

FINAL REPORT

Actively Shaken In Situ Passive Sampler Platform for Methylmercury and Organics - Phase II

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TABLE OF CONTENTS

	Page
ABSTRACT	XII
LIST OF PUBLICATIONS AND AWARDS	XIV
EXECUTIVE SUMMARY	ES-1
1.0 CHAPTER 1: IN SITU PASSIVE SAMPLING OF SEDIMENT POREWATER ENHANCED BY PERIODIC VIBRATION. (PUBLISHED PAPER)	1
1.1 ABSTRACT.....	1
1.2 INTRODUCTION	2
1.3 MATERIALS AND METHODS.....	3
1.4 RESULTS AND DISCUSSION	7
1.5 ACKNOWLEDGEMENTS.....	15
1.6 SUPPORTING INFORMATION:.....	15
1.7 REFERENCES	15
2.0 CHAPTER 2: ANALYSIS OF MEASUREMENT ERRORS IN PASSIVE SAMPLING OF POREWATER PCB CONCENTRATIONS UNDER STATIC AND PERIODICALLY VIBRATED CONDITIONS. (PUBLISHED PAPER).....	18
2.1 ABSTRACT.....	18
2.2 INTRODUCTION	19
2.3 MATERIALS AND METHODS.....	20
2.4 RESULTS AND DISCUSSION	23
2.5 ASSOCIATED CONTENT	32
2.6 AUTHOR INFORMATION.....	32
2.7 ACKNOWLEDGMENTS	32
2.8 REFERENCES	32
3.0 CHAPTER 3: DESIGN OPTIMIZATION OF PASSIVE SAMPLING PROTOTYPES WITH PERIODIC VIBRATION FOR POREWATER MEASUREMENTS OF STRONGLY HYDROPHOBIC COMPOUNDS.....	34
3.1 ABSTRACT.....	34
3.2 INTRODUCTION	35
3.3 MATERIALS AND METHODS.....	36
3.4 RESULTS AND DISCUSSION:.....	45
3.5 CONCLUSION.....	53
3.6 REFERENCES	54

TABLE OF CONTENTS (Continued)

		Page
4.0	CHAPTER 4: ANALYSIS OF TIME INTEGRATION IN EQUILIBRIUM PASSIVE SAMPLING.	56
4.1	ABSTRACT.....	56
4.2	INTRODUCTION	57
4.3	METHODS	60
4.4	RESULTS	65
4.5	CONCLUSIONS.....	69
4.6	REFERENCES	70
5.0	CHAPTER 5: OPTIMIZATION OF EQUILIBRIUM PASSIVE SAMPLING FOR SHORT-TERM SURFACE WATER MEASUREMENTS.....	74
5.1	ABSTRACT.....	74
5.2	INTRODUCTION	75
5.3	MATERIALS AND METHODS.....	76
5.4	RESULTS AND DISCUSSION.....	81
5.5	CONCLUSIONS.....	88
5.6	REFERENCES:	88
6.0	CHAPTER 6: DEVELOPMENT OF A NOVEL EQUILIBRIUM PASSIVE SAMPLING DEVICE FOR METHYLMERCURY IN SEDIMENT AND SOIL POREWATERS (PUBLISHED PAPER).....	91
6.1	ABSTRACT.....	91
6.2	INTRODUCTION	92
6.3	MATERIALS AND METHODS.....	94
	<i>Material selection and preparation</i>	94
	<i>Screening isotherms</i>	95
	<i>Sampler kinetics and mechanism of accumulation</i>	95
	<i>Activated carbon kinetics and desorption</i>	96
	<i>Soil and sediment slurries</i>	96
	<i>Static sediment microcosms</i>	97
	<i>Analytical methods</i>	98
	<i>Equilibrium speciation calculations</i>	98
6.4	RESULTS AND DISCUSSION.....	98
	<i>Screening isotherms</i>	98
	<i>Implications</i>	107
6.5	REFERENCES	108
7.0	CHAPTER 7: EVALUATING THE UPTAKE MECHANISMS OF A NOVEL, ACTIVATED CARBON-BASED EQUILIBRIUM PASSIVE SAMPLER FOR ESTIMATING POREWATER METHYLMERCURY (PUBLISHED PAPER).....	114
7.1	INTRODUCTION	115
7.2	MATERIALS AND METHODS.....	116

TABLE OF CONTENTS (Continued)

	Page
7.3 RESULTS AND DISCUSSION	120
7.4 CONCLUSIONS.....	131
7.5 REFERENCES	131
8.0 CHAPTER 8: MEASUREMENT OF MEHG DEPTH PROFILE IN SEDIMENTS	137
8.1 INTRODUCTION	138
8.2 METHODS	139
<i>Ag+AC Passive Sampler synthesis</i>	139
<i>Sediment Microcosm Set-up</i>	140
<i>Sediment Microcosm Take Down</i>	141
<i>Data Analysis and Interpretation</i>	141
8.3 RESULTS AND DISCUSSION	142
8.4 REFERENCES	145
9.0 CHAPTER 9: APPLICATION OF A NOVEL ACTIVATED CARBON BASED PASSIVE SAMPLER TO MEASURE AQUEOUS METHYLMERCURY IN SURFACE WATERS AND POREWATERS AT EAST FORK POPLAR CREEK	148
9.1 INTRODUCTION	149
9.2 MATERIALS AND METHODS.....	149
9.3 RESULTS AND DISCUSSION	152
9.4 CONCLUSIONS.....	154
9.5 REFERENCES	155
10.0 RECOMMENDATIONS FOR THE FUTURE.....	156
APPENDIX A SUPPLEMENTAL INFORMATION FOR CHAPTER 1	A-1
APPENDIX B SUPPLEMENTAL INFORMATION FOR CHAPTER 2	B-1
APPENDIX C SUPPLEMENTAL INFORMATION FOR CHAPTER 3	C-1
APPENDIX D SUPPLEMENTAL INFORMATION FOR CHAPTER 4	D-1
APPENDIX E SUPPLEMENTAL INFORMATION FOR CHAPTER 6	E-1
APPENDIX F SUPPLEMENTAL INFORMATION FOR CHAPTER 7	F-1
APPENDIX G SUPPLEMENTAL INFORMATION FOR CHAPTER 8	G-1
APPENDIX H SUPPLEMENTAL INFORMATION FOR CHAPTER 9	H-1
APPENDIX I EARLY POLYMER CHEMISTRY TRIALS IN COLLABORATION WITH AUBURN UNIVERSITY	I-1
APPENDIX J RESPONSE TO DEC 2021 IPR QUESTIONS	J-1
APPENDIX K QUESTIONS FROM THE LAST IPR	K-1

LIST OF FIGURES

	Page
Figure 1.1. Wire Diagram of a Vibrating Passive Sampler.....	4
Figure 1.2. PAH Concentration in Porewater ($\mu\text{g/L}$) and Sediment ($\mu\text{g/g}$).	8
Figure 1.3. Fractional Uptake of Chrysene in PE Passive Sampler in a) Static, b) Vibrating Systems and c) Fully-mixed.....	9
Figure 1.4. Fractional Uptake of a) Pyrene b) Chrysene and c) Benzo(a)pyrene in PE Passive Sampler in Four Differently Exposed Systems.	10
Figure 1.5. Model Simulations of Chrysene Concentration Profile Within PE and in the Sediment Side for Static and Periodic Vibration Deployments.	13
Figure 1.6. Model Simulation of Chrysene Uptake in Vibrating System with Different Pause Times of Vibration.	14
Figure 2.1. Comparison of Uptake Profile of PCBs Into PE in Static, Vibrated, and Mixed Systems.	24
Figure 2.2. Comparison of Remaining PRC Fractions in PE (f_{PRC}) in Static, Vibrated, and Mixed Systems.	25
Figure 2.3. Fractional Uptake of PCB 128 (a), PCB 180 (b), and PCB 194 (c) in PE Passive Sampler in Four Differently Exposed Systems.	26
Figure 2.4. Comparison of 56-day Mixed (True) Equilibrium Concentration in PE with PRC-corrected PE Equilibrium Concentration Measured Using 7-day and 28-day Static Exposures.	28
Figure 2.5. Comparison of 56-day Mixed Equilibrium Concentration in PE with PRC-Corrected PE Equilibrium Concentration Measured Using 7-day and 28-day Vibrated Passive Samplers.	29
Figure 2.6. Comparison of Estimated C_{free} (Cross) with the True Equilibrium C_{free} (Red Dash Lines) for Four PCBs.	31
Figure 3.1a. VibraSP3 Developed by Geosyntec.....	39
Figure 3.2b. Field Deployment of Prototype Vibra SP3 by Geosyntec in San Diego Harbor.	39
Figure 3.3c. Modified Prototype P1-14G with Extended Fins to Provide Full Exposure to PE.	39
Figure 3.2a. Vibrating Passive Sampler Prototype P2_125G That Can House 1-3 g of PE Passive Samplers and a Vibration Sensor Datalogger.....	41
Figure 3.2b. Vibrating Passive Sampler Prototype P2_110G That Can House 1.2 g of PE Passive Samplers	42
Figure 3.2c. Deployment of Static (Left) and Vibrating Passive Samplers P2-125G (Middle) and P2-110G (Right) at Kingman Lake, Washington DC on 10 December, 2019.	42
Figure 3.3. [a] Sediment Homogenization, [b] Well Mixed Jar on the Rotatory Agitator, [c] Static Sampler Deployed in Homogenized Sediment [d] Prototype P1 and [e] Prototype P2 Deployed in Homogenized Sediment [f] with at Least 6 in Gap Between Each of Them and from the Walls of the Container.	44
Figure 3.4. Effect of Vibration Frequency and Sediment TOC on the Kinetics of Uptake of PCB 128 into a Vibrating Passive Sampler.....	46

LIST OF FIGURES

	Page
Figure 3.5a. Vibration Amplitude Reported as the Vector Sum of the G Force Values, as Recorded by the Tri-axial Vibration Sensor Tag Attached to P2-125G Vibrating Device, Over a Total of 15 Days (in Two-time Segments of 6 Days (Left) and 9 Days (Right)) Deployed in the Mirror Lake Sediment Mesocosm in Laboratory Setup.	47
Figure 3.5b. Vibration Amplitude Reported as the Vector Sum of the G Force Values, as Recorded by the Tri-axial Vibration Sensor Tag Attached to P2-125G Vibrating Device, Over a Total of 10 Days Deployed in the Field at Kingman Lake, Anacostia River, Washington DC.	48
Figure 3.6. Comparison of Total (Left) and Homolog Distributed (Right) PCB Concentration Accumulated in PE from a 10-day Deployment of Static and Vibrating (P2-110G and P2-125G) Passive Samplers in the Field.	50
Figure 3.7. (a) Total Concentration and (b) Homolog Distributed Concentration of PCB Target Compounds Accumulated in the Sampler, C _{PS} [ng/g], in Static, Vibration (P1, P2), and Well Mixed Systems Exposed for 2,4,6,8 days in the Sediment.	51
Figure 3.8. Fraction Remaining of ¹³ C-labeled PCB (a) PRC 54 (tetra), (b) PRC 37 (tri), (c) PRC 111 (penta) and (d) PRC 178 (hepta) from 1 mil PE Sampler.	52
Figure 3.9. Homolog Distribution of Required PRC Corrections (tri-octa) for the Static, Vibration and Fully Mixed Systems.....	53
Figure 4.1. A Typical Passive Sampler Accumulates Target Compounds from the Surrounding Medium and Passes through the Kinetic, Curvilinear, and Equilibrium Regimes Over Its Time of Exposure.	58
Figure 4.2. (a) Actual Water Concentration and (b) Passive Sampler Predicted Water Concentration (Without PRC Correction) of PCB 37 in Two Scenarios.....	61
Figure 4.3. Comparison of Actual Time-averaged Concentration of PCB 37 Used as Input in the Model (Black Bars) with PS Predicted Concentration (Grey Bars) as Modeled by the Diffusion Equation.....	64
Figure 4.4. Fractional Uptake of PCB Compounds of Varying Hydrophobicity on a 25um Thick PE Passive Sampler, as Predicted by the Diffusion Model	66
Figure 4.5. Comparison of Actual Time-averaged Concentration of PCB Compounds from Different Homolog Groups (Black Bars) with PS Predicted Concentration (Grey Bars)	66
Figure 4.6. Correlation Between the Hydrophobicity of PCB Compounds, Time-period of Integration and Degree of Sensitivity to the Ambient Perturbation.	67
Figure 4.7. (a) Fractional Uptake of PCB 37 PE Passive Sampler of Varying Thicknesses (7.8, 17.7, 25, 50, 75 μm), As Predicted by the Diffusion Model when pulsed Perturbation Starts on the 70th Day in ambient Water. (b) Correlation Between sampler Thickness, Time-period of Integration and Degree of Sensitivity to the Ambient Perturbation.....	68

LIST OF FIGURES

	Page
Figure 4.8. 3D Correlation Between % Accuracy of Predicted Water Concentration to Actual Time-averaged Concentration (Y axis), Timing of Pulsed Perturbation in Ambient Water (Z axis) and Hydrophobicity of PCB Compounds (X axis).....	69
Figure 5.1. (a) Schematic and (b) Built Laboratory Flow Chamber for Carrying Out Ex-situ Surface Water Measurements.	78
Figure 5.2. PE Sheets Clamped to a Customized Frame to Maintain Full Exposure to Flowing Water Within the Glass Column Flow Chamber.....	78
Figure 5.3. Vibrating Passive Sampling Platforms, P1-14G (left) and P2-110G (Right)	79
Figure 5.4. Field Deployment of Optimized Passive Samplers (0.7 mil PE) in Exposed (Left) and Mesh-enclosed (Right) Configurations for Short Term Measurements of Surface Water PCB Concentrations.....	80
Figure 5.5. Desorption Profiles of C13 PCB PRCs 54, 47,37, 111, 138 and 178 from 25um Thick PE Sampler when Exposed to Different WBL Thicknesses (Modeled) and Actual Water Velocities in the Flow Chamber (Physical Experiments).	81
Figure 5.6. Desorption Profiles of C13 PCB PRCs 54, 47,37, 111, 138 and 178 from 25um Thick PE Sampler when Exposed to the Static, Vibration (Low and High Frequency) and Well Mixed Conditions.	82
Figure 5.7. Total Concentration Along with Homolog Distribution of PCBs Accumulated in PE [ng/g] at LBC1 and LBM1: Comparison of Exposed and Meshed PEs.	83
Figure 5.8. Fractional Loss of C13 PCB PRCs (54*, 47*, 37*, 111*, 138* and 178*) from 0.7mil PE Deployed at LBC1 (Blue) and LBM1 (Green) in Exposed (Solid) and Meshed (Checkered) Configurations Over an Average of 42 Hours of Storm.	84
Figure 5.9. Required PRC Corrections, (1-feq), for Tri-penta Homolog Group PCB Compounds across Passive Sampler Replicates Deployed at LBC1 and LBM1 in Exposed and Meshed Configurations.	85
Figure 5.10. Fractional Loss of C13 PCB PRCs (54*, 47*, 37*, 111*, 138* and 178*) from 0.7mil PE Deployed at Ferndale Branch, Site PT7RW03 (blue) and Olen Drive, Site OD01 (Orange) in Exposed Configuration Over an Average of 26.5 Hours of Storm.....	86
Figure 5.11. (a) Total Concentration Along with Homolog Distribution of PCBs Accumulated in PE [ng/g] at AA County Creeks, Ferndale Branch (PT7RW03) and Olen Drive (OD01). (b) Required PRC Corrections, (1-feq), for tri-penta Homolog Group PCB Compounds Across Passive Sampler Replicates Deployed at PT7RW03 and OD01.....	86
Figure 5.12. (a) Comparison of Time-integrated Measurement Over 82 Days in 2021 (left) with Short-term Measurement Over 43 Hours in 2022 (Right) of Total PCB Concentrations at Lower Beaverdam Creek (Site LBC1), Tributary to Anacostia River, Washington DC. (b) Comparison of Long-term Measurement Over 88 Days in	

LIST OF FIGURES

	Page
2020 (left) with Short-term Measurement Over 26 Hours in 2022 (Right) of Total PCB Concentrations at Ferndale Branch (Site PT7_RW03), AA County, MD.	87
Figure 5.13. Homolog distribution of the freely dissolved PCB concentration as predicted by the long-term (orange bars) and short-term measurements (blue bars) at Ferndale Barnch, AA County, MD.	88
Figure 6.1. Partitioning of (a) MeHgOH and (b) MeHgSRHA to Select Samplers in 14-d Aqueous Isotherm Tests.	99
Figure 6.2. (a) Kinetic Curves for Polymer-water Partitioning of MeHgOH (Filled circles) and MeHgSRHA (Open Circles) by ag+AC (Blue) and PET+Cys (Red).	101
Figure 6.3. Kinetics of MeHgOH Adsorption to a Coal-derived Activated Carbon(Initial $C_w = 250 \text{ ng L}^{-1}$) and Desorption of MeHg After Transfer to Water Containing No Initial MeHg. MeHg Concentrations (ng L^{-1}) in Water Over Time Are Shown as Filled in Circles; Error Bars Show ± 1 Standard Error.	103
Figure 6.4. Porewater MeHg Concentrations in (a) Slurried Soil and (b) Sediment.	105
Figure 6.5. Porewater MeHg Concentrations in Static Sediment Microcosm Experiment. (a) Unamended sediment; (b) Sediment Amended with 5% dw Activated Carbon.....	107
Figure 7.1. Partitioning of MeHg(Cys) to Bare AC Particles and Agarose with Embedded AC Particle Polymers in 14 Day Aqueous Isotherm Tests.....	121
Figure 7.2. Partitioning of Various MeHgDOM Species in 14-day Aqueous Isotherm Tests.....	123
Figure 7.3. Exchange of Isotopically Labelled MeHgSRHA from An ag+AC Polymer Over a 14-day Time Course.....	125
Figure 7.4. Direct versus Sampler-estimated Overlying Water (A) and Porewater (B) MeHg Concentrations Using $\log(K_{ps}) = 2.96$ and $\log(K_{ps}) = 3.41$ in Sediment Microcosms.....	129
Figure 8.1. Simple Conceptual Diagram of Hg Fate and Transport in Contaminated Sediments and the Implementation of a Sand and Activated Carbon Cap.	138
Figure 8.2. Passive Sampler Synthesized for Aqueous Spatial MeHg Profiling within Sediment Microcosm Experiment.	139
Figure 8.3. Setup of Sediment Microcosms (Left) and an Example PS Deployment in the Freshwater Microcosm (Right)	140
Figure 8.4. (a) A sediment Core Extracted from an Estuarine Sediment Microcosm During Take-down (One of Several Extracted from Each Microcosm), (b) a PS Extracted from a Freshwater Microcosm After Deployment, and (c) a 0.5 cm PS Segment Cut from the PS Immediately After Retrieval.....	142
Figure 8.5. MeHg and Sulfide/Sulfate Data for the Estuarine (Top) and Freshwater (Bottom) Microcosms. (Left) PS-Derived and Grab Sample [MeHg] _{aq} Profiles and Grab Sample [MeHg] _{sed} Profiles.	

LIST OF FIGURES

	Page
	The Average ($n = 3$) Initial Grab Sample [MeHg] _{PW} and [MeHg] _{sed} Are Reported as Vertical Dashed Lines and Indicated. (Right) Sulfate and Sulfide Profiles.
Figure 8.6.	143
	Calculated [MeHg] _{PW} Species Distribution in Estuarine (Right) and Freshwater (Left) Using the Lower (Top) and Upper (Bottom) Range for the Equilibrium Formation Constant of MeHgDOMRS ($\text{Log } K_f$).....
Figure 9.1.	145
Figure 9.2.	150
Figure 9.3.	151
Figure 9.4.	153
Figure 9.5.	154

LIST OF TABLES

	Page
Table 3.1. Electrical Components of the Vibrating Passive Sampler Prototypes.	41
Table 3.2a. Non-aroclor PCB Congeners Used as Performance Reference Compounds to Load PE Samplers.....	43
Table 3.2b. 13C-labeled PCB Compounds Used as Performance Reference Compounds to Load PE Samplers.....	43
Table 4.1. List of PCB Compounds in Ascending Order of Hydrophobicity (Log KOW) and the Physiochemical Properties Used in Simulating Uptake Kinetics in PE.	62
Table 5.1. List of C13 PCB PRC Compounds Used for Impregnating Passive Samplers.	76

ACRONYMS AND ABBREVIATIONS

DDT	dichlorodiphenyl trichloroethane
DoD	Department of Defense
DOM	dissolved organic matter
Hg	Mercury
HOC	Hydrophobic Organic Compound
K_{PS} or K_{PW}	sampler-water partitioning coefficient (used in MeHg PS chapters)
K_D	sediment-porewater distribution coefficient
MeHg	Methylmercury
ORNL	Oak Ridge National Laboratory
PE	polyethylene
PRC	Performance Reference Compound
PCB	polychlorinated biphenyls
PS	passive sampler
UMBC	University of Maryland Baltimore County
SERC	Smithsonian Environmental Research Center
SERDP	Strategic Environmental Research and Development Program

KEYWORDS

Passive sampler
Sediment
Porewater
Equilibrium sampling
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ABSTRACT

This full SERDP project followed a 1-year SEED project to advance passive sampling on two major fronts: 1) use of mathematical modeling and device development to enable short term passive sampling for hydrophobic pollutants, and 2) development of an equilibrium passive sampler for methylmercury in water and sediment porewater. The proof-of-concept developments in the SEED project were successfully advanced with further testing and field deployments, paving the way for the extension of passive sampling to these heretofore difficult to measure analytes/ conditions.

Passive sampling for the measurement of freely dissolved concentrations of organic pollutants in sediment pore water has emerged as a very promising approach, but *in situ* measurements are complicated by slow mass transfer of strongly hydrophobic compounds caused by the static boundary layer that develops adjacent to the sampler. Corrections of nonequilibrium using performance reference compounds become prone to large errors, especially when deviation from equilibrium is large. We address the challenge of slow kinetics by modeling the mass transfer processes and when necessary, disrupting the external aqueous boundary layer around an *in situ* passive sampler using periodic mechanical vibration. We demonstrate through numerical modeling and laboratory/field experiments that short periodic shaking of a passive sampler deployed in static sediment (by incorporating low-cost motors in the sampler platform) greatly enhances the rate of mass transfer and brings the sampler closer to equilibrium. The improvement over static sediment deployment is especially relevant for the high molecular weight compounds such as benzo(a)pyrene, high molecular weight PCBs, and dioxins. Through careful modeling of mass transfer in a passive sampler, this research showed that the time integration period in a passive sampler is different for different compounds and needs to be considered when interpreting results of long-term deployments. The research also demonstrates the feasibility of short-term water column measurements using passive samplers to capture episodic events like stormflows.

The second part of this research developed an equilibrium passive sampler for methylmercury (MeHg) that can be used in water or sediment. Our goal was to develop a sampler using the equilibrium model concept developed for hydrophobic organic chemicals (HOCs), while building on the knowledge gained from kinetic passive sampler development for MeHg to date. First, we identified sampler materials with the potential to mimic MeHg partitioning into sediments using a range of polymers embedded with suitable sorbents for MeHg. The most promising were activated carbon (AC) embedded in agarose, thiol-SAMMS embedded in agarose, and cysteine-functionalized polyethylene terephthalate. Investigation of the MeHg accumulation mechanism by AC embedded in agarose suggested sampling was kinetically influenced by MeHg interactions with AC particles and not limited by diffusion through the gel for this material. Reversible equilibrium exchange of environmentally relevant MeHg species was demonstrated through a series of dual isotope labeled exchange experiments confirming the feasibility of using isotope labeled MeHg as performance reference compounds. Isotopically labeled MeHgDOM species approached equilibrium in the samplers over 14 d while mass balance was maintained, providing strong evidence that the ag+AC polymer material is capable of equilibrium measurements of environmentally relevant MeHg species within a reasonable deployment time frame. Samplers deployed across the sediment-water interface of sediment microcosms and in the field estimated both overlying water and porewater MeHg concentrations within a factor of 2 to 4 of grab sample measurements, based on the average measured sampler-water partitioning coefficients (K_{ps}) for species of MeHg bound to natural organic matter in adsorption isotherm experiments.

Samplers provided good estimates for MeHg across a range of sediment types. A passive sampler sheet deployed in the sediment could be sectioned into 0.5 cm slices to obtain a high-resolution depth profile of porewater MeHg in sediments that can be valuable for the assessment of transport and remediation effectiveness. Taken together, our results indicate that ag+AC polymers, used as equilibrium samplers, can provide accurate MeHg estimations across many site chemistries, with a simple back calculation based on a standardized K_{ps} .

LIST OF PUBLICATIONS AND AWARDS

List of peer-reviewed publications and patent resulting from this project:

1. In situ passive sampling of sediment porewater enhanced by periodic vibration. Jalalizadeh, M. and Ghosh, U. *Environ. Sci. Technol.* 50, 8741–8749, **2016**.
2. Analysis of Measurement Errors in Passive Sampling of Porewater PCB Concentrations under Static and Periodically Vibrated Conditions. M. Jalalizadeh and Upal Ghosh. *Environ. Sci. Technol.* 51, 7018-7027, **2017**.
3. Actively Shaken In-Situ Passive Sampling Device. U. Ghosh and M. Jalalizadeh, Feb 4, **2020**. (US Patent # 10,551,283)
4. Development of a novel equilibrium passive sampling device for methylmercury in sediment and soil porewaters. Sanders, J.P.; Alyssa McBurney. A.; Gilmour, C.C.; Schwartz, G.E.; Kane Driscoll, S.B.; Brown, S.S.; Ghosh, U. *Environ. Toxicol. Chem.* 39, 323–334. **2020**.
5. Evaluation of Methylmercury Uptake Mechanisms of a Novel Activated Carbon-Based Equilibrium Passive Sampler for Prediction of Porewater Methylmercury. Washburn, S.J.; Damond, J.; Sanders, J.P.; Gilmour, C.C.; Ghosh, U. *Environ. Toxicol. Chem.* May, **2022**.

List of awards/recognitions won by publications and presentations of the research products

1. Oindrila Ghosh (Ph.D. Student) Best Student Paper Award at the Battelle International Sediment Conference. January 2023.
2. Jada Damond (Ph.D. Student) 3rd Place SETAC Chesapeake-Potomac and Hudson-Delaware Regional Chapter (CPRC-HDC) Joint Spring Meeting, April 2022.
3. Jada Damond (Ph.D. Student) 2nd Place Best Student Platform Presentation, SETAC Chesapeake Potomac Regional Chapter Annual Virtual Meeting, September 2020.
4. Oindrila Ghosh (Ph.D. Student) 3rd place Best Student Platform Presentation, SETAC Chesapeake Potomac Regional Chapter Annual Virtual Meeting, September 2020.
5. James Sanders (Ph.D. Student) 2020 Best Student Paper award from Society of Environmental Toxicology and Chemistry.
6. James Sanders (Ph.D. Student) Top 10 Exceptional Papers of 2020 by the *Journal of Environmental Toxicology and Chemistry*.
7. James Sanders (Ph.D. student), Best student poster award, Society of Environmental Toxicology and Chemistry, Hudson Delaware Chapter meeting, April 2017.

8. James Sanders (Ph.D. student), 8th Annual Geosyntec Student Paper Competition, 2nd place, 2017.
9. Mehregan Jalalizadeh (Ph.D. student) 8th Annual Geosyntec Student Paper Competition, 3rd place, 2017.
10. James Sanders (Ph.D. student), Most Popular Poster, Society of Environmental Toxicology and Chemistry, Chesapeake Potomac Regional Chapter, Virtual Poster Contest 2016.
11. Mehregan Jalalizadeh, 1st place student poster award, SETAC Hudson Delaware chapter meeting, 2016.

EXECUTIVE SUMMARY

INTRODUCTION AND REPORT LAYOUT

Accurate bioavailability measurements are needed for improved site risk assessment, proper remedy selection, and post-remediation monitoring. Passive sampling for sediment porewater and surface water has emerged as a very promising approach, but *in situ* measurements are complicated by slow mass transfer of strongly hydrophobic compounds. For methylmercury (MeHg), development of passive samplers has been hindered by the lack of an approach that adequately predicts porewater concentrations in complex milieu. This research is a follow up of a completed SEED project (ER2540) and addresses two key needs described in the SEED SON (ERSEED-15-02): i) Development of a multi-purpose passive sampling device capable of collecting data on several contaminants of interest. ii) Development of passive sampling strategies for very hydrophobic chemicals such as dioxins/furans and metals such as Hg. This full SERDP project addressed the two SONs by advancing the field of passive sampling on two major fronts: 1) Use of mathematical modeling and device development to enable short term passive sampling for strongly hydrophobic pollutants, and 2) Development of an equilibrium passive sampler for methylmercury in water and sediment porewater.

Tasks associated with these two aspects of the project are separately summarized in this executive summary and in full detail in the subsequent chapters. Each of the chapters are written as stand-alone peer-reviewed papers that have either been published or are in the process of being prepared for publication.

SHORT-TERM PASSIVE SAMPLING FOR HYDROPHOBIC ORGANICS

In our SEED project we addressed the challenge of mass transfer limitation of strongly hydrophobic compounds by using a vibrating platform for the deployment of passive sampling devices in sediments. We demonstrated through laboratory measurements and numerical modeling that the platform can greatly enhance the rate of mass transfer of 16 PAHs into PE passive samplers by disrupting the formation of a depletion layer in the vicinity of the polymer (Jalalizadeh and Ghosh, 2016). While a numerical model showed that significant improvement over static deployment is possible with lower frequency of vibration of the motors, this was not confirmed experimentally.

The first three tasks of the full proposal were aimed at taking the next steps in addressing the need for in-situ short term passive sampling of HOCs:

Task 1: Optimize vibration frequency through mathematical modeling and laboratory experiments

Task 2: Perform laboratory demonstration using two field sediments.

Task 3: Test vibrating passive sampler in the field.

These tasks are addressed in separate work products as described below. As a result of careful modeling of the transport processes in the passive sampler we were also able to examine the period of time integration for passive samplers for a range of compound hydrophobicity and extend the application of short-term sampling to the water column for potential sampling of short-term events. These work products have been written as standalone documents and are summarized below.

Analysis of Measurement Errors in Passive Sampling of Porewater PCB Concentrations under Static and Periodically Vibrated Conditions.

Task 1 is primarily addressed in a paper we published in 2017 titled: “Analysis of Measurement Errors in Passive Sampling of Porewater PCB Concentrations under Static and Periodically Vibrated Conditions” by Jalalizadeh and Ghosh, *Environ. Sci. Technol.* 2017. The key objectives of this paper were to 1) evaluate the effectiveness of periodic vibration for passive sampling of strongly hydrophobic PCBs, and 2) carefully evaluate the errors associated with PRC corrections for different deployment modes. A numerical model based on Jalalizadeh and Ghosh (2017) developed in the SEED project was used to explain the diffusion process of PCBs from sediment particles into the sediment porewater, and from porewater into passive samplers. We used a new vibrating platform, developed based on our earlier platform design, to demonstrate the effectiveness of periodic vibration for large molecular weight PCBs such as hexa-, hepta-, and octachloro-PCBs. Uptake of PCBs in PE after 7, 14, 28, and 56 days under different vibration modes was compared to that under static and mixed laboratory deployments. All PCBs reached within 95 – 100% of equilibrium after 56 days of deployment in the system vibrated briefly every 2 min, while none of the congeners achieved more than 50% of equilibrium in static deployment for the same period. Periodic vibration also increased the dissipation rate of four performance reference compounds (PRCs) from passive samplers. Higher fractional loss of PRCs and closer approach to equilibrium in the vibrated deployment resulted in estimation of corrected porewater concentrations that were statistically indistinguishable from the true equilibrium values even after a short 7-day deployment. In the static passive sampler, porewater concentrations of the strongly hydrophobic PCB congeners were overestimated by up to an order of magnitude after the same deployment time.

Shorter deployment times reduce the risk of loss, destruction, and vandalism of deployed passive sampler platforms in the field, and can reduce costs when deployment and retrieval may be performed in one mobilization to the field. Using periodic vibration for a longer deployment of a month, it may even be possible to reach so close to equilibrium that PRC corrections may not be necessary for many compounds. We expect that using the proposed vibration technique for deployment of the passive samplers would also improve the accuracy of in situ measurements of C_{free} for other strongly hydrophobic compounds such as polychlorinated dibenzo-p-dioxins/dibenzofurans since these compounds are in the same range of hydrophobicity as hexa-, hepta-, and octachloro-PCBs. Further work is needed to operationalize the vibrating passive sampler by optimizing the vibration frequency, increasing size of the devices to accommodate larger samplers, and demonstrating in the field.

Increasing the size of devices, including a sensor tag, additional testing in the lab using field sediments.

As part of Task 1, we had also proposed to increase the size of the device to allow use of a greater mass of polymer and enable measurement of low concentrations of pollutants in porewater such as dioxins and furans. We attempted two approaches to increase the size of polymer mass: increasing the thickness of polymer and increasing the overall size of the device with a larger vibration motor. We realized that the kinetics into the polymer is impacted by increases in polymer thickness (by increasing the depth of depletion zone around the polymer) and therefore focused the optimization effort on increasing the size of the device. Three larger prototypes of vibrating passive samplers were developed to address the objectives of this project. Key motivations were to increase the size of the sampling device, increasing the size of the motor, making them more robust for deployment in the field, while keeping them low-cost.

Prototype P1. The first prototype (P1 or VibraSP3) was developed in collaboration with Geosyntec. Dr. Mehregan Jalalizadeh who first worked on developing the proof-of-concept of the vibrating passive sampler at UMBC as part of the SEED project became an employee of Geosyntec and continued to develop the technology further for field deployment with additional internal support from Geosyntec. Prototype P1 is shown in Figure ES-1. The vibration device consists of a vibrating motor, a microcontroller, and a user-replaceable battery. The components of the vibration device were mounted on a waterproof housing was tested to water pressures at 30 m depth, and the microcontroller was programmed to vibrate the motors for 5 seconds in every 4 hours. The prototype was deployed in the San Diego Harbor by Geosyntec. In the first version of this prototype, the PE sampler shown in Figure ES-1 was attached to the back side of the plate holding the vibrating case. This configuration did not allow good exposure of the PE to sediment from both sides. Thus, the device was modified at UMBC to extend the frame into fins straddling the vibrating device (Prototype P1). This prototype, while larger than the ones used for proof of concept in the SEED project, is still too small to deploy 1 g of PE per sampler. Additional two versions of prototype P2 were therefore designed.

Prototypes P2-110G and P2-125G. Two additional vibrating passive samplers (prototypes P2-110G and P2-125G) were developed at UMBC that are larger in size and power to allow the deployment of 1-3 g of PE passive samplers. Figure ES-1 (middle) shows the prototype P2-110G that was built by students in the laboratory at UMBC. This prototype has three radial fins, each with 0.3 g of 2 mil PE sheets with a maximum deployed PE mass of 0.9 g. Figure ES-1 (right) shows an even larger prototype P2-125G that was built by students with the help of personnel from the UMBC machine shop and includes larger fins compared to P2-110G and also has a more powerful motor. P2-125G can also support 4 fins, each containing a 0.7 g PE sheet with a maximum total deployed mass of PE of 2.8 g. P2-125G was discontinued for lab/field testing because it proved to have negligible improvement in vibration efficiency at the cost of high-power requirement. All subsequent experiments were conducted using the prototype P2-110G.

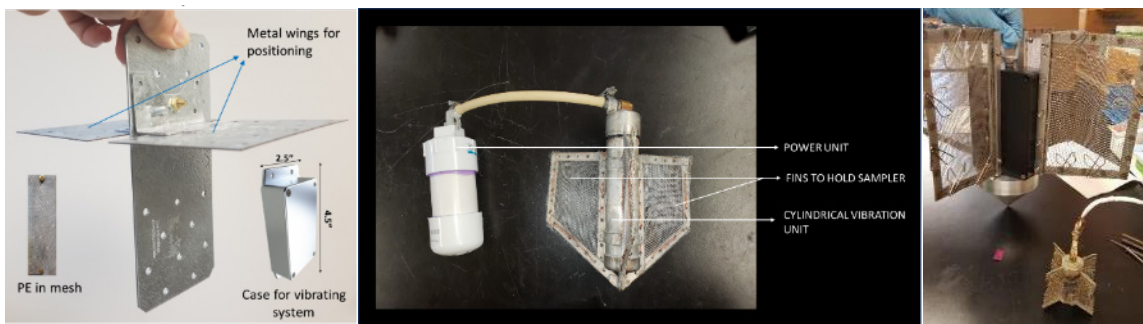


Figure ES-1. Vibrating Platform Prototypes from Left to Right: 1) Prototype P1 (VibraSP3) Samplers Built in Collaboration with Geosyntec, 2) UMBC Prototype P2-110G, and 3) UMBC Prototype P2-125G Compared with the First Small Prototype (Bottom Right) Built for Proof of Concept in the SEED Project.

Laboratory testing results of vibrating passive samplers. Prototype P2-110G was tested in the laboratory multiple times in two types of sediments: 1) a clayey freshwater sediment, and 2) a silty organic rich estuarine sediment. The prototype was first tested in the clayey sediment for two sequential deployments of 10 d each. This was followed by three sequential deployments in the silty organic rich sediments for 7 d each time. The prototype P2-110G survived all five deployments in the laboratory.

The tests demonstrated that the device was leakproof and continued to vibrate through all the deployment periods. Prototype P2-125G was successfully tested in the laboratory multiple times using a sediment mesocosm. Vibration dataloggers were attached to one of the fins of the P2-125G device and demonstrated that the prototype vibrated through the entire period of deployments and the average amplitude of vibration of the device within the sediment ranged between 2-5G over the period. As shown in Figure ES-2, the static and P1 deployments for 8 days showed little uptake of the more hydrophobic PCBs.

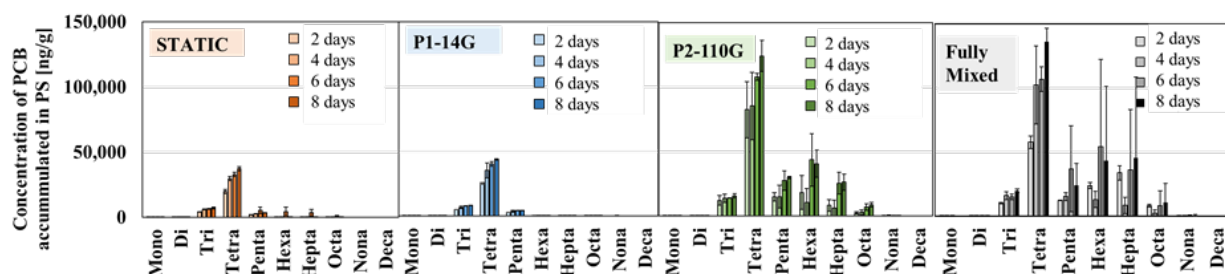


Figure ES-2. PCB Homologs Accumulated in the Vibration Samplers (P1 and P2) Compared with Static and Fully Mixed Deployments for Exposure Periods of 2, 4, 6, and 8 Days in Sediment.

In comparison, the P2-110G performed better demonstrating uptake of PCB congeners up to octachlorobiphenyls to levels close to what is observed for the fully mixed system. The P2-110G system with its more effective vibration can give a more accurate final estimate of porewater PCBs.

Field testing results of three prototypes. As per guidance from SERDP we moved forward the field deployment of the vibrating platforms to the first year of the project to evaluate the feasibility of the platform to work continuously under water and in field conditions. Geosyntec deployed the VibraSP3™ platform in a marine sediment in 10 to 15-feet of water for a time period of 7 to 14 days and demonstrated that after both the 7-day and 14-day deployments, the samplers were intact and fully-functioning, indicating a successful performance of the devices. Overall, the results of the deployment confirmed that the vibrating passive samplers enhanced the kinetics of uptake of the PCB congeners.

The two vibrating passive sampler prototypes (P2-110G and P2-125G) were deployed in the field in Kingman Lake, Anacostia River, Washington DC on Dec 10, 2019. In addition, static passive samplers that were not vibrated were also deployed alongside in sediments. The deployment was performed for a period of 10 days and all samplers were retrieved successfully at the end of the field deployment. The vibration sensor data showed that the vibrating prototype P2-125G functioned with an amplitude of about 2.5G while inside sediment throughout the deployment time (Figure ES-3). The rate of uptake of native PCBs by the vibrating sampler was 3-4 times higher in the vibrating sampler compared to the static sampler. The enhancement of uptake rate was observed not only for the lower chlorinated PCBs, but also for the higher chlorinated PCBs with 6-8 chlorines that are in the same hydrophobicity range as dioxins and furans. Correspondingly, the rate of loss of PRCs for the vibrating prototypes was faster than the static sampler over the deployment period of 10 days in the field.

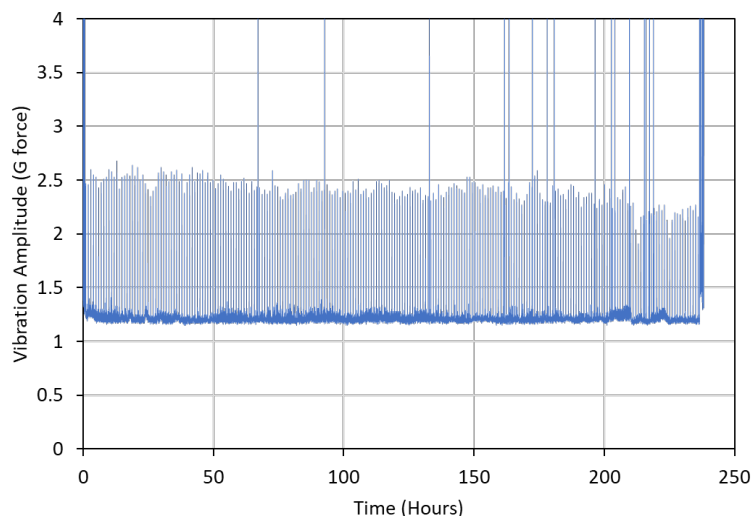


Figure ES-3. G Force Values Reported by the Tri-axial Vibration Sensor Tag Attached to the Vibrating Passive Sampler Deployed in the Field at Kingman Lake, Anacostia River, Washington DC.

Data shown for a sampling period of 240 hours.

Time period of integration of passive sampler for surface water measurements.

In the surface water, events like stormflow, industrial discharges, and tides can cause temporal variations in the ambient water concentrations of organic contaminants. Passive samplers deployed in the field for several months are expected to provide a time-weighted average concentration over the entire observation period that is important for ecological exposure assessment. The responses of single-phase equilibrium passive samplers to possible environmental situations when ambient concentrations vary linearly with time, decrease exponentially with time, constitute a pulsed event, or oscillate regularly with time have been theoretically analyzed (Hawker, 2010). The first-order response curves were found to bear a footprint of the pattern in which the ambient concentrations varied over time often with a measurable time lag. However, previous studies do not provide a comprehensive mathematical model to demonstrate the diffusive transport through internal and external resistances to PE samplers under changing ambient concentrations. We addressed this knowledge gap by using our theoretical modeling framework of exchange kinetics of PCBs in PE passive samplers using the diffusion model and the first-order model. The impact of the timing of fluctuations, hydrophobicity of the analyte, and sampler thickness on the final measurement was examined by comparing against the simulated time-averaged ambient concentration. The accuracy of the diffusion and first-order models were compared and any underlying cause of inconsistency between the predicted final water concentration by the two models explained. We considered a 10X dilution pulse in the actual water concentration outside the sampler that lasts for 10 days out of a total exposure period of 90 days. The responses of a 25 μm thick PE sampler to the pulsed perturbation in the ambient water column were simulated for the changing scenarios of increasing closeness of the starting day of the pulse to the end of exposure period. As shown in Figure ES-4, the fractional uptake into PE was different for different compounds. The lower homolog group compounds are more sensitive to the ambient perturbations, and also recover from the impact of the perturbation more quickly compared to the more hydrophobic compounds.

The optimal time-period of integration for a 25 μm PE sheet ranged from 14-15 days for a dichlorobiphenyl to 43-45 days for a hexachlorobiphenyl.

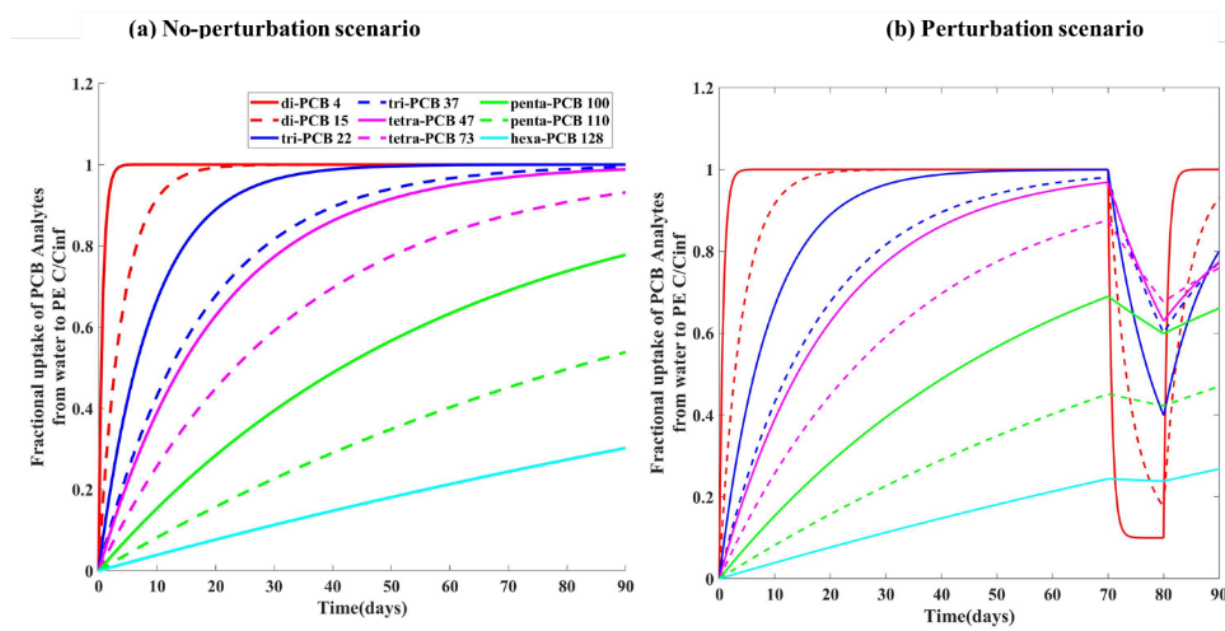


Figure ES-4. Fractional Uptake of PCB Compounds of Varying Hydrophobicity on a 25um Thick PE Passive Sampler, as Predicted by the Diffusion Model in Two Scenarios: (a) No Perturbation and (b) Pulsed Perturbation that Starts on the 70th Day in Ambient Water.

Feasibility of short term (storm event) sampling of surface water

Short-term surface water measurements are often critical in assessing inputs from episodic events. Passive sampling of surface water is often performed over an extended period of time, typically more than one month, to capture a time-integrated concentration for the duration of deployment. We hypothesized based on the observed enhancement of kinetics using the vibrating passive sampler for sediments, that it may be feasible to design a passive sampling device that is capable of measuring surface water concentrations in short term events like a storm flow. We first performed mathematical modeling of a range of simulated flow conditions in surface water with assumed water boundary layer thicknesses, followed by the setup of a laboratory flow through experiment, and finally a short-term deployment during a storm in the field. From the modeling and laboratory experiments it was concluded that by choosing a thin polymer sheet and deploying during high flow events, both internal and external mass transfer resistances can be reduced, enabling sufficient pollutant accumulation in the polymer within a day to perform a measurement of the freely dissolved concentration of PCBs up to hexachlorobiphenyls. Hence, for short-term measurements an 18-micron thick polyethylene sheet was chosen for a 1-2 day exposure during a high flow storm event in the field. We show through two field deployments (LBC and Ferndale Branch) that for high flow storm conditions, such measurements can indeed be achieved reliably up to penta or hexachlorobiphenyls. The increase in dissolved concentration during the storm event monitored at LBC suggests possible storm driven mobilization of PCBs at this site. At the Ferndale Branch site, the PCB homolog patterns are very different during baseflow and stormflow, potentially indicating mobilization of different sources at different flow conditions.

Thus, short-term integrated passive sampling measurements can provide additional information valuable for site investigations and source identification/management. We also provide proof-of-concept of the feasibility of performing short, 1-day measurements in low-flow or stagnant conditions using a continuously vibrated passive sampler deployed in surface water. These advances in passive sampling allow flexibility of sampler deployments to determine concentrations during different periods of a hydrograph that may be helpful in delineating sources when needed. For example, if the watershed and associated storm pipes are relatively clean, storm-driven high flows should be cleaner and have a dilution effect in the receiving waterbody. However, if the main pollutant sources are in the watershed land surface, one may expect to observe elevated concentration in the water after a storm driven runoff from contaminated surface soil sites.

EQUILIBRIUM PASSIVE SAMPLING FOR METHYLMERCURY

The concentration of chemically labile or bioavailable MeHg (here designated MeHg_{CL}) in surface waters and sediment porewaters is needed to make predictions about risk, and to evaluate the impact of potential remediation on risk. However, MeHg concentrations can be very low (pM in uncontaminated waters) and highly variable through time, making direct sampling and analysis challenging. The immediate focus of the present work was the development of a passive sampling device that can provide time-averaged concentration trends. By using an equilibrium approach to sampling, our objectives include obviating the use of diffusion coefficients to calculate MeHg_{CL} and limiting perturbation of the dynamic sediment:water equilibrium. Instead, [MeHg_{CL}] can be calculated directly from the measured equilibrium concentration of MeHg in the sampler [MeHg_{ps}] and the operationally defined partition coefficient between the sampler and its environment (K_{pw}):

$$[\text{MeHg}_{\text{CL}}] = [\text{MeHg}_{\text{ps}}]/K_{pw}$$

Importantly, the goal of passive sampling efforts is to assess the total pool of labile MeHg. The concentration of MeHg_{CL} will largely be determined by the equilibrium with the large pool of sediment-bound MeHg. If all of the component species of MeHg_{CL} come to equilibrium with the samplers, the concentration of MeHg accumulated in the sampler will reflect [MeHg_{CL}] regardless of MeHg speciation. Thus, the equilibrium concentration of MeHg accumulated in samplers could be used directly to assess MeHg availability. Alternatively, the absolute concentration of MeHg_{CL} can be calculated using the appropriate K_{pw} . In most environments MeHg_{DOM} species are dominant, so the use of a sufficiently representative, empirically derived K_{pw} for MeHg_{DOM} could be sufficient to determine MeHg_{CL}. The advantage of equilibrium passive sampling is that, if a standardized sampling material based on cysteine or another sorbent is properly designed, it should approach a steady-state MeHg_{CL} concentration in proportion to steady-state concentrations in benthic animals, irrespective of mechanism (Peijnenburg, Teasdale et al. 2014). The overall development of passive sampling for MeHg is addressed in tasks 4-6 of the proposal as shown below:

Task 4. Complete development of a passive sampling material that predicts pore water MeHg.

Task 5. Develop enriched stable isotope MeHg spikes as performance reference compounds for selected samplers.

Task 6. Verify MeHg equilibration with promising sampler designs in natural sediments.

These tasks are addressed in separate work products as described below.

Development of a Novel Equilibrium Passive Sampling Device for Methylmercury in Sediment and Soil Porewaters

In this research we explore the concept of equilibrium passive sampling for methylmercury (MeHg) using the strategy developed for hydrophobic organic chemicals (HOCs). Passive sampling should allow prediction of the concentration of the chemically labile fraction of MeHg in sediment porewaters (MeHg_{CL}) based on equilibrium partitioning into the sampler, without modeling diffusion rates through the sampler material. Our goals were to identify sampler materials with the potential to mimic MeHg partitioning into animals and sediments and provide reversible sorption in a time frame appropriate for in situ samplers. Candidate materials tested included a range of polymers embedded with suitable sorbents for MeHg. The most promising were activated carbon (AC) embedded in agarose, thiol-SAMMS (self-assembled monolayers on mesoporous supports) embedded in agarose, and cysteine-functionalized polyethylene terephthalate (PET), which yielded log sampler-water partition coefficients (K_{pw}) of 2.8 to 5 for MeHgOH and MeHg complexed with dissolved organic matter (Suwannee River Humic Acid). Sampler equilibration time in sediments was approximately 1 to 2 weeks. Investigation of the MeHg accumulation mechanism by AC embedded in agarose suggested sampling was kinetically influenced by MeHg interactions with AC particles and not limited by diffusion through the gel for this material. AC exhibited relatively rapid desorption of Hg and MeHg, indicating that this sorbent is capable of reversible, equilibrium measurements (see Figure ES-5). In sediment:water microcosms, porewater concentrations made with isotherm-calibrated passive samplers agreed within a factor of two (unamended sediment) or four (AC-amended sediment) with directly measured concentrations. This work demonstrates a potential new approach to passive sampling of MeHg. This sampler, along with others designed for chemisorption at reduced sulfur sites, made reasonably accurate measurements of dissolved MeHg across a range of environmentally realistic matrices including sediments with and without AC amendment. The partitioning coefficients of these samplers are such that a square piece approximately 1 cm on a side will accumulate a readily quantifiable mass of MeHg at a water concentration as low as 1 ng L⁻¹. Importantly, sampler partitioning in slurries and microcosms was generally within about half a log unit of the native K_d values in source soils and sediments. Samplers suffered no apparent degradation or fouling during deployment in sediments and soils, indicating that they should not require a potentially interfering membrane (Pham, Johnson et al. 2015).

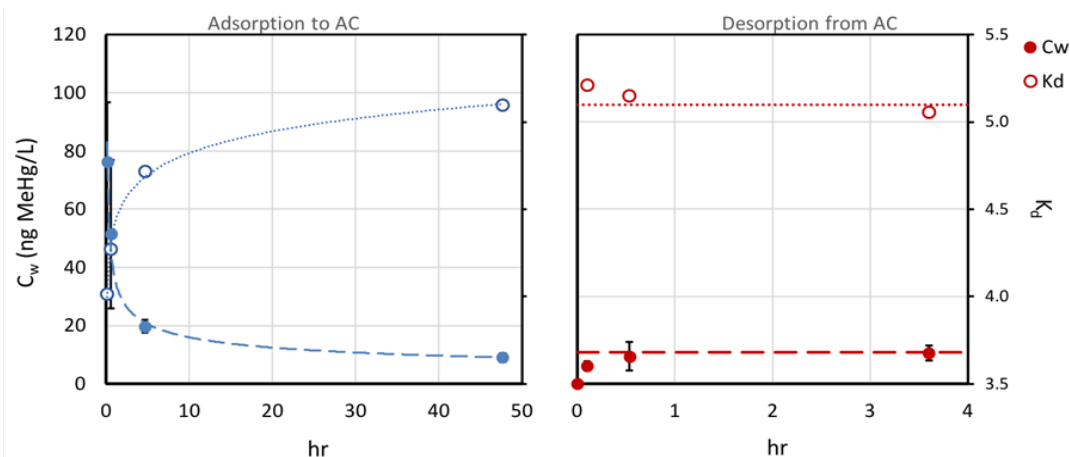


Figure ES-5. Kinetics of MeHgOH Adsorption to a Coal-derived Activated Carbon (Initial $C_w = 250 \text{ ng L}^{-1}$) and Desorption of MeHg After Transfer to Water Containing No Initial MeHg.

MeHg concentrations (ng L^{-1}) in water over time are shown as filled in circles; error bars show ± 1 standard error. Partitioning coefficients (K_d) for MeHg to activated carbon are shown with open circles. For the adsorption phase, dashed lines represent logarithmic best fit line; for the desorption phase, dashed lines represent final values observed during the adsorption phase.

Evaluating the Uptake Mechanisms of a Novel, Activated Carbon-Based Equilibrium Passive Sampler for Estimating Porewater Methylmercury

Here we describe the validation of a novel polymeric equilibrium passive sampler comprised of agarose gel with embedded activated carbon particles (ag+AC), to estimate aqueous monomethylmercury (MeHg) concentrations. In many, perhaps most, environmental settings, aqueous-phase MeHg speciation is dominated by DOM complexes. Sampler behavior was tested using a combination of idealized media and realistic sediment microcosms. Isotherm bottle experiments with ag+AC polymers were conducted to constrain partitioning to these materials by various environmentally relevant species of MeHg bound to dissolved organic matter (MeHgDOM) across a range of sizes. Partitioning coefficients ranged from $\log(K_{ps}) = 1.98 \pm 0.09$ for MeHg bound to Suwannee River Humic Acid to $\log(K_{ps}) = 3.01 \pm 0.23$ for MeHg complexed with L-cysteine. However, many of the fractionated organic matter sources used for these isotherm experiments have an exclusively terrestrial origin, and therefore may not be representative of the range of organic matters sources typically encountered in aquatic field deployments of the passive sampler. We propose using the average of the unfractionated, river-derived NOM stocks (SRNOM and UMRNOM) tested under environmentally relevant DOC concentrations, with an average $\log(K_{ps}) = 2.96$ for use in deployments with predicted predominance of MeHgDOM, as these NOM stocks are the nearest analogs to aquatic NOM of the DOM sources we have tested to date.

Reversible equilibrium exchange of environmentally relevant MeHg species was demonstrated through a series of dual isotope labeled exchange experiments confirming the feasibility of using isotope labeled MeHg as performance reference compounds. Isotopically labeled MeHgDOM species approached equilibrium in the samplers over 14 d while mass balance was maintained, providing strong evidence the ag+AC polymer material is capable of equilibrium measurements of environmentally relevant MeHg species within a reasonable deployment time frame.

Samplers deployed across the sediment-water interface of sediment microcosms estimated both overlying water and porewater MeHg concentrations within a factor of 2 to 4 of measured values, based on the average measured K_{ps} values for species of MeHg bound to natural organic matter (MeHgNOM) in the isotherm experiments. Taken together, our results indicate that ag+AC polymers, used as equilibrium samplers, can provide accurate MeHg estimations across many site chemistries, with a simple back calculation based on a standardized K_{ps} . This work successfully establishes that the ag+AC material is capable of functioning as an equilibrium passive sampler for MeHg. The demonstration of reversible equilibrium for a wide range of MeHg species also has important implications for the use of performance reference compounds to assess and potentially correct for non-equilibrium. Further work is necessary to develop performance reference compounds to account for nonequilibrium conditions and further fine-tune the measurement, and to quantify the relationship between sampler estimates of MeHg_{CL} and biotic uptake of MeHg across sediment types.

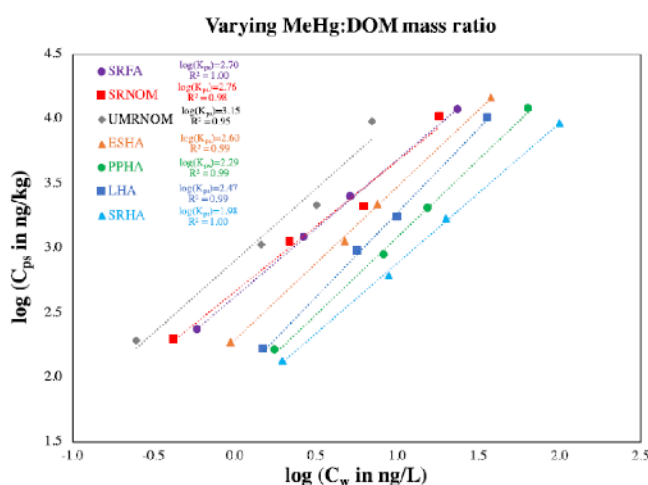


Figure ES-6. Partitioning of Various Methylmercury Dissolved Organic Matter (MeHgDOM) Species in 14-day Aqueous Isotherm Tests.

For each DOM source, log passive sampler partitioning coefficients ($\log K_{ps}$) values were determined from linear regression fitting, as were listed coefficients of determination (R^2). Isotherm data were acquired from experiments conducted at a variable MeHg:DOM mass ratio but a constant initial dissolved organic carbon concentration. See Chapter XX for DOM descriptions.

Measurement of MeHg depth profile in sediments

We conducted a sediment-water microcosm experiment to test the ability of the ag+AC polymer to estimate *in situ* MeHg concentrations in sediment porewaters and overlying surface waters. Accurately capturing the MeHg concentration gradient across the sediment-water interface, and/or a depth profile of porewater concentrations, would have numerous applications for monitoring the efficacy of Hg remediation techniques, including sediment capping with or without amendments. Passive samplers were deployed to measure the porewater profile in laboratory microcosms designed to mimic a field deployment. Elongated samplers deployed within estuarine and freshwater sediment microcosms spanned a vertical depth sufficient to capture the MeHg maxima associated with the MeHg production zone. PS-derived MeHg profiles (0.5-cm resolution) were compared to profiles obtained by porewater grab sampling at a 1 cm resolution.

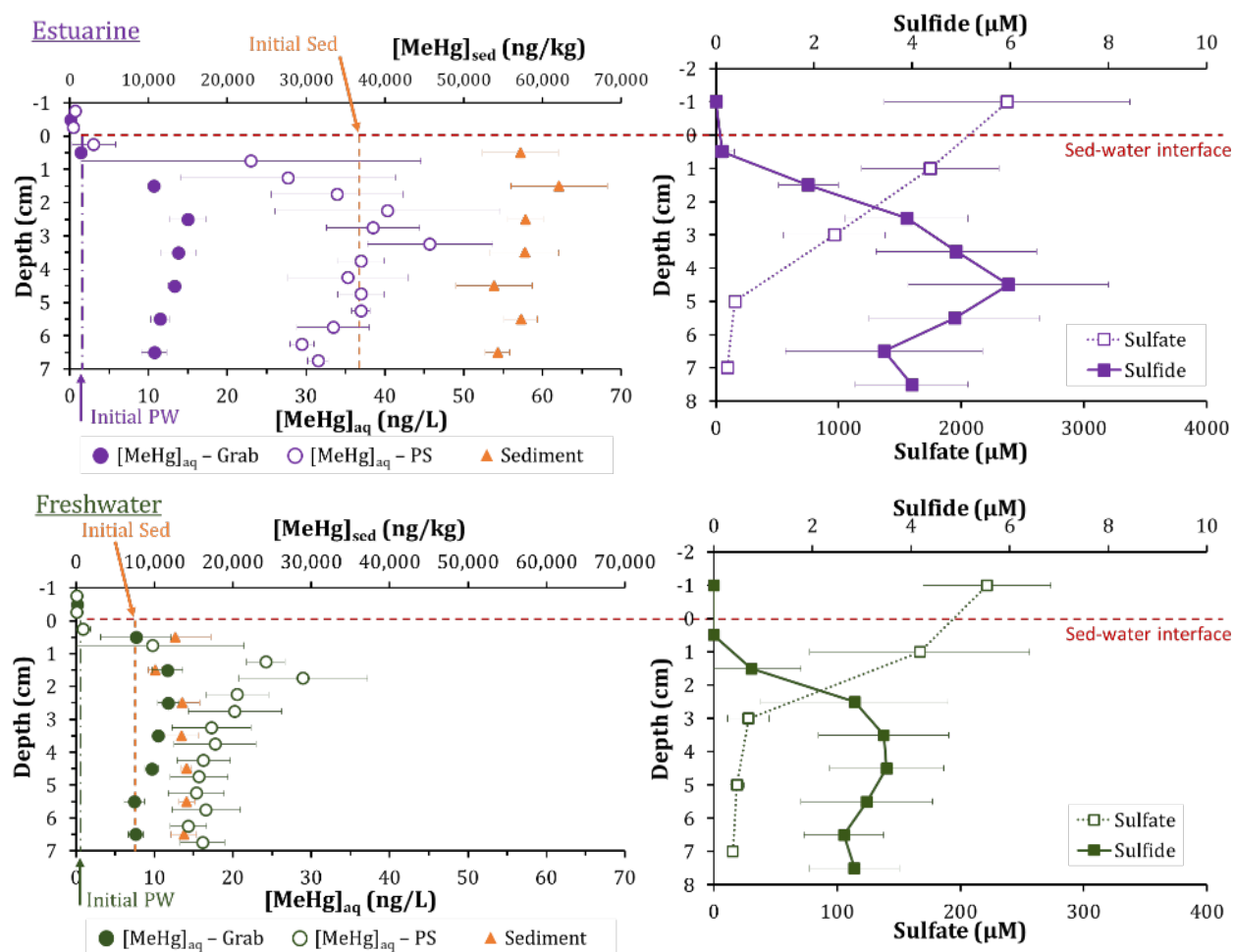


Figure ES-7. MeHg and Sulfide/Sulfate Data for the Estuarine (Top) and Freshwater (Bottom) Microcosms. (Left) PS-Derived and grab sample [MeHg]_{aq} profiles and grab sample [MeHg]_{sed} Profiles. The Average (n = 3) Initial Grab Sample [MeHg]_{PW} and [MeHg]_{sed} Are Reported as Vertical Dashed Lines and Indicated. (Right) Sulfate and Sulfide Profiles. For All Graphs, Data Points Represent an Average of Triplicate Samples, and the Error Bars Represent 1 Standard Deviation from the Average.

The porewater profiles shown in Figure ES-7 reveal the presence of a MeHg maxima. The varying porewater MeHg concentration ([MeHg]_{PW}) with depth was statistically attributed to increasing sulfide concentrations (standard least squares, $p < 0.05$, $n = 3$), and the location of the sulfide maxima in the porewater approximately corresponded to significant sulfate depletion in both microcosms. These depth-dependent observations indicate that the [MeHg]_{PW} peak results from the microbial activity of sulfate reducing bacteria (SRB) which are responsible for Hg methylation. The PS provides an excellent reflection of the porewater profile, at the finer 0.5-cm resolution (Figure ES-7). The location of the [MeHg]_{PW} maxima in the PS closely mimicked those in the centrifuged core samples, and PS-derived [MeHg]_{aq} were mostly within a factor of 2 to 4 to grab samples, using the K_{ps} chosen from the DOM isotherms ([Washburn et al. 2022](#)).

These deployments showcase the sampler's success in measuring MeHg across the sediment-water interface at a fine resolution. The 0.5-cm resolution passive sampler measurements across the sediment-water interface present the progression of increasing $[\text{MeHg}]_{\text{aq}}$ across the interface at a level unattainable by the 1-cm grab sample aqueous measurements, as demonstrated in Figure ES-7. These low-level measurements may be especially useful to determine the level of exposure to benthic organisms that reside at the sediment surface.

Field measurement of MeHg in water and sediment at ORNL

To transition the PS into a field application, PS were deployed *in situ* at East Fork Poplar Creek (EFPC) in Oak Ridge, TN. EFPC is a moderate-flow freshwater system with slightly elevated surface water MeHg, yet high sediment and fish MeHg due to Hg release from its processing as a lithium isotope separator in the mid-20th century ([Brooks and Southworth 2011](#); [Watson et al. 2016](#)). We aimed to determine how the ag+AC PS respond in an infinite flowing river system as opposed to the static finite laboratory systems in prior studies, evaluate its ability to measure surface water MeHg despite temporal changes in the environment, and assess the feasibility and robustness of porewater sampling using the PS. PS were deployed in surface waters (SW-PS) at sampling stations within EFPC; Wiltshire (EFK 16.4) and New Horizons (EFK 5.4) in Fall 2021, and at a site about 100 meters downstream from the New Horizons (EFK 5.4) station (noted throughout the report as EFK 5.3) in Summer 2022. PS were also deployed within sediments (PW-PS) at EFK 5.3 in Summer 2022 to measure $[\text{MeHg}]_{\text{pw}}$. At retrieval, surface water grab samples were collected along with SW-PS. Sediment samples were collected onsite alongside PW-PS and were shipped to MD for porewater extraction and further processing.

Regardless of low surface water MeHg concentrations ($[\text{MeHg}]_{\text{sw}}$) close to instrument detection limits, SW-PS provided aqueous concentrations that were much more detectable and very similar (within a factor of 1.6) to grab sample $[\text{MeHg}]_{\text{sw}}$ in both deployments (Figure ES-8). Further, the elevated $[\text{MeHg}]_{\text{sw}}$ measured in grab samples during the Summer 2022 deployment were reflected in the SW-PS measurements.

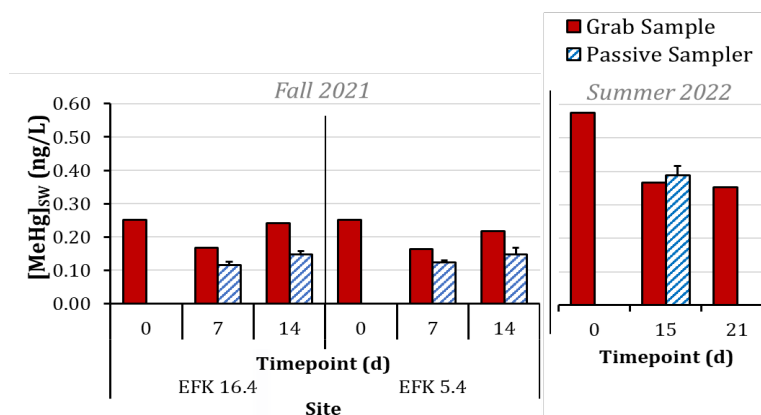


Figure ES-8. Comparison of Surface Water Concentrations Obtained by Grab Samples and SW-PS in Fall 2021 and Summer 2022 Deployments.

Summer 2022 deployments took place at a site ~100 m downstream EFK 5.4 (EFK 5.3). Grab sample bars represent direct measurement of one point. PS bars represent average measurements and error bars represent 1 standard deviation ($n = 3$).

EXECUTIVE SUMMARY REFERENCES:

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1.0 CHAPTER 1: IN SITU PASSIVE SAMPLING OF SEDIMENT POREWATER ENHANCED BY PERIODIC VIBRATION. (PUBLISHED PAPER)

Jalalizadeh, M. and Ghosh, U. *Environ. Sci. Technol.* 50, 8741–8749, **2016**.

Note: Work towards this chapter was performed as part of the proof of concept SEED project, with publication completed subsequent to the ending of the SEED project period.

1.1 ABSTRACT

Passive sampling for the measurement of freely dissolved concentrations of organic pollutants in sediment porewater has emerged as a promising approach, but in situ measurements are complicated by slow mass transfer of strongly hydrophobic compounds. The primary resistance to mass transfer arises in the sediment side where a concentration depletion layer develops in the vicinity of the polymeric passive sampling material. The slow mass transfer results in under-equilibrated passive sampler measurements that need to be corrected for equilibrium, typically by extrapolation of the loss kinetics of performance reference compounds. Such corrections are prone to large errors, especially when deviation from equilibrium is large. In this research we address the challenge of slow mass transfer by disrupting the external depletion layer around an in situ passive sampler. We report an engineering innovation of adapting low-cost vibration motors for periodically disrupting the depletion layer in a passive sampler deployed in sediments. The uptake of 16 polycyclic aromatic hydrocarbons into polyethylene passive samplers was measured after 7, 14, 28, and 56 days of exposure to sediment under static, vibrating, and fully-mixed modes. We demonstrate through laboratory experiments and numerical mass transfer modeling that short periodic shaking of a passive sampler deployed in static sediment enhances the rate of mass transfer and reduces the difference in the extent of equilibrium achieved compared to a well-mixed laboratory equilibrium. The improvement over static sediment deployment is especially evident for the high molecular weight compounds such as benzo(a)pyrene.

1.2 INTRODUCTION

The freely dissolved concentration of hydrophobic pollutants in sediment porewater is a critical measurement that is useful in assessing fate, transport, and bioavailability of these compounds.¹ Accurate measurement of low aqueous concentrations of hydrophobic compounds is challenging due to the association with colloidal and dissolved organic matter in porewater. This has led to the development of passive sampling approaches using well characterized polymeric materials. When the polymeric material is able to reach equilibrium with the sediment porewater, such as in a well-stirred laboratory measurement, the estimation of freely dissolved porewater concentration (C_{free}) becomes a trivial exercise based on the measured partition constant of the polymer.^{2,3} However, in several situations, an in situ measurement in sediment is desired. Such measurements have been challenged by the difficulty in reaching equilibrium between porewater and the passive sampler as mass transfer through the depletion layer outside the commonly used polymers (with commonly used thicknesses) becomes limiting in the absence of active mixing.⁴ It has been shown that for strongly hydrophobic compounds equilibrium may not be achieved in the field even after one year in 51 μm polyethylene (PE).⁵ Several researchers have adopted the use of performance reference compounds (PRCs) dosed in the polymer to assess the kinetics of mass transfer and correct for non-equilibrium.⁶⁻¹⁴ While corrections based on PRC loss work reasonably well for compounds with low to mid-range hydrophobicity, the corrections become increasingly erroneous for strongly hydrophobic compounds when the departure from equilibrium increases.¹⁴ Several approaches for calibration using PRC data have been suggested.⁶⁻¹⁰ In all of these approaches, the uncertainties introduced by the PRC correction are larger when the extent of equilibrium is low, which is the case for strongly hydrophobic compounds in the field.

A primary uncertainty in the PRC correction arises from the fact that nearly always it is the sediment side mass transfer in the immediate vicinity of the passive sampler that controls overall kinetics.⁴ The retarded diffusion in the sediment side is impacted by the site-specific sorption characteristics of the sediment, which can vary across orders of magnitude. For example Hawthorne et al.¹⁵ reported a 3-4 orders of magnitude range for site-specific K_{oc} values for polycyclic aromatic hydrocarbons (PAHs). Thus, to be able to correct for non-equilibrium and estimate in situ porewater concentrations we need to first have an estimate of site-specific partitioning of the analytes of interest. The loss kinetics of a few PRC compounds into sediment is used to infer the desorption behavior of a large range of analyte compounds from sediment.⁸

Thinner polymeric materials can be used to increase the surface area to volume ratio and reduce the depletion per unit area⁶ and reduce deployment time. However, even with some of the thinnest polymers practically deployable in the field (e.g. 25 μm thick PE), sediment-side mass transfer limitation can be significant.⁴ Making the polymers too thin makes them prone to damage during deployment in sediment, reduces the total mass of polymer sampling material (impacting detection limits), and also poses a physical challenge of insertion in sediments if the polymer surface area is very large.

To address these challenges, we take a very different approach of manipulating the external depletion layer in the sediment side of a passive sampler. We demonstrate for the first time a novel approach of in situ passive sampling that overcomes the slow approach to equilibrium for hydrophobic organic compounds in static sediments. Our approach involves mechanical disruption of the depletion layer outside the polymer surface using periodic vibration performed in situ.

We adapted small vibration motors used for haptic feedback in cell phones and other electronic devices to create vibrations in in situ passive sampling frames programmed to trigger at pre-determined time intervals. The concept of passive sampling still applies to the vibrated deployment because the disruptions introduced by the periodic vibration is not unlike natural sediment processes induced by burying and sediment ingesting worms that also achieve chemical equilibrium through small-scale physical disruptions in sediments. Laboratory experiments were performed using PAH-impacted field sediments to compare the approach to equilibrium under static, well-mixed, and differently shaken passive sampling modes. We also performed numerical modeling of the mass transfer process to mechanistically explain our observations and optimize the duration and periodicity of the vibrations in order to minimize the energy requirement to drive the vibration motors.

1.3 MATERIALS AND METHODS

Materials. Low density PE sheets (25 μ m thickness), manufactured by Poly-America (Grand Prairie, TX, USA) were purchased from the Home Depot. PAH and deuterated PAH stock solutions were purchased from Fisher Scientific (Pittsburg, PA, USA). Cylindrical vibrating motors with a diameter of 9 mm and length of 25 mm were purchased from Precision Microdrives (London, UK). The motors operated at a rated voltage of 3V, operating current of 130mA, and vibrating speed of 13,500 rpm. Pulse-pause timers (model 60H) were purchased from Velleman Inc. (Fort Worth, TX, USA). Prior to use, PE sheets were soaked twice in hexane/ acetone (50/50) and left on a shaker for 24 h each time to remove oligomers and any target and non-target contaminants. Clean PE sheets were then cut into 6mm $\times$ 2cm strips (2.8 mg) and were soaked in a PRC solution (80:20 methanol:water with pyrene-d10 and phenanthrene-d10) and allowed to equilibrate for 15 days on an orbital shaker.

After impregnation, all strips were removed from the PRC solution and rinsed with DI water to remove residual methanol on the surface. Two strips were extracted immediately in a 1:1 hexane and acetone mixture (3 $\times$ 24 h) to determine the initial PRC concentration in the PE strips.

In situ shaken passive sampler design. Two motors were connected in parallel to a timer and a power supply (2 rechargeable batteries 1.2 V, 700 mAh each) (Figure 1.1). The timers were powered by a 12 V power supply and were programmed to control motor vibration duration and frequency: 5 seconds pulse and 2 minutes pause (high frequency), 2 seconds pulse and 5 minutes pause (low frequency). The small PE sheets described above were enclosed in stainless steel mesh (14 mesh from TWP Inc, Berkeley, CA) and were attached like radial fins on cylindrical motors (four fins on each motor) as shown in Figure 1.1 and SI Figures S1-3.

PAH contaminated river sediment samples from the vicinity of former manufactured gas plants studied previously (identified as HD-3 and HD-5 in Khalil et al.¹⁶) were used in the present work. The two sediments were combined to obtain a sufficient quantity for the present experiments. The sediment was mixed with DI water containing 200 mg/L sodium azide to make a slurry with weight ratio of 1:2 (dry sediment/water). Water addition was performed to make the sediment more fluid and allow good mixing in the jars.³ For the well-mixed exposure, 250 mL of the sediment-water slurry and eight of the prepared PE samplers were transferred to a wide mouth jar with a Teflon-lined cap. The jar was placed on a rotary agitator and tumbled at 28 rpm. The rest of the sediment slurry was placed in a large glass tray (25cm $\times$ 35cm $\times$ 6cm). Four motors were placed inside the sediment in the tray with 10 cm separation to prevent influencing each other.

Two motors vibrated at the high frequency mode and two at the low frequency mode. Eight additional PE samplers, enclosed in stainless steel mesh without motors, were placed inside the same tray in a static mode at least 10 cm away from any vibrating motor to simulate a static deployment. The tray was then covered with aluminum foil. Two PE strips were removed from the well mixed, static, and vibrating systems and analyzed for native PAHs and PRC compounds after 7, 14, 28 and 56 days.

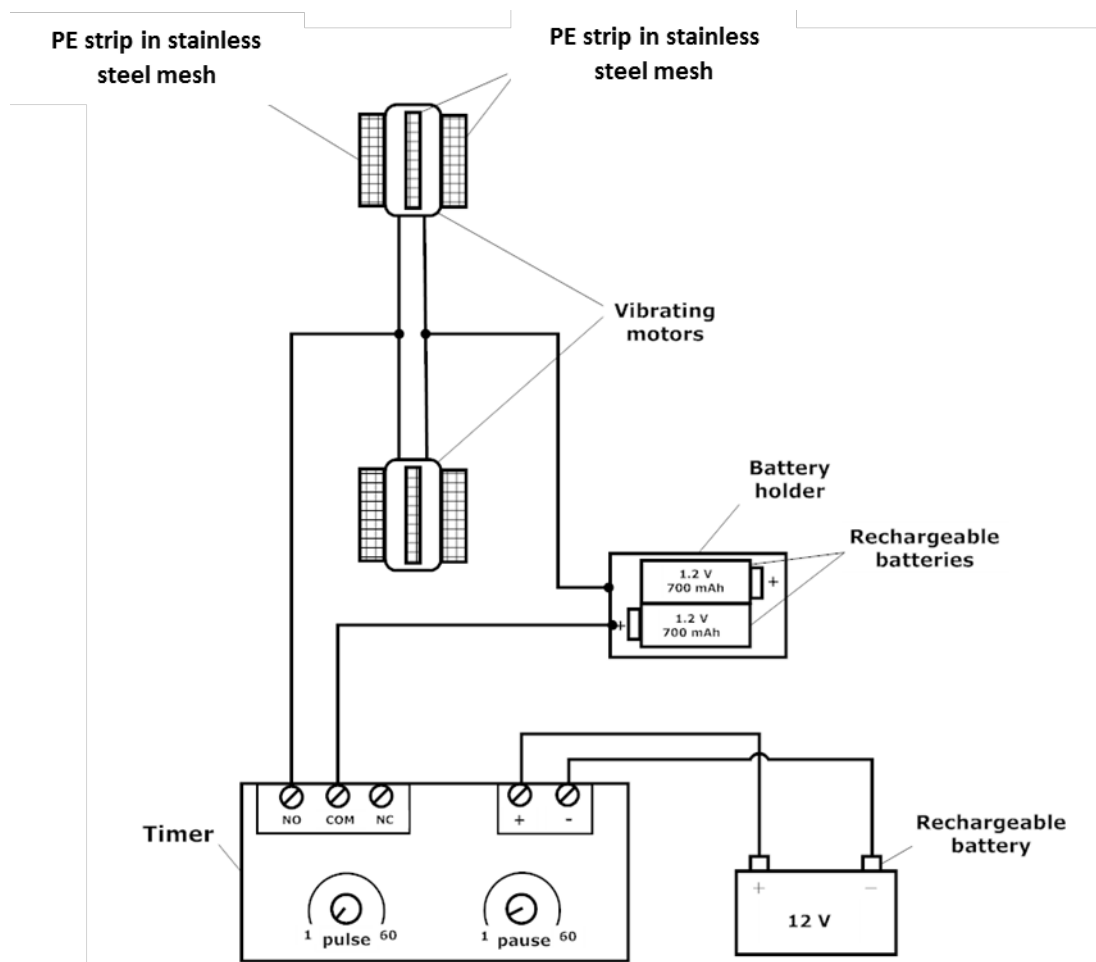


Figure 1.1. Wire Diagram of a Vibrating Passive Sampler.

PE samplers, enclosed in stainless steel mesh were attached to the motors. Two motors were connected in parallel to a timer and a power supply (2 rechargeable batteries 1.2V each). The timers were powered by a 12 V battery.

PAH extraction and analysis. Upon removal from the sediment, PE strips were rinsed with water and wiped with laboratory tissue to remove water and adhering particles. Prior to extraction anthracene-d10 surrogate was added to assess the effectiveness of sample processing, and extracts with lower than 80% surrogate recoveries were discarded. Samplers were extracted with a 1:1 hexane and acetone mixture (3 × 24 h, with sequential extracts pooled). The final extraction volumes were blown down to 1mL using a stream of nitrogen gas. PAHs from sediment were extracted by sonication (EPA method 3550B) and cleaned using activated silica gel (EPA method 3630C).

Four internal standards were added to the final extracts before analysis (1-fluoronaphthalene, p-terphenyl-d14, benzo(a)pyrene-d12, and dibenz(a,h)anthracene-d14). The 16 USEPA priority pollutant PAHs were analyzed in an Agilent 6890 gas chromatograph coupled to an Agilent 5973N MS detector as described in Khalil et al.¹⁶

Modeling uptake of analytes from sediment porewater

A numerical modeling approach was used to describe the mass transfer process involved in the static, vibrating, and well-mixed deployments of passive samplers. The modeling structure for static and vibrating deployments are similar and are described first with respective boundary conditions. Finally, the well-mixed model is described where mass transfer limitation is only in the polymer side.

Static system. Two modeling approaches were implemented to simulate mass transfer of PAHs from sediment particles into porewater, and from porewater into polymer during static deployment. The first approach is based on the one-dimensional diffusion model presented by Fernandez et al.,⁸ but solved numerically. In this model mass transfer within the sediment particle is assumed to be fast and instantaneous equilibrium between sediment particles and porewater is assumed (local equilibrium model). Mass transfer within the polymer and in porewater is described by Fick's 2nd Law of diffusion. Instantaneous equilibrium is assumed at the polymer surface boundary with porewater as done in previous work.^{4,8} This model is explained in more detail in the SI.

The second approach is based on the assumption that mass transfer from sediment particles into porewater is described by first order kinetics.^{4,18} The model was solved using two different hypothesis: 1) All PAHs are associated with the slow desorbing pool in sediment and desorption is characterized by the slow desorption rate constant. 2) All PAHs are associated with the fast desorbing pool in sediment and desorption is characterized by the fast desorption rate constant. First order desorption rate constants were obtained from a study by Ghosh et al.¹⁷, where sediment from a similar manufactured gas plant impacted site was used (see SI).

In a system containing a PE strip with the thickness of $2l_p$ and sediment/porewater with thickness of l_w on both sides, sediment concentration (S) changes following first order kinetics.^{4,18}

$$\frac{\partial S}{\partial t} = k(K_d C_w - S) \quad l_p < x < l_p + l_w \quad \text{and} \quad -l_p < x < -l_p - l_w \quad (1)$$

Where t is time (s), S is chemical concentration in sediment (ng/g), K_d is sediment-water partition coefficient (cm^3/g), k is first order desorption rate constant (s^{-1}) and C_w is chemical concentration in water (ng/cm^3)

For a PE strip with concentration C_{PE} and at point x and time t :

$$\frac{\delta C_{PE}}{\delta t} = D_{PE} \frac{\delta^2 C_{PE}}{\delta x^2} \quad -l_p < x < l_p \quad (2)$$

Where C_{PE} is chemical concentration in PE (ng/cm^3) and D_{PE} is chemical diffusivity in PE (cm^2/s)

The transport equation in porewater with concentration of C_w at point x and time t will be as follows:

$$\frac{\delta C_w}{\delta t} = D \frac{\delta^2 C_w}{\delta x^2} - \left(\frac{\rho}{\varepsilon}\right) \frac{\partial S}{\partial t} \quad l_p < x < l_p + l_w \quad \text{and} \quad -l_p < x < -l_p - l_w \quad (3)$$

Where ρ is sediment bulk density (g/cm³) and ε is porosity (cm³/cm³)

D is the diffusivity in water (D_w) after correction for tortuosity:

$$D = \frac{D_w}{1 - \ln \varepsilon^2} \quad (4)$$

Substituting Equation (1) in Equation (3), the transport equation in porewater can be re-written as:

$$\frac{\delta C_w}{\delta t} = D \frac{\delta^2 C_w}{\delta x^2} - \left(\frac{\rho}{\varepsilon}\right) k(K_d C_w - S) \quad (5)$$

Initial conditions

The polymer was initially clean and porewater was assumed to be in equilibrium with sediment.

$$C_{PE} = 0 \quad -l_p \leq x \leq l_p \quad (6)$$

$$C_{w0} = S_0/K_d \quad l_p < x < l_p + l_w \quad \text{and} \quad -l_p < x < -l_p - l_w \quad (7)$$

Where S₀ is initial chemical concentration in sediment (ng/g) and C_{w0} is initial chemical concentration in water (ng/cm³)

Boundary conditions

Continuity of flux and equilibrium condition was assumed at the PE-water boundary as done in previous work.⁸

$$D_{PE} \frac{\delta C_{PE}}{\delta x_{PE}} = D \frac{\delta C_w}{\delta x_w} \quad x = l_p \text{ and } x = -l_p, \quad t > 0 \quad (8)$$

$$C_{PE} = K_{PEW} C_w \quad x = l_p \text{ and } x = -l_p \quad (9)$$

Where K_{PEW} is the PE-water partition coefficient (cm³/cm³)

Due to symmetry the flux will be zero at the center of the PE sheet. Porewater concentration is equal to the initial concentration far away from the polymer at x=l_p+l_w and does not change over time:

$$\frac{\delta C_{PE}}{\delta x} = 0 \quad x = 0 \quad (10)$$

$$\frac{\delta C_w}{\delta t} = \frac{\delta S}{\delta t} = 0 \quad x = l_p + l_w \quad \text{and} \quad x = -l_p - l_w \quad (11)$$

Vibrating system.

In the vibrating system, when the motor is in pause mode, the mass transfer is similar to the static mode and sediment and porewater concentration in the vicinity of the polymer depletes with time. Every time the motor vibrates, the sediment and porewater in the vicinity of the polymer is mixed up. Our visual observation of the vibration system indicated that the extent of fluidized mixing was at least 1 cm from the surface of the device with pressure waves from the vibration extending to 2-3 cm from the device (SI Figure S1.3). We assumed that this mixing is enough to increase sediment concentration to the initial concentration in sediment (S_0). Porewater concentration right after each vibration pulse will also increase to the initial concentration:

$$C_w = C_{w0} ; \quad S = S_0 \quad l_p < x < l_p + l_w \quad \text{and} \quad -l_p < x < -l_p - l_w, \quad (12)$$

Fully mixed system.

Diffusion in a polymer with thickness of $2l_p$ follows Fick's second law:

$$\frac{\delta C_{PE}}{\delta t} = D_{PE} \frac{\delta^2 C_{PE}}{\delta x^2} \quad -l_p < x < l_p \quad (13)$$

The passive sampler was assumed to be initially clean. Since the system is perfectly mixed, the porewater concentration remains constant and equal to the initial value (S_0/K_d) during the deployment time. The boundary condition is defined as:

$$C_{PE} = K_{PEW} C_{w0} \quad x = l_p \text{ and } x = -l_p \quad (14)$$

The model equations were solved in Matlab using an explicit, finite-difference numerical modeling technique.¹⁹ To check the numerical model, the fractional uptake of chrysene into PE was simulated and the solution was found to be identical to the analytical solution based on Fernandez et al.⁸ Details of parameter estimation, numerical solutions and Matlab codes are provided in the SI.

1.4 RESULTS AND DISCUSSION

Equilibrium PAH concentration in sediment and porewater

The concentrations of the 16 EPA priority pollutant PAHs in sediment are shown in Figure 1.2. The four most abundant PAHs were phenanthrene, fluoranthene, pyrene, and benzo(a)pyrene. The total concentration of PAHs in the sediment was 128 $\mu\text{g/g}$. The 2-4 ring PAHs comprised 60% of the total in sediment. The equilibrium concentrations in PE ($C_{PE,eq}$) were determined by extracting the PE samplers after 56 days of deployment in the fully-mixed PE-sediment system. Another time point measurement of PE concentration after 77 days of deployment confirmed that equilibrium had reached in PE for all PAHs in 56 days (SI Table S3). Both PRCs (pyrene-d10 and phenanthrene-d10) were depleted completely in the fully-mixed exposure in 30 days (SI Figure S1.5). The freely dissolved porewater concentrations were calculated from equilibrium concentration of PAHs in PE and reported values for K_{PEW} ⁵ (Equation 9).

As shown in Figure 1.2, acenaphthene and phenanthrene are the dominant PAHs in porewater. PAHs up to chrysene contributed to 99% of the total porewater concentration at equilibrium.

Toxic units were estimated for each PAH by dividing porewater concentrations by final chronic values (FCVs).²⁰ The total toxic units of 16 PAHs measured in the sediment porewater was approximately 9.33 indicating that PAHs in this sediment likely pose narcosis toxicity to benthic invertebrates.²⁰

PAH uptake in static deployment.

As expected, the uptake of all PAHs was slowest in the static exposure. In fact, none of the PAHs from fluoranthene to indeno(1,2,3,-cd)pyrene reached equilibrium in 56 days of contact. The fractional uptake of benz(a)anthracene, benzo(k)fluoranthene and indeno(1,2,3,-cd)pyrene were only 35%, 11%, and 8%, respectively after 28 days. Previous studies have reported similar slow uptake in a static exposure,¹¹⁻¹³ especially for larger molecular weight compounds. For example, Fernandez et al.¹¹ calculated the fractional equilibration of PCBs into 25 μ m PE by measuring the fractional loss of ¹³C-labeled PCBs after 44 days of field deployment. The average fractional equilibration of penta- and hexachlorobiphenyls from different locations in the field were only 37% and 33%, respectively.

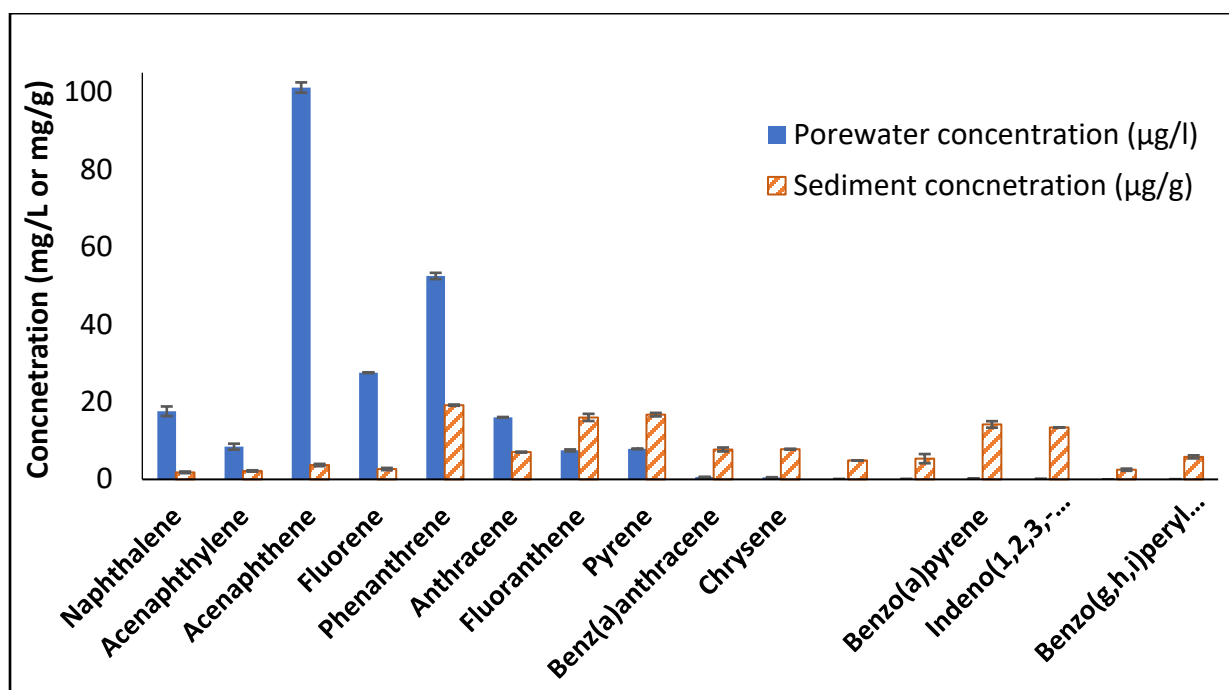


Figure 1.2. PAH Concentration in Porewater (µg/L) and Sediment (µg/g).

Sediment concentrations are mean values from triplicate measurements. Porewater concentrations were obtained using Equation 9 and $C_{PE,eq}$, which are mean values from duplicate measurements of PE concentration after 56 days of exposure in the fully-mixed system.

Effect of vibration on polymer uptake rate. Periodic vibration of the PE sampler resulted in faster uptake compared to static deployment for all PAHs measured. As shown in Figure 1.3, the uptake of chrysene after 56 days was only 40% of equilibrium in static exposure compared to 100% for the vibrating system. Even after 7 days of exposure, the vibrating system reaches 63% of equilibrium for chrysene compared to 20% in the static system. Comparison between the static and vibrating system for several other PAH compounds is shown in Figure 1-4 and SI Figure S1.4.

Both PRCs were lost more than 90% at the first time point of measurement for the vibrating systems and fully mixed systems (SI Figure S1.5), which generally agreed with the uptake of the analogous PAHs. As PRC performance was not the focus of this study, using a full range of high molecular weight PRCs and performing shorter duration measurements of PRC loss are recommended in future work in order to provide a more robust analysis of PRC performance in the vibrating system.

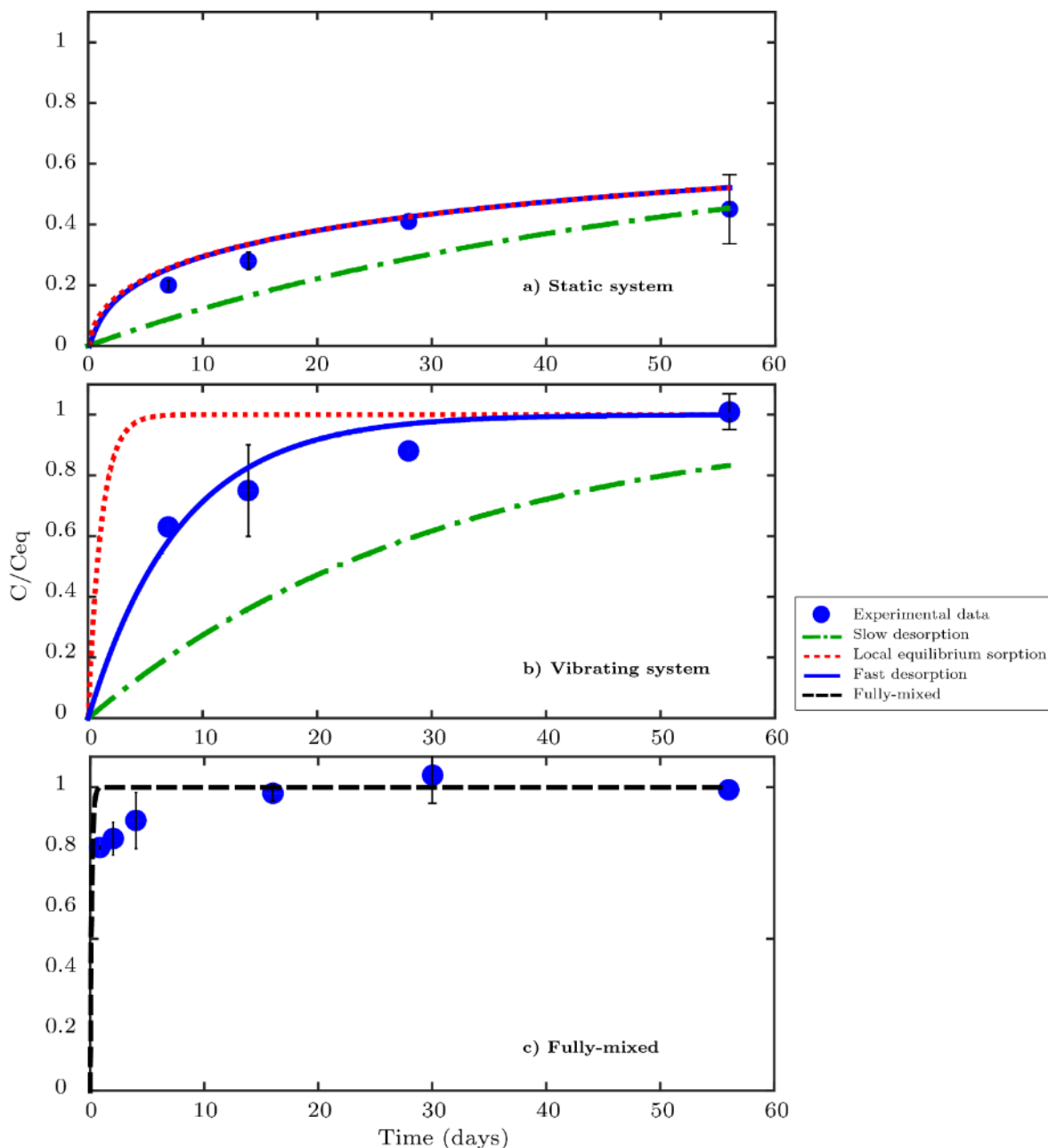


Figure 1.3. Fractional Uptake of Chrysene in PE Passive Sampler in a) Static, b) Vibrating Systems and c) Fully-mixed.

Experimental data have been shown by circles and model simulations have been shown by lines. Note that for the static system, the local equilibrium and fast desorption models overlap.

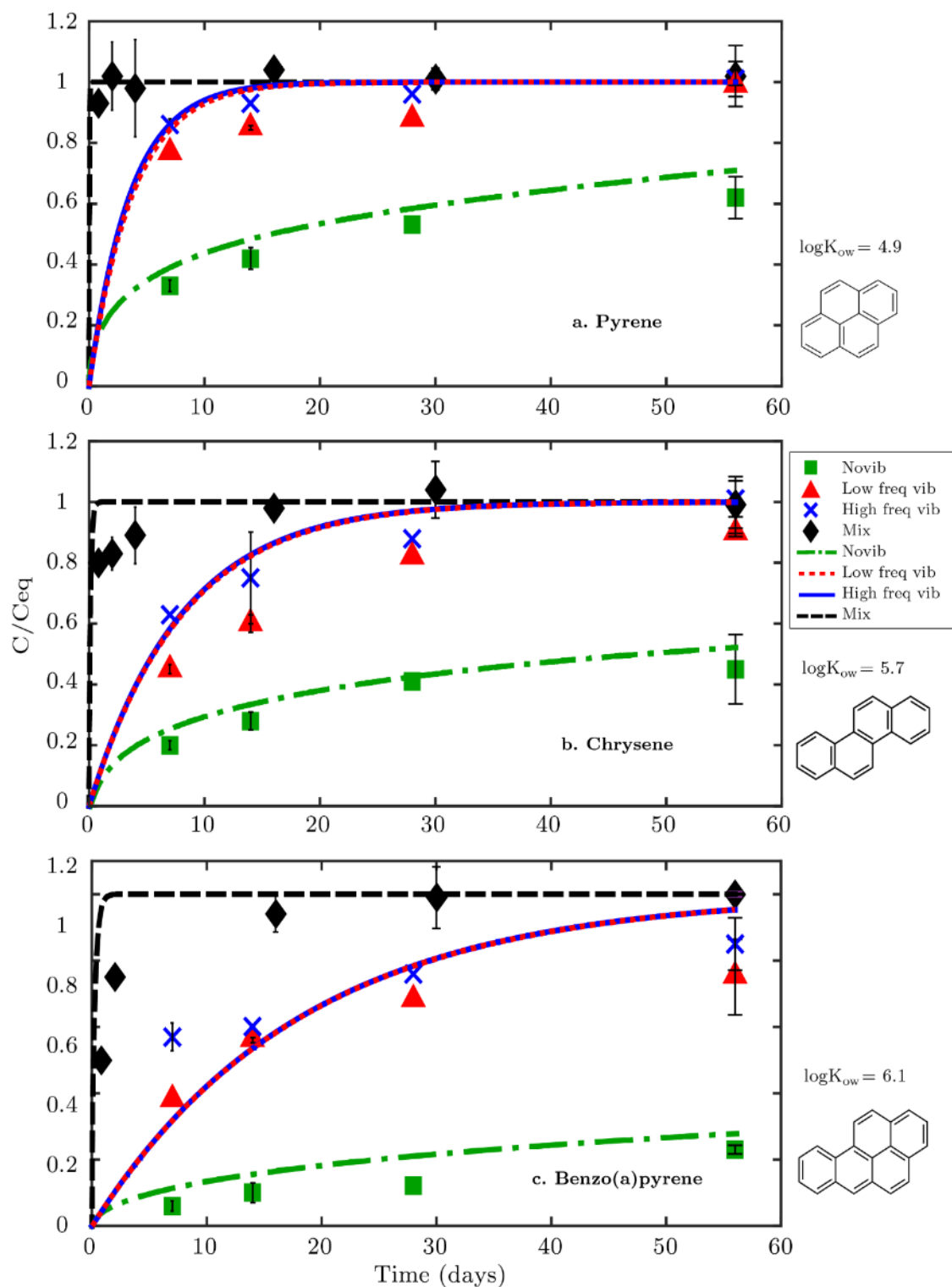


Figure 1.4. Fractional Uptake of a) Pyrene b) Chrysene and c) Benzo(a)pyrene in PE Passive Sampler in Four Differently Exposed Systems.

Experimental data have been shown by circles and fast desorption model simulations have been shown by lines

For PAH compounds less hydrophobic than chrysene (e.g., fluoranthene and pyrene), the static system showed reasonable uptake of close to 70% in 56 days while the vibrating system reached equilibrium during that exposure. When the passive sampler is close to equilibrium, the correction for non-equilibrium is relatively accurate. However, as the kinetics slow down and only a small fraction of equilibrium is achieved in the sampler, the correction for non-equilibrium becomes error-prone.⁹ This is the case for the PAH compounds that are more hydrophobic than chrysene. The improvement over static system was more evident for larger molecular weight PAHs. For example, the measured fractional uptake of benzo(a)pyrene was improved from 6% to 55% in 7 days and from 23% to 90% after 56 days. The fact that vibration was more effective on uptake rate of heavier PAHs can be explained based on the nature of the overall mass transfer resistance in a passive sampler⁶

$$\frac{1}{k_0} = \frac{\delta}{D_w} + \frac{1}{K_{PEW}D_{PE}} \quad (15)$$

Where k_0 is the overall mass transfer rate constant and δ is the diffusion distance.

The first term on the right hand side of Equation 15, describes the sediment-side mass transfer resistance. The large K_{PEW} values of the more hydrophobic compounds makes the second term smaller than the first, thereby making the first term or the water side mass transfer more dominant. The ratio of diffusivities in water and polymer (D_w/D_{PE}) also increases as the compound becomes more hydrophobic. However, K_{PEW} tends to be the dominant factor influencing which side controls mass transfer since K_{PEW} changes over a wider range of values compared to the range where the diffusivity ratios vary for different compounds.²¹ As a result, disrupting the depletion layer (decreasing apparent δ) by means of vibration will be more effective on the overall mass transfer rate of larger molecular weight PAHs. Our experimental data indicated that concentration of larger molecular weight PAHs ($\log K_{ow} > 5.5$) reached more than 50% of their equilibrium concentration in PE within 14 days of deployment in the vibrating system (SI Figure S1.4). Thus, field deployment of passive samplers with periodic vibration will encounter less challenges of non-equilibrium correction for larger molecular weight compounds.

Results from the vibration work demonstrated a great improvement of PE uptake after short exposure times (1-2 weeks). The faster exchange will also allow the use of high molecular weight PRCs to accurately correct for the remaining non-equilibrium in a vibrating system without the need for long exposure times.

Comparison of three modeling approaches in static, vibration and fully-mixed deployments. Figure 1.3-a and 1.3-b demonstrate modeling results for chrysene in static and vibrating systems based on local equilibrium, slow desorption, and fast desorption models. As shown in Figure 1.3-a, in static deployment, overall mass transfer into the polymer is slow and the predictions based on local equilibrium assumption and the fast desorption rate model are indistinguishable. Also, both predictions are close to the observed uptake of chrysene in the static deployment. However, the slow rate of desorption model predicts uptake that is slower than the observed values. Thus, it appears that for modeling static deployments, due to the rate limiting mass transfer through the depletion layer, it is adequate to assume local equilibrium between sediment and water.

For the vibrating system, assuming that the sediment is effectively mixed after vibration, the model predictions based on local equilibrium and fast rate of desorption deviated as shown in Figure 1.3-b. While the fast rate of desorption model prediction is close to the measured uptake of chrysene, the prediction based on local equilibrium greatly over-predicts uptake. The same results were observed for pyrene as indicated in SI Figure S1.6. Thus, it appears that as the depletion layer is disrupted by vibration and mass transfer is enhanced, desorption from sediment becomes limiting and local equilibrium between sediment and water can no longer be assumed. The fast desorption rate adequately predicts uptake while the slow desorption rate still under-predicts uptake in the polymer. Past work has demonstrated that PAH desorption from MGP-impacted sediments is characterized by slow and fast desorbing PAH fractions.¹⁷ However, the overall kinetics for the vibration system appear to be driven by the fast desorption kinetics and not the slow desorption likely because the sediments are not being depleted enough to reach the slow desorption regime.

For the fully-mixed system, a local-equilibrium model was implemented. As shown in Figure 1.3-c, the model agrees reasonably with the observed fast uptake of chrysene and the attainment of equilibrium in the matter of a few days. The fully mixed system brings a large volume of sediment to contribute to the required uptake by the passive sampler and hence the kinetics are fast enough to appear close to instantaneous equilibrium.

Modeling uptake of pyrene, chrysene, and benzo(a)pyrene. Experimental and modeling results for pyrene ($\log K_{ow} = 4.9$), chrysene ($\log K_{ow} = 5.7$) and benzo(a)pyrene ($\log K_{ow} = 6.1$) in static, vibrating, and fully mixed systems are shown in Figure 1.4. Based on the discussion above, only the fast desorption model was used for predicting uptake in static and vibrating systems, and a local equilibrium model was used for predicting the fully-mixed system. As shown in Figure 1.4, the model predictions reasonably agreed with the uptake profiles of the 3 PAHs in all three modes of exposure. For all three PAHs, although there were small differences between the experimental results from 2 min and 5 min pause times (not statistically significant except for pyrene at day 14), the model predicted that there should not be a significant difference between the two (see SI Tables S1.4, S1.5, and S1.6). In the model we assumed that both pulse durations are long enough to mix up the sediment to initial bulk concentration. However, in reality short pulse time (2 seconds) in the low frequency system may not be long enough to satisfy the model assumption.

To better illustrate how the periodic vibration impacts development of the sediment-side depletion layer, the concentration profiles in the sediment and half width of the PE sampler was plotted for chrysene as a function of exposure time. As shown in Figure 1.5 left panel for the static deployment, chrysene in the sediment side is depleted well into 300 μm distance from the PE surface after 20 days. The concentration values for PE plotted in Figure 1.5 has been multiplied with K_{sed-PE} to make the values directly comparable to the sediment concentration. As indicated in Figure 1.5, left panel, the concentration in PE reaches equilibrium with the depleted concentration in the sediment adjacent to the surface in 2 days or less and the mass transfer limitation is moved to the sediment-side depleted layer. Also, after the first few hours of exposure, there is no concentration gradient within the polymer indicating all mass transfer resistance is in the sediment side. In stark comparison, for the periodic vibration deployment, since the sediment side is mixed up at frequent intervals, the deep depletion layer in the sediment side is not able to develop and the mass transfer resistance is limited to a few microns near the polymer surface. In fact, as seen in the 2-day simulation for the concentration gradient within PE in the vibrating system, the model suggests that there is still some polymer-side resistance. As a result, the concentration in PE rises much more rapidly than in the static case.

For the well-mixed system, pyrene uptake is fast and modeled reasonably well by the fully mixed local-equilibrium model (Figure 1.4-a). However, the model is not accurate for early times for the more hydrophobic compounds, especially benzo(a)pyrene (Figure 1.4-c). This could be due to inaccuracy of reported diffusivity in PE, slow desorption from sediment, or inefficient mixing of the system. Inefficient mixing slows the uptake of more hydrophobic compounds since sediment-side mass transfer is dominant for high molecular weight PAHs (as described earlier) and disruption of depletion layer by efficient mixing is more important. Previous studies²² have observed slower uptake of larger PCBs in well mixed sediment-slurry systems and attributed the slow kinetics to inefficient mixing and slow desorption.

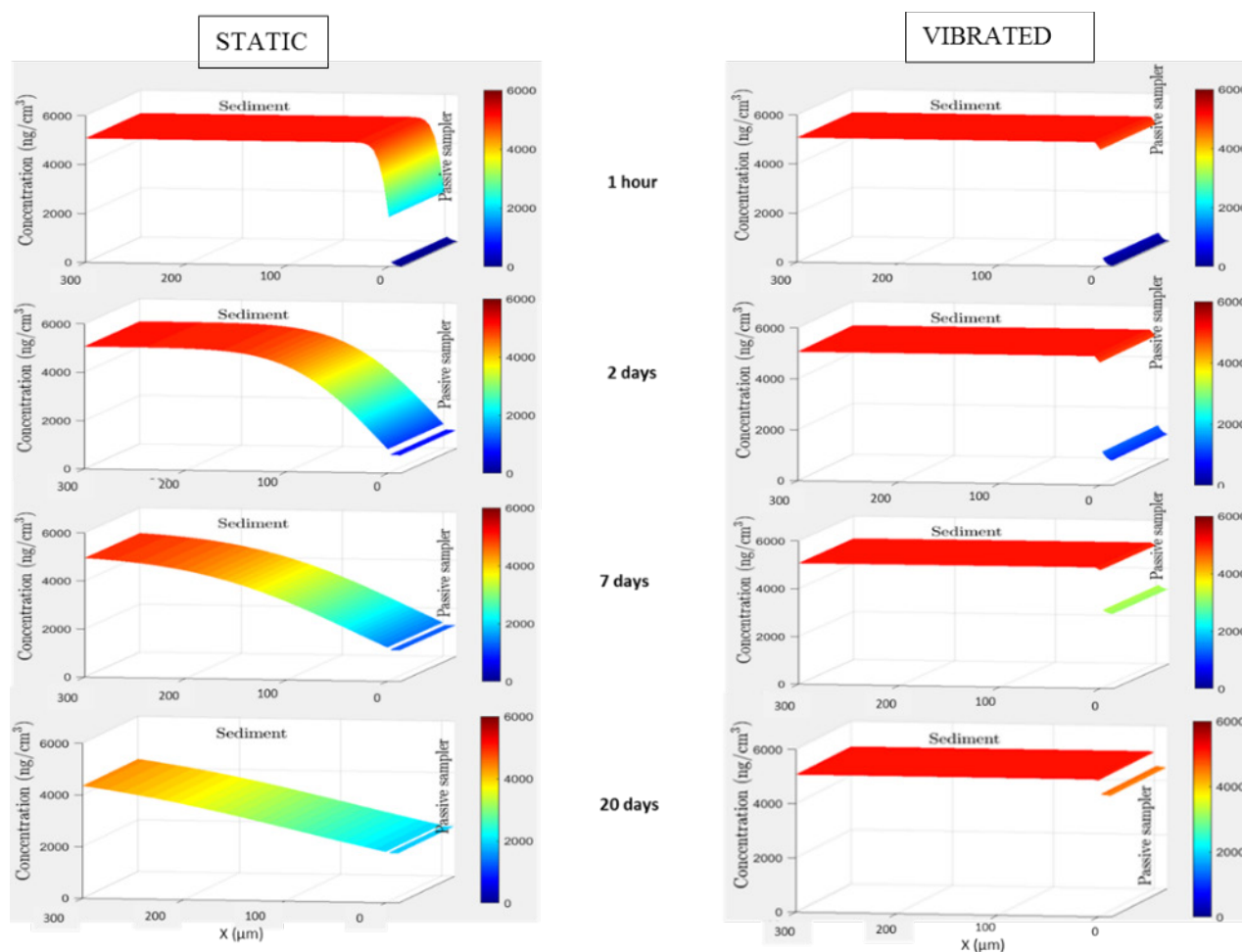


Figure 1.5. Model Simulations of Chrysene Concentration Profile Within PE and in the Sediment Side for Static and Periodic Vibration Deployments.

The values shown on the Y-axis are chrysene concentration in sediment (C_s) and concentration in PE multiplied by sediment-PE partition constant ($C_{PE} \times K_{sed-PE}$).

Optimization of vibration frequency. Results of the vibration model for PE uptake of chrysene was used to test the effect of different vibration frequencies and to optimize power requirement. All vibration frequencies had pulse duration of 5 seconds and varied in pause time.

The modeling results were based on the fast desorption model and pause times were set at: 2 min, 5 min, 6 hour, 1 day, and 5 days (Figure 1.6). Small differences (6% or less) were observed between the 2-min and 6-hour pause models (see SI Table S1.7). Even the 1-day pause model predicted an uptake profile which was not greatly different from the 2 min-pause model. The 5-day pause profile tracked the unmixed profile for the first 5 days, then jumped up to a higher uptake profile as the mixing altered the boundary condition. Although the 5 day-pause model does not show significant improvement over the static system in short deployment times (<7 days), the model still predicts 75% fractional uptake after 28 days. In comparison the fractional uptake of chrysene is only 40% in static system for the same exposure duration. These results indicate that significant improvement over the static system is possible with lower frequencies of vibration (large pause times). Increasing pause time is desirable as there is no energy consumption during the pause time when the motor is not vibrating. In order to optimize pause time, energy consumption was estimated for deploying a vibration system for 15 days and a range of pause times. The fractional uptake of three PAHs (pyrene, chrysene and benzo(a)pyrene) in PE after 15 days was also determined with the model for each pause time and plotted versus energy consumption (SI Figure S1.7). Only 30mWh is required to enhance the fractional uptake of chrysene to 80% in 15 days of deployment. In comparison, a typical AA size NiMH rechargeable battery can provide about 1000 mWh of energy. However, further enhancement of fractional uptake in PE from 80% to 82% increases the energy requirement to 2340mWh. This is also evident from Figure 1.6 where we see little enhancement of uptake when the pause time is reduced below 6 hours.

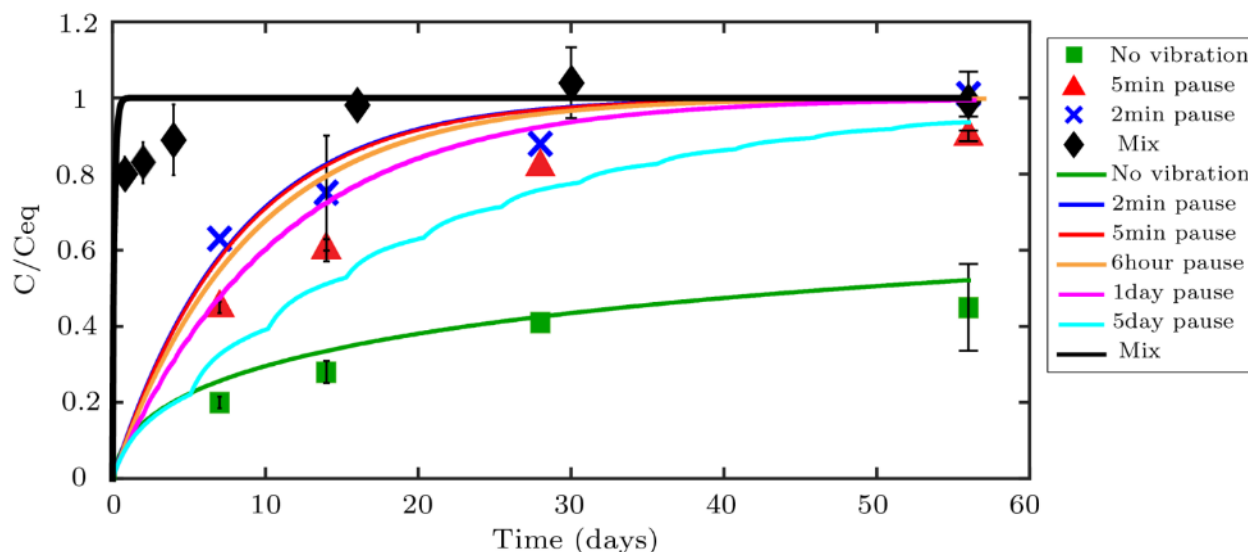


Figure 1.6. Model Simulation of Chrysene Uptake in Vibrating System with Different Pause Times of Vibration.

Lines show the fast desorption model simulation and bullets show the experimental data.

Implications. A recent review article on passive sampling by Booij et al.²³ concluded that options to reduce time for equilibrium are limited to manipulation of area/volume ratio of sampler, choice of sampler material, and flow rate. Past work has led to significant optimization of the physical aspects of the passive samplers, yet attainment of equilibrium remains difficult for strongly hydrophobic compounds especially for in situ sediment porewater measurements.

Also, there is little that can be done in the sediment environment to enhance porewater velocity. This study advances the practice of passive sampling by addressing a key bottleneck through the novel introduction of periodic vibration in the sampling platform to disrupt the depletion layer that develops in the sediment side and slows mass transfer. Through mass transfer modeling we also provide a mechanistic interpretation of how periodic vibration enhances the approach to equilibrium. While PRC corrections have allowed extension of passive sampling to compounds that do not achieve equilibrium during a reasonable period of deployment, the introduction of vibration greatly enhances approach to equilibrium, reduces deployment times, and extends the use of passive sampling in conjunction with PRCs to strongly hydrophobic compounds as shown for benzo(a)pyrene in this study. Further development is necessary to build robust prototypes and perform tests in the field. The size of the devices and motors may also need to be increased to enable deployment of larger passive samplers to target low concentrations in sediment.

1.5 ACKNOWLEDGEMENTS

The authors acknowledge financial support from the Department of Defense Strategic Environmental Research and Development Program (Project # ER-2540).

1.6 SUPPORTING INFORMATION:

Additional information is available on: 1) experimental setup, 2) details of the mathematical models used, 3) Matlab code for the numerical solution, 4) additional figures for high molecular weight PAHs, PRC desorption, energy usage, and statistical interpretation of the data. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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2.0 CHAPTER 2: ANALYSIS OF MEASUREMENT ERRORS IN PASSIVE SAMPLING OF POREWATER PCB CONCENTRATIONS UNDER STATIC AND PERIODICALLY VIBRATED CONDITIONS. (PUBLISHED PAPER)

M. Jalalizadeh and Upal Ghosh. *Environ. Sci. Technol.* 51, 7018-7027, 2017.

2.1 ABSTRACT

Although the field of passive sampling to measure freely dissolved concentrations in sediment porewater has been sufficiently advanced for organic compounds in the low- to mid-range of hydrophobicity, in situ passive sampling of strongly hydrophobic polychlorinated biphenyls (PCBs) is still challenged by slow approach to equilibrium. Periodic vibration of polyethylene (PE) passive samplers during exposure has been previously shown to enhance the mass transfer of polycyclic aromatic hydrocarbons (PAHs) from sediment into PE. Herein, we used a new vibrating platform, developed based on our earlier platform design, to demonstrate the effectiveness of periodic vibration for large molecular weight PCBs such as hexa-, hepta-, and octachloro-PCBs. Uptake of PCBs in PE after 7, 14, 28, and 56 days under different vibration modes was compared to that under static and mixed laboratory deployments. All PCBs reached within 95 – 100% of equilibrium after 56 days of deployment in the system vibrated briefly every 2 min, while none of the congeners achieved more than 50% of equilibrium in static deployment for the same period. Periodic vibration also increased the dissipation rate of four performance reference compounds (PRCs) from passive samplers. Higher fractional loss of PRCs and closer approach to equilibrium in the vibrated deployment resulted in estimation of corrected porewater concentrations that were statistically indistinguishable from the true equilibrium values even after a short 7-day deployment. Porewater concentrations of the strongly hydrophobic PCB congeners were overestimated by up to an order of magnitude in the static passive sampler after the same deployment time.

2.2 INTRODUCTION

Reliable bioavailability measurements of hydrophobic organic compounds (HOCs) such as polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) are needed for improved sediment risk assessments, proper selection of remedy, and post-remediation monitoring. Several studies have shown that freely dissolved concentrations (C_{free}) of organics in sediment porewater can be related to toxicity and bioaccumulation.^{1,2} Passive sampling for the measurement of C_{free} of organic pollutants in sediment porewater has emerged as a very promising approach, but in situ measurements are challenged by slow mass transfer of strongly hydrophobic compounds. The slow mass transfer results in under-equilibrated passive sampler measurements that need to be corrected for determining C_{free} . For a passive sampler deployed in stagnant sediment, mass transfer of the contaminants is controlled by transport through the polymer and/or sediment phase, depending on the sediment sorption characteristics and diffusivity of the pollutants in sediment porewater and polymer.³ For HOCs, the overall kinetics is often controlled by transport through the sediment phase.³⁻⁵ Under this condition, correction for non-equilibrium requires estimation of site specific sorption characteristics (e.g., retarded diffusion). The previously developed methods determined site-specific sorption characteristics from the loss kinetics of selected performance reference compounds (PRCs) and calculated corrected C_{free} from non-equilibrium polymer concentrations.^{3,6} However, even with these methods, estimating C_{free} of strongly hydrophobic compounds is prone to errors. Extrapolations based on the loss kinetics of strongly hydrophobic PRCs is challenging, since long exposure times are required to measure PRC levels that are with statistical significance different from the initially spiked PRC levels.⁶ For example, Choi et al.⁴ observed only 20% reduction in concentration of PCB 192 from 17 μm PE after 265 days of deployment in sediment. Also, high imprecisions involved in the measurement of fractional loss of PCB 192, caused a wide confidence interval for the estimated sediment sorption characteristics for this congener. In addition to the mentioned challenges with using the PRC-correction methods, it is not clear yet whether the retardation factor for HOCs that diffuse from sediment into the passive sampler is identical to the retardation factor for the PRCs that diffuse out of the passive sampler and into the sediment. Apell and Gschwend⁵ argued that PCBs exhibit the same retardation factor through the sediment when diffusing into and out of PE passive samplers. However, anisotropic exchange kinetics of PCBs and DDTs has been observed for PE and PDMS passive samplers in more recent studies.^{4,7} The mechanisms involved in anisotropic exchange kinetics are not well understood, but possibly depend on the sediment properties.⁴ Enhancing the overall kinetics by reducing the mass transfer resistance in sediment overcomes the mentioned shortcomings of PRC-correction methods. This assumption is tested further in the present study.

In our previous work,⁸ we addressed the challenge of mass transfer limitation by using a vibrating platform for the deployment of passive sampling devices in sediments. We demonstrated through laboratory measurements and numerical modeling that the platform can greatly enhance the rate of mass transfer of 16 PAHs ($3.4 < \log k_{\text{ow}} < 6.1$) into PE passive samplers by disrupting the formation of a depletion layer in the vicinity of the polymer. Dissipation amounts of pyrene-d10 and phenanthrene-d10 ($\log k_{\text{ow}} \cong 5$) from PE in the vibrating system were high and identical to those in the well-mixed system. Correction for non-equilibrium is expected to become more accurate with higher fractional loss of PRCs.⁹ However, not enough data were available to demonstrate the accuracy of this hypothesis. While a numerical model showed that significant improvement over static deployment is possible with very low frequency of vibration of the motors (5 d pause and 5 s pulse), this was not confirmed experimentally.

The objectives of the present study were to 1) evaluate the effectiveness of periodic vibration for passive sampling of strongly hydrophobic PCBs, and 2) carefully evaluate the errors associated with PRC corrections for different deployment modes. PCB-impacted sediments from the field were used in laboratory mesocosms in the present study. The uptake rates of PCBs into PE under two differently vibrated passive sampling modes (low and high frequency) were compared to the uptake under static and mixed modes. A numerical model based on Jalalizadeh and Ghosh⁸ was used to explain the diffusion process of PCBs from sediment particles into the sediment porewater, and from porewater into passive samplers. In addition, PRC-corrected equilibrium aqueous concentrations using static and vibrating passive samplers were compared to the true equilibrium concentrations, determined from mixed sampler deployments.

2.3 MATERIALS AND METHODS

Materials. Low density polyethylene (LDPE) sheets (25 μm thickness), manufactured by Poly-America (Grand Prairie, TX, USA) were purchased from the Home Depot (local store in Baltimore, MD). PCB stock solutions were purchased from Fisher Scientific (Pittsburg, PA, USA). Cylindrical vibrating motors with a diameter of 24 mm and length of 31 mm were purchased from Precision Microdrives (London, United Kingdom). The motors operated at the rated voltage of 3 V and operation current of 190 mA. Their rated vibrating speed was 5000 rpm and the normalized amplitude of vibration (measure of acceleration caused on a 100 g object) was 10 G. Pulse-pause timers (model 60H) used to control the vibration motors were purchased from Velleman Inc. (Fort Worth, TX). Prior to use, PE sheets were cleaned by soaking twice in hexane/ acetone (50/50 vol./vol.) and leaving on a shaker for 24 h each time. Clean PE sheets were cut into 20 mg (2cm $\times$ 5cm) strips. PE strips were then soaked in a 80:20 methanol/water solution containing four PRCs (2,4,5-trichlorobiphenyl (PCB 29), 2,3',4,6-tetrachlorobiphenyl (PCB 69), 2,2',4,4',6,6'-hexachlorobiphenyl (PCB 155), and 2,3,3',4,5,5',6-heptachlorobiphenyl (PCB 192)). The PRC solution was allowed to equilibrate for 15 days on an orbital shaker. After impregnation with PRCs, the strips were transferred into deionized water and left on an orbital shaker overnight to remove the methanol from PE strips. Upon removal from water, three strips were extracted immediately in hexane (3 $\times$ 24 h) to determine the initial PRC concentration.

Source of sediments. PCB contaminated sediment samples from Site 102 Abraham's Creek were used in this study. The site is located in the Marine Corps Combat Development Command (MCCDC) military training facility in Quantico, Virginia, 35 miles south of Washington, D.C.

Vibrating platform. The vibrating platform is an improvement over our earlier design⁸ with a larger frame and a more powerful motor that can house enough passive sampler to enable measurement of low levels of porewater PCB concentrations in sediment. The platform consisted of a copper pipe section, inside which the motor was located and was fabricated with assistance from the UMBC machine shop (Figure S2.2). Four fins made of copper plates and meshes were attached radially to the copper pipe. The copper wire mesh fins were designed as pockets that could hold PE sheets sandwiched within. A 20 mg PE strip (prepared as discussed above) was placed inside each pocket and the open edge was sewn with copper wire.

In situ vibrated passive sampler setup. Two platforms were connected in parallel to a timer and a power supply (2 rechargeable batteries 1.2 V, 700 mAh each). The timers were powered by a 12 V power supply and were programmed to control motor vibration duration and frequency.

Two experiments were conducted in the lab in order to measure the uptake rate of PCBs into PE under different deployment modes. In experiment 1, PE sheets were deployed in sediment under static, mixed, and high frequency vibrating modes. In experiment 2, PE sheets were deployed under static and low frequency vibrating modes. The pulse duration of vibrating motors was 5 s and the pause period was 2 min and 5 d in the high and low frequency vibrating systems, respectively. Details of experimental set up are as follows:

Experiment 1- The sediment was mixed with DI water containing 200 mg/L sodium azide to make a slurry with weight ratio of 1:2 (dry sediment/water). For the mixed exposure, three wide mouth jars with Teflon-lined lids were prepared. The sediment-water slurry (500 mL) and two of the 20 mg PE samplers were transferred into each jar. The ratio of PE to sediment mass in each jar was selected to reduce PCB depletion from sediment to <1% at equilibrium based on the guideline provided in Ghosh et al.¹⁰ The jars were placed on a rotary agitator and tumbled at a speed of 28 rpm. The rest of the sediment slurry was placed in two large glass trays (60 cm×10 cm× 10 cm). Three motors were placed inside the sediment in the trays (two of the motors were placed in one tray with 10 cm separation to prevent influencing each other). The timer was programmed to vibrate the motors with a pulse period of 5 s and pause period of 2 min. Twelve additional PE samplers with a mass of 40 mg each were enclosed in stainless steel mesh without motors and were placed inside the same trays in a static mode at least 10 cm away from the vibrating motors and 5 cm apart from each other to simulate a static system. The trays were then covered with aluminum foil. PE strips were removed from the mixed, static, and vibrating systems and analyzed for PCBs and PRC compounds after 7, 14, 28 and 56 days. At each time point, triplicate strips were collected from each system for extraction and analysis.

Experiment 2- PE deployment under static and vibrating modes was repeated in a slurry made with fresh portion from the same sediment as discussed. This time the motors vibrated with the low frequency of 5 s pulse every 5 days. PE strips were collected in triplicates from static and vibrating systems and analyzed for PCBs after 7, 14, 28 and 56 days.

PCB extraction and analysis. Upon removal from the sediment, PE strips were rinsed with water and wiped with laboratory tissue to remove water and adhering particles. Prior to extraction, PCB congeners 14 and 65 were added as surrogate standards to assess the effectiveness of sample processing, and results with lower than 80% surrogate recoveries were discarded. Samplers were extracted in 30 mL hexane (3 × 24 h, with sequential extracts pooled). The final extraction volumes were blown down to 1 mL using a stream of nitrogen gas. Sediment PCBs were extracted by sonication (EPA method 3550B). Final extracts from passive samplers and sediment were cleaned using deactivated silica gel (EPA method 3630C). Two internal standards were added to the final extracts before analysis (PCB congeners 30 and 204). PCBs were analyzed in an Agilent 6890N Gas Chromatograph with an electron capture detector (ECD) based on analytical method described in Beckingham and Ghosh.¹¹ The analyzed PCB congeners are shown in the Supporting Information Table S2.1.

PCB desorption study. The desorption rates of PCBs from sediment into water were measured based on procedures in Ghosh et al.¹¹ Briefly, Tenax beads (0.5 g) and sediment sample (5 g) were added to 12-mL glass vials. DI water (10 mL) containing sodium azide (1 g/l) was added to each vial. The vials were placed on a rotary agitator and tumbled at 28 rpm. At sampling times of 2 h, 4 h, 8 h, 12 h, and 48 h the sediment was allowed to settle and Tenax beads to float up.

Tenax beads were scooped out from each vial and a fresh portion was added. The Tenax beads were dried with anhydrous sodium sulfate, spiked with surrogate standards, and extracted by adding three volumes of 15 mL 50/50 (v/v) hexane-acetone in a 20-mL vial and shaking horizontally on a rotary shaker for 24 h. The final extraction volumes were blown down to 1 mL using a stream of nitrogen gas and were cleaned using deactivated silica gel (EPA method 3630C). The extracts were then analyzed for PCBs using GC-ECD as described above. A two-compartment model¹² was used to describe the desorption kinetics of PCBs from sediment particles into porewater. This model estimates the desorption kinetics of HOCs out of sediment particles based on the assumption that the contaminants are associated with fast and slow desorbing pools in sediment (see Supporting Information for more details). The model was fitted to the normalized desorption data for PCB 128, 183, and 194 in order to find the desorption rate constants (Supporting Information Figure S3).

PRC correction for non-equilibrium. We used the graphical user interface (GUI) by Tcaciuc et al.¹³ to calculate the extent of equilibrium of target PCBs from PRC losses. This GUI is developed based on the mass transfer model presented in Fernandez et al.⁶ PRC losses in static and vibrating systems were used to determine the extent of equilibrium of target PCBs in the corresponding systems. PCB and PRC concentrations were measured in triplicates and PRC losses from each PE strip were used to correct for nonequilibrium in the same strip.

Modeling uptake of analytes from sediment porewater. Mass transfer models described in Jalalizadeh and Ghosh, 2016⁸ were employed to describe PCB diffusion from sediment particles into porewater, and from porewater into the polymer under static, vibrated, and mixed modes. Briefly, for static deployment mass transfer within the polymer and in porewater was described by Fick's 2nd law of diffusion. Instantaneous equilibrium was assumed at the polymer surface boundary with porewater. PCB desorption from sediment particles into porewater was assumed to follow first order kinetics, and all PCBs are associated with the fast-desorbing pool in sediment. The diffusion model with the assumption of instantaneous equilibrium between sediment particles and porewater (local equilibrium model) adequately predicted the uptake in PE in a static system in some previous work.⁶ However, local equilibrium cannot be assumed in a vibrating system⁸ because mass transfer from sediment becomes limiting due to disruption of the depletion layer by vibration. For example, we showed that the overall kinetics of PAHs for the vibrating system was driven by the fast desorption kinetics and not the slow desorption, likely because the sediments are not depleted enough to reach the slow regime. The fast desorption rate constants determined from PCB desorption study were used for model simulation in the present study.

For the mixed system, mass transfer was assumed to be limited by the polymer side. Since sediment is perfectly mixed, porewater concentration remains constant and equal to the initial value during deployment time. In addition, local equilibrium was assumed between sediment particles and porewater as continuous mixing brings large volume of sediment to the vicinity of the polymer and kinetics are fast enough to appear close to instantaneous equilibrium.

Model equations were solved in Matlab using an explicit, finite-difference numerical modeling technique.¹⁴ The equations and the details of parameter estimation, numerical solution, and Matlab codes are provided in the Supporting Information.

2.4 RESULTS AND DISCUSSION

PCB Concentration in Sediment. As shown in Figure S2.1, hexa-, hepta-, and octachloro- PCBs were the most abundant homologs in the sediment. Mono- and dichloro- PCBs were not detected, and the total PCB concentration was 88 ng/g in dry sediment. The sediment had a total organic carbon content of 2.7%. This sediment was found to be suitable for the present study because our target homologs (hexa to octachloro-PCBs) were dominant. The concentrations of individual PCBs in sediment are reported in the Supporting Information Table S2.1.

True equilibrium concentration. In the mixed system, no change in concentration in the PE was observed for any of the congeners after 28 days (PE concentrations after 28 and 56 days of exposure were not significantly different as shown in Supporting Information Table S2.4). Thus, PCB concentrations in PE from the mixed system after 56 days of exposure were taken as the equilibrium concentrations for all PCB congeners and used to calculate fraction equilibrium for other modes of deployment.

Effect of high frequency vibration on PCB uptake into PE. The uptake profiles of six PCB congeners are compared in static, vibrated, and mixed systems in Figure 2.1. The congeners shown in Figure 2.2 were chosen to represent the dominant congener within each homologue group with three to eight chlorine atoms. The remaining detectable congeners are shown in Supplemental Figures S4-S6. Since measurements of PCB uptake into PE in the static system from experiment 1 and 2 were not significantly different for all PCBs (Supporting Information Tables S2 and S3), only the results from experiment 1 are shown for the static deployment. PCBs had very slow uptake rates into PE in the static exposure system especially for penta and higher chlorinated PCBs. Periodic vibration of the PE sampler every two minutes enhanced the fractional uptake of all congeners compared to the static deployment. For example, after 28 days of deployment, the fractional uptake (concentration in PE (C_{PE}) at a specific time, divided by the true equilibrium C_{PE}) of PCB 99 (penta), PCB 153 (hexa), PCB 187+182 (hepta), and PCB 203+196 (octa) were 37%, 24%, 23%, and 22%, respectively in the static system compared to 100%, 100%, 73%, and 65% in the 2-min-paused vibrating system.

All PCBs reached greater than 95% of equilibrium after 56 days of deployment in the 2-min-paused vibrating system while none of the congeners reached to more than 50% of equilibrium in static deployment for the same period. For example, the uptake of PCB 201 after 56 days was only 30% of equilibrium in static exposure compared to 100% in the vibrating system. Even after 7 days of exposure, the vibrating system reaches 35% of equilibrium for PCB 201 compared to 16% in the static system. Thus, with vibration it is apparent that in situ measurements of the full range of PCB congeners in sediments would approach high fraction equilibrium.

Effect of vibration with low frequency on PCB uptake into PE. The fractional uptake of all PCBs in the 5-d-paused vibrating system improved by a factor of 1.5 to 2 over the static system after 28 days (Figure 2.1 and Supporting Information Figures S2.4-S2.6). However, PCBs reached only 30% to 60% of equilibrium in the 5-d-paused vibrating system, except for PCB 31, PCB 70+76, and PCB 185 that reached to approximately 70%. These results indicate that the pause time between vibrations need to be less than 5 days in order to improve the uptake of larger molecular weight PCBs (hexa, hepta, and octachloro-congeners) to more than 60% in 28 days.

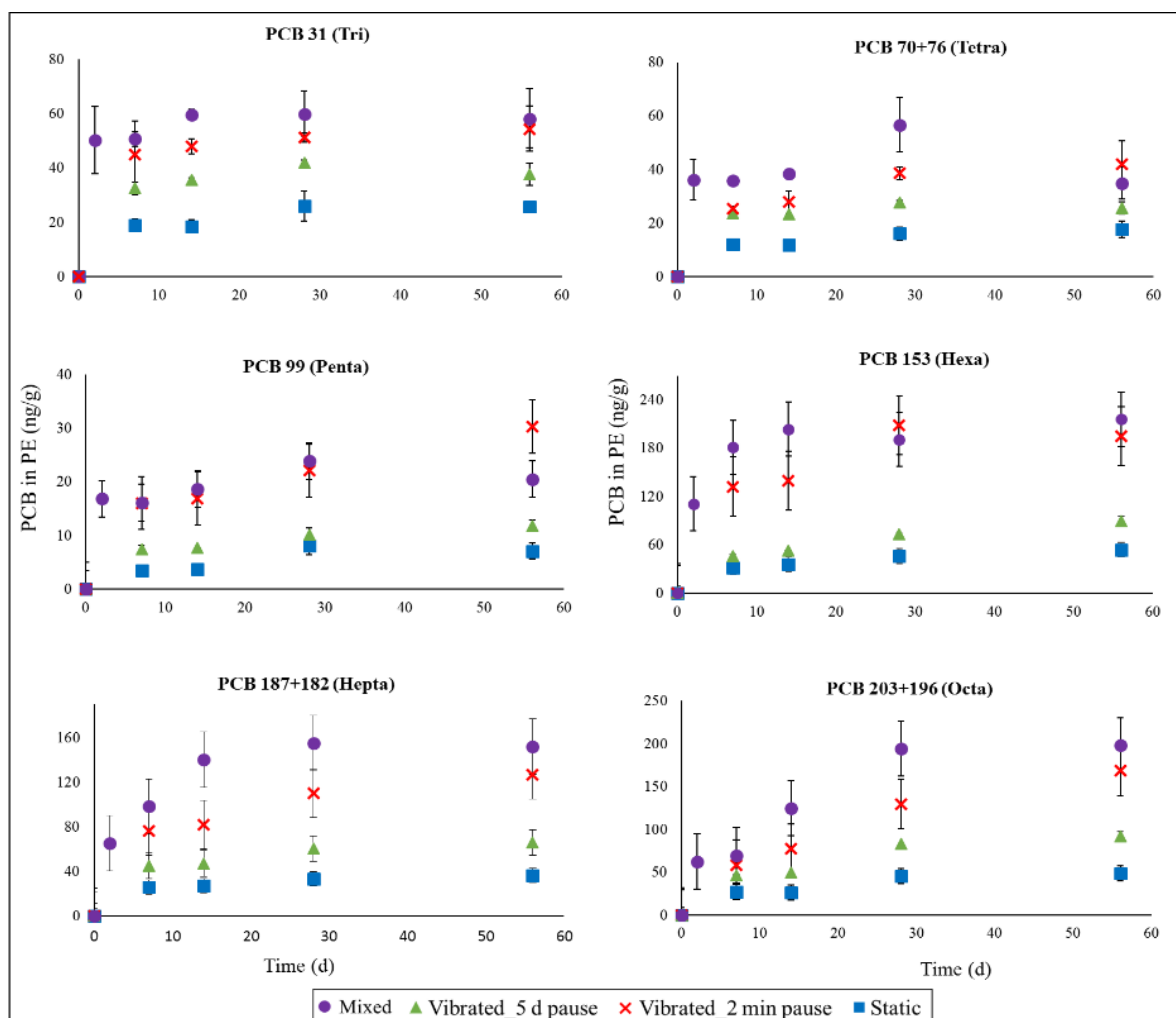


Figure 2.1. Comparison of Uptake Profile of PCBs Into PE in Static, Vibrated, and Mixed Systems.

Error bars represent the mean $\pm$ one standard deviation ($n=3$).

Effect of vibration on PRC loss from PE. The fraction of PRC remaining in PE (f_{PRC}) was measured for the four PRCs in static, vibrating, and mixed systems (Figure 2.2). The fractional losses ($1-f_{\text{PRC}}$) of lower molecular weight PRCs PCB 29 and PCB 69 in the static system were 55% and 46% respectively after 28 days of deployment. However, both PCBs were 100% dissipated from PE after the same exposure time in the high frequency (2 min-paused) vibrating system. The effect of vibration on PRC loss rate was more evident for PCB 155 and PCB 192. For example, the fractional loss was improved over the static deployment from 22% to 87% for PCB 155 (hexachloro-congener), and from 12% to 63% for PCB 192 (heptachloro-congener) after 28 days. As shown in Figure 2.2, f_{PRC} for PCB 29 and PCB 69 were nearly identical in high frequency vibrating and mixed exposures. In fact, more than 95% of both PRCs were lost in the vibrating system only after 7 days of exposure. The difference in f_{PRC} between high frequency vibrating and mixed systems was larger for more hydrophobic PRCs (PCB 155 and PCB 192). However, the fractional losses of these PRCs were still reasonably large in the high frequency vibrating system (63% after 28 days and 80% after 56 days for PCB 192).

The measured f_{PRC} values in the static system from experiment 1 and 2 were identical for all PRCs as compared in the Supporting Information Tables S2.5 and S2.6. Thus, only the results from experiment 1 are shown for the static deployment in Figure 2.2. As indicated in the figure, vibration with low frequency (5-d-paused) was not as effective in improving the dissipation rate of high molecular weight PRCs. For example, the fractional losses of PCB 29 and PCB 69 were increased to approximately 70% after 28 days in the low frequency vibrating system. However, the fractional loss was less than 60% for PCB 155, and only 25% for PCB 192.

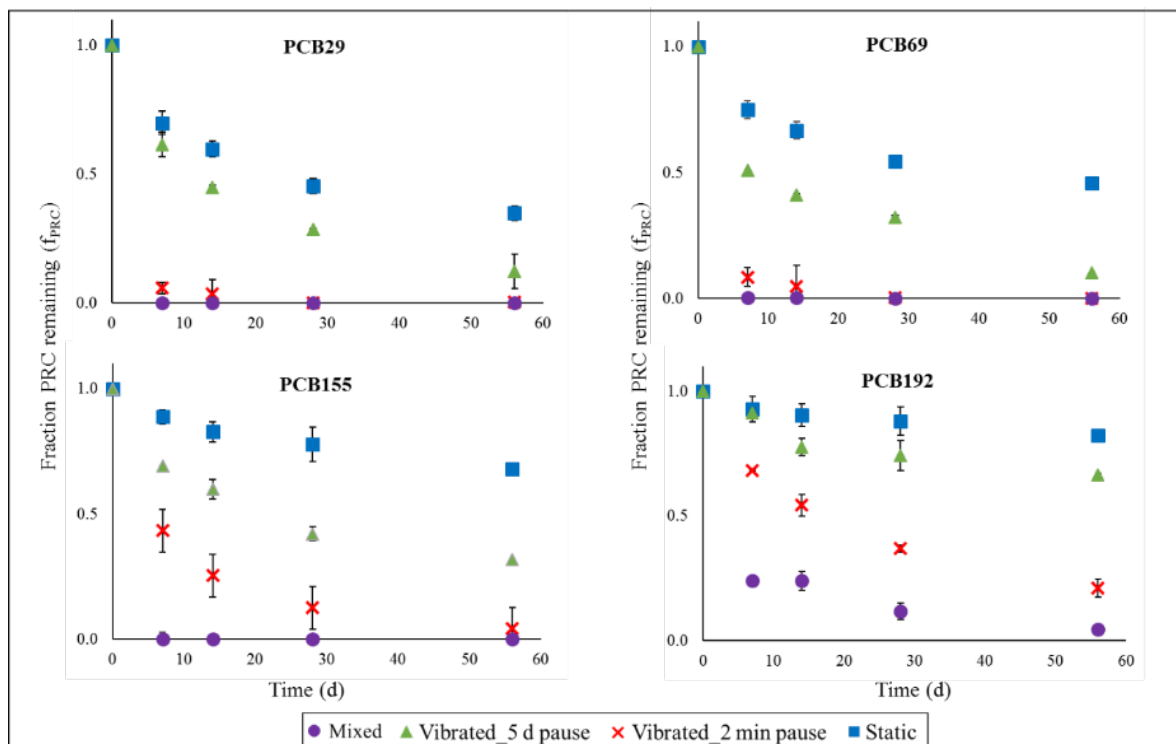


Figure 2.2. Comparison of Remaining PRC Fractions in PE (f_{PRC}) in Static, Vibrated, and Mixed Systems.

Error bars represent the mean $\pm$ one standard deviation ($n=3$).

Modeling the uptake of PCBs. Experimental and modeling results for PCB 128 (hexa), PCB 183 (hepta), and PCB 194 (octa) in static, vibrating, and mixed systems are shown in Figure 2.3. As described in the modeling section, sediment desorption rate constants are required for the modeling of mass transfer in the vibration system. The measured desorption rate constants (k_f) for the three PCB congeners were in the range of 2.4 to 2.8 d^{-1} (Supporting Information Table S9). The measured k_f values are in the same range as the values reported by Cornelissen et al.¹⁵ for sediments from Lake Oostvaardersplassen (Netherlands). However, our measured rates are approximately one order of magnitude larger compared to the reported rates by Zimmerman et al.¹⁶ for sediments from Hunters Point (CA) and those reported by Sun and Ghosh¹⁷ for sediments from Grasse River (NY). As shown in Figure 2.3, modeled uptake in PE generally had good agreement with the measured uptake of all three PCBs in static and vibrating systems with low and high frequency of vibration. This is especially noteworthy because the model uses parameters that have been independently measured or obtained from the literature (Supporting Information Table S2.7).

The mixed model over-predicted the earlier time point measurements (Figure 2.3), likely due to incomplete mixing of the sediment. While it is often assumed that a slurry of sediment in a tumbled jar is well-mixed, depending on the fluidity of the slurry, it is possible to have less than required relative movement between the passive sampler and sediment.

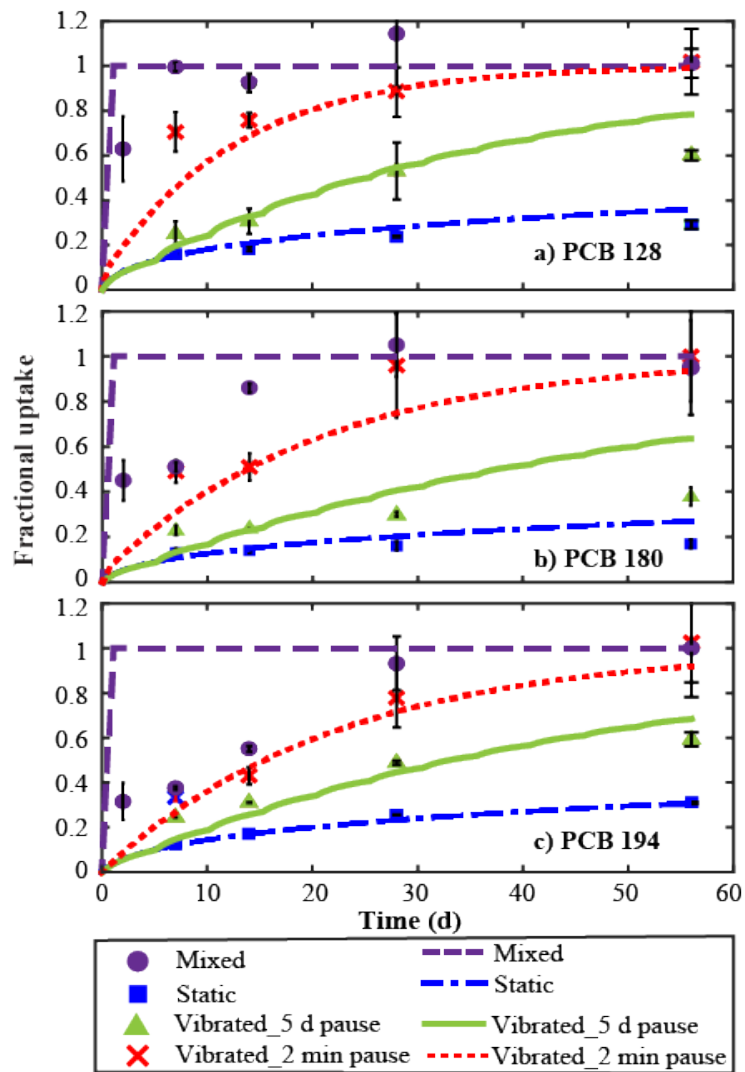


Figure 2.3. Fractional Uptake of PCB 128 (a), PCB 180 (b), and PCB 194 (c) in PE Passive Sampler in Four Differently Exposed Systems.

Experimental data are shown by symbols, and fast desorption model simulations are shown by lines. Error bars represent the mean $\pm$ one standard deviation ($n=3$).

This could cause inefficient breakup of the depletion layer⁸ that forms around the polymer. Deviations between the model simulation and experimental data for the mixed deployment were more obvious for more hydrophobic PCBs (PCB 183 and PCB 194), as mass transfer of these compounds is mostly controlled by the sediment side.⁸ Arp et al.¹⁸ also observed slow diffusion of higher molecular weight PCBs from mixed sediment slurry into POM. The authors argue that the reason for slow mass transfer of the larger molecular weight PCBs in their study could be slower desorption from the less available subdomains of the sediment.

Prediction of equilibrium concentration based on static vs. shaken deployment. Measured PCB concentrations in PE using the static and vibration deployments were corrected for non-equilibrium based on the fractional losses of PRCs. Since four PRCs were available for use in correction, the method by Fernandez et al.⁶ was used as described in the methods section. PE equilibrium concentrations were also determined from the 56-day mixed deployment. To compare the accuracy of the equilibrium estimations, the estimated C_{PE} values based on PRC-corrected concentrations in PE were compared to the true equilibrium concentrations from the mixed system. In the laboratory mesocosms with static overlying water, we expect that PCBs in porewater approach thermodynamic equilibrium with the sediment. Thus, porewater concentrations measured in the “mixed equilibrium exposures” should closely represent the true equilibrium porewater concentration to be expected in the static and vibrating passive sampler deployments. The PRC-corrected C_{PE} values measured with 7- and 28-day static and vibrated passive samplers are plotted in Figures 2.4 and 2.5, respectively and compared against the true equilibrium C_{PE} values. In both figures, the PRC-corrected C_{PE} values that are statistically different from the true values (with alpha level of 5%) are indicated with asterisks.

As shown in Figure 2.4, the tri, tetra, and pentachloro-congeners (PCB 31, 70+76, 99, and 82+151) are generally well-predicted by the static passive samplers (within a factor of 2) for both 7-day and 28-day deployments. For these moderately hydrophobic congeners, the PRC losses are high in both deployment durations and correction for non-equilibrium is relatively accurate. The measurements using static deployment start deviating strongly for the higher chlorinated PCBs (hexa and higher). There appears to be a consistent positive bias for the estimation from static deployment. For example, equilibrium C_{PE} for PCB 180 is predicted to be 7.7 fold higher from the 7-day deployment and 2.9 fold higher from the 28-day deployment. As expected, C_{PE} estimations using the 7-day deployment data in the static system were less accurate compared to the estimations using 28-day deployment data, especially for higher molecular weight PCBs. The error bars are also large, indicating poor precision. Many of the equilibrium C_{PE} prediction for the static deployment have large deviation from the true equilibrium C_{PE} (e.g., up to a factor of 10 for 7-day deployment) but often do not show statistically significant difference due to the very large associated error of the estimation. The predictions improve with length of deployment but remains poor with a factor of 5 over-prediction for several hepta- and octachloro- PCBs.

As shown in Figure 2.5, the PRC-corrected C_{PE} values from the 2-min-paused vibration deployment are much more accurate and precise compared to measurements from the static deployment. For example, the estimated equilibrium C_{PE} for PCB 180 is 291 and 346 ng/g after 7 and 28 days of deployment in the 2-min-paused vibration system, respectively. That means, equilibrium C_{PE} of PCB 180 is predicted within a factor of 1.1 of the true value of 258 ng/g even after a 7-day deployment. Even PCB 208+195, which are the most hydrophobic congeners measured, are predicted within a factor of 1.2 after 7 days deployment despite the fact that only 40% of the equilibrium concentration was reached. Both 7-day and 28-day deployments of the 2-min-paused vibrating system yield close to the true value for all measured PCBs.

Increasing pause time to 5 days made the equilibrium C_{PE} measurements less accurate than the 2-min pause vibration but was better than the static deployments. For example, C_{PE} for PCB 180 was predicted within a factor of 1.9 by the 5-d-paused deployment in 28 days compared to a factor of 2.9 for the same deployment period for the static system. Thus, even a very intermittent vibration can greatly enhance the accuracy of the C_{PE} measurement.

Higher precisions in estimation of C_{PE} using the low frequency vibration deployment results in estimated equilibrium concentrations that are statistically different from the true values, yet the absolute values are closer to the true value compared to the static deployment.

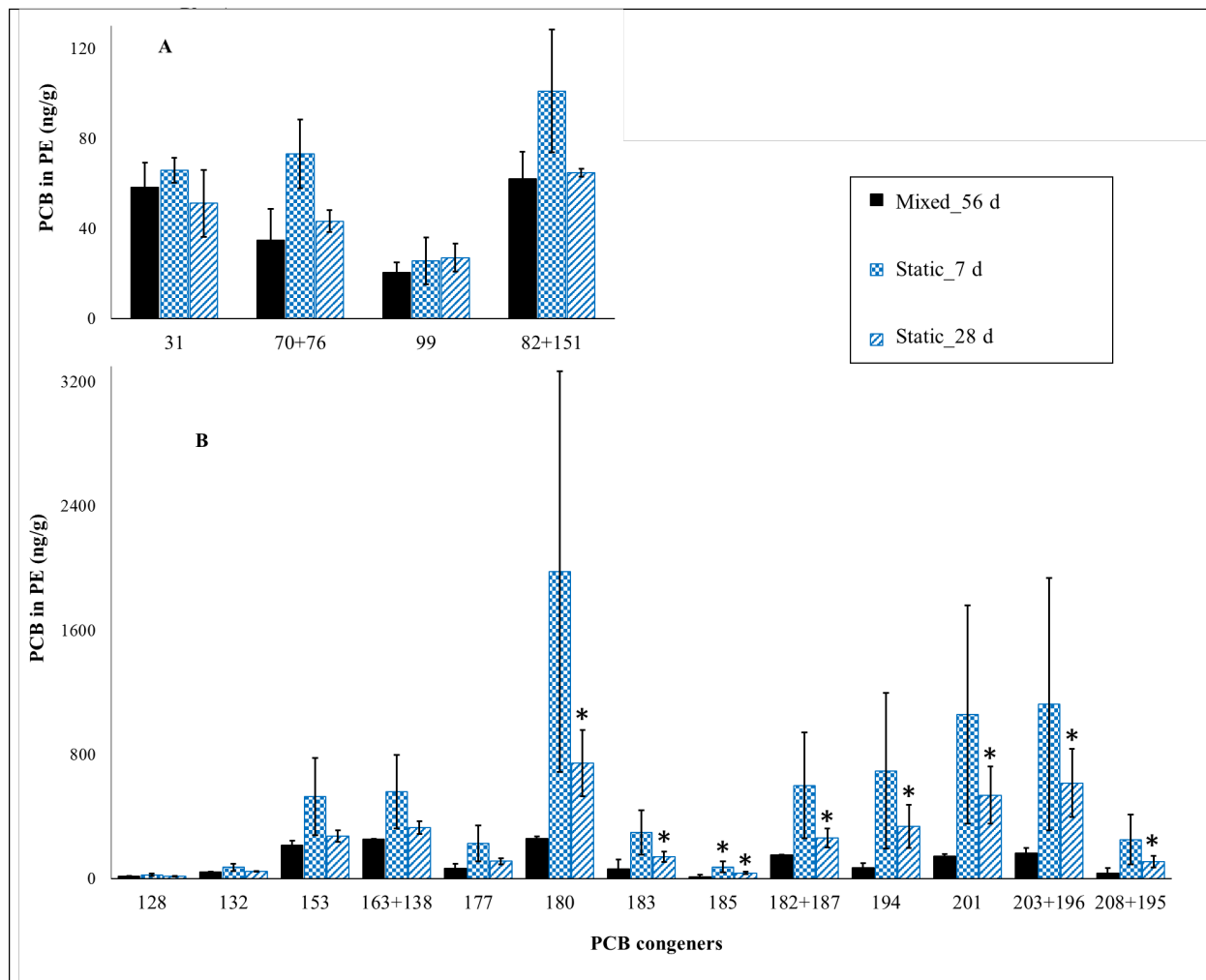


Figure 2.4. Comparison of 56-day Mixed (True) Equilibrium Concentration in PE with PRC-corrected PE Equilibrium Concentration Measured Using 7-day and 28-day Static Exposures.

Plot A shows PCB congeners that belong to pentachloro- and lower molecular weight congeners and plot B indicates congeners that belong to hexachloro- and higher molecular weight congeners. The corrected concentrations that are statistically different from the 56-day mixed equilibrium concentrations (with alpha level of 5%) are indicated with an asterisk. Error bars represent the mean $\pm$ one standard deviation ($n=3$).

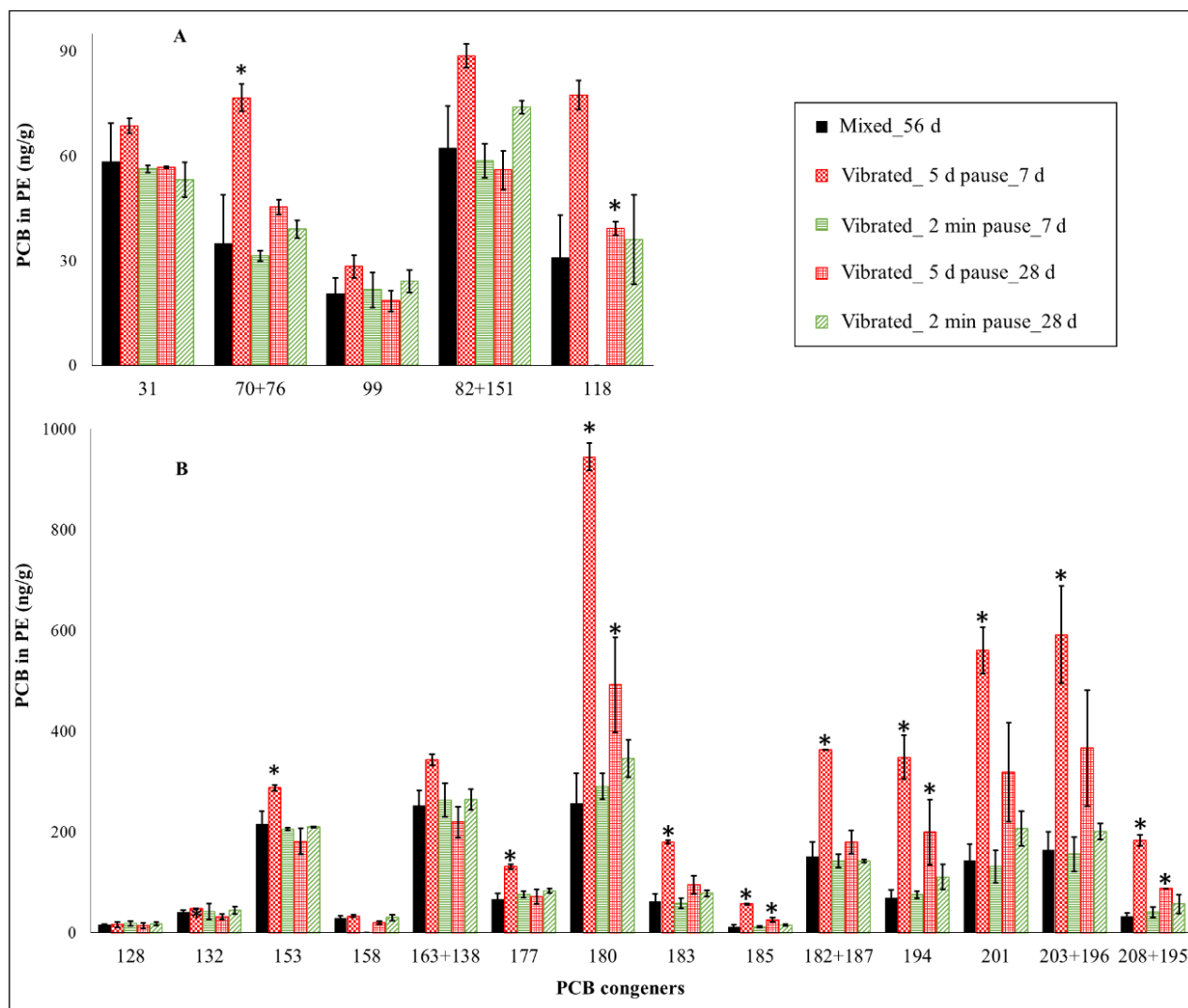


Figure 2.5. Comparison of 56-day Mixed Equilibrium Concentration in PE with PRC-Corrected PE Equilibrium Concentration Measured Using 7-day and 28-day Vibrated Passive Samplers.

Plot A shows PCB congeners that belong to pentachloro- and lower molecular weight congeners and plot B shows congeners that belong to hexachloro- and higher molecular weight congeners. The corrected concentrations that are statistically different from the 56-day mixed equilibrium concentrations values (with alpha level of 5%) are indicated with an asterisk. Error bars represent the mean $\pm$ one standard deviation ($n=3$).

Since passive sampling is often used to estimate C_{free} , PCB concentrations in PE were converted to C_{free} using the individual congener PE-water partition constants (K_{PEW}) and are presented in Supporting Information Figures S2.7 and S2.8. The K_{PEW} values for PCB congeners were estimated from the correlation provided in Ghosh et al.¹⁰ (Supporting Information Table S2.8). Conversion to C_{free} values appears to reduce the contribution of the highly chlorinated congeners towards the total PCB C_{free} . However, an important environmental impact of the pollutants in the porewater is the accumulation at the base of the aquatic food web, and partitioning into benthic organism lipids.

Predicted equilibrium concentrations in organism lipids were also calculated based on the assumption that organism lipids are similar to octanol and the lipid concentrations at equilibrium are plotted in Supporting Information Figures S2.9 and S2.10. In Figures S2.9 and S2.10 again, the contribution of the highly-chlorinated PCBs in porewater is emphasized because these compounds have a strong partitioning in lipids and thus, needs to be measured with a high degree of accuracy. This exercise illustrates the importance of assessing concentrations in the right matrix, or to convert concentrations to chemical activities as suggested in Mayer et al.¹

Apell and Gschwend⁹ using the same PRC-correction method, observed that the C_{free} estimate from 30 day and longer deployment times (up to 120 days) in static sediment, were not statistically different from the measured concentrations. However, they did not conduct the comparison for deployment times of less than 30 days and for the PCBs larger than heptachloro-congeners. In this study, we did not see significant differences between the PRC-corrected and true equilibrium C_{PE} of hexachloro- and lower molecular weight PCBs for the 28 d-deployment time, which agrees with the observations by Apell and Gschwend.⁹ In fact, the differences were significant for higher molecular weight PCBs (nona-, octa-, and some of the heptachloro congeners) (Figure 2.4). Although Apell and Gschwend⁶ concluded that uptake kinetics of PCBs into PE is identical to the release kinetics of PRCs out of the PE, more recent studies reported anisotropic exchange kinetics for diffusion of PCBs and DDTs into passive samplers. For example, Choi et al.⁴, observed slower uptake kinetics of the target PCBs compared to the release kinetics of the PRCs for PE deployed in stagnant sediment. In contrast, Bao et al.⁷, reported faster kinetics of uptake for PCBs and DDTs into PDMS compared to the release kinetics out of PDMS and into the sediment.

Comparison of exchange kinetics. To further investigate the difference between the exchange kinetics of PCBs, f_{PRC} of the four PRCs used in this study was compared to the fractional uptake (f_{target}) of four target PCBs with similar K_{ow} s. If the exchange rates are identical, then the sum of f_{target} and f_{PRC} should be equal to one for all the time point measurements. In Figure 2.6, f_{target} for PCBs 31, (70+76), 158, and 194 is compared to f_{PRC} for PCBs 29, 69, 155, and 192, respectively after 7, 14, 28, and 56 days of deployment. The sum of f_{target} and f_{PRC} deviates from one by less than 20% for all the congeners. However, the ratio of fraction PRC lost to fractional uptake (shown in Supporting Information Figure S2.11) is dramatically different from 1 for the static deployment at early times and is highly variable. The PRC-corrected C_{free} of the four PCB congeners (shown with cross) is also compared to the measured value (shown with dash lines) for all the time point measurements in Figure 2.6. For all congeners, the accuracy of C_{free} estimation improves at longer deployment times. Thus, reasonably symmetric long-term kinetic profiles for uptake of PCBs and release of their corresponding PRCs were found in this study. Therefore, we suspect that the high variability and positive bias for the estimation of C_{free} (or equilibrium C_{PE}) of highly chlorinated congeners from static deployment is likely due to small fractional losses of the larger PRCs, which cause large PRC correction errors for predicting the equilibrium concentrations. The large variability comes from the fact that at times the direction of error in analyte measurement and PRC measurement cancel each other and at other times they compound the error.

Implications. PRC corrections have allowed extension of passive sampling to compounds that do not achieve equilibrium during a reasonable period of field deployment. However, we showed that the corrections are not reliable for estimating sediment porewater concentrations of strongly hydrophobic PCBs during a typical deployment time. The introduction of periodic vibration greatly enhances the time to equilibrium, increases measurement accuracy, reduces deployment times, and extends the use of passive sampling in conjunction with PRCs to strongly hydrophobic compounds.

As demonstrated in the present work, with periodic vibration, even a 7-day deployment is adequate for a reasonably accurate in situ measurement of C_{free} for all PCB compounds. Shorter deployment times reduce the risk of loss, destruction, and vandalism of deployed passive sampler platforms in the field and can reduce costs when deployment and retrieval may be performed in one mobilization to the field. Using periodic vibration for a longer deployment of a month, it may even be possible to reach so close to equilibrium that PRC corrections may not be necessary for many compounds. We expect that using the proposed vibration technique for deployment of the passive samplers would also improve the accuracy of in situ measurements of C_{free} for other strongly hydrophobic compounds such as polychlorinated dibenzo-p-dioxins/dibenzofurans. Since these compounds are in the same range of hydrophobicity as hexa-, hepta-, and octachloro-PCBs. Further work is needed to operationalize the vibrating passive sampler through optimization of the vibration frequency, increased size of the devices to accommodate larger samplers, and field-demonstration with HOC contaminated sediments.

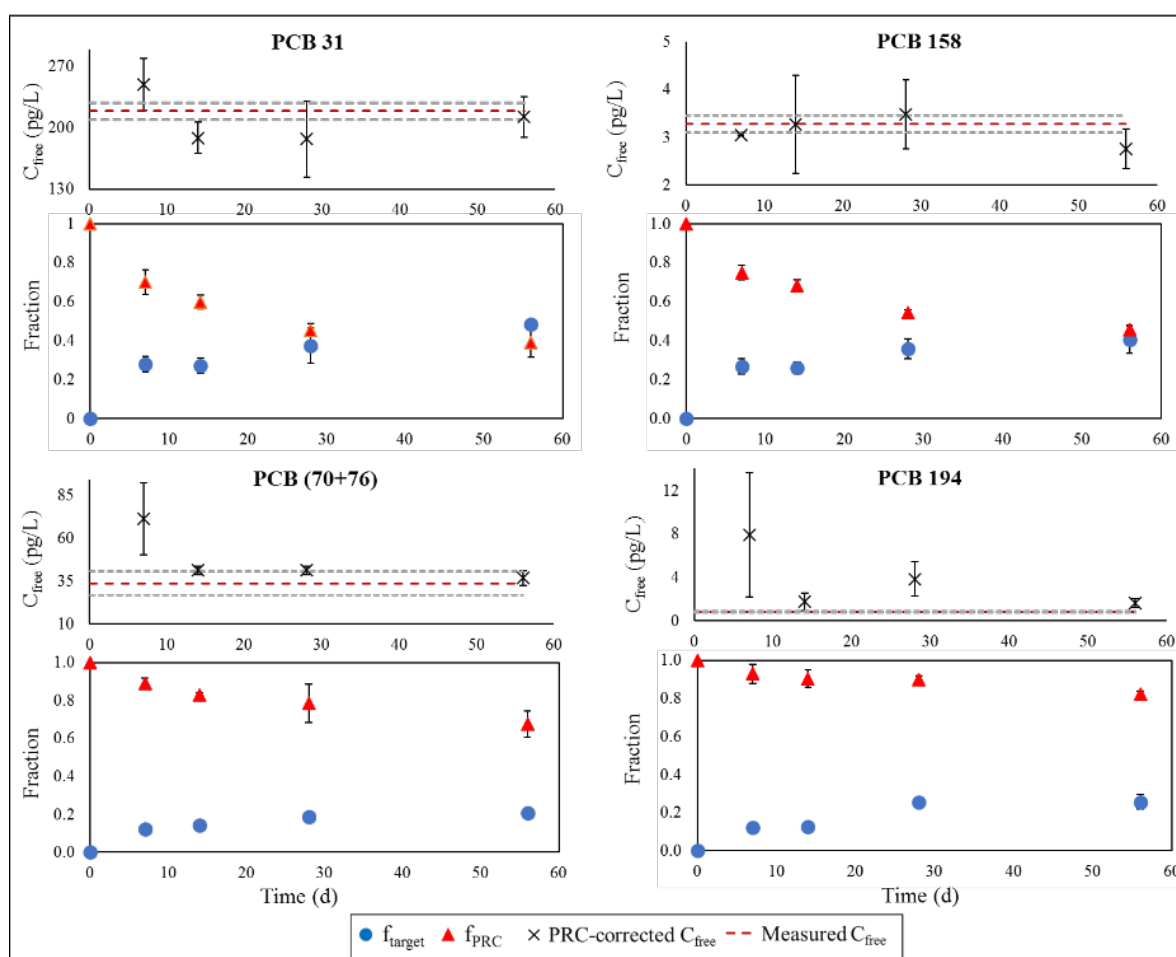


Figure 2.6. Comparison of Estimated C_{free} (Cross) with the True Equilibrium C_{free} (Red Dash Lines) for Four PCBs.

The fractional loss of PCB 29, 69, 155, and 192 at each time point measurement was used to estimate the C_{free} for the target PCBs 31, (70+76), 158, and 194, respectively. The fractional uptake of the target PCBs into PE (f_{target}) (circles) are also compared with the remaining fraction of their corresponding PRCs in PE (f_{PRC}) (triangles). Error bars and the thin dashed lines represent the mean $\pm$ one standard deviation ($n=3$).

2.5 ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: <https://pubs.acs.org/doi/10.1021/acs.est.7b01020> (1) parameter estimation; (2) model equations; (3) details of model simulations; (4) Matlab codes (5) additional figures and tables (PDF). The supporting information of this chapter is also included as Appendix 2 in this report.

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2.7 ACKNOWLEDGMENTS

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3.0 CHAPTER 3: DESIGN OPTIMIZATION OF PASSIVE SAMPLING PROTOTYPES WITH PERIODIC VIBRATION FOR POREWATER MEASUREMENTS OF STRONGLY HYDROPHOBIC COMPOUNDS.

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3.1 ABSTRACT

This chapter primarily addresses Tasks 2 and 3 of the proposal. Three larger prototypes of vibrating passive samplers were developed to address the need for the deployment of a larger mass of polymer than what was possible in the early prototypes. These prototypes were tested under different conditions in the lab and then were used to perform deployments in the field. Key motivations were to increase the size of the sampling device, increasing the size of the motor, making them more robust for deployment in the field, while keeping them low-cost. The first prototype (P1 or VibraSP3) was developed in collaboration with Geosyntec and tested successfully in the field under marine conditions. This prototype, while larger than the ones used for proof of concept in the SEED project, is still too small to deploy 1 g of PE per sampler. Additional prototypes P2-110G and P2-125G were therefore designed and developed at UMBC that are larger in size and power to allow the deployment of 1-3 g of PE passive samplers. The two P2 vibrating passive sampler prototypes were successfully tested in the field in Kingman Lake, Anacostia River, Washington DC. Vibration dataloggers were attached to one of the fins of the device and demonstrated that the prototype vibrated through the entire period of deployments and the average amplitude of vibration of the device within the sediment ranged between 2-5G over the period. The enhancement of uptake rate was observed not only for the lower chlorinated PCBs, but also more notably for the higher chlorinated PCBs with 6-8 chlorines that are in the same hydrophobicity range as dioxins and furans. Correspondingly, the rate of loss of PRCs for the vibrating prototypes was faster than the static sampler over the deployment period of 10 days in the field.

3.2 INTRODUCTION

The measurement of freely dissolved concentrations of hydrophobic organic contaminants (HOCs) in sediment porewater allows the assessment of fate, transport, and bioavailability of these compounds. [Mayer et al., 2014] Passive sampling using well characterized polymers, enables accurate measurements of low aqueous concentrations of HOCs like polychlorinated biphenyls (PCBs), which is otherwise challenging due to the strong association with colloidal and organic matter in sediment porewater that can be difficult to separate. Once the polymeric sampler reaches equilibrium with the sediment porewater, much like in a well-mixed laboratory experiment, the freely dissolved porewater concentration can be calculated using known polymer-water the partitioning coefficient. [Mayer et al., 2003; Ghosh et al., 2014] In-situ measurements of sediment porewater concentrations is challenged by slow mass transfer through the water boundary layer outside the polymer in the absence of active mixing unlike well-stirred laboratory measurements. Further, strongly hydrophobic compounds like benzo(a)pyrene (MW=252 g/mol; Log K_{ow} = 6.10) takes longer than one year to reach equilibrium in a 51 μ m PE sheet [Lohmann, 2012]. A thinner polymer can expedite mass transfer but is more prone to damage during deployment in sediment. The use of passive samplers impregnated with performance reference compounds (PRC) have been adopted for assessing the kinetics of mass transfer and account for non-equilibrium. [Huckins et al., 2006; Huckins et al., 2002; Fernandez et al., 2009a; Booij et al., 2010; Booij et al., 2003; Fernandez et al., 2014] However, PRC correction methods for compounds which are strongly hydrophobic, is prone to error. [Apell & Gschwend, 2014] These uncertainties can be attributed firstly to the site-specific sorption characteristics of the sediment which impacts the restricted diffusion in the sediment side. Secondly, the method of correction uses the depletion rate of only a few PRCs which is extrapolated to predict the exchange kinetics of a large range of analyte compounds in sediment. [Fernandez et al., 2009a]

A recent innovative approach proposes mechanical disruption of the WBL outside the polymer surface by introducing periodic vibration on the sampling platform for in-situ sediment porewater measurements [Jalalizadeh & Ghosh, 2016; Jalalizadeh & Ghosh, 2017]. Since the mass transfer kinetics is rate limited by the thickness of the WBL for most sediment porewater deployments, this approach greatly enhances the approach to equilibrium for more hydrophobic contaminants like higher chlorinated PCBs and dioxins. The proof-of-concept vibrating sampler prototypes built for in-lab measurements reported an especially evident improvement for high molecular weight compounds, over static sediment porewater measurements [Jalalizadeh & Ghosh, 2016]. With a brief vibration every 2 minutes, a 95-100% equilibrium of all PCB compounds was achieved within 56 days of deployment in sediment. The vibration also led to a higher fractional loss of the PRCs which helped in estimating corrected porewater concentrations that were statistically indistinguishable from the actual equilibrium values after a 7-day deployment [Jalalizadeh & Ghosh, 2017].

Passive sampling techniques have been extensively used in measuring the time integrative concentration of pollutants in overlying water and sediment porewater and are in the process of being adopted as a standard USEPA method. [Michalsen et al., 2020] The attainment of equilibrium can be expediting by manipulating the area/volume ratio of sampler, and periodic disruption of the WBL. for the vibrating platform, different adjustments of the frequency and strength of vibration can be made to achieve acceptable degree of uptake for highly hydrophobic compounds. In this chapter, we present results of further research towards optimizing the design of the vibrating passive sampling devices to sample PCB compounds.

The overall goal is to extend the versatility of passive sampling applications for sediment porewater measurements with the vision of operationalizing faster achievement of equilibrium by expediting mass transfer. A more efficient porewater estimation achieved through the optimization experiments through this study can provide accurate bioavailability assessments that are needed for improved site risk assessments, targeted remedy selection, and post-remedy monitoring.

The specific tasks for this study are:

- 1) Fabrication and field-testing of the actively shaken passive sampling platform for strongly hydrophobic organics.
- 2) Optimization of sampler design and vibration frequency through laboratory experiments and mathematical modeling.
- 3) Laboratory demonstration of the short-term passive sampling for contaminated sediments containing strongly hydrophobic compounds using the optimized actively shaken platform.

3.3 MATERIALS AND METHODS

Modeling framework for exchange kinetics in passive samplers in sediments:

Mass transfer within sediment involves diffusion through porous media that is filled with water and is affected by the tortuosity and sorptive exchanges in the sediment, D_{SED} can be defined as [Fernandez et al., 2009b]:

$$D_{SED} = \frac{D_W}{\tau(1+r_{SW}K_d)} \quad (1)$$

where D_W (cm^2/s) is diffusivity in water, K_d ($\text{cm}^3 \text{ sed}/\text{cm}^3 \text{ water}$) is the site-specific sediment/ water partitioning coefficient (converted to vol/vol units) and r_{SW} is the volumetric phase ratio of sediment to water and τ is tortuosity that are both calculated from porosity (n assumed to be 0.6) as:

$$r_{SW} = \frac{1}{n} \quad (2)$$

$$\tau = 1 - \ln(n^2) \quad (3)$$

In addition to D_{SED} , K_{PESED} is also a function of K_d and can be defined as:

$$K_{PESED} = \frac{K_{PEW}}{K_d} \quad (4)$$

For a static sampler, the mass exchange should be more porewater side-controlled. For a vibrating system, the porewater side control of the mass exchange kinetics should be partially replaced by control in the PE side. A one-dimensional diffusion model was used for modeling the sediment porewater concentrations C_{PW} from PE deployments. Crank's explicit finite-difference numerical solution was used to model the behavior of a vibrating system with changes to the boundary conditions as compared to the static model.

Static System:

We consider diffusion in a system consisting of two contacting media, a finite PE sheet of thickness $2L$ and an infinite sediment (/porewater) on either side, following Fick's second law:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad \text{when } -L < x < L \quad (5)$$

$$\frac{\partial C_{SED}}{\partial t} = D_{SED} \frac{\partial^2 C_{SED}}{\partial x^2} \quad \text{when } -L > x > -(L + s) \text{ and } L < x < (L + s) \quad (6)$$

where $2s$ is the thickness of the sediment/porewater layer outside the polymer C_{PE} is the mass of PCB analyte accumulated in PE (ng/cm³ of PE), C_{SED} is the concentration of analyte in the sed (ng/cm³), D_{PE} (cm²/s) and D_{SED} (cm²/s) are the diffusivity within the PE and sedimentary porous medium respectively.

The remote boundary conditions are assumed to be:

$$\frac{dC_{SED}}{dx} = 0 \quad \text{for } x=\infty \text{ and } x=-\infty \quad (7)$$

Assuming at PE-sediment interfaces diffusive fluxes match and mass is conserved:

$$D_{PE} \frac{\partial C_{PE}}{\partial x} = D_{SED} \frac{\partial C_{SED}}{\partial x} \quad \text{when } x = L \text{ and } x = -L \quad (8)$$

A local equilibrium is assumed:

$$C_{PE} = K_{PESED} C_{SED} \quad \text{when } x = L \text{ and } x = -L \quad (9)$$

where K_{PESED} is the polymer-sediment partitioning coefficient.

Vibrating system:

For the vibrating system we have two modes: the pause mode and the pulse mode. In the pause mode the system works exactly like the static system. In the pulse mode however, the sediment and the associated porewater in the vicinity of the polymer surface gets mixed up to increase the sediment concentration to the initial concentration in the sediment, $C_{SED,init}$ (ug/cm³). The governing equations in the different modes thus become:

Pause Mode:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad \text{when } -L < x < L \quad (10)$$

$$\frac{\partial C_{SED}}{\partial t} = D_{SED} \frac{\partial^2 C_{SED}}{\partial x^2} \quad \text{when } -L > x > -(L + s) \text{ and } L < x < (L + s) \quad (11)$$

Vibration Mode:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad \text{when } -L < x < L \quad (12)$$

$$C_{SED} = C_{SED,init} \quad \text{when } -L > x > -(L + s) \text{ and } L < x < (L + s) \quad (13)$$

Fully Mixed system:

For the fully mixed system, diffusion within the polymer of thickness $2L$ is governed by the equation:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad \text{when } -L < x < L \quad (14)$$

The sediment concentration remains constant at all times to the initial concentration, $C_{SED,init}$ ($\mu\text{g}/\text{cm}^3$):

$$C_{SED} = C_{SED,init} \quad \text{when } -L > x > -(L + s) \text{ and } L < x < (L + s) \quad (15)$$

The boundary condition at the PE-sediment interface only assumes local equilibrium as there are no diffusive fluxes from the sediment side to cancel out:

$$C_{PE} = K_{PESED} C_{SED} \quad \text{when } x = L \text{ and } x = -L \quad (16)$$

The fractional losses of the C13 PCB PRCs (Table 3.2) were simulated using the above model for the static, vibrating, and fully mixed conditions by assuming that the initial concentrations of these analytes in the PE are at a known higher concentration and that on the porewater side is zero.

Fabrication of vibrating passive sampler platforms and initial laboratory and early trials in sediment:

A total of three new prototypes of vibrating passive samplers were developed in this project. Key motivations were to increase the size of the sampling device from the initial proof-of-concept design, increasing the size of the motor, making them more robust for deployment in the field, all while keeping them low-cost.

Prototype P1. The first prototype (P1-14G) was developed in collaboration with Geosyntec. Dr. Mehregan Jalalizadeh who first worked on developing the proof-of-concept of the vibrating passive sampler at UMBC as part of the SEED project became an employee of Geosyntec and continued to develop the technology further for field deployment with additional internal support from Geosyntec and named their device VibraSP3, shown in Figure 3.1a. The vibration device consisted of a vibrating motor, a microcontroller, and a user-replaceable battery (which provided power for running the motor and microcontroller). The vibrating motor from Precision Microdrives was rated at 14G. The G value of these motors represent the acceleration imparted on a 100 g mass. A motor with a higher G value can create strong vibration against a load. The components of the vibration device were mounted on a 5- by 7- cm circuit board and housed in a small waterproof electrical case. The waterproof housing was tested to water pressures at 30 m depth, and the microcontroller was programmed to vibrate the motors for 5 seconds in every 4 hours. The prototype was deployed in the San Diego Harbor by Geosyntec as shown in Figure 3.1b.

In VibraSP3, the PE sampler was attached to the back side of the plate holding the vibrating case, as shown in Figure 3.1a. This configuration did not allow good exposure of the PE to sediment from both sides and was thus modified at UMBC so that the frames extended into fins, about 1.5 in wide, from either side of the body of the device as shown in Figure 3.1c. We called this modified prototype P1-14G. It could hold up to a total of 0.2 g of the 25 μm thick PE samplers in its fins. This configuration would allow good exposure of the PE to sediment from both sides. as shown in Figure 3.1c.

This prototype, while larger than the ones used for proof of concept in the SEED project, is still too small to deploy 1 g of PE per sampler. Additional prototypes were therefore designed as described below.

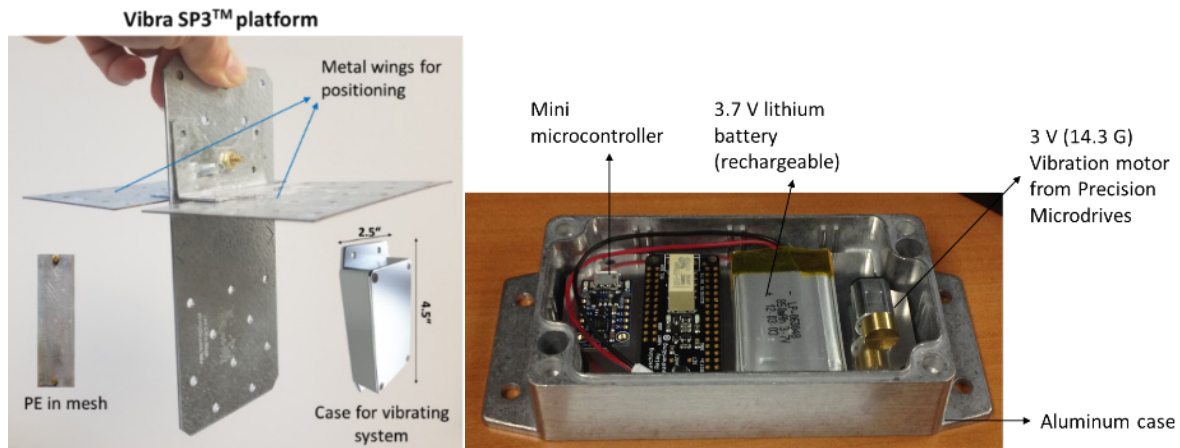


Figure 3.1a. VibraSP3 Developed by Geosyntec.

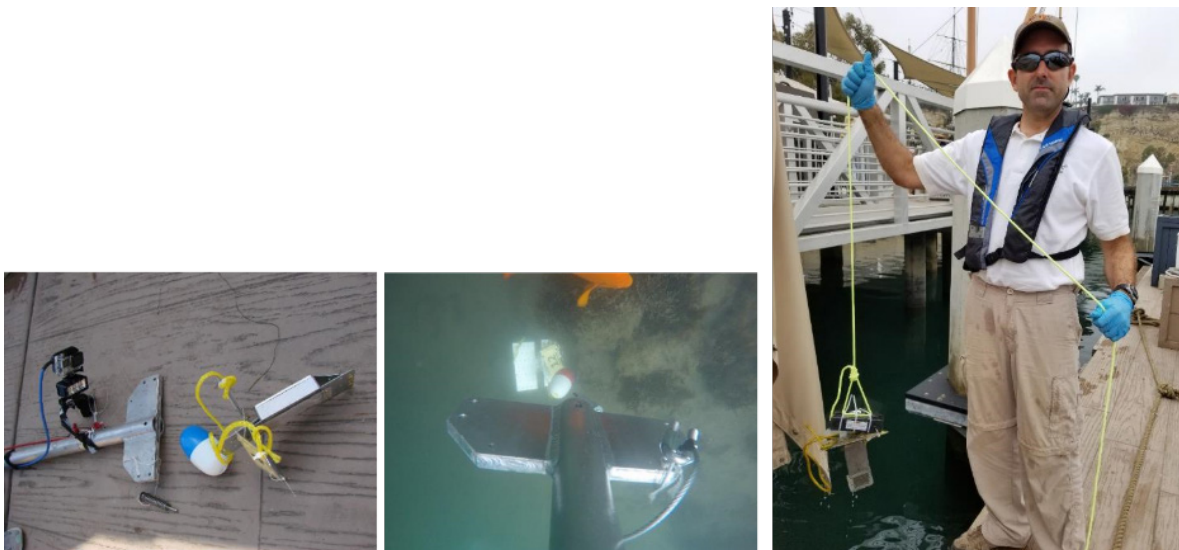


Figure 3.2b. Field Deployment of Prototype Vibra SP3 by Geosyntec in San Diego Harbor.

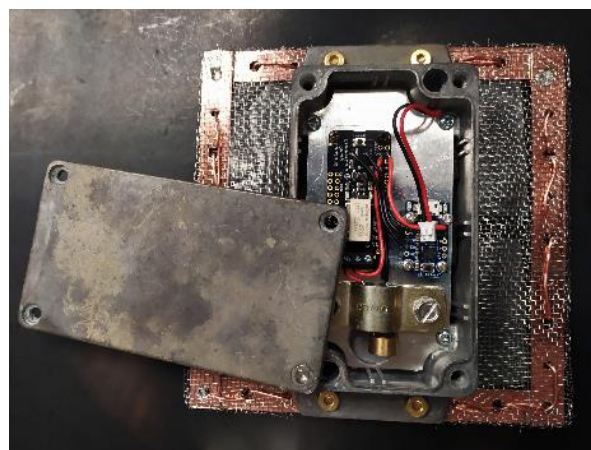


Figure 3.3c. Modified Prototype P1-14G with Extended Fins to Provide Full Exposure to PE.

Prototypes P2-110G and P2-125G. Two additional vibrating passive samplers (prototypes P2-110G and P2-125G) were developed at UMBC that are larger in size and power (larger G values) with the goal to allow the deployment of 1 g or more of PE per device. Table 3.1 lists the electrical components used in these prototypes.

P2-125G, Figure 3.2a, was built by students with the help of personnel from the UMBC machine shop. This prototype was built first and went through several stages of design modifications and provided ideas for the design of P2-110G. The body of the vibrating unit was made from a 1.5 in diameter copper pipe housing a cylindrical vibrating motor (Model No: PM 334-800, Precision Microdrives, London, UK). A unique design of this prototype had the vibration unit sealed from two ends with two detachable caps made of aluminum with a gasket to prevent leakage. This made the motor within the vibration unit accessible for replacement if damaged. However, it also made this unit prone to leakage than if the whole unit was permanently sealed. The motor within the vibration unit operated at a rated voltage of 24 V, operating current of 2000-2500 mA, vibrating speed of 7300 rpm and typical normal amplitude of 125 G. The power unit was separated from the vibration unit unlike prototype P1-14G, by a hose pipe enclosing the wires connecting the two units. The flexible hose pipe isolated the heavy battery unit from the vibration that was necessary to minimize dampening of the vibrating unit. This device required a 24V, 5000mAh rated battery. A programmable multifunction time delay relay, purchased from UCTRONICS, Amazon.com (rated at 12 V) was attached on a small acrylic board with the battery stacked under it and the whole arrangement enclosed in an aluminum waterproof electrical housing purchased from Polycase Enclosures. This device could support 4 detachable radial fins of dimensions 6 in x 3.5 in and was designed to accommodate a vibration datalogger in a waterproof housing, to be attached to one of the fins that could record the frequency and magnitude of vibration during the deployment period. However, this device was discontinued for lab testing because of the much larger power consumption, negligible improvement in intensity of vibration, and for not being very user-friendly.

P2_110G, Figure 3.2b, was built by students in the laboratory at UMBC. The vibrating unit of P2-110G housed a cylindrical vibrating motor (Model No: PM 334-410, Precision Microdrives, London, UK). The motor operated at a rated voltage of 12 V, operating current of 2400-4200 mA, vibrating speed of 6800 rpm and typical normal amplitude of 110 G. The vibrating unit in this prototype was modified to being permanently sealed with no detachable parts. This implied that when the motor was damaged, the vibration unit, including the motor fastened permanently inside a copper pipe with compatible soldered copper end caps would need replacement. Overall, this design was more optimized for cost and leakproof conditions than P2-125G. Attached to the vibrating unit were three non-detachable radial fins of dimensions 4 in x 1.5 in, made from copper brackets and soldered to the cylindrical body. The major components of the power unit remained same except for a 11.1 V, 2500 mAh rated lithium-ion battery that was compatible with the 12V rated motor in this device. The initial design of this device could support 3 radial fins (each with 0.3 g of 2 mil PE sheets with a maximum deployed PE mass of 1.2 g) and the waterproof case with the vibration datalogger inside. The prototype was tested in water and sediment mesocosms to demonstrate that the device is leakproof and continues to vibrate for the entire deployment time. Through the series of experiments, the design of this prototype was optimized to a reduced width of the fins to half of the original width so that the final dimensions were 2 in x 1.5 in. A detailed description of the design and instructions for fabrication of prototype P2_110G is provided in the appendix.

The prototypes survived several sequential in-lab deployments in two types of sediments. The tests demonstrated that the devices were leakproof through all the deployment periods and continued to vibrate throughout. A three-axis vibration datalogger was attached to one of the fins of the devices to record the frequency and magnitude of vibration during the deployment period. Both the prototypes P2-125G and P2-110G were also deployed in the field at Kingman Lake, Anacostia River, Washington DC on Dec 10, 2019, in addition to static samplers, for a period of 10 days, Figure 3.2(c).

Table 3.1. Electrical Components of the Vibrating Passive Sampler Prototypes.

Prototype No	Vibrating Motor specifications					Battery	Timer
	Motor Model	Rated operating Voltage	Rated operating Current	Rated Vibration Speed	Typical Norm Amplitude		
P2_110G	PM 334-401	12V	2400-4200 mA	6800 rpm	110G	Li-Ion Battery: 11.1V 2.5Ah	UCTRONICS DC 12V Programmable Multifunction Time Delay Relay
P2_125G	PM 334-800	24V	2000-2500 mA	7300 rpm	125G	Li-Ion Battery: 22.2V 5Ah	

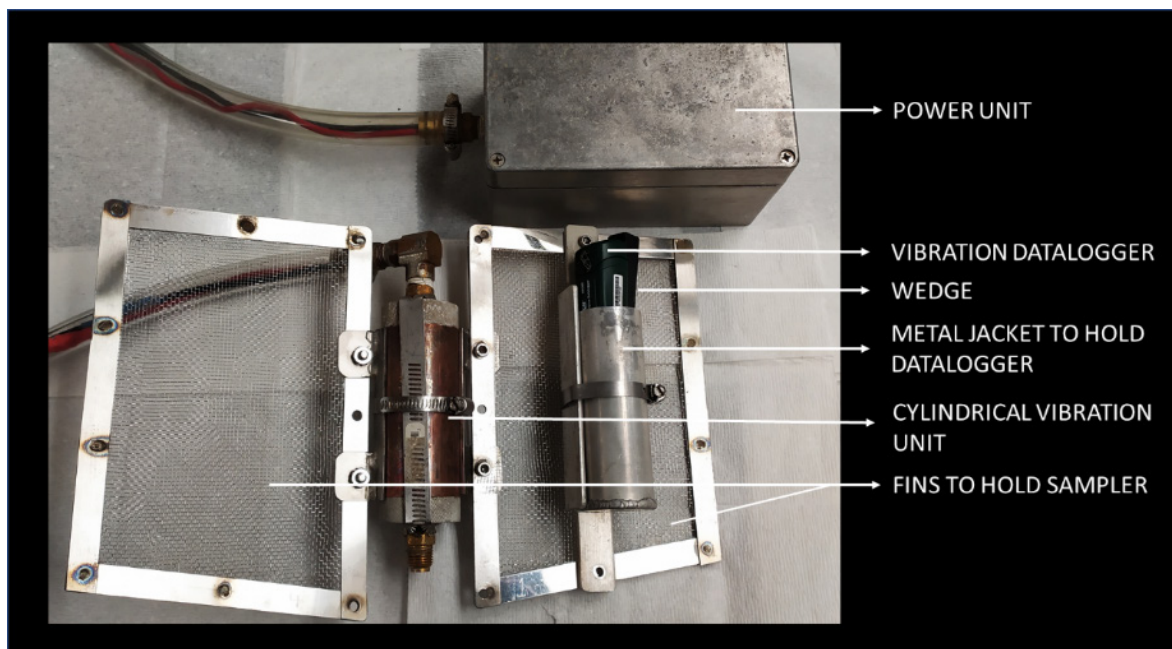


Figure 3.2a. Vibrating Passive Sampler Prototype P2_125G That Can House 1-3 g of PE Passive Samplers and a Vibration Sensor Datalogger

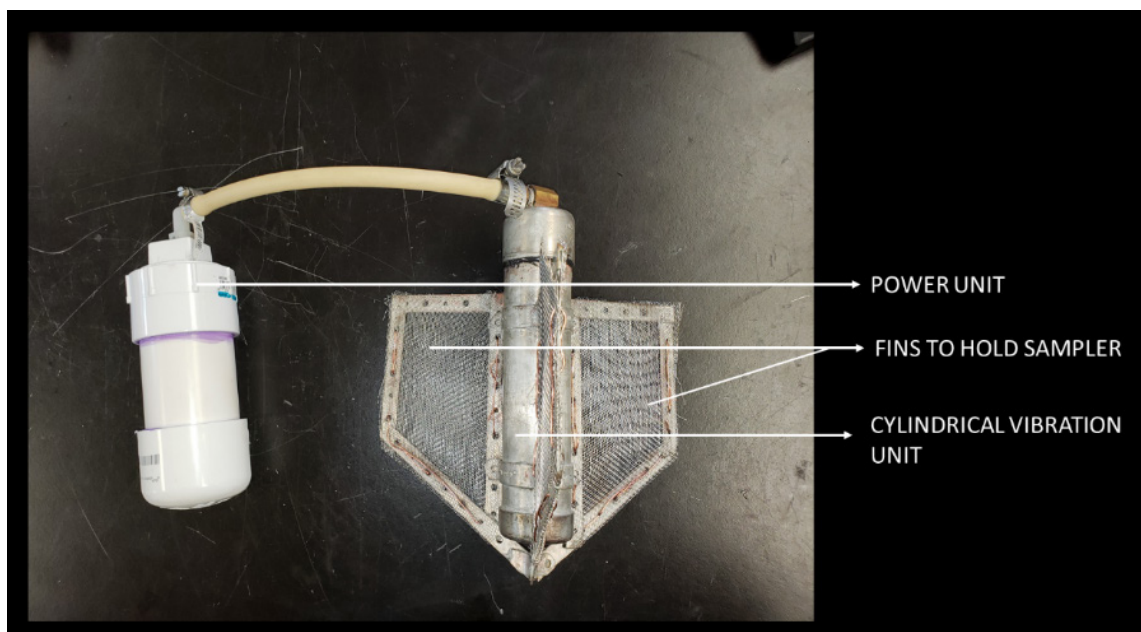


Figure 3.2b. Vibrating Passive Sampler Prototype P2_110G That Can House 1.2 g of PE Passive Samplers



Figure 3.2c. Deployment of Static (Left) and Vibrating Passive Samplers P2-125G (Middle) and P2-110G (Right) at Kingman Lake, Washington DC on 10 December, 2019.

Preparation of passive samplers:

Low density polyethylene sheets (25 μm and 50 μm thickness) manufactured by Poly-America (Grand Prairie, TX) were purchased from Home Depot. Prior to use, the 25 μm PE sheets were cut into pieces each weighing about 0.1 g and the 50 μm PE sheets were cut into pieces weighing 0.5g each. The PE sheet pieces were stacked on a stainless-steel skewer interspaced with stainless steel mesh and soaked in dichloromethane (DCM), hexane/acetone (1:1) and methanol and left on the shaker overnight in each solvent, respectively. This would remove any target and non-target contaminants from the sheets.

The clean and air-dried PE pieces were impregnated with a known concentration of rare environmental PCB PRCs by soaking in a 4L clear jar containing the loading solution (80:20 methanol: water with PCBs listed in Table 3.2a) and letting the system come to equilibrium over 2 weeks on an orbital

shaker. In another 4L jar the loading solution for ^{13}C -labeled PCB PRCs (80:20 methanol: water with ^{13}C -labeled PCBs listed in Table 3.2b) was used to load dry PE sheets over 2 weeks on an orbital shaker. After impregnation, the PE pieces were removed from the PRC loading solution, rinsed with DI water to remove any residual methanol from the surface, and stored in DI water in an amber jar. Three PE pieces were extracted from each jar immediately in hexane (3x24 hours) to determine an average initial PRC concentration on the samplers.

Table 3.2a. Non-aroclor PCB Congeners Used as Performance Reference Compounds to Load PE Samplers.

Homolog Group	PCB compd.	Molecular Weight [g/mol]	Log K_{ow} [Hawker & Connell, 1998]	Log K_{pew} [Lw/LPE] [Tcacuic et al., 2015; Ghosh et al., 2014]
Tri	PCB 29	257.54	5.60	5.27
Tetra	PCB 69	291.99	6.04	5.71
Hepta	PCB 192	395.32	7.52	7.19

Table 3.2b. ^{13}C -labeled PCB Compounds Used as Performance Reference Compounds to Load PE Samplers.

Homolog Group	PCB compd.	Molecular Weight [g/mol]	Log K_{ow} [Hawker & Connell, 1998]	Log K_{pew} [Lw/LPE] [Tcacuic et al., 2015; Ghosh et al., 2014]
Tetra	PCB 54*	291.99	5.21	4.85
Tri	PCB 37*	257.54	5.83	5.58
Tetra	PCB 47*	291.99	5.85	5.61
Penta	PCB 111*	326.43	6.76	6.68
Hexa	PCB 138*	360.88	6.83	6.76
Hepta	PCB 178*	395.32	7.14	7.13

Laboratory sediment deployment set-up:

PCBs: For sediment porewater measurements, PCB contaminated sediment from several sites studied previously, were mixed in a large container using a propeller attachment at the end of a drilling equipment (Figure 3.3a). The homogenized sediment was allowed to equilibrate for a couple of days. Three sets of experiments were run in parallel, representing the three systems: well-mixed, static, and vibrating.

For the well-mixed system, a 950 mL amber jar with a Teflon lined lid was used where this settled sediment was mixed with deionized water to make a slurry with weight ratio of 1:2 (dry sediment: water). Water was added to make the sediment more fluid and allow good mixing in the jar. Two replicates of 25 μm thick PE samplers, impregnated with ^{13}C -labeled labeled PCB PRCs, and enclosed in stainless steel mesh, were deployed in the jar, which was then placed on a rotatory agitator and tumbled at 30 rpm (Figure 3.3b). For the static system, a part of the homogenized sediment was placed in two 2L glass beakers and two replicates of PRC impregnated samplers enclosed in stainless steel mesh, were deployed in them (Figure 3.3c). For the vibrating system,

the devices P1 and P2 were deployed in the same vessel where the sediment was homogenized, with at least 6 in gap between the two devices and from the walls of the vessel (Figure 3.3d, e, f). Two replicates of PRC impregnated samplers were enclosed in the two fins of P1-14G and another two replicate samplers on the fins of P2-110G. The devices were programmed to vibrate with a frequency of 2 seconds pulse every 5 minutes. All the three systems were started on the same day and run in parallel. All the six samplers, with two replicates from each system, were retrieved at the end of 2 days and secured in labeled glass vials. After this, the sediment slurry in the big vessel and the beakers were re-homogenized. The whole exercise was repeated for three more time-steps of 4, 6, and 8 days where six fresh PRC impregnated samplers were deployed each time in the three systems and retrieved after the respective exposure periods.

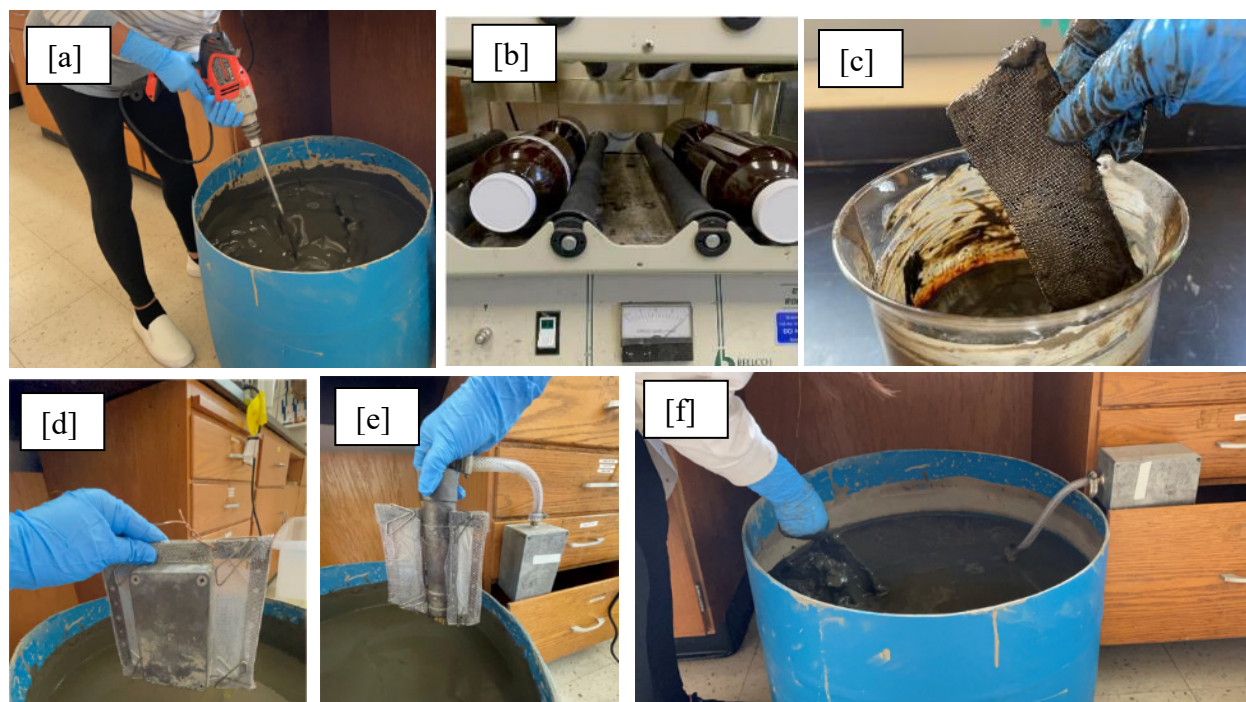


Figure 3.3. [a] Sediment Homogenization, [b] Well Mixed Jar on the Rotatory Agitator, [c] Static Sampler Deployed in Homogenized Sediment [d] Prototype P1 and [e] Prototype P2 Deployed in Homogenized Sediment [f] with at Least 6 in Gap Between Each of Them and from the Walls of the Container.

Dioxin: To check if the sediment used above had any dioxin signature, a 50um thick C13 PRC loaded PE (6 x 6 in) was exposed to one of the well mixed system conditions after the PCB experiments were completed. For this, the PRC impregnated PE sheet (not enclosed in mesh for full exposure) was inserted into the 950mL amber jar with the sediment slurry prepared with weight ratio of 1:2 (dry sediment: deionized water) and left on the TCLP rotator for 14 days. After 14 days the PE was taken out of the jar, rinsed with DI water and stored in a labeled certified 40 mL glass vial in wet conditions for some days before shipping out to a commercial lab for analysis. After it was confirmed that this sediment has the signature of at least 7 dioxin compounds, PRC impregnated 25 um thick PEs were exposed in static, vibration, and well mixed systems for 8 days, 2 replicates each. For the vibration system, the P2-110G prototype was used and set at the vibration frequency of 2 seconds pulse every 5 minutes just like before for the PCB experiments.

After 8 days, all the PE sheets were retrieved, rinsed with DI water in labeled certified 40 mL glass vials in wet conditions for some days before shipping out to a commercial lab for analysis. (Results are still pending from the commercial laboratory)

PCB extraction from passive samplers followed by sample processing. The retrieved passive samplers were cleaned of debris or deposits before extraction. PCB 14 and 65 were added as surrogate standards to all samples before extraction to check recovery. Passive samplers were extracted for PCBs in glass vials using 30 mL hexane, on an orbital shaker, overnight after which the solvent was removed, and new solvent added. This process was repeated three times to complete the extraction. All extracts were collected together and evaporated to 1-2 ml by nitrogen blowdown. PCB cleanup was based on EPA publication SW-846 (Test Methods for Evaluating Solid Waste, Physical/Chemical Methods) methods 3630C (Silica gel cleanup), 3665A (sulfuric acid cleanup) and 3660B (Sulfur removal with copper). PCB analysis was performed on an Agilent 7890B gas chromatograph, with an Agilent 5977B mass spectrometer detector. Internal standards, 2,5-dichlorobiphenyl (13C PCB 09), 2,3',4,4',5-pentachlorobiphenyl (13C PCB 118) and 2,2',3,4',5,6,6'-heptachlorobiphenyl (13C PCB 188), purchased as a mixture solution in nonane was diluted in hexane and added to all samples in desired spiking volumes.

Equilibrium corrected porewater estimations. The mass of PCB accumulated in PE samplers, C_{PS} (ng/g), associated with the well mixed, static, and vibration systems (total of 24 samples: 2 replicates x 3 systems x 4 time points) were first calculated. The fraction of PRC left in the samplers of the respective systems, $f = C_{final}/C_{initial}$, were estimated using the measured values of PRCs after the respective exposure periods. Assuming a default sediment porosity $\eta = 0.7$, the fractional loss values, $(1-f)$, of the six 13C PCB PRCs were used to calculate the fractional correction term, f_{eq} , of all 209 PCB compounds in a PRC Correction Calculator software [Teacuc, 2014] that is based on Fick's diffusion model of mass transfer. Using the above information, and the PE-water partitioning coefficients (K_{PEW}), the PRC corrected porewater concentration, C_{PW} ($\mu\text{g/L}$), was calculated using the equation:

$$C_{PW} = \frac{C_{PS}}{K_{PEW} * f_{eq}} \quad (17)$$

3.4 RESULTS AND DISCUSSION:

Effect of vibration frequency and sediment TOC on uptake in passive sampler

We simulated the effect of vibration frequency on the PCB uptake kinetics on a passive sampler using the mathematical formulation described in the methods section. For the simulation we used PCB 128 as a surrogate compound which has a log Kow value of 6.8 (close to tetra and penta dioxins and furans). As shown in Figure 3.4 (left), the uptake profile is impacted by the frequency of vibration, however, there is a diminishing rate of return with increasing intensity for pause periods shorter than 1 hr. Importantly, we predict that for PCB 128, with periodic vibration every 1 hr, the uptake is more than 50% of equilibrium value within 7 days. This is very encouraging for the application of the vibrating passive samplers for dioxins and furans.

The effect of sediment TOC on uptake was tested for a range of TOC values ranging from 1-10% with PCB 128 and a 1 hr pause vibration. As anticipated the level of TOC in sediments impacts the kinetics. The kinetics is slower for low TOC content sediment, which makes sense because the depletion layer around the sampler becomes deeper with less binding capacity in the sediment, thereby increasing the diffusive distance and slowing down the mass transfer.

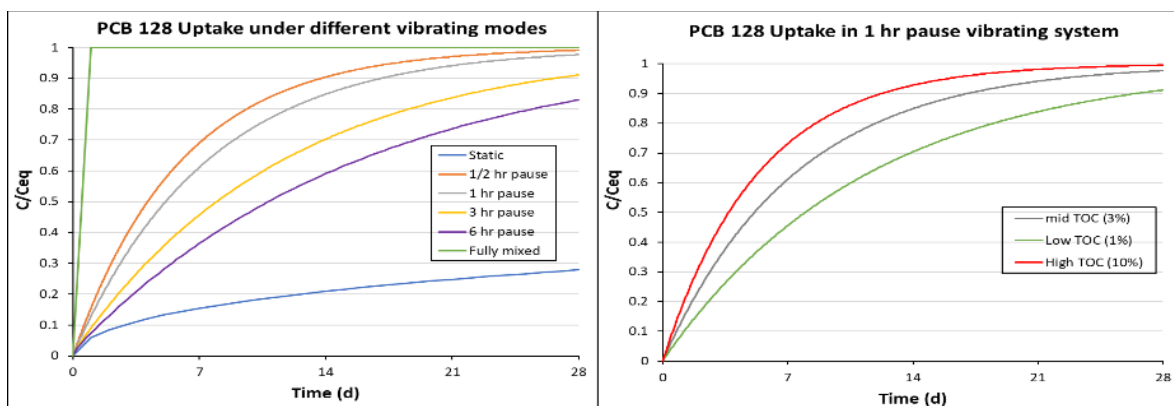


Figure 3.4. Effect of Vibration Frequency and Sediment TOC on the Kinetics of Uptake of PCB 128 into a Vibrating Passive Sampler.

Field testing results of Prototype P1 (VibraSP3™ by Geosyntec):

Geosyntec deployed the VibraSP3™ platform in a marine sediment in 10 to 15-feet of water for time periods of 7 and 14 days in order to demonstrate the platform performance and evaluate the increase in sampling rates due to the vibration (via comparison to results of the standard SP3™ device design, which is not vibrated). Four SP3™ platforms (standard/no vibrating mode) and 3 VibraSP3™ platforms (vibrating mode) were deployed in sediment using a push-pole system and an underwater camera (see Figure 3.1b). The platforms were retrieved after 7 days. Another set of platforms, including four SP3™ platforms and 4 VibraSP3™ platforms, were deployed at the same location within approximately 2 feet from each other. The second set of platforms were retrieved after 14 days.

Before retrieving each platform, Geosyntec used an underwater camera to check whether the platform was fully submerged in sediment. They also checked whether the VibraSP3 platforms were functioning by the time they were retrieved. After both the 7-day and 14-day deployments, the samplers were intact and fully-functioning, indicating a successful performance of the devices.

Problems encountered and solutions

- An inappropriate charger was used for charging the battery of three of the VibraSP3 platforms the day before the first deployment event (on July 19th). We noticed that those three platforms were not functioning on the deployment day. However, the other three VibraSP3 were functioning and were successfully deployed.
- The vibrating motor inside one of the VibraSP3 platforms was unplugged from the battery when the platform was retrieved on day 7. We proceeded with analyzing all samplers (including the unplugged one), noting that discrepancies might be observed in the results obtained from the unplugged platform.
- Two VibraSP3 platforms were partially out of sediment at retrieval time on day 14. However, the passive samplers appeared to be embedded in sediment. We proceeded with analyzing all samplers (including the partially submerged samplers), noting that discrepancies might be observed in the results obtained from the partially submerged platforms.

Overall, the results of the deployment confirmed that the vibrating passive samplers could be deployed in a marine setting and recovered without damage. Additional studies are needed to evaluate the effectiveness of the vibrations in enhancing kinetics.

Laboratory and field testing of Prototypes P2-125G and P2-110G:

Laboratory Experiments: Prototype P2-125G was first tested in a clayey freshwater sediment from Mirror Lake, DE for a total of 19 days. A vibration datalogger attached to one of the fins of the P2-125G device recorded the frequency and magnitude of vibration during the deployment period. After the first period of 6 days, the device was retrieved, and the sediment homogenized before deploying for the next period of 9 days. Figure 3.5a shows the variation in the intensity of vibration (the G force) over the period of 15 days separately for these two periods. It was observed that the prototype vibrated through the entire period of deployments and the average amplitude of vibration of the device within the sediment ranged between 2-5G over the entire period. The intensity of vibration measured by the G value decreased slightly over both the time period of deployment. Since the battery was not charged and the sediment was homogenized between experiments, the damping is not because of loss of charge from battery. A possible hypothesis for the reducing G value of the vibration is that the homogenized sediments used in the laboratory was unconsolidated at the start of the experiment. With time, the sediment consolidated, increasing the resistance to vibration and causing greater damping over time. However, this effect due to consolidation is small. The source of the additional large peaks of vibration is not clear. These could be caused by disturbance in the laboratory to the mesocosms during periodic checking of the experimental setup. Battery power was found to be enough to run the device for the period of deployment.

Both the prototypes P2-110G and P2-125G were then tested in the laboratory set-up multiple times in two more types of sediments: a silty freshwater sediment from Middle River and a silty organic rich estuarine sediment from Kingman Lake, Washington DC. The prototypes were deployed for 21-days in the Middle River sediment with two battery replacements after every 7 days and finally, for a total of 3 weeks in the Kingman Lake sediment. Prototype P2-110G survived all deployments in the laboratory. The tests demonstrated that the device was leakproof through all the deployment periods and continued to vibrate for that period of time. The copper casing and fins showed some discoloration after deployments but remained structurally sound. It was ready to go out to the field. During the final retrieval of prototype P2-125G, the top aluminum cap with the battery compartment came loose and resulted in a leak. The damage was fixed followed by a third deployment for 2 days in the laboratory in the same sediment mesocosm. No further leaks were observed and prototype P2-125G was also deemed ready for a field deployment.

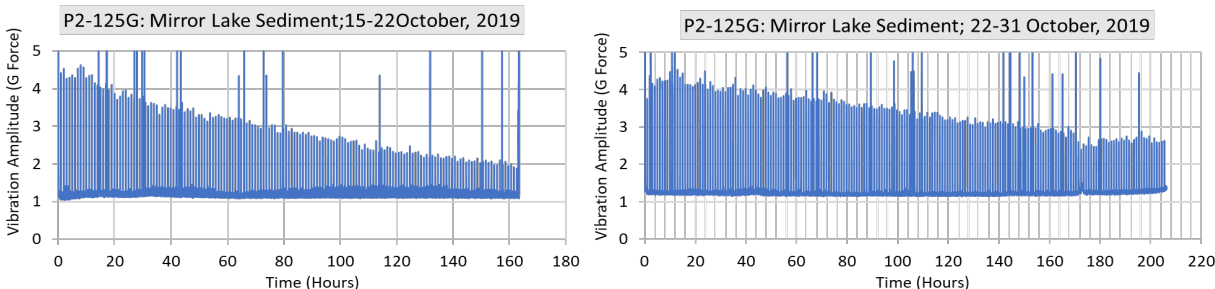


Figure 3.5a. Vibration Amplitude Reported as the Vector Sum of the G Force Values, as Recorded by the Tri-axial Vibration Sensor Tag Attached to P2-125G Vibrating Device, Over a Total of 15 Days (in Two-time Segments of 6 Days (Left) and 9 Days (Right)) Deployed in the Mirror Lake Sediment Mesocosm in Laboratory Setup.

Field Experiment: The two prototypes (P2-110G and P2-125G) were also deployed in the field in Kingman Lake, Anacostia River, Washington DC on Dec 10, 2019. In addition, static passive samplers that were not vibrated were also deployed alongside in sediments. The deployment was performed for a period of 10 days and all samplers were retrieved successfully at the end of the field deployment. The vibration sensor data showed that the vibrating prototype P2-125G vibrated with an amplitude of about 2.5G while inside sediment throughout the deployment time of 10 days until it was taken out on the day of retrieval. As seen in Figure 3.5b, the intensity of vibration was relatively constant over the 10-day deployment in the field. Thus, for consolidated field sediments, we do not observe the slow decline in G value as seen in unconsolidated sediments in the laboratory. The spikes in G value observed at the beginning and the end are likely due to manual handling during deployment and retrieval. The cause of the remaining random high spikes in G value seen during the deployment period is not clear. These could be potentially caused by unusual wave action in the field or impact from floating debris.

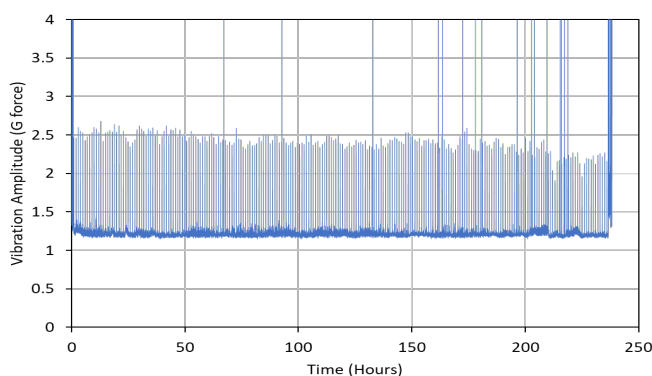


Figure 3.5b. Vibration Amplitude Reported as the Vector Sum of the G Force Values, as Recorded by the Tri-axial Vibration Sensor Tag Attached to P2-125G Vibrating Device, Over a Total of 10 Days Deployed in the Field at Kingman Lake, Anacostia River, Washington DC.

Optimization of sampler design and analytical methods through laboratory measurements of PCB compounds in sediment porewater

For the devices deployed in the laboratory, the damping resistances to the vibration were impacted by the nature of the sediments. This consequently impacted the kinetics of analyte uptake from the sediment or loss of PRCs from the PE into the sediment. The first sediment, collected from Mirror Lake was clayey in nature and with a rate of vibration at a frequency of once every hour for 5 seconds, the sediment settled and consolidated at the base of the sampler quickly and caused strong damping in the device, reducing the effectiveness of vibration. Consequently, there was barely any detectable difference in the efficiency in the performance of the static vs the vibrating platform prototypes in terms of fractional non-aroclor PCB PRC loss from the samplers. The subsequent deployment was conducted using the PE samplers loaded with non-labeled PRCs, in a silty sediment rich in organics from Middle River with high background PCB levels. The high background contamination made it difficult to analytically differentiate between the peaks corresponding to the background levels of the contaminants from those of the rare non-labeled PRCs. Thus, the GC-ECD measurements of the fractional PRC losses were highly variable and inconclusive. Finally, the prototypes P2-125G and P1-14G along with the static samplers were deployed in the mesocosm prepared using sediment from Kingman Lake. The concentration of target PCBs accumulated in the samplers in the first 7 days

showed that the background levels of the rare environmental PCB compounds that were used as PRCs were negligible in this sediment even under the influence of vibration. Thus, it would be safe to use the non-labeled PRCs for this sediment.

After the first set of experiments, we switched to using 25um thick PE loaded with C13 labeled PRCs which were more reliable as compared to the non-labeled PRCs thereby eliminating the possibility of interference from background contamination of the used PRCs. This also required us switch to a mass spectrometric analysis of the PCBs. A series of batch experiments were conducted to optimize the most effective method of loading C13 PCB PRCs on PE passive samplers in a homogenous way. It was concluded from the batch experiments that when neat C13 PCB PRC solutions in nonane were reduced to almost dryness followed by dilution in hexane and added to an 80:20 Methanol: DI water solution, it created a homogenous loading solution. About 100g of PE per batch could be loaded in 3L of this loading solution and PRC initial measurements with <10% standard deviation across replicates was achieved.

Problems encountered and solutions

We learnt the following lessons from the sequence of experiments conducted using different vibration prototypes in different sediments:

- (a) While working with non-aroclor PCB compounds as PRCs (or non-labeled PRCs), it is important to make sure that the background levels of these compounds are negligible (compared to the loaded PRC level), even under the vibration induced expedited uptake rates. Otherwise, the actual fractional loss of the PRCs is prone to error and can lead to incorrect porewater measurements. For future experiments, C13 PCB PRC loaded samplers were adopted for conducting accurate porewater measurements.
- (b) The nature of the sediment plays a significant role in determining the rate of uptake and loss kinetics of the organics into the sampler. A clayey sediment might not let enough vibration to take place for significant mass transfer. We observed that even an average vibration amplitude of 2G was not enough to break the resistance offered by the clayey sediments from Mirror Lake for accurate porewater measurements (using large fins). A new sediment mixture was prepared using PCB contaminated sediments from several sites studied previously, as shown in Figure 3.3. This new sediment mixture was used for all future lab experiments. In addition, the fin size was reduced to reduce vibration resistance.
- (c) Homogenous PRC loading of samplers is critical to measuring accurate fractional approach to equilibrium. We made sure that all the PRC impregnated samplers used in our subsequent experiments were homogeneously loaded (i.e., the initial PRC measurements from at least 3 replicate samplers from a batch had less than 10% relative standard deviation).
- (d) Prototype P2-110G proved to be a safer and leakproof prototype as compared to P2-125G because of its relatively simpler design, shorter fins (less impacted by damping action of sediments), and with less replaceable parts. The high-power consumption and negligible improvement in vibration amplitude of the P2-125G prototype made us adopt the P2-110G device for future experiments.
- (e) For subsequent studies, 25 um thick PE sheets were chosen over 50 um thick PE sheets because a thinner sampler allowed faster mass transfer (concluded from modeling experiments in Chapter 1)

PCB concentration accumulated in passive sampler:

Field Measurements: Initial field deployments were conducted at Kingman Lake, Washington DC. The total PCB concentration accumulated on the PE samplers (loaded with non-labeled PRCs at this point) enclosed in static and vibration prototypes: P2-110G and P2-125G, after 10 days of deployment are shown in Figure 3.6, left. It is observed that the uptake of native PCBs by the vibrating samplers were 2-3 times higher compared to the static sampler. The concentrations of target PCB congeners are grouped based on the number of chlorine atoms on them into the corresponding homolog groups and plotted for each sampling prototype (Figure 3.6, right). The rate of uptake in case of the static passive samplers is almost an order lower as compared to that of the vibrating platforms for the tri-penta congeners. However, there exists a large uncertainty in the measurement of concentration of the tetra group of congeners. This uncertainty can be attributed firstly to the variation in the physical conditions of the two fins due to some external source of restriction in the sediment that did not let one of the fins to vibrate as much. A second source of this uncertainty is actual local special variability in the background concentration of the target compounds. In order to eliminate the second source of uncertainty, the PRC loss from the PE should be monitored. However, the fractional losses of the PRCs were not enough and too variable for accurate corrections to be applied. Note that non-aroclor PCB congeners were used as PRCs in this study and all analyses were performed using a GC-ECD instrument. The Kingman Lake was also frozen at the time of retrieval and the low temperatures can also cause a slowdown of overall mass transfer.

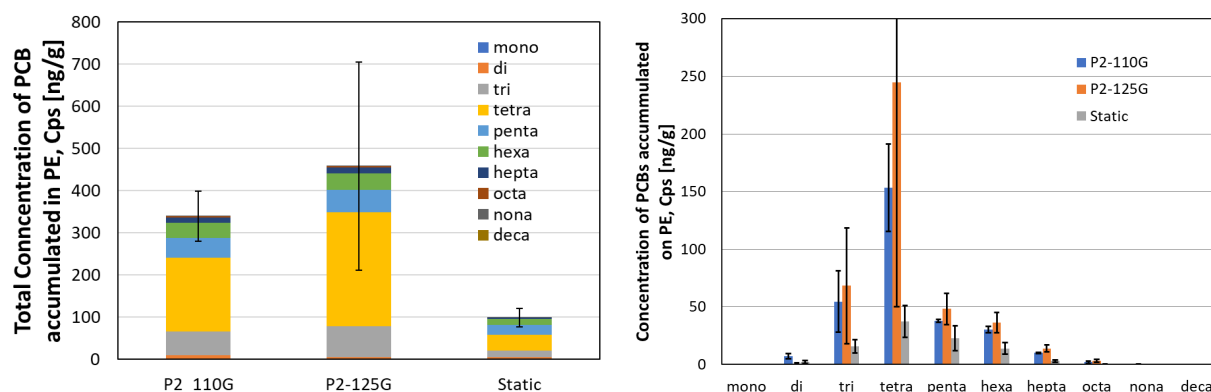


Figure 3.6. Comparison of Total (Left) and Homolog Distributed (Right) PCB Concentration Accumulated in PE from a 10-day Deployment of Static and Vibrating (P2-110G and P2-125G) Passive Samplers in the Field.

Laboratory Measurements: Learning from the lessons from the previous laboratory and modeling experiments, 25um thick PE passive samplers loaded with homogenously loaded C13 PCB PRCs were deployed in the new sediment mixture. Samplers were deployed in static and well-mixed conditions along with the optimized vibrating sampler prototypes P2-110G and P1-14G as shown in Figure 3.3.

The total concentration of PCB target analytes accumulated in the sampler at the end of 8 days (Figure 3.7a) were in the range of 50,000ng/g for both the P1 prototype and static samplers. Prototype P1 proved to have very little improvement in mass transfer over the static mode. In comparison, the total concentration of PCB target analytes accumulated in the sampler at the end

of 8 days were in the range of 250,000ng/g for both the P2 prototype (with the reduced fin-width) and well-mixed systems. The bigger motor on the P2 device was clearly able to disrupt the WBL associated with the PE in the closely packed sediment environment that helped faster desorption of the PCB compounds from the sampler.

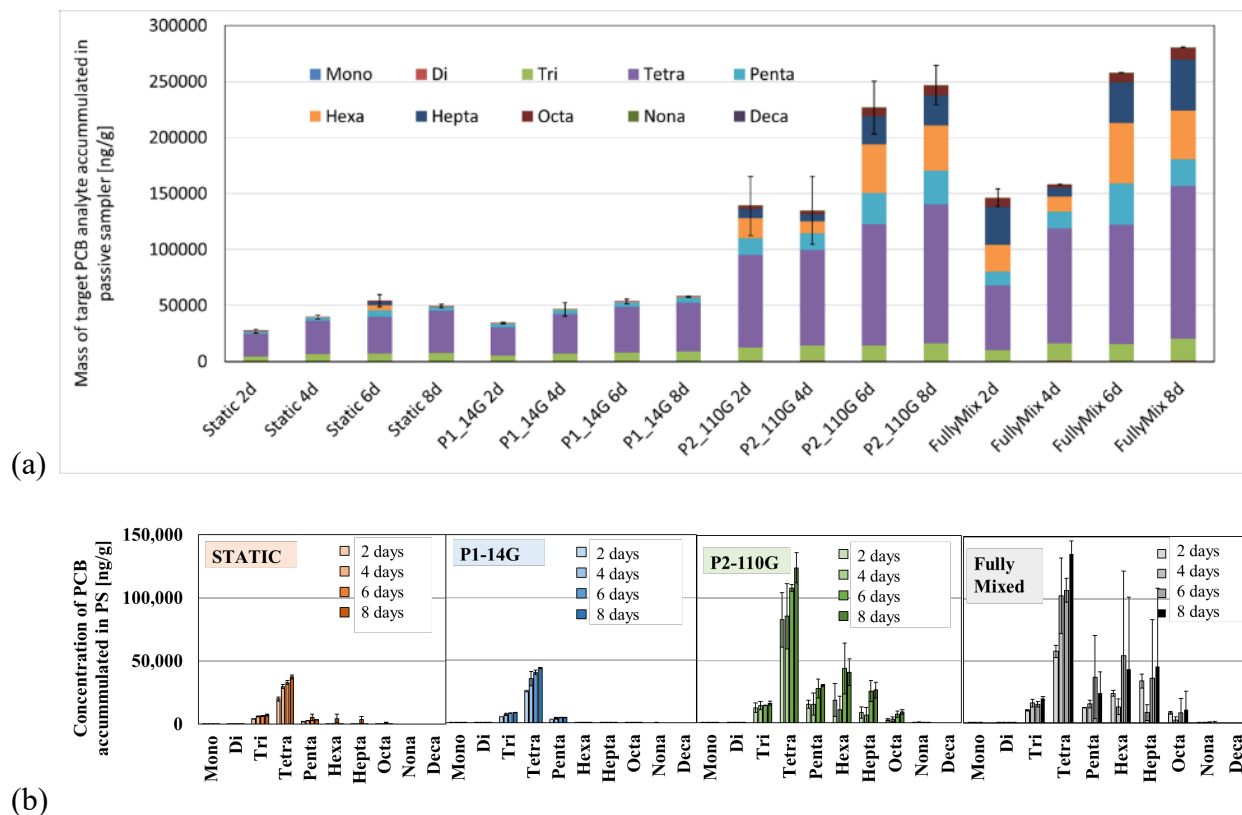


Figure 3.7. (a) Total Concentration and (b) Homolog Distributed Concentration of PCB Target Compounds Accumulated in the Sampler, C_p [ng/g], in Static, Vibration (P1, P2), and Well Mixed Systems Exposed for 2,4,6,8 days in the Sediment.

The homolog distribution plot of the accumulated PCB concentrations (Figure 3.7b) shows that the static and P1 vibration systems pick up about 10,000ng/g of tri, 40,000ng/g of tetra and about 5000 ng/g of penta PCBs. The fully mixed system picks up at least two times the concentrations of the tri, tetra and penta homolog PCBs as compared to the static and P1 systems. Additionally, the hexa, hepta and octa homolog target compounds are also accumulated that are barely measured in the static sampler. For example, after 8 days, P2-110G sampler accumulates 264-fold higher mass of heptachlorobiphenyls compared to the static deployment for the same period. The vibration induced by the P2 prototype on the passive sampling platform allows the accumulation of tri-octa homolog group target analytes from the sediment porewater to levels comparable with the fully mixed system.

Fraction of PRC loss after consecutive exposure periods: We demonstrated from the fractional loss of PRCs that, when both the prototypes were programmed to vibrate at the same frequency of 2 s pulse every 5 min pause, the P2 prototype, with the more powerful motor achieved mass transfer rate close to that of the well mixed mode. As shown in Figure 3.8, at the end of 8 days,

prototype P1 lost 50% of tetra homolog PRC (13C-labeled PCB 54) and 10% of the hepta homolog PRC (13C-labeled PCB 178) which were very comparable to the static samplers. Prototype P2 with the wide fins did not perform as efficiently and lost 60% and 10% of the tetra and hepta homolog PRCs respectively at the end of 7 days. Thus, very little improvement in the rate of approach to equilibrium over the static samplers was observed. However, when the width of the fins on P2 were reduced to half, it was able to achieve 90 % loss of the tetra homolog PRC and 35 % loss of the hepta homolog PRC, which was comparable to the well-mixed system at the end of 8 days. This implied that effective distribution of the strong vibration was an important factor in addition to having a powerful motor, to increase the rate of mass transfer and help faster approach to equilibrium of the passive sampling device. This modified design of P2 was used for our further analysis.

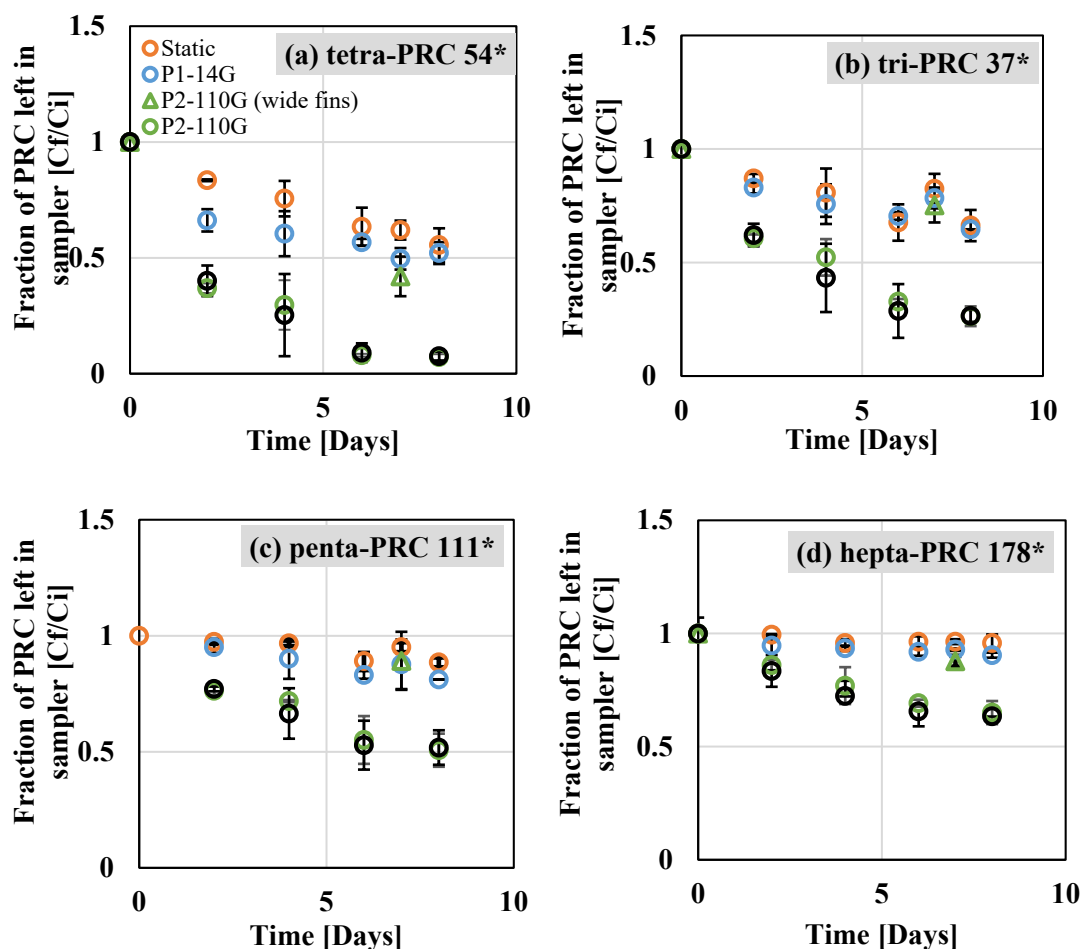


Figure 3.8. Fraction Remaining of 13C-labeled PCB (a) PRC 54 (tetra), (b) PRC 37 (tri), (c) PRC 111 (penta) and (d) PRC 178 (hepta) from 1 mil PE Sampler.

Homolog distribution of required PRC correction: The major homolog groups of target analytes ranged between the tri to octa for this sediment. The PRC fractional loss information for the six PRCs was used to calculate the fractional equilibration term (f_{eq}) for all the target analytes belonging to the tri-octa homolog groups using the PRC correction calculator. The amount of correction required for each compound was calculated as $(1-f_{eq})$ for each system and plotted as a

homolog distribution (Figure 3.9). The red dotted line corresponds to 0.9 corresponding to the requirement of a 90% correction (or 10% loss of PRC/uptake of corresponding analyte). We observe that the static system required 60-95% correction to be applied for the tri-penta homologs with the 8-day exposure sample. The amount of correction required for the higher homolog groups of hexa-octa is more than 90% and can lead to error prone porewater estimations by the static system. The P1 prototype required 60-90% correction to be applied for the tri-penta and 80-95% correction to be applied for the hexa-octa homologs respectively. While the relatively high level of corrections required for the higher homologs for this system might not be enough for an error proof porewater estimation, we see some improvement over the static system that is promising. In comparison, the P2 and fully mixed systems require only 10-40% correction for tri-penta and 50-80% correction for hexa-octa homolog group compounds. The P2 system with its more effective vibration induced approach to equilibrium requires less PRC correction for the higher homologs hexa-octa and can give a more accurate final estimate of porewater concentrations.

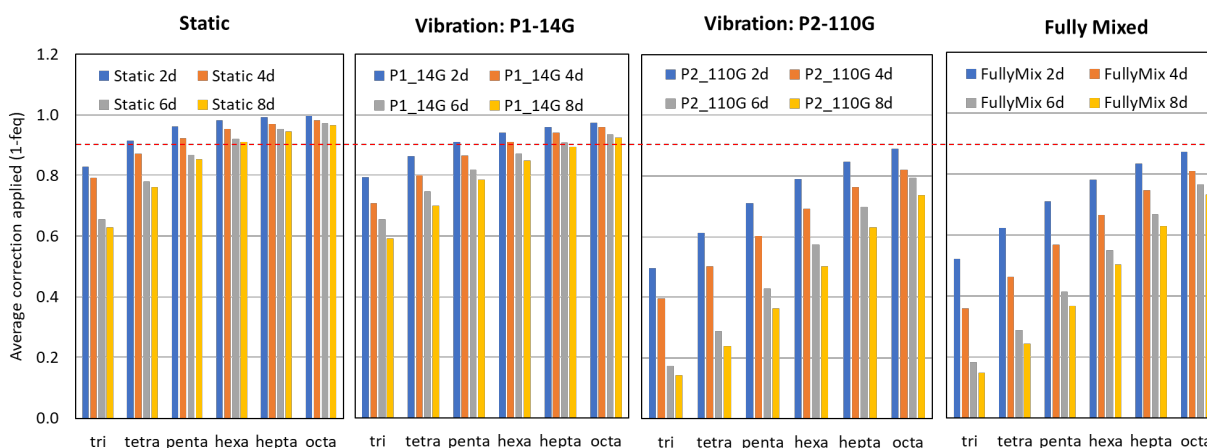


Figure 3.9. Homolog Distribution of Required PRC Corrections (tri-octa) for the Static, Vibration and Fully Mixed Systems.

3.5 CONCLUSION

In-situ measurements of more hydrophobic contaminants in sediment porewater is challenged by very low flow velocity of porewater. Introducing periodic vibration on the sampling platform disrupts the water boundary layer on the sediment side that otherwise slows down mass transfer. In this study we were able to develop robust prototypes that could survive field deployments. They were larger in size with a more effective vibration than the proof-of concept designs developed earlier. The larger device with greater mass of deployable passive sampler is suitable for targeting low porewater concentrations in the sediment. We observed that with the larger of the two prototypes we were able to achieve close to 35% equilibrium for the hepta homolog PCB compounds in only 8 days. This will help accurate PRC correction to be applied for porewater concentration measurements.

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4.0 CHAPTER 4: ANALYSIS OF TIME INTEGRATION IN EQUILIBRIUM PASSIVE SAMPLING.

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4.1 ABSTRACT

Passive samplers deployed in the field for several months is expected to provide a time-weighted average concentration over the entire observation period that is important for ecological exposure assessment. Previous studies have not provided a comprehensive mathematical model to evaluate the diffusive transport through internal and external resistances to PE samplers under changing ambient concentrations. We address this knowledge gap by using our theoretical modeling framework of exchange kinetics of PCBs in PE passive samplers using the diffusion model and the first-order model. The impact of the timing of fluctuations, hydrophobicity of the analyte, and sampler thickness on the final measurement was examined by comparing against the simulated time-averaged ambient concentration. The accuracy of the diffusion and first-order models were compared and any underlying cause of inconsistency between the predicted final water concentration by the two models explained. We considered a 10X dilution pulse in the actual water concentration outside the sampler that lasts for 10 days out of a total exposure period of 90 days. The responses of a 1 mil PE sampler to the pulsed perturbation in ambient water column were simulated for the changing scenarios of increasing closeness of the starting day of the pulse to the end of exposure period. We show that the heavier, more hydrophobic compounds are slow in transfer into the polymeric sampler and require longer times of integration compared to the less hydrophobic congeners. The optimal time-period of integration for a 25 μm PE sheet ranged from 14-15 days for a dichlorobiphenyl to 43-45 days for a hexachlorobiphenyl. We also show that a thin sampler has a shorter time-period of integration as compared to a thicker one (16 days for 0.3 mil and 40 days for 3 mil) implying that the thinner sampler recovers from the influence of the perturbation faster than the thicker one.

4.2 INTRODUCTION

Passive Sampling (PS) technology for monitoring hydrophobic organic contaminants in the environment. The freely dissolved concentration (C_{free}) of hydrophobic organic contaminants (HOCs) like polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) and pesticides provides a measure of chemical activity and is the thermodynamic driving force for partitioning into various environmental phases including biota (Ghosh et al., 2014). The conventional method of grab sampling has many shortcomings: 1) the practical volume of water sampled is often insufficient to reach detection limits of the analytical instruments used to measure these chemicals, 2) traditional grab samples of water represent concentration levels present in the water at the time of sampling and requires repetitive sampling to represent a time-weighted average concentration at the site (Alvarez et al., 2005) which can be both time consuming and expensive, 3) separation of colloidal particles can be difficult and can bias results for strongly hydrophobic compounds. In the past two decades, passive sampling technology has gained considerable interest and has been used in many overlying water and porewater monitoring applications (Adams et al., 2007; Arp et al., 2015; Fernandez, Macfarlane, et al., 2009; Lohmann, 2012). It has proved to be a good surrogate for bioaccumulation measurements and availability to benthic organisms of HOCs in many studies (Lu et al., 2011; Needham & Ghosh, 2019; Rosen et al., 2012).

Samplers are classified as kinetic (linear) or equilibrium types, depending on the accumulation stage reached during deployment. The linear (kinetic) phase extends until approximately $t = t_{1/2}$. The half-life ($t_{1/2}$), defined as the time required for the sampler to reach half the equilibrium concentration. Kinetic samplers use the rate of uptake during the linear phase to interpret the external concentration driving force for uptake.

The equilibrium sampling approach on the other hand attempts to design the sampler and exposure duration such that the sampler moves into the curvilinear stage and finally approaches equilibrium. The principle of equilibrium sampling is to bring a polymer in contact with the environmental medium (like sediment porewater or surface water) for attaining equilibrium for the target analytes while ensuring that the polymer does not deplete the concentration of the analytes in the surrounding medium (Mayer et al., 2003). The measured concentration of the analytes in the polymer can then be translated to the freely dissolved concentration by using the right thermodynamic partitioning coefficients for the analyte-polymer pair. Thin sheet single phase polymers like Polyethylene (PE), polydimethylsiloxanes (PDMS) and polyoxymethylene (POM) are some of the common materials used in equilibrium sampling (Lydy et al., 2014). While the design may not guarantee actual achievement of equilibrium, the use of performance reference compounds have enabled accurate corrections for the extent of non-equilibrium for the less mobile compounds. Sampling of complex heterogeneous sediment matrix has experimentally provided more precise results when performed in the equilibrium regime than in the kinetic uptake regime (Jahnke et al., 2012; Mayer et al., 2000).

Some of the factors that influence the time taken by a sampler to reach equilibrium are: physicochemical properties of the target analyte, environmental deployment conditions like flow velocity, temperature, biofouling, and the sorptive and physical properties of the selected polymer (Mayer et al., 2014). Often, when equilibrium passive samplers are deployed for times too short to attain equilibrium, they are impregnated with a known concentration of performance reference compounds (PRCs) that have the similar diffusivities and partitioning properties as target analytes

before deployment. As illustrated in Figure 4.1, the fractional loss of the PRC from the sampler at the end of the exposure period (f_{eq}) can be used as a measure of the system's chemical-specific fractional equilibrium of the target analyte. This is possible because the PRC desorbing from the sampler and target analyte absorbing into the sampler face identical mass transfer resistances (Adams et al., 2007; Apell & Gschwend, 2014; Fernandez, Harvey, et al., 2009).

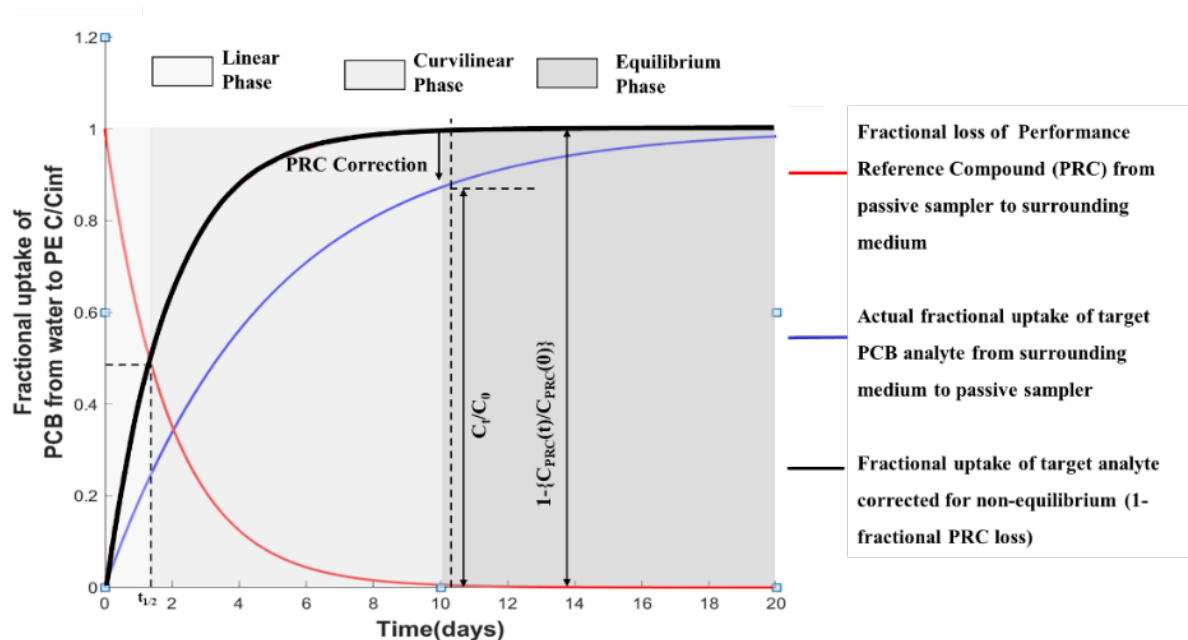


Figure 4.1. A Typical Passive Sampler Accumulates Target Compounds from the Surrounding Medium and Passes through the Kinetic, Curvilinear, and Equilibrium Regimes Over Its Time of Exposure.

Fractional loss of a known concentration of PRCs from the sampler (red) is used to correct the actual fractional uptake of target analytes (blue) to obtain the concentration the sampler would reach (black) at equilibrium.

Models used for simulation of exchange kinetics of contaminant mass

Three kinds of models are mostly used for analyzing sampler-water exchange kinetics: the chemical reaction kinetics (CRK) model, the mass transfer coefficient (MTC) model, and the diffusion model.

The CRK model is based on models describing bioconcentration (analogy with chemical reaction kinetics) where the uptake of the chemical compounds from water into sampler is the net result of the uptake and elimination reaction processes. The MTC model is based on the mathematical description of solute-mass transfer through sequential but distinct rate limiting physical environments/phases/regions. For a single-phase sampler like PE, these phases are the water boundary layer (WBL), biofilm (not always applicable), and the polymer membrane. The CRK and MTC models are very similar because they assume that the exchange process is first order with respect to reactant concentration. They differ in the way the overall exchange rate coefficient (k_o) is calculated. The k_o for the CRK model is an empirical constant. The k_o for the MTC model is defined in terms of fundamental processes that can be separately modeled (Huckins et al., 2006).

These two models are often collectively called the sampling rate models because they express the compound accumulation in terms of an equivalent sampling rate R_s which is related to k_o and the surface area of the sampler, A , by: $R_s = k_o A$. Both the CRK and the MTC models assume linear concentration profiles in the polymer and WBL sides which may or may not always capture the true nature of mass transfer. This is because the mass transfer rate coefficients on each side might vary with changes in the concentration gradients that develop over time (Tcaciuc et al., 2015).

The diffusion model, on the other hand, assumes the presence of a diffusive WBL outside the polymeric sampler. It applies Fick's second law of diffusion to both the polymer and WBL and then analyzes the concentration profiles within the polymer and the water sides (Tcaciuc et al., 2015). Under high flow rate conditions as in sewers, the exchange kinetics is not fully WBL controlled (Green & Abraham, 2000). Exchange kinetics of organic compounds between passive samplers and water can be partly or completely controlled by transport in the polymer. In such cases diffusion models have predominantly been used (Endo et al., 2019; Fernandez et al., 2009; Thompson et al., 2015). A recent study (Booij, 2021) proposed a sampling rate model, that uses the Biot number (ratio of internal/external transfer resistance) and polymer/water phase ratio as key features. This model was applied to mixed rate control by polymer and WBL under scenarios of fixed aqueous concentrations (open systems, infinite water volumes, in situ sampling) and fixed amounts (closed systems, finite water volumes, ex situ sampling).

Limited theoretical understanding of mass transfer dynamics in passive samplers under fluctuating ambient concentrations. In the field environment, events like stormflow, industrial runoff, and tides lead to temporal variation in the ambient water concentrations of organic contaminants. Passive samplers deployed in the field over a period of time is expected to provide the time-weighted average (TWA) concentration over the entire observation period that is important for ecological exposure and loading assessments. Previous studies have explored the application of kinetic passive samplers in time weighted average (TWA) measurements. Kinetic samplers like chemcatchers, POCIS, and SPMDs have been used for monitoring polar organic contaminants and heavy metals in laboratory based modeled pulse events (Allan et al., 2007; Shaw & Mueller, 2009) and in the field (Birch et al., 2013; Fernández et al., 2014; Gale, 1998; Novic, O'Brien, et al., 2017; Škodová et al., 2016). Some studies predicted the integrative capability of kinetic samplers by the response-time method and deduced that they could accurately estimate the time-averaged concentration in the linear region of the accumulation curve and for a fluctuating concentration event when the length of fluctuation is smaller than the $t_{1/2}$ (Gale, 1998; Morrison et al., 2016; Mutzner et al., 2019). One study (Birch et al., 2013) used a flow-proportional passive sampling device that assumes that the total concentration and not the dissolved fraction is captured by the samplers. The influence of episodic events on the time integrative property of diffusive gradient thin film (DGT) samplers in measuring ambient concentrations of heavy metals Cd, Cu, Ni, Pb and Zn has also been studied (Allan et al., 2007).

To accurately estimate the true TWA concentration, knowledge of the accumulation mechanisms of the contaminants of interest within equilibrium passive samplers, surrounding medium and environmental conditions is necessary. Previous studies have confirmed that exchange kinetics across sampler and water involves transport through the WBL, fouling layer, membrane, and sorbent, each step limiting the rate of exchange to a greater or smaller extent (Booij et al., 1998, 2017; Fuchte et al., 2020). The responses of single-phase equilibrium passive samplers to possible environmental situations when ambient concentrations vary linearly with time, decrease

exponentially with time, constitute a pulsed event, or oscillate regularly with time were theoretically analyzed (Hawker, 2010). The first-order response curves were found to bear a footprint of the pattern in which the ambient concentrations varied over time often with a measurable time lag. This information from the sampler response can be used, in theory, to derive the specific details of the temporal fluctuation of the contaminant in the ambient fluid.

Thus, while kinetic passive samplers have been applied for TWA measurements, the response of equilibrium passive samplers to fluctuating ambient concentration has been theoretically analyzed using the sampling rate model. None of the previous studies have provided a comprehensive mathematical model to demonstrate the diffusive transport through internal and external resistances to PE samplers under changing ambient concentrations. There exists a clear knowledge gap of a more mechanistic understanding of how the uptake of different hydrophobic organic contaminants is impacted by the design of equilibrium passive samplers (like PE sheets) under fluctuating ambient concentration scenarios that can help adapt sampling practices.

In this study we aim to address this gap by developing a comprehensive modeling framework of exchange kinetics of HOCs (PCBs here) in PE passive samplers to understand the impact of the timing of fluctuations, hydrophobicity of the analyte, and sampler physical characteristics on the final measurement. Here we try to answer the question, ‘how well do passive sampler concentrations represent the time-averaged concentration over an entire deployment period?’ In addition, we compare the predictive accuracy of the diffusion and first-order models to identify the underlying causes of any inconsistency between the two models. The overall goal of this research was to develop the mathematical framework to describe mass transfer in time-integrated passive sampling that can be applied to optimize long- and short-term deployments in the field for pore-water and surface water measurements.

4.3 METHODS

Modeling framework to understand time-integration in equilibrium passive sampling

The theoretical modeling framework of exchange kinetics of PCBs in PE passive samplers was built using the diffusion model and the first-order model. The impact of the timing of fluctuations, hydrophobicity of the analyte, and sampler thickness on the final measurement was examined by comparing against the actual time-averaged ambient concentration used in the simulated input. The accuracy of the diffusion and first-order models were compared and any underlying cause of inconsistency between the predicted final water concentration by the two models accounted for.

Modeling actual time-averaged water concentration

The first step of building the modeling framework was to decide the nature of perturbation in ambient concentration. For this, we considered a 10X dilution pulse in the actual water concentration outside the sampler that lasts for 10 days out of a total exposure period of 90 days. **Figure 2(a)** demonstrates such a dilution with pulsed perturbation starting on the 70th day. The actual time-averaged concentration of the ambient water $C_{w,Actual}$ was calculated as:

$$C_{w,Actual} = \frac{(C_w^{np} \times t^{np}) + (C_w^p \times t^p)}{t} \quad (1)$$

where C_w^{np} and C_w^p are the actual water concentration in the no-pulse and pulsed scenarios respectively, t^{np} and t^p are the time periods of no-pulse and pulse and t corresponds to the total exposure period (90 days).

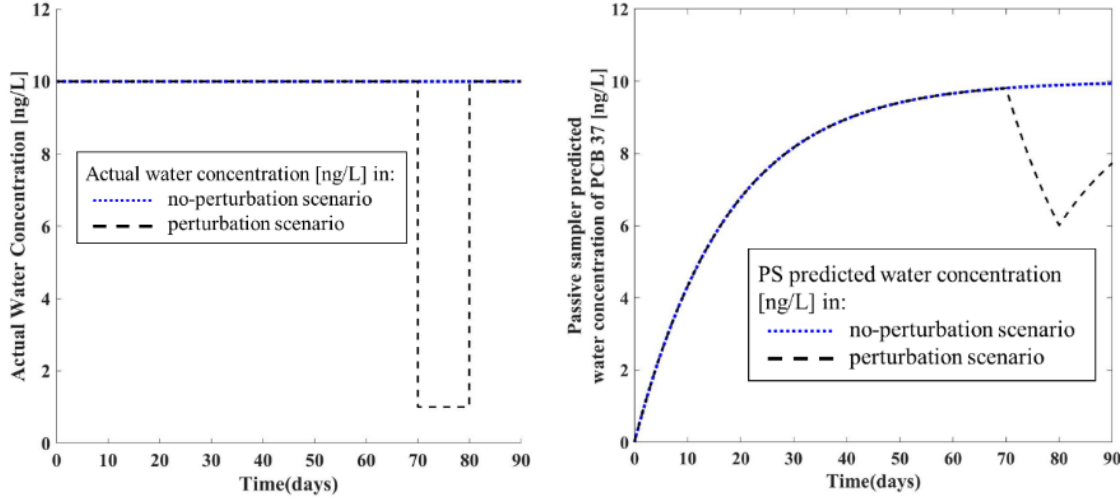


Figure 4.2. (a) Actual Water Concentration and (b) Passive Sampler Predicted Water Concentration (Without PRC Correction) of PCB 37 in Two Scenarios: (i) no Perturbation (Blue Dotted) and (ii) 10x Dilution Pulsed Perturbation Starts on the 70th Day and Ends on the 80th Day (Black Dashed).

Modeling response of PS to pulsed perturbation using Fick's diffusion model

The uptake of PCB target analytes into a PE sampler of 1 mil thickness was modeled assuming the presence of a water boundary layer of mid-range thickness of 0.02 cm on the outside of the PE sampler. Applying Fick's second law to the polymer and water boundary layer, we obtained the governing equations:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \text{ when } -L < x < L \quad (2)$$

$$\frac{\partial C_W}{\partial t} = D_W \frac{\partial^2 C_W}{\partial x^2} \text{ when } -L > x > -(L + b) \text{ and } L < x < (L + b) \quad (3)$$

Here, C_{PE} is the concentration of PCB analyte accumulated in PE (ng/g of PE), C_W is the concentration of analyte in the ambient water (ng/L). We assume that the thickness of the PE sheet is $2L$, D_{PE} is the diffusion coefficient within the PE, b is the thickness of the WBL, and D_W is the diffusion coefficient in the water. While sampling environmental systems, the amount of analyte accumulated in the sampling polymer is so small in the order of ng/g that it barely affects or changes the diffusivity of the sampler.

Thus Equation 2 controls the diffusion inside the PE, while Equation 3 controls the diffusive process within the water side. At the interface of PE and water, the mass of PCB is conserved as the diffusive fluxes are the same:

$$D_{PE} \frac{\partial C_{PE}}{\partial x} = D_W \frac{\partial C_W}{\partial x} \quad \text{when } x = L \text{ and } x = -L \quad (4)$$

A local equilibrium is assumed at the polymer surface:

$$C_{PE} = K_{PE-w} C_W \quad \text{when } x = L \text{ and } x = -L \quad (5)$$

To calculate the mass of target analyte accumulated in the PE in response to the constant (*or no-perturbation scenario*) and time-variable water concentration (*or perturbed scenario*) at the end of the exposure period, $C_{PE,t}$, Crank's explicit finite-difference numerical solution of equations 2, 3 on a flat plate (**Supplement S1**) in an infinite water bath was used (Crank, 1975). The uptake profile of PCB 37 as modeled by the diffusion equation is demonstrated in Figure 4.2(b) for both the perturbation and no-perturbation scenarios.

Modeling response of PS to pulsed perturbation using a First Order Model

In the current literature, for single phase samplers the rate of uptake of chemicals into the passive sampler is the result of competing uptake and elimination processes and can be explained in the form of a first-order one-compartment model (Bartkow et al., 2005):

$$\frac{dC_s}{dt} = k_{abs} C_w - k_{des} C_s \quad (6)$$

where C_s is the concentration in the sampler and C_w is the concentration in the water. k_{abs} and k_{des} are the first order absorption and desorption rate constants respectively (time^{-1}). The mass of contaminants accumulated on the sampler ($C'_{PE,t}$) for *constant* and *time variable* water concentration was calculated by the numerical integration of Equation 6 under both scenarios.

Table 4.1. List of PCB Compounds in Ascending Order of Hydrophobicity (Log KOW) and the Physiochemical Properties Used in Simulating Uptake Kinetics in PE.

Sl No.	Homolog Group	PCB Compound	Mol.Wt [g/mol]	Log D _{PE} (cm ² /s)	D _w (cm ² /s)	Log K _{OW}	Log K _{PE-w} [L _w /L _{PE}]
1	Di	PCB 4	223.1	-8.6	5.8E-06	4.7	4.2
2	Di	PCB 15	223.1	-8.6	5.8E-06	5.3	5.0
3	Tri	PCB 22	257.5	-8.8	5.2E-06	5.6	5.3
4	Tri	PCB 37	257.5	-8.8	5.2E-06	5.8	5.6
5	Tetra	PCB 47	292.0	-9.0	4.8E-06	5.9	5.6
6	Tetra	PCB 73	292.0	-9.0	4.8E-06	6.0	5.8
7	Penta	PCB 100	326.4	-9.2	4.4E-06	6.2	6.1
8	Penta	PCB 110	326.4	-9.2	4.4E-06	6.5	6.4
9	Hexa	PCB 128	360.9	-9.3	4.1E-06	6.7	6.7

Correction for non-equilibrium

Using the models described above, the fractional loss of the reference compounds from PE to water, was used to correct for non-equilibrium conditions.

Diffusion model: For the diffusion model, the same PCB compound was assumed to act as the reference and target analyte. In reality, the PRC can be a stable isotope labeled analog compound. The PRC modeling was done by changing the initial conditions of the model. When the analyte acts as the reference compound, its initial concentration in the PE is at a known high concentration and its conc in the water side is zero. When the analyte acts as the target compound, its initial concentration in the PE is zero while that on the water side is non-zero. The fractional loss of each of the reference compounds listed in Table 4.1, from PE to water (*feq*) was calculated at the end of running the diffusion model as the ratio of the mass of compound left in the sampler at the end of the known exposure period, M_t (ug), and the initial mass of PRC that the sampler was impregnated at, M_0 (ug):

$$feq = \frac{M_t}{M_0} \quad (7)$$

From this the corrected mass of target analyte accumulated in the PE, $C_{PE,t=\infty}$, and the corresponding water concentration at equilibrium $C_{W,t=\infty}$, was estimated for constant and time variable C_w as:

$$C_{PE,t=\infty} = \frac{C_{PE,t}}{(1-feq)} \quad (8)$$

$$C_{W,t=\infty} = \frac{C_{PE,t=\infty}}{K_{PEW}} \quad (9)$$

where $C_{PE,t}$ is the mass of PCB analyte accumulated in PE (ng/g of PE) at the end of the exposure period that is calculated by the diffusion model.

First-order model: Assuming that (a) the sampler-water exchanges can be approximated as a first-order process, (b) the rates of absorption (of target compounds) and desorption (of reference compounds) are equivalent and can be represented as an exchange rate coefficient (k_e), the k_e was calculated from the equation:

$$k_e = \frac{1}{t} \ln \frac{C_{PE,PRC}^{t=0}}{C_{PE,PRC}^t} \quad (10)$$

where $C_{PE,PRC}^{t=0}$ and $C_{PE,PRC}^t$ are the concentrations of the reference compound initially and at the end of runtime of the experiment, respectively. Since k_e is an empirical term here, it was calculated from the diffusion model predicted initial and final concentrations of all the PRC compounds for each of the five sampler thicknesses of 0.3, 0.7, 1, 2, 3 mil separately (Table S4.1). Thus, the water concentration at equilibrium ($C'_{W,t=\infty}$) as predicted by the first order model was calculated as:

$$C'_{W,t=\infty} = \frac{C'_{PE,t}}{K_{PEW}(1-e^{-k_e t})} \quad (11)$$

where $C'_{PE,t}$ is the mass of PCB analyte accumulated in PE (ng/g of PE) at the end of the exposure period that was calculated by the first-order model.

Calculating time-period of integration and % accuracy:

The responses of a 1 mil PE sampler to the pulsed perturbation in ambient water column were simulated for the changing scenarios of increasing closeness of the starting day of the pulse to the end of exposure period. From this simulation as demonstrated in Figure 4.3, the approximate time that was required by a PCB compound (PCB 37) to recover from the pulse was calculated by comparing the passive sampler predicted concentration and actual water concentration for the compound. This value was the response time or time-period of integration, characteristic of the sampler-analyte duo and specific to the 10X dilution pulse that lasted for 10 days.

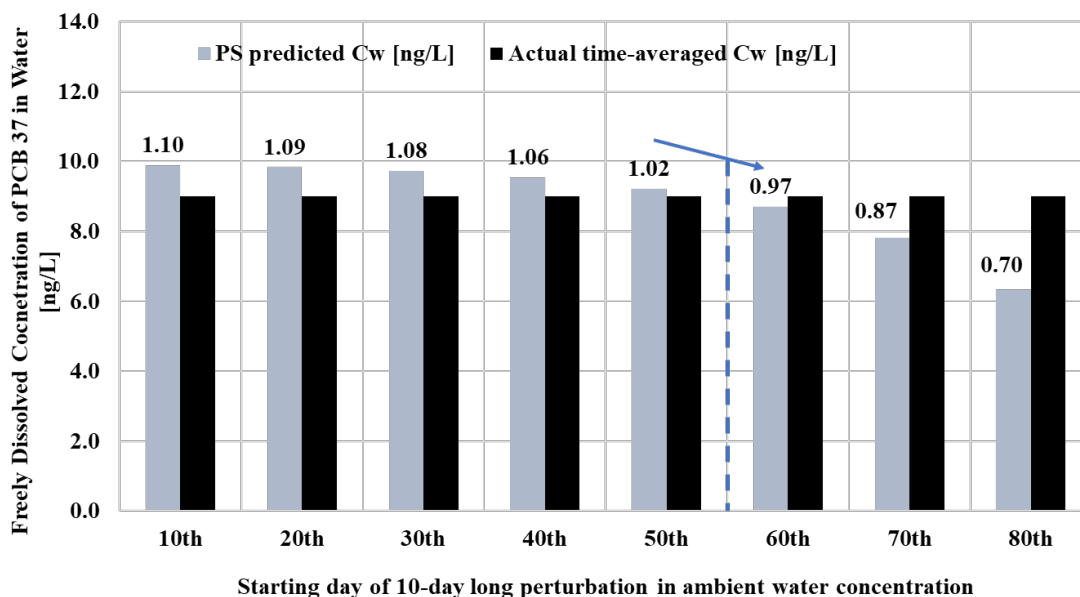


Figure 4.3. Comparison of Actual Time-averaged Concentration of PCB 37 Used as Input in the Model (Black Bars) with PS Predicted Concentration (Grey Bars) as Modeled by the Diffusion Equation, When the Starting Day of the 10-day Long Perturbation Moves Closer to the End of the Total Deployment Period, from the 10th Day to the 80th Day.

The % *accuracy* of the passive sampling system to predict the true time-averaged ambient concentration over the entire observation period was calculated as the percentage ratio of the predicted water concentration and the actual TWA concentration for all the pulse shift scenarios.

The time-period of integration and the % accuracy were calculated for the PCB analytes of varying hydrophobicity listed in Table 4.1 and PE thickness of 1-3 mil. Finally, the two models were compared for consistency in comparing the predictability of passive samplers under time variable C_w conditions.

Simulations corresponding to different scenarios were run using the modeling framework built in section 2.1-2.6 to study the impact of the timing of fluctuations, hydrophobicity of the analyte, and sampler thickness on the final measurement. The final estimates of sampler predicted water concentration under these scenarios were examined by comparing against the actual time-averaged water concentration to quantitatively analyze the nature of time-integration that a PE passive sampler can provide.

4.4 RESULTS

Impact of varying the timing of perturbation in ambient water concentration on the uptake kinetics of PCB compounds.

The influence of 10-day long pulsed perturbation introduced on different days throughout the deployment period, on the uptake of PCB 37 (Figure 4.3), demonstrated that the actual time averaged concentration stayed constant at 9 ng/L since the number of days that the perturbation lasts was constant at 10 days out of 90 days of total exposure irrespective of the day it was introduced. The passive sampler predicted water concentration, on the other hand, was not constant. It was overestimated by 10% when the perturbation starts on the 10th day of the deployment because the sampler had enough time to equilibrate post perturbation and lost its influence from the sampler memory. But, when the perturbation happened shortly before the end of the exposure, its influence was strong, and the predicted concentration was significantly lower than the actual time-integrated concentration over the 90-day deployment. The exact day when the passive sampler predicted concentration crosses over from being overpredicted to being underpredicted as compared to the actual time-averaged concentration was calculated for each compound by the method of interpolation of the over- and under-predicted concentration values and the corresponding days of introduction of perturbation. This day subtracted from the total time of deployment, was defined as the ‘time-period of integration’ for that PCB compound. It is the time, in days, that is required by the compound to recover from a 10-day long pulsed perturbation to provide the correct time averaged concentration. For PCB 37, the predicted concentration is equal to the actual time averaged concentration when the pulse starts on the 59th day (or 31 days prior to sampler retrieval) as indicated by the blue dashed line in Figure 4.3. The optimal time-period of integration for PCB 37 was thus calculated to be about 31 days when monitored using a 1 mil PE. It is the time, in days, that is required by PCB 37 to recover from a 10-day long pulsed perturbation.

Impact of compound hydrophobicity on their uptake kinetics under perturbed ambient water concentration scenario.

The impact of varying hydrophobicity of PCB congeners on their uptake kinetics under the influence of perturbation in ambient concentration was studied by plotting the fractional uptake profiles of 9 PCB compounds (Table 4.1), into a 25 μm thick PE with respect to time, as predicted by the diffusion model (Figure 4.4). We observed that when there was no ambient perturbation (Figure 4.4 a) the lower homolog group compounds, that are less hydrophobic, reached equilibrium much faster than the higher homolog group compounds that are relatively more hydrophobic. PCB 4 (solid red) reached equilibrium in less than 10 days while PCB 128 (green) reached only 25% of the actual ambient concentration in 90 days. When the ambient water concentration experienced a pulsed perturbation lasting 10 days starting on the 70th day (Figure 4b), for the same amount of change in the ambient water concentration, the fractional uptake into the 25 μm thick PE were different for different compounds. The lower homolog group compounds, which are more sensitive to the ambient perturbations, recovers from the impact of the perturbation very quickly unlike the more hydrophobic compounds. A di homolog group compound like PCB 4 for example, undergoes a very steep fall in the passive sampler concentration because of the low water concentration during the pulse event but also recovers very quickly after the pulse. In Figure 4.5 we observe that when the perturbation starts on the 70th day, the PS predicted concentration for PCB 4 at the end of 90 days is overpredicted by 11% as compared to the actual time-averaged concentration. For this

compound, thus, the minimum time required by the sampler to recover from the memory of the perturbation is as small as 15 days. The concentration of a tetra homolog group compound like PCB 47, on the other hand is underpredicted by 13% when the perturbation starts on the 70th day. Thus, the time-period of integration for PCB 47 is higher than that of PCB 4, 32 days.

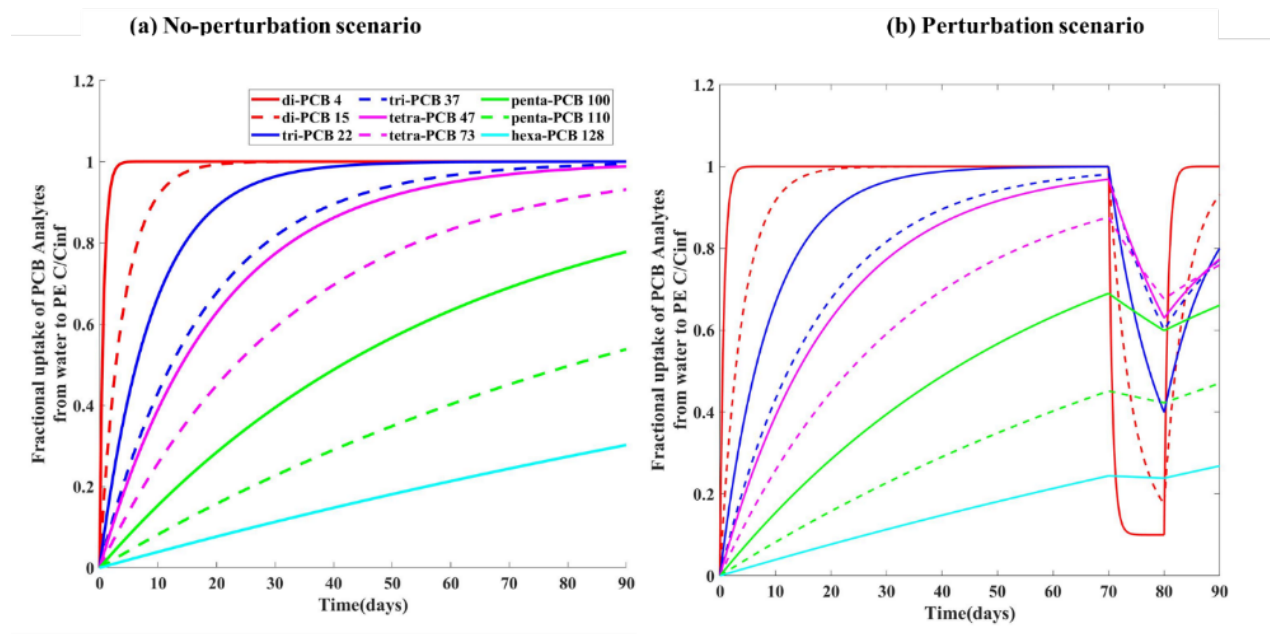


Figure 4.4. Fractional Uptake of PCB Compounds of Varying Hydrophobicity on a 25um Thick PE Passive Sampler, as Predicted by the Diffusion Model in Two Scenarios: (a) No Perturbation and (b) Pulsed Perturbation that Starts on the 70th Day in Ambient Water.

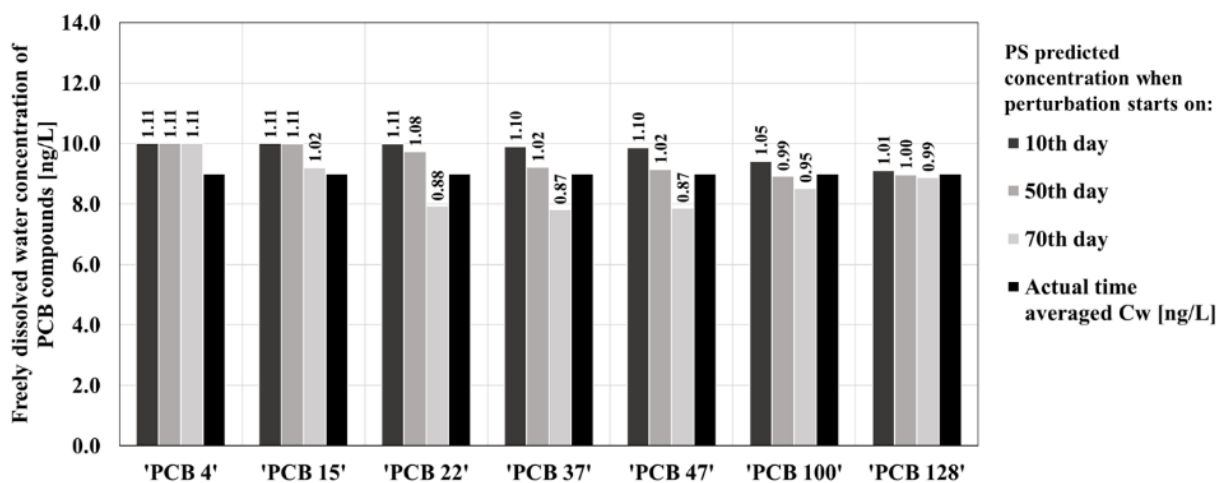


Figure 4.5. Comparison of Actual Time-averaged Concentration of PCB Compounds from Different Homolog Groups (Black Bars) with PS Predicted Concentration (Grey Bars) As Modeled by the Diffusion Equation, When the Starting Day of the 10-day Long Perturbation Moves Closer to the End of the Total Deployment Period, from the 10th day to the 80th Day.

The correlation between the hydrophobicity of PCB compounds, their corresponding time-period of integration and degree of sensitivity to the ambient perturbation is further explained in Figure 4.6. The degree of sensitivity of the compound, represented by the size of the bubbles in the diagram, is a measure of how quickly the predicted concentration is influenced by the ambient perturbation for a PCB compound. It was calculated as the sum of % deviation of the predicted concentration from the actual time averaged concentration around the day of cross-over. Thus, a tri homolog group compound like PCB 37 (Log K_{ow} 5.83) has a time-period of integration of 31 days and its predicted concentration undergoes an overall deviation from the actual concentration of 16%. In comparison, a hexa homolog group compound like PCB 128 (Log K_{ow} 6.74) has a higher time-period of integration of 43 days. However, the PS predicted concentration of the compound is not heavily impacted by the perturbation resulting in an overall deviation from the actual concentration of only 1%.

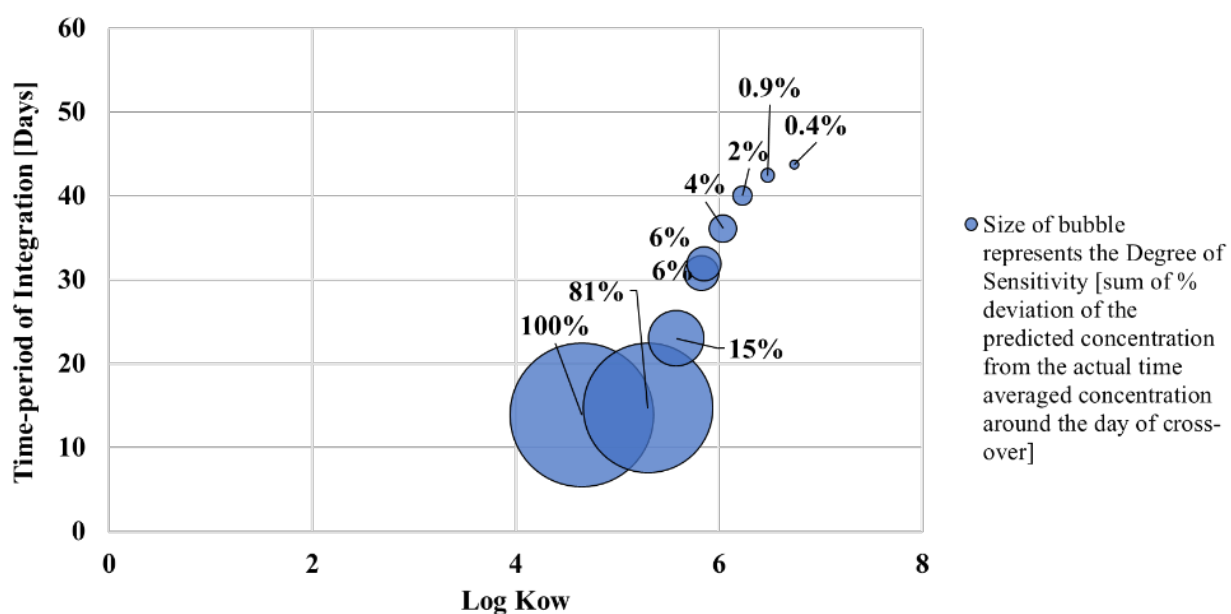


Figure 4.6. Correlation Between the Hydrophobicity of PCB Compounds, Time-period of Integration and Degree of Sensitivity to the Ambient Perturbation.

Impact of varying sampler thickness under perturbed ambient water concentration scenario.

The impact of varying sampler thickness on the uptake kinetics under perturbed ambient concentration scenario was examined by simulating the passive sampler-based water concentration profile of a PCB 37 for PE thicknesses of 0.3, 0.7, 1, 2, 3 mil in Figure 4.7a. It was observed that with increasing thickness of polymer, when the pulsed perturbation started on the 70th day, PCB 37 reached equilibrium slower. The correlation between sampler thickness, the corresponding time-period of integration and degree of sensitivity to the ambient perturbation is further explained in Figure 4.7b. A thin sampler has a shorter time-period of integration as compared to a thicker one (16 days for 0.3 mil and 40 days for 3 mil) implying that the thinner sampler responds quickly and recovers from the influence of the perturbation faster than the thicker one. The 3 mil thick PE being more resistive to the diffusive fluxes from the ambient perturbation is less impacted by the perturbation resulting in an overall deviation from the actual concentration of only 2% as compared

to a higher degree of sensitivity of 10% for the 0.3 mil thick sampler. Real world perturbations may last for shorter durations and if we would want to capture the influence of a particular perturbation event, a thinner polyethylene sampler might be an optimal choice because it is more responsive to the ambient fluctuation in concentration.

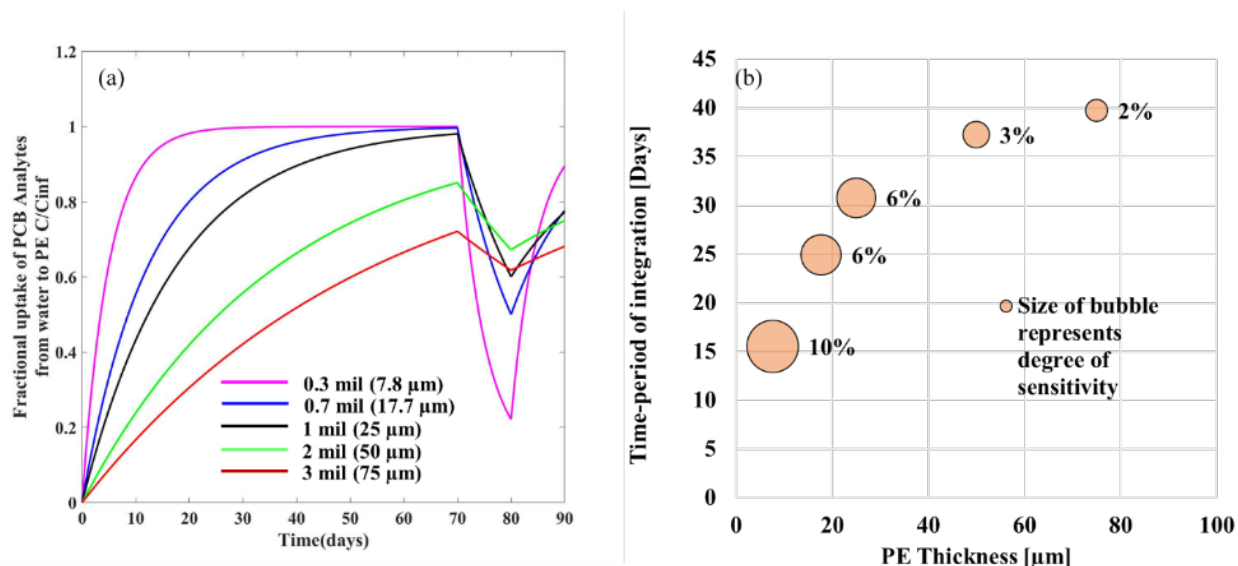


Figure 4.7. (a) Fractional Uptake of PCB 37 PE Passive Sampler of Varying Thicknesses (7.8, 17.7, 25, 50, 75 μm), As Predicted by the Diffusion Model when pulsed Perturbation Starts on the 70th Day in ambient Water. (b) Correlation Between sampler Thickness, Time-period of Integration and Degree of Sensitivity to the Ambient Perturbation.

Comparison between Diffusion and First order Model Predictions

The consistency of the Diffusion and First Order models in correcting for non-equilibrium using performance reference compounds (PRCs) for PCBs in sediment porewaters has been studied before (Sanders et al., 2018). The partial differential equations involved in the Diffusion model require numerical solutions and are often difficult to solve. The first order model, on the other hand, has been quite popular for being relatively easy to use. There exists a knowledge gap of comparing these two modeling techniques in the context of understanding the mass transfer dynamics in a single-phase equilibrium passive sampler like PE for time integrative measurement of surface water and sediment porewater measurements. The consistency of these models in predicting the water concentration under a pulsed perturbation scenario were compared for all the scenarios discussed above, by plotting a surface curve where the X, Y and Z axes correspond to Log K_{ow} of the different PCB compounds, % accuracy of the predicted concentration to the actual time-averaged concentration and the different days when the 10X dilution pulsed perturbation were introduced in the ambient water (Figure 4.8). Since all these three parameters are effective determinants of the sensitivity of the system, the similarity in the shapes of the surface curves corresponding to the first-order model (Figure 4.8a) and the diffusion model (Figure 4.8b) for a PE of thickness 0.3 mil implied that the models were consistent in their predicted water concentrations.

It was observed that for a PE of thickness 0.3 mil, when the day of perturbation varied from 10 to 80, the % accuracy varied from about 110 % to 10% for compounds of lower K_{ow} values. However, with increasing hydrophobicity of the compounds and consequently the K_{ow} values, the % accuracy varied from about 100 % to 90%. In addition, the sharper drop of accuracy over a much smaller time and K_{ow} space for the thicker PE (Figure 4.8c, d) can be attributed to the reducing sensitivity of the system to the ambient perturbation.

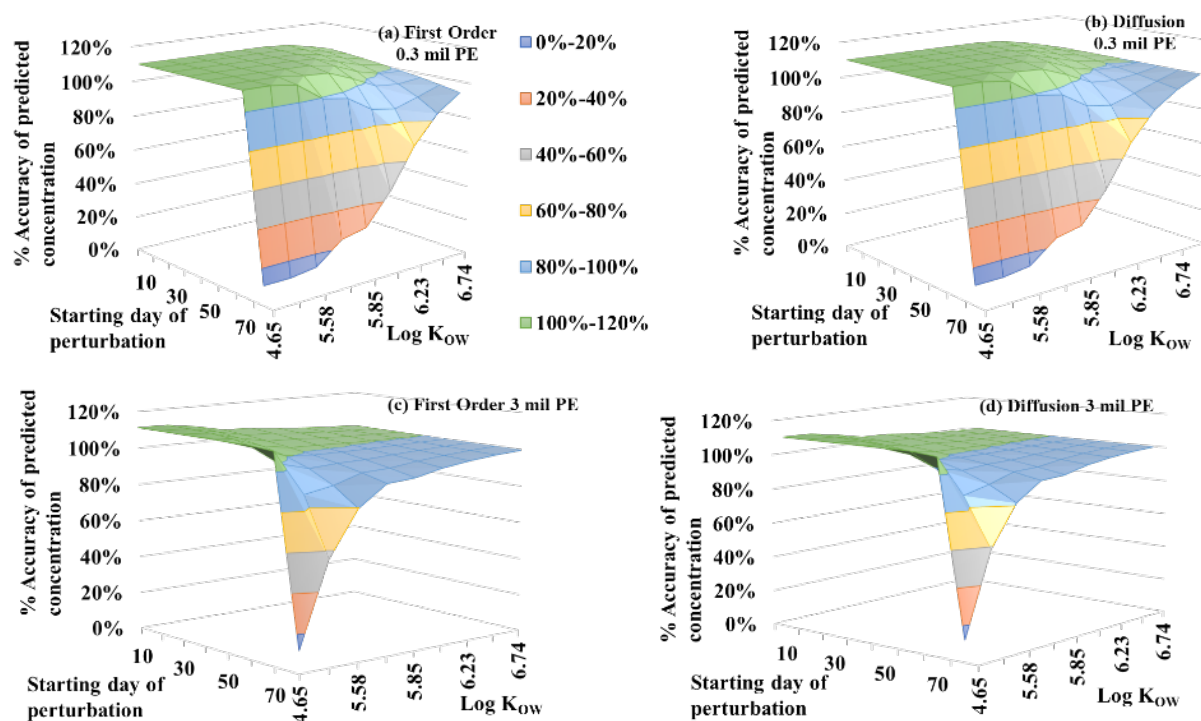


Figure 4.8. 3D Correlation Between % Accuracy of Predicted Water Concentration to Actual Time-averaged Concentration (Y axis), Timing of Pulsed Perturbation in Ambient Water (Z axis) and Hydrophobicity of PCB Compounds (X axis) for: (a) 0.3 mil PE and (c) 3 mil PE as Predicted by the First-order Model and (b) 0.3 mil PE and (d) 3 mil PE as Predicted by the Diffusion Model.

4.5 CONCLUSIONS

This research established that the nature and pattern of a perturbation in the ambient water, hydrophobicity of the compounds monitored, and the physical-chemical characteristics of the polymer used in the measurement, are important factors that determine the time period of integration of measurement by an equilibrium passive sampler. The heavier, more hydrophobic compounds are slow in transfer into the polymeric sampler and require longer times of integration compared to the less hydrophobic congeners. The optimal time-period of integration for a 25 μm PE sheet in surface water ranged from 14-15 days for a dichlorobiphenyl to 43-45 days for a hexachlorobiphenyl (for a diffusive boundary layer thickness of 0.02 cm). With the help of the modeling framework developed in this task, we could determine the period of time after which the influence of a perturbation is not reflected in the measured concentration. Using this information,

the approximate time after a known pattern of ambient concentration fluctuation can be estimated, when a sampler should be retrieved from the field, to correctly measure the true time-averaged concentration for compounds of a given range of hydrophobicity. The mechanistic understanding of the mass transfer kinetics in a passive sampler achieved in this task, also laid the fundamental groundwork for optimizing more targeted sampler design strategies for surface water and sediment porewater measurements. It is important to remember that in a real-life scenario, the perturbations can be multiple and of varying intensities. In the present study a single perturbation was modeled and water boundary layer was assumed to remain constant for simplicity. In addition, real measurements involve errors that can confound data interpretation, especially for the strongly hydrophobic compounds for which the uptake is slow and the correction for nonequilibrium can be especially prone to error. Future work can include stochastics in the modeling of the influence of perturbations in passive sampling measurements.

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5.0 CHAPTER 5: OPTIMIZATION OF EQUILIBRIUM PASSIVE SAMPLING FOR SHORT-TERM SURFACE WATER MEASUREMENTS

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5.1 ABSTRACT

Short-term surface water measurements are often critical in assessing inputs from episodic events. Passive sampling of surface water is often performed over an extended period of time, typically more than one month, to capture a time-integrated concentration for the duration of deployment. The extended period of deployment is often required to allow an approach to equilibrium conditions, especially for slow flowing water environments. We hypothesized based on the observed enhancement of kinetics using the vibrating passive sampler for sediments, that it may be feasible to design a passive sampling device that is capable of measuring surface water concentrations in short term events like a storm flow. We first performed mathematical modeling of a range of simulated flow conditions in surface water with assumed water boundary layer thicknesses, followed by the setup of a laboratory flow through experiment, and finally a short-term deployment during a storm in the field. From the modeling and laboratory experiments it was concluded that by choosing a thin polymer sheet and deploying during high flow events, both internal and external mass transfer resistances can be reduced, enabling sufficient pollutant accumulation within a day in the polymer to perform a measurement of the freely dissolved concentration of PCBs upto hexachlorobiphenyls. Hence, for short-term measurements an 18-micron thick polyethylene sheet was chosen for a 24-hour exposure during a high flow storm event in the field.

Results from the field deployment at two sites (LBC and Ferndale Branch) show initial promise of short-term passive sampling of surface water PCBs. For high flow storm conditions, such measurements can be achieved reliably upto penta or hexachlorobiphenyls using a 0.7 mil PE sheet deployed for a period of 1-2 days in the field. We also provide proof-of-concept of the feasibility of performing short, 1-day measurements in low-flow or stagnant conditions using a continuously vibrated passive sampler deployed in surface water. These advances in passive sampling allow flexibility of sampler deployments to determine concentrations during different periods of a hydrograph that may be helpful in delineating sources when needed. For example, if the watershed and associated storm pipes are relatively clean, storm-driven high flows should be cleaner and have a dilution effect in the receiving waterbody. However, if the main pollutant sources are in the watershed land surface (or storm pipes), one may expect to observe higher concentration in the water after a storm. The increase in dissolved concentration during the storm event monitored at LBC suggests possible storm driven mobilization of PCBs at this site. At the Ferndale Branch site, the PCB homolog patterns are very different during baseflow and stormflow, potentially indicating mobilization of different sources at different flow conditions. Thus, short-term integrated passive sampling measurements can provide additional information valuable for site investigations and source identification/management.

5.2 INTRODUCTION

In the past two decades, passive sampling technology has gained considerable interest and has been used in many overlying water and porewater monitoring applications (Adams et al., 2007; Arp et al., 2015; Fernandez, Macfarlane, et al., 2009; Lohmann, 2012). It has proved to be a good surrogate for bioaccumulation measurements and availability to benthic organisms of HOCs in many studies (Lu et al., 2011; Needham & Ghosh, 2019; Rosen et al., 2012). Short-term surface water measurements are often critical in assessing inputs from episodic events. Passive sampling of surface water is typically performed over an extended period of time, typically more than one month, to capture a time-integrated concentration for the duration of deployment. The extended period of deployment is often required to allow an approach to equilibrium conditions, especially for strongly hydrophobic compounds in slow flowing water environments. Grab sampling (or automated sampling) is still quite popular for short-term measurements of inputs from episodic events. Some studies have explored the application of passive samplers for short-term measurements of episodic events (Allan et al., 2007, Shaw & Mueller, 2009, Birch et al., 2013; Fernández et al., 2014; Gale, 1998; Novic, O'Brien, et al., 2017; Škodová et al., 2016).

There are two primary factors that control the rate of uptake of pollutants in a passive sampler: 1) the thickness of the polymer sheet that controls mass transfer resistance within the polymer, and 2) the flow velocity that controls the hydrodynamic boundary layer thickness and mass transfer resistance in the water side. One study (Estoppey et al., 2014) analyzed the impact of water velocity on the uptake of target PCB analytes into equilibrium samplers like PE and silicone rubber (SR) at river-like flow conditions (1 to 37 cm/s linear velocity). Samplers were exposed over a total period of 6 weeks with 2 weeks of exposure at each of the three velocities of 2 cm/s, 10 cm/s, and 30 cm/s. Though a 2-weeks long deployment is not particularly a short-term exposure, it was observed that the influence of velocity decreased with increasing hydrophobicity of PCBs when SR is used whereas the opposite effect was observed for PE. Additionally, the efficiency of PRC correction to correct for the influence of water velocity was assessed by comparing against time averaged concentration. However, the solid mechanistic interpretations could not be made partly because of the use of the sampling rate model in this study, that assumed WBL controlled uptakes for all scenarios.

There exists a knowledge gap of the theoretical understanding of the influence of water flow velocity on the exchange kinetics of compounds of varying hydrophobicity in a single-phase equilibrium passive sampler like PE that is supported by experimental validation. In this paper we explore the following hypothesis: By choosing a thin polymer sheet and deploying during high flow events, both internal and external mass transfer resistances can be reduced, enabling sufficient pollutant accumulation within a day in the polymer to perform a measurement of the freely dissolved concentration. With the final aim of optimizing passive sampling applications for short term measurement of PCBs in overlying water, we have the following specific tasks:

- (a) Optimize sampler design for fast flowing water (sampler thickness and choice of polymer) and slow flowing water (need for vibration)
- (b) Establish an empirical relationship between water velocity and the fraction of equilibrium approached by the system as a function of the WBL thickness associated with a flexible polymer sheet like PE
- (c) Determine parameters that would enable short-term measurements in the field (time, polymer material and thickness, and need for field vibration)

5.3 MATERIALS AND METHODS

The first step to optimize sampler design for short term measurements was to develop the understanding of mass transfer kinetics in PE passive samplers over a short exposure period under the influence of changing water velocity using mass transfer modeling. Two kinds of systems were modeled: (a) a moving water body like a river where the water flows with a certain velocity and (b) a stagnant water body like a pond where there is much less movement. To select the best sampler design for each of the above systems, a set of modeling and physical experiments were conducted.

Table 5.1. List of C13 PCB PRC Compounds Used for Impregnating Passive Samplers.

Homolog Group	PCB compd.	Molecular Weight [g/mol]	Log D _{pe} (cm ² /s) (Tcaciuc, 2014)	D _w (cm ² /s)	Log K _{ow} (Hawker and Connel, 1998)	Log K _{pew} [Lw/LPE] (Ghosh et al., 2014)
Tetra	PCB 54*	291.99	-8.98	4.8E-06	5.21	4.85
Tri	PCB 37*	257.54	-8.81	5.2E-06	5.83	5.58
Tetra	PCB 47*	291.99	-8.98	4.8E-06	5.85	5.61
Penta	PCB 111*	326.43	-9.16	4.4E-06	6.76	6.68
Hexa	PCB 138*	360.88	-9.33	4.1E-06	6.83	6.76
Hepta	PCB 178*	395.32	-9.40	3.9E-06	7.14	7.13

Modeling framework for short term measurements in overlying water

Moving surface water scenario with a changing water flow velocity: In the first system, the WBL outside the sampler is varied across a range of values simulating different water velocities. The typical range of WBL thickness lies between 10 µm (representative of a very turbulent water flow) to 500 µm (typical for laminar water movement) (Lohmann, 2012). The modeling framework used to simulate the loss of PRCs followed the approach used in Chapter 4.

Stagnant surface water scenario: For the second system, in stagnant water conditions like that in a lake or a pond, in addition to using a thin sampler, external periodic vibration can be used to forcefully disrupt the WBL to expedite mass transfer. Conceptually, for a static sampler, the mass transfer should be more water-side controlled. For a vibrating sampler design, the water side control of the mass exchange kinetics is partially replaced by control by the PE side. The frequency of vibration on the sampling platform can be manually programmed. In the pause mode, the exchange kinetics in the sampler simulated by Fick's Diffusion can be represented by the equations 1, 2. In the pulse mode, the WBL that develops outside the sampler is disrupted by the active shaking. The water concentration in the nearest water cell at the sampler boundary is reset to the initial concentration, C_{W,init} (ug/cm³) as represented by equations 3,4.

Pause Mode:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad \text{when } -L < x < L \quad (1)$$

$$\frac{\partial C_W}{\partial t} = D_W \frac{\partial^2 C_W}{\partial x^2} \quad \text{when } -L > x > -(L + b) \text{ and } L < x < (L + b) \quad (2)$$

Pulse Mode:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad \text{when } -L < x < L \quad (3)$$

$$C_W = C_{W,init} \quad \text{when } -L > x > -(L + b) \text{ and } L < x < (L + b) \quad (4)$$

Here, C_{PE} is the concentration of PCB analyte accumulated in PE (ng/g of PE), C_W is the concentration of analyte in the ambient water (ng/L). We assume that the thickness of the PE sheet is $2L$, D_{PE} is the diffusion coefficient within the PE, b is the thickness of the WBL, and D_W is the diffusion coefficient in the water.

Well-mixed scenario: A final best-case scenario of a well-mixed system was also simulated as a point of reference in addition to each of the above scenarios. For this, it was assumed that the water side is in a state of high turbulence so that $WBL=0$ and the mass transfer kinetics is fully sampler side controlled. This is an ideal situation when the sampler uptake is limited only by the diffusion in the polymer.

Preparation of passive samplers

Passive samplers were prepared for the measurement of freely dissolved concentrations of PCBs in surface water using the method based on the most recent guidance document for passive sampling ([U.S. EPA/SERDP/ESTCP 2017](#)). Low density polyethylene (PE) sheets of varying thicknesses of 0.7 mil (18 μm), 1 mil (25 μm) and 2 mil (50 μm) were obtained from Husky (Bolton, Ontario). 0.3 mil (8 μm) LDPE were obtained from a SARAN wrap roll. All PE sheets were cut into 1" x 6" strips. The strips were cleaned in dichloromethane, acetone/hexane (50/50 v/v), and methanol for 24 hours each solvent, dried, and then loaded with C13 labeled PCB compounds (Table 5.1), from 80:20 (vol: vol) methanol: water as recommended in previous studies ([Booij, 2002](#)).

In-lab experiments to demonstrate feasibility of short-term measurements of modeled scenarios

Experimental set up for measurements in a moving surface water scenario: To verify the modeling results from the first system of a moving water body like a river, we built a laboratory flow chamber out of a 2 in diameter glass column that drew water from a larger water reservoir using a submersible utility pump (Everbilt rated at 1/6 HP and 28 gallons per minute flow rate). The schematic and the actual set up of the flow chamber is shown in Figure 5.1. For our experiments we used DI water in the water reservoir and PRC impregnated 25 μm PE sheets were clamped to a customized frame so that they were fully exposed to the flowing water within the glass column as shown in Figure 5.2. A speed adjuster was used to control a constant water flow velocity within the glass column flow chamber. The flow velocity V_2 (cm^3/s) inside the flow chamber was calculated by measuring the volume of water coming out of the outlet that is of 1 in diameter in 1 second as follows:

$$A_1 V_1 = A_2 V_2 \quad (5)$$

where A_1 : Area of cross section of glass column = 20.25 cm^2 , V_1 : velocity of water (cm/s) inside the glass column and $A_2 V_2$ =Volume of water ejected at the outlet in a second (cm^3/s)

An activated carbon filter attached to the end of the flow chamber in the water reservoir removed PRCs desorbed from the sampler. To best represent environmental flow regimes, the flow velocities were set at 6 cm/s, 15 cm/s and 25 cm/s. PE samples were retrieved from the flow chamber after 6, 18, and 24 hours and the fractional approach to equilibrium for the respective time points measured.

The water reservoir outside the flow chamber was used as a prototype of stagnant water body (like that of a pond), required to conduct the physical experiments to verify the modeled results from our second system. Fully exposed static samplers were suspended into the water reservoir making sure they were always below the water surface. PRC loaded sampler strips were attached on the fins of the vibrating prototypes P1 and P2, developed in **Chapter 3**, in fully exposed conditions using stainless steel alligator clips. The vibrating devices were suspended below the water level in the reservoir making sure their vibration was not restricted by the container's bottom surface as shown in Figure 5.3. Two vibration frequencies were tested: a lower frequency of 1s pulse, 60s pause and a higher frequency of 1s pulse, 1s pause. The fractional approach to equilibrium was tracked after 6, 18 and 24 hours by extracting PE samples from each of the static and vibration modes.

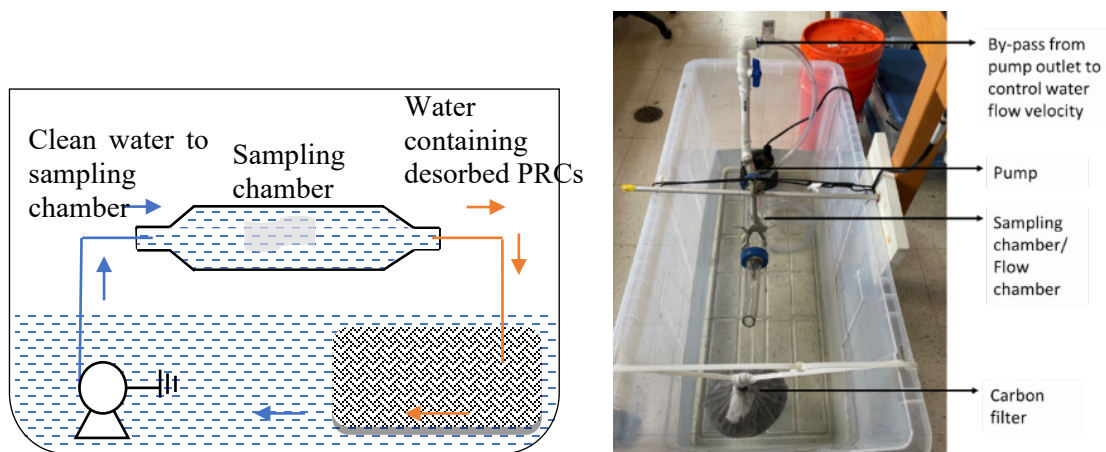


Figure 5.1. (a) Schematic and (b) Built Laboratory Flow Chamber for Carrying Out Ex-situ Surface Water Measurements.

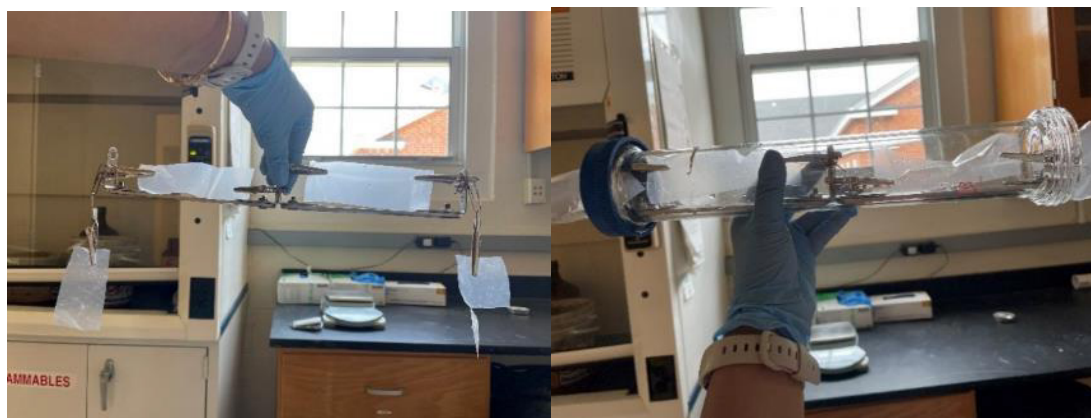


Figure 5.2. PE Sheets Clamped to a Customized Frame to Maintain Full Exposure to Flowing Water Within the Glass Column Flow Chamber.



Figure 5.3. Vibrating Passive Sampling Platforms, P1-14G (left) and P2-110G (Right), With PRC Loaded PEs Suspended in Outer Reservoir of DI Water to Track Fractional Approach to Equilibrium in Low Frequency and High Frequency Modes.

Field implementation of short-term monitoring of stormflow concentrations

From the modeling and laboratory experiments as described later, it was concluded that by choosing a thin polymer sheet and deploying during high flow events, both internal and external mass transfer resistances can be reduced, enabling sufficient pollutant accumulation within a day in the polymer to perform a measurement of the freely dissolved concentration. Hence, for short-term measurements an 18-micron thick polyethylene sheet was chosen for a 24-hour exposure during a high flow storm event.

Two sites were chosen to deploy passive samplers optimized for short-term measurements. The first site was the PCB impacted Lower Beaverdam Creek, a tributary to Anacostia River in Washington DC. PE samplers of 0.7 mil (18 micron) thickness loaded with C13 labeled PCB compounds (Table 4.1) were deployed in two configurations: within mesh envelopes and in fully exposed conditions (Figure 5.4). Approximately 1g of PE samplers in the mesh-enclosed configuration and another 1g of samplers in the exposed configuration, each consisting of two replicates were deployed in the Lower Beaverdam Creek (site LBC 1). An exactly similar set of 2g of PE samplers were deployed in downstream at the point of confluence of LBC with Anacostia River (site LBM 1). The deployment devices were secured firmly to withstand high flow conditions during a storm event. The total of 4 samplers were deployed at these two sites, right before and collected right after a storm event so that the exposure period encompasses the duration of the storm (average 42 hours).

The second site was at Ferndale Branch, a tributary to the Sawmill Creek in Anne Arundel County, Maryland. 2g of PE samplers in the exposed configuration consisting of two replicates were deployed in the Olen Drive tributary (OD-01). Another 2g of samplers were deployed in the Ferndale Branch (PT7-RW-03) in the exact same way. Samplers were deployed right before and collected right after the duration of the storm (average 26 hours).

At both sites, the short-term monitoring samplers were deployed alongside the regular samplers that were already in the field for months to provide a time-integrative measurement for each of these sites. This allowed comparison of the freely dissolved concentration in the surface water measured over the high flow period with concentrations measured over a longer duration time integration of 2-3 months.



Figure 5.4. Field Deployment of Optimized Passive Samplers (0.7 mil PE) in Exposed (Left) and Mesh-enclosed (Right) Configurations for Short Term Measurements of Surface Water PCB Concentrations.

Extraction of PCBs from samplers, cleanup and analysis

Passive samplers retrieved from the laboratory experiments and field were cleaned of debris or deposits before extraction. Sodium sulfate was added to all samples to remove excess water. PCB 14 and 65 were added as surrogate standards to all samples before extraction to check recovery. Passive samplers were extracted for PCBs in glass vials using 30 mL hexane, on an orbital shaker, overnight after which the solvent was removed, and new solvent added. This process was repeated three times to complete the extraction. All extracts were collected in a 60mL certified glass vial and evaporated to 1-2 ml by nitrogen blowdown. Samples from laboratory experiments, conducted in deionized water, were analyzed for only final PRC levels and the PCB cleanup was not necessary.

Field samples were analyzed for both PRC final and accumulated target PCB measurements and underwent the PCB cleanup step based on EPA publication SW-846 (Test Methods for Evaluating Solid Waste, Physical/Chemical Methods) methods 3630C (Silica gel cleanup), 3665A (sulfuric acid cleanup) and 3660B (Sulfur removal with copper).

PCB analysis was performed on an Agilent 7890B gas chromatograph, with an Agilent 5977B mass spectrometer detector. The GCMS was calibrated using PCB standards purchased as nonane solutions from Cambridge Isotope Laboratories (Tewksbury, MA, USA) and diluted using hexane to desired calibration levels. Internal standards, 2,5-dichlorobiphenyl (13C12 PCB 09), 2,3',4,4',5-pentachlorobiphenyl (13C12 PCB 118) and 2,2',3,4',5,6,6'-heptachlorobiphenyl (13C12 PCB 188), also purchased as a mixture solution in nonane were diluted in hexane and added to all samples in desired spiking volumes.

PRC Correction of passive sampler results

PCB concentration in the PE samplers deployed in the field, C_{PE} , was first calculated in the units of ng/g PE. The loss of individual PRCs was used to calculate the exchange rate coefficient, k_e using the equation:

$$k_e = \frac{1}{t} \ln \frac{C_{PE,PRC}^{t=0}}{C_{PE,PRC}^t} \quad (6)$$

where $C_{PE,PRC}^{t=0}$ and $C_{PE,PRC}^t$ are the concentrations of the reference compound initially and at the end of exposure period respectively. The estimated k_e for the six PRCs were used to extrapolate k_e values for the remaining analyte congeners using a k_e - K_{pew} correlation. A congener-specific

fractional correction term, $f_{eq} (= 1 - e^{-k_e t})$, was generated from the set of k_e values to account for the non-equilibrium conditions in the sampler and the PRC corrected contaminant concentration in the surface water, $C_{W,t=\infty}$, were reported as $\mu\text{g/L}$ in water using the equation:

$$C_{W,t=\infty} = \frac{C_{PE}}{K_{PEW}(1 - e^{-k_e t})} \quad (7)$$

where C_{PE} is the mass of PCB analyte accumulated in PE (ng/g of PE) at the end of the exposure period.

5.4 RESULTS AND DISCUSSION

Simulation of PRC loss with changing flow velocity

The fractional approach to equilibrium of a 25 μm thick PE sheet exposed to varying WBL thicknesses was simulated as a family of curves (Figure 5.5). The fraction of PRC compounds listed in Table 5.1 remaining in the sampler corresponding to each WBL thickness (represented by the different colors) is plotted against time by using the modeling framework developed in **Chapter 4**. The same experiment was repeated for three more PE thicknesses (8, 18, 50 μm) and a family of curves generated for each of the three PE thicknesses.

Fractional loss of PRCs under different vibrating modes in static water

The fractional approach to equilibrium of a sampler in each of the following modes of static, vibration with a low frequency (1s pulse, 60s pause) and vibration with a high frequency (1s pulse, 1s pause), were simulated as a family of curves (Figure 5.6). The fraction of PRC compounds left in a 25 μm sampler corresponding to each of the systems (represented by the different colors) were plotted against time by using the modified modeling framework discussed above (Figure S2).

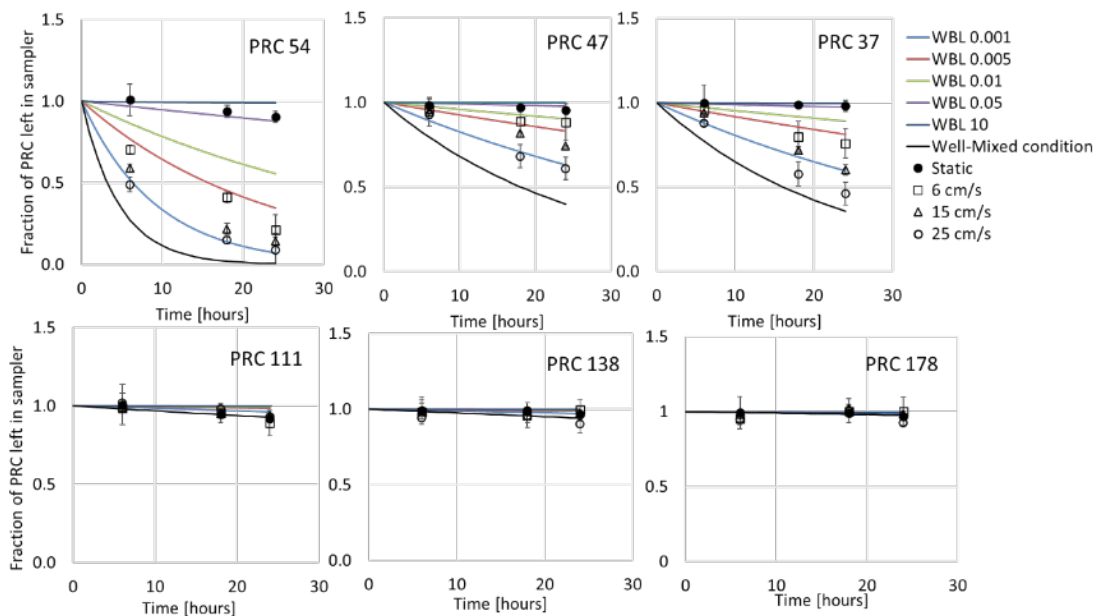


Figure 5.5. Desorption Profiles of C13 PCB PRCs 54, 47, 37, 111, 138 and 178 from 25um Thick PE Sampler when Exposed to Different WBL Thicknesses (Modeled) and Actual Water Velocities in the Flow Chamber (Physical Experiments).

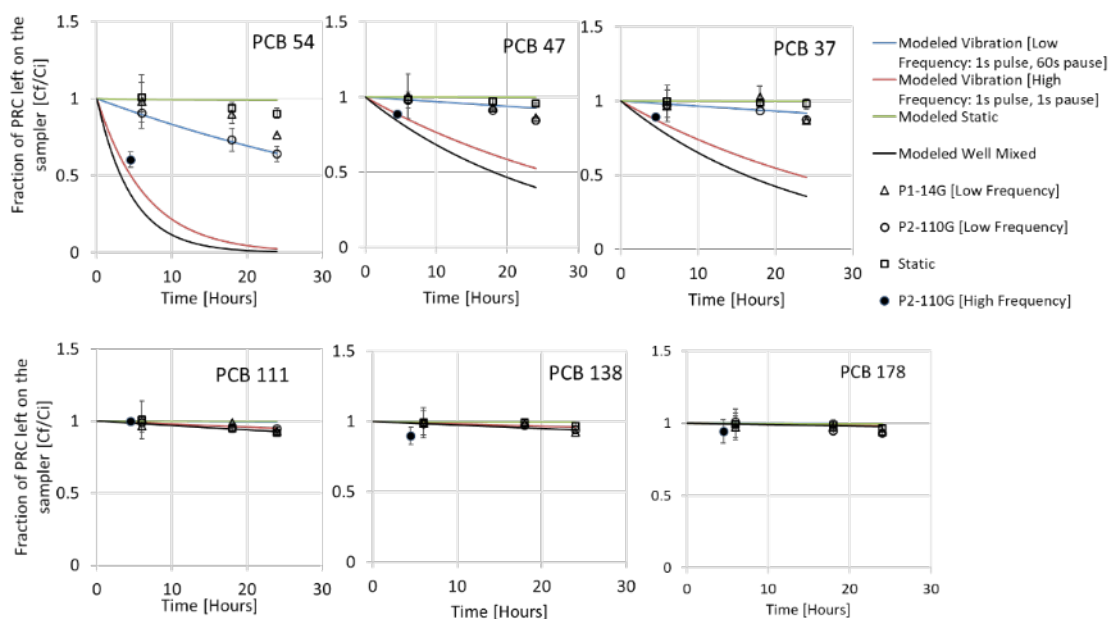


Figure 5.6. Desorption Profiles of C13 PCB PRCs 54, 47, 37, 111, 138 and 178 from 25um Thick PE Sampler when Exposed to the Static, Vibration (Low and High Frequency) and Well Mixed Conditions.

Short-term measurement of PCBs enhanced by water flow velocities: The fraction of PRC 54 remaining in the sampler when exposed to the three set water velocities (6, 15, 25 cm/s; represented by the differently shaped data points) was plotted against time (Figure 5.5) and verified against the modeled family of curves for respective WBL thicknesses (0.001-10 cm represented by the colored family of curves) associated with the sampler. The experimental fractional loss of the PRCs from the samplers in 24 hours, within the flow chamber were compared against those from the static sampler deployed in more stagnant water outside in the water reservoir. It was observed that under the influence of water flow, the samplers reached equilibrium faster than the samplers deployed in the stagnant water in the outer reservoir. Additionally, after 24 hours, the sampler exposed to the 25 cm/s water velocity lost 90% of the PRC 54 while the sampler at 6 cm/s lost 80% of PRC 54. For the static sampler, the loss of PRC 54 was less than 10% by comparison. This implied that a higher water flow velocity led to faster mass transfer and consequently an expedited approach to equilibrium. The intersection of the modeled family of curves with the measured values of fractional loss of PRC 54 indicates the apparent WBL thickness associated with the non-rigid flat surface of a PE sheet when exposed to a particular water velocity. For all PRCs, a water velocity of 6-25cm/s corresponded to a theoretical WBL thickness ranging between 0.01-0.001 cm for a 1mil PE. Additionally, in stagnant water conditions, the experimental fractional loss of PCB reference compounds corresponded to a theoretical WBL thickness of 0.05 cm. This implies that overlying water is never stagnant and natural convective movement within the water produces a background level of motion. We are yet to see how the fractional losses change for different PE thicknesses.

Short-term measurement of PCBs enhanced by vibration in stagnant water conditions: The fraction of each PRC remaining in the sampler was plotted against time (Figure 5.6) and verified against the modeled family of curves for the respective static and vibration modes. For the surface

water experiments with the vibrating prototypes in stagnant water conditions when WBL with respect to a 25 μm thick PE is close to ∞ , it was observed that at least 15-36% loss of the tri-tetra homolog PRCs could be achieved with the P2-110G prototype at low vibration frequency (1s pulse, 60s pause) within 24 hours. When set at the high frequency mode (1s pulse, 1s pause), about 10-40% loss of the tri-tetra homolog PRCs and 2-8% loss of the penta-hepta homolog PRCs could be achieved within 4.5 hours. The fractional loss % for the higher homologs may not be enough for PRC correction purposes.

Thus, a 25 μm thick PE passive sampler vibrated nearly continuously can achieve short-term measurements in 4.5 h of exposure for PCB compounds up to tetrachlorobiphenyls. Further tests need to be performed to evaluate the effectiveness of continuous vibration for the duration of 24 hours.

Short-term field measurements in surface water:

Total PCB concentration accumulated on Passive Samplers at Anacostia River, Washington DC: The concentration of total PCB accumulated in the 0.7mil PE passive samplers over the 42 hours of storm was measured at LBC1 and LBM1 are shown in Figure 5.7. It was observed that the surface water at the LBC and Anacostia River had signatures of the di, tri, tetra and penta as the major PCB homolog groups.

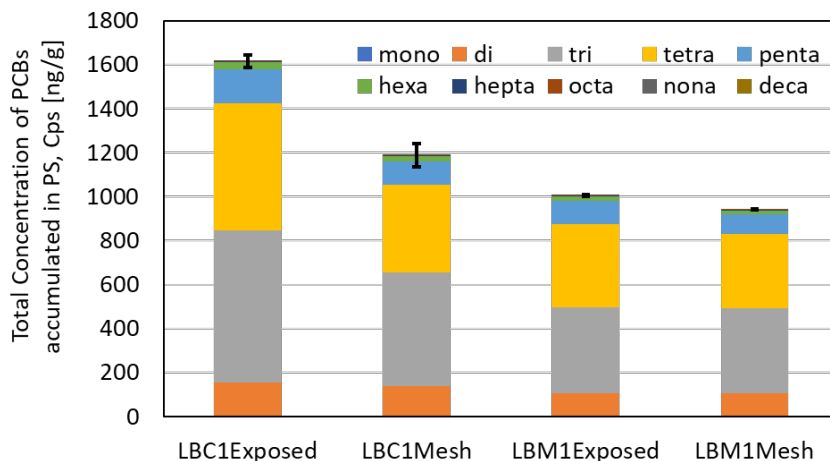


Figure 5.7. Total Concentration Along with Homolog Distribution of PCBs Accumulated in PE [ng/g] at LBC1 and LBM1: Comparison of Exposed and Meshed PEs.

It was also observed that the mesh-enclosed configuration accumulated lower total concentration than exposed configuration. The homolog distribution within the total concentration bar plot shows that at LBC1, mesh-enclosed PEs accumulated lower concentrations of the tri to penta homologs as compared to the exposed PEs. The relatively lower concentrations of target PCB analytes in the mesh-enclosed PEs can be attributed shielding of flow by the stainless steel mesh.

Fractional PRC loss and required correction for non-equilibrium: PE samplers retrieved from the field were analyzed for the fraction of PRCs left in them and compared with the initial concentration at which the samplers were loaded (Figure 5.8). The fractional loss of each of the six PRCs from the samplers deployed at the sites LBC1 and LBM1 in the exposed and meshed

configurations, normalized by the masses of PEs extracted were calculated as shown in Figure 5.8. It was observed that, over a period of 42 hours, the samplers lost an average of 55% of the tetra PRC 54, 20% of tetra PRC 47, 26% of tri PRC 37, 15% of penta PRC 111, 13% of hexa PRC 138 and 5% of hepta PRC 178. In general, the samplers at LBC1 lost a higher fraction of all PRCs and were closer to equilibrium than the samplers at LBM1 closer to the mouth of the river. This could be because the water velocity in the creek was higher during the storm as compared to closer to the point of confluence of the creek with the river where the tributary cross section widened.

Using the information of the PRC fractional loss percentages, the required correction of equilibrium values was calculated for the major homolog groups (Figure 5.9). Since we were able to achieve at least 15% of the tri, tetra and penta homolog PRCs, PRC corrections required for the major homolog groups upto penta were easily calculated to be within the range of 40% for di to 90% correction for the penta homolog compounds. At LBC1, one of the meshed replicates required more correction levels for all the homolog groups in general than that required by the other replicate. This reflects that the use of mesh to envelop PE samplers can bring about an added source of inconsistent exposure to the ambient conditions that can lead to error prone estimations of the sampler's approach to equilibrium.

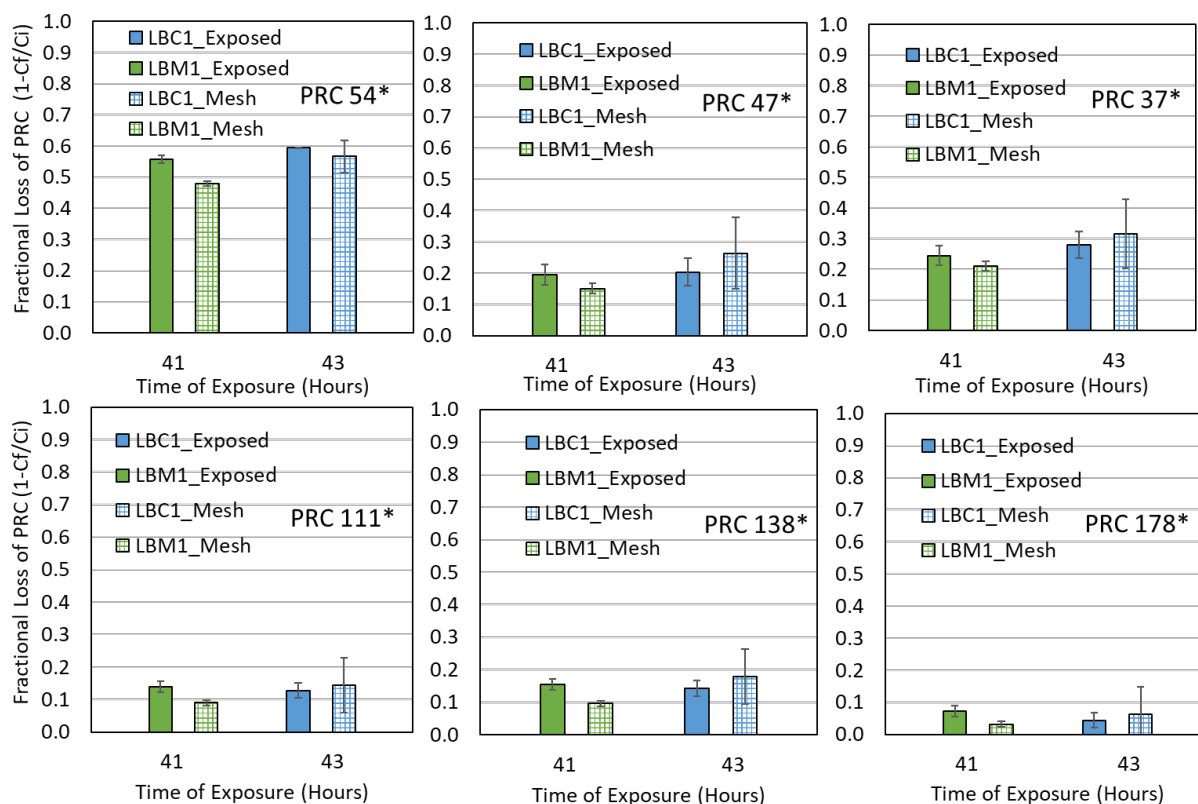


Figure 5.8. Fractional Loss of C13 PCB PRCs (54*, 47*, 37*, 111*, 138* and 178*) from 0.7mil PE Deployed at LBC1 (Blue) and LBM1 (Green) in Exposed (Solid) and Meshed (Checkered) Configurations Over an Average of 42 Hours of Storm.

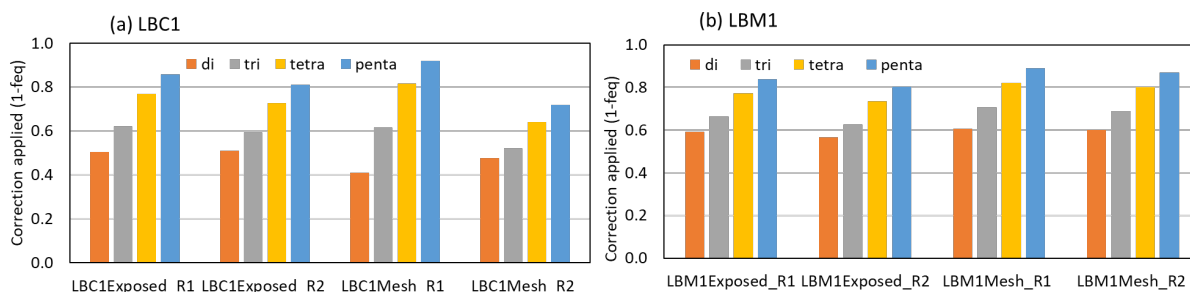


Figure 5.9. Required PRC Corrections, (1-freq), for Tri-penta Homolog Group PCB Compounds across Passive Sampler Replicates Deployed at LBC1 and LBM1 in Exposed and Meshed Configurations.

The fractional loss of each of the six PRCs from the samplers deployed at the sites OD01 and PT7RW03 in the exposed configuration, normalized by the masses of PEs extracted were calculated as shown in Figure 5.10. It was observed that, over an average of 26.5 hours of exposure, the samplers lost an average of 40% of the tetra PRC 54, 16.5% of tetra PRC 47, 19% of tri PRC 37, 5.5% of penta PRC 111, 7% of hexa PRC 138 and 5% of hepta PRC 178. The concentration of total PCB accumulated in the 0.7 mil PE passive samplers over the 26.5 hours of storm was measured for the AA County creeks (Figure 5.11a). It was observed that the surface water at both the sites had signatures of the di, tri, tetra and penta as the major PCB homolog groups. Using the information of the PRC fractional loss percentages, the required correction of equilibrium values was calculated for the major homolog groups (Figure 5.11b). PRC corrections required for the major homolog groups upto tetra were calculated to be within the range of 65% required correction for di to 85% correction for the tetra and 95% correction for the penta homolog compounds.

Comparison of long-term and short-term time integrative measurements: The long-term samplers that were deployed along with the short-term samplers in 2022 still await retrieval and processing. However, the available long-term measurements at LBC1 conducted in 2021 was compared with the 2022 short-term measurements (Figure 5.12a). At LBC1, 2 mil samplers were exposed in meshed configuration for a period of 82 days in 2020 and the surface water concentrations were predicted to be ~14 ng/L. The short-term (43 h) measurements using the meshed configuration of the 0.7 mil samplers gave concentrations that were similar to the long-term measurement in 2021. However, the exposed samplers predict a higher concentration of 19 ng/L. The homolog distribution of the target PCB compounds shows that both the long-term and short-term predict di, tri and tetra to be the major homolog groups present at LBC1.

The generally higher concentration measured during the storm flow is quite remarkable considering the large increase in flow during and after a storm event. The large increase in discharge during the storm is not diluting the concentrations, rather causing an elevation, potentially indicating a continued source from contaminated surface soils in the adjacent watershed.

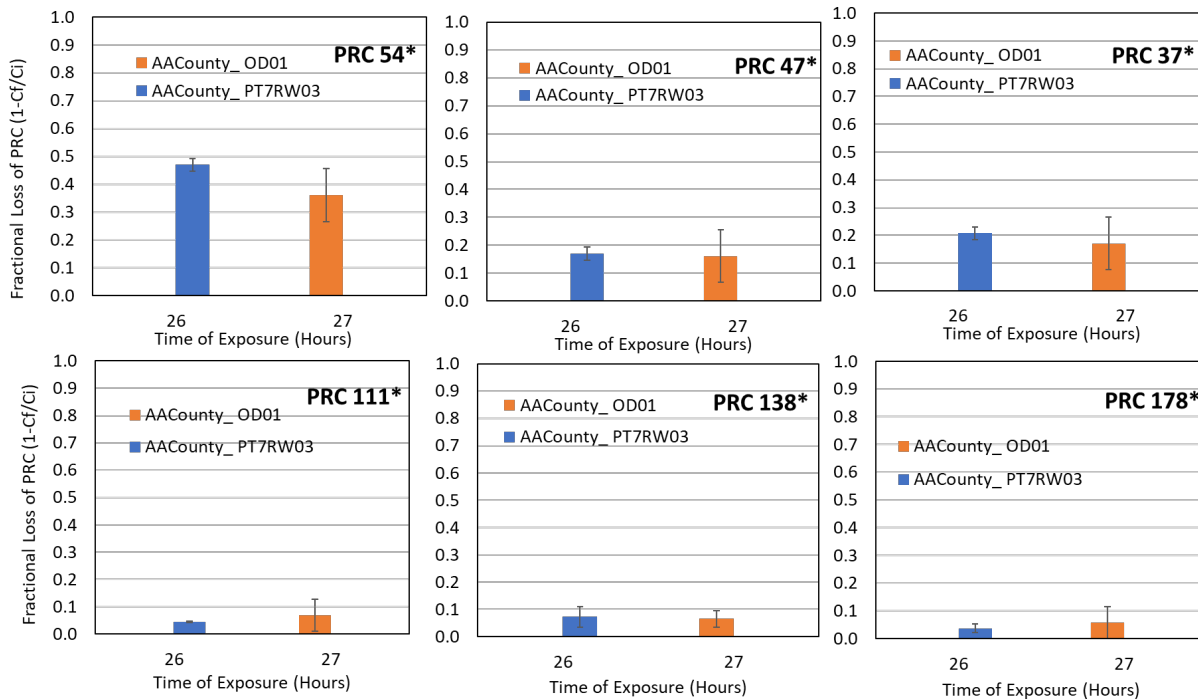


Figure 5.10. Fractional Loss of C13 PCB PRCs (54*, 47*, 37*, 111*, 138* and 178*) from 0.7mil PE Deployed at Ferndale Branch, Site PT7RW03 (blue) and Olen Drive, Site OD01 (Orange) in Exposed Configuration Over an Average of 26.5 Hours of Storm.

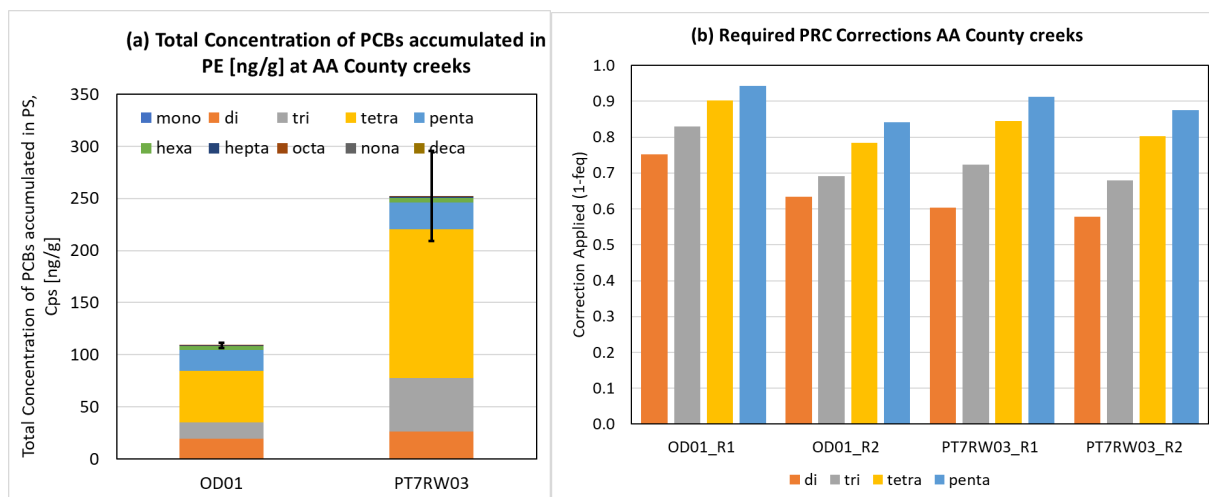


Figure 5.11. (a) Total Concentration Along with Homolog Distribution of PCBs Accumulated in PE [ng/g] at AA County Creeks, Ferndale Branch (PT7RW03) and Olen Drive (OD01). (b) Required PRC Corrections, (1-freq), for tri-penta Homolog Group PCB Compounds Across Passive Sampler Replicates Deployed at PT7RW03 and OD01.

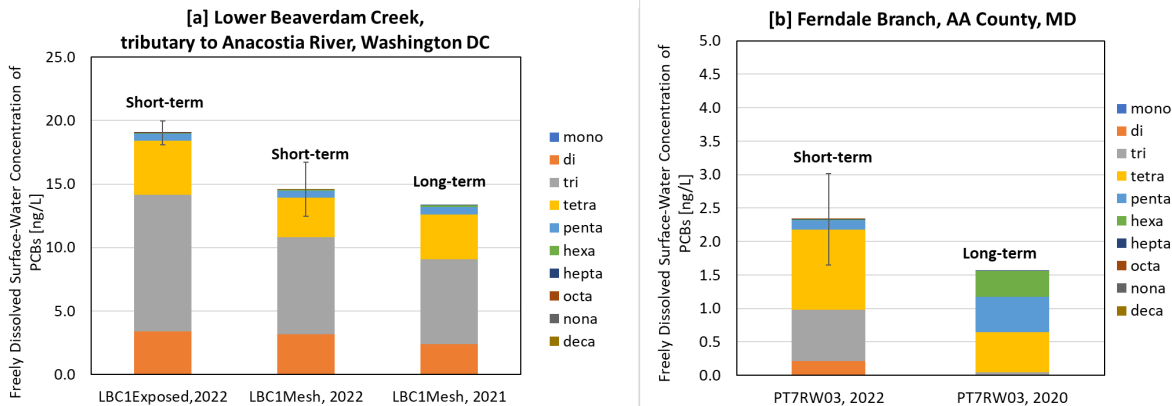


Figure 5.12. (a) Comparison of Time-integrated Measurement Over 82 Days in 2021 (left) with Short-term Measurement Over 43 Hours in 2022 (Right) of Total PCB Concentrations at Lower Beaverdam Creek (Site LBC1), Tributary to Anacostia River, Washington DC. (b) Comparison of Long-term Measurement Over 88 Days in 2020 (left) with Short-term Measurement Over 26 Hours in 2022 (Right) of Total PCB Concentrations at Ferndale Branch (Site PT7_RW03), AA County, MD.

A comparison of the long-term measurements of the surface water concentrations, conducted in 2020, at the Ferndale Branch (PT7_RW03) with the short-term measurements in 2022 is shown in Figure 5.12b. We observe that an exposed configuration of the 0.7 mil PE samplers, deployed for a short period of 26 hours, predicted slightly higher total PCB concentrations (~2.4 ng/L) as compared to the predictions from the long-term measurements of 88 days from 2020 (~1.5 ng/L). More importantly, the homolog distribution of freely dissolved PCB concentrations are very different in the short-term storm exposure, compared to the long-term measurement performed in 2020. As shown in Figure 5.13 for Ferndale Branch, for the long-term measurements (represented by the orange bars), the major homolog groups are tetra, penta, and hexa chlorobiphenyls. However, in the short-term measurements, the major homolog groups in the surface water are di, tri and tetra. Thus, it is possible for this site that different sources of PCBs are being mobilized into water during baseflow vs. stormflow conditions. This is in contrast to the observation at the LBC site, where the PCB homolog distribution during baseflow and storm were similar.

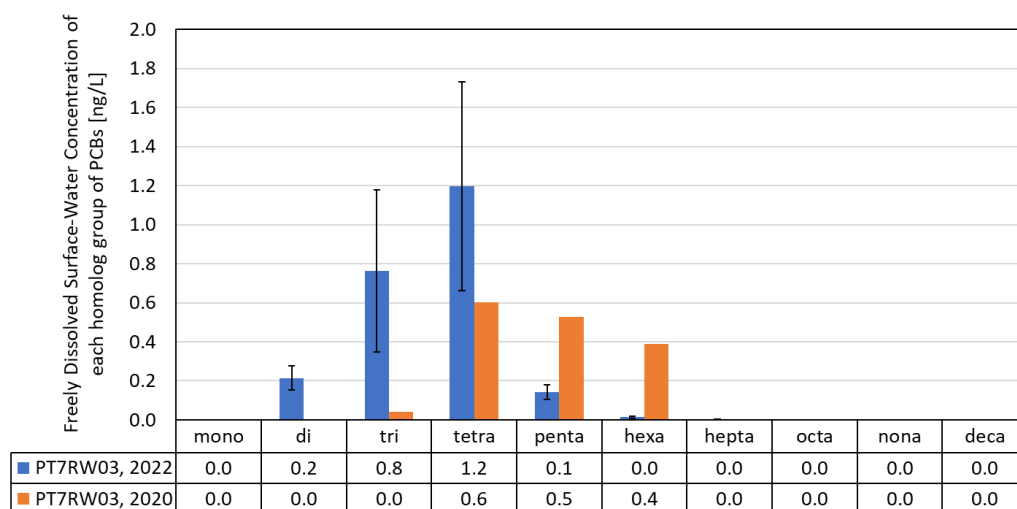


Figure 5.13. Homolog distribution of the freely dissolved PCB concentration as predicted by the long-term (orange bars) and short-term measurements (blue bars) at Ferndale Barnch, AA County, MD.

5.5 CONCLUSIONS

Results from this study show initial promise of short-term passive sampling of surface water PCBs. For high flow storm conditions, such measurements can be achieved reliably upto penta or hexachlorobiphenyls using a 0.7 mil PE sheet deployed for a period of 1-2 days in the field. We also provide proof-of-concept of the feasibility of performing short, 1-day measurements in low-flow or stagnant conditions using a continuously vibrated passive sampler deployed in surface water. These advances in passive sampling allow flexibility of sampler deployments to determine concentrations during different periods of a hydrograph that may be helpful in delineating sources when needed. For example, if the watershed and associated storm pipes are relatively clean, storm-driven high flows should be cleaner and have a dilution effect in the receiving waterbody. However, if the main pollutant sources are in the watershed land surface, one may expect to observe higher concentration in the water after a storm driven runoff from contaminated surface soil sites. The lack of dilution during the storm event monitored at LBC suggests possible storm driven mobilization of PCBs at this site. At the Ferndale Branch site, the PCB homolog patterns are very different during baseflow and stormflow, potentially indicating mobilization of different sources at different flow conditions. Thus, short-term integrated passive sampling measurements can provide additional information valuable for site investigations and source identification/management.

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6.0 CHAPTER 6: DEVELOPMENT OF A NOVEL EQUILIBRIUM PASSIVE SAMPLING DEVICE FOR METHYLMERCURY IN SEDIMENT AND SOIL POREWATERS (PUBLISHED PAPER)

Sanders, J.P.; Alyssa McBurney, A.; Gilmour, C.C.; Schwartz, G.E.; Kane Driscoll, S.B.; Brown, S.S.; Ghosh, U. *Environ. Toxicol. Chem.* 39, 323–334. **2020**.

6.1 ABSTRACT

In this study we explore the concept of equilibrium passive sampling for methylmercury (MeHg) using the strategy developed for hydrophobic organic chemicals (HOCs). Passive sampling should allow prediction of the concentration of the chemically labile fraction of MeHg in sediment porewaters (MeHg_{CL}) based on equilibrium partitioning into the sampler, without modeling diffusion rates through the sampler material. Our goals were to identify sampler materials with the potential to mimic MeHg partitioning into animals and sediments and provide reversible sorption in a time frame appropriate for in situ samplers. Candidate materials tested included a range of polymers embedded with suitable sorbents for MeHg. The most promising were activated carbon (AC) embedded in agarose, thiol-SAMMS (self-assembled monolayers on mesoporous supports) embedded in agarose, and cysteine-functionalized polyethylene terephthalate (PET), which yielded log sampler-water partition coefficients (K_{pw}) of 2.8 to 5 for MeHgOH and MeHg complexed with dissolved organic matter (Suwannee River Humic Acid). Sampler equilibration time in sediments was approximately 1 to 2 weeks. Investigation of the MeHg accumulation mechanism by AC embedded in agarose suggested sampling was kinetically influenced by MeHg interactions with AC particles and not limited by diffusion through the gel for this material. AC exhibited relatively rapid desorption of Hg and MeHg, indicating that this sorbent is capable of reversible, equilibrium measurements. In sediment:water microcosms, porewater concentrations made with isotherm-calibrated passive samplers agreed within a factor of two (unamended sediment) or four (AC-amended sediment) with directly measured concentrations. This work demonstrates a potential new approach to passive sampling of MeHg.

6.2 INTRODUCTION

Mercury is a global pollutant that can be microbially methylated in the environment and biomagnified to levels of concern in human and ecological receptors (Driscoll, Mason et al. 2013). Mercury methylation is often localized in redox transition zones near solid-water interfaces (Bigham, Murray et al. 2016), making MeHg readily available for uptake by benthic and epibenthic fauna (Chen, Borsuk et al. 2014). The concentration of chemically labile or bioavailable MeHg (here designated MeHg_{CL}) in surface waters and sediment porewaters is needed to make predictions about risk, and to evaluate the impact of potential remediation on risk. However, MeHg concentrations can be very low (pM in uncontaminated waters) and highly variable through time, making direct sampling and analysis challenging. The immediate focus of the present work was the development of a passive sampling device that can provide time-averaged concentration trends. Future work is focused on the ultimate goal of predicting MeHg uptake by biota.

Passive samplers have been extensively investigated as a tool to measure freely dissolved concentrations (sometimes designated C_{free}) of other bioaccumulating pollutants, most commonly HOCs. For HOCs, samplers are made from thin hydrophobic polymer films that allow for partitioning and concentration into the polymer matrix. Polymeric samplers for HOCs function as equilibrium samplers, so C_{free} can be calculated based on the known equilibrium partition coefficient between water and the sampling material for each HOC. Importantly, although C_{free} represents only one of multiple pathways of biotic exposure, its calculation is useful because HOCs are in thermodynamic equilibrium among water, sediment, animal, and sampler compartments (Burgess, Berry et al. 2013). This chemical activity-based approach permits the use of equilibrium partitioning coefficients to calculate unknown HOC concentrations, as well as to predict the outcome of a perturbation such as the addition of an engineered sediment amendment or an ongoing contaminant input. In this way, porewater passive sampling measurements can serve as a useful proxy for bioavailability (Marvin-DiPasquale, Lutz et al. 2009, Liu, Feng et al. 2012, Amirbahman, Massey et al. 2013).

Our goal is to develop a similar approach for MeHg, using the equilibrium model concept developed for HOCs, and building upon the knowledge gained from passive sampler development for MeHg to date. The best-studied MeHg passive sampler is the diffusive gradient in a thin film, or DGT, device (Clarisse, Lotufo et al. 2012, Liu, Feng et al. 2012, Amirbahman, Massey et al. 2013, Hong, Dan et al. 2014, Noh, Hong et al. 2016). DGT samplers are *in situ* analytical sensors (Davison and Zhang 2012) composed of an inert gel diffusion layer (generally covered by a permeable membrane) over a ligand-bearing resin appropriate to the compound of interest. DGT samplers are designed to operate as kinetic samplers, in which the amount of metal accumulated depends on the concentration in the external environment, the time of deployment, the rate of diffusion through the gel layer, and the thickness of the gel. They operate as essentially “infinite sinks,” meaning that there is a sufficient mass of ligand in the sampler to drive the metal flux from an aqueous phase into the sampler during the entire deployment period (Jiménez Piedrahita 2017). The best-developed DGT samplers for both total Hg and MeHg use thiol-functionalized silica as a ligand, overlaid by either an agarose or polyacrylamide diffusion layer (Docekalova and Divis 2005, Clarisse and Hintelmann 2006, Amirbahman, Massey et al. 2013, Lu, Hong et al. 2014). One advantage of thiol-based samplers is that they may mimic the dominant MeHg ligands in nature (Zhang, Wang et al. 2004, Jeremiason, Portner et al. 2015, Liem-Nguyen, Skyllberg et al. 2016), and so potentially provide a good predictor of the flux to aquatic organisms. As a result,

site-specific uptake by thiol-based DGT samplers (commonly referred to as C_{DGT} or DGT-labile), has been used to predict Hg availability for methylation (Ndu, Christensen et al. 2018), *de novo* MeHg production (Clarisse, Dimock et al. 2011), MeHg photodegradation rates (Fernández-Gómez, Bayona et al. 2015), and MeHg uptake by biota (Clarisse, Lotufo et al. 2012, Liu, Feng et al. 2012, Amirbahman, Massey et al. 2013).

Although DGT samplers for Hg or MeHg were originally developed as a method to estimate freely or total dissolved concentrations in porewater (C_{pw}) (Docekalova and Divis 2005, Clarisse and Hintelmann 2006, Hong, Dan et al. 2014), many studies have recognized that DGT samplers instead access a kinetically labile portion of the total Hg or MeHg pool in sediments (Merritt and Amirbahman 2007, Clarisse, Foucher et al. 2009, Peijnenburg, Teasdale et al. 2014, Ndu, Christensen et al. 2018). Thiol-based DGT samplers have generally behaved as predicted by the general form of the DGT mass accumulation equation, with linear Hg and MeHg uptake through several days, although deviations may occur during longer deployment periods (Gao, De Canck et al. 2011, Clarisse, Lotufo et al. 2012, Amirbahman, Massey et al. 2013), or due to deposition of nanoparticles on sampler membranes (Pham, Johnson et al. 2015). Another potential complication of thiol-based DGT samplers operating as an “infinite sink” for Hg and MeHg is potential perturbation of the local equilibrium among solid and aqueous phases (Peijnenburg, Teasdale et al. 2014), which could lead to overestimation of the chemically or biologically available pool depending on the resupply rate from the solid phase (Clarisse, Dimock et al. 2011).

One particular challenge in the use of DGT samplers is the choice of diffusion coefficient used for calculation of $MeHg_{CL}$ from $MeHg_{DGT}$ (Noh, Hong et al. 2016), which should ideally be consistent across sampling regimes. The distribution of aqueous MeHg forms can vary significantly among environments and these species occupy a wide range of sizes, diffusivities, and bioavailabilities (Clarisse, Foucher et al. 2009), greatly increasing uncertainty when extrapolating from DGT to the labile fraction of interest in porewater. For MeHg in typical estuarine and fresh porewaters, the dominant species of $MeHg_{CL}$ are expected to be aqueous complexes with small organic thiols, sulfide, and bulky dissolved organic matter (DOM) (Skylberg 2008, Aiken, Hsu-Kim et al. 2011, Ndu, Barkay et al. 2015, Liem-Nguyen, Skylberg et al. 2017), as well as the portion of the much larger sediment MeHg pool that is in dynamic equilibrium with aqueous complexes (Benoit, Gilmour et al. 2001, Leaner and Mason 2002). Effective diffusion coefficients range over about an order of magnitude between large MeHg-DOM complexes and small MeHg salts for DGT samplers (Clarisse, Foucher et al. 2009, Hong, Rifkin et al. 2011, Gao, De Craemer et al. 2014). One way around this issue is to use $MeHg_{DGT}$ to directly predict some measure of MeHg bioavailability in a specific environment (Clarisse, Lotufo et al. 2012), but that empirical approach can limit comparison among environments.

By using an equilibrium approach to sampling, our objectives include obviating the use of diffusion coefficients to calculate $MeHg_{CL}$ and limiting perturbation of the dynamic sediment:water equilibrium. Instead, $[MeHg_{CL}]$ can be calculated directly from the measured equilibrium concentration of MeHg in the sampler $[MeHg_{ps}]$ and the operationally defined partition coefficient between the sampler and its environment (K_{pw}):

$$[MeHg_{CL}] = [MeHg_{ps}]/K_{pw}$$

Importantly, the goal of passive sampling efforts is to assess the total pool of labile MeHg. The concentration of MeHg_{CL} will largely be determined by the equilibrium with the large pool of sediment-bound MeHg. If all of the component species of MeHg_{CL} come to equilibrium with the samplers, the concentration of MeHg accumulated in the sampler will reflect [MeHg_{CL}] regardless of MeHg speciation. Thus, the equilibrium concentration of MeHg accumulated in samplers could be used directly to assess MeHg availability. Alternatively, the absolute concentration of MeHg_{CL} can be calculated using the appropriate K_{pw} . In most environments MeHgDOM species are dominant, so the use of a sufficiently representative, empirically derived K_{pw} for MeHgDOM could be sufficient to determine MeHg_{CL}. The advantage of equilibrium passive sampling is that, if a standardized sampling material based on cysteine or another sorbent is properly designed, it should approach a steady-state MeHg_{CL} concentration in proportion to steady-state concentrations in benthic animals, irrespective of mechanism (Peijnenburg, Teasdale et al. 2014). The challenges for equilibrium passive sampling are 1) to convincingly demonstrate reversible MeHg equilibrium with the chosen sampler, 2) to establish K_{pw} for environmentally relevant MeHg species, and 3) to evaluate the relevance of sampler data in real sediment systems.

Our approach to developing a novel sampler began by identifying a suite of polymers with affinity for MeHg sufficient to concentrate it to a desirable extent, but without dramatically exceeding native sediment-water partitioning (K_d). For our purposes, this entailed a target range for logarithmic passive sampler-water linear partitioning constants ($\log K_{pw}$) of 3.0 to 4.5. This range was also selected in part to ensure accumulation of detectable masses of MeHg in a reasonably sized sampler, without causing local depletion of MeHg_{CL} through the addition of a small mass of high-affinity ligand in the sampler material. More than 30 materials were screened in isotherms for MeHg complexed with either HO⁻ or Suwannee River Humic Acid, ligands chosen to bracket a range of size and lability for relevant MeHg species. Some of the most successful materials were chosen to proceed to further, more environmentally realistic tests, first in slurried soils and sediments, then in stagnant sediment microcosms. One particularly promising material, an agarose gel containing suspended activated carbon particles, was subjected to additional experiments to investigate its kinetics of MeHg uptake and release. Several of the other materials we tested also demonstrated desirable MeHg partitioning and remain candidates for future development. The work described here represents a proof of concept for equilibrium MeHg passive sampling and sets the stage for further work toward the ultimate goal of enabling reproducible measurements of bioavailable MeHg_{CL} and improving risk assessment and management for mercury-contaminated sites.

6.3 MATERIALS AND METHODS

Material selection and preparation

The potential passive sampling materials tested in this work fall under 3 categories: (1) standard laboratory polymers not specifically designed for metal sorption; (2) polymers containing activated carbon; and (3) polymers with reduced sulfur chemical functionality. Agarose gels were prepared with an existing method (Gao, De Canck et al. 2011), but suspensions of sorbents in agarose were based on custom formulations. Sulfur-functionalized polymers were identified in the biomedical (Bernkop-Schnürch, Kast et al. 2001); (Duan and Lewis 2002, Bhalekar, Mangesh et al. 2013) or water treatment (Yu, Addai-Mensah et al. 2012) literature. A method for embedding AC in a polyvinylidene fluoride (PVDF) polymer was adapted from an electrochemistry application (Choi

2010). A complete list of 30 tested samplers and references to preparation methods is presented in Table 1, and photos of selected samplers appear in Figure S1. For all experiments except initial screening isotherms, agarose gels were prepared with uniform thickness (800 μm except where noted) by casting between glass plates separated by spacers. Spacer and gel thicknesses were verified with a 0–1” digital micrometer (iGaging).

Screening isotherms

MeHgOH isotherms. Small (ca. 1–5 cm on a side) pieces of test material were cleaned, dried, weighed, and placed in 60-mL polyethylene terephthalate glycol copolymer (PETG) bottles containing 50 mL deionized water adjusted to 3 ppt salinity with Instant Ocean® (Spectrum Brands Pet LLC). All experiments in this work were run at low salinity for consistency and to mimic the conditions at our primary field site, an oligohaline, estuarine marsh. In this experiment, $[\text{Cl}^-]$ was sufficiently low and pH sufficiently high (approximately 9 as predicted by MINEQL and verified by direct measurement) that MeHg was predominantly complexed with HO^- rather than Cl^- . The solutions were spiked with MeHg at concentrations ranging from 3 to 300 ng L^{-1} (unmodified polymers) or 30 to 3000 ng L^{-1} (modified polymers). These were chosen in consideration of analytical detection limits and anticipated partitioning. Samples were incubated for 14 d in the dark at 4 °C with orbital shaking at 120 rpm. Following incubation, sample waters were passed through 0.45- μm GD/X filters (Whatman plc, glass microfiber in propylene housing) with disposable plastic syringes. Filtrates were processed and analyzed for MeHg. In screening isotherms only, the mass-normalized sampler concentration, C_{ps} , was calculated from the difference between spiked and recovered MeHg in water. In all other experiments, samplers were directly distilled and analyzed. Sampler-water partitioning coefficients, K_{pw} , were calculated from linear regression fitting of C_{ps} and C_{w} to an isotherm model. Control bottles with no sampler were used to assess loss of MeHg to degradation or sorption to bottle walls. Fractional losses in control bottles were inversely related to initial spike concentrations, such that partitioning by unmodified samplers could have been somewhat underestimated at low spike levels. However, losses were negligible at the higher concentrations used for actual samplers containing AC or sulfhydryl functionality.

MeHgSRHA isotherms. We also evaluated partitioning of MeHg complexed with Suwannee River Humic Acid (MeHgSRHA) to several samplers. Isotherms were set up as in the MeHgOH isotherms, but with the addition of Suwannee River Humic Acid Standard II (International Humic Substances Society) in a 10^6 :1 SRHA:MeHg mass ratio in each sample and 7.5 mM NaHCO_3 to buffer pH at 8. A high SRHA:MeHg mass ratio was chosen to avoid saturating thiolic sites, which control MeHg complexation with DOM under normal environmental conditions (Haitzer, Aiken et al. 2002). To ensure a stable MeHg distribution, solutions were incubated overnight after addition of SRHA but before addition of samplers. The assumption of an overnight equilibrium between MeHg and SRHA was based on the work of (Luengen, Fisher et al. 2012). Isotherm results for all tested materials can be found in Table 6.1.

Sampler kinetics and mechanism of accumulation

In an initial, range-finding experiment, 2 samplers, an agarose gel with embedded AC particles (ag+AC) and a polyethylene terephthalate sheet covalently modified with cysteine residues (PET+Cys), were exposed to MeHgOH or MeHgSRHA solutions for 7 h, 1 d, 7 d, 14 d, or 28 d.

Solutions were sampled destructively at each time point and water filtrates and samplers were processed and analyzed for MeHg.

In a subsequent experiment, pieces of ag+AC of identical composition but contrasting thicknesses (0.80 x 5 x 5 mm vs. 0.17 x 10 x 10 mm) were exposed to MeHgSRHA to determine whether it diffuses into the sampler or is restricted to surface adsorption. A solution of 3 ppt Instant Ocean®, 7.5 mM NaHCO₃, and 5 mg L⁻¹ SRHA was prepared and passed through a 0.7-μm AQFA filter. The filtrate was spiked to 50 ng L⁻¹ MeHg and allowed to equilibrate overnight before being apportioned to exposure bottles. Samplers were added to bottles and exposed in the dark at 4 °C with orbital shaking at 60 rpm. Samples were collected destructively after 6 min, 2.4 h, 7 h, 1 d, 3 d, 7 d, 21 d, and 58 d. Waters and samplers were collected, preserved, and analyzed. Results from the 21- and 58-d time points are not reported because C_w had dropped substantially in both sampler and control bottles due to MeHg degradation.

To evaluate the effects of DOM concentration on MeHg accumulation of target sampler sorbent materials, uptake of MeHgSRHA onto granular activated carbon and granular thiol-SAMMS was investigated. 20-mL solutions of MeHgSRHA were prepared at DOM concentrations ranging from 5 to 500 mg L⁻¹, with MeHg added to reach an initial concentration of 500 ng L⁻¹. Similar to the isotherm experiments, bottles were incubated overnight in the dark at 4 °C with orbital shaking at 60 rpm to ensure equilibrium between MeHg and SRHA. Approximately 10 mg of granular sorbent material was then added to each bottle and exposed for 2 d in the dark at 4 °C with orbital shaking at 60 rpm. Waters and sorbent materials were collected after separation by centrifugation, preserved, and analyzed. Each experimental treatment was conducted in triplicate.

Activated carbon kinetics and desorption

To improve our understanding of the nature of accumulation by AC-based samplers, we investigated the kinetics of mercury sorption to activated carbon. Granular activated carbon (Calgon 80 x 325 TOG LF, CAS #7440-44-0, sieved to > 53 μm prior to use) was weighed into PETG bottles containing 50 mL of deionized water with 3 ppt Instant Ocean® and 5000 ng L⁻¹ Hg or 250 ng L⁻¹ MeHg. Control bottles without AC contained 50 ng L⁻¹ Hg or 20 ng L⁻¹ MeHg. Initial spikes were based on anticipated final concentrations and analytical detection limits. Bottles were incubated for 5 min, 30 min, 6 h, or 2 d, after which shaking was halted and AC particles were allowed to settle. Waters were carefully removed by pipet while minimizing withdrawal of AC, filtered, preserved, and analyzed. To measure desorption from AC, a fresh solution without mercury spike was added to the original exposure bottles up to the 50-mL mark, and the bottles were incubated for the same amounts of time as in the exposure step. Bottle weights were collected before and after each step to track solution volumes, and exposure times were recorded to the minute. Each adsorption and desorption time point was run in duplicate (controls) or triplicate (AC).

Soil and sediment slurries

A natural soil and sediment were used to test the predictive capabilities of select samplers in more complex and environmentally realistic chemical matrices encompassing a range of MeHg concentrations. Soil from the upper 15 cm of a Berry's Creek (Bergen County, NJ) *Phragmites* tidal marsh was collected in June 2015 in a location containing about 50 ppm total Hg and 25 ppb MeHg. Estuarine sediment was collected from the Rhode River dock at the Smithsonian

Environmental Research Center in Edgewater, MD. It contained about 0.1 ppm solid-phase Hg and less than 5 ppb MeHg. Initial sediment and soil chemistry can be found in Table S1. Slurries of each were prepared with degassed, deionized water containing 3 ppt Instant Ocean® in a 9:1 weight ratio with solids. All subsequent handling was performed in an anaerobic glove bag. Slurries were spiked with unlabeled Hg equal to 10% (soil) or 20% (sediment) of the native, dry-weight Hg content to encourage additional MeHg formation. Slurries were incubated for 7 d with a gentle shake once per day before apportionment to sample jars. Three sampler types were tested in duplicate: ag+AC, an agarose suspension of the engineered sorbent material thiol-SAMMS (ag+SAMMS), and PET+Cys. Samplers (ca. 5–25 cm on a side) were cleaned, dried, weighed, measured, and placed in small baskets prepared by folding strips of polypropylene mesh and sewing edges together with nylon thread (Figure S6.1c). Mesh and thread were washed with 1 M HNO₃ followed by deionized water prior to use. Samplers in baskets were placed in wide-mouth, glass sample jars containing 50 mL equilibrated soil or sediment slurry. Two additional “canary” jars of each slurry were prepared without samplers but with 2 mg L⁻¹ resazurin to monitor redox status. Jars were kept on ice for 20 d to minimize further MeHg production and were gently swirled once per day. After exposure, samplers were removed from jars and baskets, gently rinsed with deionized water, blotted with lab wipes, weighed, and frozen. An aliquot of overlying water was collected from each jar for pH measurements, and the remaining jar contents were transferred to tubes and centrifuged at 4200 rpm for 7 min. Supernatants were passed through 0.45 µm glass microfiber syringe filters with disposable plastic syringes into clean, 60-mL PETG bottles. Aliquots were set aside for analysis of sulfide and DOC. Remaining filtrates were acidified with 0.5% HCl and refrigerated, then processed and analyzed for MeHg, sulfide, and pH (Table S2). Pelleted solids were lyophilized and weighed repeatedly until weights were replicable, then processed and analyzed for MeHg.

Static sediment microcosms

In a further step toward simulating realistic deployment conditions, samplers were tested in static sediment microcosms. Bottom sediment was collected to a depth of 15 cm from a tidal creek in the upper part of Berry’s Creek. The sediment was silty mud with solid-phase Hg concentrations of 40–50 ppm. Sediments were collected in May 2016 in 5-gal buckets, shipped on ice to SERC and maintained at 4 °C until the start of the experiment in August. Sediments were mixed by hand and a portion was amended with 5 wt% activated carbon (Calgon Type 3055, 80 x 325 mesh, CAS #7440-44-0). For microcosms, 200 g sediment with or without AC was combined with 225 mL overlying water (5 ppt Instant Ocean®) in 800-mL plastic beakers. Beakers were loosely lidded, gently aerated, and kept at room temperature (Figure S2). Microcosms equilibrated 14 d prior to sampler insertion to allow redevelopment of a vertical redox gradient. In each beaker, one ag+AC sampler in a protective basket was fully submerged in the uppermost 0.5 cm of sediment, spanning the visually apparent redox transition zone. To assess kinetics of uptake, samples were collected destructively at 0, 8, 14, 21, and 28 d of exposure. Samplers were removed from baskets, preserved, and analyzed as before. Sediment and porewater were separated by centrifugation at 4000 rpm for 5 min and handled as in the slurry experiment. Sediment and porewater measurements reflected vertical averages of the entire depth of sediment in the microcosms (2–3 cm). Overlying water was gently replaced in remaining beakers on sampling days.

Analytical methods

MeHg in all matrices was measured by isotope dilution mass spectrometry after separation and cleanup by distillation (Gilmour, Riedel et al. 2013). Total Hg was also measured using ID-ICP-MS following SnCl_2 reduction to Hg^0 . Water samples were digested with BrCl and sediment samples with 7:4 $\text{HNO}_3\text{:H}_2\text{SO}_4$. Further details and quality assurance data are found in the SI, including Table S6.3.

Equilibrium speciation calculations

The chemical modeling program MINEQL+ v.4.6 (Environmental Research Software) was used to calculate equilibrium aqueous MeHg speciation in all experimental systems. Conditional stability constants for a variety of MeHg complexes were obtained from literature sources and added to the software's database as outlined in Table S4. All other thermodynamic constants were software defaults.

6.4 RESULTS AND DISCUSSION

Screening isotherms

MeHgOH isotherms. As shown in Table 6.1, initial isotherm tests demonstrated greatly enhanced sorptive capabilities of both AC- and thiol-modified polymers relative to unmodified hydrophobic polymers and permitted the selection of a subset of enhanced polymers to proceed to subsequent tests. Partitioning of MeHgOH by 8 unmodified hydrophobic polymers was generally well below our target range for linear partitioning $\log K_{\text{pw}}$ of 3.0 to 4.5. This outcome was to be expected given the low hydrophobicity of MeHgOH ($\log K_{\text{ow}} = -1.2$; (Mason 2001)). By contrast, partitioning of MeHgOH into many of the AC- and thiol-modified polymers fell comfortably within our target range, and sorption isotherms remained mostly linear over multiple orders of magnitude as shown for 3 selected polymers in Figure 6.1a (log transformed data) and for all 28 polymers in Table 6.1. Linear isotherms for MeHg on AC at low environmentally relevant concentrations have been published by others (Gomez-Eyles, Yupanqui et al. 2013). We also fitted partitioning data to Freundlich isotherms and found Freundlich parameters ($1/n$) less than 1 for some samplers (Table S6.5). However, curves only diverged from linearity at unrealistically high C_w (Figure S6.3) for most samplers, so reported K_{pw} values represent the regression fitted values for linear isotherms. Isotherm results were compared to the partitioning expected based on the composition of the samplers. This analysis revealed that some of the samplers permitted relatively free diffusion of MeHgOH, while others were diffusion-limited (i.e., measured partitioning was much lower than predicted). A detailed discussion of sampler permeability is found in the SI and supported by Table S6.6.

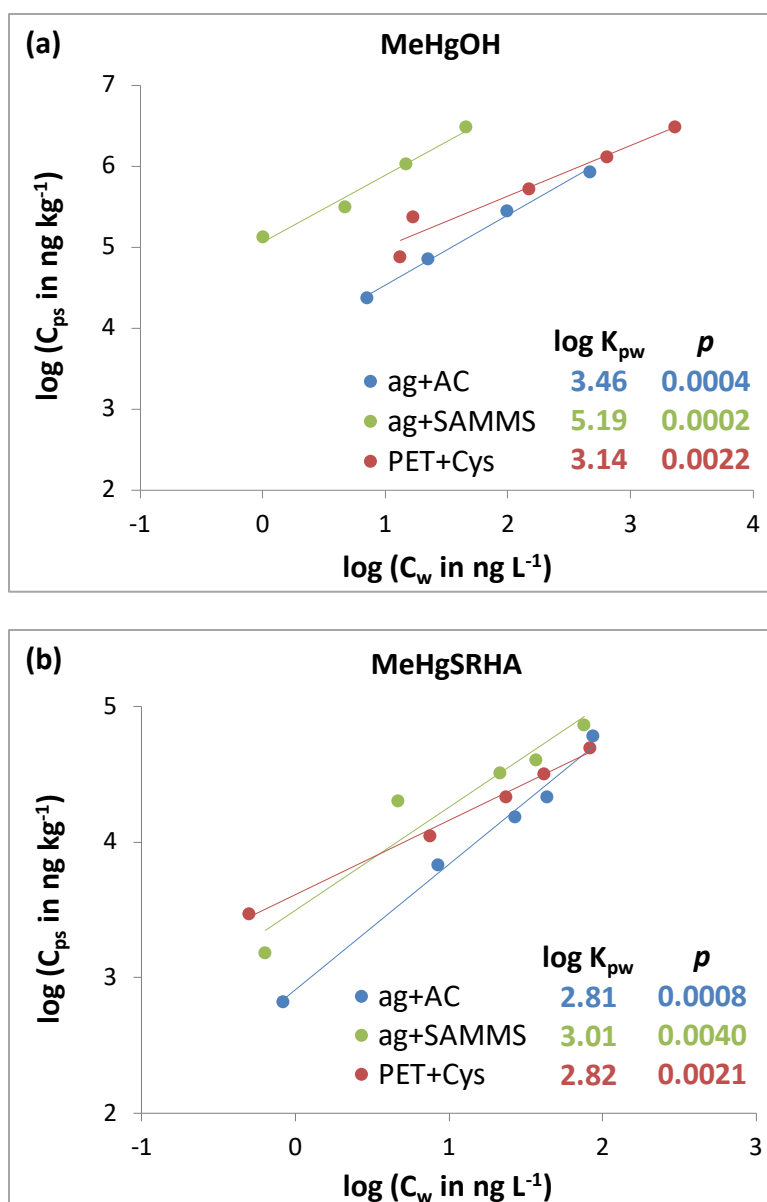


Figure 6.1. Partitioning of (a) MeHgOH and (b) MeHgSRHA to Select Samplers in 14-d Aqueous Isotherm Tests.

Note different axis scales.

Three samplers, ag+AC, ag+SAMMS, and PET+Cys, were identified as the most promising based on the strength and proportionality of their partitioning and their physical attributes. The sulfur-functionalized biomedical polymers (“thiomers”)—including thiolated chitosan and cysteinylated alginate and xyloglucans—lacked mechanical strength as prepared and were suspended in agarose to confer stability in isotherm tests. Though they also partitioned well, they were excluded from further consideration due to the additional complexity involved in their preparation and the availability of several viable alternatives. ag+MPTMS-DE, an agarose gel containing mercapto-modified diatomaceous earth, performed well in isotherm tests but was not carried forward due to sample size limitations. This material remains a good candidate for future investigation.

MeHgSRHA isotherms

Partitioning of MeHgSRHA was reduced compared to MeHgOH for all tested samplers (Figure 6.1b). Speciation modeling for isotherms run with added SRHA predicted virtually complete complexation of MeHg with SRHA. Compared to smaller MeHg complexes, MeHg complexed with DOM is both less diffusive and less bioavailable (Choi, Cech et al. 1998, Fernández-Gómez, Bayona et al. 2014). This experiment therefore represents an important contrast to the idealized scenario in the previous set of isotherms. However, in all cases partitioning remained in or near our target range and was proportional across a range of C_w ($r^2 \geq 0.93$). The lowest K_{pw} was measured for ag+AC. Under true, diffusively unconstrained equilibrium conditions, the extent of MeHg partitioning to AC particles should theoretically be the same irrespective of the other ligands present. That this didn't occur suggests that the MeHgSRHA-AC interaction may have effectively reflected an SRHA-AC interaction with MeHg incidentally associated, a hypothesis we confirmed in a separate study (Schwartz, Sanders et al. 2019).

The size of the decrease in K_{pw} from MeHgOH to MeHgSRHA varied among samplers, possibly reflecting differences in their physical structures and uptake mechanisms. For example, the K_{pw} decrease was relatively small for PET+Cys, a sampler with readily accessible binding sites on its surface and presumably not limited by diffusion. By contrast, the decrease was more pronounced for ag+SAMMS, which requires diffusion through both agarose and thiol-SAMMS, a highly structured material with pore sizes on the order of 2–20 nm (Laboratory 2009). MeHg complexed with SRHA, which forms colloids in the range of 0.5–2 nm and aggregates to some extent, may be less readily accessible to such a sampler (Balnois, Wilkinson et al. 1999, Hosse and Wilkinson 2001). Fouling of thiol-SAMMS by SRHA may also have contributed to lower-than-predicted MeHg uptake. Despite these differences, the generally positive results for several samplers in both the MeHgOH and MeHgSRHA isotherms were encouraging and indicated their potential to function across a variety of water chemistries and MeHg species.

Sampler kinetics and mechanism of accumulation

In a range-finding kinetics experiment in aqueous solution, both ag+AC and PET+Cys approached equilibrium partitioning of MeHgOH after 2 weeks (Figure 6.2a and Table S6.7). For both sampler types, the uncertainty ranges in log K_{pw} from the isotherm experiment overlap with the 95% confidence intervals at the 14-d point in this experiment (based on linear regression of log-transformed partitioning versus time). Absolute accumulation of MeHgSRHA was depressed compared to MeHgOH, with lower partitioning at each time point. The shape of the MeHgSRHA kinetic curve was also flatter, making equilibration difficult to verify.

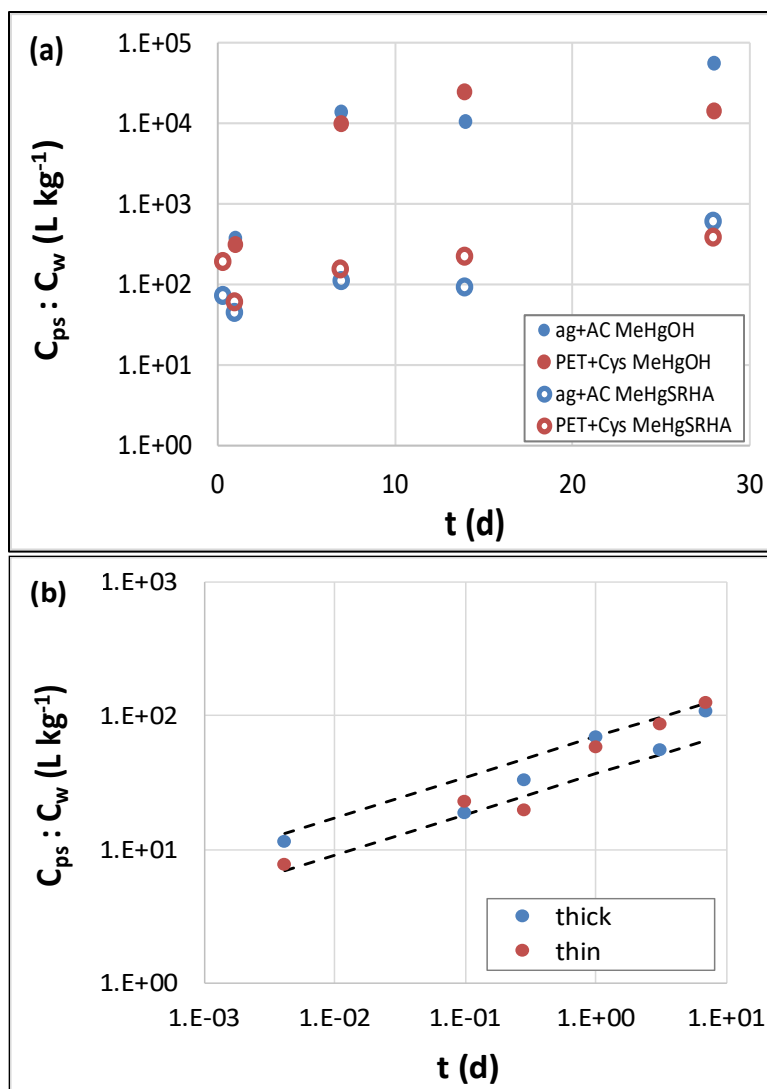


Figure 6.2. (a) Kinetic Curves for Polymer-water Partitioning of MeHgOH (Filled circles) and MeHgSRHA (Open Circles) by ag+AC (Blue) and PET+Cys (Red).

Note arithmetic vs. logarithmic axes. (b) Kinetic curves for partitioning of MeHgSRHA by ag+AC with two contrasting surface area-to-volume ratios: 3.3 mm⁻¹ ("thick", blue) and 12.2 mm⁻¹ ("thin", red). Dotted lines: upper and lower 95% confidence intervals for power fit of thick data. In both figures, each point represents $n = 1$.

In addition to kinetics, the mechanisms of MeHg accumulation by samplers are an important consideration in sampler development. An understanding of where and how sorption occurs is required to interpret sampler concentrations and optimize form factors. PET is a relatively impermeable polymer, so both the cysteinylolation of PET and the accumulation of MeHg by PET+Cys can be assumed to occur mostly on the sampler's surface. By contrast, agarose is permeable and readily permits diffusion of MeHg even in the presence of DOM (Fernández-Gómez, Bayona et al. 2014). To verify a permeation-based mechanism of accumulation by ag+AC, pieces of the material with contrasting surface area-to-volume ratios were exposed to aqueous MeHgSRHA and sampled along a time course. If internal diffusion were substantially inhibited

relative to diffusion to sampler surfaces, accumulation would increase with increasing surface area-to-volume ratio. However, this was not the case. Aside from one point, the uptake curves of the two thicknesses were indistinguishable (power fit, $p = 0.05$; Figure 6.2b; see Table S6.8 for mass balance data). This strongly suggests that even large MeHg complexes (SRHA has an average molecular weight of 1399 daltons (Waples, Nagy et al. 2005)) readily permeate the agarose matrix of ag+AC, in contrast to PVDF (see discussion of sampling mechanisms in SI). A simple modeling exercise supports this contention. The diffusion coefficient (D) in agarose of MeHg complexed with DOM from a Nordic Reservoir is $2.68 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, only 15% lower than that of MeHg without DOM (Fernández-Gómez, Bayona et al. 2014). Assuming that this value of D is similar to that of MeHgSRHA, a Fickian diffusion calculation predicts greater than 90% equilibration by agarose within 1 d at a depth of 400 μm (the half-thickness of our sampler). For comparison, our kinetic curves indicate an approach to equilibrium over several days to a week or more. It should also be borne in mind that the average pore size in our agarose gels, though not directly measured, is probably about 400 nm (Pernodet, Maaloum et al. 1997), while SRHA would have been on the order of 1 nm (Balnois, Wilkinson et al. 1999) and subject to only limited aggregation (Hosse and Wilkinson 2001). These considerations suggest that both the kinetics and equilibrium partitioning capacity of ag+AC are controlled by the included AC particles and not the agarose gel. This opens the possibility of tuning the sampler's performance by adjusting the concentration and properties of the AC or other sorbents used in its formulation. In addition, there is an opportunity to design the polymer matrix to exclude the diffusion of DOM-bound MeHg if necessary.

An experiment was conducted to understand the effect of DOM on the accumulation of MeHg species by the target sorbent materials. A gradient of SRHA concentrations was chosen to represent environmentally relevant DOM concentrations (5–50 mg L^{-1}), as well as a DOM concentration elevated above what would be expected in most environments (500 mg L^{-1}). Partitioning of MeHgSRHA to bare AC particles exhibited relatively consistent values across the environmentally relevant DOM gradient ($\log K_{AC}$ of 3.77–3.35). Similarly, partitioning of MeHgSRHA to bare thiol-SAMMS was relatively consistent across the same range ($\log K_{SAMMS}$ of 4.30 to 4.26) (Table S9). Both sorbents exhibited decreased partitioning of MeHgSRHA at elevated DOM concentrations (500 mg L^{-1}). This behavior suggests that over environmentally relevant DOM concentration ranges, even in field deployments with fluctuating DOM concentrations, both of these tested sorbent materials will provide reasonable estimates of MeHg C_{pw} when using the empirically determined K_{pw} for these materials.

Activated carbon kinetics and desorption

A separate experiment was performed to characterize adsorption onto and desorption from bare AC particles. Partitioning of MeHgOH to AC was rapid (Figure 6.3 and Figure S6.4), approaching the previously published $\log K_{AC}$ value of 4.89 within 5 h and slightly surpassing it (5.01–5.21, $n = 3$) by 2 d (Gomez-Eyles, Yupanqui et al. 2013). A model fit of MeHg adsorption is shown in Figure S4b. When MeHg-loaded AC was exposed to clean water, re-equilibration to a similar $\log K_{AC}$ (5.00–5.22, $n = 3$) occurred within 3.6 h (shown in Figure 6.3, details in Table S6.10). Because complete removal of the original exposure solutions was impossible without also removing AC, some MeHg-spiked water (usually about 2 mL) carried over into the 50 mL desorption solutions. However, the masses of MeHg released from AC exceeded the masses carried over, and MeHg in water increased with desorption time, confirming that MeHg indeed desorbed from AC. Carryover MeHg accounted for 15–30% of the totals measured in water after desorption. These findings

support the notion of a reversible, relatively rapid equilibrium between AC and MeHg in water and, by extension, between ag+AC and MeHg in water. Thus, in a field deployment, the sampler would not report the maximum concentration detected, but rather an integration of the ambient concentrations experienced throughout the exposure. The dimensions of the sampler and AC particles could be manipulated to achieve a desired timescale for exchange.

Hg_i adsorption and desorption were also rapid. The previously reported K_{AC} of 6.55 (Gomez-Eyles, Yupanqui et al. 2013) was attained (6.63–6.77, $n = 3$) within 30 min, and a similar value (6.13–6.64, $n = 2$) was measured after just 36 min of desorption in clean water. The model fit produced a higher rate constant and equilibrium concentration compared to MeHg (Figure S6.5; Table S6.11).

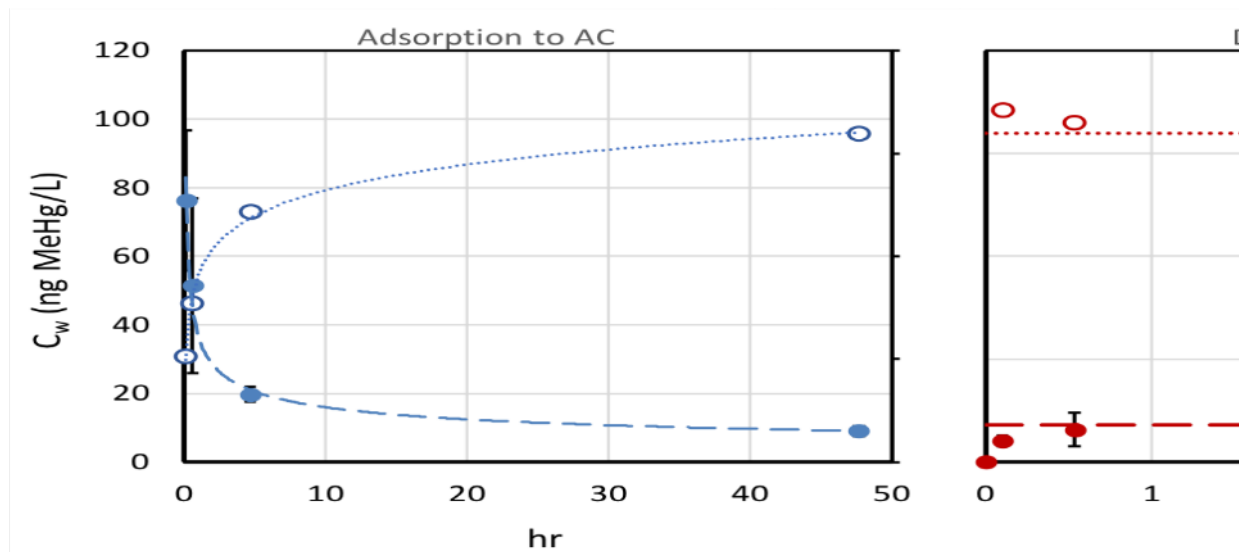


Figure 6.3. Kinetics of MeHgOH Adsorption to a Coal-derived Activated Carbon (Initial $C_w = 250 \text{ ng L}^{-1}$) and Desorption of MeHg After Transfer to Water Containing No Initial MeHg. MeHg Concentrations (ng L^{-1}) in Water Over Time Are Shown as Filled in Circles; Error Bars Show ± 1 Standard Error.

Partitioning coefficients (K_d) for MeHg to activated carbon are shown with open circles. For the adsorption phase, dashed lines represent logarithmic best fit line; for the desorption phase, dashed lines represent final values observed during the adsorption phase. The kinetics of sorption by porous media are characterized by multiple mechanistic steps, including diffusion to sorbent surfaces and intraparticle diffusion (Boyd, Adamson et al. 1947). Given the shape of the kinetic curve for MeHg on bare AC particles, it is reasonable to assume that, for ag+AC in our well-mixed systems, intraparticle diffusion was rate-limiting at later time points. However, in a passive sampler deployment in stagnant sediment, diffusion to the sampler's surface would be slower and exert a greater impact on overall rate. In that case, equilibration could be slower (Mohan, Dines et al. 2001). Further work is needed to understand the kinetics of sorption by samplers relative to those of MeHg ligand exchange in porewater and, for sulfur-based samplers, at sorbent sites.

Soil and sediment slurries

In the more chemically complex and realistic milieu of slurries, all 3 tested sampler types successfully predicted MeHg C_{pw} , giving an early indication that they may be viable for use in field conditions (Figure 6.4). All samplers were retrieved intact after 20 d of exposure. The 2 experiments, using an uncontaminated estuarine sediment (Rhode River) and a contaminated marsh soil (Berry's Creek), provided a test across sharply contrasting porewater MeHg concentrations and speciation. Redox conditions in the Rhode River sediment slurries, as indicated by a resazurin color change in the canary jars and low ($<1 \mu\text{M}$) sulfide concentrations throughout the experiment did not favor MeHg production (Tables S6.1 and S6.2). As a result, aqueous MeHg concentrations at the end of the exposure were extremely low ($0.12 \pm 0.043 \text{ ng L}^{-1}$). Both aqueous and sampler MeHg measurements were close to method detection limits (Table S3) and highly variable (one outlying value was excluded for failing a Dixon's Q -test). In comparison, the Berry's Creek soil slurry porewaters were initially strongly reducing with high sulfide concentrations ($269 \pm 1.96 \mu\text{M}$), although slurries became less reducing over the course of the exposure study, with porewater sulfide declining to $<1 \mu\text{M}$ by the end of the exposure. The contrast in redox status drove a change in MeHg speciation. Modeling results for the Berry's Creek soil slurries indicated that MeHgSH predominated at d 0 but by d 20 the balance had shifted to complexes with DOM. (In Rhode River sediment slurries, DOM complexes predominated at both time points.) No color change was observed in the corresponding Berry's Creek soil canary jars. Despite the change in redox conditions, final aqueous concentrations of MeHg were considerably higher than in Rhode River slurries ($8.7 \pm 1.5 \text{ ng L}^{-1}$), permitting more reproducible measurements of both water and samplers.

To contextualize these results, we used sampler accumulation in slurries in combination with partitioning coefficients generated in screening isotherms to calculate "predicted" C_{pw} in slurries. Figure 6.4 presents a comparison of the directly measured concentrations in centrifuged porewater with sampler-predicted values using K_{pw} obtained from independent MeHgOH and MeHgSRHA isotherms. The accuracy and replicability of sampler predictions was greater in Berry's Creek soil slurries, where both porewater and sampler concentrations were further above analytical detection limits. In general, sampler predictions based on MeHgSRHA K_{pw} values agreed with direct measurements in both Rhode River and Berry's Creek slurries. Predictions were within a factor of 2 in 4 cases and within a factor of 4 in the remaining 2. There was greater underprediction based on MeHgOH K_{pw} values. This is unsurprising given that porewater speciation was dominated by DOM. Thus, for accurate estimation of the total dissolved concentration of MeHg, it is important to use the K_{pw} value corresponding to the dominant MeHg species. In this work we have measured sampler K_{pw} for two of the most common MeHg ligands. Additional work is needed for predictions where HS^- or Cl^- may represent the dominant complexing ligand. We hypothesize that K_{pw} for MeHgCl will be similar to K_{pw} for MeHgOH, but partitioning of the bisulfide complex is more difficult to predict. Measured $\log K_{pw}$ values in Berry's Creek soil slurries (based on filtered porewater measurements) were 3.41 (ag+AC), 3.12 (ag+SAMMS), and 3.11 (PET+Cys), all within our target range and close to the independently measured K_{pw} values in MeHgSRHA isotherms. It should be emphasized that sampler measurements are time-integrative, whereas direct measurements represent snapshots of porewater concentrations. As such, some differences between the two are to be expected.

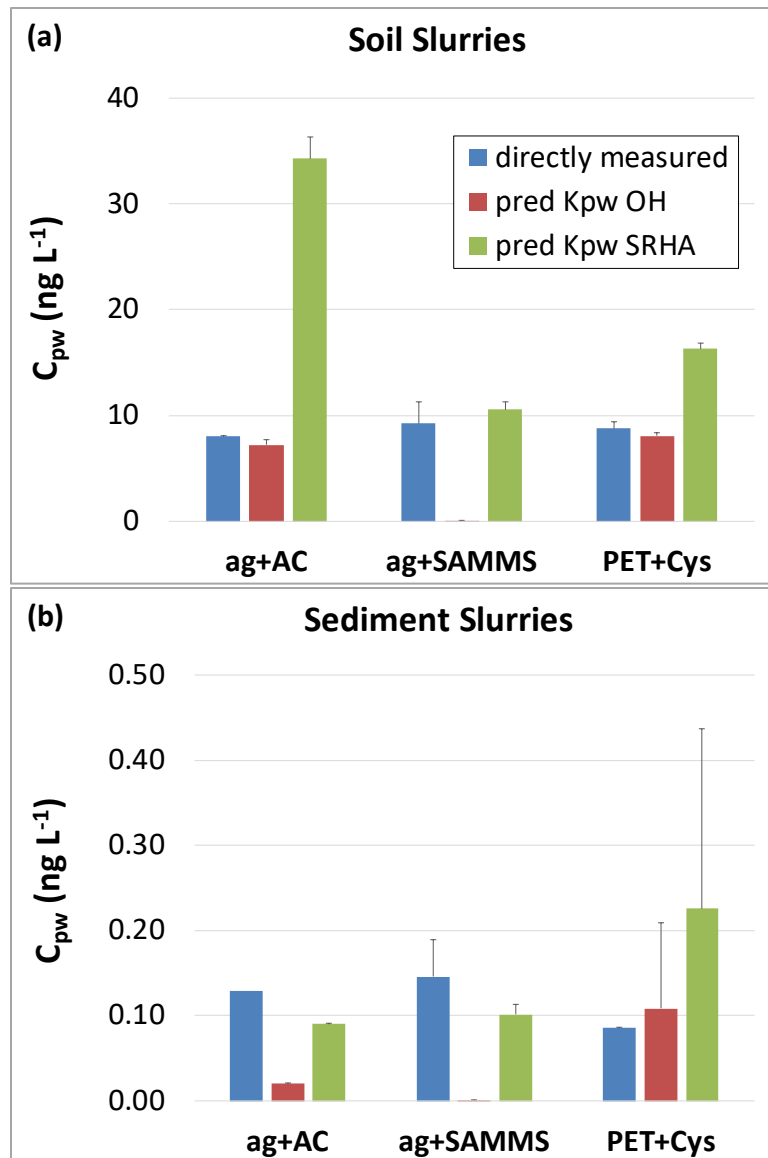


Figure 6.4. Porewater MeHg Concentrations in (a) Slurried Soil and (b) Sediment.

Blue bars: directly measured in centrifuged porewater; red bars: predicted by applying measured polymer concentrations (C_{ps}) to linear fit from MeHgOH isotherm experiment. Green bars: predicted by applying C_{ps} to linear fit from MeHgSRHA isotherm experiment. Error bars show +1 standard error ($n = 2$ except ^, $n = 1$). Note different axis scales. In (b), lower detection limits were 0.05–0.13 ng L⁻¹ for porewater and 1.03–92.16 ng kg⁻¹ for samplers.

Static sediment microcosms

As they did in well-mixed soil slurries, ag+AC samplers calibrated with K_{pw} for MeHgOH again made good predictions of MeHg concentrations in estuarine sediment porewater, here at low C_{pw} and under stagnant, poorly mixed conditions (Figure 6.5). Directly measured C_{pw} in unamended sediment collected from a different Berry's Creek location was 1.7–3.7 ng L⁻¹ across the duration of the experiment. C_{pw} predicted by samplers using K_{pw} from Berry's Creek soil slurries was 1.7–

4.6 ng L⁻¹, statistically indistinguishable from direct measurements at each of the 4 time points (*t*-test, $\alpha = 0.05$). The slurry K_{pw} was deemed most applicable because modeled MeHg speciation was similar in the two experiments (i.e., dominated by complexes with Berry's Creek DOM). The samplers' consistently accurate measurements across two experiments were notable. Interestingly, despite the modeled dominance of DOM complexes, better C_{pw} predictions were obtained from ag+AC using its isotherm K_{pw} for MeHgOH than for MeHgSRHA. This could be due to differences between SRHA and the DOM native to these estuarine sediments. SRHA is a terrestrially derived DOM occupying the high range of both aromaticity and molecular weight, and may also have a greater density of thiol sites compared to DOM native to Berry's Creek estuarine sediments (Waples, Nagy et al. 2005, Graham, Aiken et al. 2012).

Activated carbon added to sediment produced a strong effect as shown in Figure 6.5. Over the 28-d exposure period, sediment amended with AC contained significantly less MeHg in both the solid phase ($p < 0.001$, $n = 10$) and porewater ($p < 0.001$, $n = 10$) compared to unamended sediment (Figure S6.6; Tables S6.12 and S6.13). C_{pw} in amended beakers remained below 1 ng L⁻¹ throughout the study, comparable to background levels in uncontaminated sediments and soils. Sediment-water partitioning, log K_d , was 4.06 without amendment and 4.72 with AC. Sampler-water partitioning in amended sediment was somewhat stronger than in unamended sediment (log $K_{pw} = 4.09$ vs. 3.59) and led to overpredictions of C_{pw} , but even these were within 2 ng L⁻¹ of direct measurements.

To explain the apparent effect of AC on K_{pw} , we considered the possibility that AC scavenged DOM, resulting in a smaller fraction of MeHg complexed by DOM and an accordingly higher availability of MeHg to samplers. In fact, at d 14, 21, and 28, DOC was somewhat lower (not statistically significant) in AC-amended sediment, but our speciation modeling still predicted complete complexation with DOM in all beakers. However, due to the uncertainties inherent in the modeling approach—the most important of which surround the stability constants used for complexation with sulfide and DOM, as well as the fraction of -RSH groups on DOM (see Table S6.4 for details; (Liem-Nguyen, Skjellberg et al. 2016, Graham, Cameron-Burr et al. 2017)—the hypothesis that AC may alter MeHg speciation by reducing DOC and/or sulfide concentrations shouldn't be discarded at this time. Across all time points and both amendments, sampler accumulation was reasonably well correlated with directly measured C_{pw} ($r^2 = 0.69$; Figure S6.7).

The microcosm experiment also provided the first temporal results for our samplers in environmentally representative matrices (Figure 6.5). In both amendment scenarios, there was no trend in the accuracy of sampler-predicted C_{pw} with time. There was a slight increase in C_{pw} with time that was reflected in both direct and sampler measurements. In unamended sediment, the most accurate prediction (using the slurry K_{pw}) was made at 8 d, the first time point sampled (Figure 6.5a). This gives an indication that ag+AC may achieve equilibrium with porewater in a stagnant deployment on the order of 1 to 2 weeks, similar to the measured kinetics in water alone (Figure 6.2a).

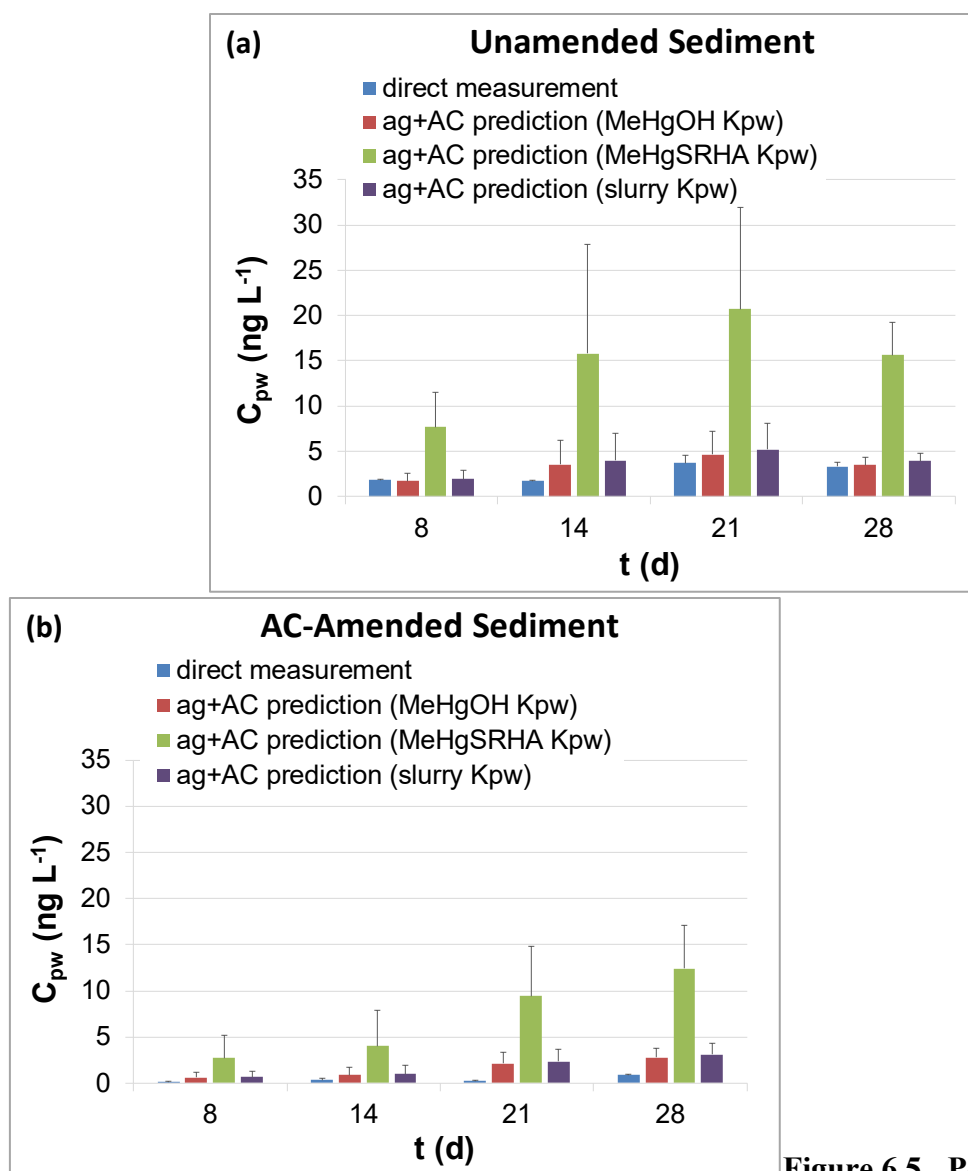


Figure 6.5. Porewater MeHg Concentrations in Static Sediment Microcosm Experiment. (a) Unamended sediment; (b) Sediment Amended with 5% dw Activated Carbon.

Values were directly measured (blue), or predicted by applying ag+AC C_{ps} to linear fits from MeHgOH isotherm (red) or MeHgSRHA isotherm (green), or by dividing C_{ps} by K_{pw} determined from soil slurry experiment (purple). Error bars show +1 standard error ($n = 2$).

Implications

We report the identification and testing of several sorbent materials with strong potential as passive samplers for MeHg_{CL} in soil and sediment porewaters, including at least one, ag+AC, which functions in a dynamic equilibrium mode. This sampler, along with others designed for chemisorption at reduced sulfur sites, made reasonably accurate measurements of dissolved MeHg across a range of environmentally realistic matrices including sediments with and without AC amendment. The partitioning coefficients of these samplers are such that a square piece approximately 1 cm on a side will accumulate a readily quantifiable mass of MeHg at a water concentration as low

as 1 ng L⁻¹. Importantly, sampler partitioning in slurries and microcosms was generally within about half a log unit of the native K_d values in source soils and sediments. Samplers suffered no apparent degradation or fouling during deployment in sediments and soils, indicating that they should not require a potentially interfering membrane (Pham, Johnson et al. 2015).

Several lines of future investigation are available. Sampler design and fabrication must be optimized and standardized for reproducibility. The potential use of stable MeHg isotopes as performance reference compounds to measure and account for nonequilibrium should be explored. The dynamics of MeHg exchange among samplers, water, and soil/sediment and among different complexing ligands must be elucidated to identify the pools accessed by the samplers and to determine the ability of samplers to respond to fluctuating C_{pw}. This will help to explain observed differences in sampler partitioning across different porewater chemistries and amendment scenarios. Because the utility of the devices will ultimately be determined by their ability to predict benthic bioavailability in diverse field conditions, tests in multiple sediments and alongside organisms in both the lab and the field will be necessary. Finally, the sorbents in our samplers have affinity for other metals, including Hg_i, Cd, Pb, Zn, and others. With additional experimentation, it should be possible to adapt this sampling strategy to measure these metals as well.

Supporting information

The Supporting Information provided in the Appendix contains photos, modeling inputs, quality assurance data, detailed analytical procedures, experimental data, and further discussion and figures.

Data Accessibility

Primary experimental data are provided in the supplemental information available online.

6.5 REFERENCES

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7.0 CHAPTER 7: EVALUATING THE UPTAKE MECHANISMS OF A NOVEL, ACTIVATED CARBON-BASED EQUILIBRIUM PASSIVE SAMPLER FOR ESTIMATING POREWATER METHYLMERCURY (PUBLISHED PAPER)

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ABSTRACT

Here we describe the validation of a novel polymeric equilibrium passive sampler comprised of agarose gel with embedded activated carbon particles (ag+AC), to estimate aqueous monomethylmercury (MeHg) concentrations. Sampler behavior was tested using a combination of idealized media and realistic sediment microcosms. Isotherm bottle experiments with ag+AC polymers were conducted to constrain partitioning to these materials by various environmentally relevant species of MeHg bound to dissolved organic matter (MeHgDOM) across a range of sizes and character. Partitioning coefficients ranged from $\log(K_{ps}) = 1.98 \pm 0.09$ for MeHg bound to Suwannee River Humic Acid to $\log(K_{ps}) = 3.15 \pm 0.052$ for MeHg complexed with Upper Mississippi River Natural Organic Matter. Reversible equilibrium exchange of environmentally relevant MeHg species was demonstrated through a series of dual isotope labeled exchange experiments. Isotopically labeled MeHgDOM species approached equilibrium in the samplers over 14 d while mass balance was maintained, providing strong evidence the ag+AC polymer material is capable of equilibrium measurements of environmentally relevant MeHg species within a reasonable deployment time frame. Samplers deployed across the sediment-water interface of sediment microcosms estimated both overlying water and porewater MeHg concentrations within a factor of 2 to 4 of measured values, based on the average measured K_{ps} values for species of MeHg bound to natural organic matter (MeHgNOM) in the isotherm experiments. Taken together, our results indicate that ag+AC polymers, used as equilibrium samplers, can provide accurate MeHg estimations across many site chemistries, with a simple back calculation based on a standardized K_{ps} .

7.1 INTRODUCTION

Accurate, direct measurement of aqueous methylmercury (MeHg) is challenging, especially in sediment porewaters. While the development of in situ porewater extraction techniques like Rhizon samplers or “sippers” has eased some of the numerous difficulties in obtaining valid sediment porewater MeHg measurements, these methods do not work in all sediment matrices equally, only provide a snapshot of MeHg concentration at the time of sampling, provide relatively coarse depth resolution, and may suffer from preferential water recovery from sediment macropores and preferential flow paths (Guedron et al., 2012; Guedron et al., 2014; Johnson et al., 2016). There remains a need for a simple, standardized passive sampling system for MeHg from which porewater MeHg concentrations and MeHg bioavailability can be calculated. A number of materials have been explored for the passive sampling of MeHg, most notably methods utilizing diffusive gradients in thin films (DGTs). Many of these methods operate in the kinetic regime and estimate concentrations based on a correlation with the kinetics of uptake of MeHg species (Taylor et al., 2019; Ndu et al., 2018; Noh et al., 2016; Clarisse et al., 2009; Clarisse et al., 2006). Equilibrium passive sampling on the other hand strives to operate at or near the equilibrium state, with corrections for departures from equilibrium as necessary (Ghosh et al., 2014). Two equilibrium passive samplers that have been used for metals include diffusion samplers such as ‘peepers’ and ‘diffusive equilibration in a thin film (DET)’ devices where the receiving phase is either water or a hydrogel (Peijnenberg et al., 2014). While these water-based samplers work for most heavy metals, often measured in the $\mu\text{g/L}$ levels in the environment, such samplers do not provide sufficient volume for accurate MeHg concentration measurements, often measured at the sub-ng/L level in environmental settings. Equilibrium passive sampling methods have been deployed successfully for a number of organic contaminants, and this approach carries numerous potential benefits for MeHg over traditional water and sediment grab sampling techniques and other passive sampling techniques deployed to date, including: 1) a time-integrated measurement of exposure concentrations over a deployment period (as opposed to a snapshot measurement in a grab sample), 2) measurement of fine-scale concentration gradients at critical mass transfer and production/degradation interfaces, 3) more accurate measurements of ultra-low concentrations that can be difficult to measure directly, and 4) improved mechanistic understanding of fate and processing of MeHg within sediment porewaters (Mayer et al., 2014).

The initial development of an equilibrium passive sampler for MeHg using activated carbon particles (Calgon PAC 3055) embedded within an agarose gel (ag+AC) was described in Sanders et al., 2020. After initial testing of a wide range of materials, Sanders et al. chose the ag+AC material because partitioning coefficients for two MeHg species were within a range that mimicked sediment porewater partitioning (typically $\log(K_d) = 3$ to 5). Additionally, AC particles exhibited reversible equilibrium sorption characteristics for the aqueous MeHgCl species. Our conceptual model for an effective equilibrium passive sampler for MeHg, as initially described in Sanders et al., 2020, is that a chemically labile pool of MeHg, MeHg_{CL}, is in equilibrium with a large sediment-bound pool of MeHg, such that the equilibrium concentration of MeHg accumulated within the passive sampler can be related to this pool regardless of MeHg speciation.

As outlined in Sanders et al., 2020, the composition of MeHg_{CL} varies significantly among environments and can encompass MeHg species occupying a wide range of sizes, diffusivities, and bioavailabilities (Clarisse et al., 2009). To make accurate estimations of MeHg_{CL}, an equilibrium passive sampler needs to be able to capture the changing equilibrium concentrations

of numerous aqueous MeHg species driven by changing environmental conditions. For MeHg in typical estuarine and fresh water sediment porewaters, the dominant species of MeHg are expected to be aqueous complexes with dissolved organic matter (DOM; typically dominated by thiolic sites within larger DOM molecules), organic thiols such as cysteine (generally to a lesser extent), and under some geochemical conditions, sulfide (Haitzer et al., 2002; Aiken et al., 2011; Liem-Nguyen et al., 2017; Ndu et al., 2015; Skjellberg, 2008). Aqueous MeHg complexes within porewaters are expected to be in dynamic equilibrium with the much larger sediment MeHg pool, and this equilibrium is impacted by the concentration and character of porewater DOM (Benoit et al., 2001; Leaner and Mason, 2002). Given the predominance of MeHgDOM species under most conditions, it is also necessary to consider the interaction of DOM molecules with AC particles. DOM interacts directly with AC particles via sorption and other physio-chemical processes that are controlled by the specific character of the DOM. The efficiency of DOM removal by AC from the aqueous phase displays a strong correlation between the pore sizes of the AC particles and the molecular size of DOM (Gibert et al., 2013; Zusman et al., 2020). The complex and dynamic nature of MeHg speciation in sediment environments, compounded by interactions of DOM with AC, necessitates a full understanding of the sorption behavior of MeHgDOM species to contextualize the ag+AC passive sampler estimates of MeHg concentration in real sediment deployments.

Sanders et al., 2020 identified several challenges in the development of an equilibrium passive sampler for MeHg within porewaters: 1) to convincingly demonstrate reversible MeHg equilibrium with a given sampler, 2) to explore the use of stable MeHg isotopes as performance reference compounds to measure and account for nonequilibrium, 3) to establish K_{ps} for environmentally relevant MeHg species, and 4) to evaluate the relevance of sampler data in real sediment systems. In the present work, we have conducted specific experiments designed to improve our ability to meet each of those key challenges for the ag+AC polymer material and standardized sampler fabrication to increase the reproducibility of MeHg estimations across most aquatic conditions. First, we conducted isotherm bottle experiments with ag+AC polymers to constrain partitioning of various environmentally relevant MeHgDOM species across a range of DOM sizes and sources, including small organic thiols using cysteine as a model ligand, as MeHgDOM is expected to be the dominant MeHg species across a wide range of aquatic environments. Reversible equilibrium was demonstrated for MeHgDOM species in a series of isotopically labeled exchange experiments, in which we also compared the kinetics of adsorption and desorption of MeHg species to evaluate the potential use of stable isotope-labeled MeHg as performance reference compounds. Finally, static sediment microcosms were used to demonstrate both the potential to make accurate estimations of MeHg_{CL} in sediment porewaters and the wide range of potential uses of these equilibrium passive samplers for monitoring transport and remediation effectiveness. The ultimate goal in the development of an equilibrium passive sampler is to enable reproducible measurements of MeHg_{CL} within aquatic environments, thereby improving risk assessment. The present work is focused on refining our understanding of the mechanisms of equilibrium partitioning of a range of MeHg species to the ag+AC polymer by addressing each of these challenges.

7.2 MATERIALS AND METHODS

An unabridged version of the Materials and Methods is included in the Supplemental Information (Appendix F SI 1.1–1.6)

Production of ag+AC Samplers

The ag+AC samplers were produced using a virgin powdered AC derived from bituminous coal (Calgon Type 3055; 80 x 325 TOG LF; C(%) = 80.9±1.4; surface area = 1116±25 m²/g; skeletal density = 1.61 g/cm³; bulk density = 0.64 g/cm³). AC particles were sieved to >53µm, then washed with DI and allowed to dry in a 30 °C oven prior to casting within gels to ensure uniformity. Following the preparation methods described in detail in Sanders et al., 2020, 0.300 g of prepared dry PAC was mixed with 0.300 g of agarose powder, then 20 mL of DI water was added, and the solution was stirred while heated in a hot water bath for 4.5 mins and allowed to cool for 1 hour. Across all experiments, ag+AC polymers were prepared identically to a uniform size and thickness (34.3 mm x 23.9 mm x 1 mm) and stored in clean DI water until use.

MeHgCys Sorption Isotherms

Partitioning of MeHg complexed with L-cysteine was evaluated for the ag+AC passive samplers. Isotherm solutions were spiked with a MeHgCl standard (Brooks Rand Laboratories) diluted to five concentrations ranging from 30 to 3000 ng/L. All experimental isotherms were conducted in 60-mL polyethylene terephthalate glycol (PETG) copolymer bottles. L-cysteine (Sigma-Aldrich, 98%) was added to each experimental bottle to maintain a 10⁵:1 molar ratio of L-cysteine to MeHg, and buffered with the addition of 1mM MOPS (3-morpholinopropane-1-sulfonic acid). Solutions were incubated overnight in the dark on a shaker table at 60 rpm at 4 °C prior to sampler addition to ensure a stable MeHg distribution. Samplers were added to experimental bottles in triplicate at each concentration level, and were allowed to equilibrate for 14 d in the dark on a shaker table at 60 rpm at 4 °C. After 14 d, ag+AC samplers were carefully removed with forceps, then stored frozen. A portion of the overlying water was acidified to 0.5% v/v with trace metal grade HCl to preserve MeHg, then stored refrigerated at 4 °C.

DOM Sorption Isotherm Experiments

Partitioning of MeHgDOM species to the ag+AC polymer material was evaluated for seven different organic matter sources with varying characteristics (summarized in Table S1; all obtained from the International Humic Substances Society) in an isotherm experiment. All MeHgDOM species were prepared by adding MeHgCl stock to a saline (3 ppt Instant Ocean, United Pet Group, Inc.) solution containing 7.5 mM NaHCO₃ (Avantor Macron Fine Chemicals) to buffer pH (8.2–8.7) at near-neutral conditions. MeHgCl-spiked DOM solutions were incubated in the dark on a shaker table at 60 rpm at 4 °C for a minimum of 24 h to ensure a stable MeHg distribution at high affinity sites within the DOM complexes. Saline experimental solution conditions were chosen to set a consistent ionic strength across experimental treatments with varying parameters.

Isotherms (referred to as “varying ratio DOM isotherms”) were conducted with DOC concentrations held constant at 5 mg/L across the range of initial MeHg concentrations (5 to 330 ng/L), resulting in DOM:MeHg mass ratios ranging from 10⁶:1 to 1.5×10⁴:1. This approach was used to avoid potential saturation of the passive sampler AC with DOM molecules. ag+AC sampler incubations mirrored those described above for the cysteine isotherm experiment.

Isotopically Labelled Experiments to Verify Equilibrium Exchange Behavior

Isotopically Labelled MeHgSRHA Experiments. A series of experiments were conducted to explicitly verify the equilibrium exchange of MeHg by the ag+AC samplers, using isotopically

labelled MeHg species to track exchange over 14-day time courses. To evaluate the exchange of an environmentally relevant MeHg species between an aqueous solution and the ag+AC polymer material, a sampler preloaded with Me¹⁹⁹HgSRHA was inserted into an aqueous solution containing Me¹⁹⁸HgSRHA. A solution containing 5 mg/L of Suwannee River Humic Acid (SRHA III, IHSS) was prepared, to which aliquots of either Me¹⁹⁸HgCl or Me¹⁹⁹HgCl were added to create solutions at a nominal concentration of 50 ng/L. SRHA was chosen as the DOM source for the exchange experiments due to the availability of published data to estimate the number of thiolic sites (Poulin et al., 2017). For the uptake phase, samplers were added to experimental bottles containing Me¹⁹⁹HgSRHA in duplicate, then allowed to equilibrate for 14 days in the dark on a shaker table at 60 rpm at 4 °C. To evaluate uptake of Me¹⁹⁹HgSRHA, after 14 days two bottles containing ag+AC samplers were separated as described in detail in Section 2.2.

After the 14-day equilibration period, ag+AC samplers were carefully removed and transferred to experimental bottles containing Me¹⁹⁸HgSRHA. Transfer of Me¹⁹⁹HgSRHA solution to bottles containing Me¹⁹⁸HgSRHA solutions was negligible. After transfer, experimental bottles were again placed onto a shaker table at 60 rpm at 4 °C in the dark. Experimental bottles were removed, separated, and preserved in duplicate over a time course to observe exchange of the isotopically labeled Me^{xxx}HgSRHA species. Bottles containing ag+AC samplers were removed after 1, 6, 24, 48, 168, and 336 h.

Isotopically Labelled MeHgCys Exchange Experiments. This experiment was designed to mimic the previous dual-isotope-label experiment, but using MeHgCys as the dominant species instead of MeHgSRHA. For both experimental phases (uptake and exchange), a solution was prepared to contain cysteine at a nominal concentration of 2.5×10^{-5} M along with 7.5 mM bicarbonate and 3 ppt Instant Ocean. The cysteine concentration was determined such that a 10^5 :1 molar ratio of cysteine to Me^{xxx}Hg would be maintained, mimicking the cysteine sorption isotherm experiments. However, concentrations of the two isotope spikes ended up being lower than anticipated in initial experimental solutions (Me¹⁹⁹HgCys = 8.75 ng/L, Me¹⁹⁸HgCys = 17 ng/L), resulting in actual molar ratios closer to 5×10^5 :1. Samplers were transferred between solution bottles following the procedure and removal timings described in Section 2.4.1.

Isotopically Labelled MeHgCys & MeHgSRHA Release Experiments Two additional exchange experiments were conducted to evaluate the exchange dynamics of MeHg species at equilibrium with the passive sampling polymer when exposed to an aqueous solution containing different environmentally relevant, high-MeHg-affinity ligands. Both uptake and exchange solutions were saline and buffered to near-neutral pH (3 ppt Instant Ocean and 7.5 mM sodium bicarbonate). One set of polymers was allowed to equilibrate with Me¹⁹⁹HgCys during the 14-day uptake phase and transferred to a solution containing SRHA for the exchange phase, and a separate set of polymers was equilibrated with Me¹⁹⁹HgSRHA during uptake and transferred to an exchange solution containing cysteine. The exchange solutions (cysteine at 2.5×10^{-5} M and SRHA at 10 mg/L DOC) for these two experimental treatments were prepared without a MeHg spike to prevent isotopic exchange between ligand-bearing species during the exchange phase that might obfuscate sampler:water MeHg partitioning. Samplers were removed following the procedure and timing outlined in Section 2.4.1.

Microcosm Experiments to Assess Passive Sampler Performance in Sediment and Water

As an initial demonstration of the potential field applications of this polymer, a sediment microcosm experiment was conducted to determine the ability of the ag+AC samplers to estimate in situ MeHg concentrations in sediment and overlying water. To mimic a moderately contaminated marsh soil (target 10 ppm total Hg), a mixture of soil from a contaminated, oligohaline *Phragmites australis* marsh in Berry's Creek, NJ, and a *Phragmites australis* marsh soil from the Smithsonian Environmental Research Center (SERC) Global Change Research wetland in Edgewater, MD was utilized. The mixture was thoroughly homogenized via paint mixer, after which 100 g of the wet soil mixture was placed into 500-mL glass jars. Artificial salt water (100 mL of 3 ppt Instant Ocean) was gently added on top of the soil layer. The microcosms were loosely capped and gently aerated at a constant rate throughout the experiment. Microcosms were allowed to equilibrate for 14 days prior to sampler insertion to allow development of redox gradients in the soil mixture.

Two configurations of passive samplers were tested: one in which separate samplers were deployed in water and sediment, and another in which a single sampler was deployed across the sediment/water interface. Full-size samplers deployed across the sediment-water interface were synthesized as described in Section 2.1. These full-size samplers (referred to throughout as “sheet-ps”) were inserted into the ~2.15 cm deep sediment layer across the sediment-water interface at a slight incline (Figure S1), such that half of the sampler mass was located in the sediment while the other half remained in the water column. To provide rigidity, the ag+AC samplers were heat-sealed in acid-cleaned polypropylene mesh (McMaster Carr, 0.21mm mesh) prior to insertion in the microcosms.

Half-sized samplers (17.2 mm by 23.9 mm, referred to throughout as “split-ps”) were deployed separately in sediment and water in a different set of microcosms to evaluate whether there was enhanced vertical diffusion of MeHg species within the agarose matrix of the full-size samplers. The sampler inserted in the sediment was tied to the sampler in the water with acid-cleaned nylon thread to anchor the sampler suspended in the water column. The sediment sampler was inserted at a slight incline into the sediment to fully submerge the portion within the sediment, while the water sampler was fully submerged within the overlying water. Microcosms without samplers (referred to as “no-ps”) served as controls to help evaluate any effects that the samplers may have on the sediment porewater chemistry or native MeHg concentration through time. The sheet-ps and split-ps pairs were deployed individually in separate microcosms, and the no-ps, sheet-ps, and split-ps microcosm configurations were constructed in triplicate.

At each experimental timepoint, passive samplers, overlying water, porewater, and sediment were collected from the microcosms for further analysis. The sheet-ps and split-ps microcosms were sampled 14 and 21 days after sampler insertion (t+14 and t+21, respectively). Sediment (*ps-sed*) and overlying water (*ps-water*) portions of split-ps samplers were separated by cutting the connecting nylon thread. Sheet-ps samplers were split at the visually determined soil-water interface with clean, DI-rinsed shears, then frozen until analysis. Overlying water was carefully pipetted from the microcosm. Subsequent handling of the sediment and porewater was performed in an anaerobic glove bag (Coy ©, Ann Arbor, MI) to maintain redox conditions after extraction. The remaining wet sediment was centrifuged to isolate the porewater.

Effects within the microcosm study were analyzed using standard least-squares models that considered time, sampler type, and sampler placement with an overall $\alpha = 0.05$. Parameters were transformed as needed to approximate normal distribution.

Analytical Methods

For all samples, MeHg was measured by isotope dilution mass spectrometry after separation by acid distillation, following the method detailed in Gilmour et al., 2013, using an Agilent 7900 ICP-MS and Brooks-Rand MERX MeHg analysis system. One adjustment was made to the distillation protocol described in Mitchell and Gilmour, 2008 and Hollwegg et al 2009, with 1% APDC (ammonium pyrrolidine dithiocarbamate, Acros Organics) replacing CuSO₄ as the main complexation agent in the distillation matrix as described in EPA Method 1630, (1998 ed.), as this was found to improve isotope dilution spike recovery for samples containing AC particles (EPA Method 1630, 1998 ed.). Me¹⁹⁹Hg isotope dilution standards were synthesized in-house (Bancon-Montigny et al., 2004) and checked for concentration and degradation by comparing SnCl₂-reducible Hg concentrations before and after BrCl digestion (De Wild et al., 2002). For all experiments described in this manuscript, MeHg mass balance was maintained throughout the duration of the experiments. MeHg quality assurance data are summarized in Table S7.2. Throughout the manuscript, log(K_{ps}) values for the ag+AC passive samplers are reported according to Equation (1):

$$(1) \quad \log(K_{ps}) = \log_{10}(C_{ps}/C_w)$$

Where C_{ps} is the MeHg concentration (ng MeHg/kg of wet polymer material) measured within the ag+AC polymer and C_w is the MeHg concentration (ng of MeHg/L) of the overlying water or porewater for a given experiment.

7.3 RESULTS AND DISCUSSION

Partitioning of MeHgCys as Determined from Sorption Isotherms

Accurate estimation of MeHg concentrations using equilibrium passive samplers requires the use of a K_{ps} appropriate to the setting (i.e., the complexation of MeHg in the site being tested). We hypothesized that the range of equilibrium K_{ps} values for MeHgNOM complexes to ag+AC passive samplers will be small enough that a single value can be used for most settings, making these passive samplers widely deployable with relative ease. To test that idea, we evaluated K_{ps} for a range of MeHgNOM complexes using the sorption isotherm approach. Cysteine represents the smallest class of organic thiols that may be generally dominant ligands for MeHg in sediment porewaters (Zhang et al., 2004; Drott et al., 2008).

We found that the sorption isotherm for MeHgCys to bare AC particles (processed Calgon PAC 3055) and ag+AC polymers (Figure 7.1 and Table S7.3) was linear over several orders of magnitude. Measurement of MeHg in both water and polymer demonstrated mass balance for the experiments, with the relative standard deviation of triplicate MeHg concentrations for all phases averaging 7.8%. For bare AC particles, a log(K_{ac}) = 5.08±0.33 was determined from a linear regression fit of the sorption isotherm data. This value is within the error of previous measurements of partitioning of both MeHgCl (linear isotherm log(K) = 4.89; Gomez-Eyles et al., 2013) and MeHgOH (log(K) = 5.00 to 5.22; Sanders et al., 2020) to this AC, suggesting that the mechanism of partitioning to this particular AC type is similar for a range of low molecular weight MeHg

species. Previous work has postulated that surface-active functional groups (hydroxyl, phenolic, carboxyl, etc.) within the activated carbon pores interact directly with charged heavy metal species via an ion-exchange mechanism, and this may be the mechanism controlling partitioning of low molecular weight MeHg species (Bussan et al., 2016).

For ag+AC polymers, $\log(K_{ps}) = 3.01 \pm 0.23$ was determined for MeHgCys from a linear regression fit of the sorption isotherm data. This value is slightly but significantly below the previously determined partitioning of MeHgOH for this polymer material ($\log(K_{ps}) = 3.46 \pm 0.07$) (Sanders et al., 2020). Using an estimate of the mass of AC particles embedded within the agarose material of each passive sampler, and assuming that all of the measured MeHgCys within the ag+AC polymer is associated with the AC particles (a reasonable assumption given the low affinity of agarose for MeHg), the MeHgCys concentration on the AC particles within the polymer material can be calculated. A linear regression of this calculated MeHgCys concentration on the AC embedded within agarose gives a $\log(K_{ps})$ value of 4.84, which is within the uncertainty of the measured $\log(K_{ac})$ for the bare AC particles (5.08 ± 0.33). The agreement of these partitioning coefficients suggests that the decreased partitioning for MeHgCys relative to MeHgOH is not driven by issues of permeability of the larger MeHgCys molecules through the agarose matrix. The agreement of K_{ac} values for MeHgCys, MeHgOH, and MeHgCl species to bare AC particles suggests that the difference in ag+AC polymer partitioning coefficients between MeHgCys and previously measured species could be caused by a combination of improvements in the reproducibility of the polymer and some differences in the sorption behavior related to the characteristics of the cysteine ligand (molecular size, thiol moiety, etc.) and AC active site interactions.

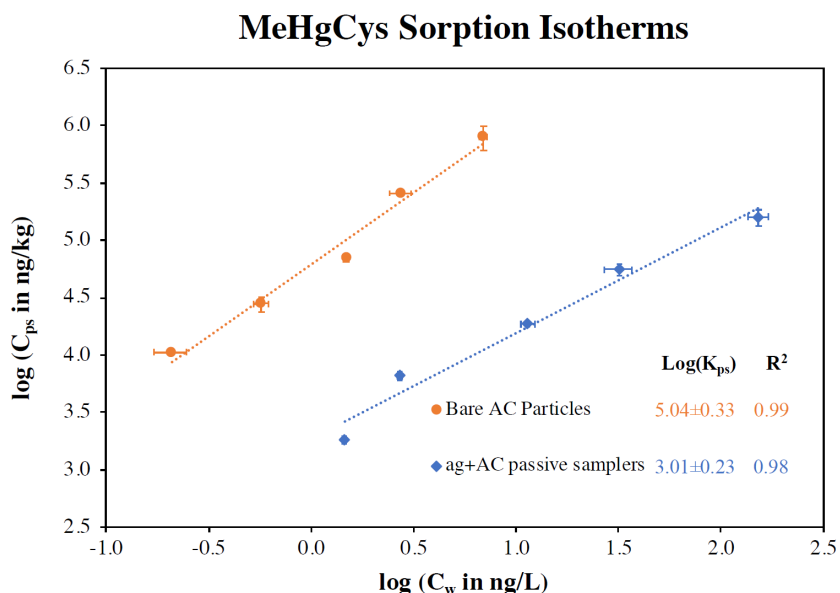


Figure 7.1. Partitioning of MeHg(Cys) to Bare AC Particles and Agarose with Embedded AC Particle Polymers in 14 Day Aqueous Isotherm Tests.

Error bars represent the ± 1 standard deviation of triplicate measurements. Partitioning of MeHg(Cys) ($\log(k_{ps}) = \log_{10} C_{ps}/C_w$) is calculated from a linear regression fitting of C_{ps} (ng MeHg/kg of wet sampler material) and C_w (ng MeHg/L of overlying water) data as were listed coefficients of determination (R^2).

Partitioning of Various Higher Molecular Weight MeHgDOM Species as Determined from Sorption Isotherms

We also estimated partitioning coefficients for a range of higher molecular weight MeHgDOM complexes using an isotherm approach. In many, perhaps most, environmental settings, aqueous-phase MeHg speciation is dominated by DOM complexes, and the characteristics of these complexes and their ability to bind MeHg range widely, depending on size, thiol content, and other attributes (Skylberg 2008; Khwaja et al., 2010; Jonsson et al., 2014; Schartup et al., 2015; Herrero Ortega et al., 2018; Jiang et al., 2018). The seven organic matter isolates tested were chosen to span a range of properties, such as aromaticity and S content, that may influence either DOM sorption to the AC particles in our samplers directly, or MeHg sorption to DOM (Table S1). The DOM isolates included unfractionated NOM from two sources (notated throughout as NOM to distinguish the unfractionated nature of these isolates), as well as fulvic and humic acids isolates, in order to test partitioning across a range of DOM chemical characteristics. Sorption of DOM to AC is impacted by the characteristics of both the organic material and AC, with adsorbability of DOM onto AC increasing with both decreasing DOM molecular size and increasing DOM aromaticity. Pore size distribution and surface charge characteristics of the AC also control the rate and efficacy of organic matter adsorption (Karanfil et al., 1999; Schreiber et al., 2005; Shimabuku et al., 2017; Shimizu et al., 2018). The adsorption of DOM by AC is controlled by multiple competing physico-chemical properties, with experiments demonstrating that increasing size of aromatic DOM compounds reduces adsorption to granular activated carbon (Zusman et al., 2020). In field deployments, AC amendments to sediments significantly decreased the aromaticity of DOM in residual porewater, suggesting that to a first order the AC particles within our passive samplers are likely to preferentially adsorb more aromatic molecules (Liu et al., 2018; Schwartz et al., 2019).

For the seven DOM isolates tested, we found a relatively small range of K_{ps} , from $\log(K_{ps}) = 1.98 \pm 0.03$ (SRHA) to $\log(K_{ps}) = 3.15 \pm 0.52$ (UMRNOM). The $\log(K_{ps})$ values for the two unfractionated NOM isolates (SRNOM and UMRNOM) differed by less than 0.5 log units. Isotherm behavior was linear for all of the DOM isolates (Figure 7.2) across the MeHg concentration ranges tested. A DOC concentration of 5 mg/L was chosen to avoid saturating the AC particles within the passive sampler matrix, and to represent a realistic value for environmental deployments. The linearity of isotherms across the MeHg concentration gradient (Table S7.4) and the similar K_{ps} values for DOM isolates and their MeHgDOM analogs show that AC particles within the sampler matrix were likely not saturated.

One goal of this study was to evaluate the range of K_{ps} values across various measures of DOM character. We found that both total S content ($p=0.056$) and the S/C ratio ($p=0.057$) of the organic matter stock were positively correlated with MeHgDOM $\log(K_{ps})$ under these experimental conditions. However, there was no significant relationship with DOM isolate aromaticity and $\log(K_{ps})$. The observed positive correlation between $\log(K_{ps})$ and DOM S content is consistent with prior observations of increased partitioning of MeHg to DOM with higher thiol content (Graham et al., 2013; Poulin et al., 2017). The greater predominance of MeHgDOM-RS under equilibrium conditions then results in a greater proportion of MeHg from the aqueous phase being indirectly associated with the AC particles as DOM complexes interact with the samplers. If the passive samplers were operating under a regime in which the AC particles were directly interacting with the MeHg moiety (rather than DOM), the expectation would be that a lower DOM sulfur content would result in a higher K_{ps} , because of reduced competition for MeHg by DOM (Liu et

al., 2016). The opposite pattern was observed, suggesting that the MeHgDOM association with the AC particles is not through direct AC-MeHg binding, but rather mainly through sorption of DOM with AC.

Organic matter facilitated sorption of MeHg to AC particles could occur either as ligand-ligand exchange of MeHg^+ ions between aqueous MeHgDOM and organic matter molecules sorbed to AC particles, or direct sorption of MeHgDOM to AC particles through AC-organic matter binding.

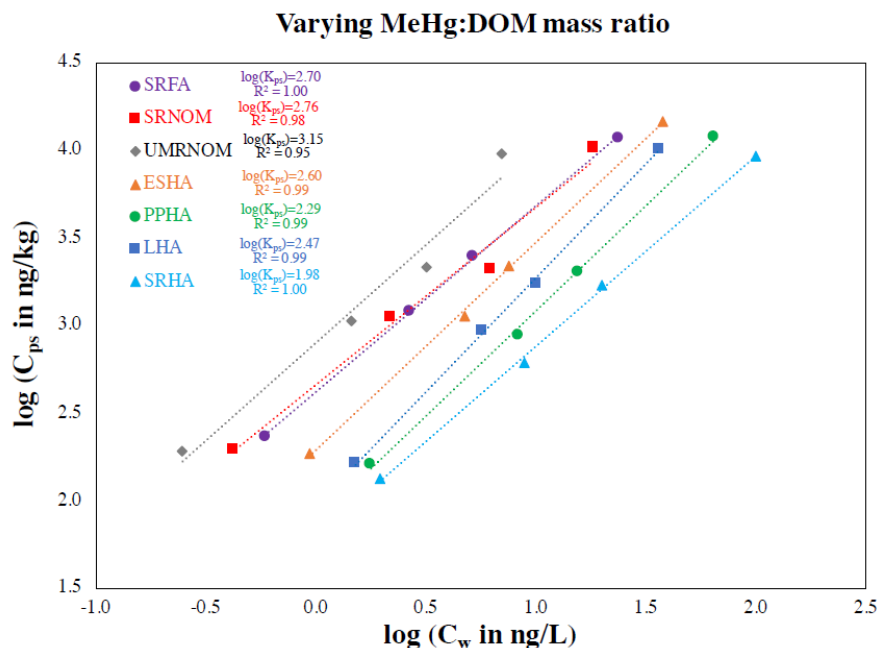


Figure 7.2. Partitioning of Various MeHgDOM Species in 14-day Aqueous Isotherm Tests.

For each DOM source, $\log(K_{ps})$ values were determined from linear regression fitting, as were listed coefficients of determination (R^2). Isotherm data acquired from experiments conducted at a variable MeHg:DOM mass ratio, but constant initial DOC concentration..

Another line of evidence supporting the proposed mechanism of AC particle-MeHg interactions being controlled by AC particle-organic matter interactions (whether direct MeHgDOM sorption or ligand-ligand exchange mechanisms) is the positive correlation between estimated DOM partitioning and $\log(K_{ps})$ values for MeHg from the varying-MeHg:DOM-ratio isotherms (Section SI 2.1). Previous work with the same AC source also suggested that MeHg sorption to AC particles was mechanistically controlled by DOM-AC interactions based on the similarity of partitioning coefficients for SRHA, MeHgSRHA and HgSRHA species in isotherm tests (Schwartz et al., 2019). The observation of relatively similar $\log(K_{ps})$ values [~ 3.5] for a number of small MeHg species (MeHgOH, MeHgCl), as compared to the relatively large MeHgDOM species with a wider range of $\log(K_{ps})$ values [1.98 to 3.15], suggest that there may be multiple interaction regimes for MeHg to the AC particles within our passive sampler. Smaller MeHg species may be operating under a regime of direct interaction between the MeHg moiety and the AC particle itself, as opposed to the DOM-AC interaction proposed for MeHgDOM. Whether this direct interaction is the result of a chemical bond or a physical process such as size exclusion of organic matter to

active sites within the AC particles due to the pore structure of the AC will need to be determined in further work.

For the ag+AC passive samplers to be useful to a wide range of potential end users aiming to make accurate estimations of porewater MeHg, it would be ideal to have a partitioning coefficient that is adequately representative of many types of DOM. Across a range of S content from ~0.4 to ~2.5% and aromaticities that ranged from ~20 to ~60%, our isotherm experiments yielded partitioning coefficients that spanned just over one log unit ($\log(K_{ps})$ of 1.98 to 3.15). The partitioning coefficient determined for MeHgCys ($\log(K_{ps}) = 3.01$) also falls within this range. This limited range in partitioning coefficients for a wide range of DOM supports the hypothesis that a single representative partitioning coefficient may be adequate for these samplers to predict aqueous MeHg concentrations in settings where MeHgNOM and small MeHg-thiols are the dominant aqueous complexes. We note that many of the fractionated DOM isolates used for these isotherm experiments have terrestrial origins, and that other sources, particularly algal and marine DOM sources should be evaluated. Therefore, for passive sampler deployments in which MeHgDOM is expected to be the dominant MeHg complex, we propose the use of $\log(K_{ps}) = 2.96$, which is the average $\log(K_{ps})$ value for the unfractionated, river-derived NOM stocks ($\log(K_{ps}) = 3.15$ for UMRNOM and $\log(K_{ps}) = 2.76$ for SRNOM).

Evaluation of Equilibrium Exchange for MeHgDOM Complexes with ag+AC Passive Sampling Material

One of the challenges in the development of an equilibrium passive sampler for MeHg is to make a convincing demonstration of reversible MeHg equilibrium, a phenomenon in which the kinetics of adsorption and desorption from the passive sampler are identical. A previous study demonstrated reversible equilibrium between MeHgOH and bare AC (Sanders et al, 2020). Here we expanded that study to test equilibrium exchange with both bare AC and the ag+AC passive sampler matrix, using environmentally relevant MeHg complexes, MeHgCys and MeHgSRHA. We observed reasonably rapid, reversible, equilibrium exchange of MeHgDOM complexes with both bare AC and with the ag+AC polymer (Figures 7.3, S7.2 and Table S7.5).

Initial exchange experiments were done with MeHgSRHA in both the uptake and exchange phases by loading the samplers with Me¹⁹⁹HgSRHA and then placing them in an exchange solution of Me¹⁹⁸HgSRHA. We observed simultaneous exchange of the MeHgSRHA complexes (Figure 7.3), with uptake of Me¹⁹⁸HgSRHA from the aqueous phase to the sorbent material and release of Me¹⁹⁹HgSRHA from the sorbent phase to the aqueous phase, with converging $\log(K_{ps})$ values of the two isotopically labeled MeHg species for both ag+AC polymers (Figure 7.3) and bare AC particles (Figure S7.2). Mass balance was maintained for both MeHg species throughout the duration of the time course such that MeHg degradation would not impact apparent removal of one species from a given phase. Overall MeHg partitioning (total MeHg partitioning, with both stable isotope species considered) was stable throughout the time course of the experiments and for both sorbent materials, indicating that exchange of MeHgSRHA from the AC particles was occurring under a reversible equilibrium regime and that the passive samplers were responding to the dominant ligand in the exchange solution. The overall partitioning of MeHgSRHA to the ag+AC passive samplers at the end of the timecourse (average $\log(K_{ps}) = 1.27$) was within the range observed for MeHgSRHA in the isotherm tests done at a constant MeHg:DOM ratio ($\log(K_{ps}) = 1.58 \pm 0.71$). The $\log(K_{ps})$ for each isotopically labeled MeHgSRHA species did not

reach the stable overall $\log(K_{ps})$ value by the end of the respective time course for either sorbent type. The timeseries data for each isotopically labeled MeHgSRHA species were fit to a model following first order kinetics with equilibrium exchange under finite volume batch conditions simulating the experimental conditions (details on model methodology contained in Appendix F SI S1.4.4, Figure S7.6). The first order kinetic coefficients for adsorption of Me^{198}Hg , k_{adsorb} , and desorption of Me^{199}Hg , k_{desorb} , were calculated, as was the time necessary for the system to reach 90% equilibrium under the given experimental conditions (summarized in Table S7.7). For the MeHgSRHA exchange experiment, the fitted k_{adsorb} value is within a factor of two compared to the fitted k_{desorb} , indicating that the desorption rate approximately matches the adsorption rate. The estimated time to 90% equilibrium (t_{90}) was 35 days for $\text{Me}^{199}\text{HgSRHA}$ and 28 days for $\text{Me}^{198}\text{HgSRHA}$, which are both longer than the duration of the experiment. This suggests that the kinetics of exchange for MeHgDOM may be slower than the 14 days that had been previously postulated in Sanders et al., 2020 and true thermodynamic equilibrium was not reached.

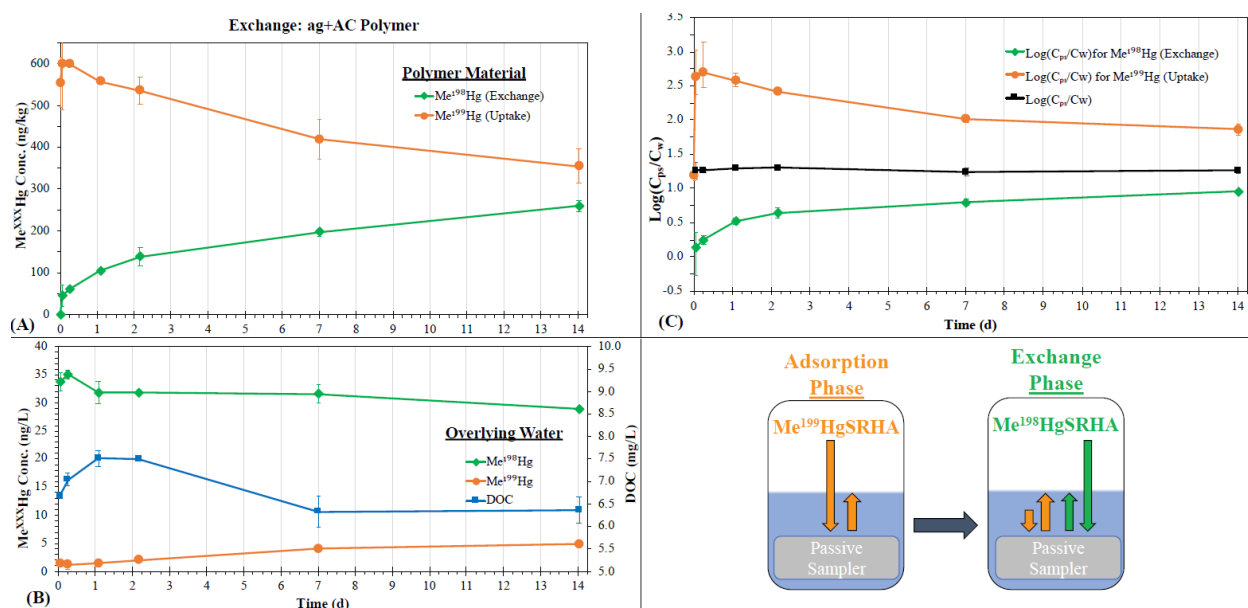


Figure 7.3. Exchange of Isotopically Labelled MeHgSRHA from An ag+AC Polymer Over a 14-day Time Course.

Polymers that had been equilibrated with $\text{Me}^{199}\text{HgSRHA}$ (orange circles) in the uptake phase for 14 days were transferred to experimental bottles containing $\text{Me}^{198}\text{HgSRHA}$ (green diamonds) in the exchange phase, where simultaneous exchange of these species was observed in both the polymer materials (panel A), and overlying water (panel B). DOC concentrations of overlying water are shown in blue squares (B). At a given timepoint, error bars represent ± 1 standard deviation of duplicates. Where error bars are not visible, error associated with that timepoint is smaller than the symbol size. Apparent partitioning coefficients (C_{ps}/C_w) for each isotopically labeled species and for total MeHg (black squares) are shown in panel C.

To more thoroughly understand the behavior of the ag+AC passive samplers with regard to MeHg species that may be found in natural porewaters of varying sizes and differing proposed AC particle interaction methods, three additional exchange experiments were conducted. First, we conducted an exchange experiment with isotopically labelled MeHgCys, set up to mirror the MeHgSRHA exchange experiment. We anticipated differing exchange behavior based on the idea that MeHgCys

interaction with AC is a direct reaction between MeHgCys and AC (either binding or surface sorption), while MeHgSRHA interaction with AC occurs via OM sorption (see section 3.2 for further discussion). Indeed, we found that equilibrium was reached faster for MeHgCys than for MeHgSRHA, with the modelled t_{90} for the MeHgCys species much shorter at 2.5 days for Me¹⁹⁹HgCys and 1.6 days Me¹⁹⁸HgCys (Figure S7.3, Table S7.7). The model fitted k_{adsorb} value was again within a factor of two compared to the fitted k_{desorb} for the MeHgCys exchange. We observed similar partitioning coefficients for both Me¹⁹⁹HgCys (average $\log(K_{\text{ps}}) = 3.78 \pm 0.15$), Me¹⁹⁸HgCys (average $\log(K_{\text{ps}}) = 3.47 \pm 0.14$), as well as MeHgCys overall (average $\log(K_{\text{ps}}) = 3.54 \pm 0.14$), at the end of the 14-day exchange experiment (Table S7.6). Equilibrium partition coefficients for both the adsorption and exchange MeHg complexes were similar despite differences in starting concentrations (Me¹⁹⁹HgCys = 8.75 ng/L, Me¹⁹⁸HgCys = 17 ng/L). The more rapid equilibrium and higher K_{ps} of MeHgCys relative to MeHgSRHA support the idea that AC complexation mechanisms are different for each compound. However, differences in experimental conditions between the MeHgCys and MeHgSRHA exchange experiments may also have contributed to differences in exchange behavior, particularly the lower overall MeHg concentrations in the MeHgCys experiment (8.5 to 17 ng/L MeHgCys compared to 42 to 54 ng/L MeHgSRHA) and differences in DOC concentrations (~0.9 mg/L in the MeHgCys experiments compared to 5 mg/L in the MeHgSRHA experiments).

Two additional exchange experiments were conducted to evaluate whether the ag+AC samplers would continue to function in a reversible equilibrium fashion under changing MeHg speciation conditions. In both studies, the exchange solution contained a different dominant ligand for MeHg than the uptake solution, to mimic changing geochemical conditions experienced in environmental deployments. Two equilibration processes were anticipated to be occurring simultaneously during the exchange phase: ligand exchange equilibration of the released MeHg species from the polymer material with the competing ligand in the aqueous solution and equilibration of the AC particles with the new solute load (mixture of MeHgCys and MeHgSRHA) in the aqueous solution. The results of these experiments are summarized in SI S2.2. In both exchange experiments with differing ligand solutions, partitioning of MeHg to the ag+AC passive samplers at the end of the exchange phases reflected the dominant ligand in the exchange solution. Cumulatively, the multiple exchange experiments convincingly demonstrated that ag+AC passive samplers respond reversibly to the thermodynamic equilibrium conditions for MeHg of the solutions in which they are deployed.

Testing ag+AC Passive Samplers in Microcosms to Assess Estimations in Sediment and Water

We conducted a sediment-water microcosm experiment to test the ability of the ag+AC polymer to estimate in situ MeHg concentrations in sediment porewaters and overlying surface waters. Accurately capturing the MeHg concentration gradient across the sediment-water interface, and/or a depth profile of porewater concentrations, would have numerous applications for monitoring the efficacy of Hg remediation techniques, including AC amendment and sediment capping techniques (Ting et al., 2018; Lewis et al., 2016; Zhang et al., 2016; Wang et al., 2020). Equilibrium passive samplers have successfully determined concentration gradients across vertical depth profiles during in situ deployments for a number of hydrophobic organic contaminants, as the adjustable nature of their physical design lends itself to overcoming the technical hurdles of traditional depth profile sampling methods (Sanders et al. 2018; Lydy et al., 2014 and references therein). Hg methylation tends to occur within the sediment column at a depth that has the chemical and redox

conditions necessary to facilitate microbial activity, hence a desirable characteristic of any equilibrium passive sampler for MeHg would be to capture the vertical concentration profile in sediment porewaters (Hsu-Kim et al. 2013).

Passive samplers were deployed across the sediment-water interface of laboratory microcosms designed to mimic a field deployment. The microcosms were constructed using a mix of marsh soil sources made to represent moderate Hg contamination, 13 ug/g total Hg, with an initial 144 ng/gdw MeHg. The mix was circumneutral in pH and highly organic (32% LOI). Microcosms were set up with 3 ppt salinity artificial seawater.

The microcosm study ran for a total of 35 days, beginning with a 14-d equilibration period (t-14 to t₀). During the equilibration period, organic matter provided sufficient oxygen demand to establish reducing conditions in the soils rapidly (Figure S7.7, Table S7.8). Microcosm sediments became slightly sulfidic, indicating some microbial sulfate reduction (Figure S7.7E). However, there was no significant sulfate depletion through time, nor depletion in porewaters relative to surface waters (Figure S7.7D), suggesting limited microbial sulfate reducing activity. We observed slightly lower pH in porewaters than in overlying water (Figure S7.7A), and a significant decline in porewater DOC through time (Figure S7.7B), which are also indicative of microbial activity in sediments. Active sulfate reduction accompanied by low levels of bisulfide accumulation are ideal conditions for MeHg accumulation in sediments and soils (Skylberg, 2008). Once established, the microcosms maintained fairly stable conditions, with no significant change in surface water pH, chloride or sulfate over time after t₀. The air-bubbled surface waters did not accumulate any sulfide. Passive samplers were placed in the microcosms at t₀.

Microcosm sediment MeHg concentrations were generally stable throughout the next 21 days at 125 ± 38 ng/g (Figure S7.7F). Filter-passing MeHg in both sediment porewaters and overlying waters declined slowly after the initial equilibration period (Figure S7.7F). Aqueous MeHg concentrations were generally about 25 times higher in porewater than in overlying water. Note that sediment data are taken from a composite of the 2.2 ± 0.2 cm of depth in the beakers, and represent averages across a redox gradient.

The presence of the samplers had small but sometimes significant effects on microcosm geochemistry. By days 14 and 21 of the study, water column MeHg concentrations were slightly (~25%) but significantly lower in the beakers that contained passive samplers than those without (Figure S7.7F). However, there were no significant differences in porewater MeHg when passive samplers were present. Surface and porewater DOC levels were significantly lower (~20%) in microcosms with samplers than without (Figure S7.7B), suggesting that the passive samplers removed a measurable amount of organic matter from the limited pool within the closed microcosm systems. The presence of samplers also had small effects on porewater sulfate and chloride (Figure S7.7), but not sulfide or pH.

MeHg uptake by the samplers placed in water and sediment reflected the different aqueous MeHg concentrations in each reservoir (Figure S8). Passive samplers in each matrix (sediment vs. water) took up significantly different amounts of MeHg, but there were no significant differences in MeHg uptake between the sheet and split sampler types deployed within each matrix. We found that the observed log(K_{ps}) was slightly (about 1.2x) but significantly higher for sediment samplers than those deployed in the water column (Figure 7.4), potentially reflecting differences in MeHg

complexation in the two matrices. Average sampler MeHg concentrations increased significantly (and about 50%) between 14 and 21 days of exposure.

One study goal was to test the ability of passive samplers deployed across the sediment-water interface to capture a gradient of MeHg concentrations, without significant vertical diffusion within the sampler material. To do so, we compared samplers deployed separately in the water column and in the sediments (split-ps) to the respective portions of the full samplers (sheet-ps), which were separated after deployment. We found no significant differences in MeHg accumulation between the two sampler designs inserted into the same physical reservoir (water vs. sediment) at the same timepoint (Figure S7.8, Table S7.8). This indicates that there was negligible vertical diffusion within the full sheet-ps samplers in comparison with the horizontal mass transfer of MeHg between each sampler portion and the surrounding aqueous phase. This supports the further development of these samplers for use for in situ deployments where it is desirable to capture the sediment-water MeHg gradient, and/or a vertical depth profile of MeHg in sediment porewater. Our observed lack of diffusional impact within the sampler matrix in static microcosms will need to be verified under non-stationary porewater flow conditions in the field.

Our main goal has been to develop an equilibrium passive sampler that can accurately estimate aqueous MeHg concentrations under a range of biogeochemical conditions. Equilibrium samplers are designed to estimate MeHg concentrations in water based on the MeHg accumulated in the sampler at equilibrium, and an assigned partition coefficient (K_{ps}) for the geochemical conditions within that environment. In developing these samplers, we targeted materials with partition coefficients that would be similar to sediment:water partition coefficients (K_d) to prevent significant perturbation of the sediment-porewater equilibrium. Our ag+AC samplers met this goal in the sediments tested here, yielding K_{ps} values within about a half an order of magnitude of the sediment:water K_d (Figure S7.9).

To choose a K_{ps} for estimation of aqueous MeHg concentrations from the samplers, we evaluated MeHg complexation in microcosm surface and porewaters using chemical equilibrium models. Speciation modeling was performed using ChemEQL with input parameters determined from average ancillary geochemical measurements in each phase, which were largely invariant during the 21 day passive sampler exposures. Our models included aqueous chloride, bisulfide and thiol complexes with MeHg. MeHg complexes with low molecular weight thiols (LMM-RS) were modeled separately from MeHg complexes with reduced exocyclic sulfur binding sites on DOM (DOM-RS). For this exercise, we used the formation constants for aqueous MeHg complexes with bisulfide given in Liem-Nguyen 2017 (see Table S7.9 for the full list of equations and equilibrium constants), except that we used the revised formation constant of MeHg_2S from Kanzler et al. 2018.

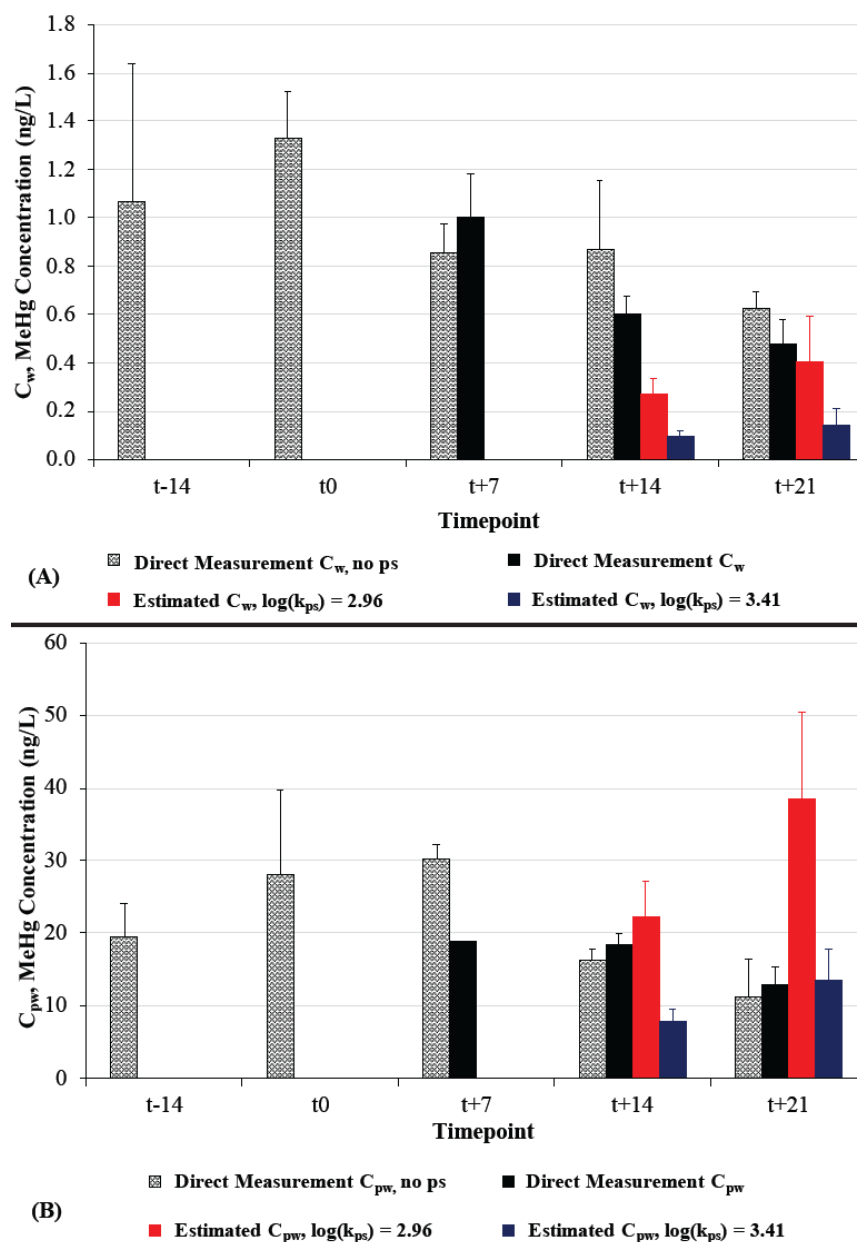


Figure 7.4. Direct versus Sampler-estimated Overlying Water (A) and Porewater (B) MeHg Concentrations Using $\log(K_{ps}) = 2.96$ and $\log(K_{ps}) = 3.41$ in Sediment Microcosms.

Direct measurements of C_w and C_{pw} are separated by microcosms without passive samplers (“no ps”, black hashed bars) and those with passive samplers (solid black bars). Estimated C_w or C_{pw} was calculated separately for each microcosm and then averaged across all microcosms; error bars represent the standard deviation of estimated C_w or C_{pw} across microcosms ($n = 6$ at each timepoint except for direct measurements without passive samplers, where $n = 3$).

Although not directly measured in this study, previous research has indicated the importance of low-molecular-weight thiols, such as L-cysteine, as ligands for MeHg in highly organic environments (e.g., Skjellberg et al., 2003). We used L-cysteine as a model low-molecular-weight thiol (LMM-SR) in our MeHg speciation modeling. Concentrations of LMM between 30 and 130 nM were previously

observed in natural porewaters (Zhang et al. 2004; Liem-Nguyen et al. 2014) so we used this range in modeling microcosm porewaters. For surface waters, we modeled MeHg complexation across an LMM thiol range of 0.3 to 30 nM. The concentration of available thiol binding sites on DOM (DOM-RS) was modeled based on reduced exocyclic sulfur binding sites on the hydrophobic organic acid (HPOA) fraction of the dissolved organic matter. DOM-RS⁻¹ site densities were estimated from porewater DOC measurements based on the equation presented in Poulin et al., 2017, which assumes that the site characteristics of the organic matter in these sediment microcosms were similar to that of Suwannee River Humic Acid:

$$[\text{DOM-RS}^{-1}] = \frac{\text{mg DOC}}{\text{L}} \cdot \frac{\text{mol C}}{12000 \text{ mg}} \cdot 0.495 \text{ HPOA fraction} \cdot \frac{9.30 \times 10^{-3} \text{ mol S}}{\text{mol C}} \cdot \frac{0.45 \text{ mol exocyclic S}}{\text{mol S}}$$

Thermodynamic equilibrium modeling showed that MeHg in microcosm surface waters was predominantly complexed with DOM-RS for all treatments and sampling times (Figure S7.10). There is significant uncertainty in the stability constant for MeHg complexes with various thiols and sulfide, as well as the fractional abundance of -RSH groups within organic matter (Liem-Nguyen et al. 2016, Graham et al. 2017). For this exercise, we modeled MeHg complexation in microcosm surface waters separately using constants that favor either DOM-RS or LMM-RS. In either case, MeHgDOM-RS predominated.

Sediment porewaters contained low concentrations of aqueous sulfide (averaging 2 µM), creating the possibility of MeHg-sulfide formation. Indeed, models showed significant aqueous MeHg-sulfide formation, but the importance of these species varied depending on choice of equilibrium constants. MeHg(DOM-RS) dominated when the highest estimated values for MeHg thiols (MeHgLMM-RS and MeHg DOM-RS) were used; but MeHg-sulfide complexes dominated using the lowest estimated stability constants for MeHg thiols (Figure S7.10a, S7.10b). In our models, the two main MeHg-sulfides (MeHg₂S and MeHgSH) were found in equal proportions.

To estimate the aqueous MeHg concentrations in the microcosms from sampler MeHg, we compared two K_{ps} values for MeHgNOM complexes. One value (log K_{ps} = 2.96) was the isotherm-derived average determined for the two NOMs tested in this study. The other was an empirically-derived value (log(K_{ps}) = 3.41) for ag+AC passive samplers deployed in similar source material (Sanders et al. 2020).

Using our experimentally derived log(K_{ps}) value of 2.96, the samplers were able to estimate directly measured surface water (C_w) and porewater (C_{pw}) MeHg concentrations within a factor of four, and in most cases a factor of two (Figure 7.4). This level of accuracy should be sufficient for most environmental deployments in which the goal is to determine the porewater MeHg risk to biota. The isotherm-derived (log(K_{ps}) = 2.96) provided the best estimate of microcosm surface water MeHg concentrations (C_w) at both timepoints. For porewaters, the partitioning coefficient which provided the most accurate estimation of C_{pw} changed from t+14 to t+21. At t+14, the lower, isotherm-derived K_{ps} value for MeHgNOM provided the best estimate, while the higher empirical value from Sanders et al. (2020) provided better estimate at t+21.

The change in sampler partitioning through time could be due to sampler non-equilibrium, although our experimental exchange data suggest that samplers approach equilibrium after approximately one month (Sanders et al. 2020 and this study). The development of an appropriate performance reference compound is another approach to evaluating passive sampler kinetics

(Sanders et al., 2018) that we are pursuing. Earlier observations of comparable adsorption and desorption kinetics show promise for the development of a stable isotope-labeled performance reference compound.

However, we believe the change in K_{ps} over time more likely reflects a change in MeHg complexation. Sediment:water partitioning increased between the two sampling dates (Figure S7.9). Porewater DOM decreased somewhat over time (Figure S7.7B), potentially favoring the formation of MeHg sulfides (Figure S7.10). A change in the DOM character over time could also account for varying MeHg complexation within the porewaters. The K_{ps} for MeHg sulfides is potentially different than MeHgNOM and small MeHg-thiol complexes and has not been measured explicitly in isotherm studies. However, the experimentally-determined K_{ps} values for MeHgNOM and small thiols (log K_{ps} around 3) have provided reasonably good C_{pw} predictions in slightly sulfidic sediments where MeHg sulfides could be important species. In both this study and in Sanders et al. 2020, predictions were within about half an order of magnitude of measured values, suggesting that K_{ps} value for MeHg sulfides into our samplers is similar to those for MeHgNOM and MeHgRS. This narrow range of partitioning values for a wide range of relevant MeHg species should enable estimations of C_{pw} across almost all sediment conditions with a single K_{ps} .

7.4 CONCLUSIONS

The ag+AC material has been demonstrated experimentally to be capable of reversible equilibrium with a wide range of environmentally relevant MeHg species. With a series of sorption isotherms, we determined the specific partitioning coefficients for a variety of DOM species that complex with MeHg. A static sediment microcosm experiment demonstrated that the ag+AC samplers successfully captured a gradient of MeHg concentration when placed across a sediment-water interface, and that these samplers have the ability to make accurate estimations of aqueous MeHg concentrations in environmentally realistic conditions. This work successfully establishes that the ag+AC material is capable of functioning as an equilibrium passive sampler for MeHg. The demonstration of reversible equilibrium for a wide range of MeHg species also has important implications for the use of AC-bearing materials in Hg remediation efforts. Further work is necessary to develop performance reference compounds to account for potential nonequilibrium conditions and to quantify the relationship between sampler estimates of MeHg_{CL} and biotic uptake of MeHg across a range of sediment environments.

Supporting Information

The Supporting Information includes an unabridged methods section, additional discussion sections, 10 figures, and 9 tables.

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8.0 CHAPTER 8: MEASUREMENT OF MEHG DEPTH PROFILE IN SEDIMENTS

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(Manuscript in preparation)

ABSTRACT

Methylmercury (MeHg) in sediments is produced by microbial activity that reaches a peak within specific redox transition zones in sediments. As a result, the concentration of MeHg in sediment porewater can vary with depth and needs to be measured to accurately assess flux from sediments and bioaccumulation in benthic organisms. Accurately measuring the MeHg concentration gradient across the sediment-water interface, and/or a depth profile of porewater concentrations, would have numerous applications for monitoring the efficacy of remediation such as sediment capping with or without amendments. Direct measurement of MeHg depth profile by porewater extraction is challenging. In this chapter we evaluated the feasibility of MeHg porewater depth profile in sediments at a 0.5 cm resolution using the MeHg passive sampler developed in the earlier chapters. We conducted a sediment-water microcosm experiment to test the ability of the ag+AC polymer to estimate in situ MeHg concentrations in sediment porewaters and overlying surface waters. Passive samplers were deployed across the sediment-water interface of laboratory microcosms designed to mimic a field deployment. Elongated samplers deployed within estuarine and freshwater sediment microcosms spanned a vertical depth sufficient to capture the MeHg maxima associated with the MeHg production zone. Passive sampler-derived MeHg profiles (0.5 cm resolution) were compared to profiles obtained by porewater grab sampling at a 1 cm resolution. The varying porewater MeHg concentration ($[MeHg]_{pw}$) with depth was statistically attributed to increasing sulfide concentrations, and the location of the sulfide maxima in the porewater approximately corresponded to significant sulfate depletion in both microcosms. These depth-dependent observations indicate that the $[MeHg]_{pw}$ peak is attributed to the microbial activity of sulfate reducing bacteria which are responsible for Hg methylation. The passive sampler provides an excellent reflection of the porewater profile, at the finer 0.5-cm resolution. The location of the $[MeHg]_{pw}$ maxima in the PS closely mimicked those in the centrifuged core samples, and PS-derived $[MeHg]_{aq}$ were mostly within a factor of 2 to 4 to grab samples, using the K_{ps} chosen from the DOM isotherms. These deployments showcase the sampler's success in measuring MeHg across the sediment-water interface at a fine resolution. The 0.5-cm resolution passive sampler measurements across the sediment-water interface present the progression of increasing $[MeHg]_{aq}$ across the interface at a level unattainable by the 1-cm grab sample aqueous measurements. These low-level measurements may be especially useful to determine the level of exposure to benthic organisms that reside at the sediment surface. The time-integration aspect of the MeHg passive sampler allows averaging of exposure concentrations over a period of change and can provide information on cumulative exposure or flux information where $[MeHg]_{pw}$ changes due to diurnal variations, collection/homogenization, or treatment application.

8.1 INTRODUCTION

Mercury (Hg) in sediments is methylated to methylmercury (MeHg) in by anaerobic microbes – typically sulfate and iron reducing microorganisms (to a lesser extent) – at a depth beneath the sediment where redox chemistry is conducive to their microbial activity ([Bigham et al. 2017](#); [Podar et al. 2015](#); [Figure 1](#)). Consequently, MeHg concentrations in sediments ($[\text{MeHg}]_{\text{sed}}$) and porewaters ($[\text{MeHg}]_{\text{pw}}$) vary spatially within the sediment ([Gilmour et al. 2018](#)). Because Hg methylation is controlled by microbial activity, the sediment biogeochemistry impacts the shape and magnitude of the vertical aqueous MeHg ($[\text{MeHg}]_{\text{aq}}$) depth profile. The ability to capture these profiles can elucidate how MeHg moves in sediment systems. Porewater profiling allows an accurate calculation of diffusive flux within the sediment column and across the sediment-water interface. Spatial $[\text{MeHg}]_{\text{pw}}$ are also useful in systems where sediment composition or concentration (i.e., in sedimentation of clean or contaminated sediment) varies with depth. Porewater concentrations are also useful for evaluating the performance of a remedial cap (like AC) for which the aim is to decrease porewater MeHg in the surface sediments ([Gilmour et al. 2018](#); [Ndungu et al. 2016](#)).

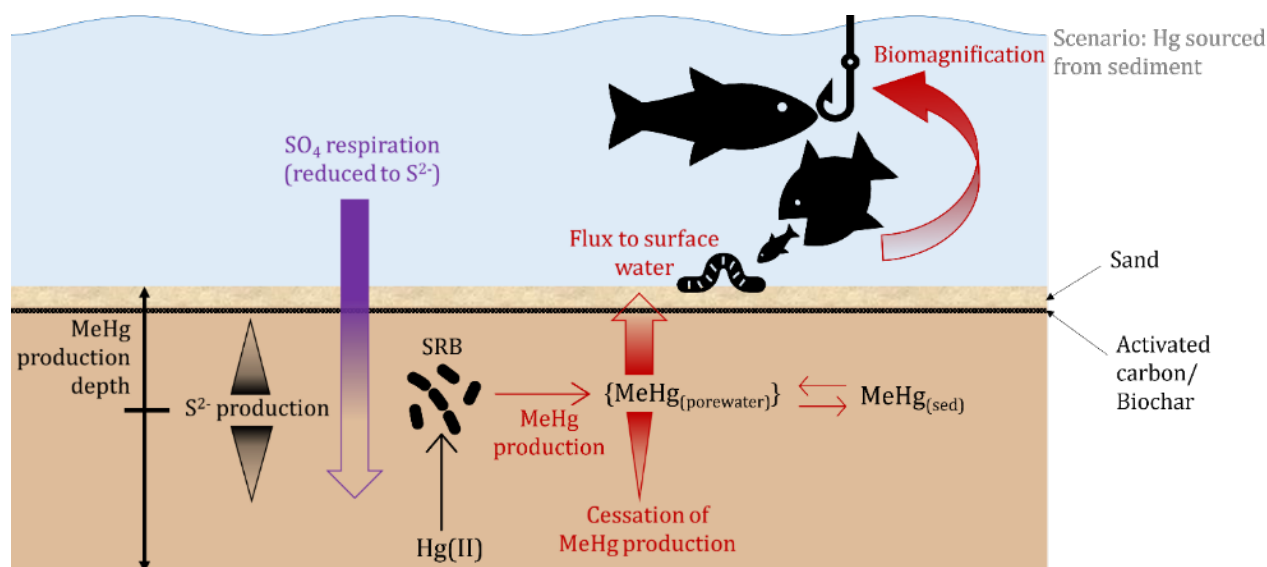


Figure 8.1. Simple Conceptual Diagram of Hg Fate and Transport in Contaminated Sediments and the Implementation of a Sand and Activated Carbon Cap.

Porewater MeHg profiles are also useful to understand bioaccumulation within epibenthic organisms. Several studies have shown that MeHg exposure is best quantified in the top sediments to epibenthic organisms, and vertical profiling is useful for understanding benthos bio-uptake ([Amirbahman et al. 2013](#); [Taylor et al. 2014](#)). Further, bioturbation by benthic organisms may impact MeHg concentrations by physical disturbance ([Benoit et al. 2009](#)) and oxidation in the top sediment layer (as postulated in ([Sanders 2018](#)), Ph.D. thesis).

Though porewater profiles are incredibly valuable, they are difficult to retrieve with traditional sampling methods. Extracting porewater from collected sediment cores is expensive and laborious, as it requires handling in an anaerobic glovebox to stabilize $[\text{MeHg}]_{\text{aq}}$ against sediment oxidation (Mason et al. 1998). Porewater sampling by syringe extraction introduces uncertainty of sampling

depth ([Gilmour et al. 2018](#)). Vertical profiling using kinetic-based samplers (i.e. DGTs) has provided porewater MeHg concentrations at a fine spatial scale, however, researchers have encountered difficulty with their interpretations due to porewater depletion by the samplers and variation of diffusion coefficients between sites ([Hong et al. 2014](#); [Noh et al. 2016](#)).

In this study, we explored the ability of our ag+AC (activated carbon in agarose gel) passive samplers to adequately produce MeHg profiles as an alternative to porewater grab sampling. As it is polymeric in nature, the PS can capture depth dependent aqueous MeHg measurements; the ag+AC PS was successful in simultaneously measuring $[\text{MeHg}]_{\text{sw}}$ and $[\text{MeHg}]_{\text{pw}}$ when placed across the sediment-water interface ([Washburn et al. 2022](#)). Our goal for this study was to determine the ability of the ag+AC sampler to measure porewater at a fine resolution. Elongated samplers were deployed within sediment microcosms to span a range sufficient to capture the MeHg maxima associated with the MeHg production zone. Samplers were deployed in estuarine and freshwater-sourced sediment microcosms to simultaneously study their applicability in two very different types of environments, both which can generate a significant amount of MeHg. In this study, we aimed to compare PS-derived MeHg profiles (0.5 cm resolution) to profiles obtained by porewater grab sampling at a 1 cm resolution.

8.2 METHODS

Ag+AC Passive Sampler synthesis

The ag+AC polymers were synthesized as mentioned in Chapter 6, however, they were cut into 4 cm by 8 cm segments to get an 8 cm vertical profile (Figure 8.2). Samplers were designed so that 1 cm was suspended in the overlying water, and the remaining 7 cm traversed the sediment. PS were enmeshed in an acid-clean polypropylene mesh to provide rigidity. Prior to deployment, enmeshed PS were deoxygenated in DI by with N_2 gas for > 30 min to minimize oxygen input into the sediment.



Figure 8.2. Passive Sampler Synthesized for Aqueous Spatial MeHg Profiling within Sediment Microcosm Experiment.

Indentations on the left side of the mesh indicated 0.5cm segments for ease of separation after retrieval from sediments. PS designed so 1 cm is suspended in the overlying water, and 7 cm traverses the sediment vertically

Sediment Microcosm Set-up

Estuarine and freshwater sediment microcosms were constructed to evaluate PS performance and compare $[\text{MeHg}]_{\text{aq}}$ profiles in the two different biogeochemical environments. Estuarine sediments comprise Hg contaminated sediment sourced from several sites in the Berry's Creek Study Area (BCSA) mixed with pristine intertidal marsh soil sourced from Global Change Research Wetlands (GCREW) at SERC (expected Hg concentration of 9.8 mg/kg). Freshwater sediments also contained Hg contaminated sediments sourced from BCSA but were mixed with soil collected from the Beaver Pond, a freshwater pond on the SERC campus (expected Hg concentration of 4.4 mg/kg). Large detritus from collected soil were removed and sediments were sieved to 2 mm. Sieved sediments were homogenized with a food processor to minimize variability between replicate microcosms. The surface water used for the estuarine microcosms were collected from the GCREW intertidal marsh (SERC) and diluted by half with DI water to maintain a salinity of about 3-4 ppt, while the freshwater surface water was sourced from a creek downstream of Beaver Pond.

Sediment mixtures were homogenized with a paint mixer immediately prior to microcosm construction. Sediment aliquots (and centrifuge-extracted porewater) were collected at the start of the experiment to assess changing concentrations over the time course of the experiment. Housed in opaque 2-gallon HDPE buckets (Figure 8.3), sediment was added to a depth of 10 cm and topped with 3 L of overlying water. For the duration of the experiment, overlying water in both microcosms was aerated by pumping air through a clean air stone. Buckets housing the microcosms were loosely capped. Samplers were inserted (Figure 8.3) 14 days after microcosm construction to allow systems to settle. Two weeks after construction, ammonia levels in the overlying water were elevated (>6 mg/L in freshwater, 0.5 – 1 mg/L in estuarine microcosms) possibly due to rotting organic matter after microcosm construction. To prevent reduction of biological activity from elevated ammonia levels, overlying water in freshwater and estuarine microcosms was drained and replenished immediately prior to sampler insertion, which brought levels back down to 0 mg/L. Additionally, 2 weeks after sampler insertion, the overlying water was replenished to make up for water evaporation over time.

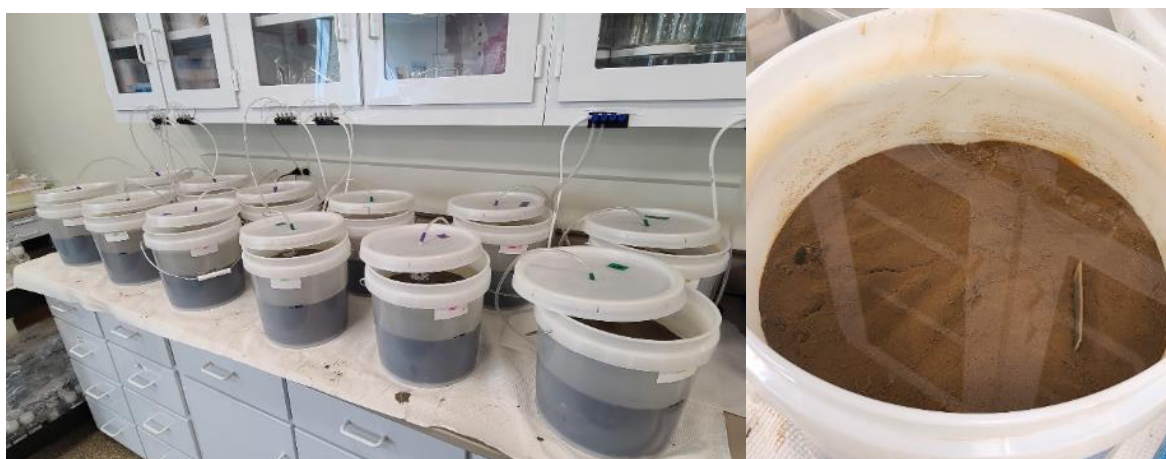


Figure 8.3. Setup of Sediment Microcosms (Left) and an Example PS Deployment in the Freshwater Microcosm (Right)

Sediment Microcosm Take Down

Sediment microcosms were deconstructed 28 days (estuarine) or 29 days (freshwater) after sampler deployment. Overlying water was drained until the sediment was covered with about an inch of overlying water to prevent sediment exposure to the air. The drained overlying water was sampled and filtered to 0.45 μm . Aliquots were immediately run for sulfide/pH or preserved for future analysis. Passive samplers were extracted, immediately sliced into 0.5 cm segments along its length, then weighed before being stored in the freezer (Figure 8.4). Multiple sediment cores were then extracted from each microcosm to extract sufficient porewater for analyses, and immediately transferred into the anaerobic chamber (95% N_2 and 5% H_2 gas). The sediment cores were segmented vertically at a 1 cm resolution using a core extruder. For each microcosm, corresponding segments from each core collected were combined before porewater extraction. Sediments were centrifuged at 4000 rpm for 20 min and overlying porewater was decanted and filtered to 0.45 μm in the anaerobic chamber. Aliquots from the filtered porewater were either immediately run for sulfide/pH or preserved for future analysis. Remaining sediment was lyophilized and stored frozen for future analysis.

Filterable MeHg was measured in overlying water and in the 1-cm resolution porewater depth profile to compare concentrations obtained from those grab samples to the concentrations derived from passive sampler measurements. Sediment MeHg was also quantified to compare sediment profiles to porewater profiles. Filterable THg and solid-phase THg will be measured to assess MeHg production in these sediment microcosms which will allow for fate and transport modeling in the future. Dissolved organic carbon (DOC), aqueous chloride, and sulfide were measured to serve as speciation modeling inputs to determine the distribution of MeHg complexes present. Aqueous chloride, sulfate, and nitrate in addition to aqueous and solid-phase elemental sulfur, iron, and manganese were also measured to assess redox chemical changes with depth, providing a clearer indication of the microbial activity responsible for Hg methylation. Because of limited porewater volume, aliquots for the measurement of anions, aqueous elements, THg, and pH were collected at a 2-cm depth resolution, rather than a 1-cm resolution. Details on sample preservation and analytical methods are given in Section X of the SI.

Data Analysis and Interpretation

Statistical analysis performed with JMP Statistical Software. Speciation calculations were performed with ChemEq1 ([Müller, Eawag](#), SI Section X).

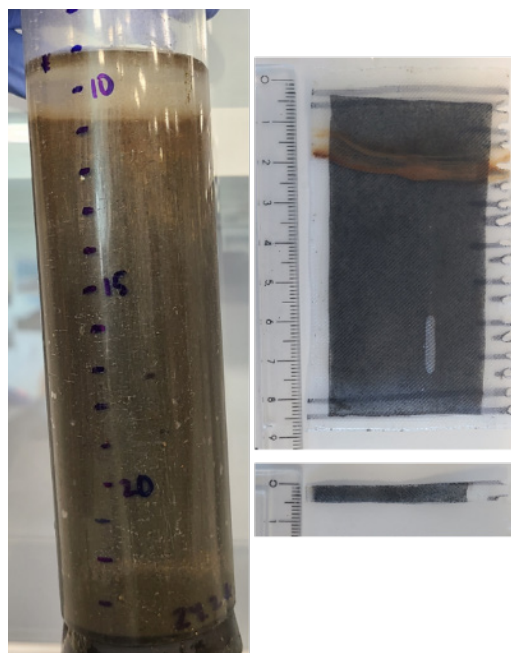


Figure 8.4. (a) A sediment Core Extracted from an Estuarine Sediment Microcosm During Take-down (One of Several Extracted from Each Microcosm), (b) a PS Extracted from a Freshwater Microcosm After Deployment, and (c) a 0.5 cm PS Segment Cut from the PS Immediately After Retrieval

8.3 RESULTS AND DISCUSSION

All passive samplers were successfully retrieved from the laboratory sediment mesocosms after a 28-day deployment period. The shape of the $[\text{MeHg}]_{\text{pw}}$ profile was better reflected by the higher-resolution PS-derived profile. With both sampling methods, the location of the $[\text{MeHg}]_{\text{pw}}$ peak is easily identifiable. Peak $[\text{MeHg}]_{\text{aq}}$ concentrations occurred where the change in sulfate with depth ($d\text{SO}_4/dx$, 2 cm resolution) was at a maximum, as can be visually indicated by the flattest slope in the sulfate vs depth curve in Figure 8.5. This correlation is expected – the elevated $d\text{SO}_4/dx$ indicates elevated activity by sulfate-reducing bacteria (SRB) in that area, which are mainly responsible for Hg methylation ([Podar et al. 2015](#)). Although, locating the peak $d\text{SO}_4/dx$ may not be a sole indication of maximum MeHg production as iron reducing bacteria (FeRB) are also responsible for Hg methylation.

The sediment MeHg profiles do not capture these peak MeHg levels observed in the porewater profiles. In fact $[\text{MeHg}]_{\text{sed}}$ dipped 1 cm below the sediment-water interface in the freshwater microcosms, where $[\text{MeHg}]_{\text{pw}}$ was at a maximum. This discrepancy may be attributed to spatial changes in sediment composition; further analysis of sediment chemistry to confirm this hypothesis will be pursued in the future. Quantifying spatial changes in sediment-porewater dynamics is important for understanding MeHg transport, as natural processes can affect transport throughout the sediment column; this is especially important for estimating breakthrough in capped sediments. Further, measuring $[\text{MeHg}]_{\text{sed}}$ alone is not enough to assess the mobile MeHg fraction that is most at risk for uptake by biota ([Biggam et al. 2017](#); [Buckman et al. 2019](#); [Hsu-](#)

[Kim et al. 2018](#)), while $[\text{MeHg}]_{\text{aq}}$ has demonstrated a good relationship with biota concentrations ([Eckley et al. 2020](#); [Gilmour et al. 2013](#)).

Comparing the estuarine and freshwater profile shapes, the freshwater $[\text{MeHg}]_{\text{PW}}$ peak was sharper and occurred closer to the sediment water interface. This could be due to the elevated microbial activity brought about by decaying organisms following microcosm construction. The DOC levels in the freshwater microcosms were substantially higher than in the estuarine microcosms, despite higher initial DOC and LOI levels in the estuarine sediment. Net MeHg production was substantial in both microcosms. Over the 42/43-day incubation, average sediment MeHg increased by 50% in estuarine microcosms and by 70% in freshwater microcosms.

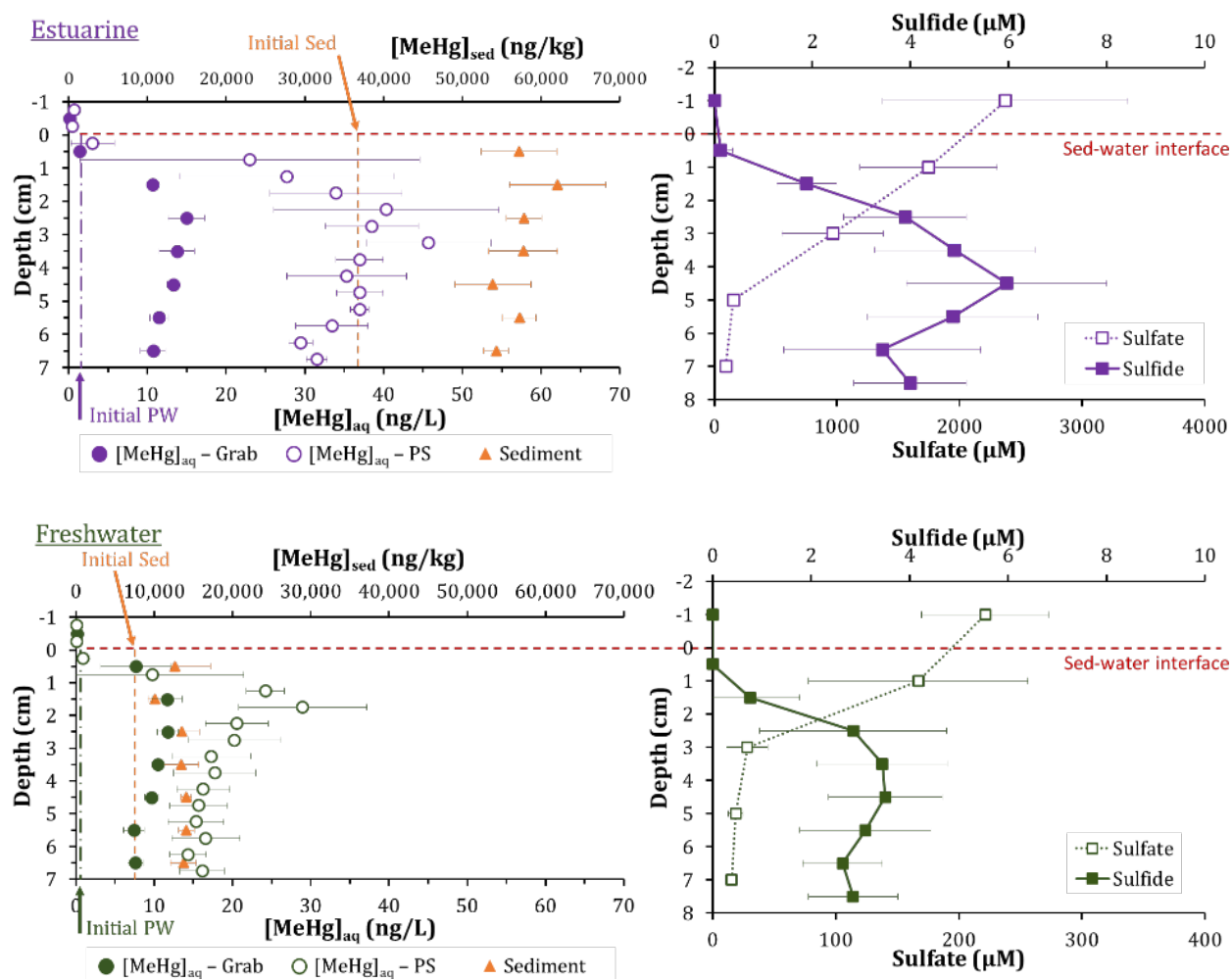


Figure 8.5. MeHg and Sulfide/Sulfate Data for the Estuarine (Top) and Freshwater (Bottom) Microcosms. (Left) PS-Derived and Grab Sample $[\text{MeHg}]_{\text{aq}}$ Profiles and Grab Sample $[\text{MeHg}]_{\text{sed}}$ Profiles. The Average ($n = 3$) Initial Grab Sample $[\text{MeHg}]_{\text{PW}}$ and $[\text{MeHg}]_{\text{sed}}$ Are Reported as Vertical Dashed Lines and Indicated. (Right) Sulfate and Sulfide Profiles.

For all graphs, data points represent an average of triplicate samples, and the error bars represent 1 standard deviation from the average.

This deployment demonstrated the versatility of the ag+AC PS in systems of varying biogeochemistry. The PS-derived $[\text{MeHg}]_{\text{aq}}$ were mostly 2 to 4 times higher than grab samples (Figure 8.5), using the K_{PS} chosen from the DOM isotherms ([Washburn et al. 2022](#)), $\log K_{\text{PS}} = 2.96$, despite differences in salinity and organic matter between the soil types. The slightly higher PS-Derived $[\text{MeHg}]_{\text{pw}}$ observed may be attributed to changing MeHg concentrations during PS deployment. It is possible that there was a spike in $[\text{MeHg}]_{\text{pw}}$ followed by a decline over time, reflected in the time integrative passive samplers, but not in the snapshot grab samples. However, MeHg concentrations throughout the incubation were not explicitly studied.

Elevated DOM in this experiment did not depress adsorption to the embedded AC in these samplers, as what was previously observed for AC ([Muller et al. 2019](#)). DOC measured at retrieval were much higher (range of 16 – 44 mg/L in estuarine and 18 to 102 mg/L in freshwater microcosms, increasing with depth) than the levels in the [Washburn et al.](#) DOM isotherms (up to 5 mg/L). However, $[\text{MeHg}]_{\text{PS}}/[\text{MeHg}]_{\text{pw}}$ ratios in this study were slightly higher than in the DOM isotherms and were relatively constant throughout the depths in this experiment. The elevated DOM did not depress K_{PS} . This observation supports the claim that DOM does not saturate the AC, as was also indicated in a study on DOM impacts on AC adsorption ([Schwartz et al. 2019](#)). The consistent partitioning behavior in this experiment demonstrates that the suggested K_{PS} in [Washburn et al.](#) is applicable over a wide range of DOC.

The presence of aqueous sulfide does not appear to influence sampler uptake in these microcosms, although sampler-water dynamics of MeHgSR have yet to be investigated. Elevated sulfide levels can shift MeHg speciation to favor MeHgSR over MeHgDOM, which is suspected to have a greater affinity to AC (1 mM sulfide, [Schwartz et al. 2019](#)). Further, aqueous sulfide can also increase the sulfur content of DOM ([Poulin et al. 2017](#)), which corresponded to increasing K_{PS} in the [Washburn et al.](#) DOM isotherms. The portion of MeHg complexed with sulfide over DOM is difficult to predict, because of the uncertainty in the formation constant for MeHgDOM ($\log K_{\text{f}}$ ranging from 15.7 to 17.5; ([Liem-Nguyen et al. 2017](#)). In this study, there is a wide range of possible MeHg species distributions (Figure 8.6); the calculated portion of MeHgSH dominates at the minimum MeHgDOM K_{f} , and vice versa for the maximum K_{f} . The influence of sulfide on K_{PS} may need to be better established in future work to confirm that MeHgSR or sulfurized DOM won't impact PS-derived measurements in systems with higher sulfide levels.

Locating the $[\text{MeHg}]_{\text{pw}}$ peak at a high-resolution and relating it to the activity of methylating organisms would facilitate the advancement of assessing and remediating Hg contamination in sediments. Profiling with the ag+AC PS offers a reliable and advantageous alternative to traditional grab sampling. In addition to the incredibly fine-resolved spatial profiling ability, the sampler eliminates the water sample requirement to detect $[\text{MeHg}]_{\text{aq}}$, increasing our bandwidth to measure other impactful analytes (i.e. sulfate, sulfide, DOC, etc.) at a higher resolution. Traditional grab sampling through core extraction requires processing in inert conditions, while PS does not. PS offers a practical advantage by eliminating the need for the expensive and laborious anaerobic glovebox. Sampling with the PS also eliminates user error associated with sediment coring, especially when sectioning at the sediment-water interface. The markings made on the PS casing guides its placement, eliminating this sampling uncertainty. Finally, filter-passing MeHg attached to small colloids in porewater grab samples can influence the measurement and interpretation of the MeHg that is bioavailable to organisms, whereas the embedded AC in the PS is size-excluding.

The versatility of the size and shape of the polymeric sampler allows alterations to meet sampling desires.

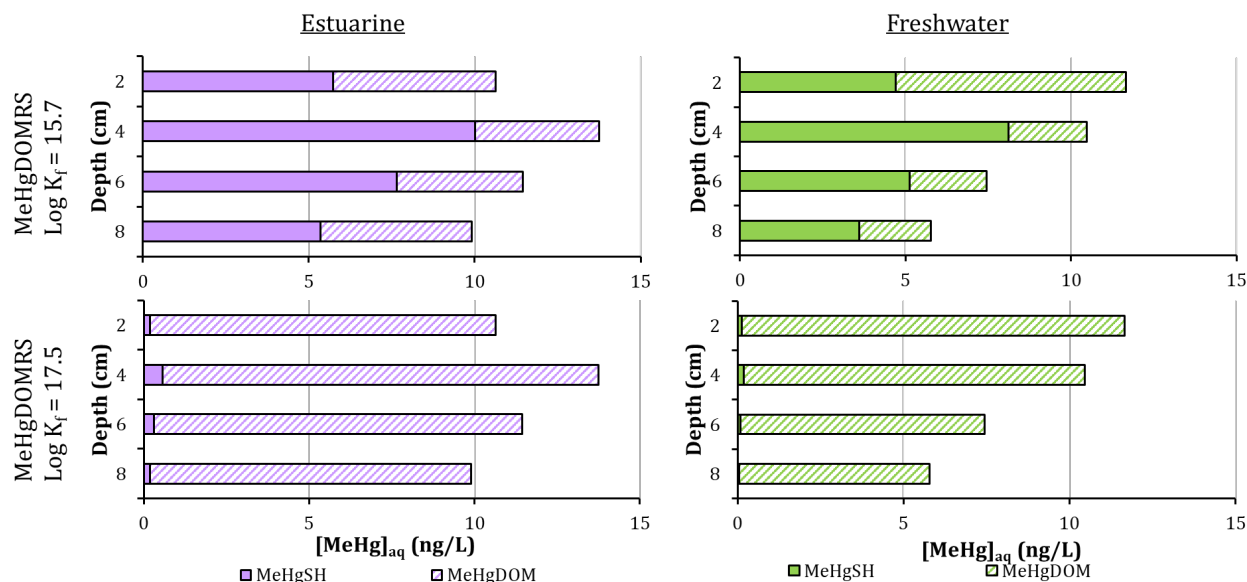


Figure 8.6. Calculated [MeHg]_{pw} Species Distribution in Estuarine (Right) and Freshwater (Left) Using the Lower (Top) and Upper (Bottom) Range for the Equilibrium Formation Constant of MeHgDOMRS (Log K_f)

This experiment successfully demonstrates the ability for the ag+AC PS to reflect spatially dependent [MeHg]_{aq} within static sediment systems. Application of PS in sediments with mid-levels of sulfide and extensive MeHg production were successful in both very different biogeochemical environments, increasing confidence in using these samplers in sediments of different chemistries. It is recommended to evaluate the effect that MeHgSH may have on the predicting power of the K_{PS} before deployment in systems with high aqueous sulfide. The time-integration aspect of the MeHg PS allows averaging of exposure concentrations over a period of change and can provide information on cumulative exposure or flux information where [MeHg]_{pw} changes due to diurnal changes, collection/homogenization, or treatment application. It is recommended to investigate the influence of short-term [MeHg]_{pw} perturbations on the PS measurements, especially for sampling in tidally influenced sites, and in recently remediated systems.

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9.0 CHAPTER 9: APPLICATION OF A NOVEL ACTIVATED CARBON BASED PASSIVE SAMPLER TO MEASURE AQUEOUS METHYLMERCURY IN SURFACE WATERS AND POREWATERS AT EAST FORK POPLAR CREEK

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ABSTRACT

To transition into a field application, the ag+AC MeHg passive sampler was deployed *in situ* at East Fork Poplar Creek (EFPC) in Oak Ridge, TN. EFPC is a moderate-flow freshwater system with low surface water MeHg, yet high sediment and fish MeHg due to Hg release from its processing as a lithium isotope separator in the mid-20th century. We aimed to determine how the ag+AC PS respond in a flowing river system as opposed to the static finite laboratory systems in prior studies, evaluate its ability to measure surface water MeHg ([MeHg]_{sw}) despite temporal changes in the environment, and assess the feasibility and robustness of porewater sampling using the passive sampler. The passive samplers (PS) were deployed in surface waters (SW-PS) at two sampling stations within EFPC in Fall 2021 and again in Summer 2022. PS were also deployed within sediments (PW-PS) at one of the locations in Summer 2022 to measure porewater MeHg ([MeHg]_{pw}). At retrieval, surface water grab samples were collected along with SW-PS. Sediment samples were collected onsite alongside Sed-PS and were shipped to MD for porewater extraction and further processing.

Regardless of low surface water MeHg concentrations ([MeHg]_{sw}) close to instrument detection limits, SW-PS provided aqueous concentration estimates that were much more detectable and very similar (within a factor of 1.6) to grab sample [MeHg]_{sw} in both deployments. Further, the elevated [MeHg]_{sw} measured in grab samples during the Summer 2022 deployment (compared to Fall 2021) were reflected in the SW-PS measurements. PS-derived [MeHg]_{pw} was 8 times higher than the grab sample porewater measurement. This discrepancy is possibly due to loss of porewater concentration during transport, or higher apparent MeHg in the passive sampler due to partial PS degradation. Additional measurements are needed to confirm this observation. The ag+AC PS were successful in obtaining surface water measurements, however, an improved PS design for *in situ* porewater sampling will need to be pursued.

9.1 INTRODUCTION

After successful testing in environmentally relevant, controlled, bench scale experiments we deployed our ag+AC passive samplers (PS) *in situ* at East Fork Poplar Creek (EFPC) in Oak Ridge, TN, to begin transitioning toward field testing. EFPC is a moderate-flow freshwater system with slightly elevated surface water methylmercury (MeHg), yet high sediment and fish MeHg due to Hg release from its use in lithium isotope separation in the mid-20th century. Despite remedial efforts, fish and sediment within EFPC continue to exhibit elevated MeHg concentrations ([Brooks and Southworth 2011](#); [Watson et al. 2016](#)). An accounting of the mercury transport within EFPC ([Watson et al. 2016](#)) reports that sediment and periphyton biofilms were found to contribute a significant portion of MeHg to fish in the creek. Surface and porewater MeHg measurements facilitated by the ag+AC PS can provide crucial information needed to understand MeHg exposure to aquatic wildlife and sediment to surface water flux.

In this field study, we tested the ability of the samplers to predict MeHg concentrations within a flowing river system as opposed to the static finite systems tested in prior bench studies. Additionally, this deployment was used to evaluate the ability of the PS to predict surface water MeHg across temporal changes in river concentrations. A field deployment provides a more robust test of PS feasibility and robustness *in situ*.

9.2 MATERIALS AND METHODS

Site Description

Currently, surface water MeHg concentrations are below 1 ng/L year-round, with increases in the warmer seasons. According to a report on mercury content in sediments at ([Brooks et al. 2017](#)), bulk sediment MeHg concentrations range from 0.55 to 10.4 µg/kg, generally decreasing downstream from the Y-12 site where the Hg processing took place. Bed sediments are mostly rocky/sandy, though there are a limited number of locations containing softer, more organic sediments. One of these areas was used for deployment of PS in sediment. Finer grained sediments generally contain higher MeHg concentrations ([Brooks et al. 2017](#)).

Deployment of Passive Samplers

There were two deployment events. In Fall 2021, passive samplers were deployed in surface waters at 2 locations in EFPC (Figure 9.1): Wiltshire (EFK 16.4) and downstream New Horizons (EFK 5.4). The numbers after EFK denote river kilometers going upstream. In Summer 2022, the samplers were deployed in surface waters *and* sediments a site about 100 meters downstream from the New Horizons (EFK 5.4) station (noted throughout the report as EFK 5.3), as this location featured soft sediments that facilitated PS deployment. Sampler material (constructed as in Chapter 7) and deployment devices described below were constructed at SERC and shipped to ORNL.

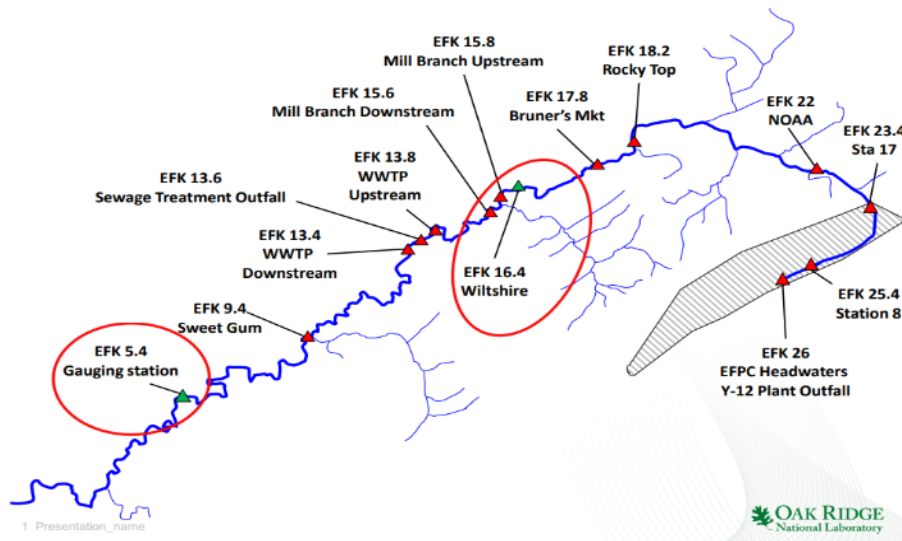


Figure 9.1. Map of East Fork Poplar Creek and ORNL Sampling Stations.

The Fall 2021 surface water deployment locations are circled in red (EFK 16.4 and EFK 5.4), and the Summer 2022 surface water/sediment deployment took place approximately 100 m downstream the EFK 5.4 site.

Surface Water PS Deployments

For surface water sampling, the ag+AC PS were deployed in a perforated casing designed to allow flow of water while protecting the soft samplers from turbulence and curious aquatic wildlife. The casing was made from a 2" OD PVC pipe cut into 8" long segments. Holes (3/16") were drilled in 4 equidistant rows (1" apart from one another in each row) around the perimeter of the PVC segment. PS were enclosed in a 69 x 69 polypropylene mesh ([McMaster-Carr](#)), that was pre-soaked in a 10% HCl solution and rinsed with DI water (or "acid-cleaned" for short). The enmeshed samplers were then placed within an acid-cleaned plastic projector slide case and secured to a plastic rod for stabilization (Figure 9.2a). This apparatus was then placed in the acid-cleaned PVC casing, enclosed with acid-cleaned PVC end fittings (Figure 9.2b). Three PS were placed in each casing for replication. To prevent drying, the hydrogel polymer samplers were kept in clean DI water until placement in the devices in the field. The casings were secured to an anchoring cinderblock in the creek (Figure 9.2c).

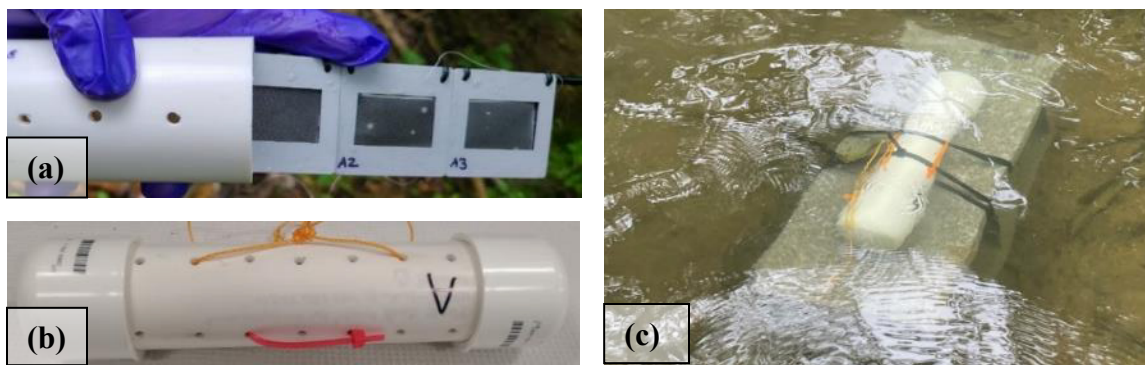


Figure 9.2. Surface Water PS Deployment Apparatus.

(a) PS in 69 x 69 polypropylene mesh secured to plastic projector slides and rod. (b) PVC casing to protect SW-PS. (c) PS-containing casings Attached to a cinderblock on the sediment bed during surface water deployment

Sediment PS Deployments

In Summer 2022, the ag+AC PS were also deployed in sediments to measure porewater MeHg. As with the SW-PS, the Sediment PS (Sed-PS) were enmeshed in acid-cleaned 69 x 69 polypropylene mesh and mounted in slide cases for protection. To hold the samplers in place in sediments, the mounted samplers were tied to an acid-cleaned acrylic frame, which was anchored to a thick ground stake (Figure 9.3). To minimize aeration of sediments to be sampled, both the enmeshed Sed-PS and acrylic frame were stored in a rigid container full of de-oxygenated DI water, minimizing headspace, until they were deployed. The Sed-PS were inserted so that the top of the sampler was placed 3 cm beneath the sediment surface and traversed approximately 2.5 cm of vertical length (Figure 9.3c), so the bottom of the PS was 5.5 cm below the surface.

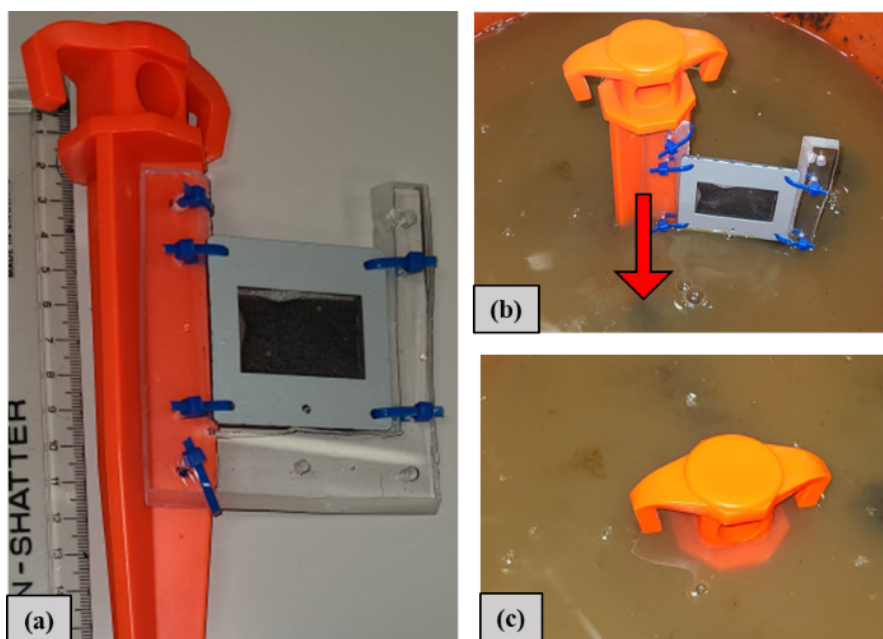


Figure 9.3. Sediment PS (Sed-PS) Deployment Apparatus.

(a) de-oxygenated enmeshed PS in projector slide case secured to acrylic frame and tied to a ground stake anchor. (b) sample picture showing deploying of apparatus in sediment until it is (c) fully submerged in sediment, as it was for the in situ deployment.

Deployment Timeframe and Sample Retrieval

A deployment time frame of 14 days was deemed sufficient when evaluating uptake kinetics ([Washburn et al. 2022](#)) of MeHg complexed with large (Suwannee River Humic Acid) and small (Cysteine) dissolved organic matter (MeHgDOM) in finite, static systems. Further, PS concentrations were equilibrated after 14 days in subsequent deployment in bench-scale sediment microcosms ([Washburn et al. 2022](#)). To determine if equilibration was reached faster in these moderate-flow semi-infinite surface waters, surface water PS (SW-PS) were deployed in triplicate at EFK 16.4 and EFK 5.4 for 7 and 14 days in Fall 2021. The deployment timeframe was longer in Summer 2022 considering the sediment PS (or Sed-PS) deployment. Equilibrium was reached previously after 14 days in static sediment porewater. We choose deployment timeframes of 14 and 21 days to ensure that equilibrium was reached here. SW-PS were deployed and retrieved alongside the Sed-PS at EFK 5.3, both in triplicate.

Upon retrieval, any dirt/sediment was gently rinsed off the surface of the PS mesh with DI water. The enmeshed PS were then placed in a plastic bag which was sealed to minimize headspace and prevent evaporation of the hydrogel polymer. The PS were kept on ice during transport to the lab. After taking final weights, the PS were immediately stored individually in sealed plastic bags and kept frozen until processing.

Surface water grab samples were retrieved at each timepoint (deployment *and* retrieval) to capture MeHg concentrations through time and to compare with aqueous MeHg concentrations estimated by the SW-PS. Surface water chemistry was also measured to calculate MeHg complexation. Surface water was collected and immediately returned to the lab on ice, where it was filtered to 0.45 μm using glass microfiber GD/X filters. Of the filtered water, an aliquot was frozen for future measurement of dissolved organic carbon (DOC) and relevant anions (Cl^- and SO_4^{2-}), and the remainder was acidified with 0.5 vol% HCl (trace metal grade) and refrigerated for future measurement of MeHg.

Sediment cores were collected adjacent to the Sed-PW at the final (21 day) timepoint for porewater MeHg analysis. Sediment cores (10 cm in length) were kept on ice until further processing at ORNL. To match the PS depth, the top 6 cm of the collected sediment core was extruded for separation of porewater in an anaerobic glovebox. Extruded sediment was kept in an air-tight polypropylene 250 mL centrifuge tube and shipped to SERC for further processing. Porewater was extracted from the sediment at SERC via centrifugation and decantation, then filtered to 0.45 μm in an anaerobic glovebox. An aliquot of the filtered water was used to immediately measure pH and aqueous sulfide concentration. The remaining porewater was preserved as above for DOC, anion, and MeHg measurements. The analytical methods for these measurements (pH, sulfide, anions, DOC, MeHg) are provided in Chapter 8.

9.3 RESULTS AND DISCUSSION

Surface water MeHg concentrations ($[\text{MeHg}]_{\text{sw}}$) derived from PS were comparable (within a factor of 1.6) to those obtained by grab sampling in both deployments (Figure 9.4). Note that the grab samples represent single timepoint measurements, whereas the passive sampler measurement is representative of a time integrated exposure concentration over the period of deployment. For the Fall 2021 deployment, the PS-derived $[\text{MeHg}]_{\text{sw}}$ at the 7-day timepoint were statistically indistinguishable from the grab sample values (2-sample Student's t-test, $p > 0.05$, $n = 2,3$). That statistical analysis was not repeated at the 14- and 15-day timepoints because of insufficient replicate surface water data. EPFC MeHg concentrations changed somewhat at both sites over the course of both deployments. In Fall 2021, there was a light rain shower before the 7-day timepoint and a statistically distinguishable dip in grab sample $[\text{MeHg}]_{\text{sw}}$ at EFK 16.4 (1-sample Student's t-test, $p = 0.03$, $n=2$), but not in EFK 5.4 ($p = 0.25$, $n = 2$). This temporal trend was reflected in the samplers; there was a significant increase in PS-derived $[\text{MeHg}]_{\text{sw}}$ between the 7- and 14- day timepoint at EFK 16.4 (2-sample Student's t-test, $p = 0.02$, $n = 3$), but not at EFK 5.4 ($p = 0.18$, $n = 3$), which supports the conclusion that equilibration occurs faster than expected in the surface water.

EPFC $[\text{MeHg}]_{\text{sw}}$ was higher during the Summer 2022 deployment, and this was reflected in the SW-PS measurements. Although there was a noticeable decrease in $[\text{MeHg}]_{\text{sw}}$ during the first 15 days, possibly due to a storm at the 14-day timepoint, SW-PS derived measurements were within error of the grab sample at the 15-day time point. All the samplers collected at the 21-day point were degraded past the point of recovery, perhaps due to stream turbulence resulting from inclement weather or aquatic worm damage after the 15-day time point.

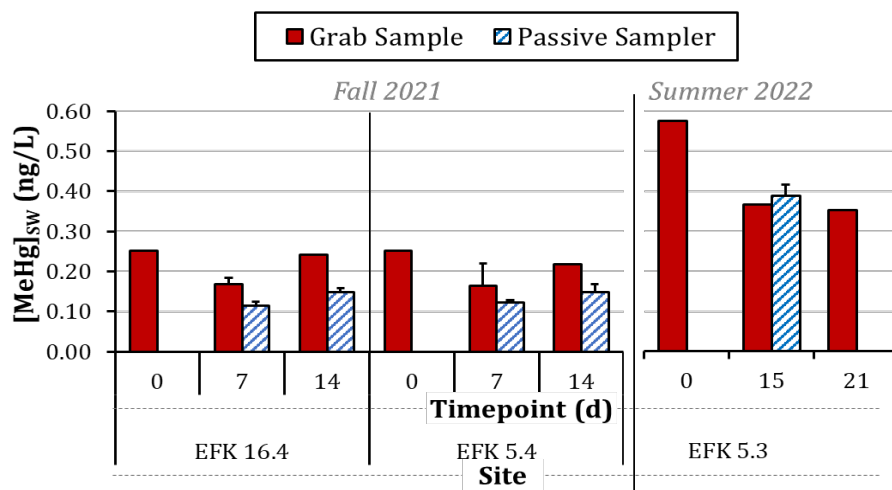


Figure 9.4. Comparison of Surface Water Concentrations Obtained by Grab Samples and SW-PS in Fall 2021 and Summer 2022 Deployments.

Summer 2022 deployments took place at a site ~100 m downstream EFK 5.4 (EFK 5.3). Due to SW-PS degradation at t+21 in Summer 2022, those data were omitted. Bars represent average concentrations and error bars represent 1 standard deviation in sample replicates (n = 2,3).

Unlike the surface water samplers, PS-derived [MeHg]_{pw} was significantly (Student's *t*-test; *p* = 0.02, *n* = 2-3) different than sediment-extracted porewater. The PS-derived [MeHg]_{pw} calculated from the suggested *K*_{PS} (Washburn et al. 2022) was 8 times higher than what was measured in the porewater grab samples (Figure 9.5). However, the [MeHg]_{pw} derived from the Sed-PS did not change significantly between the 15- and 21-day time points (Student's *t*-test, *p* = 0.20, *n* = 2-3), potentially suggesting that porewater-PS is approaching equilibrium within 15 days, as seen in the prior bench scale microcosm deployments. Additional datapoints or use of PRCs are required to confirm equilibrium.

We considered the possibility that the [MeHg]_{pw} calculated from the Sed-PS was comparatively high because the Washburn et al. *K*_{PS} used to estimate PS uptake is inappropriate for application in this setting. Our calculations suggest that MeHg speciation favors complexes with DOM, so partitioning at this site is expected to be similar to the Washburn et al. *K*_{PS}. Although a difference in DOM character can impact sampler partitioning, we do not suspect that the DOM character at this site presents a significant difference. Solutions with DOM having a higher sulfur content corresponded to higher *K*_{PS}, in the Washburn et al. MeHgDOM adsorption isotherms. Considering that native aqueous sulfide is positively correlated with S/C content in DOM (Poulin et al. 2017) and that aqueous sulfide in the EFPC porewater was measured below instrument detection limits, the sulfur content in this site's DOM is likely lower than in other sediment deployments. In other sediment deployments (Washburn et al. and in Chapter 7), PS-derived [MeHg]_{pw} were within a factor of 4 to grab sample [MeHg]_{pw} using the Washburn et al. *K*_{PS}. Therefore, we do not attribute the comparatively higher PS-derived [MeHg]_{pw} to the estimating *K*_{PS}.

One Sed-PS (at the 21-day timepoint) was degraded past the point of recovery and not included in the analysis. The remaining two Sed-PS showed partial weight loss of 10-40%. However, a 10-40% loss in weight does not explain an 8-fold difference in concentration estimates. Another potential explanation of the discrepancy of [MeHg]_{pw} in the two methods is loss of [MeHg]_{aq}

during overnight transport from ORNL to SERC (similarly observed in [Mason et al. 1998](#)). We suspect that sediment PS weight loss may be due to microbial degradation of the agarose gel backbone; but physical degradation or dessication during transport can't be ruled out. More testing will be needed to evaluate and correct this mass loss issue that occurs in some settings. Note that the passive sampler deployment in laboratory sediment mesocosms (both freshwater and brackish) in Chapter 8 showed good recovery after 28 days of deployment.

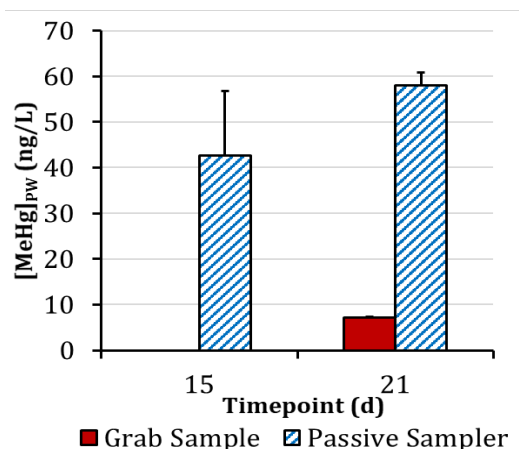


Figure 9.5. Comparison of Porewater Concentrations from Grab Sample Measurements and Sed-PS Measurements in the Summer 2022 Deployment.

Data presents average concentration and error bars represent 1 standard deviation ($n = 2$ for grab sample and Sed-PS measurements at the 21-day timepoint, $n = 3$ for PS at the 15-day timepoint).

Low (sub-ng/L) concentrations, redox and light sensitivity, and changing concentrations through time complicate field MeHg measurements and interpretation. The EFPC deployments along with several experiments detailed in this report demonstrate that the ag+AC PS offers an alternative solution to these sampling difficulties. Specifically, the samplers concentrate MeHg, making analysis easier. In EFPC, $[\text{MeHg}]_{\text{sw}}$ in grab samples was generally within a factor of 10 to the best available detection limit (~ 0.03 ng/L). MeHg was much easier to detect in the ag+AC PS, with concentrations over three orders of magnitude above instrument detection limits. Further, the samplers integrate concentrations through time, making the PS less susceptible to short-term temporal changes in water concentrations.

Passive samplers can offer additional advantages for porewater sampling. Samplers can be sliced to provide finer resolution (see Chapter 8) than most traditional porewater sampling methods (e.g., sippers). Further, use of PS can avoid the difficulties associated with maintaining redox status in porewater during sampling, transport, and handling. Because sediment:water MeHg partitioning is highly sensitive to redox, many traditional sampling methods have to use an anaerobic chamber to do porewater separation. Importantly, MeHg bound to AC in PS is stabilized against degradation during sampling.

9.4 CONCLUSIONS

In this field trial in EPFC, we were able to successfully demonstrate the use of the ag+AC PS in a dynamic flowing water setting. For both deployment events, the samplers predicted $[\text{MeHg}]_{\text{sw}}$

accurately. To calculate $[\text{MeHg}]_{\text{sw}}$, we assumed that the samplers were at equilibrium with surrounding waters, and that the equilibrium K_{PS} for MeHg was the value we had previously determined from the DOM adsorption isotherms in Washburn et al. Speciation calculations for MeHg based on measured DOM, chloride, and other constituents in EPFC show that MeHgDOM is expected to be the dominant complex, as is true for most surface waters.

However, an adequate test of ag+AC PS for porewater MeHg measurement will require additional field testing in which sampler weight loss is prevented. Several of our microcosm tests have provided robust predictions of porewater MeHg, and avoided sampler degradation over 14 days deployment. The cause of the agarose polymer weight loss as seen in the Summer 2022 deployment needs to be identified and resolved. Turbulence, biota consumption, and dessication during transport are potential causes that might be easily avoided with additional protection of the ag+AC material. To transition ag+AC PS MeHg sampling to the field, we recommend the following pursuits; 1. Examine PS predictive capabilities in a larger variety of samples sites across a broader range of water chemistry and hydrologic conditions, 2. Identify and resolve the causes of sampler degradation in some settings, and 3. Improve understanding of sampler-water equilibration times in flowing water systems (rather than in static systems) to determine the effect of rapid MeHg concentration changes on PS uptake.

9.5 REFERENCES

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10.0 RECOMMENDATIONS FOR THE FUTURE

The following recommendations are provided for future work:

- 1) The vibrating platform advances the passive sampling technology by enabling faster mass transfer of strongly hydrophobic compounds enabling rapid approach to equilibrium in slow moving water environments like sediment porewater and low flow surface waters. The technology is ready for field demonstrations. Additional field deployments in a range of flow conditions will be helpful in delineating situations where this technology is most needed and appropriate.
- 2) Further engineering advancements are possible in the vibrating sampler setup to make the system more robust and user-friendly. These include designing an integrated hermetically sealed unit with remote charging and programming capability to minimize potential for leaks.
- 3) The ag+AC passive sampler for dissolved MeHg measurements was demonstrated in the lab and field conditions. Some loss in mass was observed in the passive sampler after deployment in a few cases and needs to be investigated further to determine the cause and address as necessary.
- 4) Enhancement of the structural stability of the agarose based polymer needs to be further explored for example by using cross-linkers.
- 5) Further demonstrations under a wider range of field water quality conditions may be necessary to build more confidence in the measurements of MeHg.
- 6) We demonstrate the proof-of concept of using stable isotope labeled MeHg as performance reference compounds. Further work is necessary to demonstrate the use of performance reference compounds to account for potential nonequilibrium conditions in field deployments.
- 7) Additional work is needed to quantify the relationship between sampler estimates of MeHg_{CL} and biotic uptake of MeHg across a range of sediment environments.
- 8) It is recommended to investigate the influence of short-term MeHg concentration perturbations on the PS measurements, especially for sampling in tidally influenced sites.

APPENDIX A SUPPLEMENTAL INFORMATION FOR CHAPTER 1

IN SITU PASSIVE SAMPLING OF SEDIMENT POREWATER ENHANCED BY PERIODIC VIBRATION

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Supplemental Information (pp. 20)

Contents

Local equilibrium model for a static system

Details of model simulation

Parameter estimation

Quantification of difference between low frequency (5 min pause) and high frequency (2min pause) vibrating data

Quantification of difference between 2 min and 6 hour pause models

Matlab codes

Tables

Table S1.1. Fractional loss of PAHs from Harbor point sediment measured by Ghosh et al.⁴.

Table S1.2. Parameter values used in model simulations

Table S1.3. Comparison of PAH concentration in PE in the fully mixed system after 56 days (C56) and 77 days (C77) of exposure

Table S1.4. PAH concentration in PE in high frequency and low frequency vibrating systems at different exposure times

Table S1.5. P-values calculated for the experimental data from high and low frequency vibrating systems.

Table S1.6. Percent difference between high and low frequency model predictions at different exposure times.

Table S1.7. Percent difference between 2-min and 6-hour model predictions for chrysene

Figures

Figure S1.1. Vibrating system set up before insertion into sediment

Figure S1.2. Vibrating system set up after insertion into sediment

Figure S1.3. Motor vibration in sediment

Figure S1.4. Experimental data for fractional uptake of fluoranthene and four heavy PAHs in PE passive sampler in four different systems

Figure S1.5. Loss profile of a) deuterated phenanthrene and b) deuterated pyrene from PE exposed to sediment under different mixing conditions

Figure S1.6. Comparison of three modeling approaches for the vibrating system for pyrene

Figure S1.7. Fractional uptake of three PAHs into PE versus energy consumption of one motor after 15 days of deployment

Local equilibrium model for a static system

A one-dimensional diffusion model, based on Fernandez et al.¹ was used to describe the mass transfer in a system containing a PE strip with the thickness of $2l_p$ and sediment with thickness of l_w on both sides. Following the Fick's second law of diffusion, for a PE strip with concentration C_{PE} and at point x and time t :

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad -l_p < x < l_p \quad (S-1)$$

Where D_{PE} is chemical diffusivity in PE (cm^2/s)

Assuming instantaneous equilibrium between pore water and sediment particles, transport equation in pore water with concentration of C_w at point x and time t will be as follows:

$$\frac{1}{R} \frac{\partial C_w}{\partial t} = D \frac{\partial^2 C_w}{\partial x^2} \quad l_p < x < l_p + l_w \quad \text{and} \quad -l_p < x < -l_p - l_w \quad (S-2)$$

Where ρ is sediment bulk density (g/cm^3), R is retardation factor and D is the effective diffusivity (cm^2/s)

R and D are calculated as follows:

$$R = \varepsilon / (1 + \frac{\rho}{\varepsilon} K_d) \quad (S-3)$$

$$D = \frac{D_w}{1 - \ln \varepsilon^2} \quad (S-4)$$

Where D_w is chemical diffusivity in water (cm^2/s), K_d is sediment-water partition coefficient (cm^3/g) and ε is porosity (cm^3/cm^3)

The polymer is initially clean and sediment particles have initial concentration of S_0 .

$$C_{w0} = S_0 / K_d \quad l_p < x < l_p + l_w \quad \text{and} \quad -l_p < x < -l_p - l_w \quad (S-5)$$

$$C_{PE} = 0 \quad -l_p \leq x \leq l_p \quad (S-6)$$

At the boundary of PE-sediment, C_{PE} can be determined using the PE-water partitioning coefficient K_{PEW} and pore water concentration:

$$C_{PE} = K_{PEW} C_w \quad x = l_p \text{ and } x = -l_p \quad (\text{S-7})$$

Continuity of flux is also assumed at the boundary:

$$D_{PE} \frac{\partial C_{PE}}{\partial x_{PE}} = D \frac{\partial C_w}{\partial x_w} \quad x = l_p \text{ and } x = -l_p \quad (\text{S-8})$$

Due to symmetry the flux will be zero at the center of PE. Pore water concentration is equal to the initial concentration far away from the polymer at $x=l_p+l_w$ and does not change by time:

$$\frac{\partial C_{PE}}{\partial x} = 0 \quad x = 0 \quad (\text{S-9})$$

$$\frac{\partial C_w}{\partial t} = 0 \quad x = l_p + l_w \quad \text{and} \quad x = -l_p - l_w \quad (\text{S-10})$$

Details of model simulation

Numerical solution

Explicit, finite-difference numerical modeling techniques, as described by Crank ² were used to solve the model's equations. Briefly, the explicit method is implemented by dividing the x region with the length of L, into N intervals each of width Δx such that $x_i = i\Delta x$; $i=1, 2, \dots, N$ and $N\Delta x=L$. In this model, polymer region with the length of l_p (half of the polymer thickness) was divided into N_p intervals. Pore water and sediment regions had the same length of l_w and were divided into N_w intervals.

C_i^j is denoted for concentration in location idx and at time jdt, or in other words $C(i\Delta x, j\Delta t)$; $j=1, 2, 3, \dots$

The numerical solution to model equations in pore water, polymer and sediment regions will be as Equations S-11, S-12 and S-13, respectively:

$$\text{Pore water region: } 1 < i < N_w \quad \frac{C_i^{j+1} - C_i^j}{\Delta t} = D \frac{C_{i-1}^j - 2C_i^j + C_{i+1}^j}{\Delta x_w^2} - \left(\frac{\rho}{\varepsilon}\right) k(K_d C_i - C_{i+N}) \quad (\text{S-11})$$

$$\text{Polymer region: } N_w + 1 < i < N \quad \frac{C_i^{j+1} - C_i^j}{\Delta t} = D_{PE} \frac{C_{i-1}^j - 2C_i^j + C_{i+1}^j}{\Delta x_{PE}^2} \quad (\text{S-12})$$

$$\text{Sediment region: } N + 1 < i < N + N_w \quad \frac{C_i^{j+1} - C_i^j}{\Delta t} = k(K_d C_{i-N} - C_i) \quad (\text{S-13})$$

Where $N=N_w+N_p$, and Δx_{PE} and Δx_w are resolutions in PE and pore water region, respectively

We added an extra point at the polymer-water boundary with the concentration of C_g in order to implement the finite difference approximation of second order derivatives:

$$\frac{C_i^{j+1} - C_i^j}{\Delta t} = D \frac{C_{i-1}^j - 2C_i^j + C_g}{\Delta x_w^2} - \left(\frac{\rho}{\varepsilon}\right) k(K_d C_i - C_{i+N}) \quad \text{for } i=N_w \quad (\text{S-14})$$

$$\frac{C_i^{j+1} - C_i^j}{\Delta t} = D_{PE} \frac{K_{PEW} C_g - 2C_{i+1}^j + C_{i+2}^j}{\Delta x_{PE}^2} \quad \text{for } i=N_w \quad (\text{S-15})$$

The concentration of the extra point can be obtained using our boundary layer condition (Equation 8):

$$D_{PE} \frac{C_{N_w+1} - K_{PEW} C_g}{\Delta x_{PE}} = D \frac{C_g - C_{N_w}}{\Delta x_w} \quad (\text{S-16})$$

From Equation S-16, C_g is calculated as:

$$C_g = A * C_{N_w+1} + B * C_{N_w} \quad (\text{S-17})$$

$$A = \frac{\left(\frac{D_{PE}}{dx_p}\right)}{\frac{D_w}{\Delta x_w} + \frac{D_{PE}}{\Delta x_{PE}} K_{PEW}} \quad (\text{S-18})$$

$$B = \frac{\left(\frac{D_w}{dx_w}\right)}{\frac{D_w}{\Delta x_w} + \frac{D_{PE}}{\Delta x_{PE}} K_{PEW}} \quad (\text{S-19})$$

Substituting Equation (S-17) in Equations (S-14) and (S-15), concentrations at the water-polymer boundary can be estimated as follows:

$$\frac{C_{N_w}^{j+1} - C_{N_w}^j}{\Delta t} = \frac{D}{\Delta x_w^2} (A * C_{N_w+1} + (B - 2) * C_{N_w} + C_{N_w-1}) - \left(\frac{\rho k K_d}{\varepsilon}\right) * C_{N_w} + \left(\frac{\rho k}{\varepsilon}\right) * C_{N_w+N} \quad (\text{S-20})$$

$$\frac{C_{N_w+1}^{j+1} - C_{N_w+1}^j}{\Delta t} = \frac{D_{PE}}{\Delta x_{PE}^2} (B * K_{PEW} * C_{N_w} + (A * K_{PEW} - 2) * C_{N_w+1} + C_{N_w+2}) \quad (\text{S-21})$$

Parameter estimation

In order to calculate the slow and fast desorption rate constants of pyrene, chrysene, and benzo(a)pyrene, Equation S-22 (Ghosh et al.³) was fitted with desorption kinetics data of mentioned PAHs. The desorption data were presented for manufactured gas plant site sediments in Ghosh et al.⁴ (Table S1).

$$\frac{S}{S_0} = f e^{-k_f t} + (1 - f) e^{-k_s t} \quad (\text{S-22})$$

Where f is fraction of fast desorbing pool in sediment, k_f is first-order rate constant for fast component, and k_s is first-order rate constant for slow component.

Table S1.1. Fractional Loss of PAHs from Harbor Point Sediment Measured by Ghosh et al.⁴.

Time (day)	Pyrene	Chrysene	Benzo(a)pyrene
0	0	0	0
0.5	0.22	0.06	0.02
2	0.37	0.13	0.04
10	0.49	0.23	0.08

The equilibrium concentration of PAHs in PE ($C_{PE,eq}$) was determined by extracting the PE samplers after 56 days of deployment in the fully mixed PE-sediment system. Another time point measurement of PE concentration after 77 days of deployment confirmed that equilibrium had reached in PE for all PAHs in 56 days (The 77 data have been compared to 56 data in Table S3). The pore water initial (bulk) concentration (C_{w0}) and sediment-water partitioning coefficient (K_d) were calculated using the measured sediment concentration (C_{sed}) and reported values for K_{PEW} ³.

$$C_{w0} = \frac{C_{PE,eq}}{K_{PEW}} \quad (S-23)$$

$$K_d = \frac{C_{sed}}{C_{w0}} \quad (S-24)$$

Table S1.2 summarizes the parameter values used in model simulations for three PAHs.

Table S1.2. Parameter Values Used in Model Simulations

Parameter	Pyrene	Chrysene	Benzo(a)pyrene
Log D_{PE}^a (cm ² /s)	-9.53	-10.28	-10.59
Log D_w^b (cm ² /s)	-5.3	-5.39	-5.4
Log K_{PEW}^c (L/kg)	4.9	5.6	6.2
Log K_d (L/kg)	3.3	4.2	4.9
Log k_f^d (s ⁻¹)	-4.63	-4.76	-4.63
Log K_s^d (s ⁻¹)	-6.53	-6.73	-7.2
ε (cm ³ /cm ³)	0.6		
ρ (g/cm ³)	0.6		

a) Estimated from the correlation provided by Gschwend⁵

b) Gustafson and Dickhut⁶

c) Lohmann⁷

d) Measured by Ghosh et al.⁴

Table S1.3. Comparison of PAH concentration in PE in the fully mixed system after 56 days (C56) and 77 days (C77) of exposure.

P-value is more than 0.05 for all pairs. This indicates that the difference between the 77 and 56 data is not significant at alpha level of 5% for all congeners.

Compound	C56 (ng/mg)	C77 (ng/mg)	p-value
Phenanthrene	44.5 ± 2.7	42.0 ± 1.4	0.23
Anthracene	16.2 ± 0.8	15.3 ± 0.8	0.26
Fluoranthene	51.5 ± 3.0	45.3 ± 4.8	0.12
Pyrene	57.6 ± 3.4	51.4 ± 5.5	0.17
Benz(a)anthracene	31.1 ± 1.3	30.4 ± 3.0	0.72
Chrysene	26.1 ± 1.4	26.3 ± 2.5	0.86
Benzo(b)fluoranthene	20.1 ± 1.4	19.6 ± 1.8	0.71
Benzo(k)fluoranthene	23.2 ± 1.4	21.1 ± 1.7	0.17
Benzo(a)pyrene	48.7 ± 1.5	45.7 ± 4.0	0.25
Indeno(1,2,3-cd)pyrene	42.2 ± 0.7	30.1 ± 16	0.26
Dibenz(a,h)anthracene	4.3 ± 0.3	4.5 ± 0.5	0.76

Quantification of difference between low frequency (5 min pause) and high frequency (2min pause) vibrating data

PE concentration of pyrene, chrysene, and benzo(a)pyrene in high frequency and low frequency vibrating systems at different exposure times have been shown in Table S1.4. Due to loss of some PE strips or low recoveries, duplicate measurements were not available for 7 day and 28 day data. Thus, only 14 day and 56 day data were compared for significance of difference. As indicated in Table S1.5, except for the pyrene concentration in day 14, PE concentrations in the two systems were not significantly different at alpha level of 0.05 (p-values were more than 0.05). The maximum difference between two models' predictions is for pyrene in day 7, which is only 2% (Table S1.6).

Table S1.4. PAH concentration in PE in high frequency and low frequency vibrating systems at different exposure times

Compound	PE concentration in low frequency vibrating system (µg/g)				PE concentration in high frequency vibrating system (µg/g)			
	7 days	14 days	28 days	56 days	7 days	14 days	28 days	56 days
Pyrene	243	279 ± 2.8	279	371 ± 0.1	303	311 ± 5	326	395 ± 24
Chrysene	69.1	75 ± 19	95	113 ± 8	99	95 ± 3	105	139 ± 8
Benzo(a)pyrene	99.8	137 ± 11	123	180 ± 2	152	142 ± 2	124	201 ± 12

Table S1.5. P-values Calculated for the Experimental Data from High and Low Frequency Vibrating Systems.

Compound	P-value	
	14 days	56 days
Pyrene	0.014	0.28
Chrysene	0.28	0.08
Benzo(a)pyrene	0.62	0.13

Model prediction:

Table S1.6. Percent Difference Between High and Low Frequency Model Predictions at Different Exposure Times.

Exposure time (day)	Pyrene	Chrysene	Benzo(a)pyrene
7	2	0.69	0.31
14	0.5	0.48	0.18
28	0.1	0.2	0.12
56	0	0	0

Quantification of difference between 2 min and 6 hour pause models

The percent differences between 2-min and 6-hour models have been indicated in Table S7 for different exposure times. The maximum difference is approximately 6%.

Table S1.7. Percent Difference Between 2-min and 6-hour Model Predictions for Chrysene

Exposure time (day)	% difference
7	6.38
14	3.95
28	1.24
56	0.1

Matlab codes

Fast desorption model in static system

```

outdir = 'Output_Static';
outfile = strcat(outdir, '/', 'Output_Static.txt'); % output file
Lw = 0.1; % half-length of water region (cm)
Lp = 0.00125; % half-length of polymer region (cm)
rho = 0.6; % sediment bulk density (g/cm3)
kpew = 370000; % PE-water partition coefficient for chrysene (cm3/cm3)
kd = 10^4.2/rho; % sediment-water partitioning coefficient (cm3/g)
phi = 0.6; % porosity (cm3/cm3)
Dwater = 4*10^-6; % diffusivity in water (cm2/s)
Dw = Dwater/(1-log(phi^2)); % diffusivity in pore water (cm2/s)
Dp = 5*10^-11; % diffusivity in PE (cm2/s)
kf = 1.7e-5; % fast desorption rate constant (s-1)
Cw0 = 0.4; % initial pore water concentration (ng/cm3)

Np = 5; % discretization number on lp
Nw = 200; % discretization number on lw
dxdp = Lp/Np; % resolution of water/sediment region
dxw = Lw/Nw; % resolution of water or sediment region

A = (Dp/dxdp) / ((Dw/dxw) + (Dp*kpew/dxdp)); %parameter
B = (Dw/dxw) / ((Dw/dxw) + (Dp*kpew/dxdp)); %parameter

% initial condition
S0 = Cw0*kd; %initial sediment concentration (ng/g)
u0 = [Cw0*ones(Nw,1); zeros(Np,1); S0*ones(Nw,1)]; % Initial condition matrix

% defining the second-order differentiation operator
N = Np+Nw;
df1 = ones(Nw,1)*[1,-2,1];
Df1 = (Dw/(dxw^2))*spdiags(df1,[-1 0 1],Nw,Nw);
df2 = ones(Nw,1)*[0,(-rho*kf*kd/phi),0];
Df2 = spdiags(df2,[-1 0 1],Nw,Nw);
DfT1 = Df1+Df2;
df2_bbb = ones(Np,1)*[1,-2,1];
Df2bbbb = spdiags(df2_bbb,[-1 0 1],Np,Np);
DfT2 = [DfT1, zeros(Nw,Np); zeros(Np,Nw), Df2bbbb];
DfT2(1,:) = zeros(1,N);

```

```

DfT2(Nw,:) = [zeros(1,Nw-2), Dw/dxw^2, Dw/dxw^2*(B-2) - rho*kf*kd/phi, Dw/dxw^2*A, zeros(1,Np-1)];
DfT2(Nw+1,:) = [zeros(1,Nw-1), B*kpew, kpew*A-2, 1, zeros(1,Np-2)];
DfT2(end,:) = [zeros(1,Nw+Np-2), 2, -2];

DfT2(Nw+1:end,:) = DfT2(Nw+1:end,:)/(dxp^2)*Dp;

dfs1 = ones(Nw,1)*[0, rho*kf/phi, 0];
Dfs1 = spdiags(dfs1, [-1 0 1], Nw, Nw);
Dfs1 = [Dfs1; zeros(Np, Nw)];
Dfs1(1,:) = zeros(1, Nw);

dfs2 = ones(Nw,1)*[0, kf*kd, 0];
Dfs2 = spdiags(dfs2, [-1 0 1], Nw, Nw);
Dfs2(1,:) = zeros(1, Nw);
Dfs2 = [Dfs2, zeros(Nw, Np)];

dfs3 = ones(Nw,1)*[0, -kf, 0];
Dfs3 = spdiags(dfs3, [-1 0 1], Nw, Nw);
Dfs3(1,:) = zeros(1, Nw);
DfT = [DfT2, Dfs1; Dfs2, Dfs3];
DfT = sparse(DfT);

Mp = @(u_current)(sum(u_current(Nw+1:N)))-(u_current(Nw+1)+u_current(N))/2;
%mass per unit area of PE (ng/cm2)

u_current(:,1) = u0;
u_inf = expm(10^14*DfT)*u0; % Equilibrium concentration (ng/cm3)
M_inf = Mp(u_inf); % Equilibrium mass per unit area of PE (ng/cm2)

T_end = 56*24*3600; % deployment time (s)
tvec = 10000:10000:T_end+10000;

for jtt = 1:length(tvec)
    T_current = tvec(jtt);
    u_current(:,jtt) = expm(T_current*DfT)*u0;
    M(jtt) = Mp(u_current(:,jtt));
end

fid = fopen('Static.txt','w');
fprintf(fid, '%2.2e\n', M/M_inf);
fclose(fid);

```

Fast desorption model in high frequency vibrating system

```

outdir = 'Output_Vibration';
outfile = strcat(outdir, '/', 'Output_Vibration.txt'); % output file
Lw = 0.1; % half-length of water region (cm)
Lp = 0.00125; % half-length of polymer region (cm)
rho = 0.6; % sediment bulk density (g/cm3)
kpew = 370000; % PE-water partition coefficient for chrysene (cm3/cm3)
kd = 10^4.2/rho; % sediment-water partitioning coefficient (cm3/g)

```

```

phi = 0.6; % porosity(cm3/cm3)
Dwater = 4*10^-6; % diffusivity in water (cm2/s)
Dw = Dwater/(1-log(phi^2)); % diffusivity in pore water (cm2/s)
Dp = 5*10^-11; % diffusivity in PE (cm2/s)
kf = 1.4e-5; % fast desorption rate constant (s-1)
Cw0 = 0.4; %initial pore water concentration (ng/cm3)

Np = 5; % discretization number on lp
Nw = 200; % discretization number on lw
dxp = Lp/Np; % resolution of water/sediment region
dxw = Lw/Nw; % resolution of water or sediment region

A = (Dp/dxp) / ((Dw/dxw) + (Dp*kpew/dxp)); %parameter
B = (Dw/dxw) / ((Dw/dxw) + (Dp*kpew/dxp)); %parameter

% initial condition
S0 = Cw0*kd; %initial sediment concentration (ng/g)
u0 = [Cw0*ones(Nw,1); zeros(Np,1); S0*ones(Nw,1)]; % Initial condition matrix

% defining the second-order differentiation operator
N = Np+Nw;
df1 = ones(Nw,1)*[1,-2,1];
Df1 = (Dw/(dxw^2))*spdiags(df1,[-1 0 1],Nw,Nw);
df2 = ones(Nw,1)*[0,(-rho*kf*kd/phi),0];
Df2 = spdiags(df2,[-1 0 1],Nw,Nw);
DfT1 = Df1+Df2;
df2_bbb = ones(Np,1)*[1,-2,1];
Df2bbbb = spdiags(df2_bbb,[-1 0 1],Np,Np);
DfT2 = [DfT1,zeros(Nw,Np); zeros(Np,Nw),Df2bbbb];
DfT2(1,:) = zeros(1,N);
DfT2(Nw,:) = [zeros(1,Nw-2),Dw/dxw^2,Dw/dxw^2*(B-2)-rho*kf*kd/phi,Dw/dxw^2*A,zeros(1,Np-1)];
DfT2(Nw+1,:) = [zeros(1,Nw-1),B*kpew,kpew*A-2,1,zeros(1,Np-2)];
DfT2(end,:) = [zeros(1,Nw+Np-2),2,-2];

DfT2(Nw+1:end,:) = DfT2(Nw+1:end,:)/(dxp^2)*Dp;

dfs1 = ones(Nw,1)*[0,rho*kf/phi,0];
Dfs1 = spdiags(dfs1,[-1 0 1],Nw,Nw);
Dfs1 = [Dfs1;zeros(Np,Nw)];
Dfs1(1,:) = zeros(1,Nw);

dfs2 = ones(Nw,1)*[0,kf*kd,0];
Dfs2 = spdiags(dfs2,[-1 0 1],Nw,Nw);
Dfs2(1,:) = zeros(1,Nw);
Dfs2 = [Dfs2,zeros(Nw,Np)];

dfs3 = ones(Nw,1)*[0,-kf,0];
Dfs3 = spdiags(dfs3,[-1 0 1],Nw,Nw);
Dfs3(1,:) = zeros(1,Nw);
DfT = [DfT2,Dfs1;Dfs2,Dfs3];
DfT = sparse(DfT);

Mp = @(u_current)(sum(u_current(Nw+1:N)))-((u_current(Nw+1)+u_current(N))/2);
%mass per unit area of PE (ng/cm2)

```



```

u_current (:,1) = u0;
u_inf = expm(10^14*DfT)*u0; % Equilibrium concentration (ng/cm3)
M_inf = Mp(u_inf);          % Equilibrium mass per unit area of PE (ng/cm2)

T_end = 120;                % pause cycle duration(s)
tvec = 60:60:T_end;
n = 2;
M(1) = 0;

for k=1:(7*24*3600)/T_end

    for jtt = 1:length(tvec)
        T_current = tvec(jtt);
        u_current (:,jtt) = expm(T_current*DfT)*u0;
        M(n) = Mp(u_current (:,jtt));
        n = n+1;
    end

    u0 = [Cw0*ones(Nw,1);u_current(Nw+1:N,length(tvec));S0*ones(Nw,1)];
    % resetting the initial condition after each pause cycle
end

fid = fopen('Vibration.txt','w');
fprintf(fid,'%2.2e\n',M/M_inf);
fclose(fid);

```

Fully mixed model

```

function mixed
clc;
outdir = 'Output';
outfile = strcat(outdir, '/', 'Output_Mix'); % output file
m = 50; % discretization number in time
N = 250; % discretization number on x
L = 0.0025; % Full-length of polymer region (cm)
rho = 0.6; % sediment bulk density (g/cm3)
kpew = 370000; % PE-water partition coefficient for chrysene(cm3/ cm3)
kd = 10^4.2/rho; % sediment-water partitioning coefficient (cm3/g)
dx = L/(N-1); % resolution of polymer region
D = 5*10^-11; % pyrene diffusivity in PE (cm2/s)
T = 56*24*3600; % deployment time (sec)
dt = length(T)/m; % time interval

%initial condition
C0 = 0.4; % initial water concentration (ng/cm3)
C1= kpew*C0; % concentration at polymer-water boundary (ng/cm3)
Cp0 = [C1;zeros(N-2,1);C1]; % initial condition in polymer region

% defining the second-order differentiation operator
Df2 = D/dx^2*Df2_fd_gen(N);
Df2 = sparse(Df2);
Cp = Cp0;

```

```

for jtt = 2:m
Cp(:,jtt) = Cp(1:N,end)+dt*Df2* Cp(1:N,end);
M(jtt) = (sum(Cp(:,jtt))-( Cp(1,jtt)+ Cp(N,jtt))/2)*(L/(N-1));
end
fid = fopen('Output_Mix.txt','w');
fprintf(fid,'%2.2e\n',M);
fclose(fid);
end
function Df2 = Df2_fd_gen(N)
d = [-1; 0; 1];
B = ones(N,1)*[1,-2,1];
B(N-1,1) = 0;
B(2,3) = 0;
B(1,2) = 0;
B(N,2) = 0;
Df2 = spdiags(B,d,N,N);
end

```

Figures

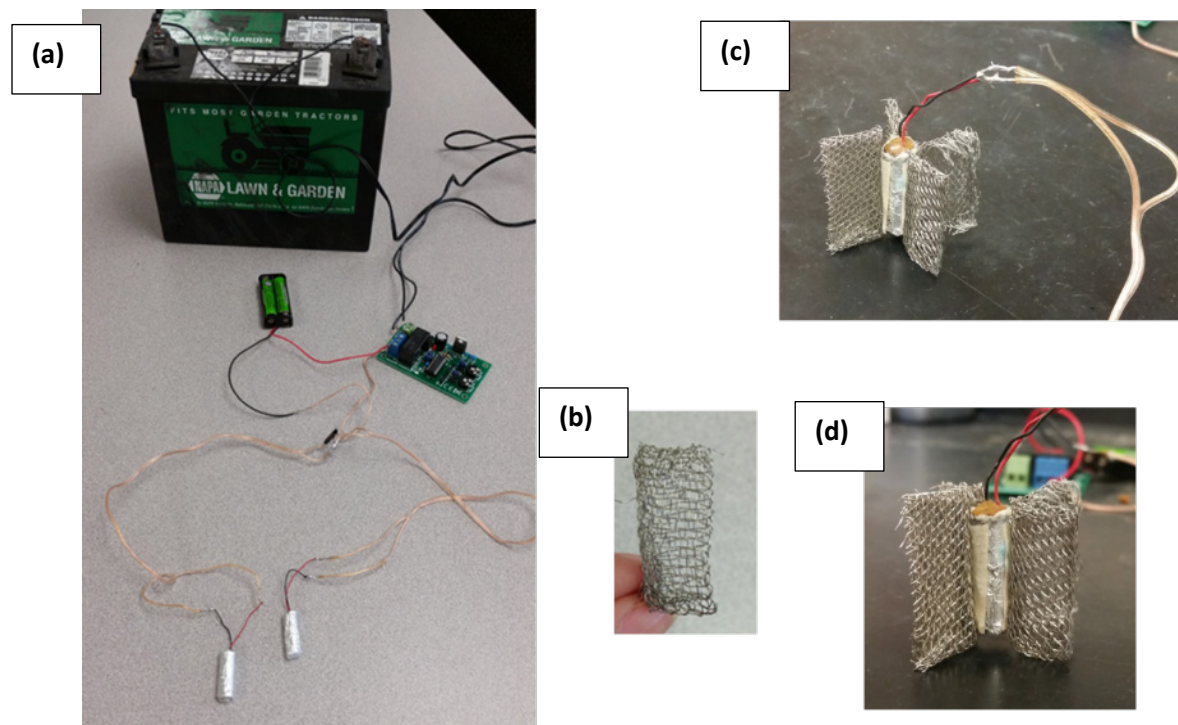


Figure S1.1. Vibrating System Set Up before Insertion into Sediment. a) Two Motors Were Connected in Parallel to a Timer and a Power Supply (2 Rechargeable Batteries 1.2V Each).

The timers were powered by a 12 V battery. b) PE strip (6mm×20mm) closed up in stainless steel mesh. c) & d) Four meshes were attached to each motor like fins.

8 PE strips, 5 cm apart (static deployment)

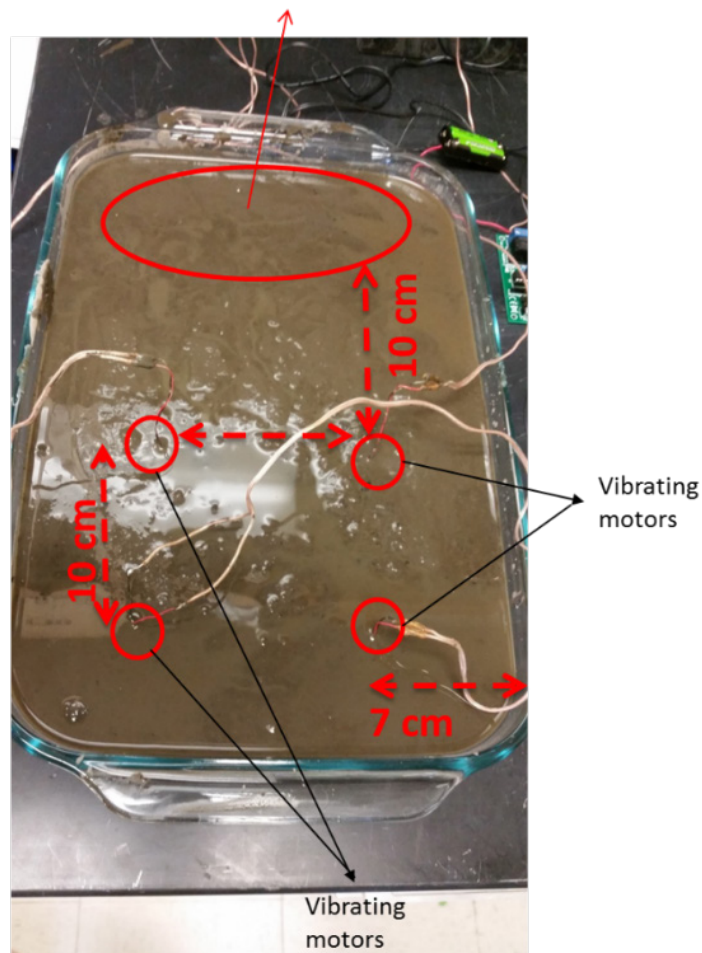


Figure S1.2. Vibrating System Set Up After Insertion into Sediment.

The sediment slurry was placed in a large glass tray (25cm×35cm×6cm). Four motors were placed inside the sediment. Eight additional PE samplers, enclosed in stainless steel meshes without motors, were placed inside the same tray in a static mode far from the vibrating motors



Figure S1.3. Motor Vibration in Sediment.

Based on our visual observation of vibration in sediment, the extent of mixing appears to extend at least 1 cm from the surface of the fins. As shown in the figure (taken with the platform slightly lifted from the sediment surface while vibrating), the vibration causes pressure waves to extend several cm away from the device, with actual fluidized mixing limited to about 1 cm around the sampler fins. The vibration effect is well beyond the thickness of the depletion layer at the end of each pause mode, which is only a few microns.

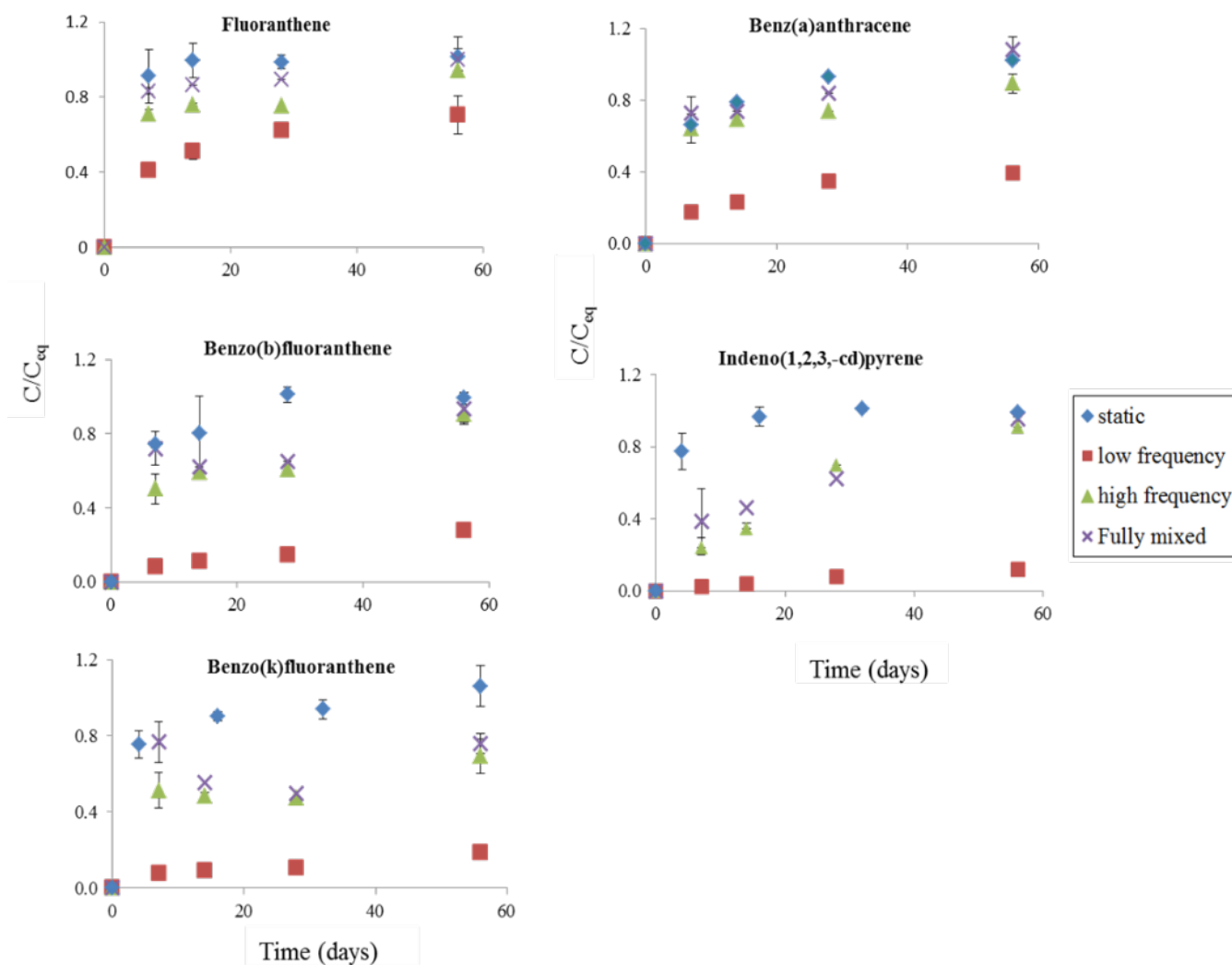


Figure S1.4. Experimental Data for Fractional Uptake of Fluoranthene and Four Heavy PAHs in PE Passive Sampler in Four Different Systems.

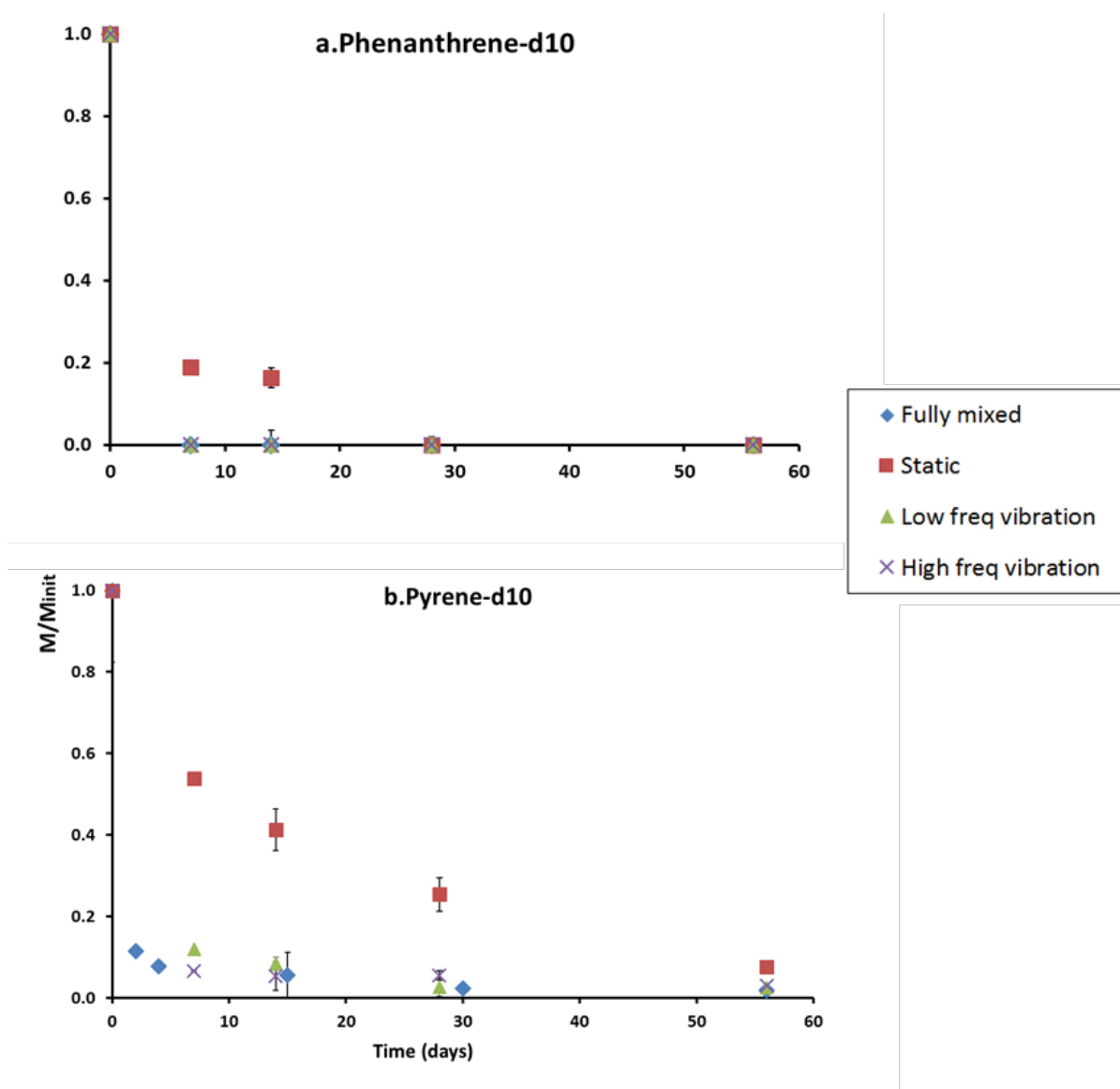


Figure S1.5. Loss Profile of a) Deuterated Phenanthrene and b) Deuterated Pyrene from PE Exposed to Sediment Under Different Mixing Conditions.

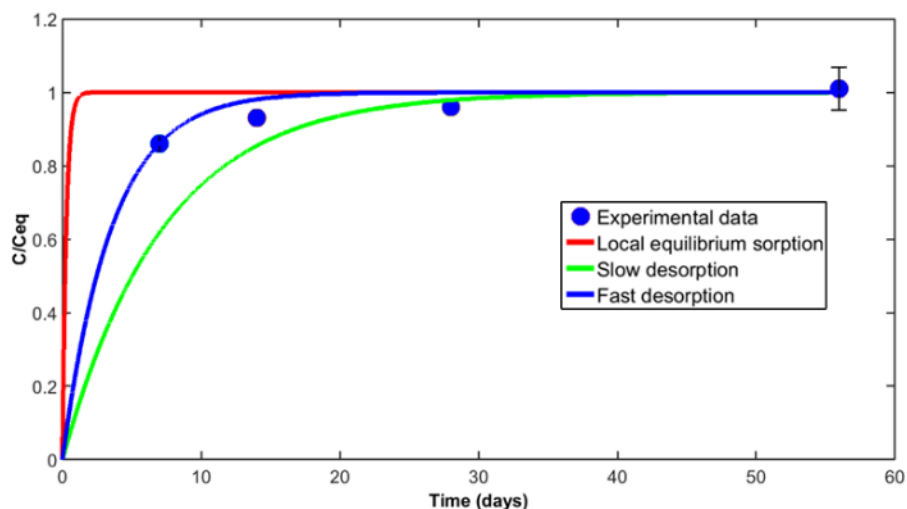


Figure S1.6. Comparison of Three Modeling Approaches for the Vibrating System for Pyrene.

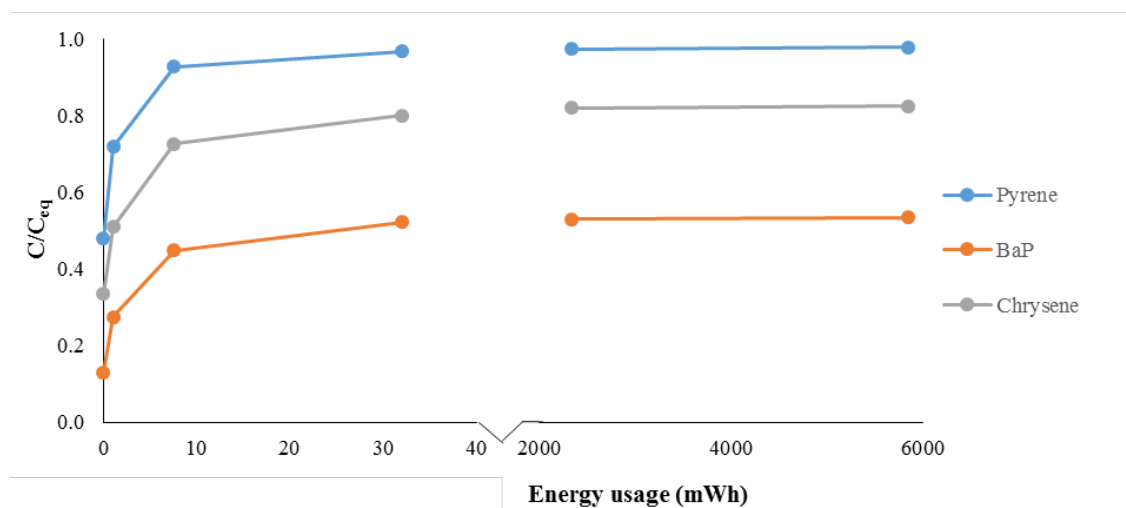


Figure S1.7. Fractional Uptake of Three PAHs into PE Versus Energy Consumption of One Motor After 15 Days of Deployment

Literature Cited

- (1) Fernandez, L. A.; Harvey, C. F.; Gschwend, P. M. Using performance reference compounds in polyethylene passive samplers to deduce sediment porewater concentrations for numerous target chemicals. *Environ. Sci. Technol.* 2009, 43, 8888–8894.
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APPENDIX B SUPPLEMENTAL INFORMATION FOR CHAPTER 2

ANALYSIS OF MEASUREMENT ERRORS IN PASSIVE SAMPLING OF POREWATER PCB CONCENTRATIONS UNDER STATIC AND PERIODICALLY VIBRATED CONDITIONS

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Supporting Information (pp. 17)

Contents

Parameter estimation

Model equations

Details of model simulation

Matlab codes

Tables

Table S2.1. PCB concentrations in sediment based on the mean of three measurements

Table S2.2. PCB concentration in static PE at different exposure times from experiment 1 and 2

Table S2.3. P-values calculated for the PCB concentrations in static PE from experiment 1 and experiment 2

Table S2.4. Comparison of PCB concentration in PE in the mixed system after 28 days (C28) and 56 days (C56) of exposure

Table S2.5. PRC fraction remaining in PE (f_{PRC}) deployed in static system after different exposure times.

Table S2.6. P-values calculated for f_{PRC} in static system from experiment 1 and experiment 2

Table S2.7. Parameter values used in model simulations

Table S2.8. Log K_{PEW} of PCB congeners. For PCB (70+76), PCB (82+151), PCB (163+138), PCB (182+187) the average log K_{PEW} of the two PCBs was used

Table S2.9. Parameters estimated by fitting dual compartment model to normalized desorption data for three PCBs

Figures

Figure S2.1. PCB Homolog distribution in sediment based on the mean of three measurements. Error bars indicate the mean $\pm$ one standard deviation.

Figure S2.2. Prototype of in situ vibrating passive sampler built with copper casing

Figure S2.3. Normalized desorption data for three PCBs and dual compartment model fit

Figure S2.4. Comparison of uptake profile of hexachloro-congeners into PE in static, vibrated, and mixed systems

- Figure S2.5. Comparison of uptake profile of heptachloro-congeners into PE in static, vibrated, and mixed systems
- Figure S2.6. Comparison of uptake profile of octachloro-congeners into static, vibrated, and mixed systems
- Figure S2.7. Comparison of PRC-corrected C_{free} using 7-day and 28-day static samplers with the true equilibrium C_{free} .
- Figure S2.8. Comparison of PRC-corrected C_{free} using 7-day and 28-day vibrated samplers with the true equilibrium C_{free} .
- Figure S2.9. Comparison of PRC-corrected C_{lipid} using 7-day and 28-day static samplers with the true equilibrium C_{lipid} .
- Figure S2.10. Comparison of PRC-corrected C_{lipid} using 7-day and 28-day vibrated samplers with the true equilibrium C_{lipid} .
- Figure S2.11. The ratio of fractional loss of PRCs ($1 - f_{\text{PRC}}$) to the fractional uptake of their corresponding target PCBs into PE (f_{target}) at each time point measurement. Error bars and the thin dashed lines represent the mean $\pm$ one standard deviation ($n=3$).

Parameter estimation

PCB concentrations in PE after 56 days of deployment in the fully mixed PE-sediment system were used as the equilibrium concentration of PCBs in PE ($C_{\text{PE,eq}}$). Since no change was observed in the PE concentrations after 28 days of exposure in this system (The 28 data have been compared to 56 data in Table S1.5). The porewater initial (bulk) concentration (C_{w0}) and sediment-water partitioning coefficient (K_d) were calculated using the measured PCB concentrations in sediment (S) and reported values for K_{PEw} .¹

$$C_{\text{w0}} = \frac{C_{\text{PE,eq}}}{K_{\text{PEw}}} \quad (\text{S-1})$$

$$K_d = \frac{S}{C_{\text{w0}}} \quad (\text{S-2})$$

A two compartment model² was used to describe the desorption kinetics of PCBs from sediment particles into porewater:

$$\frac{S}{S_0} = f e^{-k_f t} + (1 - f) e^{-k_s t} \quad (\text{S-3})$$

Where S is PCB concentration in sediment, S_0 is PCB initial concentration in sediment, f is fraction of fast desorbing pool in sediment, k_f is first-order rate constant for fast component, and k_s is first-order rate constant for slow component.

The model was fitted to the normalized desorption data for PCB 128, 183, and 194 in order to determine in f , k_f , and k_s in Equation S-3 (Figure S1.6). These parameters are reported in Table S1.7.

Table S1.1 summarizes the parameter values used in model simulations for three PCBs.

Model equations

Static system

In a system containing a PE strip with the thickness of $2l_p$ and sediment/porewater with thickness of l_w on both sides, sediment concentration (S) changes following first order kinetics.^{3,4}

$$\frac{\partial S}{\partial t} = k(K_d C_w - S) \quad l_p < x < l_p + l_w \quad \text{and} \quad -l_p < x < -l_p - l_w \quad (\text{S-4})$$

Where t is time (s), S is chemical concentration in sediment (ng/g), K_d is sediment-water partition coefficient (cm^3/g), k is first order desorption rate constant (s^{-1}) and C_w is chemical concentration in water (ng/cm^3)

For a PE strip with concentration C_{PE} and at point x and time t:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad -l_p < x < l_p \quad (\text{S-5})$$

Where C_{PE} is chemical concentration in PE (ng/cm^3) and D_{PE} is chemical diffusivity in PE (cm^2/s)

The transport equation in porewater with concentration of C_w at point x and time t will be as follows:

$$\frac{\partial C_w}{\partial t} = D \frac{\partial^2 C_w}{\partial x^2} - \left(\frac{\rho}{\epsilon}\right) \frac{\partial S}{\partial t} \quad l_p < x < l_p + l_w \quad \text{and} \quad -l_p < x < -l_p - l_w \quad (\text{S-6})$$

Where ρ is sediment bulk density (g/cm^3) and ϵ is porosity (cm^3/cm^3)

D is the diffusivity in water (D_w) after correction for tortuosity:

$$D = \frac{D_w}{1 - \ln \epsilon^2} \quad (\text{S-7})$$

Combining Equations S-4 and S-6, the transport equation in porewater can be re-written as:

$$\frac{\partial C_w}{\partial t} = D \frac{\partial^2 C_w}{\partial x^2} - \left(\frac{\rho}{\epsilon}\right) k(K_d C_w - S) \quad (\text{S-8})$$

Initial conditions

The polymer was initially clean and porewater was assumed to be in equilibrium with sediment.

$$C_{PE} = 0 \quad -l_p \leq x \leq l_p \quad (\text{S-9})$$

$$C_{w0} = S_0/K_d \quad l_p < x < l_p + l_w \quad \text{and} \quad -l_p < x < -l_p - l_w \quad (\text{S-10})$$

Where S_0 is initial chemical concentration in sediment (ng/g) and C_{w0} is initial chemical concentration in water (ng/cm³)

Boundary conditions

Continuity of flux and equilibrium condition was assumed at the PE-water boundary:

$$D_{PE} \frac{\partial C_{PE}}{\partial x_{PE}} = D \frac{\partial C_w}{\partial x_w} \quad x = l_p \text{ and } x = -l_p, \quad t > 0 \quad (\text{S-11})$$

$$C_{PE} = K_{PEW} C_w \quad x = l_p \text{ and } x = -l_p \quad (\text{S-12})$$

Where K_{PEW} is the PE-water partition coefficient (cm³/cm³)

Due to symmetry, the flux will be zero at the center of the PE sheet. Porewater concentration is equal to the initial concentration far away from the polymer at $x=l_p+l_w$ and does not change over time:

$$\frac{\partial C_{PE}}{\partial x} = 0 \quad x = 0 \quad (\text{S-12})$$

$$\frac{\partial C_w}{\partial t} = \frac{\partial S}{\partial t} = 0 \quad x = l_p + l_w \quad \text{and} \quad x = -l_p - l_w \quad (\text{S-13})$$

Vibrating system

In the vibrating system, when the motor is in pause mode, the mass transfer is similar to the static mode and sediment and porewater concentration in the vicinity of the polymer depletes with time. Every time the motor vibrates, the sediment and porewater at the vicinity of the polymer is mixed up. We assumed that this mixing is enough to increase sediment concentration to the initial concentration in sediment (S_0). Porewater concentration right after each vibration pulse will also increase to the initial concentration:

$$C_w = C_{w0} ; \quad S = S_0 \quad l_p < x < l_p + l_w \quad \text{and} \quad -l_p < x < -l_p - l_w, \quad (\text{S-14})$$

Mixed system

Diffusion in a polymer with thickness of $2l_p$ follows Fick's second law:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad -l_p < x < l_p \quad (\text{S-15})$$

The passive sampler was assumed to be initially clean. Since the system is perfectly mixed, the porewater concentration remains constant and equal to the initial value (S_0/K_d) during the deployment time. The boundary condition is defined as:

$$C_{PE} = K_{PEW} C_{w0} \quad x = l_p \text{ and } x = -l_p \quad (\text{S-16})$$

Details of model simulation

Numerical solution

Explicit, finite-difference numerical modeling techniques, as described by Crank⁵ were used to solve the model's equations. Briefly, the explicit method is implemented by dividing the x region with the length of L, into N intervals each of width Δx such that $x_i = i\Delta x$; $i=1, 2, \dots, N$ and $N\Delta x = L$. In this model, polymer region with the length of l_p (half of the polymer thickness) was divided into N_p intervals. Porewater and sediment regions had the same length of l_w and were divided into N_w intervals.

C_i^j is denoted for concentration in location idx and at time jdt, or in other words, $C(i\Delta x, j\Delta t)$; $j=1, 2, 3, \dots$

The numerical solution to model equations in pore water, polymer and sediment regions will be as Equations S-11, S-12 and S-13, respectively:

$$\text{Porewater region: } 1 < i < N_w \quad \frac{C_i^{j+1} - C_i^j}{\Delta t} = D \frac{C_{i-1}^j - 2C_i^j + C_{i+1}^j}{\Delta x_w^2} - \left(\frac{\rho}{\varepsilon}\right) k(K_d C_i - C_{i+N}) \quad (\text{S-17})$$

$$\text{Polymer region: } N_w + 1 < i < N \quad \frac{C_i^{j+1} - C_i^j}{\Delta t} = D_{PE} \frac{C_{i-1}^j - 2C_i^j + C_{i+1}^j}{\Delta x_{PE}^2} \quad (\text{S-18})$$

$$\text{Sediment region: } N + 1 < i < N + N_w \quad \frac{C_i^{j+1} - C_i^j}{\Delta t} = k(K_d C_{i-N} - C_i) \quad (\text{S-19})$$

Where $N = N_w + N_p$, and Δx_{PE} and Δx_w are resolutions in PE and pore water region, respectively

We added an extra point at the polymer-water boundary with the concentration of C_g in order to implement the finite difference approximation of second order derivatives:

$$\frac{C_i^{j+1} - C_i^j}{\Delta t} = D \frac{C_{i-1}^j - 2C_i^j + C_g}{\Delta x_w^2} - \left(\frac{\rho}{\varepsilon}\right) k(K_d C_i - C_{i+N}) \quad \text{for } i = N_w \quad (\text{S-20})$$

$$\frac{C_i^{j+1} - C_i^j}{\Delta t} = D_{PE} \frac{K_{PEW} C_g - 2C_{i+1}^j + C_{i+2}^j}{\Delta x_{PE}^2} \quad \text{for } i = N_w \quad (\text{S-21})$$

The concentration of the extra point can be obtained using our boundary layer condition (Equation 8):

$$D_{PE} \frac{C_{N_w+1} - K_{PEw} C_g}{\Delta x_{PE}} = D \frac{C_g - C_{N_w}}{\Delta x_w} \quad (S-22)$$

From Equation S-22, C_g is calculated as:

$$C_g = A * C_{N_w+1} + B * C_{N_w} \quad (S-23)$$

$$A = \frac{\left(\frac{D_{PE}}{dx_p}\right)}{\frac{D_w}{\Delta x_w} + \frac{D_{PE}}{\Delta x_{PE}} K_{PEw}} \quad (S-24)$$

$$B = \frac{\left(\frac{D_w}{dx_w}\right)}{\frac{D_w}{\Delta x_w} + \frac{D_{PE}}{\Delta x_{PE}} K_{PEw}} \quad (S-25)$$

Substituting Equation (S-23) in Equations (S-20) and (S-21), concentrations at the water-polymer boundary can be estimated as follows:

$$\frac{C_{N_w}^{j+1} - C_{N_w}^j}{\Delta t} = \frac{D}{\Delta x_w^2} (A * C_{N_w+1} + (B - 2) * C_{N_w} + C_{N_w-1}) - \left(\frac{\rho k k_d}{\varepsilon}\right) * C_{N_w} + \left(\frac{\rho k}{\varepsilon}\right) * C_{N_w+N} \quad (S-26)$$

$$\frac{C_{N_w+1}^{j+1} - C_{N_w+1}^j}{\Delta t} = \frac{D_{PE}}{\Delta x_{PE}^2} (B * K_{PEw} * C_{N_w} + (A * K_{PEw} - 2) * C_{N_w+1} + C_{N_w+2}) \quad (S-27)$$

Matlab codes

Fast desorption model in static system for PCB 128

```

outdir = 'Output_Static';
outfile = strcat(outdir, '/', 'Output_Static.txt'); % output file
Lw = 0.1; % half-length of water region (cm)
Lp = 0.00125; % half-length of polymer region (cm)
rho = 0.9; % sediment bulk density (g/cm3)
kpew = 10^6.6*0.93; % PE-water partition coefficient for chrysene (cm3/cm3)
kd = 10^5.47; % sediment-water partitioning coefficient (cm3/g)
phi = 0.7; % porosity (cm3/cm3)
Dwater = 10^-5.41; % diffusivity in water (cm2/s)
Dw = Dwater/(1-log(phi^2)); % diffusivity in pore water (cm2/s)
Dp = 10^-9.35; % diffusivity in PE (cm2/s)
kf = 3.33e-5; % fast desorption rate constant (s-1)
Cw0 = 0.4; % initial pore water concentration (ng/cm3)

Np = 5; % discretization number on lp
Nw = 200; % discretization number on lw
dxp = Lp/Np; % resolution of water/sediment region

```

```

dxw = Lw/Nw; % resolution of water or sediment region

A = (Dp/dxp) / ((Dw/dxw) + (Dp*kpew/dxp)); %parameter
B = (Dw/dxw) / ((Dw/dxw) + (Dp*kpew/dxp)); %parameter

% initial condition
S0 = Cw0*kd; %initial sediment concentration (ng/g)
u0 = [Cw0*ones(Nw,1); zeros(Np,1); S0*ones(Nw,1)]; % Initial condition matrix

% defining the second-order differentiation operator
N = Np+Nw;
df1 = ones(Nw,1)*[1,-2,1];
Df1 = (Dw/(dxw^2))*spdiags(df1,[-1 0 1],Nw,Nw);
df2 = ones(Nw,1)*[0,(-rho*kf*kd/phi),0];
Df2 = spdiags(df2,[-1 0 1],Nw,Nw);
DfT1 = Df1+Df2;
df2_bbb = ones(Np,1)*[1,-2,1];
Df2bbbb = spdiags(df2_bbb,[-1 0 1],Np,Np);
DfT2 = [DfT1, zeros(Nw,Np); zeros(Np,Nw), Df2bbbb];
DfT2(1,:) = zeros(1,N);
DfT2(Nw,:) = [zeros(1,Nw-2), Dw/dxw^2, Dw/dxw^2*(B-2) - rho*kf*kd/phi, Dw/dxw^2*A, zeros(1,Np-1)];
DfT2(Nw+1,:) = [zeros(1,Nw-1), B*kpew, kpew*A-2, 1, zeros(1,Np-2)];
DfT2(end,:) = [zeros(1,Nw+Np-2), 2, -2];

DfT2(Nw+1:end,:) = DfT2(Nw+1:end,:)/(dxp^2)*Dp;

dfs1 = ones(Nw,1)*[0, rho*kf/phi, 0];
Dfs1 = spdiags(dfs1,[-1 0 1],Nw,Nw);
Dfs1 = [Dfs1; zeros(Np,Nw)];
Dfs1(1,:) = zeros(1,Nw);

dfs2 = ones(Nw,1)*[0, kf*kd, 0];
Dfs2 = spdiags(dfs2,[-1 0 1],Nw,Nw);
Dfs2(1,:) = zeros(1,Nw);
Dfs2 = [Dfs2, zeros(Nw,Np)];

dfs3 = ones(Nw,1)*[0, -kf, 0];
Dfs3 = spdiags(dfs3,[-1 0 1],Nw,Nw);
Dfs3(1,:) = zeros(1,Nw);
DfT = [DfT2, Dfs1; Dfs2, Dfs3];
DfT = sparse(DfT);

Mp = @(u_current)(sum(u_current(Nw+1:N)))-(u_current(Nw+1)+u_current(N))/2;
%mass per unit area of PE (ng/cm2)

u_current(:,1) = u0;
u_inf = expm(10^14*DfT)*u0; % Equilibrium concentration (ng/cm3)
M_inf = Mp(u_inf); % Equilibrium mass per unit area of PE (ng/cm2)

T_end = 56*24*3600; % deployment time (s)
tvec = 10000:10000:T_end+10000;

for jtt = 1:length(tvec)
    T_current = tvec(jtt);

```

```

        u_current(:,jtt) = expm(T_current*DfT)*u0;
        M(jtt) = Mp (u_current(:,jtt));
    end

fid = fopen('Static.txt','w');
fprintf(fid,'%2.2e\n',M/M_inf);
fclose(fid);

```

Fast desorption model in two min-pause vibrating system for PCB 128

```

outdir = 'Output_Vibration';
outfile = strcat(outdir, '/', 'Output_Vibration.txt'); % output file
Lw = 0.1; % half-length of water region (cm)
Lp = 0.00125; % half-length of polymer region (cm)
rho = 0.6; % sediment bulk density (g/cm3)
kpew = 10^6.6*0.93; % PE-water partition coefficient for chrysene (cm3/cm3)
kd = 10^5.47; % sediment-water partitioning coefficient (cm3/g)
phi = 0.7; % porosity (cm3/cm3)
Dwater = 10^-5.41; % diffusivity in water (cm2/s)
Dw = Dwater/(1-log(phi^2)); % diffusivity in pore water (cm2/s)
Dp = 10^-9.35; % diffusivity in PE (cm2/s)
kf = 3.33e-5; % fast desorption rate constant (s-1)
Cw0 = 0.4; % initial pore water concentration (ng/cm3)

Np = 5; % discretization number on lp
Nw = 200; % discretization number on lw
dxp = Lp/Np; % resolution of water/sediment region
dxw = Lw/Nw; % resolution of water or sediment region

A = (Dp/dxp) / ((Dw/dxw) + (Dp*kpew/dxp)); %parameter
B = (Dw/dxw) / ((Dw/dxw) + (Dp*kpew/dxp)); %parameter

% initial condition
S0 = Cw0*kd; %initial sediment concentration (ng/g)
u0 = [Cw0*ones(Nw,1); zeros(Np,1); S0*ones(Nw,1)]; % Initial condition matrix

% defining the second-order differentiation operator
N = Np+Nw;
df1 = ones(Nw,1)*[1,-2,1];
Df1 = (Dw/(dxw^2))*spdiags(df1,[-1 0 1],Nw,Nw);
df2 = ones(Nw,1)*[0,(-rho*kf*kd/phi),0];
Df2 = spdiags(df2,[-1 0 1],Nw,Nw);
DfT1 = Df1+Df2;
df2_bbb = ones(Np,1)*[1,-2,1];
Df2bbbb = spdiags(df2_bbb,[-1 0 1],Np,Np);
DfT2 = [DfT1,zeros(Nw,Np); zeros(Np,Nw),Df2bbbb];
DfT2(1,:) = zeros(1,N);
DfT2(Nw,:) = [zeros(1,Nw-2), Dw/dxw^2, Dw/dxw^2*(B-2) - rho*kf*kd/phi, Dw/dxw^2*A, zeros(1,Np-1)];
DfT2(Nw+1,:) = [zeros(1,Nw-1), B*kpew, kpew*A-2, 1, zeros(1,Np-2)];
DfT2(end,:) = [zeros(1,Nw+Np-2), 2, -2];

DfT2(Nw+1:end,:) = DfT2(Nw+1:end,:)/(dxp^2)*Dp;

```



```

dfs1 = ones(Nw,1)*[0, rho*kf/phi, 0];
Dfs1 = spdiags(dfs1, [-1 0 1], Nw, Nw);
Dfs1 = [Dfs1; zeros(Np, Nw)];
Dfs1(1,:) = zeros(1, Nw);

dfs2 = ones(Nw,1)*[0, kf*kd, 0];
Dfs2 = spdiags(dfs2, [-1 0 1], Nw, Nw);
Dfs2(1,:) = zeros(1, Nw);
Dfs2 = [Dfs2, zeros(Nw, Np)];

dfs3 = ones(Nw,1)*[0, -kf, 0];
Dfs3 = spdiags(dfs3, [-1 0 1], Nw, Nw);
Dfs3(1,:) = zeros(1, Nw);
DfT = [DfT2, Dfs1; Dfs2, Dfs3];
DfT = sparse(DfT);

Mp = @(u_current)(sum(u_current(Nw+1:N)) - ((u_current(Nw+1) + u_current(N))/2));
%mass per unit area of PE (ng/cm2)

u_current(:,1) = u0;
u_inf = expm(10^14*DfT)*u0; % Equilibrium concentration (ng/cm3)
M_inf = Mp(u_inf); % Equilibrium mass per unit area of PE (ng/cm2)

T_end = 120; % pause cycle duration(s)
tvec = 60:60:T_end;
n = 2;
M(1) = 0;

for k=1:(7*24*3600)/T_end

    for jtt = 1:length(tvec)
        T_current = tvec(jtt);
        u_current(:,jtt) = expm(T_current*DfT)*u0;
        M(n) = Mp(u_current(:,jtt));
        n = n+1;
    end

    u0 = [Cw0*ones(Nw,1); u_current(Nw+1:N, length(tvec)); S0*ones(Nw,1)];
    % resetting the initial condition after each pause cycle
end

fid = fopen('Vibration.txt', 'w');
fprintf(fid, '%2.2e\n', M/M_inf);
fclose(fid);

```

Mixed model for PCB 128

```

function mixed
clc;
outdir = 'Output';
outfile = strcat(outdir, '/', 'Output_Mix'); % output file
m = 50; % discretization number in time

```

```

N = 250; % discretization number on x
L = 0.0025; % Full-length of polymer region (cm)
rho = 0.6; % sediment bulk density (g/cm3)
kpew = 10^6.6*0.93; % PE-water partition coefficient for chrysene(cm3/cm3)
kd = 10^5.47; % sediment-water partitioning coefficient (cm3/g)
dx = L/(N-1); % resolution of polymer region
D = 10^-9.35; % pyrene diffusivity in PE (cm2/s)
T = 56*24*3600; % deployment time (sec)
dt = length(T)/m; % time interval

%initial condition
C0 = 0.4; % initial water concentration (ng/cm3)
C1= kpew*C0; % concentration at polymer-water boundary (ng/cm3)
Cp0 = [C1;zeros(N-2,1);C1]; % initial condition in polymer region

% defining the second-order differentiation operator
Df2 = D/dx^2*Df2_fd_gen(N);
Df2 = sparse(Df2);
Cp = Cp0;
for jtt = 2:m
Cp(:,jtt) = Cp(1:N,end)+dt*Df2* Cp(1:N,end);
M(jtt) = (sum(Cp(:,jtt))-( Cp(1,jtt)+ Cp(N,jtt))/2)*(L/(N-1));
end
fid = fopen('Output_Mix.txt','w');
fprintf(fid,'%2.2e\n',M);
fclose(fid);
end
function Df2 = Df2_fd_gen(N)
d = [-1; 0; 1];
B = ones(N,1)*[1,-2,1];
B(N-1,1) = 0;
B(2,3) = 0;
B(1,2) = 0;
B(N,2) = 0;
Df2 = spdiags(B,d,N,N);
end

```

Tables

Table S2.1. PCB Concentrations in Sediment Based on the Mean of Three Measurements

PCB congener number	Concentration in sediment (ng/g dry sediment)	PCB congener number	Concentration in sediment (ng/g dry sediment)	PCB congener number	Concentration in sediment (ng/g dry sediment)
(1)	0.00	101	1.98	199	0.39
(3)	0.00	99	0.66	170 + 190	4.40
(4+10)	0.00	83	0.00	198	0.11
(7+9)	0.00	97	0.16	201	3.77
6	0.00	81 + 87	0.67	203 + 196	4.43
008 + 005	0.00	85	0.36	208 + 195	1.06
19	0.00	136	1.14		
12 + 13	0.00	110 + 77	0.00		
18	0.00	82 + 151	2.54		
17 + 15	0.14	135 + 144	1.52		
24 + 27	0.00	107	0.40		
16 + 32	0.43	149 + 123	4.91		
26	0.04	118	0.74		
25	0.15	134	0.00		
31	0.51	114 + 131	0.00		
28	0.00	146	1.65		
21 + 33 + 53	0.34	153	5.53		
51	0.00	132	2.13		
22	0.42	105	0.03		
45	2.35	141	1.28		
46	0.00	137 + 176 + 130	0.00		
52 + 43	0.76	163 + 138	6.90		
49	0.33	158	0.99		
47	0.28	178 + 129	1.64		
48	0.00	175	0.21		
44	0.47	187 + 182	2.64		
37	0.00	183	1.21		
42	0.12	128	0.51		
41 + 71	0.27	185	0.31		
64	0.20	174	1.98		
40	0.19	177	2.03		
100	0.02	202 + 171 + 156	0.00		
63	0.45	157 + 200	0.28		
74	0.43	172 + 197	1.57		
70 + 76	0.52	180	7.74		
66 + 95	2.25	193	1.80		

Table S2.2. PCB Concentration in Static PE at Different Exposure Times from Experiment 1 and 2.

Compound	Experiment 1				Experiment 2			
	7 d	14 d	28 d	56 d	7 d	14 d	28 d	56 d
PCB 31	19.9 ± 2.3	18.5 ± 2.4	26.1 ± 5.6	25.7 ± 4.6	15.7 ± 1.9	16.8 ± 1.8	18.5 ± 2.2	18.1 ± 2.1
PCB 70+ 76	12.1 ± 1.9	11.7 ± 1.5	16.1 ± 2.4	17.7 ± 3.1	10.3 ± 1.2	11.1 ± 1.3	12.4 ± 1.4	12.3 ± 1.4
PCB 99	3.5 ± 0.3	3.7 ± 0.6	8.1 ± 1.7	7.1 ± 1.5	3.6 ± 0.6	4.6 ± 0.5	5.4 ± 0.03	6.2 ± 0.5
PCB 146	15.4 ± 0.6	17.3 ± 1.6	22.0 ± 0.4	26.5 ± 2.7	14.9 ± 0.4	22.3 ± 1.3	21.8 ± 2.2	21.5 ± 1.1
PCB 153	31.5 ± 6.5	36.0 ± 3	45.8 ± 0.9	54.0 ± 5.8	25.7 ± 1.4	28.2 ± 3.7	42.1 ± 8.3	42.3 ± 4.6
PCB 132	6.7 ± 1.4	9.0 ± 0.9	11.3 ± 0.3	13.6 ± 1.1	4.5 ± 0.4	7.2 ± 1	10.4 ± 1.9	10.9 ± 1.1
PCB 163+PCB 138	38.6 ± 0.2	44.7 ± 4.6	56.7 ± 1	66.4 ± 6.4	34.4 ± 2.6	29.2 ± 4.8	49.9 ± 9.9	52.2 ± 5.4
PCB 158	3.1 ± 0.4	3.9 ± 0.3	5.1 ± 0.1	5.9 ± 0.7	2.6 ± 0.4	2.9 ± 0.9	4.6 ± 1.2	4.8 ± 0.4
PCB 178+PCB 129	5.2 ± 0.3	8.6 ± 0.9	11.0 ± 0.8	12.7 ± 1.7	4.3 ± 0.6	7.9 ± 5.3	8.8 ± 1.4	9.8 ± 1.3
PCB 187+PCB 182	25.4 ± 1.7	27.0 ± 2.7	33.2 ± 1.9	36.6 ± 4.5	22.7 ± 1.7	25.3 ± 2.6	31.8 ± 4.8	33.8 ± 4.8
PCB 183	8.3 ± 0.3	10.6 ± 1	17.5 ± 1	19.1 ± 2.4	7.2 ± 0.5	9.2 ± 1.3	13.9 ± 2.1	14.6 ± 2.2
PCB 128	2.5 ± 0.1	2.9 ± 0.2	3.8 ± 0.1	4.7 ± 0.5	1.5 ± 0.1	1.9 ± 0.4	3.6 ± 0.8	3.7 ± 0.4
PCB 185	3.8 ± 0.1	4.0 ± 0.4	4.7 ± 0.4	5.1 ± 0.7	2.1 ± 0.3	2.7 ± 0.4	3.8 ± 0.7	3.9 ± 0.6
PCB 201	24.4 ± 1.6	26.3 ± 3.2	41.2 ± 3.1	43.8 ± 5.7	21.5 ± 2.1	21.3 ± 3.5	35.1 ± 6.5	36.5 ± 5.9
PCB 203+PCB 196	26.4 ± 0.5	28.2 ± 3	45.5 ± 3.7	48.6 ± 5.9	23.5 ± 2.4	26.9 ± 4	39.4 ± 6.7	40.5 ± 6.5
PCB 208+PCB 195	5.7 ± 0.7	6.9 ± 0.9	8.1 ± 0.6	8.8 ± 1.1	3.5 ± 0.3	3.7 ± 0.6	6.8 ± 1.2	7.4 ± 1.1
PCB 194	12.0 ± 0.8	18.1 ± 2	21.0 ± 2.3	21.6 ± 2.2	10.0 ± 1.5	8.5 ± 0.7	17.9 ± 3.4	18.0 ± 2.9

Table S2.3. P-values Calculated for the PCB Concentrations in Static PE from Experiment 1 and Experiment 2.

P-value is more than 0.05 for all pairs. This indicates that the difference between PCB uptake in two experiments is not significant at alpha level of 5% for all congeners.

Compound	P-value			
	7 d	14 d	28 d	56 d
PCB 31	0.1	0.45	0.17	0.12
PCB 70+ 76	0.38	0.64	0.2	0.1
PCB 99	0.7	0.18	0.13	0.51
PCB 146	0.19	0.07	0.87	0.24
PCB 153	0.2	0.08	0.51	0.14
PCB 132	0.27	0.11	0.5	0.10
PCB 163+ 138	0.1	0.07	0.35	0.12
PCB 158	0.34	0.18	0.56	0.26
PCB 178+ 129	0.11	0.83	0.1	0.18
PCB 187+ 182	0.11	0.07	0.68	0.57
PCB 183	0.06	0.27	0.08	0.17
PCB 128	0.06	0.05	0.73	0.15
PCB 185	0.08	0.068	0.14	0.18
PCB 201	0.09	0.11	0.26	0.30
PCB 203+ 196	0.08	0.35	0.28	0.29
PCB 208+ 195	0.15	0.05	0.2	0.27
PCB 194	0.07	0.14	0.31	0.21

Table S2.4. Comparison of PCB Concentration in PE in the Mixed System after 28 Days (C28) and 56 Days (C56) of Exposure.

P-value is more than 0.05 for all pairs. This indicates that the difference between the 28 and 56 data is not significant at alpha level of 5% for all congeners.

Compound	C28 (ng/g)	C56 (ng/g)	P-values
PCB 31	60.2 ± 8.3	58.4 ± 10.9	0.71
PCB 70+ 76	56.7 ± 10.1	34.9 ± 6.01	0.52
PCB 99	23.91 ± 2.8	20.5 ± 4.5	0.36
PCB 146	61.5 ± 23.8	50.8 ± 8.9	0.51
PCB 153	208.6 ± 84.6	178.7 ± 35.1	0.60
PCB 132	52.6 ± 27.9	38.0 ± 8.4	0.47
PCB 163+PCB 138	294.3 ± 156.3	221.1 ± 46.5	0.52
PCB 158	40.1 ± 31.2	26.5 ± 7.4	0.54
PCB 178+PCB 129	48.8 ± 19.9	42.7 ± 8	0.66
PCB 187+PCB 182	109.9 ± 15.3	118.3 ± 18	0.57
PCB 183	63.0 ± 15.9	62.3 ± 12.3	0.95
PCB 128	26.2 ± 20.8	16.3 ± 5.3	0.50
PCB 185	11.8 ± 1.8	12.4 ± 2.2	0.74
PCB 201	115.3 ± 17	136.6 ± 22.1	0.25
PCB 203+PCB 196	129.5 ± 22	155.8 ± 27.7	0.26
PCB 208+PCB 195	26.0 ± 5.4	30.8 ± 5.4	0.34
PCB 194	54.3 ± 9.2	64.9 ± 14.6	0.36

Table S2.5. PRC Fraction Remaining in PE (f_{PRC}) Deployed in Static System after different Exposure Times.

Compound	Experiment 1				Experiment 2			
	7 d	14 d	28 d	56 d	7 d	14 d	28 d	56 d
PCB 29	0.7 ± 0.04	0.6 ± 0.03	0.45 ± 0.03	0.32 ± 0.03	0.63 ± 0.02	0.60 ± 0.02	0.46 ± 0.02	0.32 ± 0.02
PCB 69	0.75 ± 0.03	0.67 ± 0.03	0.54 ± 0.02	0.39 ± 0.02	0.73 ± 0.01	0.71 ± 0.01	0.56 ± 0.00	0.39 ± 0.04
PCB 155	0.89 ± 0.02	0.83 ± 0.04	0.78 ± 0.07	0.64 ± 0.00	0.82 ± 0.03	0.81 ± 0.01	0.76 ± 0.09	0.64 ± 0.06
PCB 192	0.93 ± 0.05	0.9 ± 0.05	0.88 ± 0.06	0.74 ± 0.01	0.94 ± 0.01	0.86 ± 0.04	0.90 ± 0.04	0.74 ± 0.01

Table S2.6. P-values Calculated for f_{PRC} in Static System from Experiment 1 and Experiment 2.

P-value is more than 0.05 for all pairs. This indicates that the difference between PRC loss in two experiments is not significant at alpha level of 5% for all congeners.

Compound	P-value			
	7 d	14 d	28 d	56 d
PCB 29	0.3	0.84	0.90	0.22
PCB 69	0.56	0.94	0.21	0.30
PCB 155	0.13	0.54	0.41	0.48
PCB 192	0.85	0.32	0.17	0.21

Table S2.7. Parameter Values used in Model Simulations

Parameter	PCB 128	PCB 180	PCB 194
Log D_{PE}^a (cm ² /s)	-9.35	-9.53	-9.7
Log D_w^b (cm ² /s)	-5.41	-5.44	-5.47
Log K_{PEW}^c (L/kg)	6.7	7.4	7.9
Log K_d (L/kg)	5.47	6.13	6.8
k_f (s ⁻¹)	3.33×10^{-5}	3.06×10^{-5}	2.78×10^{-5}
ε (cm ³ /cm ³)	0.7		
ρ (g/cm ³)	0.9		

- a) Lohmann⁶
b) Gustafson and Dickhut⁷
c) Ghosh et al.¹

Table S2.8. Log K_{PEW} of PCB Congeners.

For PCB (70+76), PCB (82+151), PCB (163+138), PCB (182+187) the average log K_{PEW} of the two PCBs was used

PCB congener	log K_{ow}^a		log K_{PEW}^b
31	5.67		5.43
70+76	6.2		6.06
76	6.13		5.97
99	6.39		6.28
82+151	6.2		6.06
118	6.74		6.69
128	6.74		6.69
132	6.58		6.50
138	6.99		6.99
151	6.32		6.20
153	6.92		6.91
158	7.02		7.02
163+138	6.83		6.80
177	7.08		7.09
180	7.36		7.42
183	7.2		7.24
185	7.11		7.13
182+187	7.2		7.24
187	7.17		7.20
194	7.8		7.94
195	7.56		7.66
196	7.65		7.77
201	7.62		7.73
203	7.65		7.77
208	7.71		7.84

- a) Hawker and Connell⁸
b) Ghosh et al.¹

Figures

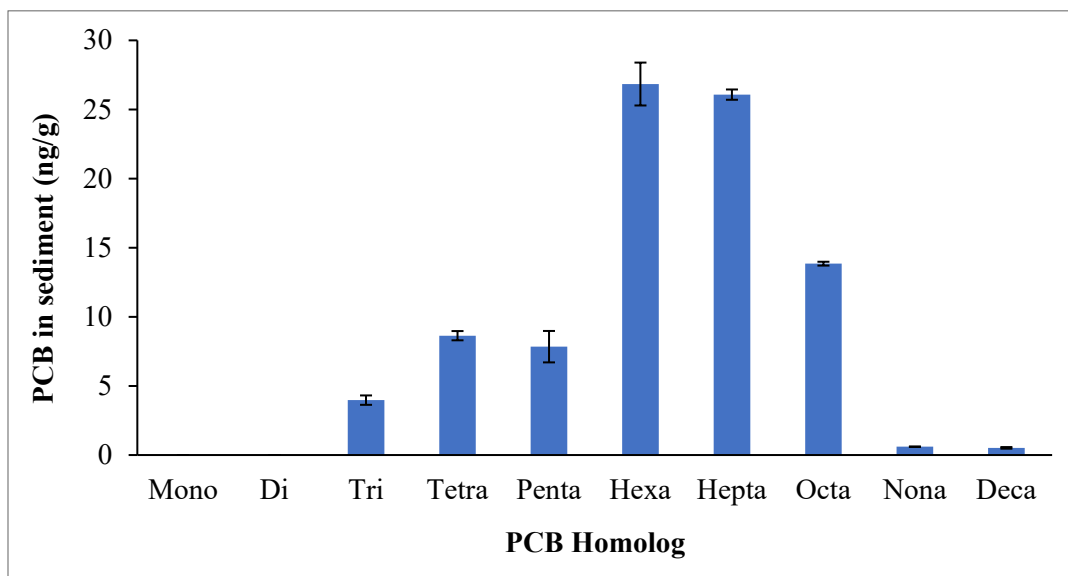


Figure S2.1. PCB Homolog Distribution in Sediment Based on the Mean of Three Measurements.

Error bars indicate the mean $\pm$ one standard deviation ($n=3$).

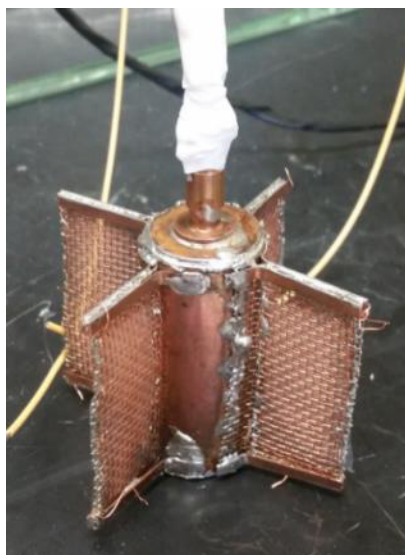


Figure S2.2. Prototype of In Situ Vibrating Passive Sampler Built with Copper Casing

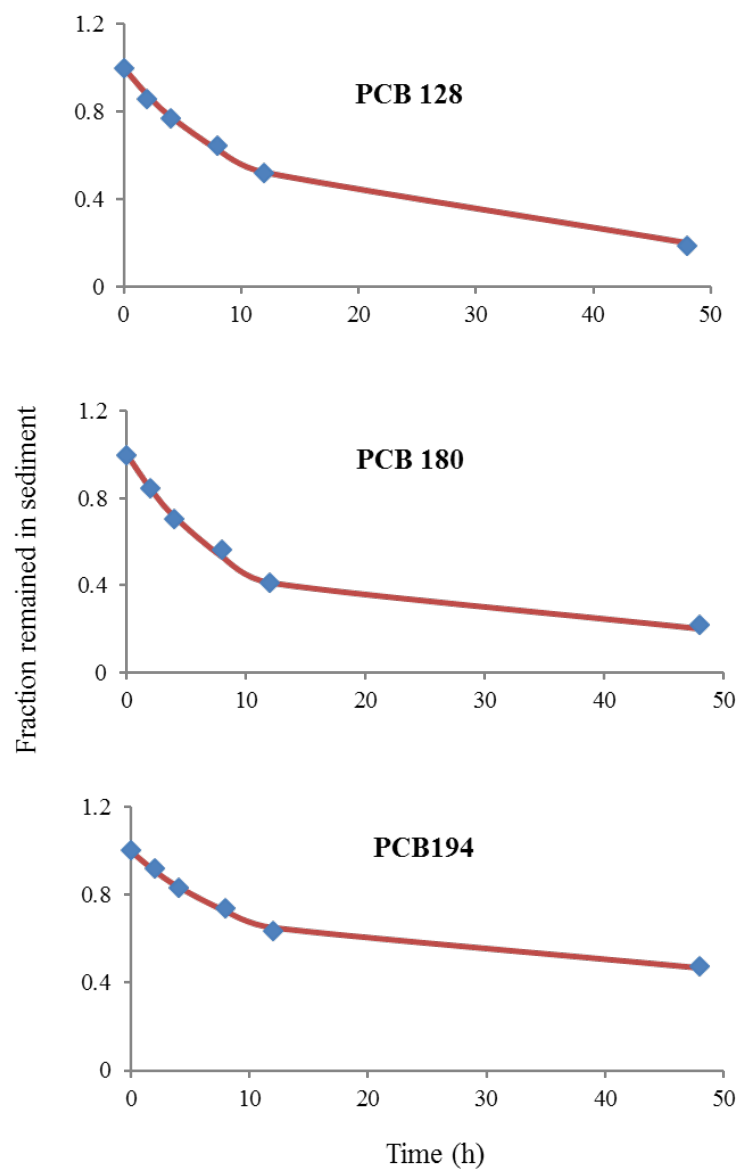


Figure S2.3. Normalized Desorption Data for Three PCBs and Dual Compartment Model Fit.

Table S2.9. Parameters Estimated by Fitting Dual Compartment Model to Normalized Desorption Data for Three PCBs

Compound	f	$k_f (s^{-1})$	$k_s (s^{-1})$
PCB 128	0.48	3.33×10^{-5}	5.56×10^{-6}
PCB 180	0.8	3.06×10^{-5}	7×10^{-7}
PCB 194	0.48	2.78×10^{-5}	7×10^{-7}

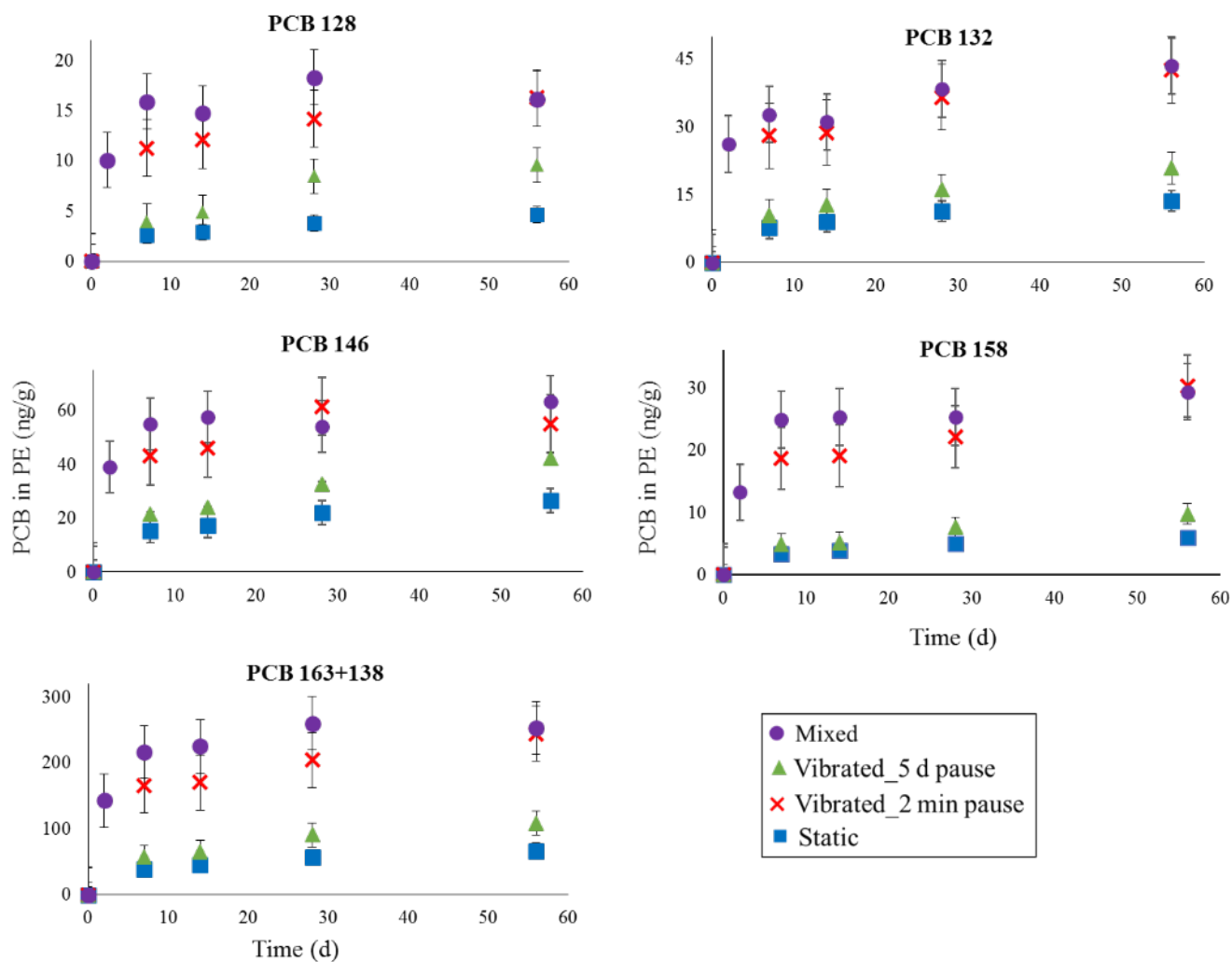


Figure S2.4. Comparison of Uptake Profile of Hexachloro-congeners into PE in Static, Vibrated, and Mixed Systems.

Error bars represent the mean $\pm$ one standard deviation (n=3).

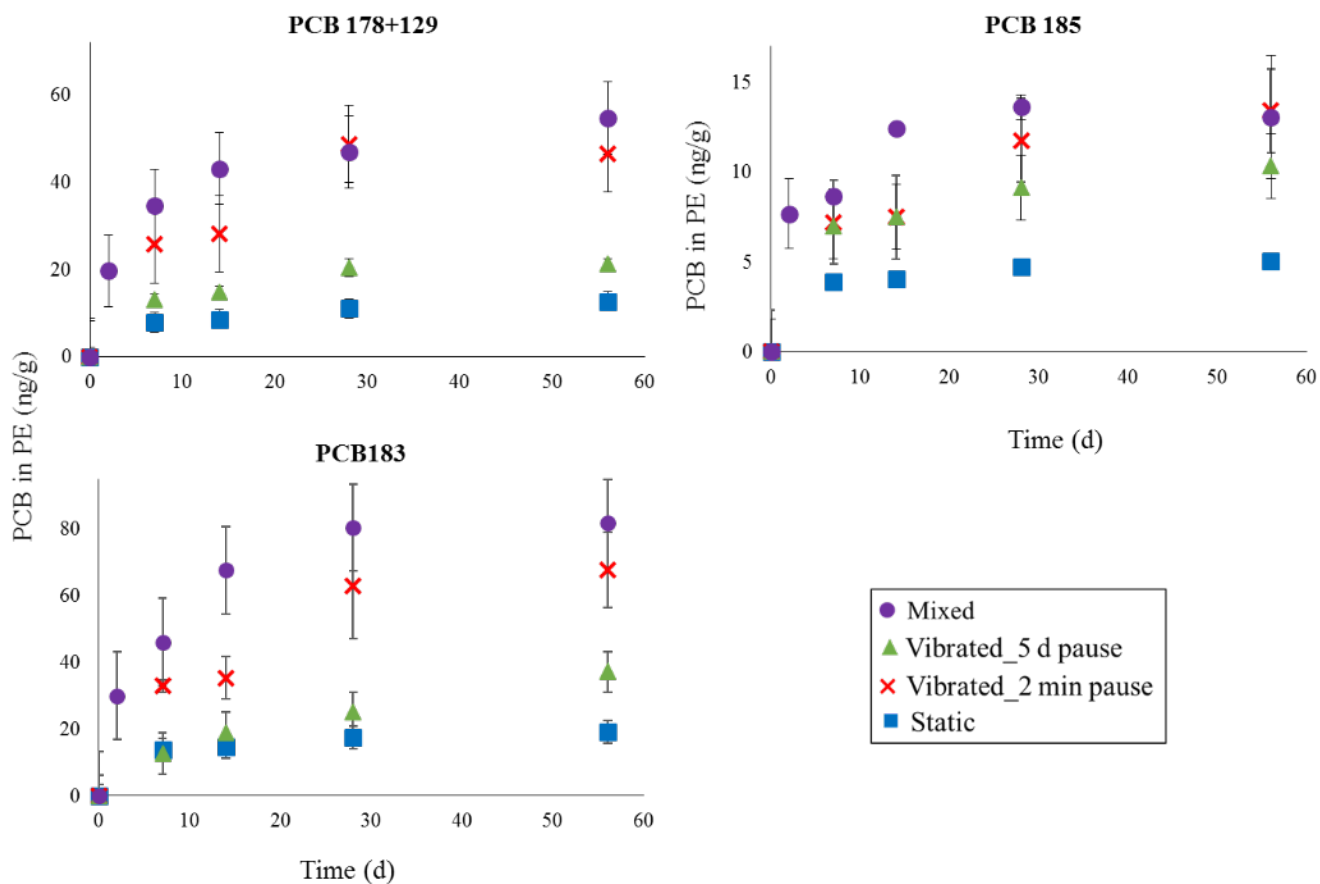


Figure S2.5. Comparison of Uptake Profile of Heptachloro-congeners Into PE in Static, Vibrated, and Mixed Systems.

Error bars represent $\pm$ the mean $\pm$ one standard deviation ($n=3$).

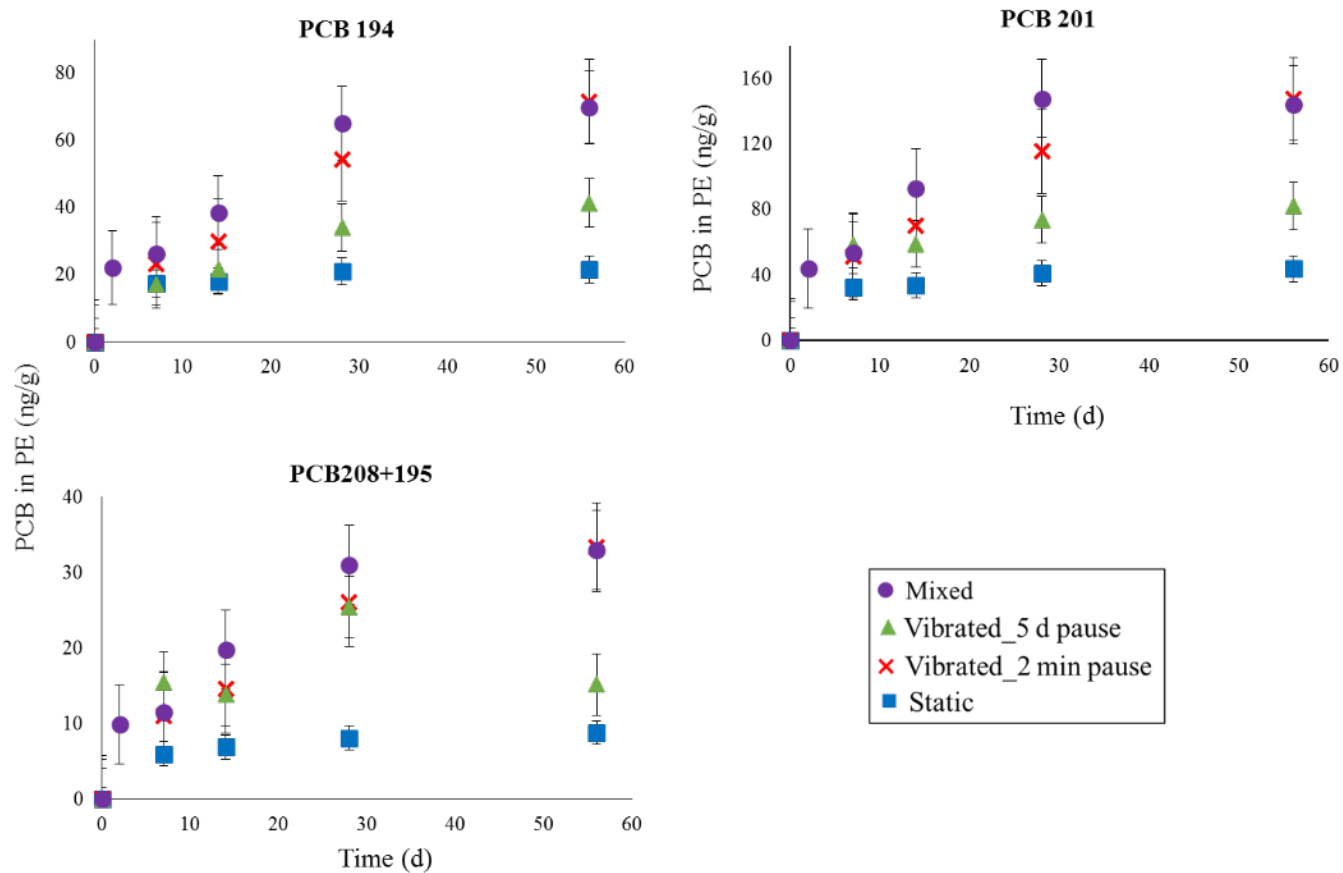


Figure S2.6. Comparison of Uptake Profile of Octachloro-congeners into PE in Static, Vibrated, and Mixed Systems.

Error bars represent the mean $\pm$ one standard deviation ($n=3$).

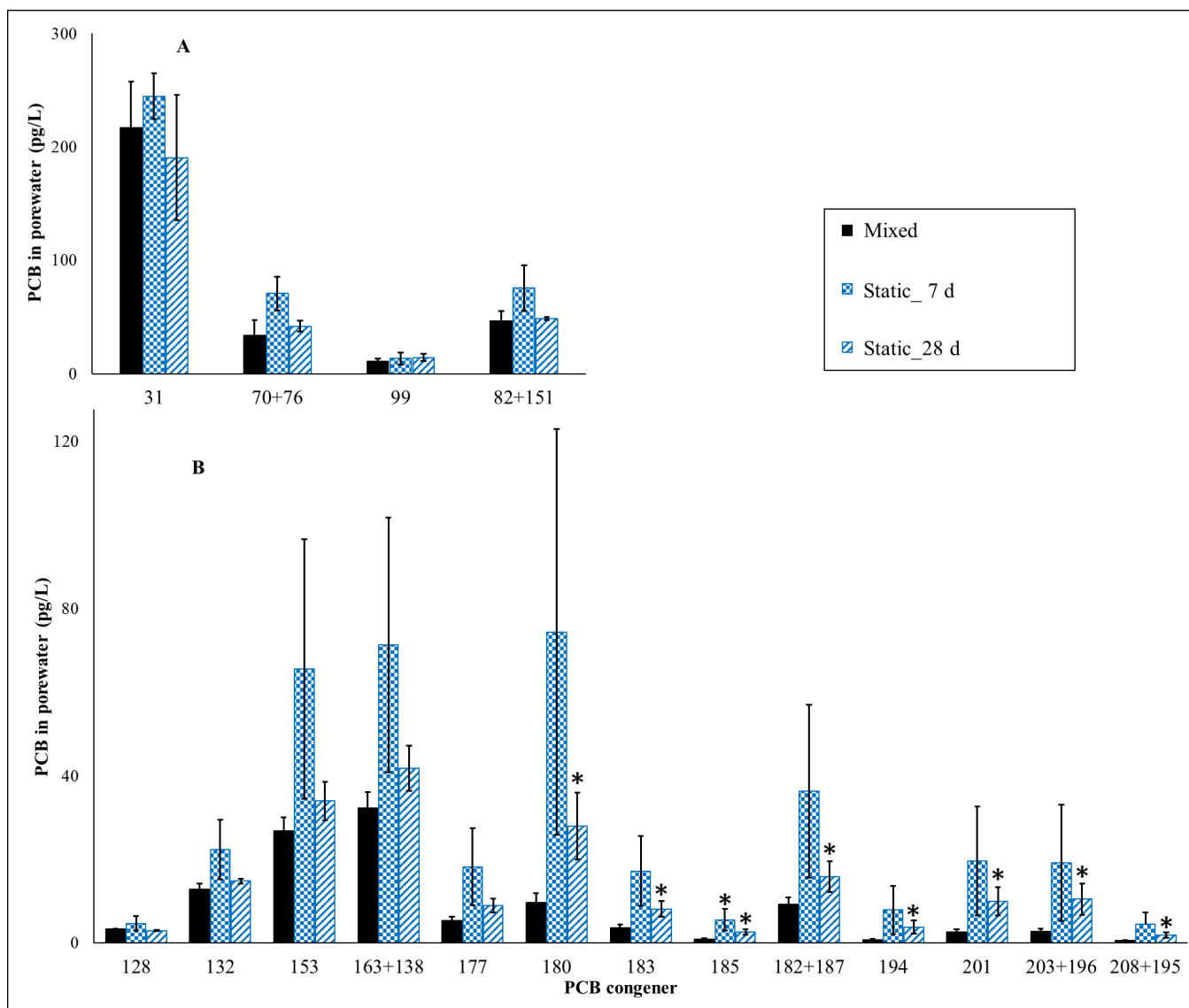


Figure S2.7. Comparison of PRC-corrected C_{free} Using 7-day and 28-day Static Samplers with the True Equilibrium C_{free} .

Plot A shows PCB congeners that belong to pentachloro- and lower molecular weight congeners and plot B indicates congeners that belong to hexachloro- and higher molecular weight congeners. The measured C_{free} was estimated based on the measured equilibrium concentration in PE after 56 days of deployment in the mixed system. The corrected C_{free} was calculated based on the PRC-corrected PE equilibrium concentration in static system. PE equilibrium concentrations were converted to C_{free} using the correlations provided by Ghosh et al.¹ The corrected concentrations that are statistically different from the measured C_{free} values (with alpha level of 5%) are indicated with an asterisk. Error bars represent the mean $\pm$ one standard deviation ($n=3$).

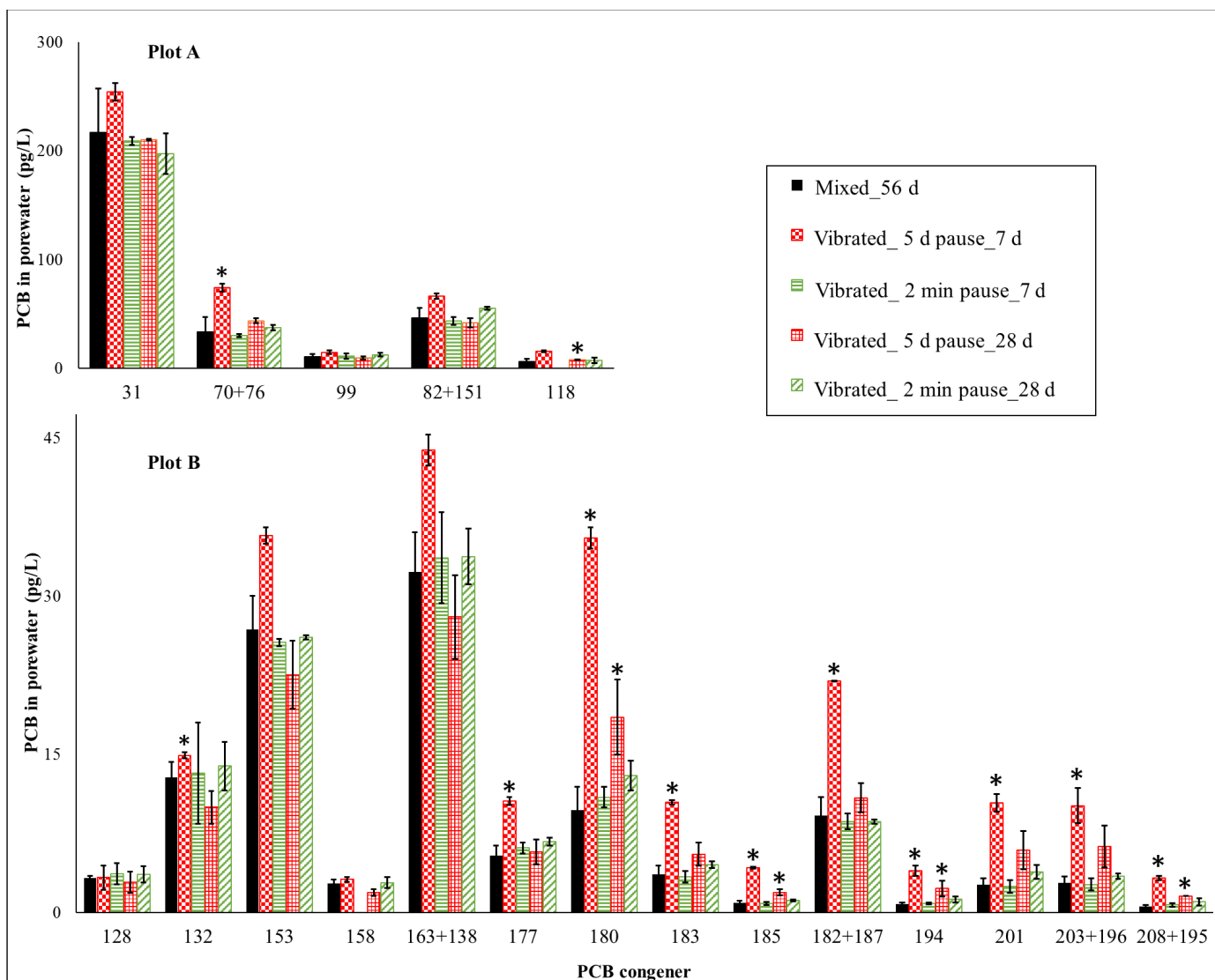


Figure S2.8. Comparison of PRC-corrected C_{free} Using 7-day and 28-day Vibrated Samplers with the True Equilibrium C_{free} .

Plot A shows PCB congeners that belong to pentachloro- and lower molecular weight congeners and plot B indicates congeners that belong to hexachloro- and higher molecular weight congeners. The measured C_{free} was estimated based on the measured equilibrium concentration in PE after 56 days of deployment in the mixed system. The corrected C_{free} was calculated based on the PRC-corrected PE equilibrium concentration in vibrating system. PE equilibrium concentrations were converted to C_{free} using the correlations provided by Ghosh et al.¹ The corrected concentrations that are statistically different from the measured C_{free} values (with alpha level of 5%) are indicated with an asterisk. Error bars represent the mean $\pm$ one standard deviation ($n=3$).

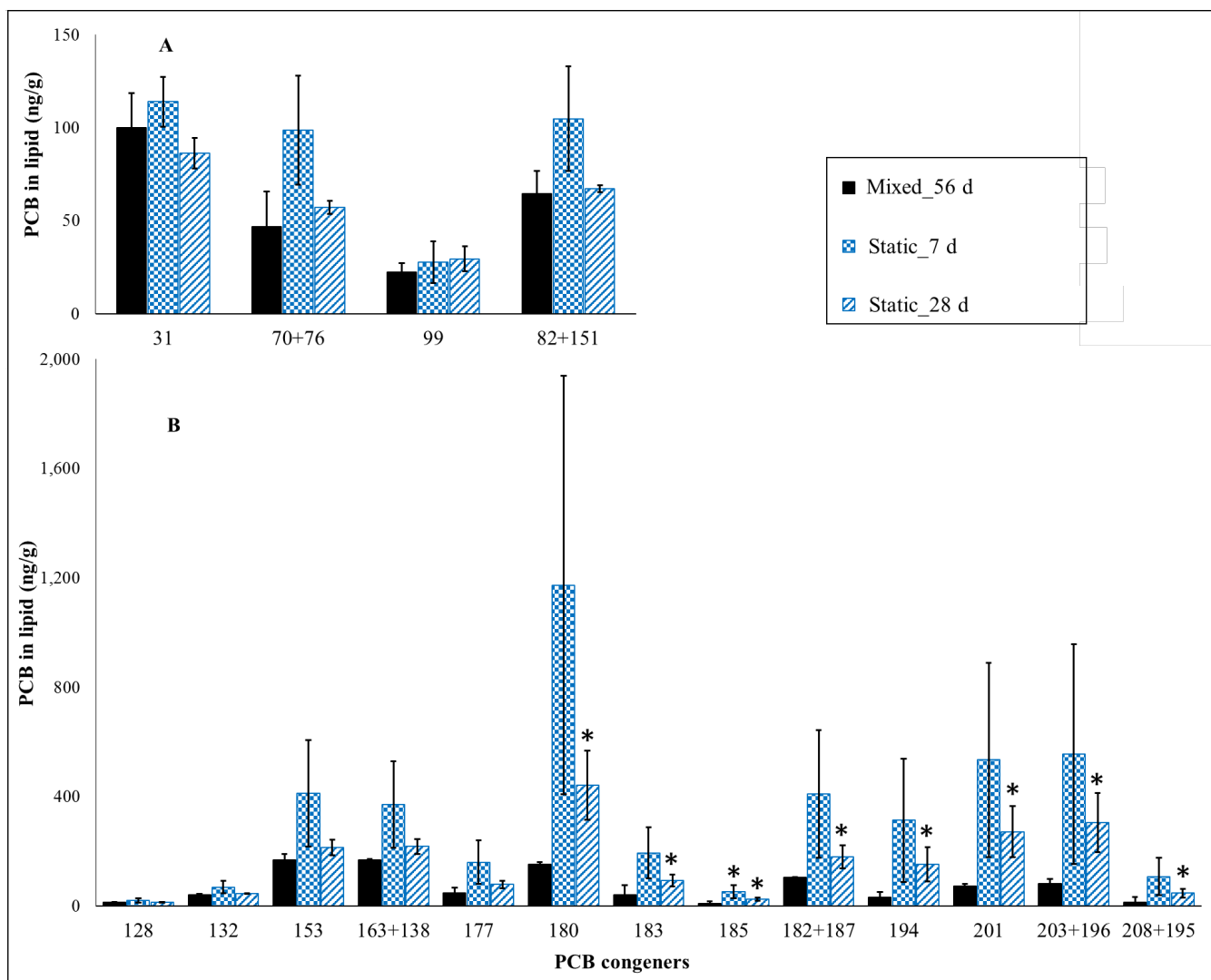


Figure S2.9. Comparison of PRC-corrected C_{lipid} Using 7-day and 28-day Static Samplers with the True Equilibrium C_{lipid} .

Plot A shows PCB congeners that belong to pentachloro- and lower molecular weight congeners and plot B indicates congeners that belong to hexachloro- and higher molecular weight congeners. The measured C_{lipid} was estimated based on the measured equilibrium concentration in PE after 56 days of deployment in the mixed system. The corrected C_{lipid} was calculated based on the PRC-corrected PE equilibrium concentration in static system. PE equilibrium concentrations were converted to C_{free} and C_{lipid} using the correlations provided by Ghosh et al.¹, and Werner et al.⁹, respectively. The corrected concentrations that are statistically different from the measured C_{lipid} values (with alpha level of 5%) are indicated with an asterisk. Error bars represent the mean $\pm$ one standard deviation ($n=3$).

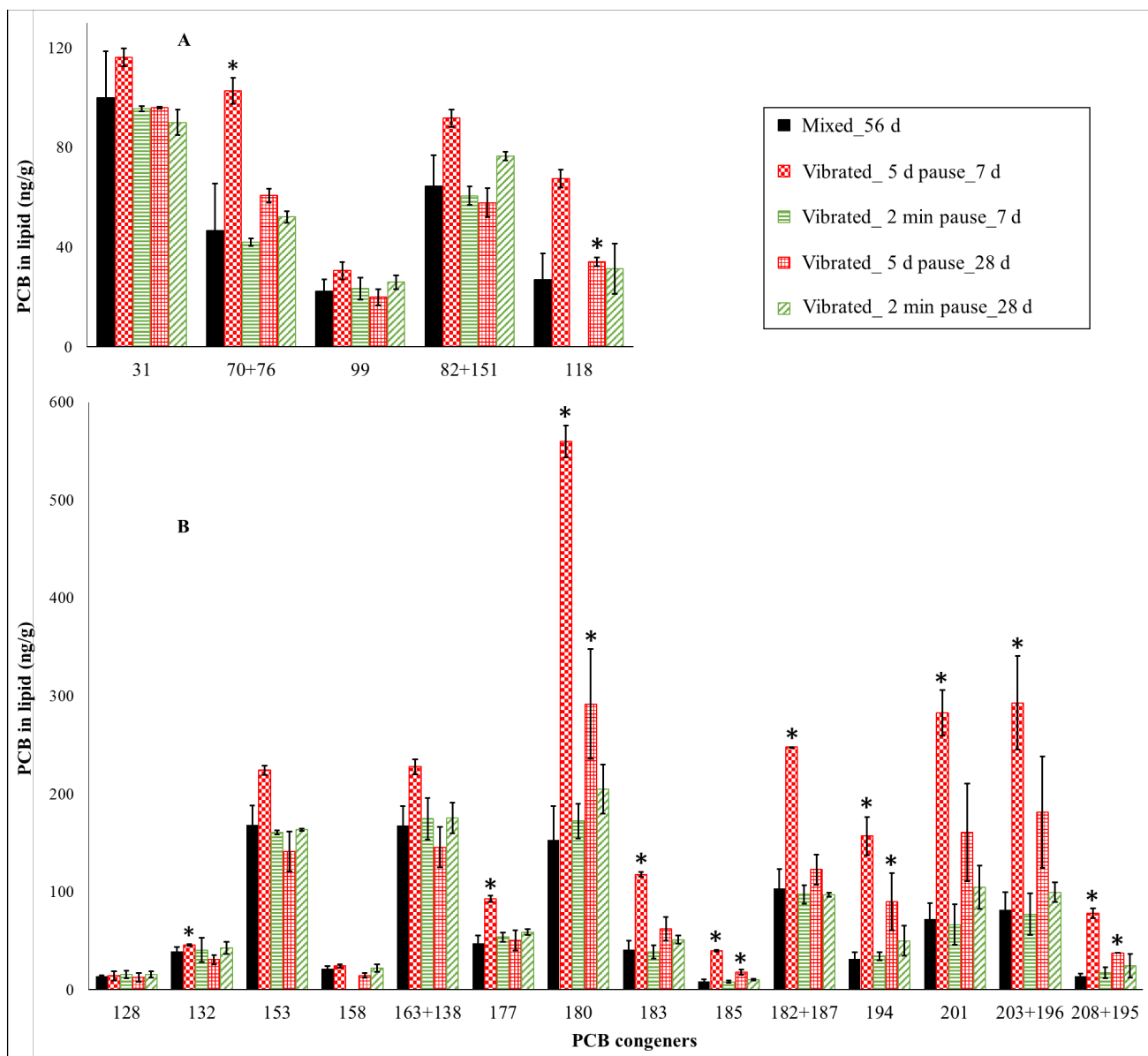


Figure S2.10. Comparison of PRC-corrected C_{lipid} Using 7-day and 28-day Vibrated Samplers with the True Equilibrium C_{lipid} .

Plot A shows PCB congeners that belong to pentachloro- and lower molecular weight congeners and plot B indicates congeners that belong to hexachloro- and higher molecular weight congeners. The measured C_{lipid} was estimated based on the measured equilibrium concentration in PE after 56 days of deployment in the mixed system. The corrected C_{lipid} was calculated based on the PRC-corrected PE equilibrium concentration in vibrating system. PE equilibrium concentrations were converted to C_{free} and C_{lipid} using the correlations provided by Ghosh et al.¹, and Werner et al.⁹, respectively. The corrected concentrations that are statistically different from the measured C_{lipid} values (with alpha level of 5%) are indicated with an asterisk. Error bars represent the mean $\pm$ one standard deviation ($n=3$).

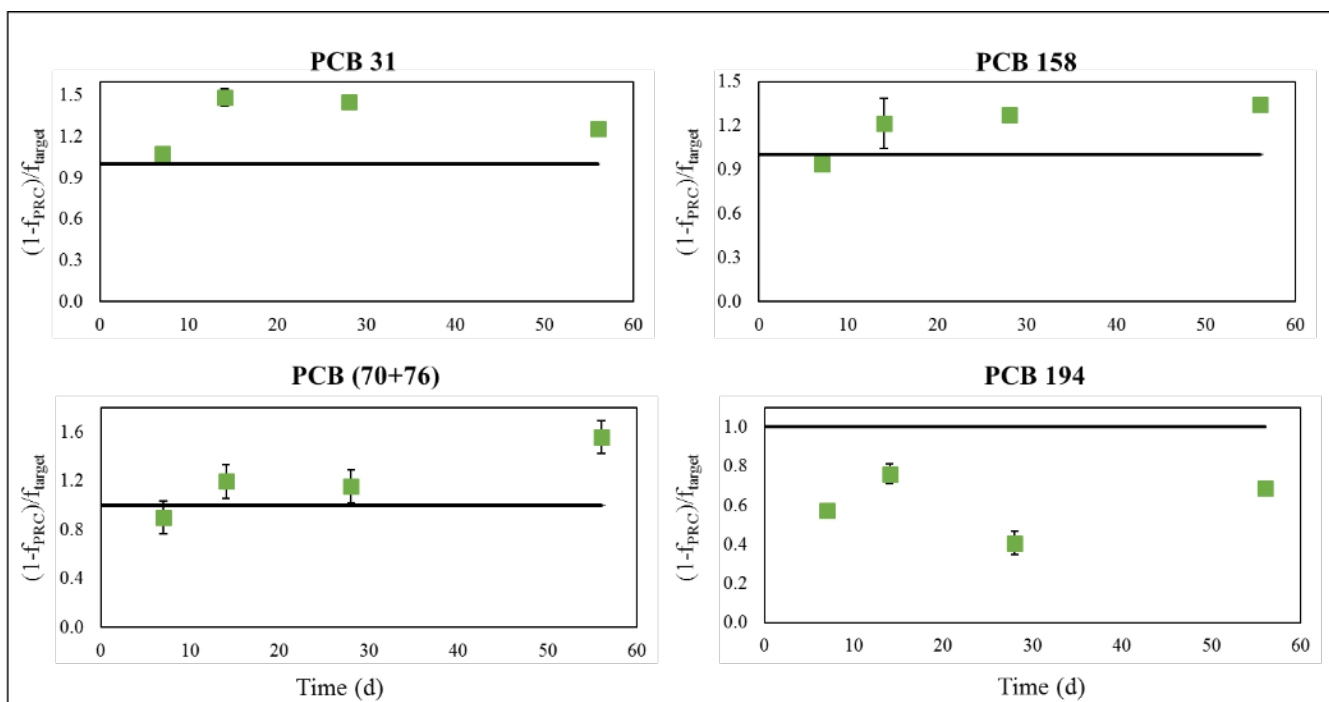


Figure S2.11. The Ratio of Fraction Loss of PRCs ($1-f_{\text{PRC}}$) to the Fractional Uptake of Their Corresponding Target PCBs into PE (f_{target}) at Each Time Point Measurement.

Error bars and the thin dashed lines represent the mean $\pm$ one standard deviation ($n=3$).

References

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APPENDIX C SUPPLEMENTAL INFORMATION FOR CHAPTER 3

VIBRATING SAMPLER P2 FABRICATION GUIDE

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1 – Materials and Costs

Table 3.1: The Material List and Total Cost to Produce a Single Vibrating Sampler

Material For sampler	Vendor	Quantity	Price per unit	Total Price
1 ½ in. ID 10-foot copper pipe	Ferguson Plumbing	1, 7 ¼ inch section	\$69	~ \$4.17
1 ¼ in Slip copper coupling pipe	Ferguson Plumbing	1	\$8.655	\$8.66
1 ½ in copper end cap	Ferguson Plumbing	2	\$8.933	\$17.87
¾ in. copper pipe strap 50 – pack	Home Depot	6 pipe straps	\$18.53	~ \$2.22
Brass pipe – street elbow 3/8 in MIP x 3/8 in FIP	Home Depot	1	\$5.96	\$5.96
Hose barb – Adapter 3/8 in ID x 3/8 in MIP	Home Depot	1	\$3.74	\$3.74
2 in. PVC Spigot x Cleanout Adaptor with Plug	Home Depot	1	\$2.40	\$2.40
2 in. PVC Sch. 40 Socket Cap	Home Depot	1	\$1.44	\$1.44
3/8 in. ID x 1/4 in. MIP Plastic 90-Degree Hose Barb	Home Depot	1	\$2.36	\$2.36
Stainless Steel Hose Clamp	Home Depot	1	\$0.87	\$0.87
¾ in x 12 in. Tubing Hanger	Home Depot	3	\$1.87	\$5.61
34mm Vibration Motor – 30mm Model 334-401	Precision Microdrive	1	\$16.59	\$16.59
Uctronics DC 12V Programmable Multifunction Time Delay	Amazon	1	\$12.99	\$12.99
			Estimated price per sampler = \$85.75	

2 - Initial 3D Rendering of the Vibrating Sampler Design

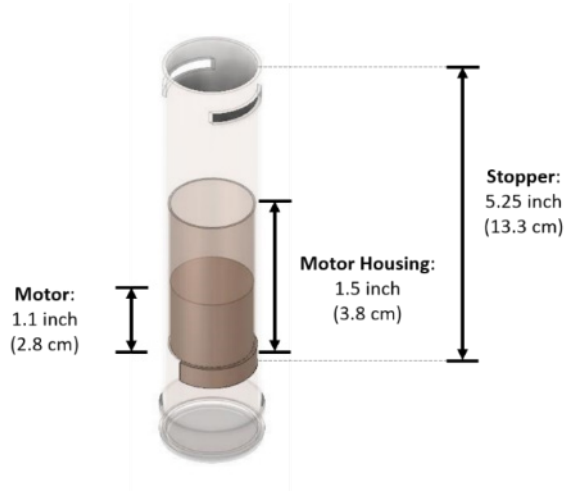


Figure S3.1. The copper body, coupling, and motor dimension Were Displayed.

The motor and coupling were fixed together and that slides into the copper body.



Figure S3.2. A semi-circle piece (black arrow) of copper was soldered below the motor to act as a stop for the motor.

The press (red arrow) consisted of two metal pieces, the top piece sits in slits made on the main body while the bottom piece sits on top of the coupling. The top piece is threaded so a 3/8 in. bolt can be screwed in and apply pressure on the bottom piece. This will hold the motor into place.

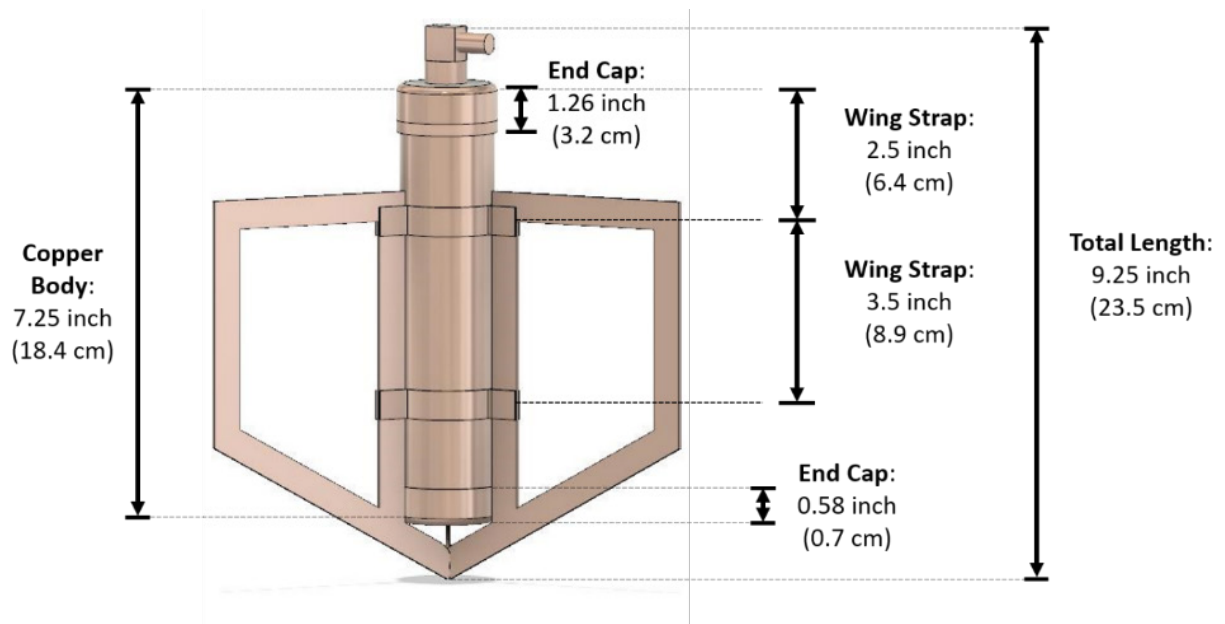


Figure S3.3: The Wings, Straps that Hold the Wings, and End Cap Dimension Were Shown in this Rendering.

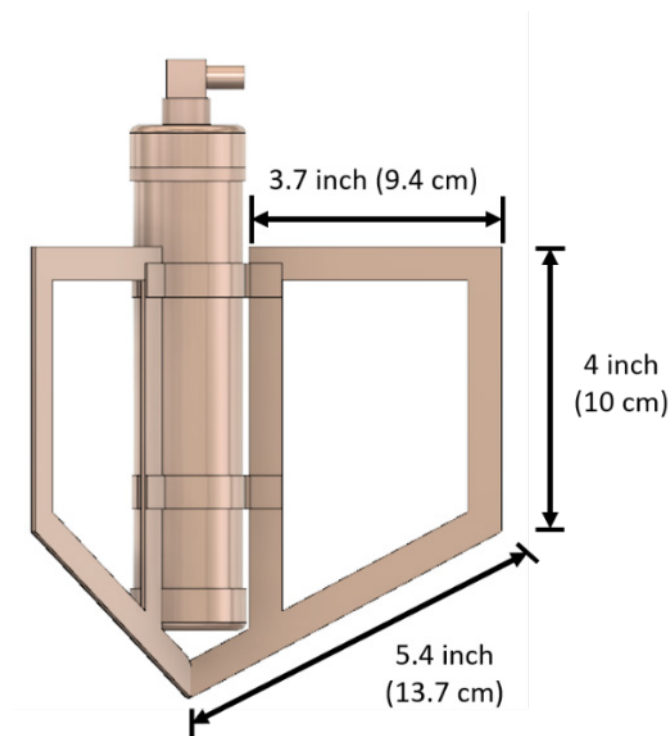


Figure S3.4: Dimensions of the Wings.

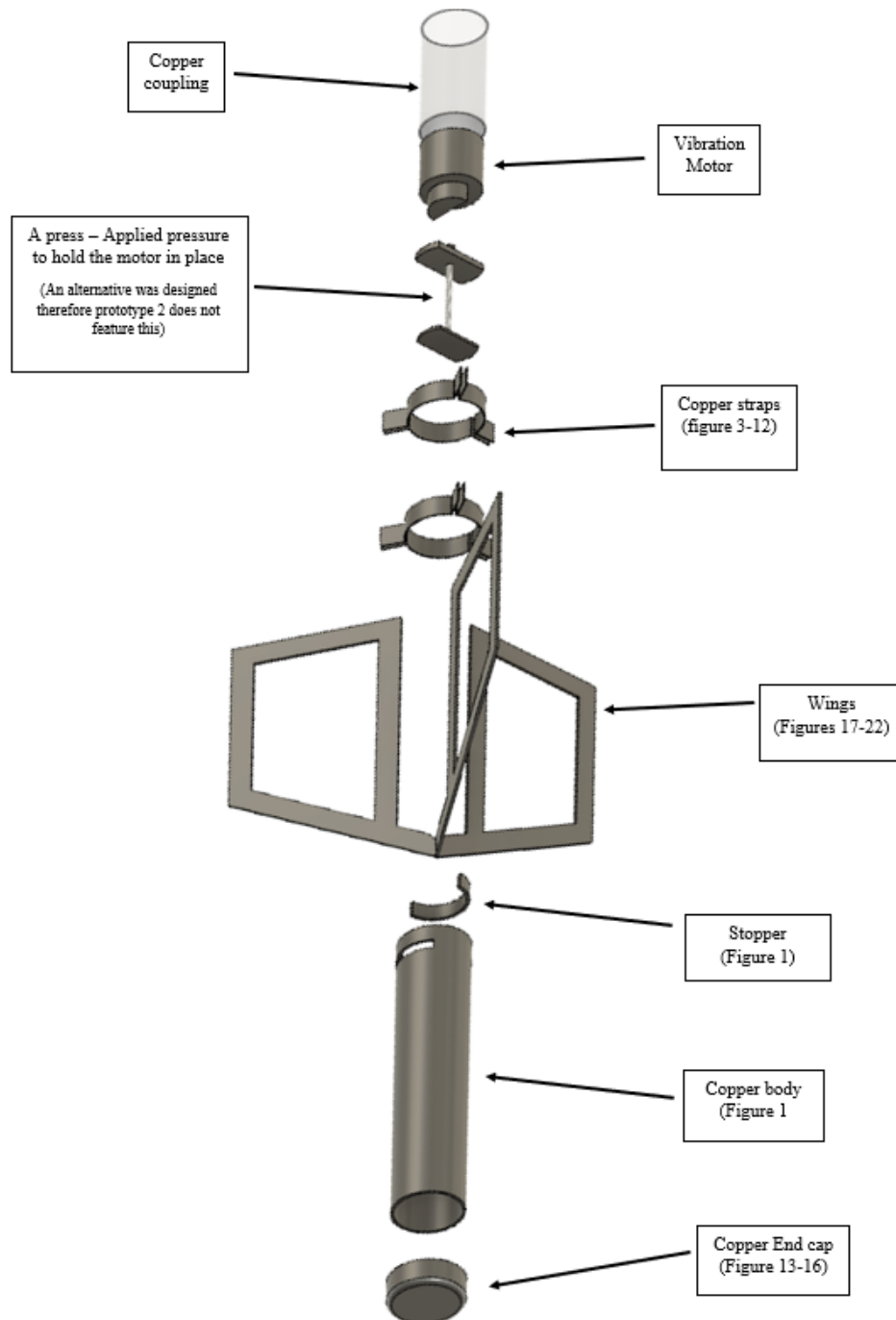


Figure S3.5: Exploded View of the Vibrating Sampler

3 - Instructions

Copper was used for a majority of the design because of its readily availability and the ability for the components to be soldered together. It was also easily workable due the nature of the material. All the copper to copper joints were soldered together to create a strong bond between the metal. The most important step to soldering was to add flux. The flux removed and prevented any oxidation of the copper to occur, allowing the tin-based solder to exhibit a capillary effect.



Figure S3.1. Miter Saw was Used to Cut the 1 ½ in. ID Copper Pipe to 7.25 in.



Figure S3.2. The Corner of the ¼ in. Pipe Tube Strap Was Bent Using Pliers.



Figure S3.3. The Straps Were Then Placed on a Scrap Piece of Pipe that Has the Same Diameter as the Body of the Vibrator Sampler.

A hammer was used to lightly tap the strap into the rough curve of the pipe.



Figure S3.4. The Final Rough Shape of the Strap After Shaping it with a Hammer.



Figure S3.5. To Shape the Strap into the Final Form of the Vibrating Body a Pipe Clamp Was Used.



Figure S3.6. The Strap Was Placed on the Same Scrape Pipe.



Figure S3.7. The Pipe Clamp Was Placed on Top of the Strap.

Using an impact driver, the pipe clamp is tightened to conform the strap to the curve of the body. A hammer was used to make any small adjustments on the strap while the pipe clamp was tightened.



Figure S3.8. A Side-by-side Comparison of the Strap Before (Left) and After (Right) Shaping them.



Figure S3.9. Before and After Shaping the Strap to the Body of the Vibrating Sampler.



Figure S3.10. The Straps Are Used to Attach the Wings to the Body of the Sampler.

A small section of the strap was bent to allow the strap to be soldered to the wing. The strap was placed in a vise and bent. The right picture showed the strap before being bent and the left picture is after it was bent.

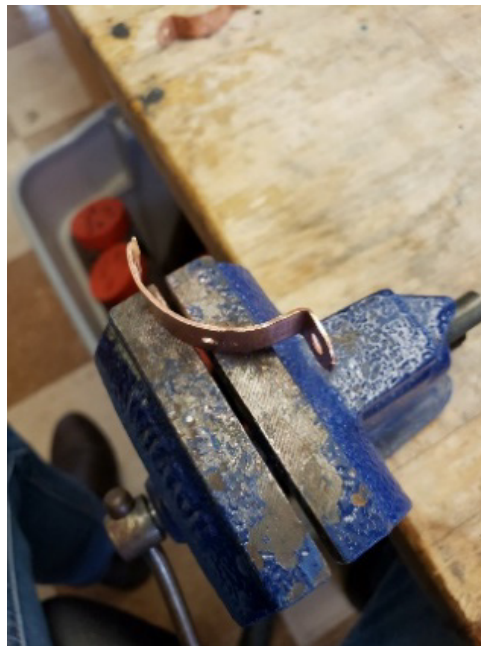


Figure S3.11. This Is the Final Shape of the Strap with Only One Side Bent.
Both sides will be bent.

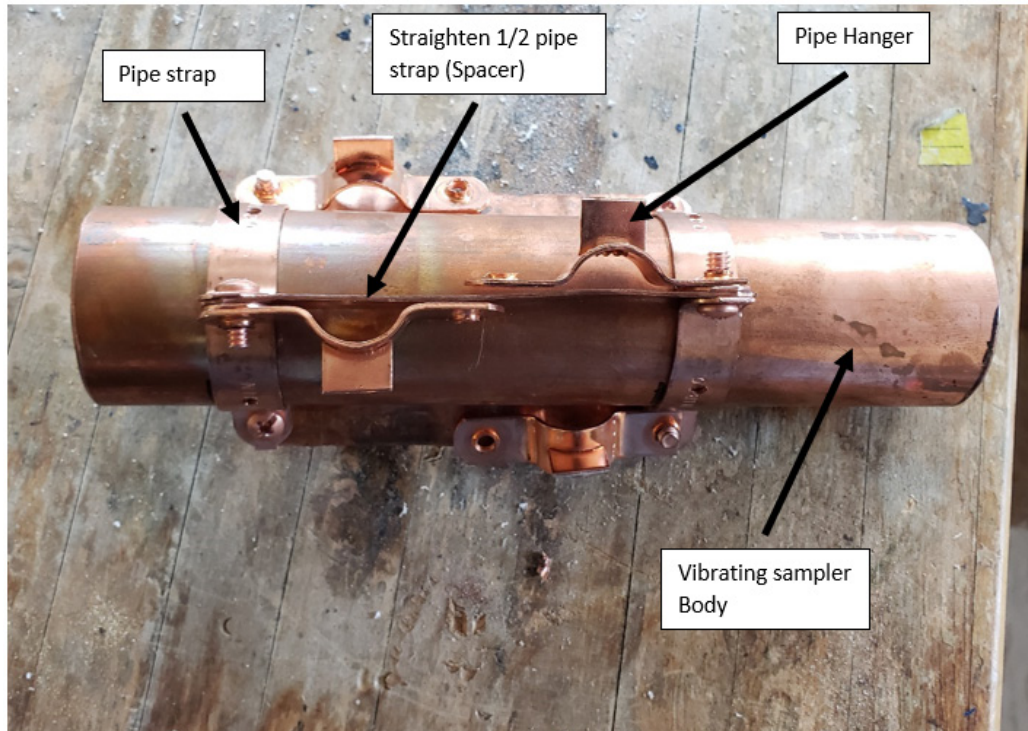


Figure S3.12. The Straps Needed to Be Soldered to the Body of the Sampler.

A jig was created to hold the strap in place in order to solder it to the body properly. This jig was made using scrape pieces and a 1/2 in. pipe strap that was bent straight as a spacer. All the straps were then soldered into place and the jig was removed.



Figure S3.13. A 1 1/2 in. ID End Cap Is Used to Seal on End of the Sampler.

The length of the end cap was reduced to remove weight of the total sampler. It was then soldered on.



Figure S3.14. The End Result of Soldering the End Cap to the Sampler.



Figure S3.15. The Setup Used for This Process.



Figure S3.16. The Completed Attachment of Straps.

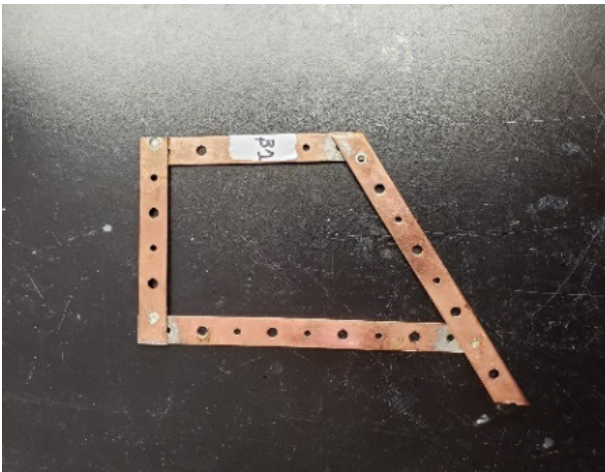


Figure S3.17. The Wing Was Constructed But Cutting of the Pipe Clamp on a Tubing Hanger.

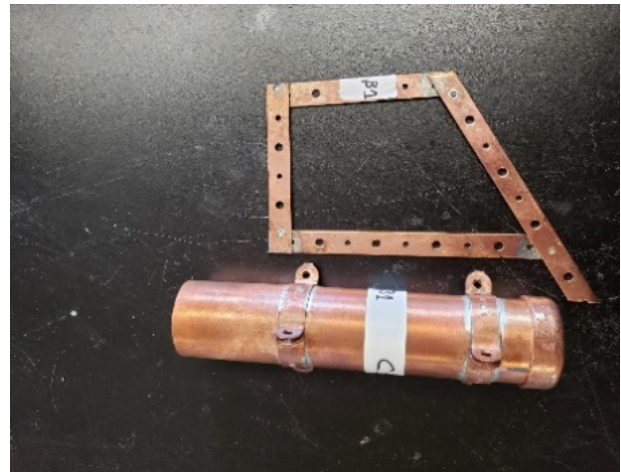


Figure S3.18. The Wings Was Attached to the Body by Soldering It to the Pipe Straps.

The copper stripes were soldered together



Figure S3.19. The Setup that Was Used to Hold the Sampler in Place while Soldering them Onto the Body.



Figure S3.20. Before Soldering.



Figure S3.21. After Soldering



Figure S3.22. The Sampler After Attaching the Wings.



Figure S3.23. A Scrap Piece of Copper Was Bent to Conform to the Angle of the Wings.

This was soldered on to reinforce the point.



Figure S3.24. The Result of Soldering.



Figure S3.25. The Cap Was Made Using a 1/2 in Copper End Cap, Brass Hose Barb, and a Brass Street Elbow.

These parts were soldered together



Figure S3.26. The Battery and Timer Compartment Were Made with PVC Cleanout Adaptor with Plug, PVC Socket Cap, and a 90-Degree Hose Barb.

The joints were attached with PVC cement and JB weld.

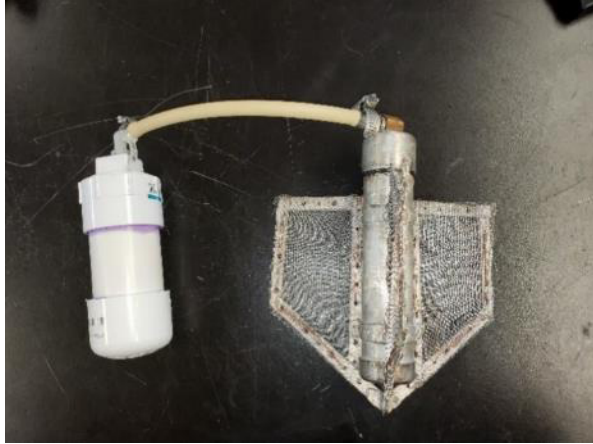


Figure S3.27. The Vibrating Sampler After the Completion.

The body and wing were tin plated to prevent corrosion, but this set was unnecessary. This picture was the taken before placing the sampler through an experiment



Figure S3.28. During the Experiment the Clay-like Mud Clumped onto the Sampler.



Figure S3.29. The Vibrating Sampler After the First Experiment in Mud.

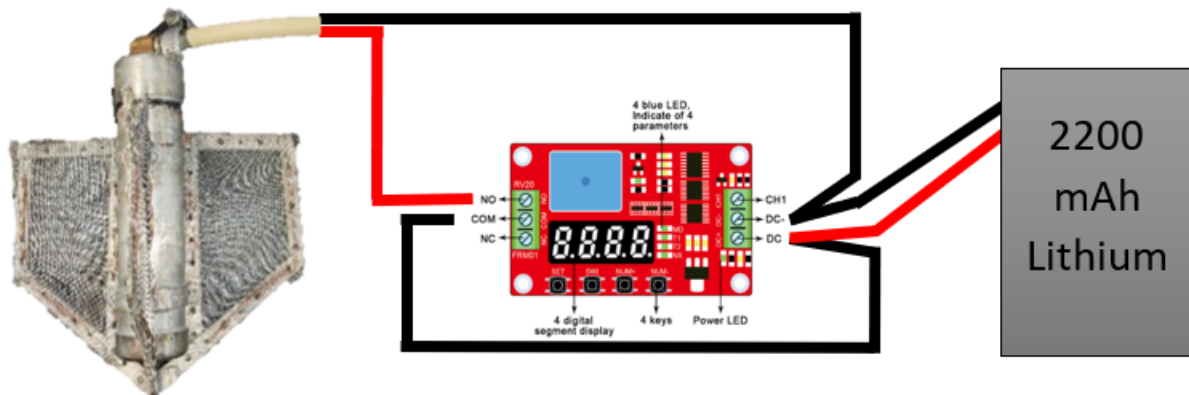


Figure S3.30. A Schematic Representing the Wiring of the Vibrating Sampler with the Timer and Battery.

The vibrating will vibrate for 5 seconds every hour (idle for 3595 seconds and vibrates for 5 seconds)

$$\text{Timer: } \frac{3595 \text{ sec pause}}{1 \text{ hour}} \times \frac{24 \text{ hour}}{1 \text{ day}} \times \frac{7 \text{ day}}{1 \text{ week}} \times \frac{1 \text{ hour}}{3600 \text{ sec}} \times 2.5 \text{ weeks} \times 4 \text{ mA} = 1677.67 \text{ mAh}$$

$$\text{Motor: } \frac{5 \text{ sec run time}}{1 \text{ hour}} \times \frac{24 \text{ hour}}{1 \text{ day}} \times \frac{7 \text{ day}}{1 \text{ week}} \times \frac{1 \text{ hour}}{3600 \text{ sec}} \times 2.5 \text{ weeks} \times 400 \text{ mA} = 233.3 \text{ mAh}$$

$$\text{Total mA required for the sampler} = 1677.67 \text{ mAh} + 233.3 \text{ mAh} = \mathbf{1911 \text{ mAh}}$$



Figure S3.31. Power Bank Displaying the Current Required to Run the Vibrating ~4mA



Figure S3.32. Power Bank displaying the Current Required to Run the Vibrating ~400 mA

APPENDIX D SUPPLEMENTAL INFORMATION FOR CHAPTER 4

ANALYSIS OF TIME INTEGRATION IN EQUILIBRIUM PASSIVE SAMPLING

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S1. Crank's numerical solution of Fick's diffusion in a flat plate

From Fick's second law of diffusion, in a plane sheet of thickness L and constant diffusion coefficient D:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{-Eq S1}$$

Dimensionless constants:

$$X = \frac{x}{L}; T = \frac{Dt}{L^2}; c = \frac{c}{c_0}$$

Substituting dimensionless constants into Eq S1:

$$\frac{\partial c}{\partial T} = \frac{\partial^2 c}{\partial X^2} \quad \text{-Eq S2}$$

Assuming the sheet to occupy the space $0 \leq X \leq 1$ and X be divided into equal intervals of dX and time into intervals of dT, the X-T region is covered by a grid of rectangles each of size dX,dT. The coordinates of a representative grid point would be (idX, jdT) and the c at that point would be $c_{i,j}$ where i and j are integers. Applying Taylor's series in X, T directions, the numerical solution to Eq S072 by finite difference approximation would be:

$$\begin{aligned} c_{i,j+1} &= c_{i,j} + \frac{dT}{(dX)^2} (c_{i-1,j} - 2c_{i,j} + c_{i+1,j}) \\ &= c_{i,j} + res (c_{i-1,j} - 2c_{i,j} + c_{i+1,j}) \end{aligned} \quad \text{-Eq S3}$$

where $\frac{dT}{(dX)^2} = res \leq 0.5$ needs to be maintained.

Table S4.1: First Order Rate Constants, k_e for Various PCB Compounds Corresponding to Different PE Thicknesses.

SI No.	# Cl atoms	PCB congener	k_e [0.3mil PE]	k_e [0.7mil PE]	k_e [1mil PE]	k_e [2mil PE]	k_e [3mil PE]
1	2	PCB 4	5.39	2.06	1.46	0.70	0.47
2	2	PCB 15	0.92	0.35	0.25	0.12	0.08
3	3	PCB 22	0.39	0.16	0.11	0.05	0.04
4	3	PCB 37	0.20	0.08	0.06	0.03	0.02
5	4	PCB 47	0.18	0.07	0.05	0.02	0.02
6	4	PCB 73	0.11	0.04	0.03	0.01	0.01
7	5	PCB 100	0.06	0.02	0.02	0.01	0.01
8	5	PCB 110	0.03	0.01	0.01	0.00	0.00
9	6	PCB 128	0.01	0.01	0.00	0.00	0.00

S2. Impact of varying day of introduction of perturbation in ambient water concentration.

The influence of 10-day long pulsed perturbation introduced on different days throughout the deployment period on the uptake of PCB #37 was examined by comparing the passive sampler-based water concentration as predicted by the First Order model and the actual time-averaged concentration on each of these events (**Figure S4.1**). It was observed that the time averaged concentration stayed constant at 9 ng/L. The passive sampler-based water concentration as predicted by the First Order model, of PCB 37, crosses over from being overestimated, when the pulse starts on the 50th day, to being underestimated, when the pulse starts on the 60th day. Thus, the cross-over happens on the 59th day when the predicted value is equal to the actual water concentration. Hence, the optimal time-period of integration for PCB 37 was about $(90-59)= 31$ days which is same as the time-period of integration for PCB 37 as predicted by the Diffusion model. Hence the two models are consistent.

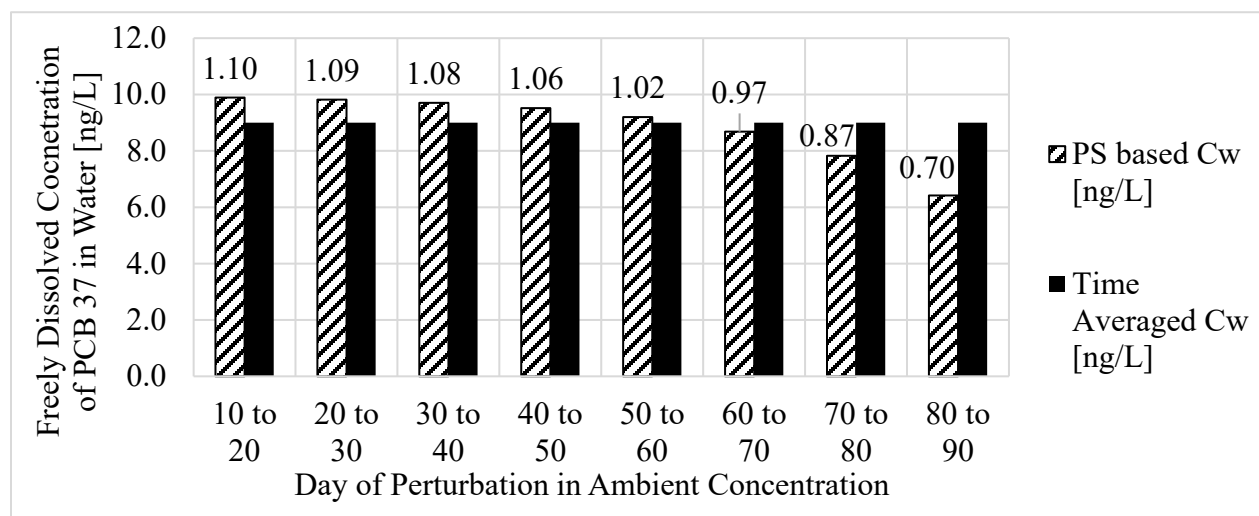


Figure S4.1: Impact of day of introduction of pulsed perturbation on the uptake of PCB 37 into PE:

Comparison of actual time averaged concentration and passive sampler-based water concentration as measure by the First-Order model.

S3. Impact of perturbation on the uptake of PCB congeners as a function of their hydrophobicity.

The modeled simulation of varying rates of fractional uptake of PCB congeners from water as a function of time, when there was no perturbation in the ambient concentration versus when the perturbation was introduced on the 70th day, as predicted by the First Order model, is shown in **Figure S4.2 (a) and (b)** respectively. With a constant concentration of PCBs in the ambient fluid, a lower homolog group congener (PCB #4, for example) reached equilibrium faster (in less than 10 days) than one from a higher homolog group (PCB #128, for example, reached only 20% of the actual ambient concentration in 90 days).

The first order-model-predicted and actual time-integrated water concentrations for varying days of introduction of perturbation were compared to examine the percent difference between these estimates for various PCB congeners (**Figure S4.3**). It was observed that while a pulse on the 60th day overestimated the predicted water concentration of PCB #15 by about 10%, the same pulse occurring on the 80th day led to an underestimation of predicted concentration by about 88%.

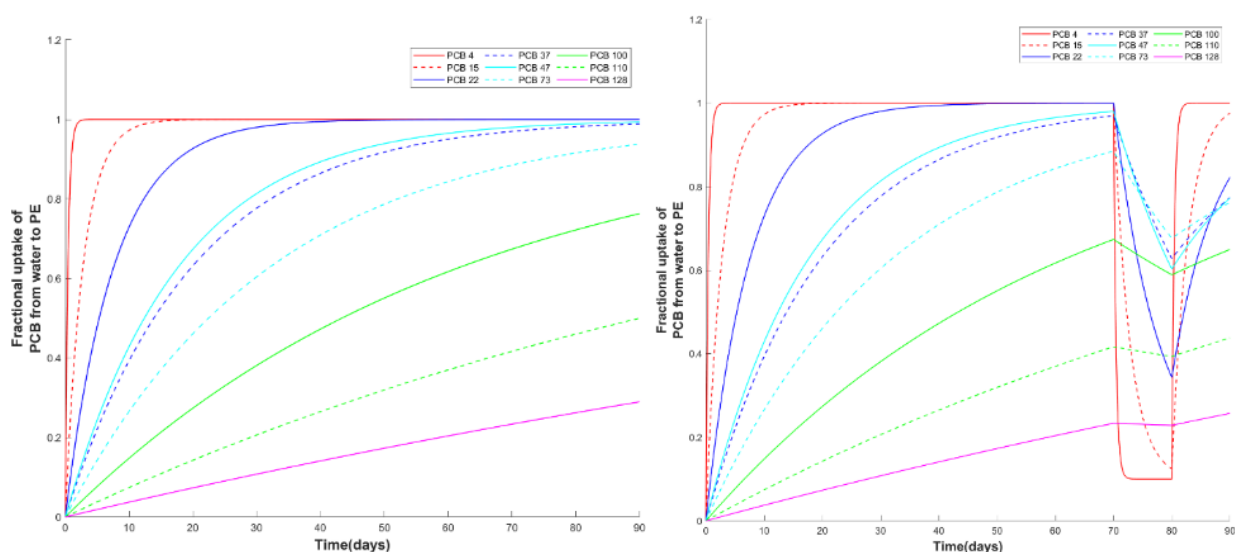


Figure S4.2. Passive Sampler-based Water Concentration Profile of 10 PCB Congeners #4, #15, #22, #37, #47, #73, #100, #110, #128, #180 into PE of Thickness 25 μ m with Respect to Time, with (a) Constant Ambient Concentration and (b) Pulsed Perturbation in Ambient Concentration on the 80th Day of Deployment Scenarios as Measured by the First-Order Model.

The time-period of integration as predicted by the first-order model, was correlated with PCB congener hydrophobicity ($\log K_{ow}$) and the percentage crossover as shown in Figure S5 with the size of the bubble representing the degree of sensitivity of a congener. It was observed that a congener of $\log K_{ow}$ of 4.5, has a time-period of integration of 14 days, which means that it requires only about 2 weeks to recover from a pulsed perturbation and return the true time-integrated concentration, while a congener of $\log K_{ow}$ of 6.0 needs at least 35 days to recover from a pulsed perturbation to return the true time-integrated water concentration value.

Additionally, the predicted value of concentration of PCB #15 ($\log K_{ow}=5.30$) crosses over from being overestimated from the true concentration by 9% when the pulse originates on the 70th day

to being underestimated from the true concentration by 86% when the pulse originates on the 80th day. The actual day of crossover was calculated by the method of interpolation to be the 75th day which is 15 days from the end of the deployment. Hence, in **Figure S4**, PCB #15 corresponds to time integration period of 15 days and a bubble size corresponding to a percent crossover value of (86%+9%=95%). PCB #128 (log K_{ow} =6.74) corresponds to a time integration value of 37 days and a crossover percent value of 0.5% which means, it takes the passive sampler at least 53 days to predict the actual water concentration.

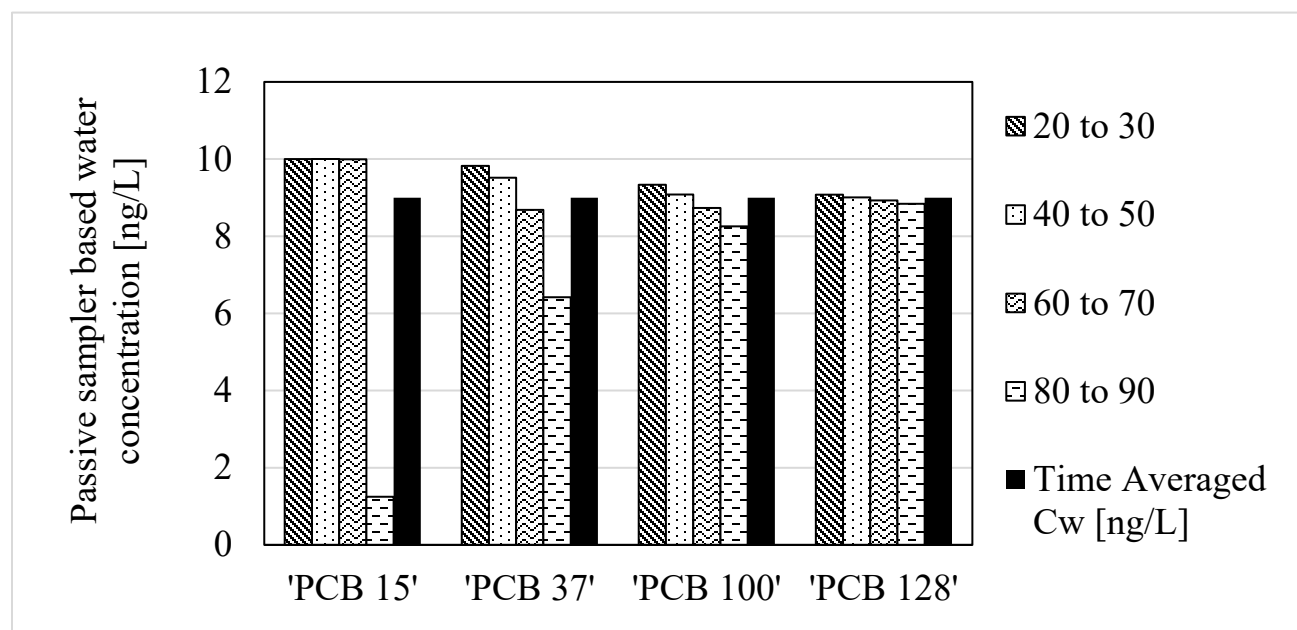


Figure S4.3. Comparison of Actual Time Averaged Concentration and Passive Sampler-Based Water Concentration, as Measured by the First-order Model, of PCB Congeners #15, #37, #100 and #128 with Varying Days of Introduction of 10-day Long Pulsed Perturbations.

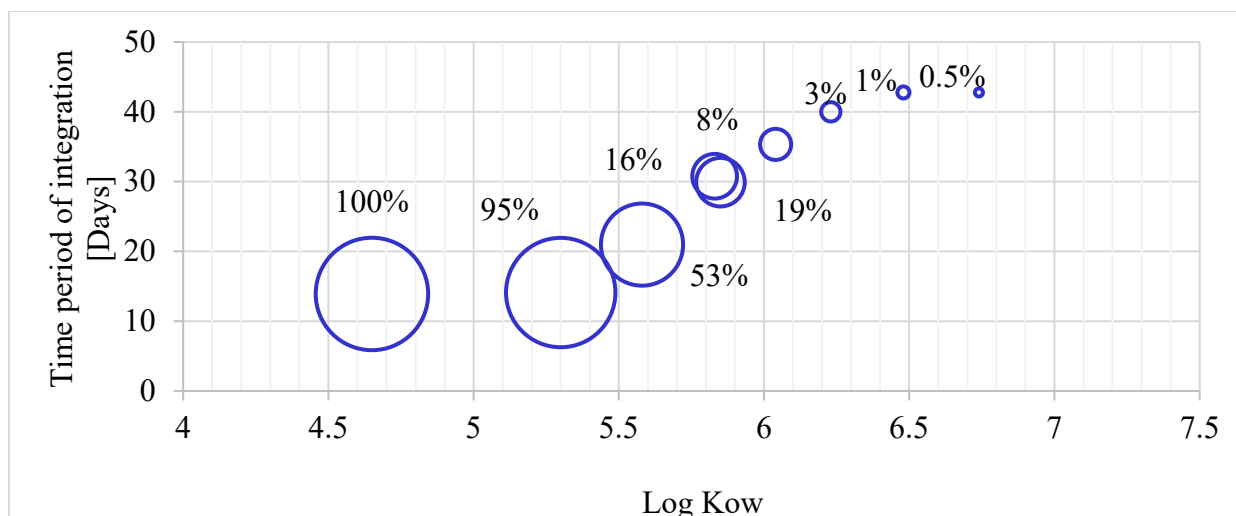


Figure S4.4. Effect of Varying Hydrophobicity of PCB Congeners with Time-period of Integration and Percentage of Cross-over from Under-prediction to Over-prediction of Passive Sampler-based Water Concentration, as Measured by the First-order Model, with Respect to Actual-time Averaged Concentration.

S4. Varying sampler thickness under fluctuating ambient concentration scenario.

The percent difference in passive sampler-based water concentration as predicted by the first-order model and actual time averaged concentration for PCB#37, as a function of the time of introduction of perturbation, was calculated for various PE thicknesses 1mil (25 μ m), 2mil (50 μ m), 3mil (75 μ m). The corresponding shift in the time-period of integration with changing thicknesses of PE and the consequent change in the percent crossover values was analyzed for the congener (**Figure S4.5**). It was observed that with increasing PE thickness, the time-period of integration for PCB#37 varied from 31days for 25 μ m PE to 38 days for 50 μ m PE to 40 days for 75 μ m PE. The sensitivity of the system decreased from 16% for 25 μ m PE to 3% for 50 μ m PE to 2% for 75 μ m PE.

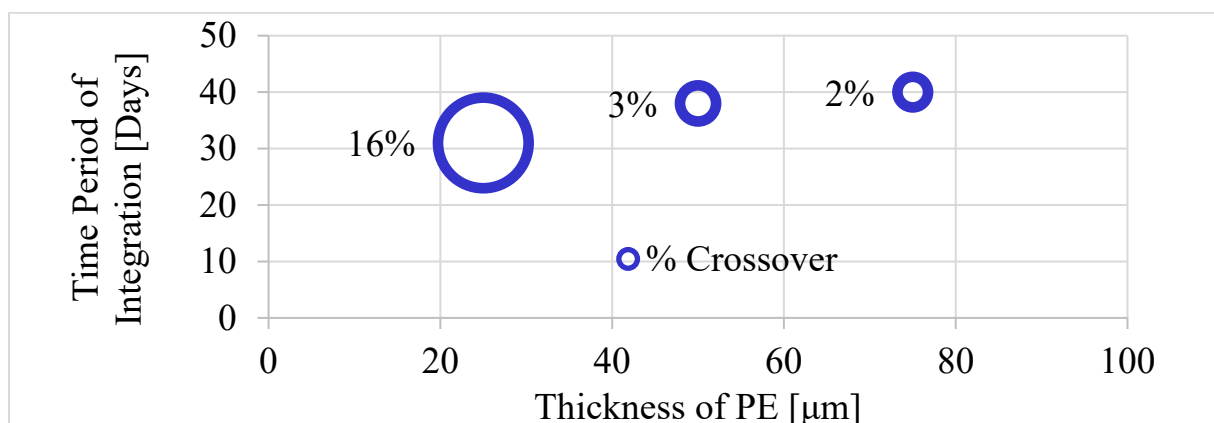


Figure S4.5. Effect of Varying PE Thicknesses 1mil (25 μ m) to 2mil(50 μ m) to 3mil (75 μ m) under the Influence of a Pulsed Perturbation of Ambient Concentration on the 70th Day of Deployment on the Time-period of Integration of PCB #37, as Measured by the First-order Model.

MATLAB script for modeling mass transfer kinetics involved in the uptake of PCBs from a well mixed water bath across water-side boundary layer into PE using the 1-D Fick's Diffusion model.

(i) No Pulse

```
clear all;
close all;

%% Defining Parameters
Wbl=0.02;           % water side boundary layer (cm)
runtime=90*24;      % enter time in hours
PEmass=1;           % Mass of PE (g)
PEthick=12.5*10^-4; % PE thickness in (cm)
PEarea=(PEmass/0.92)/PEthick; %(cm^2 for two sides)
dt=1;               % time step (sec)
r=0.3;

%define chemical properties
Comp_names={'PCB 4','PCB 15','PCB 22','PCB 37','PCB 47','PCB 73','PCB 100','PCB 110','PCB 128'};
MW= [223.1 223.1 257.54 257.54 291.99 291.99 326.43 326.43 360.88];
Dpe=10.^[-8.64 -8.64 -8.81 -8.81 -8.98 -8.98 -9.16 -9.16 -9.33];
Kpew= 10.^[4.23 4.99 5.32 5.62 5.64 5.87 6.09 6.39 6.69];
Kwpe=Kpew.^-1;
Dw=(2.7*10^-4)./(MW.^0.71); % Diffusivity of PCB37 in water (cm^2/s)
%colors for plotting
linespec_array1={'-r','-r','-b','-b','-c','-c','-g','-g','-m'}; %matlab linespecs
%for n=1:length(Comp_names)
for n=1
    dxpe=((Dpe(n)*dt)/r)^0.5; % (cm)
    dxwat=((Dw(n)*dt)/r)^0.5; % (cm)
    %Sections in PE
    pesections=PEthick/dxpe;
    PE=round(pesections);
    %Sections in Water
    wsections=Wbl/dxwat;
    WAT=round(wsections);

    %%
    % Initial conditions for GAIN function
    G_CoinPE=0; % GAIN: Initial concentration in the PE (ug/cm^3 PE)
    G_CoinW=10*10^-6; % GAIN: Initial concentration in the water (ug/cm^3)
    % G_C matrix with concentration across entire cross section at any given time
    G_C(1,1:PE)=G_CoinPE; % Setting the PE section equal to Co in PE
    G_C(1,PE+1:PE+WAT+1)=G_CoinW; % setting the WAT section equal to Co in water

    G_MinWinit=0; %Mass in water initially
    G_MinWinit=G_MinWinit+G_C(1,PE+1:PE+WAT+1)*dxwat*PEarea;

    %Initial Conditions for LOSS function
```

```

L_CoinPE=100; % LOSS: Initial concentration in the PE (ug/cm^3 PE)
L_CoinW=0; % LOSS: Initial concentration in the water (ug/cm^3)
% L_C matrix with concentration across entire cross section at any given time
L_C(1,1:PE)=L_CoinPE;
L_C(1,PE+1:PE+WAT+1)=L_CoinW;

L_MinPEinit=0; %Mass in PE initially
L_MinPEinit=L_MinPEinit+L_C(1,1:PE)*dxpe;

% Initial Conditions for TIME AVERAGED function
Cw_Sum=0;

%Boundary Conditions
G_Coboundary=G_CoinPE; % GAIN: Setting boundary layer within PE equal to Co in PE
G_CinW=G_CoinW; % GAIN: Setting boundary layer in Water equal to Co in water
L_Coboundary=L_CoinPE; % LOSS: Setting boundary layer within PE equal to Co in PE
L_CinW=L_CoinW; % LOSS: Setting boundary layer in Water equal to Co in water

G_CPE=zeros((runtime*3600)/dt,1); % GAIN: Conc taken up in PE (averaged over the PE sections) as
a function of time [ug/cm^3 of PE]
time=0;
% Solving Diffusion Equations wrt Time
for j=1:((runtime*3600)/dt)
    time=time+dt;
    x(j)=(j*dt/(3600*24)); % time as plotted on x axis

    Cw_Time(j,1)=G_CoinW*10^6; %TIME AVERAGED: Cw wrt time [ng/L]
    Cw_Sum= Cw_Sum+Cw_Time(j); % TIME AVERAGED: Total Cw [ng/L]

    G_Coboundary=G_Coboundary+2*r*(G_C(1)-G_Coboundary); % GAIN: no flux boundary
    G_C(1)=G_C(1)+r*(G_Coboundary-2*G_C(1)+G_C(2)); % GAIN: first pe point
    L_Coboundary=L_Coboundary+2*r*(L_C(1)-L_Coboundary); % LOSS: no flux boundary
    L_C(1)=L_C(1)+r*(L_Coboundary-2*L_C(1)+L_C(2)); % LOSS: first pe point

    for i=2:PE-1
        G_C(i)=G_C(i)+r*(G_C(i-1)-2*G_C(i)+G_C(i+1)); % pe points
        L_C(i)=L_C(i)+r*(L_C(i-1)-2*L_C(i)+L_C(i+1)); % pe points
    end

    G_C(PE)=(((G_C(PE+1)*Dw(n)*dxpe)+(G_C(PE-1)*Dpe(n)*dxwat))*Kpew(n))/((Dw(n)*dxpe)+(Dpe(n)*dxwat*Kpew(n))); %Wall boundary: last PE
    point
    G_C(PE+1)=G_C(PE+1)+r*((G_C(PE)/Kpew(n))-2*G_C(PE+1)+G_C(PE+2)); % Wall boundary:
    first wat point
    L_C(PE)=(((L_C(PE+1)*Dw(n)*dxpe)+(L_C(PE-1)*Dpe(n)*dxwat))*Kpew(n))/((Dw(n)*dxpe)+(Dpe(n)*dxwat*Kpew(n))); %last PE point
    L_C(PE+1)=L_C(PE+1)+r*((L_C(PE)/Kpew(n))-2*L_C(PE+1)+L_C(PE+2)); %first wat point

    for i=PE+2:PE+WAT
        G_C(i)=G_C(i)+r*(G_C(i-1)-2*G_C(i)+G_C(i+1)); % rest of wat points
        L_C(i)=L_C(i)+r*(L_C(i-1)-2*L_C(i)+L_C(i+1)); % rest of wat points
    end

```

```

end

G_MinPE=0; % Mass of PCB gained in PE after the diffusion [ug/cm^2 of PE]
for i=1:PE
    G_MinPE=G_MinPE+G_C(1,i)*dxpe*PEarea;
    G_CPE(j,1)=G_CPE(j,1)+G_C(1,i)/PE; %Cpe [ug/cm^3]
    G_CPE_ngL(j,1)=G_CPE(j,1)*10^6;%Cpe [ng/L]
end
G_MinW=0;% Mass in Water after the diffusion [ug/cm^2 of Water]
G_MinW=G_MinW+G_C(1,PE+1:PE+WAT)*dxwat*PEarea;
G_CinW=G_CoinW;
G_C(1,PE+WAT+1)=G_CinW; % boundary condition

L_MinPE=0;
L_MinPE=L_MinPE+L_C(1,1:PE)*dxpe;
L_C(PE+WAT+1)=L_CoinW; % boundary condition
feq_arr(j,1)=1-(L_MinPE/L_MinPEinit); %fractional equilibration term (fraction of PCB
accumulated in PE) over time
end

Cw_TA=Cw_Sum/((runtime*3600)/dt); %TIME AVG: Time Averaged Cw [ng/L]

% CPE to Cw conversions
G_Cw(1:(runtime*3600)/dt,1)=(G_CPE(1:(runtime*3600)/dt,1)*10^6)/Kpew(n); % Conc in Water as a
function of time [ug/cm^3] acquired from CPE
CPE_Before_PRC_Correction=(G_CPE((runtime*3600)/dt))*10^6;
Cw_Before_PRC_Correction=(G_Cw((runtime*3600)/dt,1));
CPE_Eqlb=CPE_Before_PRC_Correction/feq_arr((runtime*3600)/dt,1);
Cw_Eqlb=CPE_Eqlb/Kpew(n);
for i=1:length(G_CPE_ngL)
    frac_uptake(i,1)=G_CPE_ngL(i,1)/CPE_Eqlb;
end
%% Data Assimilation
C_data(1,2:6)={'Cw','Cw Eqlb','Cw Time Avg','CPE','CPE Eqlb'};
C_data(n+1,1)=Comp_names(n);
C_data{n+1,2}=Cw_Before_PRC_Correction;
C_data{n+1,3}=Cw_Eqlb;
C_data{n+1,4}=Cw_TA;
C_data{n+1,5}=CPE_Before_PRC_Correction;
C_data{n+1,6}=CPE_Eqlb;

%% Plot
hold on
figure(1)
plot(x, frac_uptake, linespec_array1{n}, 'linewidth', 1)
xlabel('Time(days)', 'fontweight', 'bold', 'fontsize', 14)
ylabel('Fractional uptake of; PCB from water to PE', 'fontweight', 'bold', 'fontsize', 14)
xlim([0 90])
ylim([0 1.2])
legend(Comp_names())
set(legend, 'NumColumns', 3)

```

```

hold on
figure(2)
plot(x, G_CPE_ngL, linespec_array1{n}, 'linewidth', 1)
xlabel('Time(days)', 'fontweight', 'bold', 'fontsize', 14)
ylabel('Concentration of PCB accumulated in PE (ng/L)', 'fontweight', 'bold', 'fontsize', 14)
xlim([0 90])
legend(Comp_names())
set(legend, 'NumColumns', 3)
end

```

(ii) Pulsed

```

clear all;
%close all;

%% Defining Parameters
Wbl=0.02; % water side boundary layer (cm)
runtime=90*24; % enter time in hours
PEmass=1; % Mass of PE (g)
PEthick=37.5*10^-4; % PE thickness in (cm)
PEarea=(PEmass/0.92)/PEthick; % (cm^2 for two sides)
dt=1; % time step (sec)
r=0.3;
%define chemical properties
Comp_names={'PCB 4', 'PCB 15', 'PCB 22', 'PCB 37', 'PCB 47', 'PCB 73', 'PCB 100', 'PCB 110', 'PCB 128'};
MW= [223.1 223.1 257.54 257.54 291.99 291.99 326.43 326.43 360.88];
Dpe=10.^[-8.64 -8.64 -8.81 -8.81 -8.98 -8.98 -9.16 -9.16 -9.33];
Kpew= 10.^[4.23 4.99 5.32 5.62 5.64 5.87 6.09 6.39 6.69];
Kwpe=Kpew.^-1;
Dw=(2.7*10^-4)./(MW.^0.71); % Diffusivity of PCB37 in water (cm^2/s)
%colors for plotting
linespec_array1={'-r', '-r', '-b', ':b', '-c', '--c', '-g', '--g', '-m'}; %matlab linespecs
%for n=1:length(Comp_names)
for n=4
    dxpe=((Dpe(n)*dt)/r)^0.5; % (cm)
    dxwat=((Dw(n)*dt)/r)^0.5; % (cm)
    %Sections in PE
    pesections=PEthick/dxpe;
    PE=round(pesections);
    %Sections in Water
    wsections=Wbl/dxwat;
    WAT=round(wsections);

```

```

%%
% Initial conditions for GAIN function
G_CoinPE=0; % GAIN: Initial concentration in the PE (ug/cm^3 PE)
G_CoinW=10*10^-6; % GAIN: Initial concentration in the water (ug/cm^3)
% G_C matrix with concentration across entire cross section at any given time
G_C(1,1:PE)=G_CoinPE; % Setting the PE section equal to Co in PE
G_C(1,PE+1:PE+WAT+1)=G_CoinW; % setting the WAT section equal to Co in water

G_MinWinit=0; %Mass in water initially
G_MinWinit=G_MinWinit+G_C(1,PE+1:PE+WAT+1)*dxwat*PEarea;

%Initial Conditions for LOSS function
L_CoinPE=100; % LOSS: Initial concentration in the PE (ug/cm^3 PE)
L_CoinW=0; % LOSS: Initial concentration in the water (ug/cm^3)
% L_C matrix with concentration across entire cross section at any given time
L_C(1,1:PE)=L_CoinPE;
L_C(1,PE+1:PE+WAT+1)=L_CoinW;

L_MinPEinit=0; %Mass in PE initially
L_MinPEinit=L_MinPEinit+L_C(1,1:PE)*dxpe;

% Initial Conditions for TIME AVERAGED function
Cw_Sum=0;

%Boundary Conditions
G_Coboundary=G_CoinPE; % GAIN: Setting boundary layer within PE equal to Co in PE
G_CinW=G_CoinW; % GAIN: Setting boundary layer in Water equal to Co in water
L_Coboundary=L_CoinPE; % LOSS: Setting boundary layer within PE equal to Co in PE
L_CinW=L_CoinW; % LOSS: Setting boundary layer in Water equal to Co in water

G_CPE=zeros((runtime*3600)/dt,1); % GAIN: Conc taken up in PE (averaged over the PE sections) as
a function of time [ug/cm^3 of PE]
time=0;

%%
%Solving Diffusion Equations wrt Time
for j=1:((runtime*3600)/dt)
    time=time+dt;
    x(j)=(j*dt/(3600*24)); % time as plotted on x axis

    G_Coboundary=G_Coboundary+2*r*(G_C(1)-G_Coboundary); % GAIN: no flux boundary
    G_C(1)=G_C(1)+r*(G_Coboundary-2*G_C(1)+G_C(2)); % GAIN: first pe point
    L_Coboundary=L_Coboundary+2*r*(L_C(1)-L_Coboundary); % LOSS: no flux boundary
    L_C(1)=L_C(1)+r*(L_Coboundary-2*L_C(1)+L_C(2)); % LOSS: first pe point

```



```

for i=2:PE-1
    G_C(i)=G_C(i)+r*(G_C(i-1)-2*G_C(i)+G_C(i+1)); % pe points
    L_C(i)=L_C(i)+r*(L_C(i-1)-2*L_C(i)+L_C(i+1)); % pe points
end

G_C(PE)=(((G_C(PE+1)*Dw(n)*dxpe)+(G_C(PE-1)*Dpe(n)*dxwat))*Kpew(n))/((Dw(n)*dxpe)+(Dpe(n)*dxwat*Kpew(n))); %Wall boundary: last PE point
G_C(PE+1)=G_C(PE+1)+r*((G_C(PE)/Kpew(n))-2*G_C(PE+1)+G_C(PE+2)); % Wall boundary: first wat point
L_C(PE)=(((L_C(PE+1)*Dw(n)*dxpe)+(L_C(PE-1)*Dpe(n)*dxwat))*Kpew(n))/((Dw(n)*dxpe)+(Dpe(n)*dxwat*Kpew(n))); %last PE point
L_C(PE+1)=L_C(PE+1)+r*((L_C(PE)/Kpew(n))-2*L_C(PE+1)+L_C(PE+2)); %first wat point

for i=PE+2:PE+WAT
    G_C(i)=G_C(i)+r*(G_C(i-1)-2*G_C(i)+G_C(i+1)); % rest of wat points
    L_C(i)=L_C(i)+r*(L_C(i-1)-2*L_C(i)+L_C(i+1)); % rest of wat points
end

G_MinPE=0; % Mass of PCB gained in PE after the diffusion [ug/cm^2 of PE]
for i=1:PE
    G_MinPE=G_MinPE+G_C(1,i)*dxpe*PEarea;
    G_CPE(j,1)=G_CPE(j,1)+G_C(1,i)/PE; %Cpe [ug/cm^3]
    G_CPE_ngL(j,1)=G_CPE(j,1)*10^6;%Cpe [ng/L]
end
G_MinW=0;% Mass in Water after the diffusion [ug/cm^2 of Water]
G_MinW=G_MinW+G_C(1,PE+1:PE+WAT)*dxwat*PEarea;
% entering pulse
if ((time/(3600*24))>70 && (time/(3600*24))<80)
    G_CinW=G_CoinW/10;
else
    G_CinW=G_CoinW;
end
G_C(PE+WAT+1)=G_CinW; % boundary condition

L_MinPE=0;
L_MinPE=L_MinPE+L_C(1,1:PE)*dxpe;
L_C(PE+WAT+1)=L_CoinW; % boundary condition
feq_arr(j,1)=1-(L_MinPE/L_MinPEinit); %fractional equilibration term (fraction of PCB accumulated in PE) over time

if ((time/(3600*24))>70 && (time/(3600*24))<80)
    Cw_Time(j,1)=(G_CoinW*10^6)/10;

```

```

else
    Cw_Time(j,1)=G_CoinW*10^6;
end
Cw_Sum= Cw_Sum+Cw_Time(j);
end
Cw_TA=Cw_Sum/((runtime*3600)/dt); %TIME AVG: Time Averaged Cw [ng/L]

% CPE to Cw conversions
G_Cw(1:(runtime*3600)/dt,1)=(G_CPE(1:(runtime*3600)/dt,1)*10^6)/Kpew(n); % Conc in Water as a
function of time [ug/cm^3] acquired from CPE
CPE_Before_PRC_Correction=(G_CPE((runtime*3600)/dt))*10^6;
Cw_Before_PRC_Correction=(G_Cw((runtime*3600)/dt,1));

CPE_Eqlb=CPE_Before_PRC_Correction/feq_arr((runtime*3600)/dt,1);
Cw_Eqlb=CPE_Eqlb/Kpew(n);

%Actual conc normalized by Eqlb Conc
CPE_Eqlb_NoPulse=[169824.3652 977237.2209 2089296.131 4168693.835 4365158.322
7413102.413 12302687.71 24547089.16 48977881.94]
for i=1:length(G_CPE_ngL)
    frac_uptake(i,1)=G_CPE_ngL(i,1)/CPE_Eqlb_NoPulse(n);
end
%% Data Assimilation
C_data(1,2:6)={'Cw','Cw Eqlb','Cw Time Avg','CPE','CPE Eqlb'};
C_data(n+1,1)=Comp_names(n);
C_data{n+1,2}= Cw_Before_PRC_Correction;
C_data{n+1,3}= Cw_Eqlb;
C_data{n+1,4}= Cw_TA;
C_data{n+1,5}= CPE_Before_PRC_Correction;
C_data{n+1,6}= CPE_Eqlb;

%% Plot
hold on
figure(1)
plot(x, frac_uptake, linespec_array1{n}, 'linewidth', 1)
xlabel('Time(days)', 'fontweight', 'bold', 'fontsize', 14)
ylabel({'Fractional uptake of'; 'PCB from water to PE'}, 'fontweight', 'bold', 'fontsize', 14)
xlim([0 90])
ylim([0 1.2])
legend(Comp_names())
set(legend, 'NumColumns', 3)

hold on
figure(2)

```

```

plot(x, G_CPE_ngL, linespec_array1{n}, 'linewidth', 1)
xlabel('Time(days)', 'fontweight', 'bold', 'fontsize', 14)
ylabel('Concentration of PCB accumulated; in PE (ng/L)', 'fontweight', 'bold', 'fontsize', 14)
xlim([0 90])
legend(Comp_names())
set(legend, 'NumColumns', 3)
end

```

Matlab script for modeling mass transfer kinetics involved in the uptake of PCBs from a well-mixed water bath across water-side boundary layer into PE using the First Oder model.

(i) No Pulse

```

%%%
clear all
close all
clc
%%%
Start_t = 0;                %%% t = 0 days
End_t = 90;                 %%% t = 90 days
N = 3600*24*End_t;          %%% N = Time in seconds
t = linspace(Start_t, End_t, N); %%% Time points
dt = (End_t - Start_t)/N;    %%% Interval between consecutive time points
CW = zeros(N, 1);           %%% matrix for storing water concentration values
CW(1:N, 1) = 10*10^-6;      % concentration in the water (ug/cm^3)
CPE = zeros(N, 1);

Comp_names = {'PCB 4', 'PCB 15', 'PCB 22', 'PCB 37', 'PCB 47', 'PCB 73', 'PCB 100', 'PCB 110', 'PCB 128'};
MW = [223.1 223.1 257.54 257.54 291.99 291.99 326.43 326.43 360.88];
Kpew = 10.^[4.23 4.99 5.32 5.62 5.64 5.87 6.09 6.39 6.69]; % L/kg
%ke = [2.4268 0.3600 0.1308 0.0500 0.0560 0.0309 0.0160 0.0077 0.0038 0.0005]; %25um thick PE
%ke = [0.6911 0.11 0.0499 0.025 0.0233 0.0136 0.0078 0.0039 0.0019 0.0003]; %50um thick PE
ke = [0.4654 0.0750 0.0337 0.0167 0.0157 0.0092 0.0052 0.0027 0.0013 0.0002]; %75um thick PE
linespec_array1 = {'-r', '--r', '-b', '--b', '-c', '--c', '-g', '--g', '-m'}; %matlab linespecs
for k = 1:length(Comp_names)
    %for k= 1
        for j = 2:N
            CPE(j) = CPE(j-1) + (ke(k)*Kpew(k)*CW(j)*dt) - (ke(k)*CPE(j-1)*dt); % Concentration in PE
            based on CW
        end
        Cw_noneqlb = CPE(N)/Kpew(k);
        CPE_Eqlb = CPE(N)/((1-exp(-ke(k)*End_t))); %%% Concentration in PE at
        equilibrium??
    end
end

```

```

Cw_Eqlb = CPE_Eqlb/Kpew(k);
Cw_Sum=0;
for i=1:N
    x(i)=(i*dt); % time as plotted on x axis
    frac_uptake(i,1)=CPE(i)/CPE_Eqlb;
    Cw_Time(i,1)=CW(i); %TIME AVERAGED: Cw wrt time [ng/L]
    Cw_Sum= Cw_Sum+Cw_Time(i); % TIME AVERAGED: Total Cw [ng/L]
end
Cw_TA=Cw_Sum/(N); %TIME AVG: Time Averaged Cw [ng/L]%% Concentration in water based
on PE

```

```

%% Data Assimilation
C_data(1,2:6)={'Cw','Cw Eqlb','Cw Time Avg','CPE','CPE Eqlb'};
C_data(k+1,1)=Comp_names(k);
C_data{k+1,2}= Cw_noneqlb*10^6;
C_data{k+1,3}= Cw_Eqlb*10^6;
C_data{k+1,4}= Cw_TA*10^6;
C_data{k+1,5}= CPE(N)*10^6;
C_data{k+1,6}= CPE_Eqlb*10^6;
%% Plot
hold on
figure(1)
plot(x, frac_uptake, linespec_array1{k}, 'linewidth', 1)
xlabel('Time(days)', 'fontweight', 'bold', 'fontsize', 14)
ylabel({'Fractional uptake of'; 'PCB from water to PE'}, 'fontweight', 'bold', 'fontsize', 14)
xlim([0 90])
ylim([0 1.2])
legend(Comp_names())
set(legend, 'NumColumns', 3)
end

```

(ii) Pulse

```

%%
clear all
close all
clc
%%
Start_t = 0; %%% t = 0 days
End_t = 90; %%% t = 90 days
N = 3600*24*End_t; %%% N = Time in seconds
t = linspace(Start_t, End_t, N); %%% Time points
dt = (End_t - Start_t)/N; %%% Interval between consecutive time points
CW = zeros(N,1); %%% matrix for storing water concentration values
CPE = zeros(N,1);

```

```

Comp_names={'PCB 4','PCB 15','PCB 22', 'PCB 37','PCB 47','PCB 73', 'PCB 100','PCB 110', 'PCB
128'};
MW=[223.1 223.1 257.54 257.54 291.99 291.99 326.43 326.43 360.88];
Kpew= 10.^[4.23 4.99 5.32 5.62 5.64 5.87 6.09 6.39 6.69]; % L/kg
ke= [2.4268 0.3600 0.1308 0.0500 0.0560 0.0309 0.0160 0.0077 0.0038 0.0005]; %25um thick PE
%ke=[0.6911 0.11 0.0499 0.025 0.0233 0.0136 0.0078 0.0039 0.0019 0.0003]; %50um thick PE
%ke=[0.4654 0.0750 0.0337 0.0167 0.0157 0.0092 0.0052 0.0027 0.0013 0.0002]; %75um thick PE
linespec_array1={'-r','--r','-b','--b','-c','--c', '-g', '--g','-m'}; %matlab linespecs

%%% Introducing Storm
N_startofstorm=3600*24*20;
N_endofstorm=3600*24*30;
CW(1:N_startofstorm,1)=10*10^-6; % concentration in the water (ug/cm^3)
CW(N_startofstorm:N_endofstorm,1)=1*10^-6; % concentration in the water (ug/cm^3)
CW(N_endofstorm:N,1)=10*10^-6; % concentration in the water (ug/cm^3)
%%%
%for k= 1:length(Comp_names)
for k= 4
    for j = 2:N
        CPE(j) = CPE(j-1) + (ke(k)*Kpew(k)*CW(j)*dt) - (ke(k)*CPE(j-1)*dt); % Concentration in PE
based on CW
    end
    Cw_noneqlb= CPE(N)/Kpew(k);
    CPE_Eqlb = CPE(N)/((1-exp(-ke(k)*End_t))); %%% Concentration in PE at
equilibrium??
    Cw_Eqlb = CPE_Eqlb/Kpew(k);
    CPE_Eqlb_NoPulse=[169824.3652 977237.2209 2089296.131 4168693.869 4365158.35 7413102.481
12302687.51 24547087.73 48977877.55];
    Cw_Sum=0;
    for i=1:N
        x(i)=(i*dt); % time as plotted on x axis
        frac_uptake(i,1)=(CPE(i)*10^6)/ CPE_Eqlb_NoPulse(k);
        Cw_Time(i,1)=CW(i); %TIME AVERAGED: Cw wrt time [ng/L]
        Cw_Sum= Cw_Sum+Cw_Time(i); % TIME AVERAGED: Total Cw [ng/L]
    end
    Cw_TA=Cw_Sum/(N); %TIME AVG: Time Averaged Cw [ng/L]%% Concentration in water based
on PE

%%% Data Assimilation
C_data(1,2:6)={'Cw','Cw Eqlb','Cw Time Avg','CPE','CPE Eqlb'};
C_data(k+1,1)=Comp_names(k);
C_data{k+1,2}= Cw_noneqlb*10^6;
C_data{k+1,3}= Cw_Eqlb*10^6;

```

```

C_data{k+1,4}= Cw_TA*10^6;
C_data{k+1,5}= CPE(N)*10^6;
C_data{k+1,6}= CPE_Eqlb*10^6;
%% Plot
hold on
figure(1)
plot(x, frac_uptake,linespec_array1{k},'linewidth',1)
xlabel('Time(days)','fontweight','bold','fontsize',14)
ylabel({'Fractional uptake of';'PCB from water to PE'},'fontweight','bold','fontsize',14)
xlim([0 90])
ylim([0 1.2])
legend(Comp_names())
set(legend, 'NumColumns',3)
end

```

APPENDIX E SUPPLEMENTAL INFORMATION FOR CHAPTER 6

DEVELOPMENT OF A NOVEL EQUILIBRIUM PASSIVE SAMPLING DEVICE FOR METHYLMERCURY IN SEDIMENT AND SOIL POREWATERS

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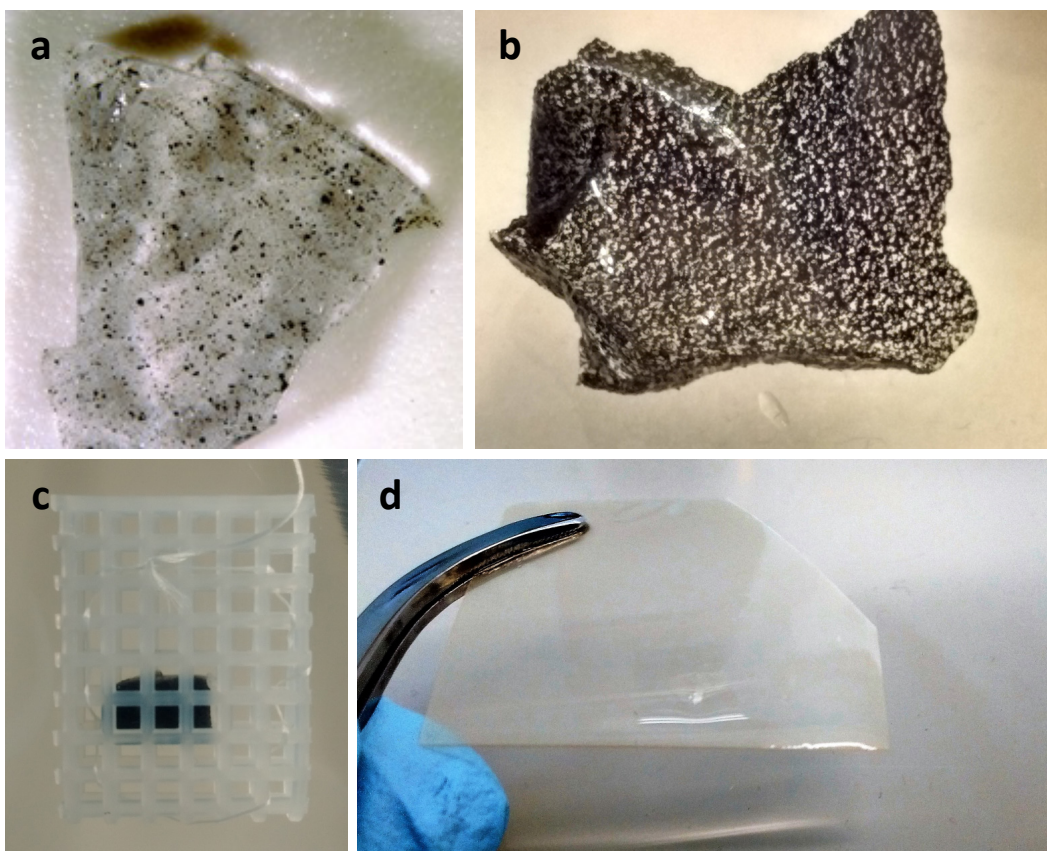


Figure S6.1. Photos of Select Sampling Materials.

(a) ag+AC under light microscope; (b) PVDF+AC under light microscope; (c) ag+AC in protective basket; (d) PET+Cys.

Table S6.1. Raw Data and Calculations from Sediment and Soil Slurry Experiment at d 0.^a

Matrix	Rep	Sampler	Sulfide	pH	C _s	C _{pw}	log K _d
			(μM)		(ng kgdw ⁻¹)	(ng L ⁻¹)	log (L kgdw ⁻¹)
sediment	1	n/a	0.69	7.06	945	0.5	3.31
sediment	2	n/a	0.69	6.98	1149	0.3	3.55
sediment	3	n/a	0.69	6.80	993	0.5	3.33
soil	1	n/a	267.00	7.04	74877	93.1	2.91
soil	2	n/a	270.92	7.07	45118	90.6	2.70
soil	3	n/a	268.95	7.04	44690	79.6	2.75

^a C_s and C_{pw} are concentrations of MeHg in solids and porewater, respectively.

Table S6.2. Raw Data and Calculations from Sediment and Soil Slurry Experiment at d 20.^a

Matrix	Rep	Sampler	Sulfide	pH	C _s	C _{pw}	log K _d	C _{ps}	C _{pw} Pred. w. K _{SRHA}	Avg.	Std. Error	log K _{pw}
			(μM)		(ng kgdw ⁻¹)	(ng L ⁻¹)	log (L kgdw ⁻¹)	(ng kg ⁻¹)	(ng L ⁻¹)	(ng L ⁻¹)	(ng L ⁻¹)	log (L kg ⁻¹)
sediment	1	ag+AC	0.09	6.88	554	0.58*	n.d.	58	0.09			n.d.
sediment	2	ag+AC	0.05	7.10	562	0.13	3.64	59	0.09	0.09	0.00	2.66
sediment	1	ag+SAMMS	0.07	7.24	518	0.19	3.44	116	0.11			2.79
sediment	2	ag+SAMMS	0.08	7.30	614	0.10	3.78	92	0.09	0.05	0.01	2.95
sediment	1	PET+Cys	0.07	7.25	587	0.09	3.83	289	0.44			3.52
sediment	2	PET+Cys	0.05	7.13	623	0.09	3.86	10	0.01	0.08	0.07	2.05
soil	1	ag+AC	0.54	7.14	44049	8.07	3.74	19433	30.10			3.38
soil	2	ag+AC	0.87	7.10	48468	7.96	3.78	22123	34.26	30.73	1.99	3.44
soil	1	ag+SAMMS	0.95	7.15	45573	7.17	3.80	12227	11.95			3.23
soil	2	ag+SAMMS	0.65	7.11	41233	11.30	3.56	10791	10.55	5.64	0.35	2.98
soil	1	PET+Cys	1.06	7.21	46701	9.41	3.70	11546	17.48			3.09
soil	2	PET+Cys	0.62	7.17	47668	8.14	3.77	10761	16.29	5.72	0.20	3.12

^a All concentrations are of MeHg.

* Excluded from calculations for failing *Q*-test.

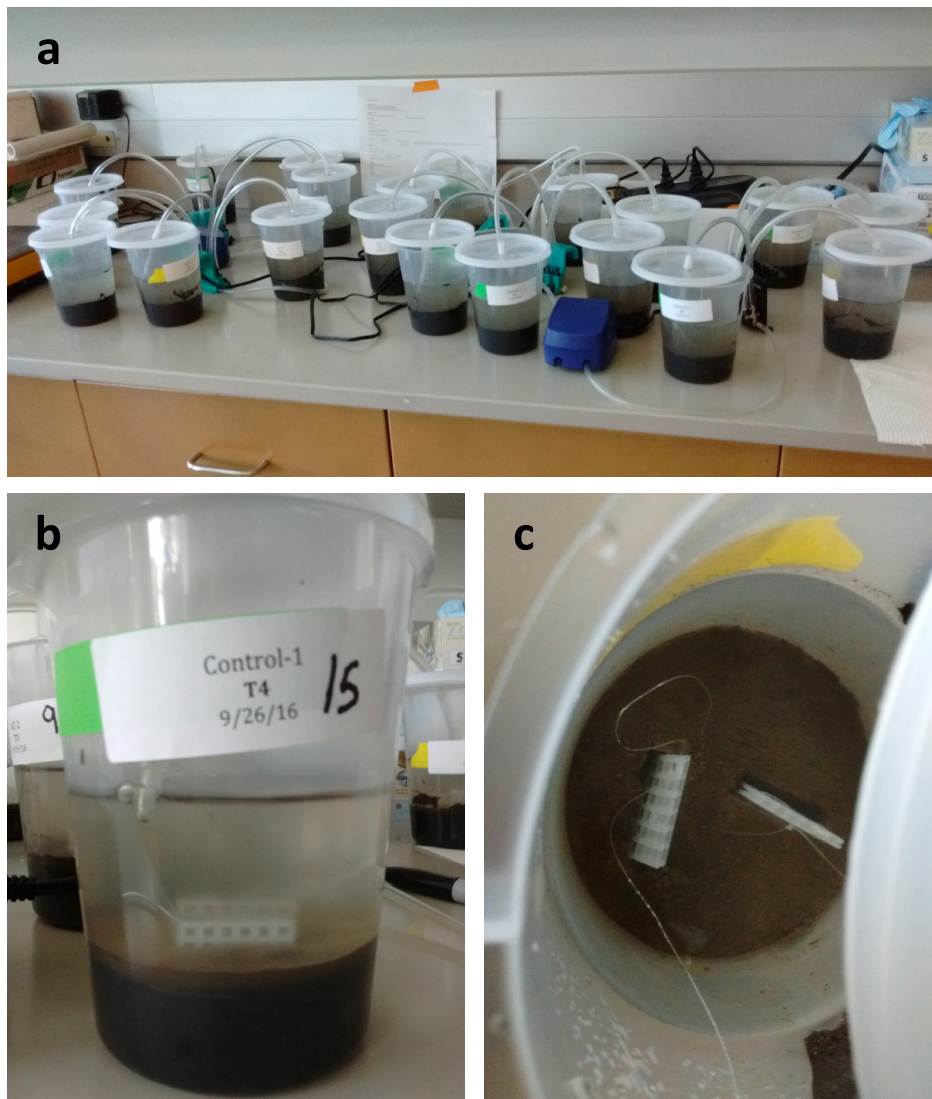


Figure S6.2. Photos of Sediment Microcosm Experiment.

(a) Overview of setup; (b, c) detail views of one beaker from the side and above. Note placement of baskets to expose passive samplers to visibly apparent redox transition zone.

Analytical Methods. MeHg samples were distilled in H_2SO_4 as described by Horvat and others (1993) and analyzed following the method outlined by Mitchell and Gilmour (2008). Briefly, a spike consisting of enriched, stable Hg isotope (Oak Ridge National Laboratories) was added, the samples were buffered with acetate, derivatized with sodium tetraethylborate to facilitate volatilization, purged and concentrated on a Tenax trap with a BrooksRand autosampler, thermally desorbed, separated on an OV-3/Chromosorb column, and introduced into a Perkin Elmer Elan DRC II ICP-MS for detection. THg was also measured as in Mitchell and Gilmour (2008). Concentrations were determined by digesting samples in 7:4 HNO_3 : H_2SO_4 , heating to achieve loss of color, oxidizing organics with BrCl , reducing Hg(II) to Hg(0) with SnCl_2 , and analyzing via ICP-MS. Isotopic dilution calculations were performed to enhance the accuracy and precision of MeHg and THg measurements (Mitchell and Gilmour 2008). MeHg quality assurance data are

summarized in Table S3. Sulfide was measured by mixing samples 1:1 with sulfide antioxidant buffer (2.0 M NaOH, 0.2 M ascorbic acid, and 0.2 M Na₂EDTA in deoxygenated, deionized water prepared anaerobically) and analyzing with a sulfide ion-selective electrode calibrated by lead titration of a saturated sulfide standard. DOC was measured on a Shimadzu organic carbon analyzer. Cations were measured on a Perkin Elmer Optima 8300 ICP-OES. Where not directly measured, major ion concentrations used in speciation modeling were estimated from the chemical composition of Instant Ocean provided by the manufacturer (Spectrum Brands 2008).

Table S6.3. Quality Assurance Data for MeHg Analyses in this Work.^a

Matrix	RPD Duplicates	CRM Recovery	ID Spike Recovery	Distillation Blanks	DL	Units
water	6.2 ± 2.4%	95.8 ± 1.9%	70.3 ± 1.1%	0.52 ± 0.28	1.02 ± 0.27	ng L ⁻¹
sediment/ soil	22.6 ± 0.7%	105.1 ± 4.2%	59.8 ± 3.8%	0.51 ± 0.13	66.3 ± 11.2	ng kgdw ⁻¹
ag+AC	n/a	97.3 ± 2.2%	54.8 ± 2.3%	0.06 ± 0.01	228.66 ± 52.53	ng kgww ⁻¹
PET+Cys	n/a	99.7 ± 4.4%	61.1% ± 3.4%	0.05 ± 0.01	188.63 ± 27.84	ng kgww ⁻¹

^a Analysis was done by isotope dilution ICP-MS, i.e. with internal stable isotope standards. Relative percent differences (RPD) are for duplicate analyses of the same prepared sample. CRMs were NIST 1566b oyster tissue. Detection limits were estimated as three times the standard error of blanks across samples.

Table S6.4. Additional Reactions Used in MINEQL+ Equilibrium Speciation Modeling.

Reaction	log K	Reference
$H^+ + DOMRS^- \rightleftharpoons DOMRSH$	9.000	(Karlsson and Skjellberg 2003; Liem-Nguyen and others 2016)
$MeHg^+ + SO_4^{2-} \rightleftharpoons MeHgSO_4^-$	0.940	(Rabenstein and others 1976)
$MeHg^+ + Br^- \rightleftharpoons MeHgBr$	6.620	(Schwarzenbach and Schellenberg 1965)
$MeHg^+ + Cl^- \rightleftharpoons MeHgCl$	5.400	(Loux 2007)
$MeHg^+ + F^- \rightleftharpoons MeHgF$	1.500	(Schwarzenbach and Schellenberg 1965)
$MeHg^+ + DOMRS^- \rightleftharpoons MeHgDOMRS$	17.500	(Karlsson and Skjellberg 2003; Liem-Nguyen and others 2016; Qian and others 2002; Reid and Rabenstein 1981)
$2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$	-2.150	(De Robertis and others 1998)
$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$	-4.500	(Loux 2007)
$MeHg^+ + CO_3^{2-} \rightleftharpoons MeHgCO_3^-$	6.100	(Rabenstein and others 1976)
$MeHg^+ + H^+ + CO_3^{2-} \rightleftharpoons MeHgHCO_3$	12.950	(Loux 2007)
$MeHg^+ + HS^- \rightleftharpoons MeHgS^- + H^+$	7.300	(Schwarzenbach and Schellenberg 1965)
$MeHg^+ + HS^- \rightleftharpoons MeHgSH$	14.500	(Dyrssen and Wedborg 1991)
$2MeHg^+ + HS^- \rightleftharpoons (MeHg)_2S + H^+$	23.600	(Loux 2007; Schwarzenbach and Schellenberg 1965)

^a Two components were added to the software's database: MeHg (+1 charge), and DOMRS, representing a model reduced exocyclic sulfur binding site in Suwannee River Humic Acid (-1 charge). DOMRS site densities were estimated from DOC measurements with the following equation, under the assumption that DOM characteristics were similar to SRHA (Graham and others 2017; Manceau and Nagy 2012; IHSS 2017):

$$[\text{DOMRS}] = \frac{\text{mg DOC}}{\text{L}} \times \frac{\text{mg SRHA}}{0.5263 \text{ mg DOC}} \times \frac{0.0054 \text{ mg S}}{\text{mg SRHA}} \times \frac{0.236 \text{ mg reduced exocyclic S}}{\text{mg S}} \\ \times \frac{\text{mol reduced exocyclic S}}{32065 \text{ mg reduced exocyclic S}}$$

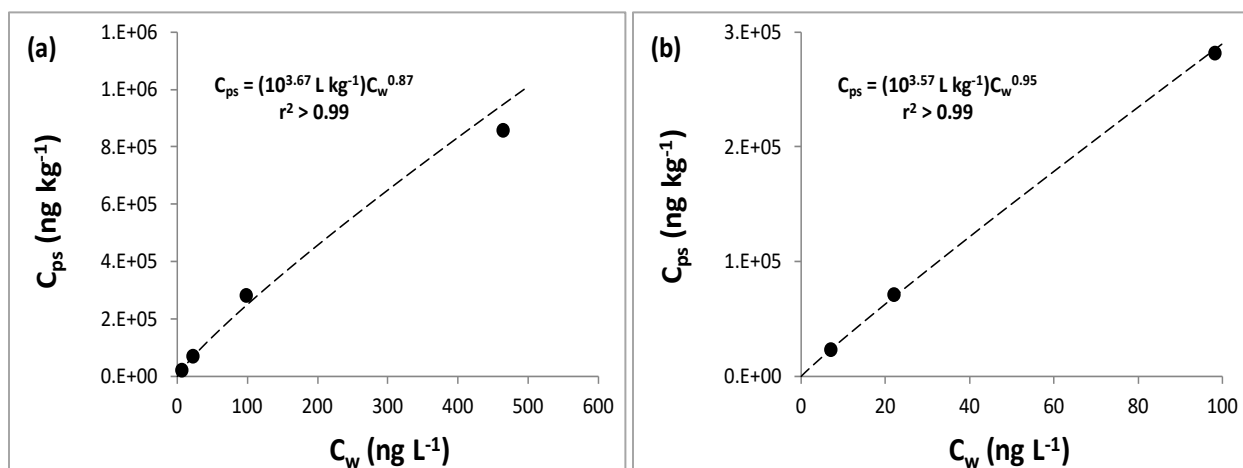


Figure S6.3. Freundlich Model Fits of Sorption Isotherm Data for MeHgOH on ag+AC.

Points: measured data. Dashed lines: model fits (equations shown on plots). (a) All four points; (b) first three points only.

Sampling Mechanisms. Using MeHg partitioning coefficients for bare AC (Gomez-Eyles and others 2013) and Thiol-SAMMS (the present work), we conducted a simple, mass-weighted partitioning analysis for the samplers containing suspensions of these sorbent materials, as follows:

$$K_{pw, \text{predicted}} = f_{\text{polymer}} K_{\text{polymer}} + f_{\text{sorbent}} K_{\text{sorbent}} \quad (\text{S1})$$

where f is the fractional contribution of each component to the total mass of the material. Because these calculations involved K values separated by multiple orders of magnitude, they were accompanied by substantial uncertainty. Even so, a comparison of measured K_{pw} to $K_{pw, \text{predicted}}$ provided a semiquantitative indication of the relative contributions of internal diffusion and surface adsorption to the overall mechanisms of sampler accumulation (Table S5). Notably, the agarose-based samplers performed more closely to model predictions than did the PVDF-based samplers, indicating that the former were more permeable and amenable to suffusion by MeHgOH. Indeed, MeHg species are known to pass readily through agarose, which is sometimes used as the diffusive gel in DGT samplers (Fernández-Gómez and others 2014; Gao and others 2014). A diffusive mechanism for ag+AC was confirmed in the subsequent kinetics experiment.

In an attempt to enhance the permeability of PVDF samplers, variants were prepared with either water or 1:1 methanol:water as nonsolvent to produce contrasting membrane pore structures

(Sukitpaneemit and Chung 2009). The measured partitioning by the methanol:water-prepared sampler, which was formulated to encourage a more globular microstructure with fewer macrovoids, was somewhat greater than that of the water-prepared sampler ($\log K_{pw} = 3.73$ vs. 3.16). However, both remained well below their model-predicted partitioning, likely due to the dense outer skin that is characteristic of PVDF membranes regardless of the nonsolvent used in preparation (Sukitpaneemit and Chung 2009). Thus, it appears likely that partitioning by all of the PVDF samplers in this study was dominated by surface adsorption and that most of the included sorbent particles were not accessed by MeHgOH. An analogous method to modulate the permeability of agarose was also explored. Alternate versions of ag+AC and ag+SAMMS were prepared with a polyethylene glycol dopant to promote macroporosity in the gel (agPEG+AC and agPEG+SAMMS; Charlionet and others 1996). The effects of this modification on isotherm partitioning were ambiguous. While their measured and predicted K_{pw} values were in better agreement than those of ag+AC and ag+SAMMS, this was due to increased partitioning by agPEG+AC on one hand and decreased partitioning by agPEG+SAMMS on the other; no overall trend was apparent. Additionally, the agPEG gels themselves were slushier and less mechanically robust than standard agarose, making them poorly suited for deployment in sediment and soil, so the idea was abandoned.

Table S6.5. Freundlich Fitting Parameters for MeHg Isotherm Experiments^a

Abbreviation	Material	Target Sorbent Conc.	MeHgOH			MeHgSRHA		
			log K _{pw} ^b	p-value	1/n	log K _{pw} ^b	p-value	1/n
ag	agarose	n/a	3.18 ± 0.12	0.0014	0.54	n.d.	n.d.	
ag+AC	activated carbon suspended in agarose	10% w/w AC	3.67 ± 0.08	0.0005	0.86	2.91 ± 0.08	<0.0001	0.93
ag+Cys	L-cysteine dissolved in agarose	2% w/w Cys	2.84 ± 0.23	0.0011	1.04	n.d.	n.d.	n.d.
ag+Cys-alg	L-cysteine-functionalized alginate suspended in agarose	5% w/w Cys	4.12 ± 0.24	<0.0001	0.70	n.d.	n.d.	n.d.
ag+Cys-xylo	L-cysteine-functionalized xyloglucans suspended in agarose	5% w/w Cys	3.47 ± 0.24	0.0005	0.73	n.d.	n.d.	n.d.
ag+MAA-chit	mercapto-functionalized chitosan suspended in agarose	0.3% w/w mercapto	3.47 ± 0.19	0.0004	0.88	n.d.	n.d.	n.d.
ag+MPTMS-DE	mercapto-functionalized diatomaceous earth suspended in agarose	1% w/w mercapto	4.23 ± 0.09	<0.0001	0.73	3.29 ± 0.07	<0.0001	0.82
ag+SAMMS	thiol-SAMMS suspended in agarose	2% w/w SAMMS	4.95 ± 0.16	<0.0001	1.03	3.50 ± 0.15	0.00	0.76
agPEG	agarose doped with polyethylene glycol and glycerol	n/a	3.28 ± 0.23	0.00007	0.46	n.d.	n.d.	n.d.
agPEG+AC	activated carbon suspended in PEG-doped agarose	3% w/w AC	4.11 ± 0.15	0.0001	0.72	3.21 ± 0.20	0.0005	0.78
agPEG+SAMMS	thiol-SAMMS suspended in PEG-doped agarose	2% w/w SAMMS	4.01 ± 0.04	<0.0001	0.96	2.81 ± 0.06	<0.0001	1.14
CA	cellulose acetate	n/a	2.95 ± 0.07	<0.0001	0.63	n.d.	n.d.	n.d.
CA+MA	mercapto-functionalized cellulose acetate	20% w/w mercapto	2.21 ± 0.19	0.0075	1.06	n.d.	n.d.	n.d.
CN	cellulose nitrate	n/a	3.22 ± 0.18	0.0004	0.69	n.d.	n.d.	n.d.
DE	diatomaceous earth	n/a	3.16 ± 0.13	<0.0001	0.69	n.d.	n.d.	n.d.
MPTMS-DE	mercapto-functionalized diatomaceous earth	3% w/w mercapto	5.52 ± 0.07	<0.0001	1.24	n.d.	n.d.	n.d.

Abbreviation	Material	Target Sorbent Conc.	MeHgOH			MeHgSRHA		
			$\log K_{pw}^b$	p-value	1/n	$\log K_{pw}^b$	p-value	1/n
Parafilm	paraffin	n/a	1.93 ± 0.20	0.0023	1.07	n.d.	n.d.	n.d.
PDMS	polydimethylsiloxane	n/a	2.56 ± 0.04	0.0006	0.57	n.d.	n.d.	n.d.
PES	polyethersulfone	n/a	2.78 ± 0.38	0.0052	0.76	n.d.	n.d.	n.d.
PET+Cys	L-cysteine-functionalized polyethylene terephthalate	8 nmol Cys cm ⁻²	4.39 ± 0.21	0.0002	0.62	3.61 ± 0.07	<0.0001	0.55
POM38	polyoxymethylene (38 μ m thick)	n/a	2.58 ± 0.13	0.0003	0.54	n.d.	n.d.	n.d.
PTFE	polytetrafluoroethylene	n/a	2.58 ± 0.11	0.0002	0.67	n.d.	n.d.	n.d.
PVDFm+AC	activated carbon suspended in PVDF prepared with 1:1 methanol:water nonsolvent	10% w/w AC	3.74 ± 0.32	0.007	0.89	n.d.	n.d.	n.d.
PVDFw	polyvinylidene fluoride prepared with water nonsolvent	n/a	2.77 ± 0.29	0.0102	0.68	n.d.	n.d.	n.d.
PVDFw+AC	activated carbon suspended in PVDF prepared with water nonsolvent	10% w/w AC	3.39 ± 0.20	0.0036	0.92	3.51 ± 0.02	<0.0001	0.62
PVDFw+Cys	L-cysteine dissolved in PVDF	6% w/w Cys	5.27 ± 0.11	<0.0001	0.55	n.d.	n.d.	n.d.
PVDFw+SAMMS	thiol-SAMMS suspended in PVDF	5% w/w SAMMS	4.41 ± 0.15	<0.0001	0.82	2.85 ± 0.10	0.0001	1.12
SAMMS	thiol-SAMMS	n/a	n.d.	n.d.	n.d.	5.17 ± 0.16	<0.0001	n.d.

^a Experimental data fit to a Freundlich adsorption isotherm model.

^b Partition coefficient $\pm$ 1SE

References or sources for polymers and sorbents: ag: Gao and others 2011; Cys+alg: Bernkop-Schnürch and others 2001; Cys+xylo: Bhalekar and others 2013; ag+MAA-chit: Kast and Bernkop-Schnürch 2001; ag+MPTMS-DE: Yu and others 2012; SAMMS: Steward Environmental Solutions; agPEG: Charlionet and others 1996; CA: Membrane Filtration Products Inc.; MA: Aoki and others 2007; CN: Membrane Filtration Products Inc.; DE: Honeywell, Muskegon, MI; MPTMS-DE: Yu and others 2012; parafilm: Bemis, Oshkosh, WI; PDMS: Altec, St. Austell, UK; PES: Goodfellow Cambridge, Inc. Huntington, UK; PET+Cys: Duan and Lewis 2002; POM38: CS Hyde, Lake Villa, IL; PTFE: Grainger, Lake Forest, IL.

Table S6.6. Comparison of Measured Sampler Partitioning in Isotherm Studies ($\log K_{pw}$) to Mass-weighted Predictions Based on Fractional Compositions of Polymer ($f_{polymer}$) and Sorbent ($f_{sorbent}$).

Abbreviation	Material		$\log K_{pw}$	p	$f_{polymer}$	$f_{sorbent}$	$\log K_{pw,predicted}$	Ratio $K_{pw}: K_{pw,predicted}$
ag	agarose		2.06	0.0018	n/a	n/a	n/a	n/a
agPEG	agarose doped with polyethylene glycol and glycerol		2.17	0.0367	n/a	n/a	n/a	n/a
PVDFw	poly(vinylidene fluoride) prepared with water nonsolvent		2.11	0.0009	n/a	n/a	n/a	n/a
AC	activated carbon		5.22	0.0004	n/a	n/a	n/a	n/a
ag+AC	activated carbon suspended in agarose		3.46	0.0004	0.96	0.04	3.8	0.43
agPEG+AC	activated carbon suspended in PEG-doped agarose		3.28	0.0001	0.97	0.03	3.4	0.76
PVDFw+AC	AC suspended in PVDF prepared with water nonsolvent		3.16	0.0003	0.89	0.11	3.9	0.17
PVDFm+AC	AC suspended in PVDF prepared with 1:1 methanol:water nonsolvent		3.73	0.0003	0.89	0.11	4.3	0.29

^a See text above for prediction equation.

Table S6.7. Raw Data and Calculations for Initial Passive Sampler Kinetics Experiment.

Sorbate	Sampler	t (min)	C _w (ng L ⁻¹)	C _{ps} (ng kg ⁻¹)	ng on ps	ng in Water	Mass Bal.	% Recov.	C _{ps} :C _w	log (C _{ps} :C _w)	Frac. Equil. vs. Isotherm
MeHgOH	ag+AC	1411	1.75	666	0.018	0.087	0.106	46%	381	2.58	0.14
MeHgOH	ag+AC	10029	0.16	2210	0.021	0.008	0.028	12%	13984	4.15	4.96
MeHgOH	ag+AC	20077	0.10	1042	0.017	0.005	0.021	9%	10582	4.02	3.75
MeHgOH	ag+AC	40250	0.03	1799	0.010	0.002	0.012	5%	56340	4.75	19.99
MeHgOH	PET+Cys	1390	3.13	977	0.017	0.159	0.176	76%	312	2.49	0.06
MeHgOH	PET+Cys	10008	0.12	1184	0.021	0.006	0.026	11%	9937	4.00	1.85
MeHgOH	PET+Cys	20056	0.06	1559	0.025	0.003	0.028	12%	25002	4.40	4.66
MeHgOH	PET+Cys	40231	0.09	1281	0.017	0.004	0.021	9%	14575	4.16	2.71
MeHgSRHA	ag+AC	433	11.22	806	0.010	0.566	0.576	58%	72	1.86	0.11
MeHgSRHA	ag+AC	1405	6.42	287	0.007	0.330	0.337	34%	45	1.65	0.07
MeHgSRHA	ag+AC	10018	12.56	1370	0.024	0.634	0.657	66%	109	2.04	0.16
MeHgSRHA	ag+AC	20067	8.69	813	0.016	0.442	0.458	46%	93	1.97	0.14
MeHgSRHA	ag+AC	40240	3.43	2049	0.034	0.175	0.209	21%	597	2.78	0.88
MeHgSRHA	ag+AC	79404	0.85	554	0.012	0.043	0.055	5%	651	2.81	0.96
MeHgSRHA	PET+Cys	429	11.30	2155	0.048	0.569	0.617	62%	191	2.28	0.10
MeHgSRHA	PET+Cys	1389	15.00	899	0.020	0.767	0.787	79%	60	1.78	0.03
MeHgSRHA	PET+Cys	10001	2.57	400	0.009	0.129	0.138	14%	155	2.19	0.08
MeHgSRHA	PET+Cys	20050	6.40	1441	0.019	0.328	0.347	35%	225	2.35	0.12
MeHgSRHA	PET+Cys	40223	2.14	825	0.017	0.104	0.121	12%	386	2.59	0.20
MeHgSRHA	PET+Cys	79388	0.48	1997	0.022	0.024	0.047	5%	4139	3.62	2.12

^a All concentrations are of MeHg. Mass balances in samples showed loss of MeHg over time, especially in isotherms without added SRHA. This resulted in artificially reduced C_w at later time points and partitioning that surpassed the 14-d K_{pw} values generated in screening isotherms. Mass balances in MeHgSRHA samples were somewhat more favorable, indicating a preservative effect of either SRHA or the accompanying buffer.

Table S6.8. Mass Balance Data for ag+AC Thick/Thin Sampler Kinetics Experiment.

Time Pt.	ag+AC	g Water	Final C _w (ng L ⁻¹)	ng in Water	ng in Sampler	Total ng	Frac. Recov.
0	none	37.437	45.77	1.713	0.000	1.713	92%
0	thick	40.317	48.76	1.966	0.018	1.984	98%
0	thin	39.320	49.78	1.957	0.022	1.979	101%
1	none	36.519	48.25	1.762	0.000	1.762	97%
1	thick	38.434	47.71	1.834	0.028	1.862	97%
1	thin	37.636	48.59	1.829	0.040	1.869	99%
1	none	39.413	48.92	1.928	0.000	1.928	98%
1	thick	39.840	45.99	1.832	0.028	1.860	93%
1	thin	37.262	46.44	1.730	0.037	1.767	95%
2	none	35.790	51.99	1.861	0.000	1.861	104%
2	thick	38.035	50.68	1.928	0.031	1.958	103%
2	thin	39.596	50.66	2.006	0.050	2.056	104%
3	none	37.717	48.47	1.828	0.000	1.828	97%
3	thick	39.623	49.97	1.980	0.066	2.046	103%
3	thin	38.236	47.71	1.824	0.096	1.920	100%
4	none	36.918	49.62	1.832	0.000	1.832	99%
4	thick	38.405	51.84	1.991	0.165	2.156	112%
4	thin	39.172	50.90	1.994	0.222	2.216	113%
5	none	39.288	48.11	1.890	0.000	1.890	96%
5	thick	39.138	42.42	1.660	0.240	1.900	97%
5	thin	39.306	49.67	1.952	0.432	2.384	121%
5	none	39.027	51.73	2.019	0.000	2.019	103%
5	thick	40.596	52.98	2.151	0.237	2.388	118%
5	thin	39.471	44.78	1.768	0.293	2.060	104%
6	none	37.938	45.68	1.733	0.000	1.733	91%
6	thick	40.371	39.30	1.586	0.518	2.104	104%
6	thin	39.435	36.16	1.426	0.607	2.033	103%
7	none	40.326	49.90	2.012	0.000	2.012	100%
7	thick	38.901	32.21	1.253	0.297	1.550	80%
7	thin	38.012	33.87	1.288	0.308	1.596	84%

^a All concentrations are of MeHg. All samples were spiked to an initial concentration of 50 ng L⁻¹. Average fractional recovery was 102 ± 7% (s.d. among all 30 samples).

Activated Carbon Kinetics Modeling. The MeHg-AC kinetic data (Figure S4a) were fitted with pseudo-first order (Lagergren 1898) and pseudo-second order (Ho and McKay 1998) (Figure S4b) kinetic models. Both models provided good fits of the data ($r^2 = 0.98$ and 1.0, respectively),

suggesting a Langmuir-type adsorption mechanism (Tien and Ramarao 2017). The apparent sorption rate constants, which depend on experimental conditions including initial C_w , were $k_1 = 0.31 \text{ h}^{-1}$ and $k_2 = 2.1 \times 10^{-4} \text{ kg ng}^{-1} \text{ h}^{-1}$. The equilibrium C_{AC} predicted by the pseudo-second order model was $1.2 \times 10^6 \text{ ng kg}^{-1}$. It should be emphasized that this does not represent this AC's maximum adsorptive capacity. In Gomez-Eyles et al., the MeHg sorption isotherm of this carbon remained log-linear for initial C_w values up to 6000 ng L^{-1} under conditions nearly identical to ours. There, the final C_{AC} was $2.8 \times 10^7 \text{ ng kg}^{-1}$ (Gomez-Eyles and others 2013). This, along with the proportionality of our screening isotherms, indicates that there is little danger of saturating an ag+AC sampler with MeHg at environmentally realistic C_{pw} . We also evaluated the kinetics of inorganic mercury sorption to AC (Table S9 and Figure S5).

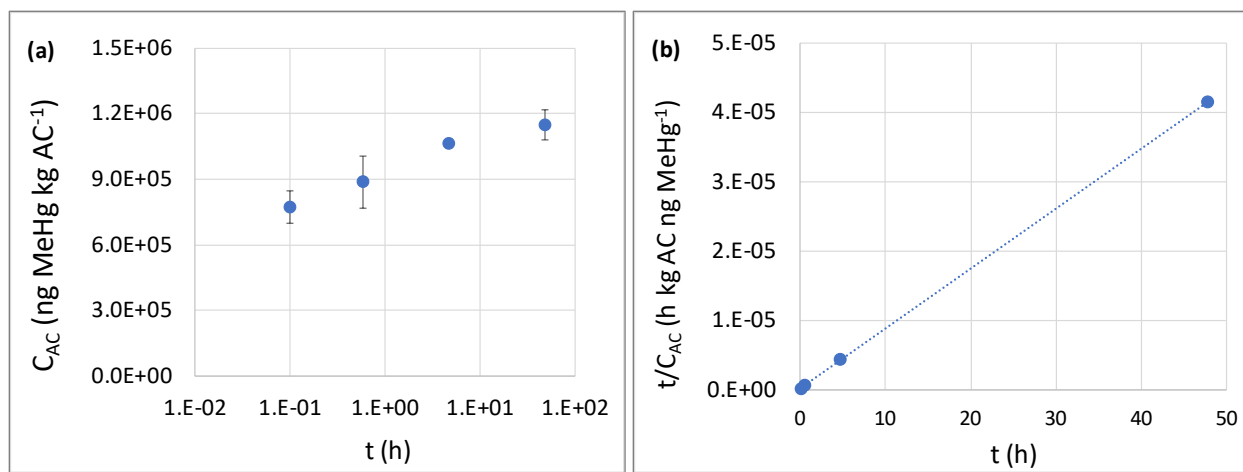


Figure S6.4. Kinetics of MeHgOH Adsorption to a Coal-derived Activated Carbon (Initial $C_w = 250 \text{ ng L}^{-1}$).

(a) MeHg concentrations on AC over time; error bars show ± 1 standard error. (b) Pseudo-second order model fit. $k_2 = 2.1 \times 10^{-4} \text{ kg ng}^{-1} \text{ h}^{-1}$; $C_{AC,eq} = 1.2 \times 10^6 \text{ ng kg}^{-1}$.

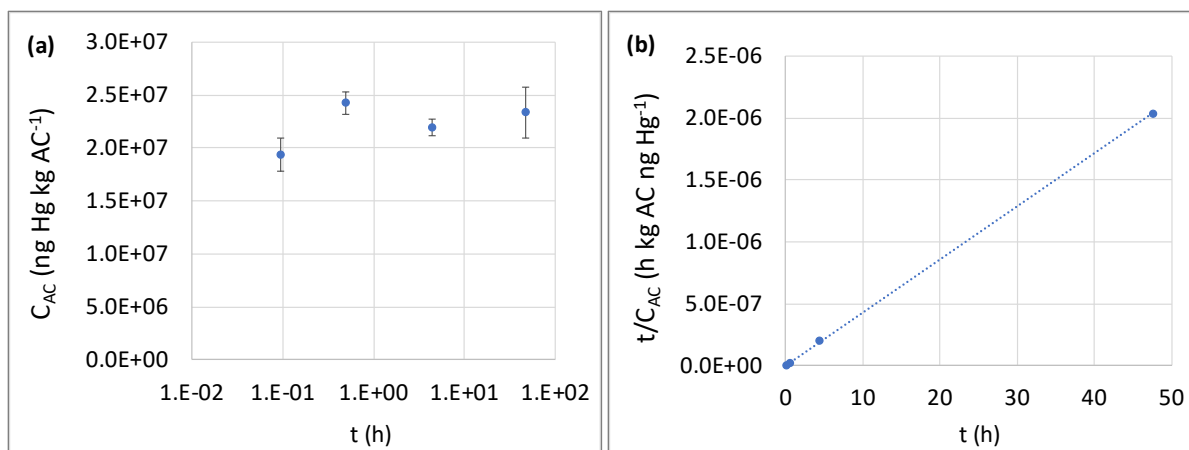


Figure S6.5. Kinetics of Hg(OH)_2 Adsorption to a Coal-derived Activated Carbon (Initial $C_w = 5000 \text{ ng L}^{-1}$).

(a) Hg Concentrations on AC over time; error bars show ± 1 standard error. (b) Pseudo-second order model fit. $k_2 = 1.1 \times 10^{-5} \text{ kg ng}^{-1} \text{ h}^{-1}$; $C_{AC,eq} = 2.3 \times 10^7 \text{ ng kg}^{-1}$.

Table S6.9. Raw Data and Calculations for SRHA Gradient Experiment.

Sorbent	SRHA (mg L ⁻¹)	C _w (ng L ⁻¹)	m _w MeHg (ng)	m _{sorbent} MeHg (ng)	m sorbent (mg)	C _{sorbent} (ng g ⁻¹)	log K _d	Treatment Average log K _d
CAC-Coal	5	0.15	2.94	9.33	12	777.83	3.72	
CAC-Coal	5	0.14	2.75	9.52	10	952.17	3.84	3.77
CAC-Coal	5	0.15	2.95	9.32	11	847.00	3.76	
CAC-Coal	25	0.22	4.32	5.68	10	557.28	3.41	
CAC-Coal	25	0.29	5.76	4.24	10	423.64	3.17	3.29
CAC-Coal	25	0.23	4.56	5.44	13	431.81	3.28	
CAC-Coal	50	0.22	4.37	7.90	12	657.99	3.48	
CAC-Coal	50	0.33	6.62	5.65	10	565.35	3.23	3.35
CAC-Coal	50	0.26	5.24	7.03	12	586.23	3.35	
CAC-Coal	500	0.52	10.37	1.90	11	172.92	2.52	
CAC-Coal	500	0.30	6.03	6.24	12	520.02	3.24	2.86
CAC-Coal	500	0.45	9.00	3.27	11	297.19	2.82	
thiol-SAMMS	5	0.04	0.83	9.17	11	833.75	4.30	
thiol-SAMMS	5	0.04	0.72	9.28	12	773.14	4.33	4.30
thiol-SAMMS	5	0.04	0.89	9.11	11	827.83	4.27	
thiol-SAMMS	50	0.05	1.00	9.00	10	900.16	4.26	
thiol-SAMMS	50	0.05	0.97	9.03	10	903.28	4.27	4.26
thiol-SAMMS	50	0.05	0.98	9.02	10	902.37	4.27	
thiol-SAMMS	500	0.23	5.53	6.74	12	561.45	3.38	
thiol-SAMMS	500	0.07	1.78	10.49	11	873.80	4.07	3.84
thiol-SAMMS	500	0.08	1.89	10.38	10	943.53	4.07	

Table S10. Raw Data and Calculations for MeHg AC Kinetics and Desorption Experiment.

Sorbent	Time Pt.	Rep	t (h)	C _w (ng L ⁻¹)	m _{tot} (ng)	m in Water (ng)	Frac. as Carry-over	ng on AC	mg AC	C _{AC} (ng kg ⁻¹)	C _{AC} :C _w (L kg ⁻¹)	Avg. log K
none	a1	1	0.08	6.60	0.976	0.32	n/a	n/a	n/a	n/a	n/a	
none	a1	2	0.08	10.44	0.989	0.52	n/a	n/a	n/a	n/a	n/a	
CAC-Coal	a1	1	0.10	90.81	11.762	4.27	n/a	7.490	10.70	699961	7708	
CAC-Coal	a1	2	0.10	61.80	13.103	3.24	n/a	9.864	11.61	849629	13749	4.03
none	a2	1	0.60	8.42	0.986	0.41	n/a	n/a	n/a	n/a	n/a	
none	a2	2	0.60	9.84	1.037	0.51	n/a	n/a	n/a	n/a	n/a	
CAC-Coal	a2	1	0.57	33.52	12.505	1.68	n/a	10.828	10.75	1007266	30054	
CAC-Coal	a2	2	0.58	69.52	12.658	3.52	n/a	9.138	11.89	768530	11055	4.31
none	a3	1	4.60	7.74	0.982	0.38	n/a	n/a	n/a	n/a	n/a	
none	a3	2	4.62	9.94	1.013	0.50	n/a	n/a	n/a	n/a	n/a	
CAC-Coal	a3	1	4.67	17.57	12.916	0.91	n/a	12.008	10.90	1101662	62691	
CAC-Coal	a3	2	4.67	19.64	12.732	1.00	n/a	11.732	11.33	1035469	52715	
CAC-Coal	a3	3	4.68	21.98	12.606	1.11	n/a	11.498	10.84	1060663	48262	4.74
none	a4	1	47.63	10.12	0.987	0.50	n/a	n/a	n/a	n/a	n/a	
none	a4	2	47.65	10.05	1.009	0.51	n/a	n/a	n/a	n/a	n/a	
CAC-Coal	a4	1	47.67	7.42	12.670	0.38	n/a	12.294	10.31	1192438	160639	
CAC-Coal	a4	2	47.68	9.97	12.872	0.51	n/a	12.359	9.95	1242066	124554	
CAC-Coal	a4	3	47.68	9.88	12.378	0.49	n/a	11.888	11.74	1012640	102455	5.11
none	d1	1	0.08	0.22	0.657	0.01	0.27	n/a	n/a	n/a	n/a	
none	d1	2	0.08	0.23	0.476	0.01	0.34	n/a	n/a	n/a	n/a	
CAC-Coal	d1	1	0.08	3.73	7.694	0.19	1.10	7.509	10.70	701737	188322	
CAC-Coal	d1	2	0.10	5.77	10.044	0.29	0.61	9.749	11.61	839700	145601	5.27
none	d2	1	0.57	0.23	0.574	0.01	0.25	n/a	n/a	n/a	n/a	
none	d2	2	0.57	0.26	0.531	0.01	0.32	n/a	n/a	n/a	n/a	
CAC-Coal	d2	1	0.53	3.37	10.878	0.17	0.29	10.710	10.75	996271	295649	
CAC-Coal	d2	2	0.53	8.86	9.259	0.46	0.26	8.796	11.89	739792	83479	5.28
none	d3	1	3.58	0.29	0.606	0.01	0.26	n/a	n/a	n/a	n/a	
none	d3	2	3.60	0.30	0.513	0.01	0.23	n/a	n/a	n/a	n/a	
CAC-Coal	d3	1	3.58	6.49	12.043	0.31	0.11	11.731	10.90	1076277	165899	
CAC-Coal	d3	2	3.60	10.06	11.777	0.49	0.09	11.284	11.33	995906	98970	
CAC-Coal	d3	3	3.60	10.08	11.536	0.50	0.08	11.041	10.84	1018515	101051	5.09
none	d4	1	43.28	0.24	0.493	0.01	0.43	n/a	n/a	n/a	n/a	
none	d4	2	43.28	0.27	0.505	0.01	0.26	n/a	n/a	n/a	n/a	
CAC-Coal	d4	1	43.30	1.62	12.312	0.08	0.22	12.231	10.31	1186325	733212	
CAC-Coal	d4	2	43.32	1.96	12.376	0.10	0.18	12.278	9.95	1233927	630749	
CAC-Coal	d4	3	43.33	1.26	11.906	0.07	0.25	11.835	11.74	1008112	798736	5.86

^a All concentrations are of MeHg.

Table S6.11. Raw Data and Calculations for Hg_i AC Kinetics and Desorption Experiment.

Sorbent	Time Pt.	Rep	t (h)	C _w (ng L ⁻¹)	m _{tot} (ng)	m in Water (ng)	Frac. as Carry-over	ng on AC	mg AC	C _{AC} (ng kg ⁻¹)	C _{AC} :C _w (L kg ⁻¹)	Avg. log K
none	a1	1	0.08	11.50	2.411	0.55	n/a	1.857	n/a	n/a	n/a	
none	a1	2	0.08	16.79	2.578	0.87	n/a	1.713	n/a	n/a	n/a	
CAC-Coal	a1	1	0.08	275.81	249.045	13.74	n/a	235.307	10.85	21687300	78631	
CAC-Coal	a1	2	0.12	123.07	244.370	6.01	n/a	238.355	11.90	20029845	162754	
CAC-Coal	a1	3	0.08	46.75	255.985	2.39	n/a	253.591	15.53	16329124	349250	5.29
none	a2	1	0.52	7.00	2.465	0.35	n/a	2.119	n/a	n/a	n/a	
none	a2	2	0.52	7.24	2.536	0.37	n/a	2.169	n/a	n/a	n/a	
CAC-Coal	a2	1	0.48	5.43	249.790	0.27	n/a	249.519	10.78	23146463	4264877	
CAC-Coal	a2	2	0.48	3.94	242.045	0.19	n/a	241.854	10.47	23099726	5858536	
CAC-Coal	a2	3	0.50	6.07	250.410	0.30	n/a	250.106	9.46	26438249	4353121	6.68
none	a3	1	4.32	11.63	2.497	0.58	n/a	1.916	n/a	n/a	n/a	
none	a3	2	4.32	19.26	2.523	0.97	n/a	1.552	n/a	n/a	n/a	
CAC-Coal	a3	1	4.33	9.51	255.325	0.49	n/a	254.839	11.28	22592138	2375327	
CAC-Coal	a3	2	4.35	11.97	249.750	0.60	n/a	249.152	12.24	20355561	1700461	
CAC-Coal	a3	3	4.38	16.34	249.340	0.82	n/a	248.525	10.89	22821393	1396340	6.26
none	a4	1	47.57	4.68	2.432	0.23	n/a	2.204	n/a	n/a	n/a	
none	a4	2	47.58	15.43	2.554	0.79	n/a	1.766	n/a	n/a	n/a	
CAC-Coal	a4	1	47.57	1.71	246.040	0.08	n/a	245.956	13.23	18590770	10876228	
CAC-Coal	a4	2	47.57	1.36	247.125	0.07	n/a	247.058	9.36	26395060	19401360	
CAC-Coal	a4	3	47.60	8.40	255.055	0.43	n/a	254.626	10.16	25061642	2981984	7.04
none	d1	1	0.08	1.18	1.861	0.06	0.07	n/a	n/a	n/a	n/a	
none	d1	2	0.10	0.89	1.719	0.05	0.13	n/a	n/a	n/a	n/a	
CAC-Coal	d1	1	0.08	10.72	236.095	0.57	1.38	235.526	10.85	21707439	2024606	
CAC-Coal	d1	2	0.10	10.76	238.690	0.60	0.55	238.086	11.90	20007199	1859099	
CAC-Coal	d1	3	0.10	29.23	253.730	1.57	0.09	252.155	15.53	16236656	555568	6.17
CAC-Coal	d2	1	0.58	17.11	249.526	0.85	0.01	248.676	10.78	23068300	1347896	
CAC-Coal	d2	3	0.60	6.12	250.116	0.29	0.04	249.828	9.46	26408852	4316890	6.45
none	d3	1	3.78	0.59	1.920	0.03	0.06	n/a	n/a	n/a	n/a	
none	d3	2	3.82	0.69	1.559	0.03	0.04	n/a	n/a	n/a	n/a	
CAC-Coal	d3	1	3.82	8.19	254.864	0.45	0.03	254.413	11.28	22554311	2754905	
CAC-Coal	d3	2	3.83	8.01	249.185	0.40	0.08	248.781	12.24	20325208	2538295	
CAC-Coal	d3	3	3.82	14.17	248.582	0.73	0.09	247.853	10.89	22759688	1606712	6.36
none	d4	1	43.22	0.73	2.206	0.04	0.12	n/a	n/a	n/a	n/a	
none	d4	2	43.23	0.97	1.773	0.05	0.11	n/a	n/a	n/a	n/a	
CAC-Coal	d4	2	43.28	0.56	247.061	0.03	1.24	247.034	9.36	26392487	47329082	
CAC-Coal	d4	3	43.30	0.66	254.640	0.04	0.19	254.600	10.16	25059095	38016674	7.63

^a All concentrations are of Hg_i.

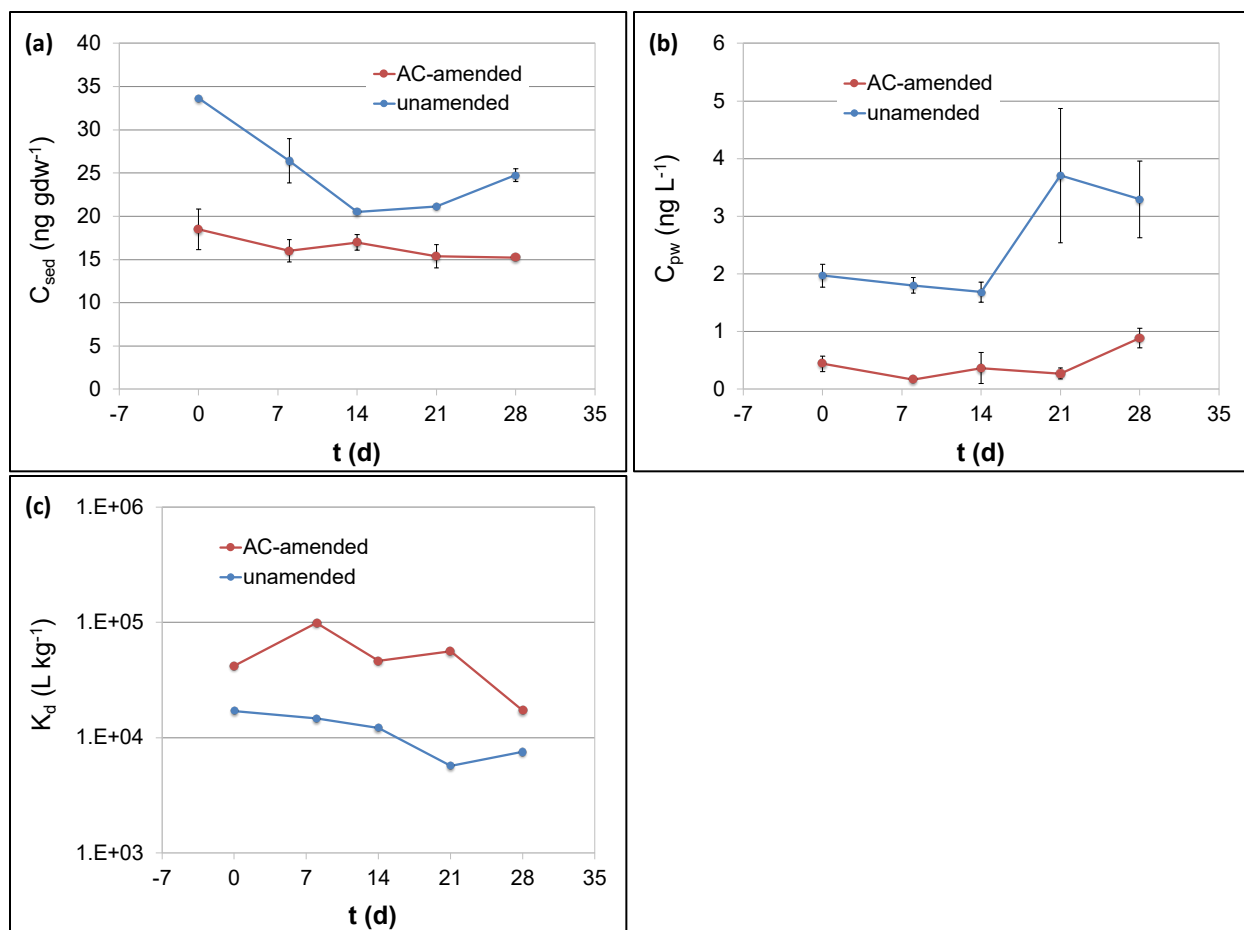


Figure S6.6. MeHg Concentrations in (a) Sediment and (b) Porewater (Directly Measured); (c) Sediment-water Partitioning in Microcosm Experiment.

Error bars show ± 1 standard deviation ($n = 2$).

Table S6.12. Porewater Chemistry in Unamended Sediment Used in Microcosm Experiment.

Parameter	Units	0 d	8 d	14 d	21 d	28 d
Al	mg L ⁻¹	2.06 ± 0.65	1.7 ± 0.57	1.31	1.03 ± 0.57	0.55 ± 0.4
B	mg L ⁻¹	0.98 ± 0.04	1 ± 0.12	1.1	1.13 ± 0.04	1.37 ± 0.16
Ba	mg L ⁻¹	1.15 ± 0.02	0.83 ± 0.25	0.79	1 ± 0.14	0.85 ± 0.46
Ca	mg L ⁻¹	81 ± 7	89 ± 18	111	125 ± 19	152 ± 16
DOC	mg L ⁻¹	n.d.	19.09 ± 1.92	17.02 ± 1.74	15.18 ± 1.01	35.91 ± 33.2
Fe	mg L ⁻¹	2.11 ± 0.34	3.44 ± 2.13	8.5	10.45 ± 8.7	14.08 ± 9.22
FMeHg	ng L ⁻¹	1.97 ± 0.19	1.8 ± 0.14	1.68 ± 0.17	3.71 ± 1.16	3.29 ± 0.67
FTHg	ng L ⁻¹	473.65 ± 145.59	414.37 ± 0.61	367.82	244.75 ± 59.89	143.69 ± 86.71
K	mg L ⁻¹	62.03 ± 7.83	54.1 ± 2.83	78.9	60.1 ± 9.48	91.05 ± 1.06
Mg	mg L ⁻¹	157 ± 7	167 ± 17	185	195 ± 22	254 ± 41
Mn	mg L ⁻¹	0.8 ± 0.1	0.92 ± 0.37	1.3	1.51 ± 0.65	2 ± 0.77
Na	mg L ⁻¹	1427 ± 21	1460 ± 14	1440	1495 ± 7	1935 ± 205
P	mg L ⁻¹	4.84 ± 0.18	5.94 ± 1.21	4.97	5.66 ± 0.64	5.61 ± 1.05
pH		6.95 ± 0.01	7.01 ± 0.47	6.54 ± 0.02	6.53 ± 0.18	6.45 ± 0.24
S	mg L ⁻¹	43.07 ± 10.29	55.85 ± 18.88	77.2	97.2 ± 37.9	138.15 ± 54.94
Si	mg L ⁻¹	15.33 ± 0.21	16.9 ± 0.42	16.9	15.4 ± 0.57	16.65 ± 0.78
Sr	mg L ⁻¹	1.22 ± 0.09	1.29 ± 0.21	1.56	1.7 ± 0.22	2.15 ± 0.3
sulfide	μM	0.44	0.82	1.42 ± 0.08	2.52 ± 0.35	1.32 ± 0.43
Zn	mg L ⁻¹	0.32 ± 0.02	0.3 ± 0.05	0.35	0.34 ± 0.03	0.36 ± 0.01
MeHg (solid)	ng gdw ⁻¹	33.64 ± 0.07	26.41 ± 2.56	20.52	21.13 ± 0.12	24.75 ± 0.76
THg (solid)	μg gdw ⁻¹	45.71 ± 0.59	48.22 ± 0.58	46.78 ± 0.54	47.89 ± 1.56	49.25 ± 1.26

^a Final two rows are solid-phase concentrations. Sediment was a silty mud collected to a depth of 15 cm from a tidal creek in the upper part of Berry's Creek in Bergen County, NJ. Values represent averages ± one s.d. (no s.d. denotes *n* = 1).

Table S6.13. Porewater Chemistry in AC-amended Sediment Used in Microcosm Experiment.

Parameter	Units	0 d	8 d	14 d	21 d	28 d
Al	mg L ⁻¹	0.79 ± 0.3	0.2 ± 0.1	0.57 ± 0.08	0.13 ± 0.1	0.57 ± 0.16
B	mg L ⁻¹	1 ± 0.02	0.99 ± 0.05	1.1 ± 0.04	1.22 ± 0.13	1.21 ± 0.07
Ba	mg L ⁻¹	0.84 ± 0.26	0.71 ± 0.36	0.46 ± 0.06	0.47 ± 0.1	0.53 ± 0.15
Ca	mg L ⁻¹	84 ± 3	94 ± 14	122 ± 18	143 ± 13	146 ± 20
DOC	mg L ⁻¹	n.d.	28.3 ± 19.34	6.77 ± 0.14	6.42 ± 0.35	17.02 ± 8.66
Fe	mg L ⁻¹	2.56 ± 0.79	2.96 ± 2.45	7.48 ± 2.35	18.3 ± 6.22	16.96 ± 14.91
FMeHg	ng L ⁻¹	0.44 ± 0.13	0.16 ± 0.01	0.37 ± 0.27	0.27 ± 0.09	0.89 ± 0.17
FTHg	ng L ⁻¹	259.85 ± 108.12	87.33 ± 18.03	251.98 ± 2.5	65.78 ± 35.19	168.25 ± 23.26
K	mg L ⁻¹	103.7 ± 15.99	105.1 ± 8.34	107.5 ± 7.78	138 ± 12.73	126 ± 14.14
Mg	mg L ⁻¹	164 ± 3	173 ± 16	197 ± 21	259 ± 1	249 ± 16
Mn	mg L ⁻¹	0.92 ± 0.05	1.03 ± 0.3	1.34 ± 0.21	2.16 ± 0.45	1.95 ± 0.95
Na	mg L ⁻¹	1457 ± 23	1450 ± 28	1545 ± 120	1895 ± 64	1875 ± 92
P	mg L ⁻¹	4.98 ± 0.12	4.28 ± 0.64	4.01 ± 0.4	3.16 ± 0.04	5.25 ± 1.34
pH		6.75 ± 0.01	6.78 ± 0.11	6.61 ± 0.06	6.42 ± 0.11	6.46 ± 0.26
S	mg L ⁻¹	58.03 ± 10.71	68.35 ± 15.63	112.15 ± 19.59	181 ± 4.24	154.5 ± 55.86
Si	mg L ⁻¹	14.6 ± 0.52	14.7 ± 0.57	15.2 ± 0.14	16.3 ± 0.57	16.8 ± 1.13
Sr	mg L ⁻¹	1.25 ± 0.03	1.37 ± 0.16	1.69 ± 0.23	2.03 ± 0.26	2.06 ± 0.32
sulfide	μM	0.28	0.45 ± 0.03	0.66 ± 0.15	0.65 ± 0.17	1.81 ± 0.32
Zn	mg L ⁻¹	0.35 ± 0.01	0.27	0.35 ± 0.01	0.38 ± 0.02	0.32 ± 0.03
MeHg (solid)	ng gdw ⁻¹	16.82	15.99 ± 1.3	16.34	15.35 ± 1.34	15.2 ± 0.17
THg (solid)	μg gdw ⁻¹	46.24 ± 0.74	47.88 ± 2.43	47.91 ± 3.34	47.45 ± 0.81	47.61 ± 1.85

^a The final two rows are solid-phase concentrations. Sediment was a silty mud collected to a depth of 15 cm from a tidal creek in the upper part of Berry's Creek in Bergen County, NJ. Sediment was amended with 5 wt% activated carbon (Calgon Type 3055, 80 x 325 mesh, CAS #7440-44-0). Values represent averages ± one s.d. (no s.d. denotes $n = 1$).

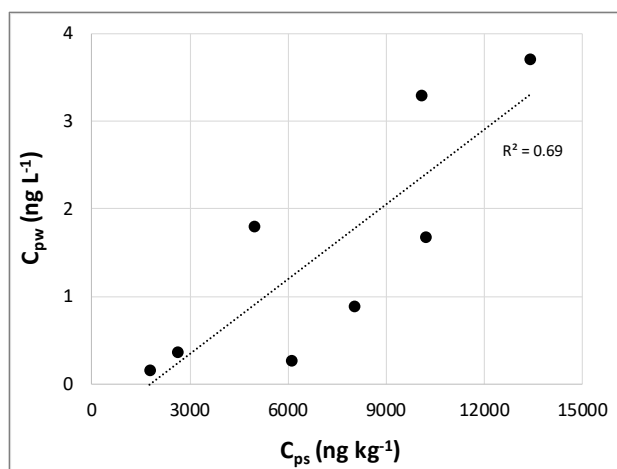


Figure S6.7. Correlation Between Passive Sampler Uptake and Directly Measured Porewater Concentrations in Sediment Microcosm Experiment Across Both Amendment Types and All Time Points.

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APPENDIX F SUPPLEMENTAL INFORMATION FOR CHAPTER 7

UPTAKE MECHANISMS OF A NOVEL, ACTIVATED CARBON-BASED EQUILIBRIUM PASSIVE SAMPLER FOR ESTIMATING POREWATER METHYLMERCURY

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SI 1. Materials and Methods

SI 1.1 Production of ag+AC polymer samplers

The ag+AC polymers were produced using a virgin powdered AC derived from bituminous coal (Calgon Type 3055; 80 x 325 TOG LF; C(%) = 80.9±1.4; surface area = 1116±25 m²/g; skeletal density = 1.61 g/cm³; bulk density = 0.64 g/cm³). AC particles were sieved to >53µm, then washed with DI and allowed to dry in a 30 °C oven prior to casting within gels or indirect experimental use to ensure uniformity. Following the preparation methods described in detail in Sanders et al., 2020, 0.300 g of prepared dry PAC was mixed with 0.300 g of agarose powder, then 20 mL of DI water was added, and the solution was stirred while heated in a hot water bath for 4.5 mins. Across all experiments, ag+AC polymers were prepared identically to a uniform thickness (1 mm) by casting the agarose gel suspension between two acid-cleaned glass plates separated by spacers (Gao et al., 2011; Gomez-Eyles et al., 2013; Sanders et al., 2020). Gels were allowed to cool for 1 hour, then cut to a uniform size of 34.3 mm by 23.9 mm and stored in clean DI water until use. The gel was sufficiently rigid that transfer between experimental bottles was accomplished using acid-cleaned forceps to gently transfer samplers.

SI 1.2 MeHgCys Sorption Isotherms

Partitioning of MeHg complexed with L-Cysteine was evaluated for both the ag+AC passive samplers and bare AC particles. Isotherm solutions were spiked with a MeHgCl standard (Brooks Rand Laboratories) diluted to five concentrations ranging from 3 to 300 ng/L (bare AC particles) or 30 to 3000 ng/L (ag+AC polymers). All experimental isotherms were conducted in 60-mL polyethylene terephthalate glycol (PETG) copolymer bottles. L-cysteine (Sigma-Aldrich, 98%) was added to each experimental bottle to maintain a 10⁵:1 molar ratio of L-cysteine to MeHg, and buffered with the addition of 1mM MOPS (3-Morpholinopropane-1-sulfonic acid). Solutions were incubated overnight in the dark on a shaker table at 60 rpm at 4 °C prior to sampler addition to ensure a stable MeHg distribution. Samplers or ~0.010g of bare AC particles were added to experimental bottles in triplicate at each concentration level, and were allowed to equilibrate for 14 days in the dark on a shaker table at 60 rpm at 4 °C. After 14 days, ag+AC samplers were carefully removed with forceps, and bare AC particles were separated from overlying solution with centrifugation followed by careful pipetting. After separation, sorbents were stored frozen. A portion of the overlying water was acidified to 0.5% v/v with trace metal grade HCl to preserve MeHg, then stored refrigerated at 4 °C. Aliquots of overlying water after 14 days were taken from one treatment of each triplicate to evaluate pH and sulfide concentration within the experimental solutions to monitor for cysteine degradation. All solutions were below detection limit (BDL) for

sulfide. DI water blanks and control bottles containing the sorbents and the cysteine solution without a MeHg spike were processed in tandem with the experimental samples. All blanks and controls exhibited negligible amounts of MeHg.

SI 1.3 DOM Sorption Isotherm Experiments

Partitioning of MeHgDOM species to the ag+AC polymer material was evaluated for seven different organic matter sources with varying characteristics (summarized in Table S5; all obtained from the International Humic Substances Society) in an isotherm experiments. All MeHgDOM species were prepared by adding MeHgCl stock to a saline (3 ppt Instant Ocean, United Pet Group, Inc.) solution containing 7.5 mM NaHCO₃ (Avantor Macron Fine Chemicals) to buffer pH (8.2-8.7) at near-neutral condition. MeHgCl spiked DOM solutions were incubated in the dark on a shaker table at 60 rpm at 4 °C for a minimum of 24 hours to ensure a stable MeHg distribution at high affinity sites within the DOM complexes. Saline experimental solution conditions were chosen to set a consistent ionic strength across experimental treatments with varying parameters.

Isotherms (referred to as “varying ratio DOM isotherms”) were conducted with DOC concentrations held constant at 5 mg/L across the range of initial MeHg concentrations ranging from 5 to 330 ng/L, resulting in DOM:MeHg mass ratios ranging from 10⁶:1 to 1.5×10⁴:1. This approach was used to avoid potential saturation of the passive sampler AC with DOM molecules. For these isotherms, one ag+AC sampler was added to an experimental bottle containing the DOM stock but without a MeHgCl spike to evaluate DOM partitioning in the absence of MeHg (ag+AC DOC blank). DOM-containing blanks and MeHg controls (at an initial MeHg spike of ~50 ng/L) for each DOM source were processed in tandem with the ag+AC sampler treatments.

ag+AC samplers were added to each PETG bottle, and were incubated in the dark on a shaker table at 60 rpm at 4 °C. After 14 days, ag+AC samplers were carefully removed with acid cleaned forceps. Aliquots of overlying water were removed from each bottle to evaluate pH, DOC concentration, and sulfide concentration within the experimental solutions. All solutions were BDL for sulfide. All blanks exhibited negligible amounts of MeHg, and controls displayed insignificant degradation of MeHg over the 14-day incubation period.

SI 1.4 Isotopically-Labelled Experiments to Verify Equilibrium Exchange Behavior

SI 1.4.1 Isotopically-Labelled MeHgSRHA Experiments

A series of experiments were conducted to explicitly verify the equilibrium exchange of MeHg by the ag+AC samplers, utilizing isotopically-labelled MeHg species to track exchange over 14-day time courses. To evaluate the exchange of MeHg between an environmentally relevant MeHg species and the ag+AC polymer material, a solution containing 5 mg/L of Suwannee River Humic Acid (SRHA III, IHSS) was prepared. To this SRHA solution, aliquots of either Me¹⁹⁸HgCl or Me¹⁹⁹HgCl were added to create solutions at a nominal concentration of 50 ng/L. SRHA was chosen as the DOM source for the exchange experiments due to the availability of published data to estimate the number of thiolic sites (Poulin et al., 2017). Solutions were incubated overnight in the dark on a shaker table at 60 rpm at 4 °C prior to sampler addition to ensure a stable MeHgSRHA distribution. Samplers were added to experimental bottles containing Me¹⁹⁹HgSRHA in duplicate, then allowed to equilibrate for 14 days in the dark on a shaker table at 60 rpm at 4 °C. To evaluate

uptake of $\text{Me}^{199}\text{HgSRHA}$, after 14 days 2 bottles containing bare AC particles and two containing ag+AC samplers were separated as described in detail in Section S1.2.

After the 14-day equilibration period, ag+AC samplers were carefully removed with acid-cleaned forceps and transferred to experimental bottles containing $\text{Me}^{198}\text{HgSRHA}$. The same general procedure was followed for bare AC particles, with the following exceptions: equilibration time was only 48 hours, transfer of bare AC particles involved separation from $\text{Me}^{199}\text{HgSRHA}$ solution by centrifugation followed by careful pipetting, and washing of the centrifuge tubes with $\text{Me}^{198}\text{HgSRHA}$ solutions to ensure complete mass transfer. Transfer of $\text{Me}^{199}\text{HgSRHA}$ solution to bottles containing $\text{Me}^{198}\text{HgSRHA}$ solutions was minimal ($\ll 0.5\text{mL}$) for both transfer methods. After transfer, experimental bottles were again placed onto a shaker table at 60 rpm at 4 °C in the dark. Experimental bottles were removed, separated, and preserved in duplicate over a time course to observe exchange of the isotopically-labeled $\text{Me}^{\text{xxx}}\text{HgSRHA}$ species. Bottles containing bare AC particles were removed after 0.25, 1, 3, 6, 24, and 48 hours, while ag+AC containing bottles were removed after 1, 6, 24, 48, 168, and 336 hours.

In tandem with experimental solutions, bottles containing blank and control solutions of both $\text{Me}^{\text{xxx}}\text{HgSRHA}$ species were prepared. Control solutions were preserved for analysis at the start and end of both the uptake and exchange phases. SRHA blanks were negligible for MeHg, and control solutions indicated that there was minimal degradation of MeHgSRHA species over the experiment duration.

SI 1.4.2 Isotopically-Labelled MeHgCys Exchange Experiments

This experiment was designed to mimic the previous dual isotope label experiment, but using MeHgCys as the dominant species instead of MeHgSRHA. For both experimental phases (uptake and exchange) a solution was prepared to contain cysteine at a nominal concentration of $2.5\text{E-}5\text{ M}$ along with 7.5 mM bicarbonate and 3ppt Instant Ocean. The cysteine concentration was determined such that a $10^5\text{:}1$ molar ratio of cysteine to $\text{Me}^{\text{xxx}}\text{Hg}$ would be maintained, mimicking the cysteine sorption isotherm experiments. However, concentrations of the two isotope spikes ended up being lower than anticipated in initial experimental solutions ($\text{Me}^{199}\text{HgCys} = 8.75\text{ ng/L}$, $\text{Me}^{198}\text{HgCys} = 17\text{ ng/L}$), resulting in actual molar ratios closer to $5\times 10^5\text{:}1$. Samplers were allowed to equilibrate with the exchange phase solution containing $\text{Me}^{199}\text{HgCys}$ for 14 days on a shaker table at 60 rpm at 4 C in the dark, then carefully transferred to new PETG bottles containing the $\text{Me}^{198}\text{HgCys}$ solution. Samplers were removed in triplicate at the following times: 1 hr, 6 hr, 24 hr, 48 hr, 96 hr, 7 days, 14 d, with an additional 3 samplers preserved prior to insertion in the exchange phase solution during the switchover process to evaluate $\text{Me}^{199}\text{HgCys}$ uptake. Experimental blanks exhibited negligible MeHg, and control bottles for both $\text{Me}^{199}\text{HgCys}$ and $\text{Me}^{198}\text{HgCys}$ exhibited minimal degradation over the respective 14-day equilibration periods.

SI 1.4.3 Isotopically-Labelled MeHgCys & MeHgSRHA Release Experiments

Two additional exchange experiments were conducted to evaluate the exchange dynamics of MeHg species at equilibrium with the passive sampling polymer when exposed to an aqueous solution containing differing environmentally-relevant high MeHg affinity ligands. Both uptake and exchange solutions were saline and buffered to near neutral pH (3 ppt Instant Ocean and 7.5 mM sodium bicarbonate). One set of polymers was allowed to equilibrate with $\text{Me}^{199}\text{HgCys}$ during

the 14-day uptake phase and transferred to a solution containing SRHA for the exchange phase, and separate set of polymers equilibrated with Me¹⁹⁹HgSRHA during uptake and transferred to an exchange solution containing cysteine. The exchange solutions (cysteine at 2.5E-5 M conc., and SRHA at 10 mg/L DOC) for these two experimental treatments were prepared without a MeHg spike to prevent isotopic exchange between ligand-bearing species during the exchange phase that might obfuscate sampler:water MeHg partitioning. Samplers were removed in duplicate at the following times for each experimental treatment: 1 hr, 6 hr, 24 hr, 48 hr, 96 hr, 7 days, 14 d, with 2 additional samplers preserved prior to insertion in the exchange phase solutions to evaluate either Me¹⁹⁹HgCys or Me¹⁹⁹HgSRHA uptake. Solution blanks for all phases were negligible for MeHg, and uptake phase MeHg control bottles exhibited minimal degradation. DOC concentrations were measured in overlying waters for the Me¹⁹⁹HgSRHA uptake phase bottles, and in the overlying waters of both exchange phase solutions.

SI 1.4.4 Kinetic Modelling of Isotopically-Labelled Exchange Experiment

The timeseries data to the dual-isotopic exchange experiments using MeHgSRHA and MeHgCys were each fitted to a model following first order kinetics with equilibrium exchange under finite volume batch conditions simulating the experimental conditions. The first order kinetic coefficients for adsorption of Me¹⁹⁸Hg, k_{adsorb} , and desorption of Me¹⁹⁹Hg, k_{desorb} , were calculated independently. Likewise, the time it takes for the system to reach 90% equilibrium under experimental conditions was calculated for each isotopic species.

The sampler concentrations through time were fitted to a first order kinetic model with equilibrium exchange, shown in Equation 1,

$$\frac{dC_{ps,t}}{dt} = -k \cdot (C_{ps,t} - C_{ps,eq}) \quad (1)$$

where $C_{ps,t}$ [ng/kg] is the sampler concentration at time t (d), k (d⁻¹) is the kinetic coefficient describing adsorption, and $C_{ps,eq}$ is the sampler concentration at equilibrium with the water concentration at time t . This kinetic equation was used to model the desorption of the preloaded Me¹⁹⁹Hg and the adsorption of Me¹⁹⁸Hg, independently. The $(C_{ps,t} - C_{ps,eq})$ term represents the concentration gradient driving the shift towards equilibrium. Using the equilibrium partitioning relationship, $C_{ps,eq}$ can thus be replaced with the product of the concentration in the water at time t multiplied by the equilibrium partitioning coefficient, $C_{w,t}K_{ps}$, as in Equation 2.

$$\frac{dC_{ps,t}}{dt} = -k \cdot (C_{ps,t} - C_{w,t}K_{ps}) \quad (2)$$

K_{ps} [L/kg] was calculated as the overall $C_{ps,t}/C_{w,t}$ ratio at the final 14-day timepoint, inclusive of both isotopic species; $\log K_{ps} = 1.26$ was used for the experiments using MeHgSRHA and $\log K_{ps} = 3.54$ was used for experiments using MeHgCys. $C_{w,t}$ is related to $C_{ps,t}$ via the following mass balance equation for Me¹⁹⁹Hg,

$$^{199}C_{w,t} = \frac{^{199}C_{ps,0}m_{ps} - ^{199}C_{ps,t}m_{ps}}{V_w} \quad (3)$$

where m_{ps} is the mass of the sampler [kg], V_w is the volume of the exchange solution [L], and $^{199}C_{ps,0}$ is the initial Me¹⁹⁹Hg concentration in the sampler (ng/kg), which was estimated under the assumption that the entire mass of Me¹⁹⁹Hg was initially present in the preloaded sampler. Substituting $^{199}C_{w,t}$ into Equation 2,

$$\frac{d^{199}C_{ps,t}}{dt} = -k \cdot \left[^{199}C_{ps,t} - \frac{K_{ps}m_{ps}}{V_w} (^{199}C_{ps,0} - ^{199}C_{ps,t}) \right] \quad (4)$$

expanding,

$$\frac{d^{199}C_{ps,t}}{dt} = -k \cdot \left[\left(1 + \frac{K_{ps}m_{ps}}{V_w}\right) ^{199}C_{ps,t} - \frac{K_{ps}m_{ps}}{V_w} ^{199}C_{ps,0} \right] \quad (5)$$

reducing constant terms $(1 + K_{ps}m_{ps}/V_w)$ to constant a , and term $K_{ps}m_{ps}^{199}C_{ps,0}/V_w$ to constant b ,

$$\frac{d^{199}C_{ps,t}}{dt} = -k \cdot [a^{199}C_{ps,t} - b] \quad (6)$$

then isolating $^{199}C_{ps,t}$ yields the following.

$$\frac{d^{199}C_{ps,t}}{dt} = -ka \cdot \left[^{199}C_{ps,t} - \frac{b}{a} \right] \quad (7)$$

Separating variables,

$$\frac{d^{199}C_{ps,t}}{^{199}C_{ps,t} - \frac{b}{a}} = -ka \, dt \quad (8)$$

then integrating leads to the following solution,

$$\ln \left| ^{199}C_{ps,t} - \frac{b}{a} \right| = -kat + Q \quad (9)$$

where Q is an undefined constant. Rearranging,

$$^{199}C_{ps,t} - \frac{b}{a} = Q \exp(-kat) \quad (10)$$

Q is solved by substituting $C_{ps,0}$ for $C_{ps,t}$ at $t = 0$ as such.

$$^{199}C_{ps,0} - \frac{b}{a} = Q \exp(-kat) \quad (11)$$

Plugging Q back into the solved equation and isolating $^{199}\text{C}_{ps,t}$ yields the final solution for Me^{199}Hg .

$$^{199}\text{C}_{ps,t} = \left[^{199}\text{C}_{ps,0} - \frac{b}{a} \right] \exp(-kat) + \frac{b}{a} \quad (12)$$

A similar approach is taken for Me^{198}Hg . $^{198}\text{C}_{w,t}$ is defined with the following mass balance equation,

$$^{198}\text{C}_{w,t} = \frac{^{198}\text{C}_{w,0}V_w - ^{198}\text{C}_{ps,t}m_{ps}}{V_w} \quad (13)$$

where $^{198}\text{C}_{w,0}$ is the initial concentration of Me^{198}Hg in the exchange solution (ng/L). $^{198}\text{C}_{w,0}$ was estimated using data at each timepoint by assuming the entire Me^{198}Hg mass in the system at time t was initially present in the solution. Substituting $^{198}\text{C}_{w,t}$ into Equation 2,

$$\frac{d^{198}\text{C}_{ps,t}}{dt} = -k \cdot \left[^{198}\text{C}_{ps,t} - \frac{K_{ps}}{V_w} (^{198}\text{C}_{w,0}V_w - ^{198}\text{C}_{ps,t}m_{ps}) \right] \quad (14)$$

then rearranging yields the following.

$$\frac{d^{198}\text{C}_{ps,t}}{dt} = -k \cdot \left[\left(1 + \frac{K_{ps}m_{ps}}{V_w} \right) ^{198}\text{C}_{ps,t} - K_{ps} ^{198}\text{C}_{w,0} \right] \quad (15)$$

Reducing the term $(1 + K_{ps}m_{ps}/V_w)$ to constant a (as the with Me^{199}Hg equation) and the term $K_{ps} ^{198}\text{C}_{w,0}$ to constant d ,

$$\frac{d^{198}\text{C}_{ps,t}}{dt} = -k \cdot \left[a^{198}\text{C}_{ps,t} - d \right] \quad (16)$$

and isolating $^{198}\text{C}_{ps,t}$ gives the following.

$$\frac{d^{198}\text{C}_{ps,t}}{dt} = -ka \cdot \left[^{198}\text{C}_{ps,t} - \frac{d}{a} \right] \quad (17)$$

Separating variables,

$$\frac{d^{198}\text{C}_{ps,t}}{^{198}\text{C}_{ps,t} - \frac{d}{a}} = -ka \, dt \quad (18)$$

then integrating yields the following solution,

$$\ln \left| ^{198}\text{C}_{ps,t} - \frac{d}{a} \right| = -kat + S \quad (19)$$

where S is an undefined constant. Transforming,

$$^{198}C_{ps,t} - \frac{d}{a} = S \exp(-kat) \quad (20)$$

S is solved by substituting 0 for $^{198}C_{ps,t}$ at $t = 0$ as such,

$$-\frac{d}{a} = S \exp(-kat) \quad (21)$$

Plugging S back into the solved equation and isolating $^{198}C_{ps,t}$ yields the final solution for Me¹⁹⁸Hg.

$$^{198}C_{ps,t} = \frac{d}{a} [1 - \exp(-kat)] \quad (22)$$

The kinetic coefficient k was estimated by iterating its value to maximize the coefficient of determination, R^2 , between the estimated and measured sampler concentrations. A model dataset was built using the obtained k values with the average $C_{ps,0}$, $C_{w,0}$, and m_{ps} . The model is plotted with the experimental data in Figures S6a and S6b.

It should be noted that the measured initial and final Me¹⁹⁹HgCys concentrations were indistinguishable (t -test, $\alpha = 0.05$), so it is hard to visibly see the desorption of Me¹⁹⁹HgCys in Figure S6B. Despite this minor change over time, the first order model provides a good fit for this dataset, and the kinetic coefficient k is similar to that of Me¹⁹⁸HgCys.

The estimated time for the system to reach 90% equilibrium conditions was calculated by using Equations 12 and 22 to solve for t at the $C_{ps,t90}$ defined by Equation 23.

$$C_{ps,t90} = C_{ps,0} - 0.9 \cdot (C_{ps,0} - C_{ps,eq}) \quad (23)$$

where

$$^{199}C_{ps,eq} = \frac{^{199}C_{ps,0}m_{ps}}{m_{ps} + \frac{V_w}{K_{ps}}} \quad (24)$$

and

$$^{198}C_{ps,eq} = \frac{^{198}C_{w,0}V_w}{m_{ps} + \frac{V_w}{K_{ps}}} \quad (25)$$

The average $C_{ps,0}$, $C_{w,0}$, and m_{ps} were used to estimate t_{90} .

SI 1.5 Microcosm Experiments to Determine Passive Sampler Predictive Capability in Sediment and Water

As an initial demonstration of the potential field applications of this passive sampling polymer, a sediment microcosm experiment was conducted to determine to a first order the ability of the ag+AC samplers to predict *in situ* MeHg concentrations in sediment and overlying water. To mimic a moderately contaminated marsh soil (target 10 ppm total Hg), a mixture of soil from an oligohaline *Phragmites australis* marsh in Berry's Creek, NJ, and a *Phragmites australis* marsh soil from the Smithsonian Environmental Research Center (SERC) Global Change Research wetland in Edgewater, MD was utilized. Prior to the study, this soil mixture had been used in a 18 month field mesocosm experiment in a tidal creek at SERC (Schwartz, unpublished data). Soils collected after the mesocosm study were stored at 4 °C for an additional 26 months prior to the current experiment. Immediately prior to the passive sampler experiment, measured MeHg concentration in the mixture was 19.5 ng/g wet soil. The mixture was thoroughly homogenized via paint mixer, after which 100 g of the wet soil mixture was placed into 500 mL glass jars. Artificial salt water (100 mL of 3 ppt Instant Ocean) was gently added on top of the soil layer. The microcosms were loosely capped and gently aerated at a constant rate throughout the experiment. Microcosms were allowed to equilibrate for 14 days prior to sampler insertion to allow development of redox gradients in the soil mixture.

Two configurations of passive samplers were tested; one in which separate samplers were deployed in water and sediment, and another in which a single sampler was deployed across the sediment/water interface. Full-size samplers deployed across the sediment-water interface were synthesized as described in Section 2.1. These full-size samplers (referred to throughout as “sheet-ps”), were inserted across the sediment-water interface at a slight incline (Figure S8), such that half of the sampler mass was located in the sediment while the other half remained in the water column. To provide rigidity, the ag+AC samplers were heat sealed in acid cleaned polypropylene mesh (McMaster Carr, 0.21mm mesh) prior to insertion in the microcosms.

Half-sized samplers (17.2 mm by 23.9 mm) denoted as “split-ps,” were deployed separately in sediment and water in a different set of microcosms to evaluate whether there was significant vertical diffusion of MeHg species within the agarose matrix of the samplers. The sampler inserted in the sediment was tied to the sampler in the water with acid-cleaned nylon thread to anchor the sampler suspended in the water column. The sediment sampler was inserted at a slight incline into the sediment, while the water sampler was fully submerged within the overlying water. Microcosms without samplers (referred to as “no-ps”) served as controls to help evaluate any effects that the samplers may have on the sediment porewater chemistry or native MeHg concentration through time. The sheet-ps and split-ps pairs were deployed individually in separate microcosms, and the no-ps, sheet-ps, and split-ps microcosm configurations were constructed in triplicate.

At each experimental time point, passive samplers, overlying water, porewater, and sediment were collected from the microcosms for further analysis. The sheet-ps and split-ps microcosms were sampled 14 and 21 days after sampler insertion (t+14 and t+21, respectively), with an additional sheet-ps microcosm take down 7 days after insertion (t+7). Upon removal, the sheet-ps and split-ps were gently rinsed with DI water to remove sediment particles. Sediment (*ps-sed*) and overlying water (*water-ps*) portions of split-ps samplers were separated by cutting the connecting nylon

thread. Sheet-ps samplers were split at the visually determined soil-water interface with clean, DI-rinsed shears, then frozen until analysis. Sacrificial no-ps microcosms were sampled hours after microcosm construction (t-14), at sampler insertion (t+0), and at each sampler retrieval date (t+7, t+14, and t+21). A sacrificial beaker filled with DI water was deployed alongside the microcosm, from which water was taken at the t0, t+7, t+14, and t+21 timepoint as a quality control blank. A passive sampler was deployed in this beaker and retrieved at t+21 for the same purpose.

At each experimental time point, overlying water was carefully pipetted from the microcosm. Subsequent handling of the sediment and porewater was performed in an anaerobic glove bag (Coy ©, Ann Arbor, MI) to maintain redox conditions after extraction. The bag was filled with 95% N₂:5% H₂. Anaerobic conditions were maintained with a Pd catalyst system to remove O₂. The remaining wet sediment was centrifuged to separate out the porewater, which was then decanted with a pipette. Both overlying- and pore- waters were filtered with a 0.45 µm glass microfiber syringe filter into clean 60mL PETG bottles, from which aliquots were taken for analysis of sulfide, pH, anions, and DOC. Filtrates were then preserved with 0.5% HCl and stored at 4 °C prior to MeHg analysis. An aliquot of the centrifuged sediment was frozen and then lyophilized prior to MeHg analysis.

Effects within the microcosm study were analyzed using standard least squares models that considered time, sampler type, and sampler placement with an overall $\alpha = 0.05$. Parameters were transformed as needed to approximate normal distribution.

SI 1.6 Analytical Methods

For all samples, MeHg was measured by isotope dilution mass spectrometry after separation by acid distillation, following the method detailed in Gilmour et al., 2013, using an Agilent 7900 ICP-MS and Brooks-Rand MERX MeHg analysis system. One adjustment was made to the distillation protocol described in Mitchell and Gilmour, 2008 and Hollwegg et al 2009, with 1% APDC (ammonium pyrrolidine dithiocarbamate, Acros Organics) replacing CuSO₄ as the main complexation agent in the distillation matrix as described in EPA Method 1630, (1998 ed.), as this was found to improve isotope dilution spike recovery for samples containing AC particles (EPA Method 1630, 1998 ed.). Me¹⁹⁹Hg isotope dilution standards were synthesized in-house (Bancon-Montigny et al., 2004) and checked for concentration and degradation by comparing SnCl₂-reducible Hg concentrations before and after BrCl digestion (De Wild et al., 2002). MeHg standards and dilutions were maintained in 0.1% (v/v) TMG HCl and 0.5 % (v/v) acetate buffer, and stored in the dark at 4 °C. For all experiments described in this manuscript, MeHg mass balance was maintained throughout the duration of the experiments. MeHg quality assurance data are summarized in Table S4. Throughout the manuscript, log(K_{ps}) values for the ag+AC passive samplers are reported according to Equation (26):

$$(26) \log(K_{ps}) = \log_{10}(C_{ps}/C_w)$$

Where C_{ps} is the MeHg concentration (ng MeHg/kg of wet polymer material) measured within the ag+AC polymer and c_w is the MeHg concentration (ng of MeHg/L) of the overlying water for a given experiment.

Sulfide was measured by mixing samples 1:1 with sulfide antioxidant buffer (2.0 M NaOH, 0.2 M ascorbic acid, and 0.2 M Na₂EDTA in deoxygenated, deionized water prepared anaerobically) and

analyzing with a sulfide ion-selective electrode calibrated by lead titration of a saturated sulfide standard. DOC was measured on a Shimadzu TOC-V organic carbon analyzer.

SI 2.1 Additional Discussion of the Partitioning Behavior of Various MeHgDOM Species as Determined from Sorption Isotherms

To test the idea that MeHgDOM partitioning to our samplers reflects the equilibrium of DOM with AC in the samplers (rather than a direct equilibrium between AC and MeHg), we measured DOM sorption to the samplers directly for comparison at a single DOC concentration. The test was done as part of the MeHgDOM isotherm experiments at a varying MeHg:DOM ratios, with partitioning estimated based on the change in aqueous DOC concentration in the experimental solutions over 14 days for a solution without added MeHg spike. Estimated DOM partitioning to the samplers was indeed similar to MeHg partitioning, with $\log(K_{ps})$ values for MeHg from the varying-MeHg:DOM-ratio isotherms displaying a positive correlation with estimated DOM partitioning, although this correlation is insignificant at the $\alpha=0.05$ level ($p=0.09$).

One additional isotherm that was not discussed in the main text was conducted under the varying MeHg:DOM mass ratios with SRHA, but for this isotherm the experimental solution contained no Instant Ocean or sodium bicarbonate buffer, which resulted in a lower ionic strength and pH (4.2 instead of 8.4). Although MeHg partitioning did not appear to be depressed in this treatment compared to the buffered treatment ($\log(K_{ps}) = 2.00 \pm 0.80$, $R^2 = 0.76$; compared to $\log(K_{ps}) = 1.98 \pm 0.03$), the highest MeHg concentration point appears to be driving this apparent high partitioning, as it is the only point that diverges from linear behavior. Without this data point, the linear regression results in a $\log(K_{ps}) = 0.95$ with an $R^2 = 0.99$. As this experiment was not conducted at any level of replication, it is difficult to determine whether the partitioning observed at the highest MeHg concentration is spurious. Partitioning of DOC to the passive sampler was depressed in this isotherm compared to the SRHA isotherm conducted in an aqueous solution containing Instant Ocean and sodium bicarbonate ($\log(K_{DOC}) = 1.02$ compared to $\log(K_{DOC}) = 1.62$, respectively). Previous research has suggested that changes in pH, ionic strength, and DOM concentration all likely affect the macromolecular structure of DOM aggregates, and such changes would fundamentally alter the DOM-AC interactions (Schreiber et al., 2007). Decreased DOM partitioning driven by changes in the pH or ionic strength was likely responsible for decreased MeHg partitioning. A similar depression of partitioning coefficients in lower pH and ionic strengths solutions was also observed in the isotopically labelled MeHgCys exchange experiments. Overall partitioning of MeHgCys to the ag+AC material ($\log(K_{ps}) = 3.54 \pm 0.14$ at 14 d) was greater than what was observed during the cysteine isotherm experiment ($\log(K_{ps}) = 3.01 \pm 0.23$), a difference that is likely driven by the differing experimental conditions between the isotherm and exchange experiments, with the isotherms conducted at lower pH and ionic strength. A thorough understanding of the role both pH and ionic strength play in the partitioning of MeHg to AC particles will be critical for extending the use of these passive samplers to a wide range of porewater environments and may have implications for the efficacy of AC as a remediation strategy.

SI 2.2 Additional Discussion of Equilibrium Exchange Experiments with Changing MeHg Speciation

In the exchange experiment with passive samplers initially equilibrated with $\text{Me}^{199}\text{HgCys}$ and transferred into a solution containing SRHA, Me^{199}Hg concentrations were observed to decrease

in the ag+AC polymers and rise correspondingly in the overlying water over the 14 day time course (Figure S5, Table S6). DOC concentrations fell in the overlying water throughout the 14-day time course (from 9.4 mg/L to 5.6 mg/L DOC), suggesting active partitioning of SRHA to the AC particles. At the end of the exchange phase, $\log(K_{ps}) = 2.41$ for Me¹⁹⁹Hg, elevated above the $\log(K_{ps})$ value observed in the SRHA isotherms ($\log(K_{ps}) = 1.98$), but below the previously measured $\log(K_{ps}) = 3.01 \pm 0.23$ observed in the Cys isotherms. This elevated partitioning could be the result of a number of potential scenarios. First, it may reflect a slower exchange of MeHg between passive sampler and overlying water due to the additional interaction of MeHg ligand exchange onto high affinity sites within the organic matter, such that true equilibrium conditions were not met within the 14-day timeframe. It is also possible that larger organic molecules functioned as a physical barrier that prevented efficient release of the relatively smaller MeHgCys molecules from the pore spaces of the AC particles, again resulting in non-equilibrium at the 14-day sampling timepoint.

For the experiment with initial equilibration of the samplers with Me¹⁹⁹HgSRHA and subsequent transfer into a solution containing cysteine, Me¹⁹⁹Hg concentrations remained relatively constant in both the passive samplers and water (although there is only data for Me¹⁹⁹Hg concentrations in the water for timepoints at 48 h, 7 d, and 14 d) (Fig. S5, Table S6). MeHg partitioning is stable for the portion of the time course for which data are available at $\log(K_{ps}) = 3.24$ to 3.17, slightly lower than observed in the MeHgCys:MeHgCys exchange experiments ($\log(K_{ps}) = 3.54 \pm 0.14$), but within the error of the partitioning as determined in the cysteine isotherm experiments ($\log(K_{ps}) = 3.01 \pm 0.23$). The observed K_{ps} value is higher than observed in the MeHgSHRA:MeHgSHRA exchange experiments ($\log(K_{ps}) = 1.98$). DOC concentrations mirrored MeHg concentrations in the overlying water during the exchange phase in that they were largely invariant over time (0.88 mg/L DOC at 1 hr and 0.89 mg/L at 14 days), and these concentrations were in good agreement with the estimated amount of DOC in solution that would be contributed by cysteine in the initial solution prior to passive sampler insertion (0.90 mg/L). Following the proposed equilibration processes, partitioning of MeHg onto the passive sampler material responded to the dominant ligand in solution, in this case cysteine, as demonstrated by the $\log(K_{ps})$ values in good agreement with the cysteine isotherm experiments.

SI 2.3 Additional Discussion of the Sediment Microcosm Experiment

The elevated average MeHg concentration observed in the t+21 split-ps sediment sampler compared to both the t+14 split-ps and the t+21 sheet-ps samplers could reflect changes in a number of factors, including the amount or character of the organic matter within these particular microcosms, potentially altering the partitioning behavior of MeHg. At t+21, the DOC concentrations in the porewater and overlying water of the split-ps treatment were significantly lower than in the sheet-ps treatment, suggesting degradation of organic matter could have contributed to this difference in MeHg uptake between sampler types.

MeHg concentrations in the ag+AC passive sampler portions that were deployed within the overlying water can also be used to predict MeHg C_w . Generally, predictions were less accurate for C_w than they were for C_{pw} when using $\log(K_{ps})$ values of 2.96 and 3.41, particularly at the t+14 timepoint (Figure S7.7). Using the $\log(K_{ps})$ values for MeHgNOM provided a more accurate prediction of C_w at both timepoints, within a factor 3 at t+14 and within a factor of 2 at t+21 for both sampler types. The empirically derived partitioning coefficient ($\log(K_{ps}) = 3.41$) provided

poor predictions at both t+14 (within a factor of 7) and t+21 timepoints (within a factor of 6), suggesting that the presence of μM amounts of sulfide and elevated DOC concentrations within the porewaters of the sediment microcosms are impacting the partitioning of MeHg to the ag+AC samplers, likely due to differences in MeHg speciation driven by the presence of sulfide.

Supplemental Figures



Figure S7.1. Sediment Microcosm Displaying a Sheet-ps Sampler Inserted Across the Sediment-water Interface.

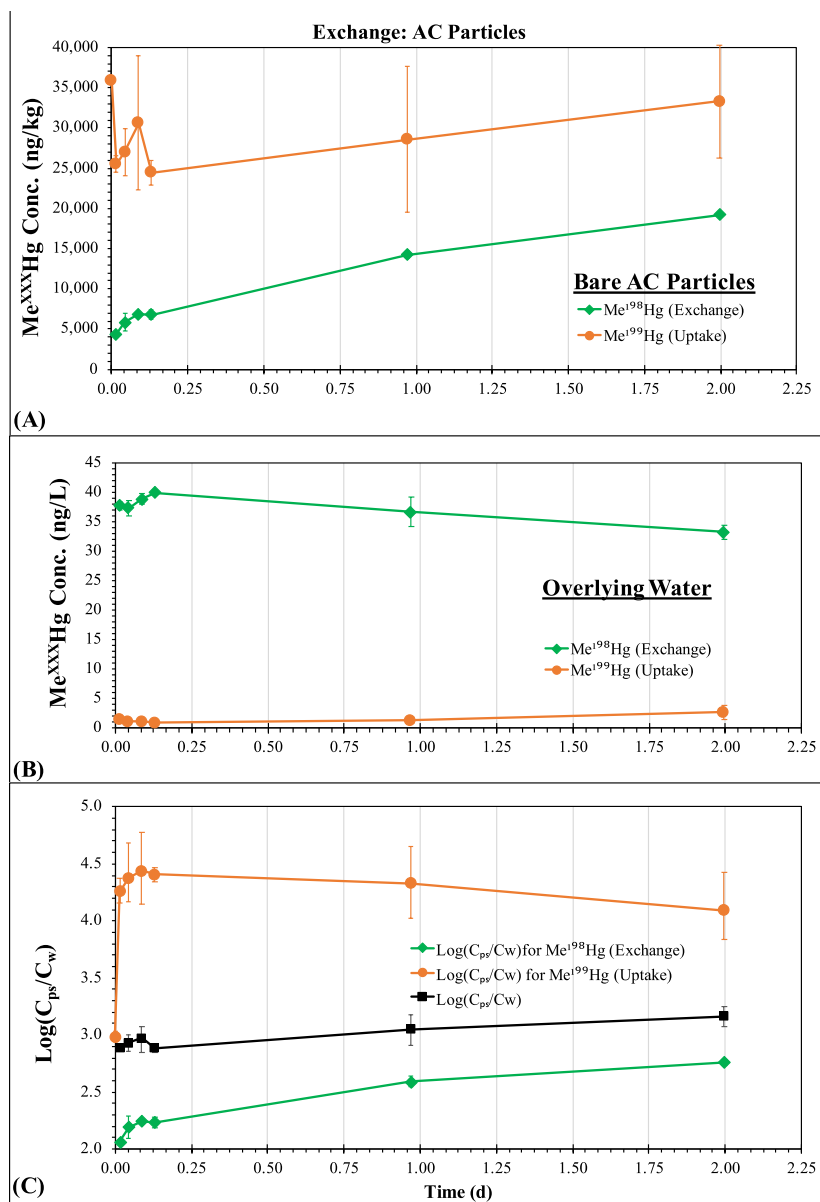


Figure S7.2. Exchange of Isotopically Labelled MeHgSRHA from Bare AC Particles (CAC-coal) Over a 2-d Time Course.

AC particles that had been equilibrated with Me¹⁹⁹HgSRHA (orange circles) during an initial 2-d uptake period were transferred to experimental bottles containing Me¹⁹⁸HgSRHA (green diamonds), and exchange of these species was observed in both the AC particle sorbents (panel A), and overlying water (panel B). At each timepoint, error bars represent ± 1 standard deviation of duplicates. Apparent partitioning coefficients (C_{ps}/C_w) for each isotopically labeled species and for total MeHg (black squares) are shown in panel C.

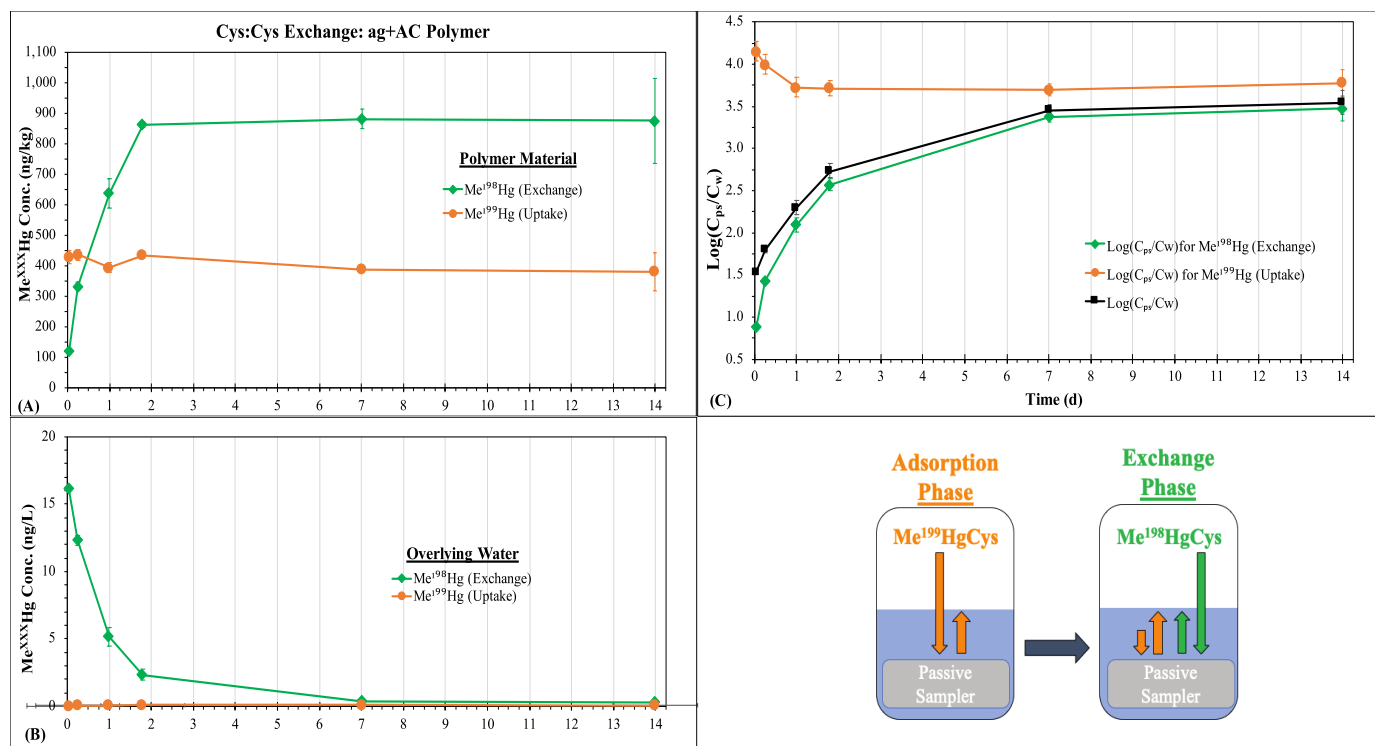


Figure S7.3. Exchange of Isotopically Labeled Me¹⁹⁹HgCys from an ag+AC Polymer Placed in a Solution Containing Me¹⁹⁸HgCys Over a 14-d Time Course.

Polymers that had been equilibrated with Me¹⁹⁹HgCys (orange circles) during an initial 14-d uptake period were transferred to experimental bottles containing Me¹⁹⁸HgCys (green diamonds), and exchange of these species was observed in both the polymer materials (panel A), and overlying water (panel B). At each timepoint, error bars represent ± 1 standard deviation of duplicates. Where error bars are not visible, error associated with that timepoint is smaller than the symbol size. Apparent partitioning coefficients (C_{ps}/C_w) for each isotopically labeled species and for total MeHg (black squares) are shown in panel C.

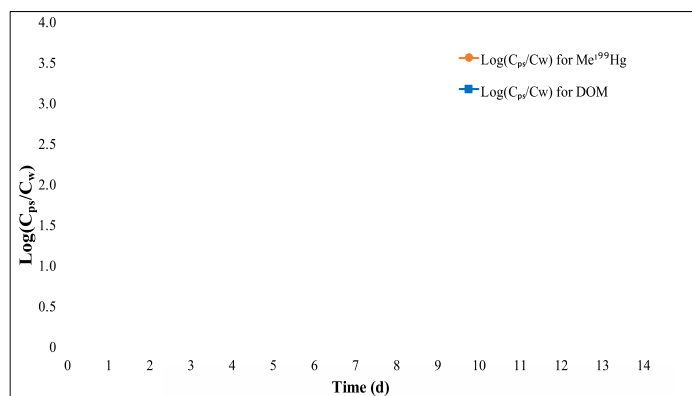


Figure S7.4. Exchange of Isotopically Labelled Me¹⁹⁹HgCys from an ag+AC Polymer in an SRHA Solution Without MeHg Over a 14-d Time Course.

Polymers that had been equilibrated with Me¹⁹⁹HgCys (orange circles) during an initial 14-d uptake period were transferred to experimental bottles containing SRHA in solution, and desorption from the polymer, as well as exchange of MeHg between these species, were observed in both the polymer materials (panel A) and overlying water (panel B). DOC concentrations in overlying water are shown in blue squares (B). At a given timepoint, error bars represent ± 1 standard deviation of duplicates. Where error bars are not visible, error associated with that timepoint is smaller than the symbol size. Apparent partitioning coefficients (C_{ps}/C_w) for Me¹⁹⁹HgCys and organic matter are shown in panel C.

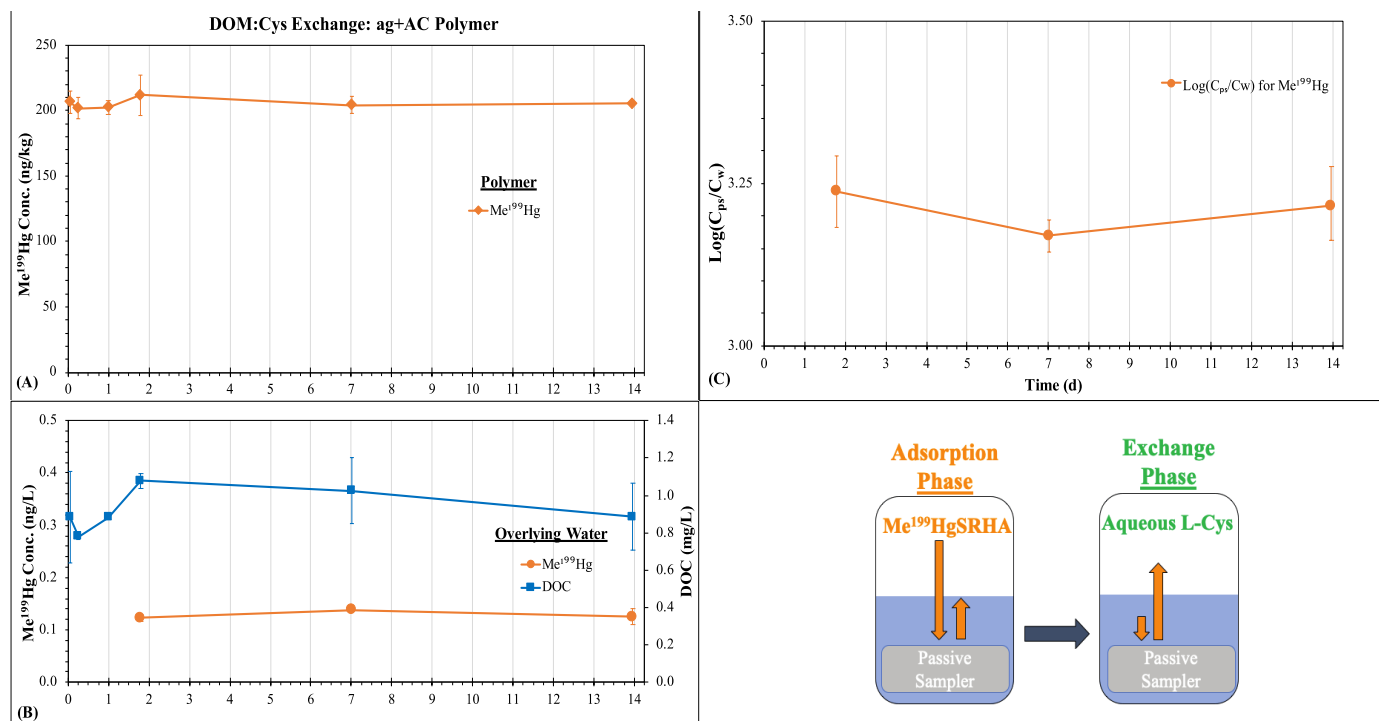


Figure S7.5. Exchange of Isotopically-labelled Me¹⁹⁹HgSRHA from an ag+AC Polymer in a L-Cysteine Containing Solution Without Any MeHg Over a 14-day Time Course.

Polymers that had been equilibrated with Me¹⁹⁹HgSRHA (orange circles) during an initial 14-d uptake period were transferred to experimental bottles containing L-Cys, and desorption from the polymer, as well as exchange of MeHg between these species was observed in both the polymer materials (panel A), and overlying water (panel B). DOC concentrations of overlying water are shown in blue squares (B). At a given timepoint, error bars represent ± 1 standard deviation of duplicates. Where error bars are not visible, error associated with that timepoint is smaller than the symbol size. Apparent partitioning coefficients (C_{ps}/C_w) for Me¹⁹⁹HgCys are shown in panel C.

Figure S6

Time series data and first order kinetic model for MeHgSRHA dual-isotopic exchange isotherms (A) and MeHgCys dual-isotopic exchange isotherms (B). Data points represent average values of measured concentrations and error bars represent 1 SD.

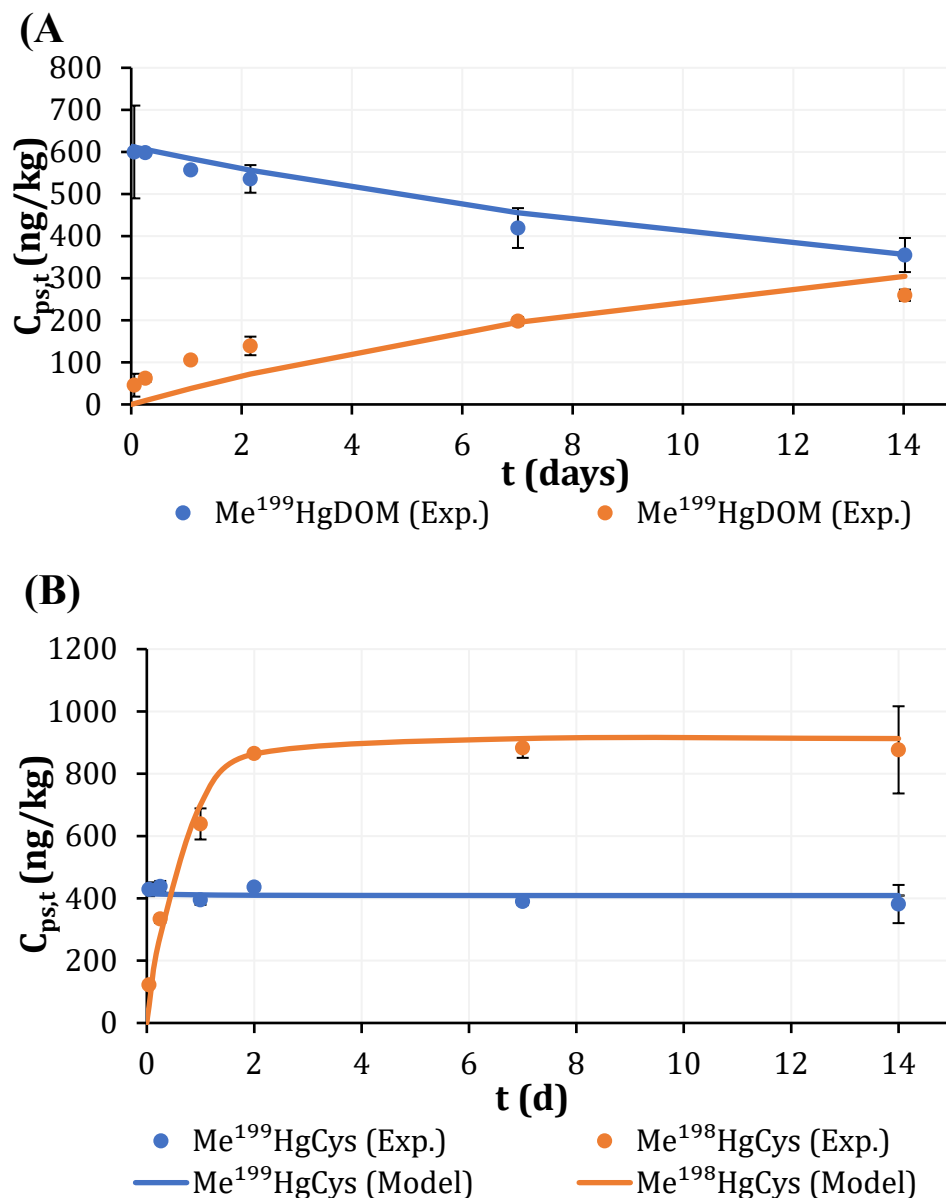


Figure S7.7. Sediment, Water and Porewater Chemistry Over Time in Sediment/Water Microcosms.

Bars show average $\pm$ 1 standard deviation for triplicate microcosms at each time point. Colored bars represent three treatments, no passive sampler (green), sheet-ps (blue) or split-ps (orange). For sediment porewater and passive sampler measurements, microcosms were sacrificed at each time point. Sediment and porewater samples were processed under anaerobic conditions.

Fig. S7A. Surface and porewater pH.

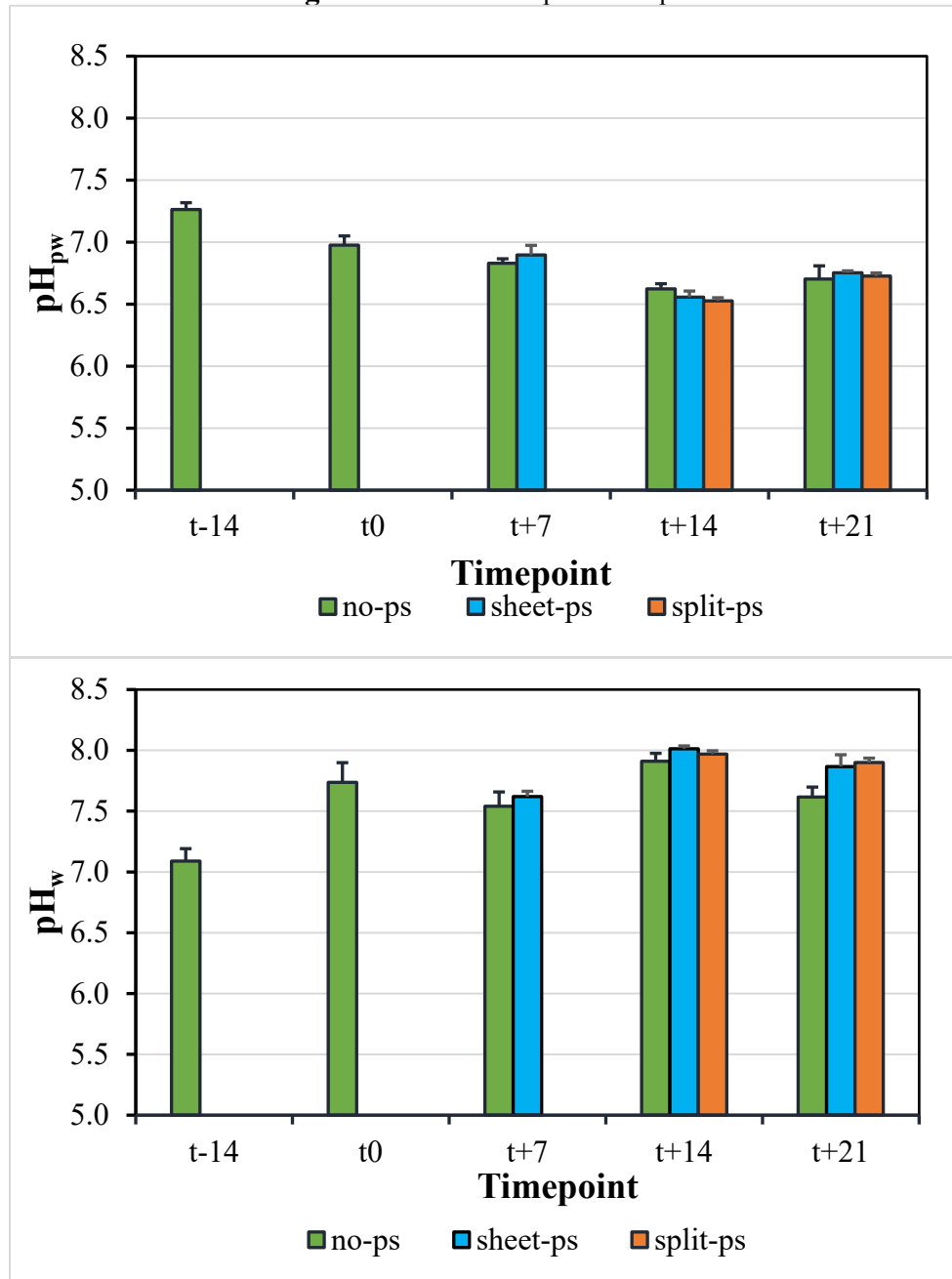


Figure S7.7B. DOC Concentrations in Porewater, but Not Surface Water Declined Significantly Over time.

For days 14 and 21, DOC levels were lower in microcosms (porewater and surface water) with passive samplers than those without ($p < 0.003$).

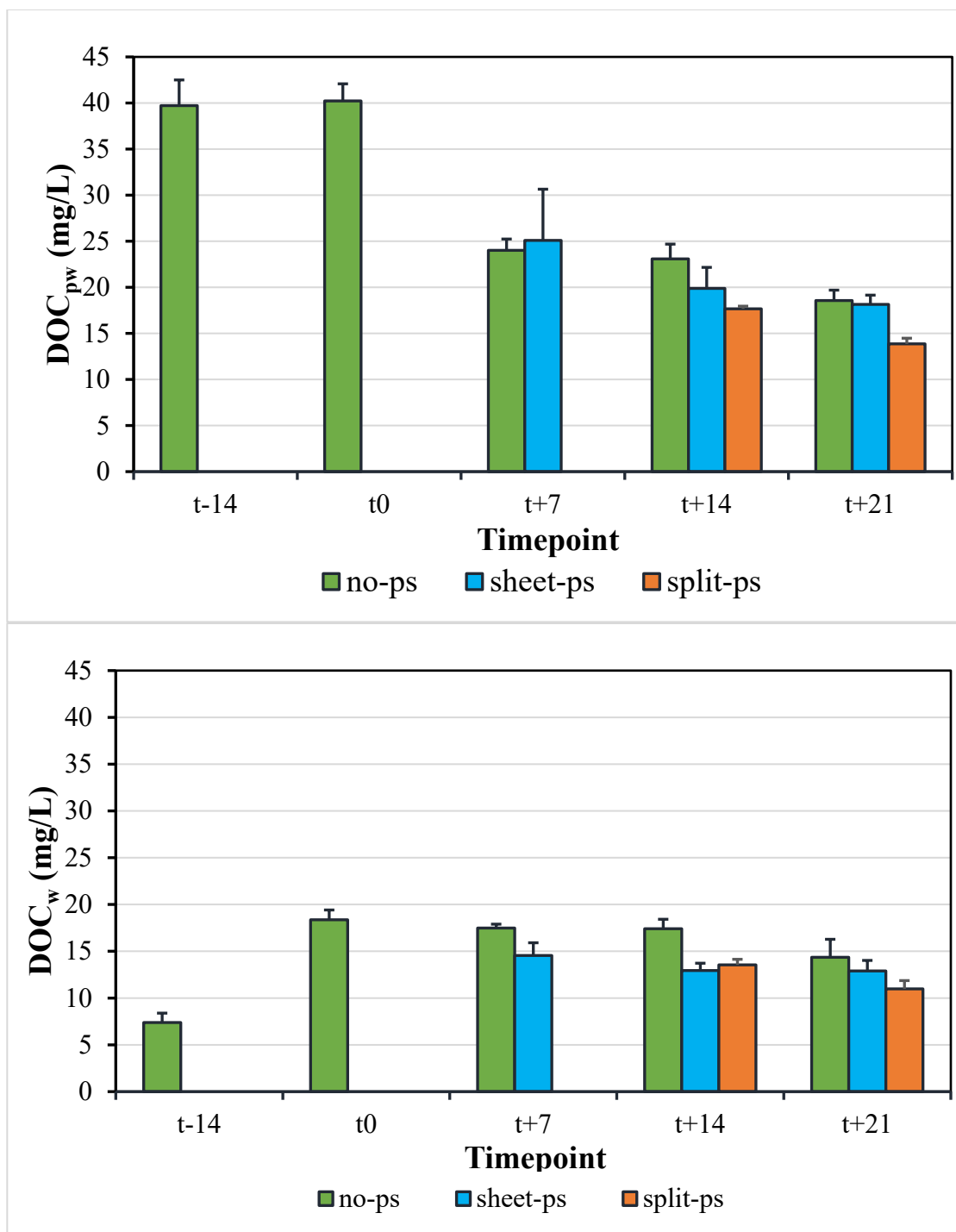


Figure S7.7C. Chloride in Surface and Porewater.

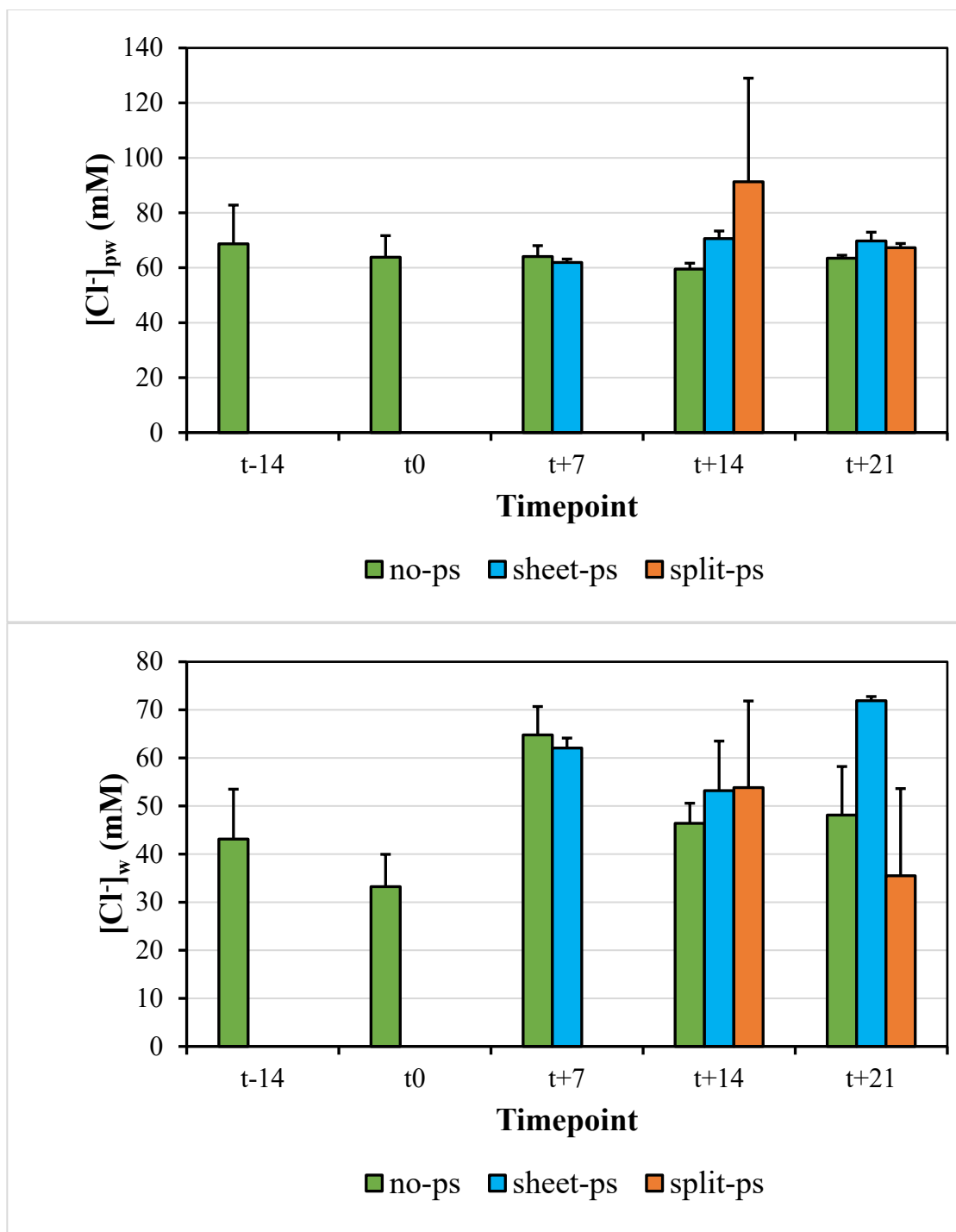


Figure S7.7D. Sulfate in Surface and Porewater.

There was no significant sulfate depletion through time, or depletion in porewaters relative to surface waters, suggesting limited microbial sulfate reducing activity. Across the last three sampling dates, sulfate in both porewaters and surface waters was higher in the presence of samplers ($n=20$, $p<0.046$).

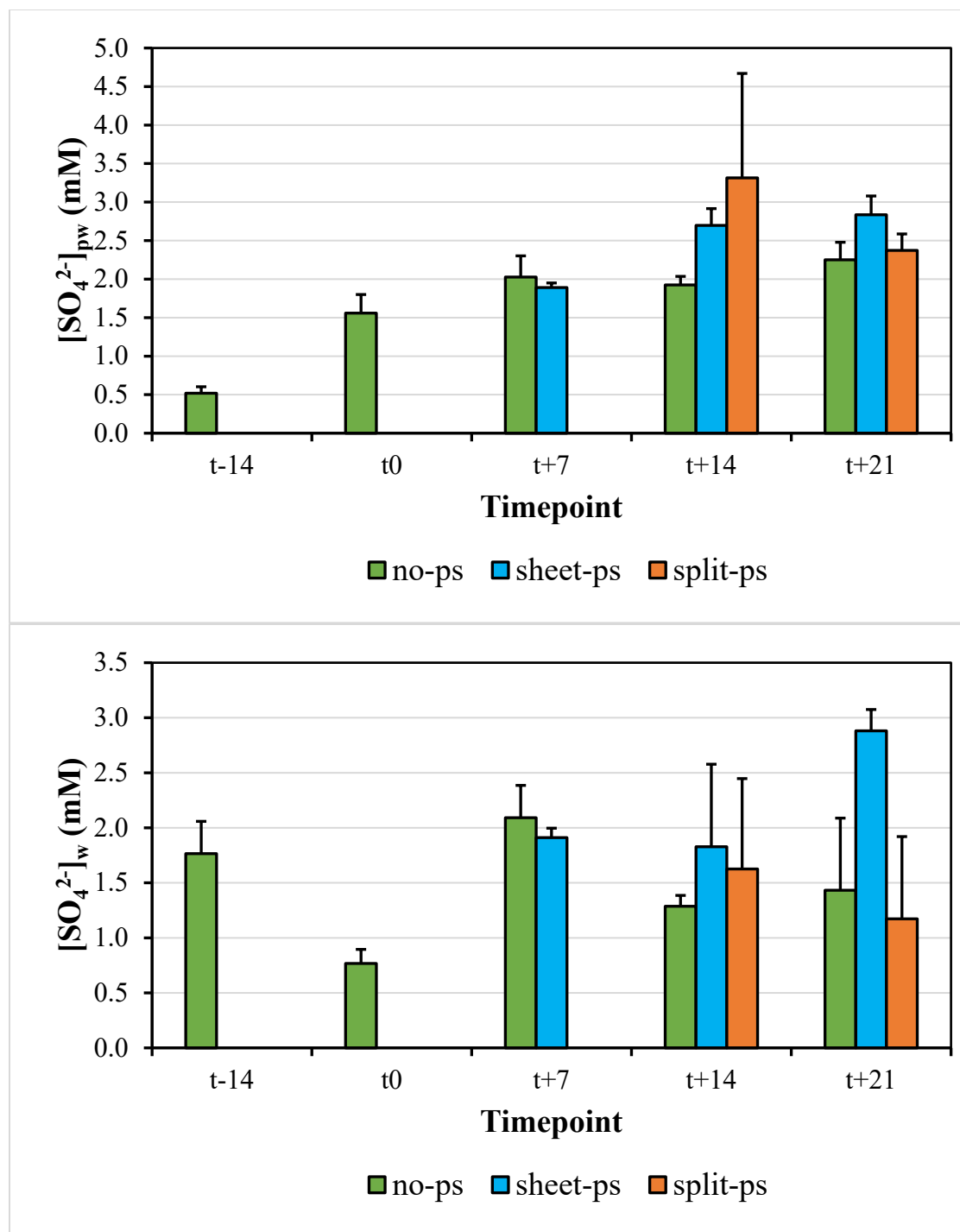


Figure S7.7E. Porewater Sulfide.

Sulfide in porewaters was low (1-4 μ M) but detectable at all time points. There was no change in porewater sulfide over time. The presence of samplers did not affect porewater sulfide concentrations. There was no detectable sulfide in microcosm surface waters (DL = 0.5 μ M).

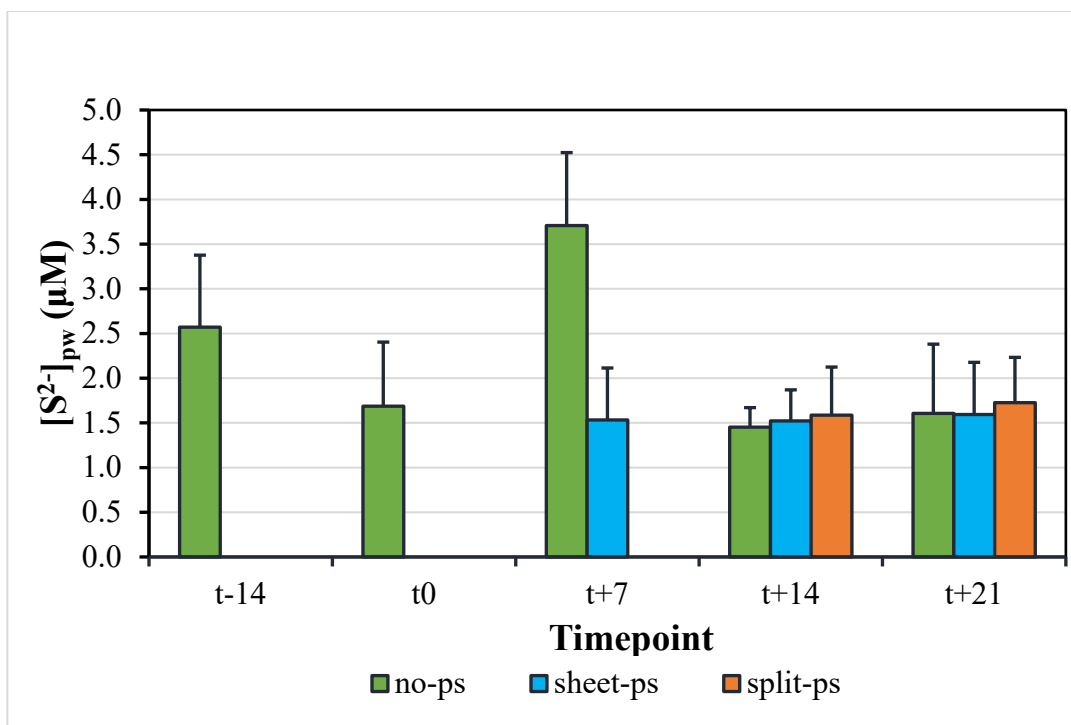


Figure S7.7F. MeHg in Microcosm Surface Water (A), Porewater (B), Sediment (C), and Sediment:water MeHg Partitioning (D).

By days 14 and 21, water column MeHg concentrations were slightly (~25%) but significantly less in the beakers that contained passive samplers than those without (two-way ANOVA on sampling date and presence of sampler, $p < 0.007$). There were no significant differences in porewater MeHg when passive samplers were present. Sediment MeHg concentrations did not change over time, nor were they impacted by the presence of the samplers.

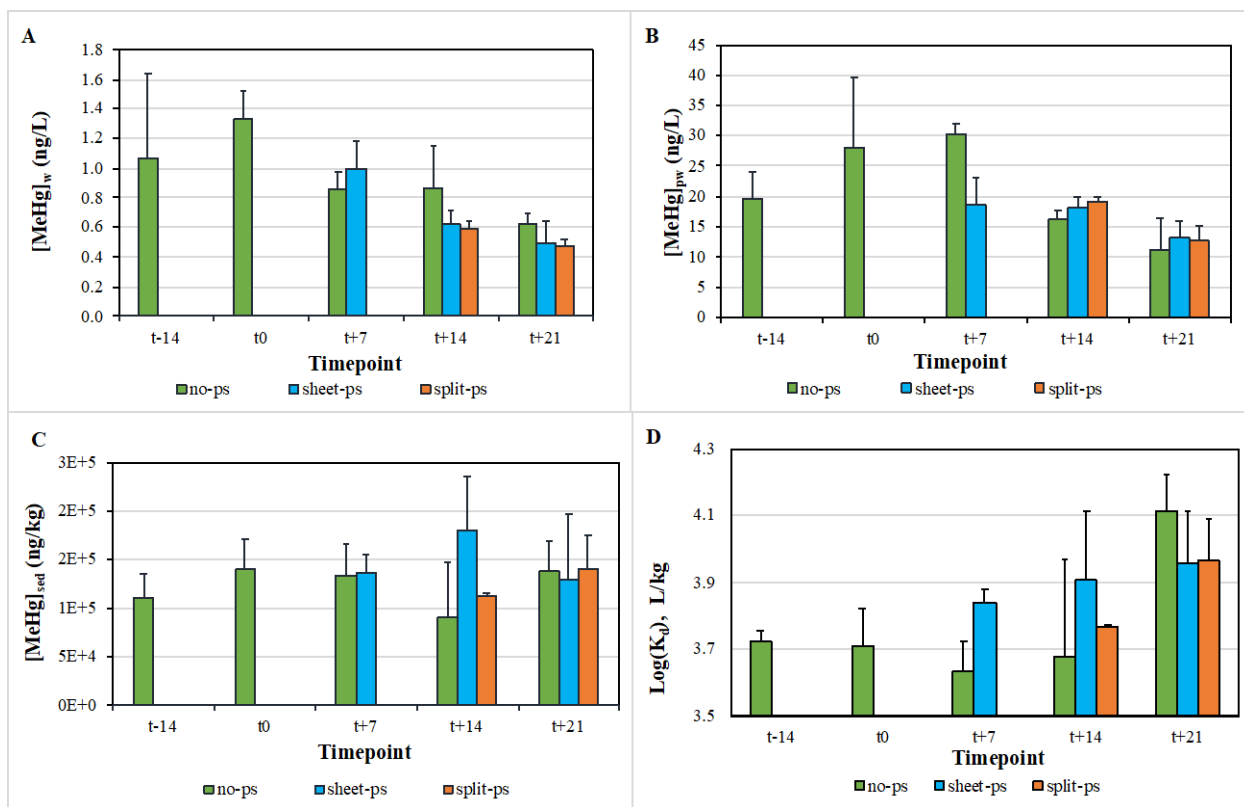


Figure S7.8. A Comparison of Aqueous MeHg Concentrations with MeHg Accumulation by ag+AC Samplers.

Mean overlying water and porewater MeHg concentrations at (A) 14 days after sampler insertion and (B) 21 days after sampler insertion (left panel). Error bars depict one standard deviation. MeHg concentrations in ag+AC samplers inserted in the sediment and suspended in water, (A) 14 days after sampler insertion and (B) 21 days after sampler insertion (right panel). Error bars depict one standard deviation.

Passive sampler MeHg concentrations rose significantly in both water and sediment between days 14 and 21 of exposure. There were no significant differences in MeHg uptake between sheet and split samplers deployed within each matrix (sediment vs. water). Analysis based on standard least squares models that considered time, sampler type, and sampler placement with an overall $\alpha=0.05$.

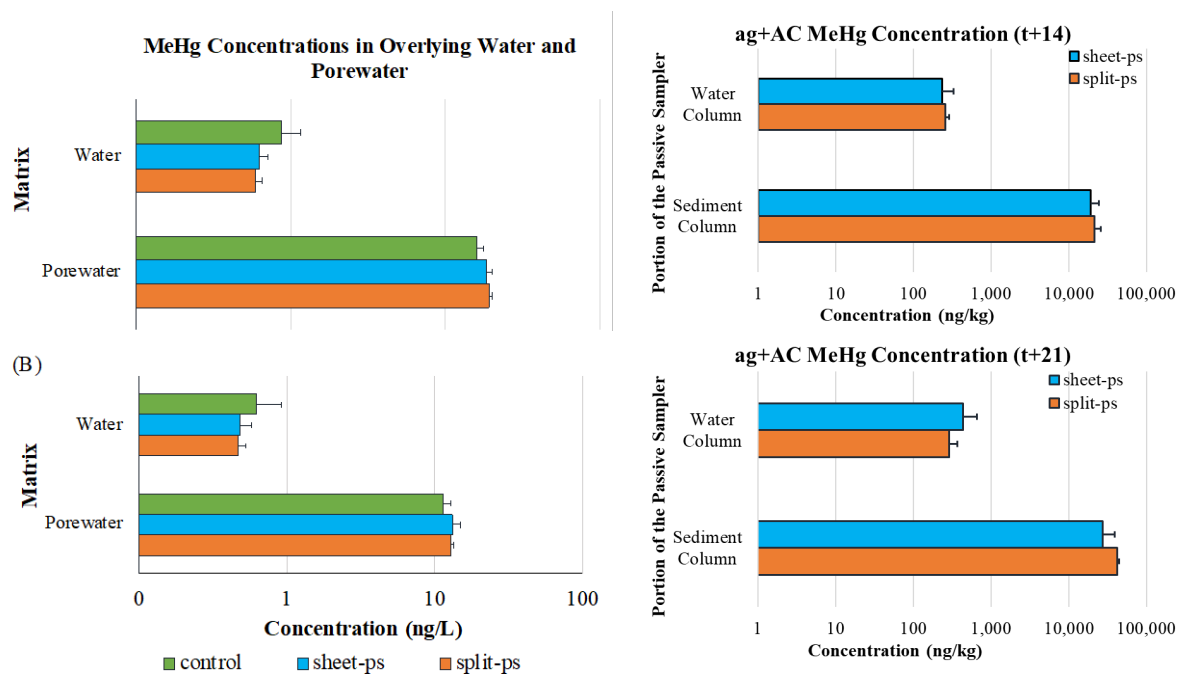


Figure S7.9. Comparison of log(K) Values for Partitioning of MeHg from Porewater to Either Sediment (solid bars) or Passive Samplers Inserted within the Sediment Phase (Dashed Bars) in Sediment Microcosms at 14 Days and 21 Days After Passive Sampler Deployment.

Bars show average 1 standard deviation for triplicate microcosms at each time point. Colored bars represent three treatments: no passive sampler (green), sheet-ps (blue) or split-ps (orange).

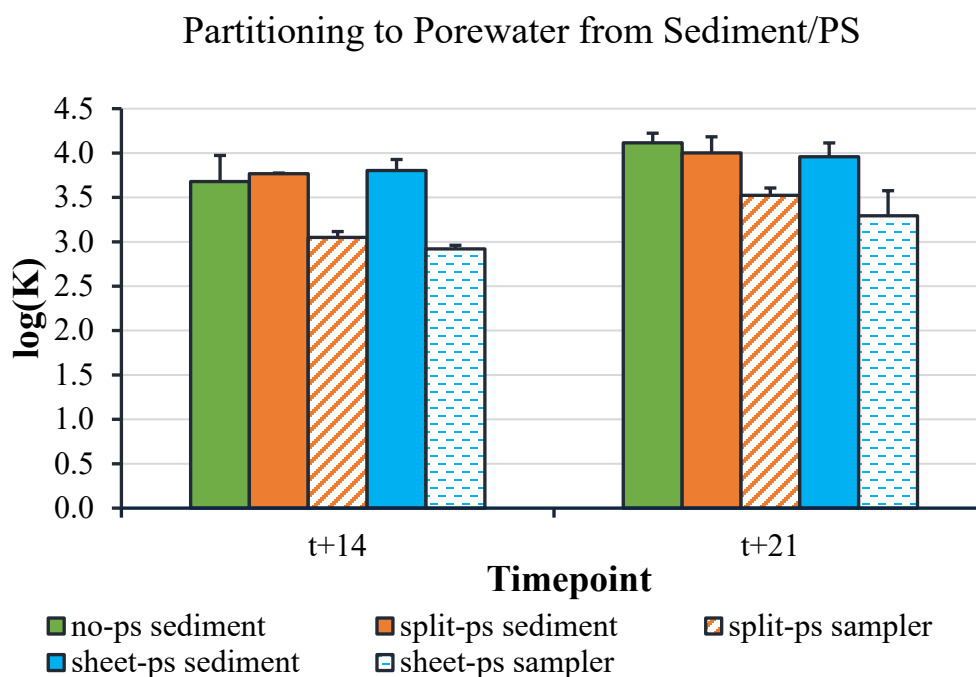
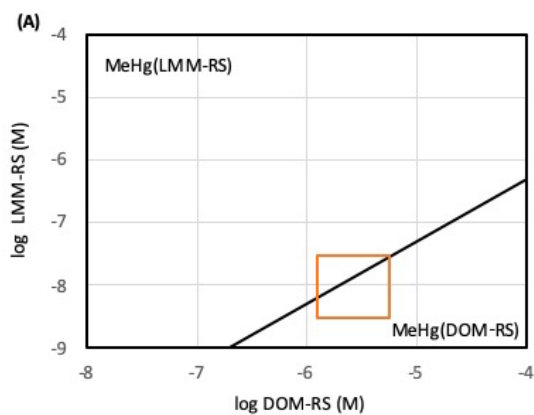


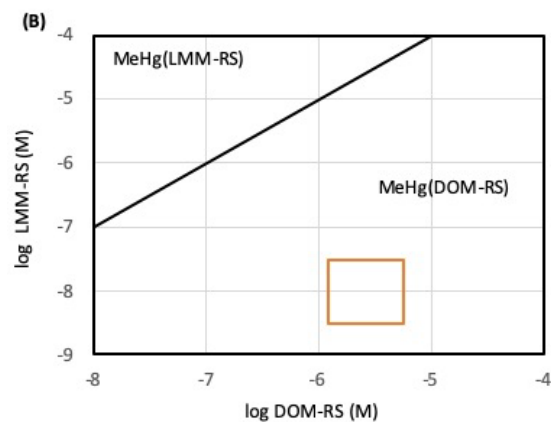
Figure S7.10. Calculated MeHg Speciation in Microcosm Surface Waters and Porewaters as a Function of the DOM Thiol Concentration (DOM-RS) and the Sum of Low Molecular Weight Thiols.

Calculations were performed using minimum and maximum estimated values of the formation constants (K_f) for MeHg complexes with low molecular weight thiols and DOM thiols, see Table S9 for equations and references. For surface water models (A & B), $pH = 7.7$, $Cl^- = 5 \times 10^{-2} M$, and sulfide = 0 M, while for porewater models (C & D), $pH = 6.8$, $Cl^- = 6.5 \times 10^{-2} M$, and sulfide = $2 \times 10^{-6} M$, average measured conditions for the microcosms. A) Formation constants most favoring MeHg(LMM-RS) complexes in surface water; B) formation constants most favoring MeHg(DOM-RS) complexes in porewater, C) formation constants most favoring MeHgSH over MeHg(LMM-RS) and MeHg(DOM-RS) complexes in porewater; D) formation constants most favoring MeHg(LMM-RS) and MeHg(DOM-RS) complexes over MeHgSH in porewater. Orange boxes show the estimated range of LMM-RS and DOM-RS in microcosm surface water or porewater (see text).

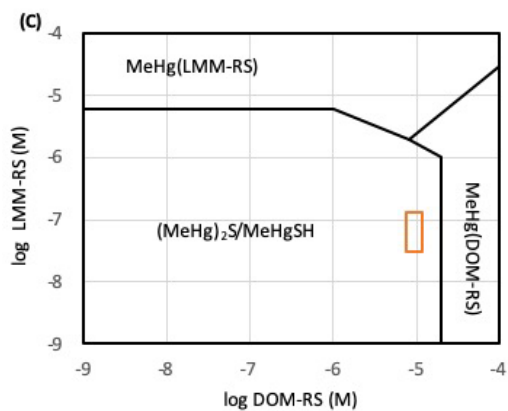
A. $\log K_f \text{MeHg(LMM-RS)} = 17.5$
 $\log K_f \text{MeHg(DOM-RS)} =$



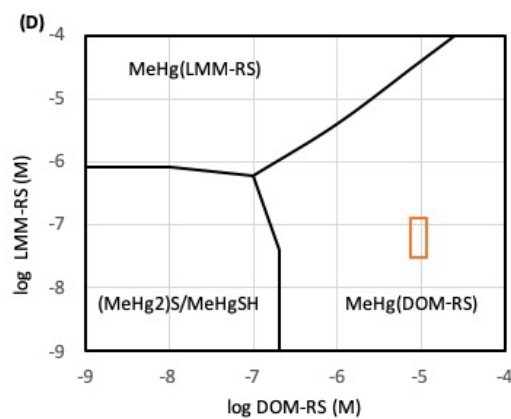
B. $\log K_f \text{MeHg(LMM-RS)} = 15.7$
 $\log K_f \text{MeHg(DOM-RS)} = 17.1$



D. $\log K_f \text{MeHg(LMM-RS)} = 17.5$
 $\log K_f \text{MeHg(DOM-RS)} = 17.1$



C. $\log K_f \text{MeHg(LMM-RS)} = 15.7$
 $\log K_f \text{MeHg(DOM-RS)} = 15.6$



Supplemental Tables

Table S7.1. Reference Organic Matter Stock Elemental Composition and C Distributions.
All Data Are Taken from IHSS.

OM Source	Abbreviation	C content (mass %)	S content (mass %)	S/C	Aromaticity (% of C)
Suwannee River Humic Acid III	SRHA	54.59	0.55	0.010	35.3
Suwannee River Fulvic Acid II	SRFA	52.34	0.46	0.009	22
Elliott Soil Humic Acid V	ESHA	58.75	0.43	0.007	48.3
Pahokee Peat Humic Acid II	PPHA	56.37	0.71	0.013	47
Leonardite Humic Acid	LHA	63.81	0.76	0.012	58
Suwannee River Natural Organic Matter	SRNOM	50.7	1.78	0.035	23
Upper Mississippi River Natural Organic Matter	UMRNOM	49.98	2.62	0.052	19

Table S7.2. Quality Assurance Data for MeHg Analyses in This Work.^a

Matrix	RPD Duplicates	Concentration	ID Spike Recovery	CRM Recovery	DL	Units
water	5.4 ± 5.0%	NA	83.3 ± 12.9%	NA	0.48 ± 0.74	ng L ⁻¹
sediment	15.7%	NA	82.1 ± 21.5%	NA	2057 ± 673	ng kgdw ⁻¹
ag+AC	n/a	NA	65.8 ± 12.5%	NA	83.7 ± 207	ng kgdw ⁻¹
bare AC particles	n/a	NA	47.6% ± 9.7%	NA	0.36 ± 0.35	ng kgdw ⁻¹
CRM	NA	13.06 ± 1.59	87.5% ± 9.7%	95.3% ± 10.3%	NA	µg gdw ⁻¹
distillation blanks	NA	0.11 ± 0.10	72.2% ± 12.2%	NA	NA	ng L ⁻¹

^a Analysis was done by isotope dilution ICP-MS, i.e., with internal stable isotope standards. Relative percent differences (RPD) are for duplicate analyses of the same prepared sample. Certified Reference Materials (CRM) were NIST 1566b oyster tissue, certified concentration of 13.2 µg/g MeHg. Detection limits were estimated as three times the standard error of blanks across samples.

Table S7.3. Summary of MeHgCys Isotherm Experiment Data.

MeHg Spike Level (ng/L)	Replicate	Sample Type	Sorbent	Mass (g)	MeHg Conc. (ng/L or ng/kg)	Treatment Avg. MeHg Conc. (ng/L or ng/kg)	1 SD of MeHg Conc.	Log(C _w)	Log(C _{ps})
DI Blank	A	Water	Blank	40	0.21				
DI Blank	B	Water	Blank	40	0.21	0.20	0.03		
DI Blank	C	Water	Blank	40	0.17				
Control Blank	A	Water	Blank	40	0.14				
Control Blank	B	Water	Blank	40	0.16	0.14	0.02		
Control Blank	C	Water	Blank	40	0.12				
Control Blank	A	Water	AC	30	0.16				
Control Blank	B	Water	AC	30	0.16	0.16	0.00		
Control Blank	C	Water	AC	30	0.16				
Control Blank	A	Particles	AC	0.0098	299				
Control Blank	B	Particles	AC	0.0094	314	282.31	43.06		
Control Blank	C	Particles	AC	0.0101	233				
3	A	Water	AC	30	0.25				
3	B	Water	AC	30	0.21	0.21	0.04	-0.68	
3	C	Water	AC	30	0.17				
3	A	Particles	AC	0.0093	11132				
3	B	Particles	AC	0.0094	9797	10580.62	696.84		4.02
3	C	Particles	AC	0.0098	10812				
10	A	Water	AC	30	0.59				
10	B	Water	AC	30	0.51	0.57	0.05	-0.24	
10	C	Water	AC	30	0.61				
10	A	Particles	AC	0.0104	26920				
10	B	Particles	AC	0.0113	24398	27990.92	4231.42		4.45
10	C	Particles	AC	0.0092	32655				
30	A	Water	AC	30	1.48				
30	B	Water	AC	30	1.49	1.49	0.01	0.17	
30	C	Water	AC	30					
30	A	Particles	AC	0.0117	64533				
30	B	Particles	AC	0.0099	73860	69525.97	4698.11		4.84
30	C	Particles	AC	0.0105	70185				
100	A	Water	AC	30	2.39				
100	B	Water	AC	30	2.80	2.75	0.34	0.44	
100	C	Water	AC	30	3.06				
100	A	Particles	AC	0.0109	253118				
100	B	Particles	AC	0.0108	253231	255437.07	3919.14		5.41
100	C	Particles	AC	0.0104	259962				
300	A	Water	AC	30	7.04				
300	B	Water	AC	30	6.63	6.94	0.28	0.84	
300	C	Water	AC	30	7.16				
300	A	Particles	AC	0.0117	652425				
300	B	Particles	AC	0.011	720921	793755.64	188608.05		5.90

MeHg Spike Level (ng/L)	Replicate	Sample Type	Sorbent	Mass (g)	MeHg Conc. (ng/L or ng/kg)	Treatment Avg. MeHg Conc. (ng/L or ng/kg)	1 SD of MeHg Conc.	Log(C _w)	Log(C _{ps})
300	C	Particles	AC	0.0105	1007921				
Control Blank	A	Water	ag+AC	30	0.13				
Control Blank	B	Water	ag+AC	30	0.15	0.13	0.01	-0.87	
Control Blank	C	Water	ag+AC	30	0.13				
Control Blank	A	Sampler	ag+AC	0.446	5				
Control Blank	B	Sampler	ag+AC	0.43	5	5.64	0.58		
Control Blank	C	Sampler	ag+AC	0.45	6				
30	A	Water	ag+AC	30	1.44				
30	B	Water	ag+AC	30	1.45	1.45	0.02	0.16	
30	C	Water	ag+AC	30	1.47				
30	A	Sampler	ag+AC	0.468	1952				
30	B	Sampler	ag+AC	0.478	1826	1821.37	132.92		3.26
30	C	Sampler	ag+AC	0.491	1686				
100	A	Water	ag+AC	30	2.67				
100	B	Water	ag+AC	30	2.79	2.71	0.07	0.43	
100	C	Water	ag+AC	30	2.66				
100	A	Sampler	ag+AC	0.445	6612				
100	B	Sampler	ag+AC	0.405	7190	6596.39	601.51		3.82
100	C	Sampler	ag+AC	0.481	5987				
300	A	Water	ag+AC	30	10.52				
300	B	Water	ag+AC	30	11.44	11.41	0.89	1.06	
300	C	Water	ag+AC	30	12.29				
300	A	Sampler	ag+AC	0.481	18942				
300	B	Sampler	ag+AC	0.459	18087	18628.48	471.19		4.27
300	C	Sampler	ag+AC	0.463	18857				
1000	A	Water	ag+AC	30	36.80				
1000	B	Water	ag+AC	30	32.43	32.05	4.94	1.51	
1000	C	Water	ag+AC	30	26.93				
1000	A	Sampler	ag+AC	0.471	59993				
1000	B	Sampler	ag+AC	0.594	48463	55398.41	6111.18		4.74
1000	C	Sampler	ag+AC	0.465	57740				
3000	A	Water	ag+AC	30	173.54				
3000	B	Water	ag+AC	30	141.20	153.09	17.79	2.18	
3000	C	Water	ag+AC	30	144.53				
3000	A	Sampler	ag+AC	0.43	180870				
3000	B	Sampler	ag+AC	0.543	130424	159927.52	26290.22		5.20
3000	C	Sampler	ag+AC	0.475	168488				

Table S7.4. Summary of Experimental Data from MeHgDOM Isotherm Experiments.
DOM Source Abbreviations Are Taken from Table S7.1.

Isotherm Experiment	Adsorbate	Sample Type	DOM Source	Mass of Reservoir (g)	MeHg (ng/L or ng/kg)	DOC (mg/L)
Varying DOM:MeHg	Blank	Water	SRFA	35	0.13	1.09
Varying DOM:MeHg	MeHg	Water	SRFA	35	0.59	4.15
Varying DOM:MeHg	MeHg	Water	SRFA	35	2.69	1.22
Varying DOM:MeHg	MeHg	Water	SRFA	35	5.22	1.35
Varying DOM:MeHg	MeHg	Water	SRFA	35	23.76	1.63
Varying DOM:MeHg	Blank	Polymer	SRFA	0.85	8.34	
Varying DOM:MeHg	MeHg	Polymer	SRFA	0.718	232.19	
Varying DOM:MeHg	MeHg	Polymer	SRFA	0.748	1199.58	
Varying DOM:MeHg	MeHg	Polymer	SRFA	0.736	2480.47	
Varying DOM:MeHg	MeHg	Polymer	SRFA	0.667	11680.83	
Varying DOM:MeHg	Blank	Water	SRNOM	35	0.08	1.07
Varying DOM:MeHg	MeHg	Water	SRNOM	35	0.42	4.01
Varying DOM:MeHg	MeHg	Water	SRNOM	35	2.19	1.20
Varying DOM:MeHg	MeHg	Water	SRNOM	35	6.23	1.16
Varying DOM:MeHg	MeHg	Water	SRNOM	35	18.30	1.03
Varying DOM:MeHg	Blank	Polymer	SRNOM	0.809	5.57	
Varying DOM:MeHg	MeHg	Polymer	SRNOM	0.728	196.39	
Varying DOM:MeHg	MeHg	Polymer	SRNOM	0.767	1109.07	
Varying DOM:MeHg	MeHg	Polymer	SRNOM	0.8	2097.87	
Varying DOM:MeHg	MeHg	Polymer	SRNOM	0.813	10375.62	
Varying DOM:MeHg	Blank	Water	UMRNOM	35	0.01	1.10
Varying DOM:MeHg	MeHg	Water	UMRNOM	35	0.25	4.11
Varying DOM:MeHg	MeHg	Water	UMRNOM	35	1.46	1.29
Varying DOM:MeHg	MeHg	Water	UMRNOM	35	3.18	1.23
Varying DOM:MeHg	MeHg	Water	UMRNOM	35	7.02	1.37
Varying DOM:MeHg	Blank	Polymer	UMRNOM	0.815	7.29	
Varying DOM:MeHg	MeHg	Polymer	UMRNOM	0.851	193.55	
Varying DOM:MeHg	MeHg	Polymer	UMRNOM	0.836	1065.83	
Varying DOM:MeHg	MeHg	Polymer	UMRNOM	0.803	2167.44	
Varying DOM:MeHg	MeHg	Polymer	UMRNOM	0.819	9567.57	
Varying DOM:MeHg	Blank	Water	ESHA	35	0.00	2.48
Varying DOM:MeHg	MeHg	Water	ESHA	35	0.94	5.73
Varying DOM:MeHg	MeHg	Water	ESHA	35	4.73	3.02
Varying DOM:MeHg	MeHg	Water	ESHA	35	7.52	2.18
Varying DOM:MeHg	MeHg	Water	ESHA	35	37.75	2.65
Varying DOM:MeHg	Blank	Polymer	ESHA	0.809	0.23	
Varying DOM:MeHg	MeHg	Polymer	ESHA	0.835	185.83	
Varying DOM:MeHg	MeHg	Polymer	ESHA	0.766	1124.06	
Varying DOM:MeHg	MeHg	Polymer	ESHA	0.819	2183.05	
Varying DOM:MeHg	MeHg	Polymer	ESHA	0.768	14541.28	
Varying DOM:MeHg	Blank	Water	PPHA	35	0.00	1.94
Varying DOM:MeHg	MeHg	Water	PPHA	35	1.78	4.55
Varying DOM:MeHg	MeHg	Water	PPHA	35	8.33	1.93
Varying DOM:MeHg	MeHg	Water	PPHA	35	15.49	2.04
Varying DOM:MeHg	MeHg	Water	PPHA	35	64.44	2.48
Varying DOM:MeHg	Blank	Polymer	PPHA	0.8	1.85	
Varying DOM:MeHg	MeHg	Polymer	PPHA	0.842	162.45	
Varying DOM:MeHg	MeHg	Polymer	PPHA	0.819	887.05	
Varying DOM:MeHg	MeHg	Polymer	PPHA	0.783	2018.64	
Varying DOM:MeHg	MeHg	Polymer	PPHA	0.803	11933.00	
Varying DOM:MeHg	Blank	Water	LHA	35	0.00	1.26
Varying DOM:MeHg	MeHg	Water	LHA	35	1.51	4.54

Isotherm Experiment	Adsorbate	Sample Type	DOM Source	Mass of Reservoir (g)	MeHg (ng/L or ng/kg)	DOC (mg/L)
Varying DOM:MeHg	MeHg	Water	LHA	35	5.71	1.50
Varying DOM:MeHg	MeHg	Water	LHA	35	10.11	1.59
Varying DOM:MeHg	MeHg	Water	LHA	35	36.35	2.22
Varying DOM:MeHg	Blank	Polymer	LHA	0.921	0.00	
Varying DOM:MeHg	MeHg	Polymer	LHA	0.805	163.50	
Varying DOM:MeHg	MeHg	Polymer	LHA	0.904	936.34	
Varying DOM:MeHg	MeHg	Polymer	LHA	0.838	1739.44	
Varying DOM:MeHg	MeHg	Polymer	LHA	1.039	10213.95	
Varying DOM:MeHg	Blank	Water	SRHA	35	0.00	2.86
Varying DOM:MeHg	MeHg	Water	SRHA	35	1.95	6.10
Varying DOM:MeHg	MeHg	Water	SRHA	35	8.92	3.11
Varying DOM:MeHg	MeHg	Water	SRHA	35	19.95	2.91
Varying DOM:MeHg	MeHg	Water	SRHA	35	99.78	3.67
Varying DOM:MeHg	Blank	Polymer	SRHA	0.779	0.93	
Varying DOM:MeHg	MeHg	Polymer	SRHA	0.877	134.14	
Varying DOM:MeHg	MeHg	Polymer	SRHA	0.871	612.39	
Varying DOM:MeHg	MeHg	Polymer	SRHA	0.848	1690.84	
Varying DOM:MeHg	MeHg	Polymer	SRHA	0.838	9300.67	
Constant DOM:MeHg	MeHg	Water	ESHA	30	1.50	
Constant DOM:MeHg	MeHg	Water	ESHA	30	7.20	
Constant DOM:MeHg	MeHg	Water	ESHA	30	12.85	
Constant DOM:MeHg	MeHg	Polymer	ESHA	0.732	318.21	
Constant DOM:MeHg	MeHg	Polymer	ESHA	0.61	943.69	
Constant DOM:MeHg	MeHg	Polymer	ESHA	0.466	1864.54	
Constant DOM:MeHg	MeHg	Water	LHA	30	2.28	
Constant DOM:MeHg	MeHg	Water	LHA	30	8.65	
Constant DOM:MeHg	MeHg	Water	LHA	30	13.86	
Constant DOM:MeHg	MeHg	Polymer	LHA	0.862	267.22	
Constant DOM:MeHg	MeHg	Polymer	LHA	0.899	574.11	
Constant DOM:MeHg	MeHg	Polymer	LHA	0.823	860.72	
Constant DOM:MeHg	MeHg	Water	PPHA	30	0.80	
Constant DOM:MeHg	MeHg	Water	PPHA	30	5.49	
Constant DOM:MeHg	MeHg	Water	PPHA	30	11.06	
Constant DOM:MeHg	MeHg	Polymer	PPHA	0.755	353.41	
Constant DOM:MeHg	MeHg	Polymer	PPHA	0.741	1156.81	
Constant DOM:MeHg	MeHg	Polymer	PPHA	0.77	1203.97	
Constant DOM:MeHg	MeHg	Water	SRFA	30	0.09	
Constant DOM:MeHg	MeHg	Water	SRFA	30	1.38	
Constant DOM:MeHg	MeHg	Water	SRFA	30	8.00	
Constant DOM:MeHg	MeHg	Water	SRFA	30	59.82	
Constant DOM:MeHg	MeHg	Polymer	SRFA	0.827	8.15	
Constant DOM:MeHg	MeHg	Polymer	SRFA	0.731	332.24	
Constant DOM:MeHg	MeHg	Polymer	SRFA	0.845	477.15	
Constant DOM:MeHg	MeHg	Polymer	SRFA	0.816	956.89	
Constant DOM:MeHg	MeHg	Water	SRNOM	30	0.06	
Constant DOM:MeHg	MeHg	Water	SRNOM	30	0.09	
Constant DOM:MeHg	MeHg	Water	SRNOM	30	0.70	
Constant DOM:MeHg	MeHg	Water	SRNOM	30	6.41	
Constant DOM:MeHg	MeHg	Water	SRNOM	30	46.29	
Constant DOM:MeHg	MeHg	Polymer	SRNOM	0.749	9.29	
Constant DOM:MeHg	MeHg	Polymer	SRNOM	0.694	40.60	
Constant DOM:MeHg	MeHg	Polymer	SRNOM	0.758	337.34	
Constant DOM:MeHg	MeHg	Polymer	SRNOM	0.807	560.59	
Constant DOM:MeHg	MeHg	Polymer	SRNOM	0.999	944.41	
Constant DOM:MeHg	MeHg	Water	UMRNOM	30	0.13	

Isotherm Experiment	Adsorbate	Sample Type	DOM Source	Mass of Reservoir (g)	MeHg (ng/L or ng/kg)	DOC (mg/L)
Constant DOM:MeHg	MeHg	Water	UMRNOM	30	0.04	
Constant DOM:MeHg	MeHg	Water	UMRNOM	30	0.70	
Constant DOM:MeHg	MeHg	Water	UMRNOM	30	5.90	
Constant DOM:MeHg	MeHg	Water	UMRNOM	30	41.30	
Constant DOM:MeHg	MeHg	Polymer	UMRNOM	0.829	8.51	
Constant DOM:MeHg	MeHg	Polymer	UMRNOM	0.873	32.95	
Constant DOM:MeHg	MeHg	Polymer	UMRNOM	0.844	308.96	
Constant DOM:MeHg	MeHg	Polymer	UMRNOM	0.795	611.45	
Constant DOM:MeHg	MeHg	Polymer	UMRNOM	0.868	1451.39	
Constant DOM:MeHg	MeHg	Water	SRHA	30	0.96	
Constant DOM:MeHg	MeHg	Water	SRHA	30	3.02	
Constant DOM:MeHg	MeHg	Water	SRHA	30	20.98	
Constant DOM:MeHg	MeHg	Water	SRHA	30	26.98	
Constant DOM:MeHg	MeHg	Polymer	SRHA	0.73	221.52	
Constant DOM:MeHg	MeHg	Polymer	SRHA	0.793	352.45	
Constant DOM:MeHg	MeHg	Polymer	SRHA	0.639	1479.10	
Constant DOM:MeHg	MeHg	Polymer	SRHA	0.736	954.55	

Table S7.5. Summary of Isotopically Labelled MeHgSRHA:MeHgSRHA Exchange Experiment Data.

Samples are broken down by whether they were a part of the uptake or exchange phase, whether the MeHg concentrations were measured in overlying water or sorbent material, and by sorbent. Control samples contained Me^{xxx}HgSRHA spikes, but no sorbent materials. Averages and standard deviation of Me^{xxx}Hg concentrations are shown for triplicate treatments at each timepoint.

Phase	Sample Type	Sorbent	Replicate	Time (min)	Mass of Reservoir (g)	Me ¹⁹⁹ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁹ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁹ Hg	Me ¹⁹⁸ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁸ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁸ Hg	Overall Log(K _{ps})	DOC (mg C/L)	Treatment Avg. DOC	1SD
Uptake	Water	Blank	A	21500	30	0.00				0.00							
Uptake	Water	Blank	B	21500	30	0.00	0.00	0.00		0.00	0.00	0.00					
Uptake	Water	Blank	C	21500	30	0.00				0.00							
Uptake	Water	Control	A	0	30	50.81				0.00							
Uptake	Water	Control	B	0	30	46.07	49.52	3.03		0.00	0.01	0.01					
Uptake	Water	Control	A	0	30	51.70				0.02							
Uptake	Water	Control	A	2850	30	47.44				0.00					5.41		
Uptake	Water	Control	B	2850	30	50.92	50.43	2.78		0.00	0.00	0.00			5.85	5.92	0.56
Uptake	Water	Control	C	2850	30	52.94				0.00					6.51		
Uptake	Water	Control	A	21500	30	54.71				0.00					5.65		
Uptake	Water	Control	B	21500	30	55.06	53.78	1.92		0.00	0.00	0.00			5.67	5.53	0.24
Uptake	Water	Control	C	21500	30	51.57				0.00					5.255		
Uptake	Sorbent	ag+AC Sampler	A	21500	0.84	593.85				3.22							
Uptake	Sorbent	ag+AC Sampler	B	21500	0.90	515.27	554.56	55.56		3.79	3.51	0.40					
Uptake	Water	ag+AC Sampler	A	21500	30	31.20				0.00					4.68		
Uptake	Water	ag+AC Sampler	B	21500	30	30.67	30.94	0.38	1.194	0.00	0.00	0.00	NA	1.194	3.84	4.26	0.59
Uptake	Water	ag+AC Sampler	A	21500	30	35.48				0.00					3.96		
Uptake	Water	ag+AC Sampler	B	21500	30	34.89				0.00					4.54		
Uptake	Water	ag+AC Sampler	C	21500	30	38.25				0.00					4.37		
Uptake	Water	ag+AC Sampler	D	21500	30	36.64				0.00					5.49		
Uptake	Water	ag+AC Sampler	E	21500	30	35.13				0.00					4.29		
Uptake	Water	ag+AC Sampler	F	21500	30	36.71	36.22	1.37		0.00	0.00	0.00			4.256	4.27	0.48

Phase	Sample Type	Sorbent	Replicate	Time (min)	Mass of Reservoir (g)	Me ¹⁹⁹ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁹ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁹ Hg	Me ¹⁹⁸ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁸ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁸ Hg	Overall Log(K _{ps})	DOC (mg C/L)	Treatment Avg. DOC	1SD
Uptake	Water	ag+AC Sampler	G	21500	30	36.52				0.00					4.151		
Uptake	Water	ag+AC Sampler	H	21500	30	36.50				0.00					3.923		
Uptake	Water	ag+AC Sampler	I	21500	30	38.71				0.00					3.569		
Uptake	Water	ag+AC Sampler	J	21500	30	36.52				0.00					3.87		
Uptake	Water	ag+AC Sampler	K	21500	30	35.46				0.00					4.29		
Uptake	Water	ag+AC Sampler	L	21500	30	33.85				0.00					4.52		
Uptake	Sorbent	Bare AC Particle	A	2850	0.0111	35913.44				653.61							
Uptake	Sorbent	Bare AC Particle	B	2850	0.0112	35836.77	35875.10	54.22		0.00	326.80	462.17					
Uptake	Water	Bare AC Particle	A	2850	30	36.85				0.24					6.66		
Uptake	Water	Bare AC Particle	B	2850	30	34.02	35.43	2.00	2.98	0.00	0.12	0.17	NA	2.98	5.89	6.27	0.55
Uptake	Water	Bare AC Particle	A	2850	30	33.54				0.19					4.74		
Uptake	Water	Bare AC Particle	B	2850	30	33.34				0.00					3.84		
Uptake	Water	Bare AC Particle	C	2850	30	35.49				0.00					4.011		
Uptake	Water	Bare AC Particle	D	2850	30	31.84				0.00					4.65		
Uptake	Water	Bare AC Particle	E	2850	30	31.69	31.75	4.27		0.00	0.02	0.06			4.35	4.56	0.49
Uptake	Water	Bare AC Particle	I	2850	30	27.29				0.00					4.039		
Uptake	Water	Bare AC Particle	J	2850	30	37.28				0.00					5.475		
Uptake	Water	Bare AC Particle	K	2850	30	32.24				0.00					5.19		
Uptake	Water	Bare AC Particle	L	2850	30	23.05				0.00					4.86		
Uptake	Water	Bare AC Particle	F	2850	30	NA				NA					4.28		
Uptake	Water	Bare AC Particle	G	2850	30	NA				NA					4.78		
Uptake	Water	Bare AC Particle	H	2850	30	NA				NA					4.472		
Exchange	Water	Blank	A	20194	30	0.00				0.00					0.67		
Exchange	Water	Blank	B	20194	30	0.00	0.00	0.00		0.00	0.00	0.00			0.557	0.57	0.08
Exchange	Water	Blank	C	20194	30	0.00				0.00					0.50		

Phase	Sample Type	Sorbent	Replicate	Time (min)	Mass of Reservoir (g)	Me ¹⁹⁹ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁹ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁹ Hg	Me ¹⁹⁸ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁸ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁸ Hg	Overall Log(K _{ps})	DOC (mg C/L)	Treatment Avg. DOC	1SD
Exchange	Water	Control	A	0	30	0.43				41.44							
Exchange	Water	Control	B	0	30	0.45	0.44	0.01		44.93	43.19	2.47					
Exchange	Water	Control	A	0	30	0.34				42.30					7.23		
Exchange	Water	Control	B	0	30	0.39	0.37	0.03		41.63	41.96	0.48			7.22	7.23	0.01
Exchange	Water	Control	A	187	30	1.97				39.43							
Exchange	Water	Control	B	187	30	0.54	1.37	0.74		43.91	42.00	2.31					
Exchange	Water	Control	C	187	30	1.61				42.66							
Exchange	Water	Control	A	2875	30	0.26				40.89					5.20		
Exchange	Water	Control	B	2875	30	0.00	0.19	0.17		44.07	42.17	1.68			5.22	5.15	0.10
Exchange	Water	Control	C	2875	30	0.31				41.54					5.026		
Exchange	Water	Control	A	10094	30	0.09				34.97							
Exchange	Water	Control	B	10094	30	0.04	0.04	0.04		38.19	37.60	2.38					
Exchange	Water	Control	C	10094	30	0.00				39.63							
Exchange	Water	Control	A	20194	30	0.00				33.55					6.524		
Exchange	Water	Control	B	20194	30	0.00	0.00	0.00		34.63	34.84	1.40			7.030	6.94	0.38
Exchange	Water	Control	C	20194	30	0.00				36.33					7.273		
Exchange	Sorbent	ag+AC Sampler	A	81	0.83	522.00				64.90							
Exchange	Sorbent	ag+AC Sampler	B	81	0.77	677.96	599.98	110.28		26.49	45.69	27.16					
Exchange	Water	ag+AC Sampler	A	81	30	0.89				34.84					6.72		
Exchange	Water	ag+AC Sampler	B	81	30	1.87	1.38	0.70	2.638	32.54	33.69	1.62	0.132	1.265	6.639	6.68	0.06
Exchange	Sorbent	ag+AC Sampler	A	369	0.74	595.65				55.97							
Exchange	Sorbent	ag+AC Sampler	B	369	0.70	601.15	598.40	3.89		68.05	62.01	8.54					
Exchange	Water	ag+AC Sampler	A	369	30	1.75				35.60					7.14		
Exchange	Water	ag+AC Sampler	B	369	30	0.66	1.20	0.77	2.696	34.49	35.04	0.79	0.248	1.261	6.94	7.04	0.14
Exchange	Sorbent	ag+AC Sampler	B	1556	0.74	554.04				102.64							
Exchange	Sorbent	ag+AC Sampler	A	1556	0.75	560.14	557.09	4.32		108.42	105.53	4.09					

Phase	Sample Type	Sorbent	Replicate	Time (min)	Mass of Reservoir (g)	Me ¹⁹⁹ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁹ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁹ Hg	Me ¹⁹⁸ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁸ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁸ Hg	Overall Log(K _{ps})	DOC (mg C/L)	Treatment Avg. DOC	1SD
Exchange	Water	ag+AC Sampler	B	1556	30	1.71				30.40					7.65		
Exchange	Water	ag+AC Sampler	A	1556	30	1.25	1.48	0.32	2.575	33.30	31.85	2.05	0.520	1.298	7.39	7.52	0.18
Exchange	Sorbent	ag+AC Sampler	A	3111	0.76	512.73				123.45							
Exchange	Sorbent	ag+AC Sampler	B	3111	0.71	559.19	535.96	32.85		154.64	139.04	22.06					
Exchange	Water	ag+AC Sampler	A	3111	30	2.04				31.87					7.491		
Exchange	Water	ag+AC Sampler	B	3111	30	2.04	2.04	0.00	2.420	31.67	31.77	0.15	0.641	1.300	7.503	7.50	0.01
Exchange	Sorbent	ag+AC Sampler	A	10094	0.71	452.67				204.77							
Exchange	Sorbent	ag+AC Sampler	B	10094	0.71	385.72	419.19	47.34		191.04	197.90	9.71					
Exchange	Water	ag+AC Sampler	A	10094	30	3.98				30.45					6.09		
Exchange	Water	ag+AC Sampler	B	10094	30	4.04	4.01	0.04	2.020	32.73	31.59	1.62	0.797	1.239	6.572	6.33	0.34
Exchange	Sorbent	ag+AC Sampler	A	20194	0.78	383.71				250.09							
Exchange	Sorbent	ag+AC Sampler	B	20194	0.69	326.43	355.07	40.51		268.93	259.51	13.32					
Exchange	Water	ag+AC Sampler	A	20194	30	5.10				29.05					6.15		
Exchange	Water	ag+AC Sampler	B	20194	30	4.68	4.89	0.30	1.861	28.74	28.89	0.22	0.953	1.260	6.57	6.36	0.30
Exchange	Sorbent	Bare AC Particle	A	21	0.0106	24741.86				4322.80							
Exchange	Sorbent	Bare AC Particle	B	21	0.0116	26219.36	25480.61	1044.75		4392.47	4357.63	49.26					
Exchange	Water	Bare AC Particle	A	21	30	1.60				37.21					5.64		
Exchange	Water	Bare AC Particle	B	21	30	1.21	1.41	0.28	4.26	38.10	37.66	0.63	2.06	2.88	5.24	5.44	0.28
Exchange	Sorbent	Bare AC Particle	A	63	0.0115	24926.04				5065.46							
Exchange	Sorbent	Bare AC Particle	B	63	0.0115	29088.31	27007.18	2943.17		6626.15	5845.81	1103.57					
Exchange	Water	Bare AC Particle	A	63	30	1.48				36.40					4.93		
Exchange	Water	Bare AC Particle	B	63	30	0.77	1.13	0.50	4.38	38.12	37.26	1.21	2.20	2.93	5.029	4.98	0.07
Exchange	Sorbent	Bare AC Particle	A	126	0.0117	24748.38				6834.24							
Exchange	Sorbent	Bare AC Particle	B	126	0.0115	36469.18	30608.78	8287.86		6840.43	6837.33	4.38					
Exchange	Water	Bare AC Particle	A	126	30	0.78				38.16					5.26		
Exchange	Water	Bare AC Particle	B	126	30	1.45	1.12	0.47	4.44	39.42	38.79	0.89	2.25	2.97	5.25	5.26	0.00
Exchange	Sorbent	Bare AC Particle	A	187	0.0101	25481.07				7249.31							

Phase	Sample Type	Sorbent	Replicate	Time (min)	Mass of Reservoir (g)	Me ¹⁹⁹ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁹ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁹ Hg	Me ¹⁹⁸ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁸ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁸ Hg	Overall Log(K _{ps})	DOC (mg C/L)	Treatment Avg. DOC	1SD
Exchange	Sorbent	Bare AC Particle	B	187	0.0106	23393.02	24437.05	1476.47		6389.71	6819.51	607.82					
Exchange	Water	Bare AC Particle	A	187	30	0.91				40.20					4.912		
Exchange	Water	Bare AC Particle	B	187	30	1.01	0.96	0.07	4.41	39.62	39.91	0.41	2.23	2.88	5.41	5.16	0.35
Exchange	Sorbent	Bare AC Particle	B	1397	0.0107	22189.30				14578.29							
Exchange	Sorbent	Bare AC Particle	A	1397	0.0108	34949.82	28569.56	9023.05		13902.54	14240.41	477.83					
Exchange	Water	Bare AC Particle	B	1397	30	0.98				38.47					3.83		
Exchange	Water	Bare AC Particle	A	1397	30	1.70	1.34	0.51	4.33	34.83	36.65	2.57	2.59	3.05	5.28	4.55	1.03
Exchange	Sorbent	Bare AC Particle	B	2875	0.0103	38280.51				18869.22							
Exchange	Sorbent	Bare AC Particle	A	2875	0.0105	28372.35	33326.43	7006.13		19557.70	19213.46	486.83					
Exchange	Water	Bare AC Particle	B	2875	30	1.86				32.40					4.39		
Exchange	Water	Bare AC Particle	A	2875	30	3.52	2.69	1.18	4.09	34.05	33.22	1.17	2.76	3.17	4.349	4.37	0.03

Table S7.6. Summary of Isotopically Labelled MeHgCys:MeHgCys Exchange, DOM:Cys Exchange, and Cys:DOM Exchange Experiments Data.

Samples are broken down by whether they were a part of the uptake or exchange phase, whether the MeHg concentrations were measured in overlying water or polymer material, and by sorbent. Control samples contained Me^{xxx}HgXXX spikes, but no sorbent materials. Averages and standard deviation of Me^{xxx}Hg concentrations are shown for triplicate or duplicate treatments at each timepoint.

Phase	Sample Type	Sorbent	Aqueous Ligand	Replicate	Time (min)	Experiment Course	Mass of Reservoir (g)	Me ¹⁹⁹ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁹ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁹ Hg	Me ¹⁹⁸ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁸ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁸ Hg	Overall Log(K _{ps})	DOC (mg C/L)
Uptake	Water	Blank	Me ¹⁹⁹ HgCys	A	20165	Cys:Cys	40	0.00									
Uptake	Water	Blank	Me ¹⁹⁹ HgSRHA	B	20165	Cys:Cys	40	0.00									
Uptake	Water	Control	Me ¹⁹⁹ HgCys	A	20165	Cys:Cys	40	8.73									
Uptake	Water	Control	Me ¹⁹⁹ HgCys	B	20165	Cys:Cys	40	8.67									
Uptake	Water	Control	Me ¹⁹⁹ HgCys	C	20165	Cys:DOM	40	8.67									
Uptake	Water	Control	Me ¹⁹⁹ HgSRHA	A	20165	DOM:Cys	40	8.74									
Uptake	Water	Control	Me ¹⁹⁹ HgSRHA	B	20165	DOM:Cys	40	8.79									
Uptake	Water	Control	Me ¹⁹⁹ HgSRHA	C	20165	DOM:Cys	40	8.76									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	A	20036	Cys:Cys	40	0.11	0.10	0.02	3.79						
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	B	20036	Cys:Cys	40	0.10									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	C	20036	Cys:Cys	40	0.11									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	D	19952	Cys:Cys	40	0.13									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	E	19952	Cys:Cys	40	0.10									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	F	20075	Cys:Cys	40	0.13									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	G	20075	Cys:Cys	40	0.14									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	H	20075	Cys:Cys	40	0.06									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	I	20219	Cys:Cys	40	0.08									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	J	20219	Cys:Cys	40	0.07									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	K	20219	Cys:Cys	40	0.09									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	L	20249	Cys:Cys	40	0.12									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	M	20249	Cys:Cys	40	0.09									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	N	20249	Cys:Cys	40	0.11									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	O	20275	Cys:Cys	40	0.08									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	P	20219	Cys:Cys	40	0.06									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	Q	20219	Cys:Cys	40	0.08									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	R	20165	Cys:Cys	40	0.07									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	S	20165	Cys:Cys	40	0.07									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	T	20165	Cys:Cys	40	0.09									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	A	20039	Cys:DOM	40	0.07	0.09	0.01	3.67						
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	B	20039	Cys:DOM	40	0.06									

Phase	Sample Type	Sorbent	Aqueous Ligand	Replicate	Time (min)	Experiment Course	Mass of Reservoir (g)	Me ¹⁹⁹ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁹ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁹ Hg	Me ¹⁹⁸ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁸ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁸ Hg	Overall Log(K _{ps})	DOC (mg C/L)
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	C	19958	Cys:DOM	40	0.08									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	D	19958	Cys:DOM	40	0.10									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	E	20079	Cys:DOM	40	0.09									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	F	20079	Cys:DOM	40	0.07									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	G	20223	Cys:DOM	40	0.09									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	H	20223	Cys:DOM	40	0.09									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	I	20254	Cys:DOM	40	0.08									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	J	20254	Cys:DOM	40	0.10									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	K	20279	Cys:DOM	40	0.10									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	L	20279	Cys:DOM	40	0.11									
Uptake	Water	ag+AC	Me ¹⁹⁹ HgCys	M	20165	Cys:DOM	40	0.09	4.34	0.26	1.71						
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	A	20043	DOM:Cys	40	4.62									5.801
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	B	20043	DOM:Cys	40	4.11									5.185
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	C	19965	DOM:Cys	40	4.15									5.542
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	D	19965	DOM:Cys	40	4.48									5.699
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	E	20083	DOM:Cys	40	4.29									5.574
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	F	20083	DOM:Cys	40	4.24									5.176
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	G	20227	DOM:Cys	40	4.19									5.532
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	H	20227	DOM:Cys	40	4.04									5.421
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	I	20258	DOM:Cys	40	4.40									5.518
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	J	20258	DOM:Cys	40	4.07									5.534
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	K	20283	DOM:Cys	40	4.40									5.569
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	L	20283	DOM:Cys	40	4.20									5.387
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	M	20165	DOM:Cys	40	4.83									5.540
Uptake	Water	ag+AC	Me ¹⁹⁹ HgSRHA	N	20165	DOM:Cys	40	4.81									5.579
Uptake	Polymer	ag+AC	Me ¹⁹⁹ HgCys	R	20165	Cys:Cys	0.74	476.80	472.01	15.40							
Uptake	Polymer	ag+AC	Me ¹⁹⁹ HgCys	S	20165	Cys:Cys	0.73	484.46									
Uptake	Polymer	ag+AC	Me ¹⁹⁹ HgCys	T	20165	Cys:Cys	0.78	454.78									
Uptake	Polymer	ag+AC	Me ¹⁹⁹ HgCys	N	20165	Cys:DOM	0.73	479.74	479.74	NA							
Uptake	Polymer	ag+AC	Me ¹⁹⁹ HgSRHA	M	20165	DOM:Cys	0.81	215.42	220.31	6.92							
Uptake	Polymer	ag+AC	Me ¹⁹⁹ HgSRHA	N	20165	DOM:Cys	0.78	225.21									
Exchange	Water	Blank	Me ¹⁹⁸ HgCys	A	20165	Experiment	40	0.00				0.00					
Exchange	Water	Control	Me ¹⁹⁸ HgCys	A	20165	Experiment	40	-0.01				18.64					
Exchange	Water	Control	Me ¹⁹⁸ HgCys	B	20165	Experiment	40	0.01				18.47					

Phase	Sample Type	Sorbent	Aqueous Ligand	Replicate	Time (min)	Experiment Course	Mass of Reservoir (g)	Me ¹⁹⁹ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁹ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁹ Hg	Me ¹⁹⁸ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁸ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁸ Hg	Overall Log(K _{ps})	DOC (mg C/L)
Exchange	Water	Control	Me ¹⁹⁸ HgCys	C	20165	Experiment	40	0.00				18.73					
Exchange	Water	Blank	SRHA, no MeHg	A	20165	Experiment	40	0.00									
Exchange	Water	Control	SRHA, no MeHg	B	20165	Experiment	40	0.00									
Exchange	Water	Control	L-Cys, no MeHg	A	20165	Experiment	40	0.00									
Exchange	Water	Control	L-Cys, no MeHg	B	20165	Experiment	40	0.00									
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	A	63	Cys:Cys	40	0.04	0.03	0.01	4.14	16.06	16.13	0.14	0.88	1.53	
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	B	64	Cys:Cys	40	0.03				16.30					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	C	65	Cys:Cys	40	0.02				16.03					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	D	364	Cys:Cys	40	0.04	0.04	0.01	3.99	12.11	12.33	0.35	1.43	1.80	
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	E	365	Cys:Cys	40	0.06				12.74					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	F	367	Cys:Cys	40	0.04				12.14					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	G	1434	Cys:Cys	40	0.07	0.08	0.02	3.72	5.87	5.16	0.67	2.09	2.30	
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	H	1435	Cys:Cys	40	0.10				4.54					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	I	1436	Cys:Cys	40	0.06				5.09					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	J	2581	Cys:Cys	40	0.09	0.08	0.01	3.71	1.88	2.34	0.41	2.57	2.73	
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	K	2582	Cys:Cys	40	0.07				2.46					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	L	2583	Cys:Cys	40	0.10				2.67					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	M	10101	Cys:Cys	40	0.08	0.08	0.01	3.69	0.33	0.37	0.05	3.38	3.45	
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	N	10103	Cys:Cys	40	0.07				0.37					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	O	10105	Cys:Cys	40	0.09				0.42					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	P	20104	Cys:Cys	40	0.06	0.06	0.01	3.78	0.25	0.30	0.05	3.47	3.54	
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	Q	20161	Cys:Cys	40	0.08				0.34					
Exchange	Water	ag+AC	Me ¹⁹⁸ HgCys	R	20163	Cys:Cys	40	0.05				0.29					
Exchange	Water	ag+AC	SRHA, no MeHg	A	64	Cys:DOM	40	0.12	0.10	0.03	3.58						9.290
Exchange	Water	ag+AC	SRHA, no MeHg	B	66	Cys:DOM	40	0.09									9.441
Exchange	Water	ag+AC	SRHA, no MeHg	C	363	Cys:DOM	40	0.17	0.17	0.01	3.38						8.427
Exchange	Water	ag+AC	SRHA, no MeHg	D	366	Cys:DOM	40	0.17									8.452
Exchange	Water	ag+AC	SRHA, no MeHg	E	1434	Cys:DOM	40	0.38	0.37	0.02	3.05						7.392
Exchange	Water	ag+AC	SRHA, no MeHg	F	1436	Cys:DOM	40	0.36									7.641
Exchange	Water	ag+AC	SRHA, no MeHg	H	2581	Cys:DOM	40	NA	0.48	0.00	2.92						7.264
Exchange	Water	ag+AC	SRHA, no MeHg	H	2583	Cys:DOM	40	0.48									7.227
Exchange	Water	ag+AC	SRHA, no MeHg	I	10102	Cys:DOM	40	0.95	0.96	0.01	2.62						6.06
Exchange	Water	ag+AC	SRHA, no MeHg	J	10104	Cys:DOM	40	0.97									5.27
Exchange	Water	ag+AC	SRHA, no MeHg	K	20105	Cys:DOM	40	1.34	1.36	0.03	2.41						5.40
Exchange	Water	ag+AC	SRHA, no MeHg	L	20106	Cys:DOM	40	1.38									5.85

Phase	Sample Type	Sorbent	Aqueous Ligand	Replicate	Time (min)	Experiment Course	Mass of Reservoir (g)	Me ¹⁹⁹ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁹ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁹ Hg	Me ¹⁹⁸ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁸ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁸ Hg	Overall Log(K _{ps})	DOC (mg C/L)
Exchange	Water	ag+AC	L-Cys, no MeHg	A	64	DOM:Cys	40	NA									1.06
Exchange	Water	ag+AC	L-Cys, no MeHg	B	66	DOM:Cys	40	NA									0.71
Exchange	Water	ag+AC	L-Cys, no MeHg	C	361	DOM:Cys	40	NA									0.77
Exchange	Water	ag+AC	L-Cys, no MeHg	D	363	DOM:Cys	40	NA									0.79
Exchange	Water	ag+AC	L-Cys, no MeHg	E	1434	DOM:Cys	40	NA									0.88
Exchange	Water	ag+AC	L-Cys, no MeHg	F	1436	DOM:Cys	40	NA									0.88
Exchange	Water	ag+AC	L-Cys, no MeHg	G	2580	DOM:Cys	40	0.12	0.12	0.01	3.24						1.11
Exchange	Water	ag+AC	L-Cys, no MeHg	H	2582	DOM:Cys	40	0.13									1.05
Exchange	Water	ag+AC	L-Cys, no MeHg	I	10101	DOM:Cys	40	0.14	0.14	0.00	3.17						1.15
Exchange	Water	ag+AC	L-Cys, no MeHg	J	10103	DOM:Cys	40	0.14									0.90
Exchange	Water	ag+AC	L-Cys, no MeHg	K	20104	DOM:Cys	40	0.14	0.13	0.02	3.22						1.01
Exchange	Water	ag+AC	L-Cys, no MeHg	L	20106	DOM:Cys	40	0.11									0.76
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	A	63	Cys:Cys	0.83	426.15	429.27	22.08		128.01	122.48	5.08			
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	B	64	Cys:Cys	0.87	408.92				118.01					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	C	65	Cys:Cys	0.81	452.75				121.43					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	D	364	Cys:Cys	0.80	439.01	438.05	17.81		347.49	333.90	12.87			
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	E	365	Cys:Cys	0.78	455.36				332.32					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	F	367	Cys:Cys	0.86	419.79				321.88					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	G	1434	Cys:Cys	0.92	383.57	395.02	15.62		588.79	638.88	49.88			
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	H	1435	Cys:Cys	0.86	412.82				688.55					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	I	1436	Cys:Cys	0.87	388.68				639.28					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	J	2581	Cys:Cys	0.83	423.74	436.20	10.84		874.07	864.91	8.25			
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	K	2582	Cys:Cys	0.80	443.51				858.07					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	L	2583	Cys:Cys	0.80	441.34				862.58					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	M	10101	Cys:Cys	0.85	400.64	389.90	11.66		915.01	883.15	32.15			
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	N	10103	Cys:Cys	0.88	391.58				883.73					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	O	10105	Cys:Cys	0.87	377.49				850.72					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	P	20104	Cys:Cys	0.96	349.72	381.78	61.31		805.21	876.67	139.93			
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	Q	20161	Cys:Cys	0.78	452.47				1037.90					
Exchange	Polymer	ag+AC	Me ¹⁹⁸ HgCys	R	20163	Cys:Cys	1.00	343.14				786.89					
Exchange	Polymer	ag+AC	SRHA, no MeHg	A	64	Cys:DOM	0.83	416.01	396.87	27.07							
Exchange	Polymer	ag+AC	SRHA, no MeHg	B	66	Cys:DOM	0.86	377.73									
Exchange	Polymer	ag+AC	SRHA, no MeHg	C	363	Cys:DOM	0.79	428.04	405.34	32.10							
Exchange	Polymer	ag+AC	SRHA, no MeHg	D	366	Cys:DOM	0.86	382.65									
Exchange	Polymer	ag+AC	SRHA, no MeHg	E	1434	Cys:DOM	0.80	408.70	414.18	7.74							

Phase	Sample Type	Sorbent	Aqueous Ligand	Replicate	Time (min)	Experiment Course	Mass of Reservoir (g)	Me ¹⁹⁹ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁹ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁹ Hg	Me ¹⁹⁸ Hg (ng/L or ng/kg)	Treatment Avg. Me ¹⁹⁸ Hg	1 SD	Log(K _{ps}) Me ¹⁹⁸ Hg	Overall Log(K _{ps})	DOC (mg C/L)
Exchange	Polymer	ag+AC	SRHA, no MeHg	F	1436	Cys:DOM	0.79	419.65									
Exchange	Polymer	ag+AC	SRHA, no MeHg	G	2581	Cys:DOM	0.78	409.58	401.49	11.44							
Exchange	Polymer	ag+AC	SRHA, no MeHg	H	2583	Cys:DOM	0.83	393.40									
Exchange	Polymer	ag+AC	SRHA, no MeHg	I	10102	Cys:DOM	0.81	386.19	396.49	14.56							
Exchange	Polymer	ag+AC	SRHA, no MeHg	J	10104	Cys:DOM	0.79	406.79									
Exchange	Polymer	ag+AC	SRHA, no MeHg	K	20105	Cys:DOM	0.80	338.37	349.22	15.34							
Exchange	Polymer	ag+AC	SRHA, no MeHg	L	20106	Cys:DOM	0.81	360.07									
Exchange	Polymer	ag+AC	L-Cys, no MeHg	A	64	DOM:Cys	0.83	200.11	206.33	8.80							
Exchange	Polymer	ag+AC	L-Cys, no MeHg	B	66	DOM:Cys	0.79	212.55									
Exchange	Polymer	ag+AC	L-Cys, no MeHg	C	361	DOM:Cys	0.80	207.29	201.58	8.09							
Exchange	Polymer	ag+AC	L-Cys, no MeHg	D	363	DOM:Cys	0.78	195.86									
Exchange	Polymer	ag+AC	L-Cys, no MeHg	E	1434	DOM:Cys	0.80	206.11	202.34	5.33							
Exchange	Polymer	ag+AC	L-Cys, no MeHg	F	1436	DOM:Cys	0.87	198.57									
Exchange	Polymer	ag+AC	L-Cys, no MeHg	G	2580	DOM:Cys	0.80	200.82	211.83	15.57							
Exchange	Polymer	ag+AC	L-Cys, no MeHg	H	2582	DOM:Cys	0.74	222.84									
Exchange	Polymer	ag+AC	L-Cys, no MeHg	I	10101	DOM:Cys	0.83	204.54	204.03	6.39							
Exchange	Polymer	ag+AC	L-Cys, no MeHg	J	10103	DOM:Cys	0.82	206.16									
Exchange	Polymer	ag+AC	L-Cys, no MeHg	K	20104	DOM:Cys	0.78	199.51	205.35	1.14							
Exchange	Polymer	ag+AC	L-Cys, no MeHg	L	20106	DOM:Cys	0.80	208.56									

Table S7.7. Kinetic Parameters Obtained from Fitting Time-series Data to a First-order Adsorption Model with Equilibrium Exchange.

	k_{desorb} (d⁻¹)	(R²)_{desorb}	-k_{adsorp} (d⁻¹)	(R²)_{adsorb}	k_{adsorb}:k_{desorb}	¹⁹⁹t₉₀	¹⁹⁸t₉₀
MeHgSRHA	-0.046	0.86	-0.057	0.52	1.23	34.56	28.00
MeHgCys	-0.0126	1.00	-0.0197	0.98	1.57	2.48	1.58

Table S7.8. Full Crosstab of Analyte Concentrations in Passive Sampler (ps) Portions in the Sediment (ps-sed) and in the Overlying Water (ps-water), Sediment (sed), Overlying Water (w), and Porewater (pw).

Sulfide concentrations below detection limit of 0.5 μM have been denoted “< 0.5.” Partitioning coefficients calculated are expressed as the log transform of the aqueous concentration in ng/L divided by the solid concentration in ng/kg. MeHg concentrations in a quality control blank were measured in the aqueous phase at t0, t+7, t+14, and t+21 and in a passive sampler at t+21 in a jar filled with plain DI water.

Sample Type	Rep	Time Point	C _{sed} (ng/kg)	C _w (ng/L)	C _{pw} (ng/L)	C _{ps-water} (ng/kg)	C _{ps-sed} (ng/kg)	Sed:Water log K _d	log K _{ps:pw}	log K _{ps:w}	[S ²⁻] _w (μM)	pH _w	DOC _w (mg/L)	[Cl ⁻] _w (mM)	[SO ₄ ²⁻] _w (mM)	[S ²⁻] _{pw} (μM)	pH _{pw}	DOC _{pw} (mg/L)	[Cl ⁻] _{pw} (mM)	[SO ₄ ²⁻] _{pw} (mM)
no-ps	a	t-14	121022	1.72	24.69			3.69			0.57	7.11	8.53	42.17	1.81	3.45	7.2	37.68	55.91	0.49
no-ps	b	t-14	102228	0.83	18.18			3.75			< 0.5	6.98	6.96	33.23	1.45	2.40	7.29	39.67	83.80	0.61
no-ps	c	t-14	85646	0.65	15.88			3.73			< 0.5	7.18	6.65	53.94	2.03	1.86	7.3	41.80	66.42	0.46
no-ps	a	t ₀	172409	1.45	41.45			3.62			< 0.5	7.82	17.21	33.37	0.80	2.50	6.95		69.27	1.80
no-ps	b	t ₀	111192	1.44	23.07			3.68			0.53	7.84	18.91	39.89	0.88	1.40	7.06	41.54	67.38	1.56
no-ps	c	t ₀	136289	1.11	20.05			3.83			< 0.5	7.55	18.47	26.47	0.63	1.16	6.92	38.90	54.84	1.31
no-ps	a	t+7	171671	0.81	31.57			3.74			0.61	7.41	17.60	71.50	2.43	4.45	6.86	23.78	66.82	2.31
no-ps	b	t+7	112522	0.99	31.06			3.56			0.52	7.57	17.85	62.46	1.93	3.83	6.84	22.90	65.86	2.01
no-ps	c	t+7	114789	0.76	28.18			3.61			< 0.5	7.64	16.91	60.43	1.92	2.84	6.79	25.34	59.49	1.76
sheet-ps	a	t+7	135573	0.80	21.95	369	52339	3.79	3.38	2.67	< 0.5	7.6	16.01	63.14	1.91	1.46	6.92	30.98	62.00	1.85
sheet-ps	b	t+7	147547	1.07	20.67	223	25912	3.85	3.10	2.32	< 0.5	7.67	14.31	59.70	1.82	2.15	6.81	24.34	63.11	1.96
sheet-ps	c	t+7	101852	1.13	13.62	314	39722	3.87	3.46	2.44	< 0.5	7.59	13.32	63.38	2.00	0.99	6.96	19.94	60.63	1.86
no-ps	a	t+14	79485	0.63	17.96			3.65			< 0.5	7.84	18.32	42.42	1.23	1.70	6.59	22.87	57.51	1.83
no-ps	b	t+14	37434	0.78	14.75			3.40			< 0.5	7.92	16.66	46.02	1.23	1.38	6.61	23.38	59.22	2.04
no-ps	c	t+14	152607	1.19	15.68			3.99			< 0.5	7.97	18.02	50.76	1.40	1.28	6.67	22.73	61.78	1.91
sheet-ps	a	t+14	97909	0.70	18.89	163	16800	3.71	2.95	2.37	< 0.5	8.04	13.61	48.37	1.54	1.82	6.5	18.23	67.55	2.64
sheet-ps	b	t+14	217431	0.64	16.35		25059	4.12	3.19		< 0.5	8	12.08	46.19	1.27	1.14	6.59	18.95	72.99	2.51
sheet-ps	c	t+14	151360	0.53	19.47	302	15155	3.89	2.89	2.75	< 0.5	8	13.13	65.04	2.68	1.61	6.58	22.48	71.23	2.94
split-ps	a	t+14	111161	0.53	19.36	248		3.76		2.67	< 0.5	7.94	13.35	74.01	2.56	2.18	6.5	17.37	123.93	4.49
split-ps	b	t+14	114571	0.63	19.59	294	24450	3.77	3.10	2.67	< 0.5	7.99	14.21	48.12	1.31	1.43	6.55	17.92	59.68	2.25
split-ps	c	t+14	108326	0.61	18.21	230	18315	3.77	3.00	2.58	< 0.5	7.98	13.07	39.40	1.01	1.14	6.53	17.73	57.59	2.04

Sample Type	Rep	Time Point	C _{sed} (ng/kg)	C _w (ng/L)	C _{pw} (ng/L)	C _{ps-water} (ng/kg)	C _{ps-sed} (ng/kg)	Sed:Water log K _d	log K _{ps:pw}	log K _{ps:w}	[S ²⁻] _w (μM)	pH _w	DOC _w (mg/L)	[Cl ⁻] _w (mM)	[SO ₄ ²⁻] _w (mM)	[S ²⁻] _{pw} (μM)	pH _{pw}	DOC _{pw} (mg/L)	[Cl ⁻] _{pw} (mM)	[SO ₄ ²⁻] _{pw} (mM)
no-ps	a	<i>t</i> +21	136416	0.61	10.23			4.12			< 0.5	7.58	16.57	58.97	2.17	1.32	6.59	19.87	64.53	2.51
no-ps	b	<i>t</i> +21	169021	0.57	16.88			4.00			< 0.5	7.56	13.15	46.38	1.21	2.48	6.72	17.84	62.42	2.09
no-ps	c	<i>t</i> +21	107749	0.70	6.53			4.22			< 0.5	7.71	13.37	39.01	0.92	1.02	6.8	17.97	63.49	2.15
sheet-ps	a	<i>t</i> +21	105134	0.60	14.60	688	14231	3.86	2.99	3.06	< 0.5	7.76	13.86	72.85	3.09	1.30	6.75	18.81	72.18	3.11
sheet-ps	b	<i>t</i> +21	75585	0.55	9.98	377	34971	3.88	3.54	2.84	< 0.5	7.89	13.17	71.18	2.83	1.22	6.74	18.65	66.11	2.67
sheet-ps	c	<i>t</i> +21	205552	0.31	14.97	254	33364	4.14	3.35	2.91	< 0.5	7.95	11.67	71.72	2.71	2.27	6.77	17.00	70.91	2.72
split-ps	a	<i>t</i> +21	112685	0.49	14.66	327	40540	3.89	3.44	2.83	< 0.5	7.86	11.50	22.58	0.62	2.21	6.75	14.39	66.16	2.13
split-ps	b	<i>t</i> +21	110577	0.50	13.63	343	45227	3.91	3.52	2.83	< 0.5	7.93	11.49	27.72	0.87	1.76	6.73	14.02	69.04	2.54
split-ps	c	<i>t</i> +21	126309	0.41	9.80	198	39682	4.11	3.61	2.68	< 0.5	7.91	9.95	56.22	2.02	1.20	6.7	13.19	66.60	2.44
blank	-	<i>t</i> ₀		0.03																
blank	-	<i>t</i> +7		0.03																
blank	-	<i>t</i> +14		0.16																
blank-ps	-	<i>t</i> +21		-0.01		7.22														

Table S7.9. Equilibrium Constants Used for Modeling MeHg Speciation in Sediment: Water Microcosms.

educts			products		Species	Notes	Log Kf	Reference
H ₂ O		<=>	OH ⁻	H ⁺	OH ⁻	for 25° C	14.0	NIST Critical
Sulfide protonation								
H ₂ S		<=>	HS ⁻	H ⁺	HS ⁻		7.0	Millero 1986; NIST Critical
HS ⁻		<=>	S ₂ ⁻	H ⁺			13.9	Smith and Martell 1976
Thiol protonation								
RS ⁻	H ⁺	<=>	RSH		cysteine	value for cysteine	8.6	Liem-Nguyen 2017; Skyllberg 2003
NOM-RS	H ⁺	<=>	NOM-RSH		LMM thiols		9.0	Jalilehvand 2013
Aquo MeHg compounds								
MeHg ⁺	H ₂ O	<=>	MeHgOH	H ⁺	MeHgOH		-4.8	Loux 2007; DeRobertis et al. (1998)
2(MeHg ⁺)	H ₂ O	<=>	(MeHg)2OH ⁺		(MeHg)2OH ⁺		-2.3	Loux 2007; DeRobertis et al. (1998)
MeHg ⁺	Cl ⁻	<=>	MeHgCl		MeHgCl		5.4	Loux 2007; DeRobertis et al. (1998)
MeHg ⁺	HS ⁻	<=>	MeHgSH		MeHgSH		14.5	Dyrssen and Wedborg 1991
MeHg ⁺	HS ⁻	<=>	MeHgS ⁻	H ⁺	MeHgS ⁻		7.00	Schwarzenbach and Schellenberg 1965
2MeHg ⁺	HS ⁻	<=>	(MeHg)2S	H ⁺	(MeHg)2S		26.0	Kanzler et al 2018
MeHg ⁺	RS ⁻	<=>	MeHgRS		MeHgRS	values for cysteine	15.7	Loux 2007; Friedman 1973
							15.7-17.5	Liem Nguyen 2017; Reid et al 1981
MeHg ⁺	NOM-RS ⁻	<=>	MeHg(NOM-RS)		MeHg(NOM-RS)		16.3-16.7	Qian 2002
							15.6-17.1	Karlsson and Skyllberg 2003

APPENDIX G SUPPLEMENTAL INFORMATION FOR CHAPTER 8

MEASUREMENT OF MeHg DEPTH PROFILE IN SEDIMENTS

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Supporting Information for Measurement of a Porewater Depth Profile using the ag+AC PS

Table S8.1. Overlying Water Monitoring Over the Microcosm Incubation.

Salinity was measured with a handheld analog refractometer, ammonia measured with LAMOTTE InstaTest® Analytic Ammonia test strips (0 to 6 ppm), pH with colorpHast® indicator test strips, and ORP with a Mettler Toledo InLab® Redox microelectrode (Ag/AgCl reference).

Timepoint	Event	Microcosm ID	O. Water ORP (mV, AgCl)	pH	NH ₃ (mg/L)	Salinity (mg/L)	Vol. O.Water before Event (L)	Anaerobic PW ORP (mV, AgCl)*	Anaerobic PW Depth (cm)*
t-14	Microcosm Construction								
t-7	Level Check	A2	308	6.5	0.5				
		A3	313	6.5	0.5				
		A4	313	6.5	0.5				
		B1	436	5	6				
		B2	433	5	6				
		B3	433	5	6				
t0	Sampler insertion. O. water replaced (prior to insertion) to lower NH ₄ levels	A2					2		
		A3		6.5	<1	4	2.3		
		A4					2.4		
		B1		4.5	6	0	2.5		
		B2					2		
		B3		4.5	6	0	2.2		
t+2 (A2, B1, B2), t+3 (A3, A4, B3)	Level Check	A2	271	6.5	0	3			
		A3	281	6.5	0	3			
		A4	287	6.5	0	3			
		B1	422	4.5	0.5	0			
		B2	419	4.5	0	0			
		B3	420	4.5	0	0			
t+14	O. water gently added to maintain 3 L	A2	241	7	0	3	2.3		
		A3	263	7	0	3	2.3		
		A4	253	7	0	3	2.35		
		B1	375	4.5	0	0	2.4		
		B2	375	4.5	0	0	2.3		
		B3	403	4.5	0	0	2.1		
t+28 (A2, A3, A4) t+29 (B1, B2, B3)	Sampler retrieval & microcosm deconstruction	A2	212	7.5	0	5	2.2	-1.5	1.5
		A3	190	7	0.5	4	2.6	-5.4	1.7
		A4	191	7	0.5	5	2	0.4	1.3
		B1	305	5	0	0	2.1	3.1	1.6
		B2	262	5	0	0	2.1	-1.2	1.4
		B3	297	5	0.5	1	1.9	3	1.8

* ORP probe inserted into sediment until anaerobic ORP (=0 mV for AgCl meter) was reached. Measured depth of anaerobic porewater under the sediment-water interface. Blank values indicate no measurement at that timepoint.

Table S8.2. Analytical Measurements of Samples Taken at Microcosm Construction and At the End of the PS Deployment.

ow = overlying water, *BDL* = below detection limit. Empty cells indicate a lost sample, or a sample that was not measured, for each microcosm replicate and each analyte, bold/double underlined values represent the maximum value and bold/single underlined values represent the minimum (besides samples BDL).

Sediment	Rep	Depth (cm)	PS Depth (cm)	[MeHg] _{ps} (ng/kgPS)	PS-Derived [MeHg] _{aq} (ng/L)	PS- Derived [MeHg] _{aq} (1 cm res, ng/L)	Grab Sample [MeHg] _{aq} (ng/L)	Log [K _{ps} (L/kg)]	[MeHg] _{sed} (ng/kg-dw)	Log [K _b (L/kg)]	DOC (mg/L)	Sulfide (μM)	pH	Fe (μM)	Mn (μM)	S (μM)	Cl (μM)	SO4 (μM)	NO3 (μM)
<i>Initial Measurements</i>																			
Estuarine	a										2.39	0.42	7.43				34,894	2286	392
	b										2.52	0.47	7.31				24,271	1107	208
	c										2.17	0.48	7.32				28,177	1410	222
Freshwater	b										3.16	0.15	6.32				626	122	22
	a										3.21	0.13	6.54				873	169	23
	c										3.39	0.15	6.58				914	171	23
Estuarine	a						2.02		32,208	4.20	29.37	0.41	7.21				132,619	4719	968
	b						1.24		37,705	4.48	28.24	0.34	7.29				150,070	6026	673
	c						1.39		40,356	4.46	28.19	0.40	7.22				97,672	2870	911
Freshwater	a						0.53		6,827	4.11	11.86	0.19	3.92				10,774	2265	68
	b						0.56		8,999	4.21	16.39	0.28	3.91				9,641	1488	28
	c						0.60		6,892	4.06	14.92	0.25	4.11				12,211	4810	35
<i>Measurements after taken down</i>																			
Estuarine	A2	ow	-0.75	90	0.10	0.06	BDL	2.78			7.14	BDL	8.20	0	0.0	2416	46,019	1500	354
			-0.25	27	0.03														
		1	0.25	522	0.57	1.49	2.00	2.83	62,165	4.49	20.24	0.51	7.10	121	26.6	1863	45,159	1103	478
			0.75	2,200	2.41														
		2	1.25	11,113	12.19	18.39	10.76	3.19	62,022	3.76	25.78	1.06	7.10	121	26.6	1863	45,159	1103	478
			1.75	22,422	24.58														
		3	2.25	28,216	30.94	32.65	12.42	3.38	59,689	3.68	30.08	2.15	6.98	239	39.1	892	84,338	1365	831
			2.75	31,340	34.36														
		4	3.25	50,034	54.86	47.15	12.91	3.52	61,756	3.68	38.53	2.79	6.98	239	39.1	892	84,338	1365	831
			3.75	35,971	39.44														
		5	4.25	40,169	44.04	41.99	14.05	3.44	50,761	3.56	35.95	3.15	7.12	173	41.2	177	53,973	121	621
			4.75	36,419	39.93														

Sediment	Rep	Depth (cm)	PS Depth (cm)	[MeHg] _{ps} (ng/kgPS)	PS-Derived [MeHg] _{aq} (ng/L)	PS- Derived [MeHg] _{aq} (1 cm res, ng/L)	Grab Sample [MeHg] _{aq} (ng/L)	Log [K _{ps} (L/kg)]	[MeHg] _{sed} (ng/kg-dw)	Log [K _D (L/kg)]	DOC (mg/L)	Sulfide (μM)	pH	Fe (μM)	Mn (μM)	S (μM)	Cl (μM)	SO4 (μM)	NO3 (μM)		
		6	5.25	33,887	37.16	33.14	10.14	3.47	54,856	3.73	45.44	2.33	7.24	210	<u>43.6</u>	<u>120</u>	80,416	<u>90</u>	<u>914</u>		
			5.75	26,559	29.12																
		7	6.25	25,582	28.05	30.44	8.89	3.49	54,787	3.79	43.88	1.39									
			6.75	29,950	32.84																
		8					10.05		<u>50,685</u>	3.70	<u>48.19</u>	2.91									
Freshwater	B1	ow	-0.75	135	0.15	<u>0.13</u>	<u>0.20</u>	2.79			<u>6.82</u>	BDL	6.55	<u>2</u>	<u>3.8</u>	<u>299</u>	<u>3,402</u>	<u>168</u>	43		
			-0.25	<u>108</u>	<u>0.12</u>																
		1	0.25	366	0.40	1.33	11.63	<u>2.02</u>	15,305	3.12	25.86	<u>1.28</u>	<u>6.45</u>	891	16.7	175	4,436	102	24		
			0.75	2,056	2.25																
		2	1.25	19,486	21.37	<u>29.55</u>	12.87	<u>3.32</u>	11,044	<u>2.93</u>	48.41	2.82	6.58	2113	27.9	<u>133</u>	4,834	19	<u>24</u>		
			1.75	<u>34,406</u>	<u>37.73</u>																
		3	2.25	22,389	24.55	25.62	<u>13.35</u>	3.24	12,611	2.98	70.76	2.39	6.68	2653	37.2	173	6,405	14	67		
			2.75	24,340	26.69																
		4	3.25	20,593	22.58	21.39	10.92	3.25	<u>15,799</u>	3.16	81.76	<u>3.31</u>	6.73	<u>2718</u>	<u>39.5</u>	180	<u>7,248</u>	<u>14</u>	<u>77</u>		
			3.75	18,415	20.19																
		5	4.25	17,706	19.41	18.57	10.42	3.21	14,697	3.15	94.21	3.26	6.73	<u>2718</u>	<u>39.5</u>	180	<u>7,248</u>	<u>14</u>	<u>77</u>		
			4.75	16,163	17.72																
		6	5.25	16,912	18.54	18.42	8.46	3.30	13,987	3.22	104.96	2.72	6.73	<u>2718</u>	<u>39.5</u>	180	<u>7,248</u>	<u>14</u>	<u>77</u>		
			5.75	16,688	18.30																
		7	6.25	13,659	14.98	15.99	8.67	3.23	13,840	3.20	<u>106.16</u>	2.52	6.73	<u>2718</u>	<u>39.5</u>	180	<u>7,248</u>	<u>14</u>	<u>77</u>		
			6.75	15,504	17.00																
		8					3.66		<u>8,668</u>	<u>3.37</u>	105.56	1.74	6.73	<u>2718</u>	<u>39.5</u>	180	<u>7,248</u>	<u>14</u>	<u>77</u>		
		Estuarine	A3	ow	-0.75	<u>485</u>	<u>0.53</u>	<u>0.61</u>	<u>0.09</u>	3.77			<u>6.34</u>	BDL	<u>8.34</u>	<u>0</u>	<u>0.0</u>	<u>2277</u>	<u>84,905</u>	<u>3461</u>	<u>422</u>
					-0.25	621	0.68														
1	0.25			5,537	6.07	25.77	1.21	<u>4.29</u>	52,557	<u>4.64</u>	14.82	BDL	7.30	84	23.8	1953	65,268	2035	640		
	0.75			<u>41,476</u>	<u>45.48</u>																
2	1.25			34,665	38.01	37.25	11.23	3.48	55,994	3.70	19.53	<u>2.35</u>	7.06	<u>262</u>	33.8	968	<u>65,186</u>	989	658		
	1.75			33,286	36.50																
3	2.25			30,348	33.28	39.29	<u>15.45</u>	<u>3.37</u>	55,351	<u>3.55</u>	24.83	5.01	<u>7.06</u>	<u>262</u>	33.8	968	<u>65,186</u>	989	658		
	2.75			41,320	45.31																

Sediment	Rep	Depth (cm)	PS Depth (cm)	[MeHg] _{ps} (ng/kgPS)	PS-Derived [MeHg] _{aq} (ng/L)	PS- Derived [MeHg] _{aq} (1 cm res, ng/L)	Grab Sample [MeHg] _{aq} (ng/L)	Log [K _{ps} (L/kg)]	[MeHg] _{sed} (ng/kg-dw)	Log [K _d (L/kg)]	DOC (mg/L)	Sulfide (μM)	pH	Fe (μM)	Mn (μM)	S (μM)	Cl (μM)	SO4 (μM)	NO3 (μM)																																					
		4	3.25	37,957	41.62	<u>39.72</u>	12.08	3.48	53,132	3.64	30.67	6.38	7.28	186	42.6	218	83,628	196	<u>916</u>																																					
			3.75	34,491	37.82																																																			
		5	4.25	28,453	31.20	34.09	12.54	3.39	51,414	3.61	30.86	<u>7.60</u>								7.39	200	<u>43.2</u>	<u>140</u>	68,138	<u>95</u>	794																														
			4.75	33,733	36.99																																																			
		6	5.25	32,583	35.73	34.34	12.47	3.40	<u>58,038</u>	3.67	39.16	6.29															7.39	200	<u>43.2</u>	<u>140</u>	68,138	<u>95</u>	794																							
			5.75	30,057	32.96																																																			
		7	6.25	28,377	31.11	31.28	11.54	3.39	55,568	3.68	<u>44.91</u>	5.41																						7.39	200	<u>43.2</u>	<u>140</u>	68,138	<u>95</u>	794																
			6.75	28,686	31.45																																																			
		8					9.18		<u>51,356</u>	3.75	38.21	5.61																													7.39	200	<u>43.2</u>	<u>140</u>	68,138	<u>95</u>	794									
		Freshwater	B2	ow	-0.75	<u>93</u>	<u>0.10</u>	<u>0.11</u>	<u>0.16</u>	<u>2.81</u>																																						<u>6.31</u>	BDL	6.61	<u>1</u>	<u>7.0</u>	<u>364</u>	<u>3,480</u>	<u>226</u>	30
					-0.25	108	0.12																																																	
1	0.25			1,828	2.00	12.59	8.50	3.13	15,213	3.25	21.91	BDL	6.55	896	17.4	231	4,330	130	<u>24</u>																																					
	0.75			21,141	23.18																																																			
2	1.25			23,473	25.74	<u>26.70</u>	<u>12.72</u>	3.28	<u>9,806</u>	<u>2.89</u>	49.86	<u>1.58</u>	6.55	896	17.4	231	4,330	130	<u>24</u>																																					
	1.75			<u>25,234</u>	<u>27.67</u>																																																			
3	2.25			18,792	20.60	19.91	10.91	3.22	<u>16,068</u>	3.17	67.76	2.05	<u>6.73</u>	2181	29.3	<u>130</u>	4,955	18	27																																					
	2.75			17,516	19.21																																																			
4	3.25			15,265	16.74	19.00	9.80	3.25	13,216	3.13	86.96	<u>2.18</u>	<u>6.73</u>	2181	29.3	<u>130</u>	4,955	18	27																																					
	3.75			19,385	21.25																																																			
5	4.25			15,276	16.75	17.34	9.82	3.21	14,174	3.16	97.21	1.95	6.65	2738	38.2	171	6,254	17	<u>63</u>																																					
	4.75			16,350	17.93																																																			
6	5.25			14,594	16.00	17.92	5.96	<u>3.44</u>	15,160	<u>3.41</u>	102.31	1.98	6.65	2738	38.2	171	6,254	17	<u>63</u>																																					
	5.75			18,084	19.83																																																			
7	6.25			14,782	16.21	17.31	6.84	3.36	12,062	3.25	<u>110.46</u>	1.92	<u>6.48</u>	<u>2919</u>	<u>41.4</u>	183	<u>7,009</u>	<u>15</u>	28																																					
	6.75			16,799	18.42																																																			
8							7.10		12,110	3.23	105.46	1.92	<u>6.48</u>	<u>2919</u>	<u>41.4</u>	183	<u>7,009</u>	<u>15</u>	28																																					
Estuarine	A4	ow	-0.75	1,373	1.51	<u>1.08</u>	<u>0.08</u>	<u>4.10</u>			<u>7.29</u>	BDL	<u>8.35</u>	<u>0</u>	<u>0.0</u>	<u>2567</u>	61,194	<u>2157</u>	<u>239</u>																																					
			-0.25	<u>593</u>	<u>0.65</u>																																																			
		1	0.25	2,313	2.54	11.81	1.06	4.01	56,884	<u>4.73</u>	12.13	BDL	7.22	89	24.3	2068	67,248	2106	663																																					

Sediment	Rep	Depth (cm)	PS Depth (cm)	[MeHg] _{ps} (ng/kgPS)	PS-Derived [MeHg] _{aq} (ng/L)	PS- Derived [MeHg] _{aq} (1 cm res, ng/L)	Grab Sample [MeHg] _{aq} (ng/L)	Log [K _{ps} (L/kg)]	[MeHg] _{sed} (ng/kg-dw)	Log [K _D (L/kg)]	DOC (mg/L)	Sulfide (μM)	pH	Fe (μM)	Mn (μM)	S (μM)	Cl (μM)	SO4 (μM)	NO3 (μM)
			0.75	19,232	21.09														
		2	1.25	30,069	32.97	36.84	9.93	3.53	<u>68,256</u>	3.84	17.21	<u>1.78</u>							
			1.75	37,133	40.72														
		3	2.25	<u>51,822</u>	<u>56.82</u>	<u>46.34</u>	<u>16.98</u>	3.40	58,479	<u>3.54</u>	24.84	3.88	<u>7.02</u>	<u>269</u>	38.1	1025	<u>47,192</u>	542	385
			2.75	32,710	35.87														
		4	3.25	37,049	40.62	37.11	16.27	<u>3.32</u>	58,292	3.55	30.68	5.96							
			3.75	30,642	33.60														
		5	4.25	28,000	30.70	32.37	13.26	3.35	59,413	3.65	38.13	<u>7.31</u>	7.04	190	<u>44.5</u>	246	58,399	151	661
			4.75	31,049	34.04														
		6	5.25	34,636	37.98	38.11	11.74	3.47	58,825	3.70	37.71	5.29							
			5.75	34,884	38.25														
		7	6.25	26,676	29.25	29.75	11.67	3.37	<u>52,561</u>	3.65	40.66								
6.75	27,580		30.24																
8					10.49		59,986	3.76	<u>45.12</u>	3.79									
Freshwater	B3	ow	-0.75	68	0.07	<u>0.07</u>	<u>0.04</u>	3.18			<u>5.61</u>	BDL	<u>5.41</u>	<u>2</u>	<u>11.7</u>	<u>440</u>	<u>4,563</u>	<u>272</u>	<u>52</u>
			-0.25	<u>53</u>	<u>0.06</u>														
		1	0.25	320	0.35	2.12	2.77	<u>2.84</u>	<u>7,439</u>	<u>3.43</u>	7.06	BDL	6.27	447	15.5	362	4,734	269	36
			0.75	3,546	3.89														
		2	1.25	<u>23,258</u>	<u>25.50</u>	<u>23.49</u>	9.38	<u>3.36</u>	9,390	<u>3.00</u>	19.96	<u>1.96</u>	6.27	447	15.5	362	4,734	269	36
			1.75	19,593	21.48														
		3	2.25	15,132	16.59	15.76	<u>11.04</u>	3.11	11,915	3.03	40.51	3.91	6.49	1463	22.5	<u>138</u>	5,164	48	37
			2.75	13,617	14.93														
		4	3.25	11,441	12.54	12.14	10.68	3.02	11,362	3.03	53.86	<u>4.04</u>	6.49	1463	22.5	<u>138</u>	5,164	48	37
			3.75	10,695	11.73														
		5	4.25	11,535	12.65	12.06	8.76	3.10	13,442	3.19	69.86	3.50	6.64	2261	32.4	148	5,916	25	38
			4.75	10,465	11.48														
		6	5.25	10,479	11.49	11.56	7.93	3.12	13,155	3.22	78.21	3.45	6.64	2261	32.4	148	5,916	25	38
			5.75	10,612	11.64														
		7	6.25	10,732	11.77	12.37	7.28	3.19	<u>15,357</u>	3.32	83.81	3.18	<u>6.76</u>	<u>2863</u>	<u>41.1</u>	170	<u>6,897</u>	<u>17</u>	<u>31</u>
			6.75	11,838	12.98														
8						6.55		12,349	3.28	<u>94.51</u>	2.85								

Sediment	Rep	Depth (cm)	PS Depth (cm)	[MeHg] _{ps} (ng/kgPS)	PS-Derived [MeHg] _{aq} (ng/L)	PS- Derived [MeHg] _{aq} (1 cm res, ng/L)	Grab Sample [MeHg] _{aq} (ng/L)	Log [K _{ps} (L/kg)]	[MeHg] _{sed} (ng/kg-dw)	Log [K _d (L/kg)]	DOC (mg/L)	Sulfide (μM)	pH	Fe (μM)	Mn (μM)	S (μM)	Cl (μM)	SO4 (μM)	NO3 (μM)
Estuarine (no-ps)	A (no-ps)	ow					<u>0.05</u>		BDL	BDL	<u>6.53</u>	BDL	<u>8.44</u>				<u>45,699</u>	1569	<u>268</u>
		1					1.65		62,162	<u>4.58</u>	10.64	BDL	6.99				65,692	<u>1900</u>	539
		2					12.12		<u>73,903</u>	3.79	21.21	<u>2.34</u>							
		3					<u>13.42</u>		69,274	<u>3.71</u>	25.69	4.51	<u>6.90</u>				56,255	480	304
		4					11.13		59,304	3.73	31.05	4.44							
		5					11.55		64,830	3.75	35.86	<u>5.77</u>	7.07				<u>80,506</u>	150	<u>888</u>
		6					9.74		60,466	3.79	38.35	5.54							
		7					7.25		62,107	3.93	22.06	3.47	7.30				74,621	<u>91</u>	839
		8					6.82		<u>50,739</u>	3.87	<u>40.67</u>	3.64							
Freshwater (no-ps)	B (no-ps)	ow					BDL				4.68	0.00	5.81				4,353	327	41
		1					5.66		13,791	3.39	<u>15.55</u>	<u>2.13</u>	<u>6.45</u>				4,712	<u>149</u>	<u>35</u>
		2					<u>9.99</u>		14,166	<u>3.15</u>		<u>5.68</u>							
		3					7.86		15,910	3.31	49.38	5.06	6.69				<u>4,332</u>	15	46
		4					5.91		<u>18,131</u>	3.49	<u>73.88</u>	4.81							
		5					5.05		13,120	3.42	56.78	4.81	6.81				5,793	<u>13</u>	<u>56</u>
		6					<u>2.74</u>		12,248	<u>3.65</u>	68.63	3.21							

Sediment	Rep	Depth (cm)	PS Depth (cm)	[MeHg] _{ps} (ng/kgPS)	PS-Derived [MeHg] _{aq} (ng/L)	PS- Derived [MeHg] _{aq} (1 cm res, ng/L)	Grab Sample [MeHg] _{aq} (ng/L)	Log [K _{ps} (L/kg)]	[MeHg] _{sed} (ng/kg-dw)	Log [K _D (L/kg)]	DOC (mg/L)	Sulfide (μM)	pH	Fe (μM)	Mn (μM)	S (μM)	Cl (μM)	SO4 (μM)	NO3 (μM)
		7					4.14		10,511	3.40	56.78	3.96	<u>6.84</u>						
		8					3.87		<u>9,594</u>	3.39	71.13	2.89					<u>7,390</u>	13	38

Table S8.3. ChemEq1 MeHg Speciation Model Inputs and Outputs.

DOMRS was calculated (as in Washburn et al 2022) from measured dissolved organic carbon (DOC), and the average of the following values from Poulin et al (2017): fraction of hydrophobic organic acid (HPOA) in dissolved organic matter (DOM), atomic S/C in the HPOA fraction of DOM, and the exocyclic sulfur content in the HPOA fraction of DOM. Values were input at the lowest analyte resolution (2 cm), averaging across the three microcosm replicates for each sediment type.

							Model Outputs			
Model Inputs							Log K _f = 15.7		Log K _f = 17.5	
Microcosm	Depth (cm)	[MeHg] _{aq} (M)	[Cl ⁻] _{aq} (M)	[HS] _{aq} (M)	DOMRS (M)	H(M)	MeHgSH (ng/L)	MeHgDOMRS (ng/L)	MeHgSH (ng/L)	MeHgDOMRS (ng/L)
Estuarine	2	4.93E-11	5.92E-02	1.73E-06	3.59E-06	6.21E-08	5.72E+00	4.91E+00	1.93E-01	10.4
	4	6.38E-11	6.56E-02	5.05E-06	5.73E-06	9.55E-08	1.00E+01	3.74E+00	5.60E-01	13.2
	6	5.31E-11	6.53E-02	4.63E-06	7.02E-06	7.13E-08	7.65E+00	3.80E+00	3.05E-01	11.1
	8	4.59E-11	7.39E-02	4.10E-06	7.55E-06	5.17E-08	5.35E+00	4.56E+00	1.81E-01	9.7
Freshwater	2	5.41E-11	4.50E-03	2.12E-06	6.79E-06	3.77E-07	4.70E+00	6.96E+00	1.23E-01	11.5
	4	4.85E-11	4.98E-03	3.18E-06	1.28E-05	2.51E-07	8.11E+00	2.35E+00	1.78E-01	10.3
	6	3.45E-11	6.19E-03	2.71E-06	1.64E-05	2.20E-07	5.13E+00	2.32E+00	8.17E-02	7.4
	8	2.68E-11	7.05E-03	2.17E-06	1.75E-05	2.20E-07	3.60E+00	2.18E+00	4.74E-02	5.7

APPENDIX H SUPPLEMENTAL INFORMATION FOR CHAPTER 9

Supporting info from the EFPC deployments

Supporting Information for Chapter 9: Application of a Novel Activated Carbon Based Passive Sampler to Measure Aqueous Methylmercury in Surface Waters and Porewaters at East Fork Poplar Creek

Table S9.1. Methylmercury Concentrations [Average $\pm$ 1 Standard Deviation (Number of Samples)] in Surface Water (SW) and Porewater (PW) Measured by Grab Sample and Derived from Passive Samplers (PS), Passive Samplers Deployed in Surface Water (SW-PS) and Sediment Porewaters (Sed-PS), and Sediments.

Event	Site	Coll. Time	Grab Sample SW	PS-Derived SW	Grab Sample PW	PS-Derived PW	SW-PS	Sed-PS	Sediment
		d	ng/L	ng/L	ng/L	ng/L	ng/kg-PS	ng/kg-PS	ng/kg-dw
Fall 2021	EFK 16.4	0	0.25 (1)		-	-	-	-	-
		7	0.17 $\pm$ 0.02 (2*)	0.11 $\pm$ 0.01 (3)	-	-	105 $\pm$ 9 (3)	-	-
		14	0.24 (1)	0.15 $\pm$ 0.01 (3)	-	-	135 $\pm$ 9 (3)	-	-
	EFK 5.4	0	0.25 (1)		-	-	-	-	-
		7	0.16 $\pm$ 0.06 (2*)	0.12 $\pm$ 0.01 (3)	-	-	112 $\pm$ 5 (3)	-	-
		14	0.22 (1)	0.15 $\pm$ 0.02 (3)	-	-	134 $\pm$ 19 (3)	-	-
Summer 2022	EFK 5.3	0	0.57 (1)		-	-	-	-	-
		15	0.36 (1)	0.37 $\pm$ 0.03 (3)	-	43 $\pm$ 14 (2)	341 $\pm$ 23 (3)	45,548 $\pm$ 12,950 (2)	-
		21	0.35 $\pm$ 0.01 (2*)	-	7.2 $\pm$ 0.09 (2)	58 $\pm$ 3 (2)	-	37,962 $\pm$ 17,996 (2)	28,134 $\pm$ 2,178 (2)

*duplicate from instrument run.

Missing values indicate no measurement made for that sample.

Table S9.2. Ancillary Chemical Measurements [Average $\pm$ 1 Standard Deviation (Number of Samples)] in Aqueous Samples.

Event	Site	Coll. Time (d)	DOC (mg/L)		[Cl ⁻] (μ M)		[SO ₄ ²⁻] (μ M)		[NO ₃ ⁻] (μ M)	
			SW	PW	SW	PW	SW	PW	SW	PW
Fall 2021	EFK 16.4	0	1.7 (1)	-	217 (1)	-	191 (1)	-	66 (1)	-
		7	1.6 (1)	-	267 (1)	-	121 (1)	-	225 (1)	-
		14	2.8 (1)	-	173 $\pm$ 0.3 (2*)	-	141 $\pm$ 0.01 (2*)	-	57 $\pm$ 0.1 (2*)	-
	EFK 5.4	0	2.3 (1)	-	312 (1)	-	154 (1)	-	208 (1)	-
		7	2.1 (1)	-	204 (1)	-	197 (1)	-	85 (1)	-
		14	2.1 (1)	-	225 (1)	-	119 (1)	-	165 (1)	-
Summer 2022	EFK 5.3	0	2.5 (1)	-	429 (1)	-	183 (1)	-	221 (1)	-
		15	1.6 (1)	-	255 (1)	-	131 (1)	-	128 (1)	-
		21	2.1 (1)	6.1 $\pm$ 2.5 (2)	278 (1)	349 $\pm$ 5 (2)	123 (1)	7.3 $\pm$ 0.04 (2)	160 (1)	8 $\pm$ 0.93 (2)

*duplicate from instrument run.

Missing values indicate no measurement made for that sample.

APPENDIX I EARLY POLYMER CHEMISTRY TRIALS IN COLLABORATION WITH AUBURN UNIVERSITY

Collaboration with Dr. Brian Beckingham, Auburn University

SYNTHESIS AND EVALUATION OF THE PEGDA-MATAS POLYMER MATERIAL

Development of PEGDA-MATATS Polymer

As part of a SERDP award for the development of equilibrium passive samplers for methylmercury new polymer chemistry platforms were attempted. These chemistries must be robust and chemically stable for placement in environmental systems. Chemistries which allow for the incorporation of thiol ($R-SH$) groups are of particular interest and it is desired that the thiol content be tunable. Additionally, formed polymer films with appropriate free-volume pathways (i.e. average pore size or mesh size) for the timely diffusion of dissolved organic matter were sought. Two systems were conceived for this purpose. Both systems seek to achieve the above-stated design criteria and have been designed to facilitate iterative testing through modular and tunable chemistries.

Polymer Chemistry Platform 1: Thiol-bearing ion-containing hydrogels

Based on the work of ([Elias et al. 2018](#)), a thiol-bearing ionomer hydrogel was designed. ([Elias et al. 2018](#)) prepared ion gels of a task-specific ionic liquid (trioctylmethylammonium thiosalicylate, TOMATS) and a polymer (cellulose triacetate). In this system, the polymer acts as a scaffold within which the ionic liquid (TOMATS), which contains a thiol group that is responsible for coordination to Hg, is dispersed.

As shown in Figure I-1, we have designed a platform which tethers the ionic cation to the polymer backbone while, for comparison, leveraging the same thiosalicylate anion for Hg coordination. We propose a polymerized-ionic-liquid architecture as opposed to the ion gels presented by ([Elias et al. 2018](#)). By covalently bonding one of the ionic species to the polymer backbone, the potential for ion leakage is decreased and physical properties can be improved by limiting plasticization. This chemistry is amenable to manipulation of the physical properties (mechanical strength, water swelling) through the molecular weight of the poly(ethylene glycol)-diacrylate (PEGDA) used, water content of pre-polymerization mixtures and manipulation of the thiol-content through the relative amount of MATATS ([Dobić et al. 2012](#); [Galizia et al. 2016](#); [Ju et al. 2010, 2009](#); [Kalakkunnath et al. 2005](#); [Kim and Cha 2018](#); [Wu et al. 2010](#)).

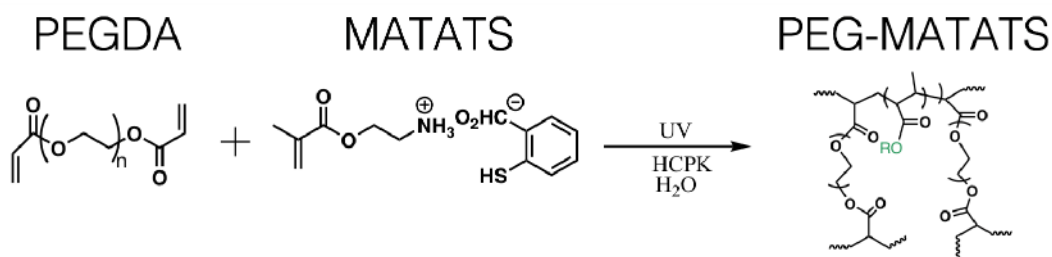


Figure I-1. Synthesis of Thiol-bearing Ion-containing Hydrogels Using UV-Photopolymerization of PEGDA and MATATS.

Various molecular weights of PEGDA are commercially available but a broader range of molecular weights are possible if necessary by synthesis in house. MATATS is a novel structure conceived by us and based on the thiol ionic liquid used by (Elias et al. 2018)., however is not commercially available. It will be prepared by ion-exchange of [2-(Methacryloyloxy)ethyl]trimethylammonium chloride and sodium thiosalicylate as shown in Figure I-2. Successful ion exchange can be verified using 60 MHz ¹H-NMR comparing the acrylate and thiol protons. One concern with the chemistry in Figure I-1. is the potential reactivity of the thiol group with the acrylates during polymerization. This potential will be examined and if necessary, the ion exchange to MATATS will be performed post polymerization.

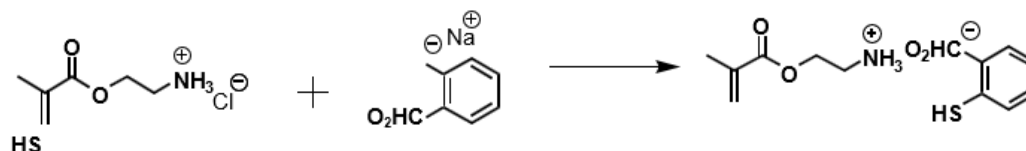


Figure I-2. Synthesis of MATATS

Polymer Chemistry Platform 2: Cysteine-functionalized Hydrogels

A second polymer platform has been designed which covalently tethers a cysteine residue to the polymer; as shown in Figure I-3. Here, the pendant double bonds on poly(allyl glycidyl ether) (PAGE) are converted to alcohols through thiol-ene click chemistry with thioglycol. The number of groups converted can be controlled through the reaction stoichiometry. These alcohol groups are then susceptible to EDAC-mediated conjugation with L-cysteine yielding a cysteine-functionalized polyether. Additionally, the remaining pendant alkenes can be utilized, if desired, to crosslink the structure for mechanical stability. Upon review, there are several potential issues with this chemistry as it relies on a series of click reactions which can be tough to optimize properly. This chemistry will be attempted as we have synthesized PAGE and thioglycol on hand with which to test this route. However, we are actively investigating more a more facile route to either tethered thiols or cysteine residues; likely using polyester chemistry.

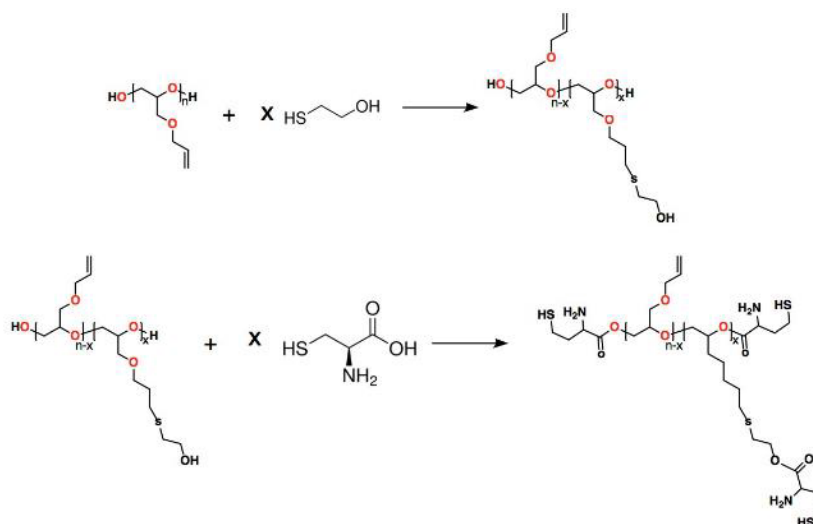


Figure I-3. Synthesis of Cysteine-functionalized PAGE.

General Characterization

Chemical structures of synthesized small molecules and polymers will be verified using ¹H NMR spectroscopy and/or FTIR spectroscopy. PAGE molecular size will be determined using size exclusion chromatography. Using known parameters for poly(ethylene glycol) and the Peppas-Merrill equation below, the effective molecular weight between crosslinks (M_c) and the effective mesh size (S_M) for these membranes will both be estimated from water-swelling experiments as:

$$\frac{1}{M_c} = \frac{2}{M_n} - \frac{\frac{V}{V_1} [\ln(1-V_{2,s}) + V_{2,s} + \chi V_{2,s}^2]}{V_{2,r} \left[\left(\frac{V_{2,s}}{V_{2,r}} \right)^{1/3} - 0.5 \left(\frac{V_{2,s}}{V_{2,r}} \right) \right]} \quad \text{and} \quad S_M = l \left(3 \frac{M_c}{M_r} \right)^{1/2} V_{2,s}^{-1/3} C_n$$

where M_n is the PEGDA number average molecular weight, V_1 is the molar volume of water, χ is the Flory-Huggins interaction parameter for PEG-water, l is the average bond length (1.50 Å), M_r is the molar mass of the PEG repeat unit (44 g/mol), C_n is the characteristic ratio for PEG (3.8) and $V_{2,r}$ and $V_{2,s}$ are the equilibrium polymer volume fraction before and after swelling respectively ([Cruise et al. 1998](#); [Ju et al. 2009](#); [Mellott et al. 2001](#); [Peppas and Merrill 1976](#); [Stringer and Peppas 1996](#)). Additionally, water uptake (W_U) will be measured and used as a relative measure of membrane fractional free volume (volume within the material available for molecular transport).

$$W_U = \frac{W_S - W_D}{W_S} * 100$$

where W_S and W_D are the weights of the water-swollen and dry polymer membrane respectively. Pore structures will be visualized, where applicable, using SEM.

Evaluation of PEGDA-MATATS Polymer

Materials and Methods

Before conducting extensive material characterization of the synthesized polymers, a series of MeHg sorption tests were performed. Testing involved a variety of different formulations of the PEGDA-MATATS (shortened to “PM” throughout) polymer (shown in Figure I-4), that varied both the density of the thiol-bearing ligand within the polymer (ranged from 1.5 pmol ligand/g polymer to 0.44 μmol/g), and the porosity of material [defined by the Beckingham group as the water swelling capability of the material] for one ligand density (0.15 nmol/g; the larger porosity material referred to throughout as “LP”).

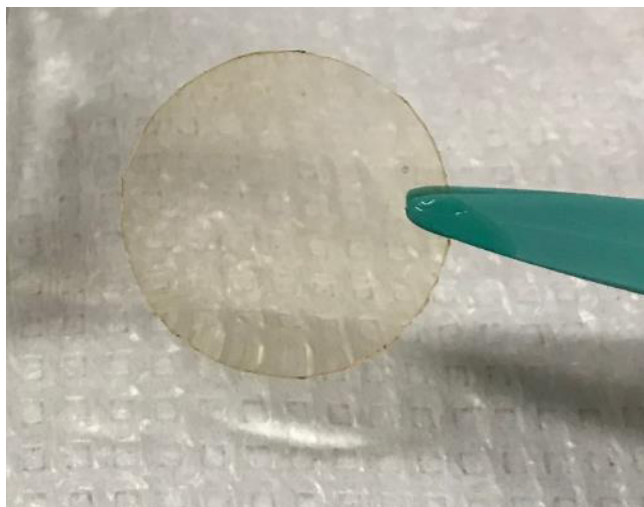


Figure I.4. The PEGDA_MATAS Polymer Synthesized by Dr. Beckingham, Photographed by Dr. Washburn

Kinetics of Uptake of MeHgSRHA into the PM polymers. This experiment served to evaluate uptake into the PM polymers (0.15 nmol/g, both porosities) over a 14-day time course while comparing the differing porosities. Polymers were added to solution containing ~430ng/L MeHgSRHA, with the SRHA concentration nominally at 10 mg/L. Polymers were carefully removed after 1hr, 3hr, 6hr, 24hr, 48hr, 96hr, 7d, and 14d.

Comparison of MeHg Distillation methods for recovery of MeHg isotope spike from PM polymers. An initial round of testing with the PM polymers indicated some lower-than-average recoveries of the MeHg isotope spike added to distillations to monitor and account for recovery. To test whether using different a distillation method would improve recovery, isotherms for both 0.15 nmol/g and 0.15 nmol/g LP were conducted with MeHgCl and MeHgSRHA. Polymers and waters were then distilled with either 1% APDC or CuSO₄.

Comparison of varying ligand densities within PM polymers for uptake of MeHgCl and MeHgDOM. 14-day isotherm experiments were conducted with MeHgCl and MeHgSRHA to determine the variation in uptake between the PM polymers of varying thiol ligand density. In an additional experiment, 14-day isotherm experiments were conducted with 0.15 nmol/g and 0.15nmol/g LP polymers with three additional DOM sources: SRNOM, SRFA, UMRNOM. These experiments began approximately one month after the initial isotherm tests. The polymers were stored in DI water in the refrigerator for this period, but appeared to have degraded.

Results & Discussion

Kinetics of Uptake of MeHgSRHA into the PM polymers. Uptake for both polymers (Figure I-5) appears to have occurred relatively rapidly, with the 0.15nmol/g polymers reaching a steady state MeHgSRHA concentration within 96 hrs, while the 0.15nmol/g LP polymers reached a steady state concentration after just 48 hrs, in line with the hypothesis that the larger porosity should facilitate faster uptake of the larger MeHgDOM species.

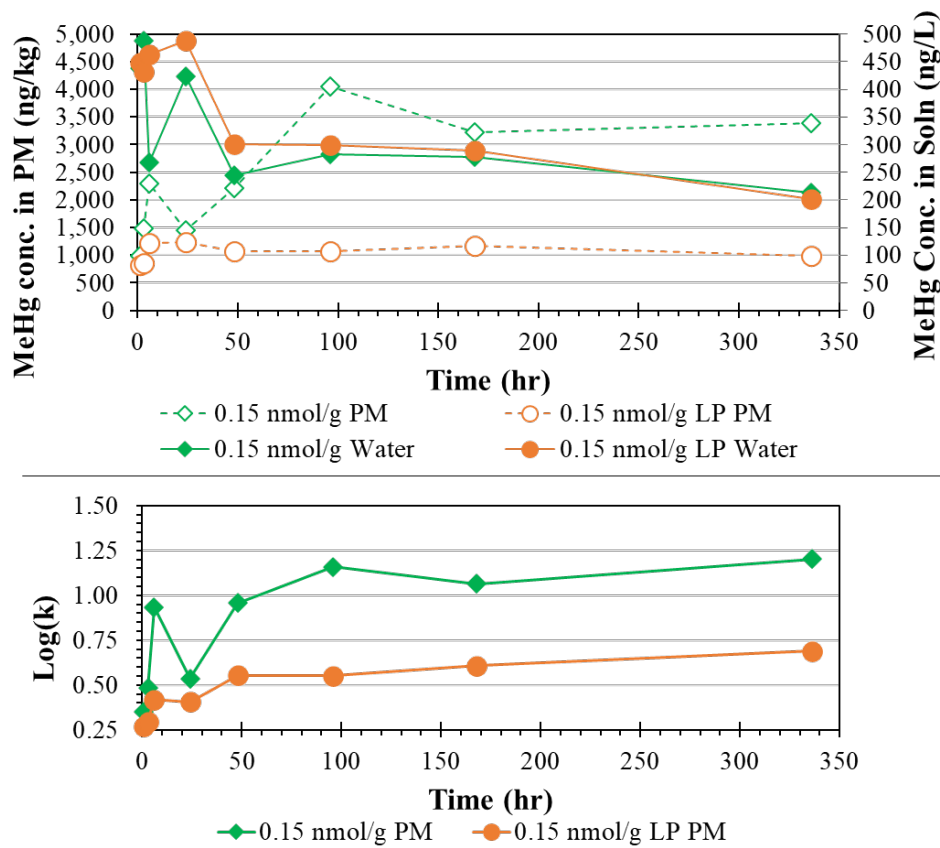


Figure I-5. (Top) Concentration of Polymer and Solution and (Bottom) Partitioning Through Time in Uptake Isotherms with the PM Polymer

Comparison of MeHg Distillation methods for recovery of MeHg isotope spike from PM polymers (Figure I-6). Across the treatments, isotope spike recovery was improved in this second round of testing compared to the first round. The two distillation methods did not produce significantly different results, except in the case of MeHgSRHA partitioning to 0.15nmol/g PM. This discrepancy appears to be related to variability in uptake rather than the result of isotope spike recovery, as spike recovery was similar for the two distillation methods.

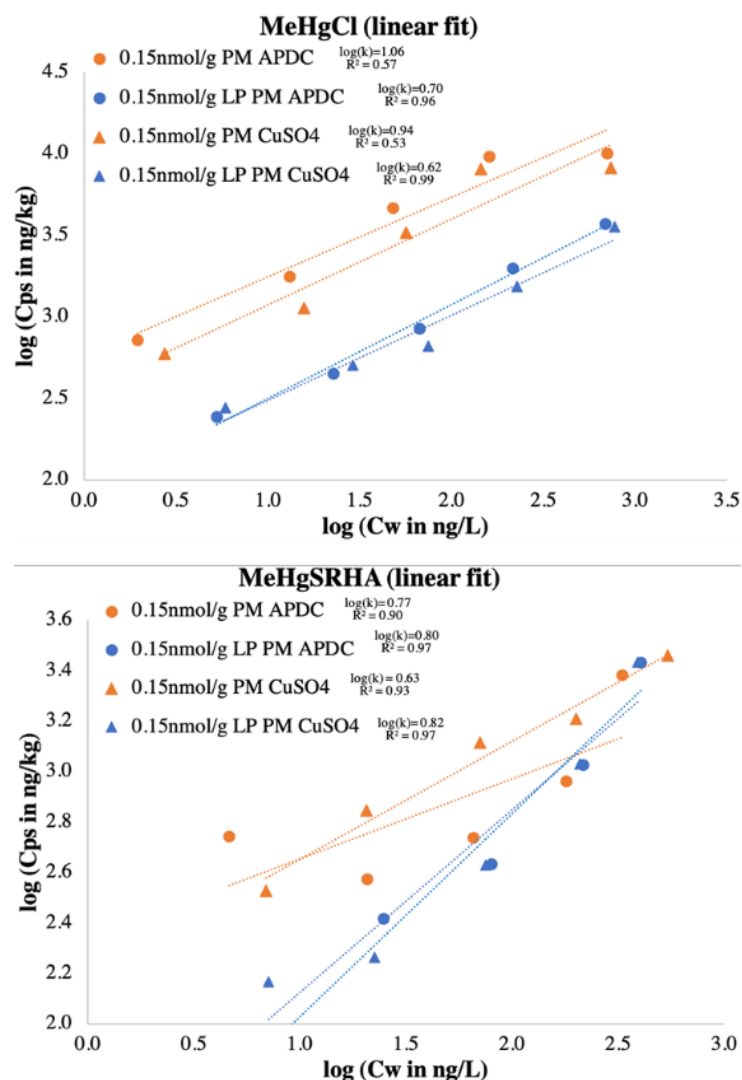


Figure I-6. Adsorption Isotherms of MeHgCl and MeHgSRHA Uptake to the Standard and Low-porosity PM Polymers and Comparison of Distillation Techniques for MeHg Extraction from the PM Polymer.

Comparison of varying ligand densities within PM polymers for uptake of MeHgCl and MeHgDOM (Figure I-7). 14-day isotherm experiments were conducted with MeHgCl and MeHgSRHA to determine the variation in uptake between the PM polymers of varying thiol ligand density. $\log(K_{ps})$ values were low across all thiol-ligand densities, regardless of the method used to calculate partitioning. Many of the treatments also displayed depressed uptake into the polymers at high C_w (~100 to 800 ng/L), which caused $\log(K_{ps})$ calculated from linear fitting to be significantly depressed compared to averaged $\log(K_{ps})$ values. Somewhat surprisingly, partitioning was not always suppressed for MeHgSRHA as compared to MeHgCl for a given polymer material, with 0.15 nmol/g LP, and the 100 nmol/g density polymers exhibiting greater $\log(K_{ps})$ for MeHgSRHA (this pattern does not hold if Avg. $\log(K_{ps})$ are considered). $\log(K_{ps})$ values did not exhibit any trend with thiol ligand densities of the polymers, with the highest partitioning for MeHgCl actually observed the lowest density polymer ($\log(K_{ps})=1.17$ for 0.0015 nmol/g. In isotherms with MeHg complexed with various DOM species, the PM polymers did not concentrate

MeHg whatsoever, suggesting that the polymers degraded in some way (no visible difference was observed), perhaps related the release of the thiol-containing functional group.

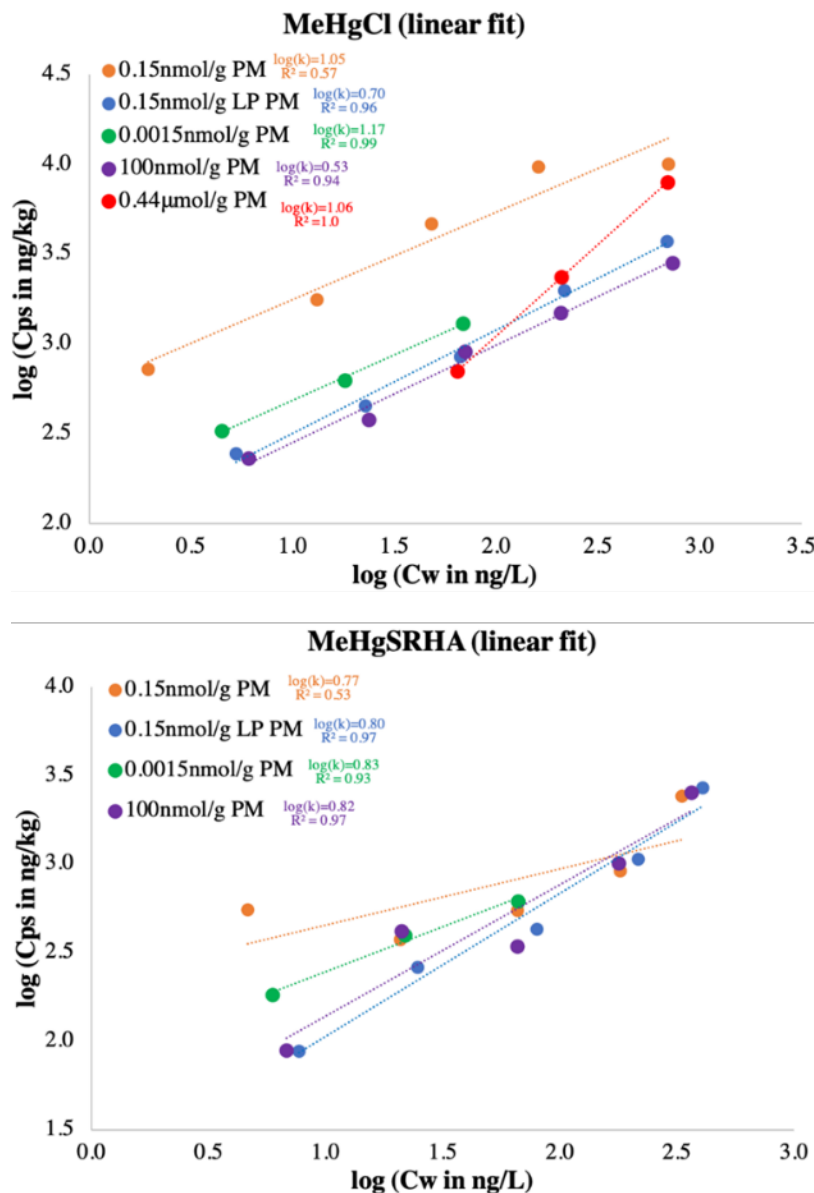


Figure I-7. Adsorption Isotherms of MeHgCl and MeHgSRHA Uptake to the Various PM Polymers Types

The lack of a significant difference in partitioning between different polymer formulations suggests that either the polymer is not functioning in a ligand exchange mode, or that the polymers are degrading before testing at SERC which is supported by the very poor results observed for the DOM isotherms. Sulfide levels in the solutions after the experiment were below detection limit, indicating that the thiol itself is not being degraded. Because of the observed lack of reproducibility, we decided to discontinue further exploration of the PM polymer.

SUPPORTING INFORMATION FOR PEGDA-MATAS EARLY POLYMER TESTING

Table I.1. Data from Kinetics of Uptake of MeHgSRHA into the PM Polymers

Polymer	Time (hr)	PS Mass (g)	[MeHg] _{aq} (ng/L)	[MeHg] _{ps} (ng/kg)	Log(k)
0.15nmol/g	1	0.496	438	979	0.35
0.15nmol/g	3	0.448	488	1,478	0.48
0.15nmol/g	6	0.455	268	2,303	0.93
0.15nmol/g	24	0.438	423	1,452	0.54
0.15nmol/g	48	0.445	244	2,205	0.96
0.15nmol/g	96	0.44	282	4,057	1.16
0.15nmol/g	168	0.419	277	3,219	1.07
0.15nmol/g	336	0.403	213	3,387	1.20
0.15nmol/g LP	1	0.451	350	828	0.37
0.15nmol/g LP	3	0.426	431	850	0.30
0.15nmol/g LP	6	0.425	385	1,213	0.50
0.15nmol/g LP	24	0.342	488	1,238	0.40
0.15nmol/g LP	48	0.373	300	1,074	0.55
0.15nmol/g LP	96	0.381	299	1,067	0.55
0.15nmol/g LP	168	0.35	268	1,170	0.64
0.15nmol/g LP	336	0.403	201	982	0.69

Table I.2. Data from Comparison of Distillation Methods (14-day Isotherm)

Species	Distillation Method:			APDC		CuSO ₄	
	Polymer	Level	PS Mass (g)	[MeHg] _{aq} (ng/L)	[MeHg] _{ps} (ng/kg)	[MeHg] _{aq} (ng/L)	[MeHg] _{ps} (ng/kg)
MeHgCl	0.15nmol/g	1	0.414	1.9	727	2.7	594
		2	0.434	13.1	1,769	15.7	1,135
		3	0.406	47.8	4,664	56.4	3,302
		4	0.385	160.4	9,663	144.9	8,065
		5	0.496	701.3	10,065	735.5	8,170
	0.15nmol/g LP	1	0.303	5.3	246	5.9	279
		2	0.306	22.7	453	29.0	509
		3	0.365	66.5	850	74.8	664
		4	0.338	215.0	1,995	227.1	1,537
		5	0.319	687.6	3,736	771.5	3,567
MeHgSRHA	0.15nmol/g	1	0.392	4.6	556	6.9	337
		2	0.398	20.8	376	20.6	700
		3	0.413	65.5	550	70.5	1,306
		4	0.413	179.6	918	199.7	1,617
		5	0.398	330.3	2,427	542.2	2,891
	0.15nmol/g LP	1	0.288	7.7	88	7.1	147
		2	0.324	24.6	262	22.5	184
		3	0.352	79.6	431	75.3	426
		4	0.364	215.4	1,068	208.2	1,071
		5	0.356	404.9	2,713	390.5	2,711

Table I.3. Comparison of Varying Ligand Densities within PM Polymers for Uptake of MeHgCl and MeHgDOM

Ligand Density	Species	Level	[MeHg] _{aq} (ng/L)	[MeHg] _{ps} (ng/kg)	Log(k)
0.0015nmol/g	MeHgCl	1	4.5	329	1.17
		2	18.0	631	
		3	68.3	1,301	
	MeHgSRHA	1	5.9	183	0.83
		2	21.8	398	
		3	66.0	615	
100 nmol/g	MeHgCl	1	6.1	232	0.53
		2	23.6	379	
		3	70.2	909	
		4	206.4	1,496	
		5	731.8	2,817	
	MeHgSRHA	1	6.8	89	0.82
		2	21.1	418	
		3	65.9	345	
		4	177.5	1,017	
		5	364.6	2,544	
0.44 μ mol/g	MeHgCl	3	64.5	704	1.06
		4	208.6	2,366	
		5	696.5	7,958	

Table I.4. Data from Comparing Varying PM Porosity for Uptake of MeHgDOM

DOM Complex	Polymer	Level	PS Mass (g)	[MeHg] _{aq} (ng/L)	[MeHg] _{ps} (ng/kg)
SRHA	0.15nmol/g	1	0.429	4.6	556
		2	0.441	20.8	376
		3	0.412	65.5	550
		4	0.382	179.6	918
		5	0.395	330.3	2427
	0.15nmol/g LP	1	0.323	7.7	88
		2	0.319	24.6	262
		3	0.314	79.6	431
		4	0.311	215.4	1068
		5	0.32	404.9	2713
SRFA	0.15 nmol/g	1	0.479	0.2	1
		2	0.479	1.2	2
		3	0.461	9.5	23
		4	0.456	22.0	38
		5	0.456	88.3	115
	0.15 nmol/g LP	1	0.416	0.2	0
		2	0.418	0.9	4
		3	0.414	9.7	18
		4	0.422	22.4	26
		5	0.428	89.1	56
SRNOM	0.15 nmol/g	1	0.438	0.2	2
		2	0.431	0.9	3
		3	0.44	8.9	31
		4	0.464	22.1	43

DOM Complex	Polymer	Level	PS Mass (g)	[MeHg] _{aq} (ng/L)	[MeHg] _{ps} (ng/kg)
	0.15 nmol/g LP	5	0.479	84.8	119
		1	0.423	0.2	1
		2	0.419	0.9	3
		3	0.432	9.4	21
		4	0.402	22.0	49
		5	0.432	87.4	107
UMRNOM	0.15 nmol/g	1	0.515	0.2	2
		2	0.455	0.8	6
		3	0.471	9.3	27
		4	0.494	21.6	45
		5	0.466	85.7	142
	0.15 nmol/g LP	1	0.419	0.2	2
		2	0.401	0.9	8
		3	0.418	9.7	20
		4	0.416	22.2	41
		5	0.441	85.7	91

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APPENDIX J RESPONSE TO DEC 2021 IPR QUESTIONS

Questions from the last IPR:

- 1) In a White Paper, provide a comparison of data from independent direct observations of porewater measurements of (1) v-passive sampler measures, and (2) standard measurements of porewater PCBs, dioxins, and MeHg in "standard" analytical tools (e.g. centrifugation), with your model predictions.

Response: We responded to this through SEMS on Jan 24, 2022 as shown below:

We would like to request the program office to provide additional clarification on what is really being asked here. Please provide additional explanation of what underlying concern is driving the early request for this additional white paper. Our understanding is that each of the comparisons being asked for has already been presented by us multiple times as described below and will form part of our final project report. 1) For MeHg passive sampling we have already performed and reported on the comparison between the passive sampler measured and directly measured concentrations in both water phase and in sediment porewater. This was the central theme of the recently published paper: Sanders et al. Environmental Toxicology and Chemistry, 2020;39:323–334 which won the Top 10 Exceptional Papers of 2020 Award from the journal. (see fig 4 and 5 in the paper). We also presented additional measurements comparing methylmercury directly measured and predicted using passive samplers in our most recent IPR (see IPR slides 26, 28, 29). These latter results are also in the process of being published and will constitute a significant portion of our final report. 2) For hydrophobic organics like PCBs and dioxins, multiple studies have reported comparisons between directly measured and passive sampler estimated concentrations. Most recently in our work in ER201735, we compared directly measured porewater PCBs and PAHs in sediment porewater and demonstrated good comparison with concentrations estimated using passive samplers that were deployed in static sediments and also in well mixed sediments. Thus, shaking of the sediments or vibration of the passive sampler does not alter equilibrium concentrations measured. We do not see the need for repeating experiments that have already been completed by us in related projects.

- 2) There are passive samplers that can be deployed for short periods of time (e.g. SPMDs or others). Though field work is costly, mobilizing a crew to retrieve a “traditional” passive sampler should be compared to the cost of the vibrating passive samplers. This can be addressed in the Final Report.

Response: The total cost of production of the vibrating passive samplers is quite low. We are not able to assess commercial production costs including labor, but anticipate material cost to be less than \$100 per unit (see cost of parts in the fabrication guide provided in the appendix). This is quite low compared to typical hourly cost of labor for sampler setup and field deployments even without accounting for travel and lodging costs if the sites are located out of town. Finally, the cost benefit analysis will also depend on the number of samplers deployed at a site per sampling event.

- 3) In the Final Report, discuss the potential deployment issues and retrieval success of using this in situ passive sampling platform vs deployment methods and platforms currently used without being actively shaken. The question is how this technology compares to traditional deployment and retrieval of other passive sampling platforms, and will the inclusion of an active shaker in the current platform lead to potential lesser rates of retrieval (e.g. sampler doesn't remain in the sediment because vibration causes it to detach/become removed from the sediment inserted into?)

Response: Field deployment experiences are described in the Final Report Chapter 3. In none of our deployments in the laboratory or in the field we experienced any issues with the sampler not remaining embedded within sediments.

- 4) In the Final Report, discuss the potential field deployment considerations for this type of passive sampler (e.g., advantages, disadvantages, limitations, etc.)

Response: The advantages of the vibrating passive samplers are discussed in detail in the Final report.

The main disadvantage/limitations are:

- 1) The inclusion of vibrating motor and associated electronics and power makes the device more expensive than a simple metal frame attachment
- 2) The vibration setup does add to the complexity of procurement and deployment and will have to be weighed against the disadvantages of long-term deployments and will be dependent on site/project-specific considerations.
- 3) If the units are not sealed properly, or lost after deployment, there can be potential concerns of littering or release of metals and other battery-associated chemicals into the aquatic environment. Therefore, steps should be taken to eliminate potential for losses after deployment.

APPENDIX K QUESTIONS FROM THE LAST IPR

- 1) In a White Paper, provide a comparison of data from independent direct observations of porewater measurements of (1) v-passive sampler measures, and (2) standard measurements of porewater PCBs, dioxins, and MeHg in "standard" analytical tools (e.g. centrifugation), with your model predictions.

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- 2) There are passive samplers that can be deployed for short periods of time (e.g., SPMDs or others). Though field work is costly, mobilizing a crew to retrieve a “traditional” passive sampler should be compared to the cost of the vibrating passive samplers. This can be addressed in the Final Report.

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