Development and Application of Passive Samplers for Assessing Air and Freely Dissolved Concentrations of Hydrophobic Organic Contaminants

by

Adesewa A. Odetayo, B.Tech., M.Sc.

A Dissertation

In

Civil, Environmental and Construction Engineering

Submitted to the Graduate Faculty
of Texas Tech University in
Partial Fulfillment of
the Requirements for
the Degree of

DOCTOR OF PHILOSOPHY

Approved

Dr. Danny D. Reible
Chair of Committee

Dr. Chongzong Na

Dr. Weile Yan

Dr. Mark Sheridan
Dean of the Graduate School

December 2020

Acknowledgements

This research was supported by funding from U.S Army Corps of Engineer (USACE) and U.S Army Engineer Research Development Center (ERDC) (contract # W912HZ-17-2-0019), and the Environmental Security Technology Certificate Program (ESTCP) (contract # ER 201735). Special thanks to the crew from ERDC for their support during all the field sampling trips.

Firstly, my sincere appreciation goes to my supervisor, Dr. Danny Reible for his help, guidance, and tremendous support throughout the course of my doctoral study, without whom I would have accomplished this milestone. I would like to also extend my gratitude to my committee members for their time and constructive inputs to my research.

My Doctoral research experience was made possible because of so many individuals starting with Magdalena Rakowska, who is always available to help and provide intellectual insights pertaining my research. My adopted brother, Uriel de Jesús Garza Rubalcava who cheered me up and always available to help. Tariq Hussain and Alex Smith who I would most likely meet in the Lab at nights or weekends working on their individual research and fellow passive sampling buddy. My office pals, Hasti Ziaei and Ilektra Drygiannaki, who provided multiple layers of fun to my Ph.D. experience. A special thank you to Brad Thornhills and the Reible research group for your various support during my Ph.D. journey.

To my amazing husband, Oluwaseyi who shared this journey with me, always ready to help with proofreading and put up with me or the absence of me. I sincerely appreciate your love, moral support, patience, and sacrifice for the past five years. I would like to also thank my parents, siblings, family-in-love and friends for their supports, prayers, and words

of encouragement. You are all shades of amazing, I couldn't have achieved this without you.

Last and most importantly, my deepest gratitude goes to the maker of my life, the orchestrator of all things, the foundation of the world, my lord and savior, Jesus Christ. Thank you, Lord, for the assurance I have in your words, you are the lamp unto my feet and the light unto my path.

Table of Contents

Abstract

This research focuses on the use of passive sampling techniques to assess air concentration of hydrophobic organic contaminants (HOCs) such as the polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) around a confined disposal facility. An effective method for managing dredged contaminated sediments from the bottom of waterbodies is the confined disposal facility (CDF). However, volatile losses of HOCs such as PCBs and PAHs from CDFs during placement and disposal of contaminated sediments is of substantial concern to surrounding communities. To address this concern, the air concentrations of PCBs and PAHs are measured using conventional high-volume samplers. However, this method is labor-intensive, expensive, and in addition, does not provide long time-averaged exposure concentrations. This drawback necessitated the development of a passive sampling technique using polyoxymethylene (POM) sorbents to absorb air concentrations of PCBs and PAHs.

Laboratory evaluations with POM were used to assess the uptake kinetics, average equilibrium time, and estimate the POM-air partition coefficients ($K_{POM\text{-}A}$) of 16 PCB congeners. The uptake kinetics defined the effective averaging time for air sampling and differs depending on the hydrophobicity of the compounds of interest but averaged from a week for compounds with $K_{POM\text{-}A} < 10^{6.75}$ to about 5 weeks for compounds with $10^{6.75} > K_{POM\text{-}A} < 10^{8}$ and greater than 5 weeks for $K_{POM\text{-}A} > 10^{8}$. Field sampling at 10 stations surrounding the CDF was conducted three times (two fall/winter and one summer) over two years. Preliminary field application primarily for PCB air concentrations at an average temperature of 3.5 ^{o} C indicated a ∑PCB averaged 0.3 ng/m^3. Subsequent field applications showed the highest concentrations (∑PCB~13 ng/m^3, ∑PAH~65 ng/m^3) occurred during

the summer active dredged material placement when the ambient temperature was 23 ^{o}C. Partitioning to the POM during the fall/winter when the average temperature was ~5 ^{o}C showed a concentration of $\sum$PCB~3 ng/m^3 and $\sum$PAH~45 ng/m^3 during the post dredged material placement. The concentrations during the fall/winter were corrected for temperature effects which may increase uncertainty in the measured concentration. The partitioning POM air sampler (PAS) measurements agreed well with weekly 24-hour HVAS samples averaged over the POM uptake time for lower congener number PCBs (15, 18, 20/28 and 31) and naphthalene but were about 10 times lower than HVAS for high molecular weight PAHs. The difference was likely the result of the greater association of these PAHs with particulates and sources other than evaporation from the CDF. The POM air sampler achieved the goal of providing a long-term average air concentration without having to collect, analyze and average multiple HVAS samples.

This research also demonstrates the reproducibility of the passive sampling approach using polydimethylsiloxane (PDMS). Standardized procedures were developed for measuring freely dissolved concentrations of HOCs through phased inter-laboratory efforts to achieve increased commercial availability and promote public acceptance. The results of the inter-laboratory study towards standardizing passive sampling using PDMS to measure freely dissolved concentrations in sediment porewater indicated that the objectives of the research study was achieved based on desired accuracies of ±30% and ±50% for target and PRC compounds respectively, and precisions of $\leq$ 20% for both targets and PRCs. In general, the achieved success rate based on the desired accuracies and precisions ranged from 71 – 100% for the phase 1. During phase 2, using revised SOP, all laboratories achieved a 100 % success rate based on the desired ±50% accuracy and 20%

precision for PRCs, and phase 3 results showed that participating laboratories measured porewater concentrations of native PCBs and PAHs within a factor of 2. The overall project outcomes include standardized methods and increased commercial availability to end users.

List of Tables

List of Figures

Chapter 1

Introduction

1.1. Background and Motivation

Hydrophobic organic compounds (HOCs) encompass a range of potentially toxic pollutants that are distributed into the environment through natural and anthropogenic activities. These activities include industrial discharge, sewage, forest fire, coal burning, and volcanic eruptions that are discharged into the environment mostly via the atmosphere and into receiving waterbodies. Once contaminated wastes are released into water bodies, the HOCs can evaporate into the atmosphere, and/or settle and accumulate in underlying sediment (silt and mud) at the bottom of rivers, lakes, and estuaries [1, 2]. HOCs in the atmosphere exist in gaseous and particulate phases, while, in sediment and overlying water, HOCs exist in three phases namely freely dissolved, associated with dissolved organic carbon and sorbed to particles [3, 4]. Examples of HOCs include polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans (PCDDs), and several other agricultural and industrial chemicals. Most of these compounds became regulated or banned after evidence implicated them in causing a range of health issues in the nervous, reproductive, endocrine, and immune system of animals and humans [5-8]. Furthermore, gaseous ambient and freely dissolved concentrations have been directly linked to exposure and risk to aquatic life, wildlife, and humans [9]. Hence, mitigating the adverse health effects from these toxic and persistent pollutants are very important and mainly achieved through effective environmental management and control [2, 10].

Conventional techniques of monitoring HOCs in air, water or sediment is often conducted using methods such as active air sampling systems, and alum flocculation or sediment centrifugation for assessing freely dissolved concentrations in water and sediment [2, 11, 12]. In the case of air monitoring, the sampler requires a power supply to operate, is bulky, expensive, and often at risk of vandalism. In general, these conventional sampling methods require elaborate analytical cleaning procedures, are limited to some target compounds (EPA method TO-15), and gives low volume for toxicity testing in the case of sampling freely dissolved concentration in sediment. These limitations necessitated alternative monitoring methods and led to the development of passive samplers [2].

Passive sampling techniques have shown a great deal of promise in providing a potentially reliable and cost-effective means of augmenting current conventional techniques. Passive samplers can provide information about contaminants in sediment, water or air by sorbing and concentrating contaminants onto polymeric materials, therefore allowing for the analysis of the typically low concentration HOCs [13]. The concentration of contaminants accumulated on the polymeric material is related, at equilibrium to the concentration of contaminants in the environmental media. Several studies have shown the application of passive samplers in assessing contaminants' concentrations in different environmental media, that is, air [14-20], sediment [21-25] and water columns [10, 26]. Depending on the type of sorbent and design, the passive samplers can be deployed at numerous locations inaccessible with traditional active sampling equipment. Common sorbents used include semipermeable membrane devices (SPMDs), polyurethane foam (PUF) samplers, XAD resin-based samplers, polyethylene-based (PE) samplers, polyoxymethylene (POM) and polydimethylsiloxane (PDMS).

Studies have indicated that passive sampling techniques provide low detection limits for contaminants and present accurate measurement of gaseous and freely dissolved concentration that is indicative of bioaccumulation, bioconcentration, toxicity and bioavailability to aquatic organisms and wildlife [2]. It was also shown that it is very relevant in the evaluation of the effectiveness of environmental management and monitoring programs such as sediment remedial programs [27, 28], ambient air, and water quality monitoring [13, 26, 29-32]. For instance, Lampert et al [27] evaluated the effectiveness of active capping using PDMS by monitoring PAHs concentration. These results have indicated that passive sampling can be a useful risk decision making tool for stakeholders at multiple stages in the process of assessing and managing contaminated sediment sites.

1.2. Research Objectives

The overall objective of this research is to develop, improve public acceptance of, and standardize passive sampling techniques capable of assessing freely dissolved concentrations by,

1. Develop polymeric passive samplers to measure air concentration of hydrophobic organic contaminants (HOCs) in simulated field applications.
2. Assess the performance of the passive sampling technique in measuring air concentrations in field applications.
3. Evaluate the performance of the passive polymeric sampler approach by comparing with conventional air sampling method in field applications.
4. Demonstrate standardized passive polymeric sampler procedure for assessing freely dissolved concentrations in sediment porewater.

Objectives one through three will be achieved through a set of laboratory and field studies using passive polyoxymethylene sampler. While objective 4 will be achieved using polydimethylsiloxane (PDMS) through inter-laboratory cooperation between multiple participatory commercial and academic laboratories.

1.3. Dissertation Outline

In addressing these objectives, the report is divided into the following chapters as follow:

1. This introduction
2. A literature review of hydrophobic organic compounds of interest in the environment, health implications and environmental regulations, the risks predictor and indicator, passive sampling methods, theory and application in the evaluation and monitoring contaminants in the environment.
3. An overview of the study area, study methodologies including the analytical instruments used, sediment, water, and air sampling.
4. A discussion on the development of the passive polyoxymethylene sampler for assessing PCB air concentrations during lab and field study.
5. A discussion on the application of polyoxymethylene air sampler at a confined disposal facility and comparing the passive sampling method with the conventional high-volume air sampler.
6. A discussion of the results of the participatory laboratories for the purpose of standardizing the polymeric polydimethylsiloxane sampler procedures for measuring freely dissolved concentrations, towards promoting acceptance and increased use.
7. A summary of the main conclusions from the research study and recommendations for future research work.

References

1. Cui, X.; Mayer, P.; Gan, J., Methods to assess bioavailability of hydrophobic organic contaminants: principles, operations, and limitations. *Environmental Pollution* 2013, *172*, 223-234.
2. Greenwood, R.; Mills, G.; Vrana, B., *Passive sampling techniques in environmental monitoring*. Elsevier: 2007.
3. Pan, B.; Ning, P.; Xing, B., Part IV—sorption of hydrophobic organic contaminants. *Environmental Science and Pollution Research* 2008, *15*, (7), 554-564.
4. Council, N. R., *A risk-management strategy for PCB-contaminated sediments*. National Academies Press: 2001.
5. Ross, G., The public health implications of polychlorinated biphenyls (PCBs) in the environment. *Ecotoxicology and environmental safety* 2004, *59*, (3), 275-291.
6. EPA, U., Polycyclic aromatic hydrocarbons (PAHs)-EPA fact sheet. *Washington DC: National Center for Environmental Assessment, office of Research and Development* 2008.
7. ASTDR Polychlorinated Biphenyls (PCBs) ToxicityWhat Standards and Regulations Exist for PCB Exposure? https://www.atsdr.cdc.gov/csem/csem.asp?csem=30&po=8 2018.
8. ATSDR, A. Polycyclic Aromatic Hydrocarbons (PAHs)What are the Standards and Regulations for PAHs Exposure? https://www.atsdr.cdc.gov/csem/csem.asp?csem=13&po=8 2013.
9. Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental organic chemistry*. John Wiley & Sons: 2016.
10. Lohmann, R.; Booij, K.; Smedes, F.; Vrana, B., Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. *Environmental Science and Pollution Research* 2012, *19*, (6), 1885-1895.
11. Edmunds, W. M.; Bath, A. H., Centrifuge extraction and chemical analysis of interstitial waters. *Environ Sci Technol* 1976, *10*, (5), 467-472.
12. Ghosh, U.; Gillette, J. S.; Luthy, R. G.; Zare, R. N., Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles. *Environ Sci Technol* 2000, *34*, (9), 1729-1736.
13. Ghosh, U.; Kane Driscoll, S.; Burgess, R. M.; Jonker, M. T.; Reible, D.; Gobas, F.; Choi, Y.; Apitz, S. E.; Maruya, K. A.; Gala, W. R., Passive sampling methods for contaminated sediments: practical guidance for selection, calibration, and implementation. *Integrated environmental assessment and management* 2014, *10*, (2), 210-223.

14. Herkert, N. J.; Spak, S. N.; Smith, A.; Schuster, J. K.; Harner, T.; Martinez, A.; Hornbuckle, K. C., Calibration and evaluation of PUF-PAS sampling rates across the Global Atmospheric Passive Sampling (GAPS) network. *Environmental Science: Processes & Impacts* 2018, *20*, (1), 210-219.

15. Jaward, F. M.; Zhang, G.; Nam, J. J.; Sweetman, A. J.; Obbard, J. P.; Kobara, Y.; Jones, K. C., Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. *Environ Sci Technol* 2005, *39*, (22), 8638-8645.

16. Khairy, M. A.; Lohmann, R., Field validation of polyethylene passive air samplers for parent and alkylated PAHs in Alexandria, Egypt. *Environ Sci Technol* 2012, *46*, (7), 3990-3998.

17. Odetayo, A. A.; Reible, D. D.; Acevedo-Mackey, D.; Price, C.; Thaic, L., Development of polyoxymethylene passive sampler for assessing air concentrations of PCBs at a confined disposal facility (CDF). *Environmental Pollution* 2020, 114720.

18. Huckins, J. N.; Tubergen, M. W.; Manuweera, G. K., Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavaiiability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* 1990, *20*, (5), 533-552.

19. Schummer, C.; Tuduri, L.; Briand, O.; Appenzeller, B. M.; Millet, M., Application of XAD-2 resin-based passive samplers and SPME–GC–MS/MS analysis for the monitoring of spatial and temporal variations of atmospheric pesticides in Luxembourg. *Environmental pollution* 2012, *170*, 88-94.

20. Okeme, J. O.; Yang, C.; Abdollahi, A.; Dhal, S.; Harris, S. A.; Jantunen, L. M.; Tsirlin, D.; Diamond, M. L., Passive air sampling of flame retardants and plasticizers in Canadian homes using PDMS, XAD-coated PDMS and PUF samplers. *Environmental pollution* 2018, *239*, 109-117.

21. Nam, G.-U.; Bonifacio, R. G.; Kwon, J.-H.; Hong, Y., Kinetics and equilibrium partitioning of dissolved BTEX in PDMS and POM sheets. *Environmental Science and Pollution Research* 2016, *23*, (18), 18901-18910.

22. Hawthorne, S. B.; Jonker, M. T.; van der Heijden, S. A.; Grabanski, C. B.; Azzolina, N. A.; Miller, D. J., Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Analytical chemistry* 2011, *83*, (17), 6754-6761.

23. Lang, S.-C.; Hursthouse, A.; Mayer, P.; Kötke, D.; Hand, I.; Schulz-Bull, D.; Witt, G., Equilibrium passive sampling as a tool to study polycyclic aromatic hydrocarbons in Baltic Sea sediment pore-water systems. *Marine pollution bulletin* 2015, *101*, (1), 296-303.

24. Arp, H. P.; Hale, S. E.; Elmquist Krusa, M.; Cornelissen, G.; Grabanski, C. B.; Miller, D. J.; Hawthorne, S. B., Review of polyoxymethylene passive sampling

methods for quantifying freely dissolved porewater concentrations of hydrophobic organic contaminants. *Environ Toxicol Chem* 2015, *34*, (4), 710-20.

25. Choi, Y.; Wu, Y.; Luthy, R. G.; Kang, S., Non-equilibrium passive sampling of hydrophobic organic contaminants in sediment pore-water: PCB exchange kinetics. *Journal of hazardous materials* 2016, *318*, 579-586.

26. Zabiegała, B.; Kot-Wasik, A.; Urbanowicz, M.; Namieśnik, J., Passive sampling as a tool for obtaining reliable analytical information in environmental quality monitoring. *Analytical and bioanalytical chemistry* 2010, *396*, (1), 273-296.

27. Lampert, D. J.; Lu, X.; Reible, D. D., Long-term PAH monitoring results from the Anacostia River active capping demonstration using polydimethylsiloxane (PDMS) fibers. *Environmental Science: Processes & Impacts* 2013, *15*, (3), 554-562.

28. Thomas, C.; Lampert, D.; Reible, D., Remedy performance monitoring at contaminated sediment sites using profiling solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers. *Environmental Science: Processes & Impacts* 2014, *16*, (3), 445-452.

29. Adams, R. G.; Lohmann, R.; Fernandez, L. A.; MacFarlane, J. K.; Gschwend, P. M., Polyethylene devices: Passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. *Environ Sci Technol* 2007, *41*, (4), 1317-1323.

30. Bao, L. J.; Xu, S. P.; Liang, Y.; Zeng, E. Y., Development of a low-density polyethylene-containing passive sampler for measuring dissolved hydrophobic organic compounds in open waters. *Environmental toxicology and chemistry* 2012, *31*, (5), 1012-1018.

31. Vrana, B.; Mills, G.; Greenwood, R.; Knutsson, J.; Svensson, K.; Morrison, G., Performance optimisation of a passive sampler for monitoring hydrophobic organic pollutants in water. *Journal of Environmental Monitoring* 2005, *7*, (6), 612-620.

32. Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C., Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environ Sci Technol* 2004, *38*, (1), 34-41.

Chapter 2

Literature Review

2.1. Hydrophobic Organic Contaminants (HOCs)

Hydrophobic organic contaminants (HOCs) are generally persistent in the environment and have resulted in widespread environmental contamination due to long-time indiscriminate disposal or release. The HOCs of interest are the polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs).

2.1.1. Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a class of organic compounds with a biphenyl base that consist of two (2) hexagonal rings of carbon atoms connected by double bonds with substituted chlorine atoms (Figure 2.1) that can range from 1 to 10 and are referred to as homologs[1]. The position and number of the chlorine atoms in the structure of a PCB determines its physical and chemical properties, leading to 209 forms (congeners) of PCBs with molecular weights ranging from 188.65 to 493.63 g/mole. PCBs are majorly from anthropogenic sources, are commercially manufactured and were used from 1929 to 1977 [1-3]. They are of industrial relevance due to their chemical properties such as chemical and thermal stability, dielectric properties, non-flammability and miscibility with other organic compounds. Some of the consumer products include but not limited to electrical equipment, cable insulators, dyes, plastics, and transformers. However, mounting scientific evidences pointed to the fact that PCBs accumulate in the environment and have adverse health effects. These evidences coupled with concerns for workers and human health led to the enactment of PCB regulations in 1976 and their eventual production ban in 1979 by the Toxic Substances Control Act (TSCA). Even after their ban and till now, PCBs disposal into the environment remains reviewed and regulated [4].

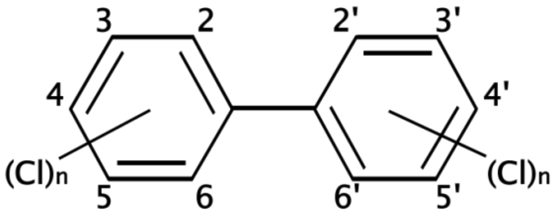


Figure 2.1. Structure of polychlorinated biphenyls.

2.1.2. Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds made of two or more aromatic rings consisting of only carbons and hydrogens (Figure 2.2). PAHs sources stem from both natural and anthropogenic emissions. Natural emission of PAHs include forest fires and volcanic eruptions while the anthropogenic emission which is the predominant source of PAHs include the incomplete combustion of organic materials such as coal and crude oil, gas flaring, residential heating, oil spill and are usual components of plastics, paints and dyes[5-7]. Hence, they are pollutants that are commonly detected in air, water, and soil due to the multiple sources of entry into the environment. The ring system in PAHs can be configured in multiple ways and arrangements leading to a range of semi volatile compounds which are distributed in the air, water, and sediment [8]. In general, PAHs are nonpolar, lipophilic and their aqueous solubility decreases as the molecular weight increases. PAHs can be distributed in the environment through non-point sources such as the release from landfill, drainage, seepage, water bodies and disposal facilities (such as dredged material disposal areas) [9]. PAHs in the environment presents potential risks to aquatic organisms, wildlife and humans. In humans, the exposure pathway include inhalation and ingestion of food grown in contaminated soil or air and studies indicated that cancer is the main health risk presented by PAHs. Carcinogenic tendency of PAHs depends on its structure, PAHs can be either genotoxic and initiate cancer or non-genotoxic and progress cancer [10]. Therefore, some PAHs are more environmentally significant than others[11], USEPA identified sixteen (16) of these PAHs which are referred to as priority PAHs [12] (Fig 2.2).

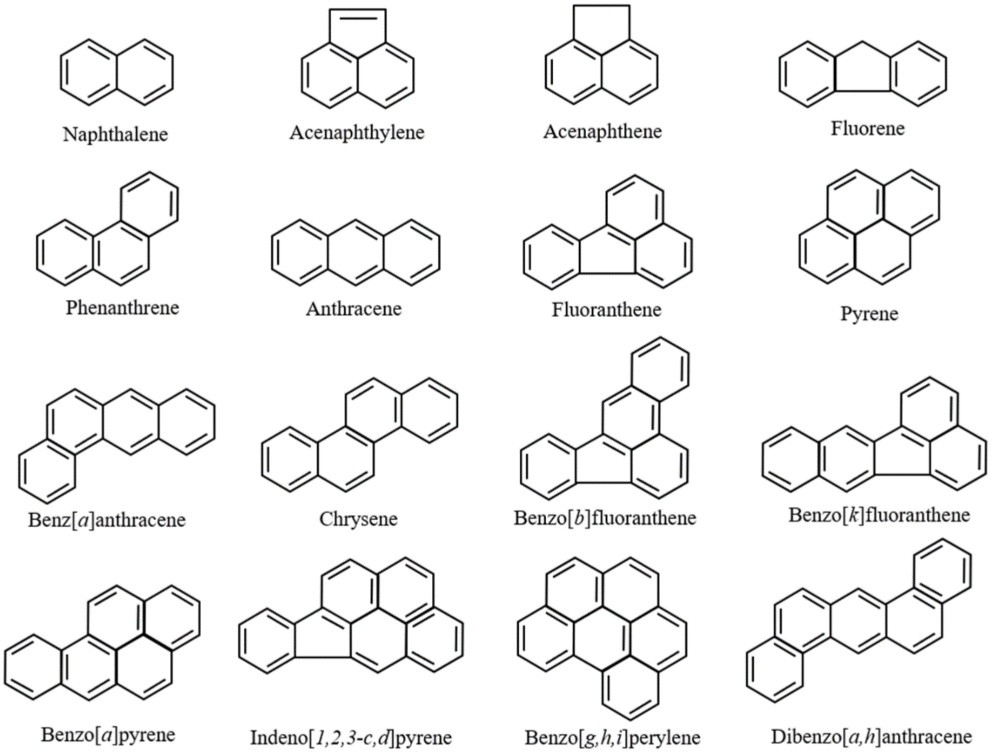


Figure 2.2. Structure of polycyclic aromatic hydrocarbons.

2.2. Health implications of HOCs uptake

Human and wildlife exposure to HOCs can be via direct contact with contaminated air, sediments, or water, and indirectly through diet. Over the years, concerns have arisen not only over the amounts of hydrophobic contaminants discharged into the environment, but also because of the effects on aquatic, wildlife, and human health. PCBs for example, even decades after their ban, degrade slowly in the environment due to their chemical stability properties, and eventually end up in the food chain [13, 14]. Most agencies have categorized PCBs as animal carcinogens and probable human carcinogens [2] due to indefinite evidence linking increased level of PCBs to increased cancer risk[14]. Zani Claudia et al[15] studied the effect of human exposure to PCBs through the ingestion of rice grown on PCB contaminated soil, and an association between PCB levels in humans and non-Hodgkin lymphomas was observed, however, no definite conclusion was drawn. Engel and Wolff indicated potential association between child neurodevelopment and PCB exposure[16], some other studies have also provided meaningful evidences that PCBs are carcinogenic in humans [17, 18]. As a consequence of these studies, the International Agency for Research on Cancer and U.S Environmental Protection Agency (USEPA), classify PCBs as a probable human carcinogen. Other health implications include possible damage to immune system, nervous system, skin irritation, and eye irritation [19], hence, the need for regulation and standardized laws.

PAHs are found everywhere and enter the environment predominantly through wide varieties of anthropogenic activities. They have been identified as contaminants of concern due to their adverse health effects. Exposure to PAHs can be through the ingestion and inhalation of air contaminated with vehicle exhaust, wood smoke, coal smoke, and cigarette smoke among others [20]. The health effects of PAHs depends on the amount, length, and duration of exposure, however, the impact of the exposure to low levels of PAHs are unknown[21]. Exposure to high levels of naphthalene causes eyes and lungs irritation, liver and blood abnormalities[21, 22]. Li et al[23] established genetic effects among workers exposed to coke-oven and tobacco smoke. Findings also indicated positive relationships between unitary PAHs and natural menopause in U.S women[24]. Long time exposure to other PAHs and mixtures have been reported to be cancer-causing [25] and Myers et al established a cause and effect relationship between exposure to PAHs and neoplastic live lesions in humans [26].

Obvious evidences of the health and risk implications of PCBs and PAHs led to the regulation of emissions and discharges of these HOCs materials/wastes into various compartments of the environment. Regulations and policies also require adopting safe practices that effectively reduce, impede, and control the impacts of these contaminants to humans. Table 2.1 and Table 2.2 summarizes the levels or allowable concentrations of PCBs and PAHs to be discharged in air and water.

Table 2.1. Standards and regulations for PCBs [27]

Agency	**Focus**	**Level**
OSHA	Workplace air	1.0 mg/m^3 for PCBs with 42% Cl 0.5 mg/m^3 for PCBs with 54% Cl
NIOSH	Workplace air	1.0 µg/m^3
EPA	Drinking water, environment	0.0005 ppm
FDA	Food: environment	0.2-3.0 ppm (all foods) 2.0 ppm (fish) 10 ppm (paper food-packaging materials)
WHO FAO	Food: environment	6.0 µg/kg per day

where OSHA – Occupational Safety and Health Administration.
NIOSH – National Institute for Occupational Safety and Health.
EPA – Environmental Protection Agency
FDA – Food and Drug Agency
WHO- World Health Organization
FAO – Food and Agriculture Organization

Table 2.2. Standards and regulations for PAHs [28]

Agency	**Focus**	**Level**
American Conference of Governmental Industrial Hygienists	Air: workplace	0.2 milligrams per cubic meter (mg/m^3) for benzene-soluble coal tar pitch fraction
National Institute for Occupational Safety and Health	Air: workplace	0.1 mg/m^3 for coal tar pitch volatile agents
Occupational Safety and Health Administration	Air: workplace	0.2 mg/m^{3}for benzene-soluble coal tar pitch fraction
U.S. Environmental Protection Agency	Water	0.0001 milligrams per liter (mg/L)
		0.0002 mg/L
		0.0003 mg/L
		0.04 L

2.3. Environmental Risk Prediction, Assessment, and Indication

Understanding the risks posed by the hydrophobic organics require a proper understanding of their fate, transport, and distribution in the environment. HOCs discharged into the environment undergo chemical, physical and biological transformation, are redistributed and partition to various environmental media including sediment, water, air and biota [29]. Effective risk assessment helps with efficient decision making by various stakeholders of the environment, including regulators, consultants, natural resource managers and the public [30, 31]. Earlier risk assessors used sediment contaminant load as an indicator or measure of risks [32]. However, this assessment has been deemed inadequate in assessing the risks posed by these hydrophobic organics to environmental health [33]. For instance, to estimate risks posed to an organism, bioaccumulation factor (BAF) is often used as indicated in equation (2.1). However, estimating contaminants' concentration in environmental media such as the sediment have been noted to be complicated. These complicating factors are the different components existing among sediments and the varying interactions of contaminants within these components. Hence, providing significantly different contaminants' concentrations that affects accurate BAF estimation [34]. Research over the years continued to find better approaches for understanding risk and toxicity from contaminated sediments. And so far, studies have indicated that risk and toxicity to the environment is directly linked to truly or freely dissolved concentrations (C_{free}) [33-34]. In sediment, the truly dissolved concentrations or C_{free} is referred to contaminants' concentrations not bound to organic matters in the sediment. In aquatic media, truly dissolved concentrations is referred to contaminants' concentrations not bound to dissolved organic matters in water, and in the air media, truly dissolved contaminants are concentrations in the truly gaseous concentration. Overall, contaminants that are truly or freely available are concentrations not bound to organic matters, colloids, and particulate matters [35]. In any environmental media, truly available contaminant concentration has been noted attractive to be an effective indicator and predictor of risk regarding the fate, transport, bioaccumulation, and toxicity of these contaminants to aquatic life, wildlife, and human health [35, 36].

$$BAF = \frac{C_{organism}}{C_{media}} \tag{2.1}$$

2.3.1. Freely dissolved concentrations in sediment or aquatic systems

The freely dissolved concentration (C_{free}) is the actual concentration in sediment or aquatic environment and represents the fraction of contaminants not bound to colloidal matters or dissolved organic matters [35]. C_{free} can be measured through, a.) direct measurement using alum flocculation [37], or sediment centrifugation [38] or b.) passive sampling methods using polymeric sorbents such as PDMS [39, 40] , PE [41, 42] and POM [43-45]. Generally, freely dissolved concentrations are difficult to measure and direct measurement methods do not provide enough volume required for toxicity testing, [46] and accurate measurement of higher molecular weights organics remains challenging. Passive sampling methods provide a diffusion-based alternative approach that allows contaminants from sediment and water media without disturbance to sorb on the polymeric sorbent [47]. Freely dissolved concentration helps environmental stakeholders understand contaminants' uptake, fate, distribution, and partitioning behavior with respect to the environment.

2.3.2. Airborne concentrations

Through atmospheric transport and transformation, HOCs are found in the gaseous and particulate phases in ambient air. These HOCs in ambient air are compounds that have low vapor pressure and low henry's constant. Most often, these HOCs in air serve as a pathway for the settling of these contaminants into the water and sediment [36]. Airborne contaminants are either from the primary emission of HOCs due to direct leakage of chemicals from source or by secondary emission through volatilization from a contaminated reservoir or water bodies. Continued air quality monitoring and assessment are employed using conventional or passive sampling methods. Conventional methods for assessing the air concentration includes low volume air sampling, high volume air sampling, and air canisters. Most often, these conventional sampling methods are expensive, require specialized labor, electricity in the collection of known volume of samples, and generally provide an ambient concentration over a short timescale of sampling [36]. While, the alternative, the passive sampling method is often cheaper, is diffusion based, and allows the accumulation of contaminants onto the sorbent long enough until equilibrium is attained which can take as long as weeks or months. So far, passive samplers include sorbents like polyurethane foam (PUF), XAD-2, semipermeable devices using low density polyethylene (LDPE), and PDMS. These passive samplers are discussed in the following sections.

2.4. Passive sampling methods

2.4.1. Emergence of passive sampling methods

The passive sampling approach's popularity continues to soar and has become widely used for the determination of air and freely dissolved concentrations by equilibrating over time with the environmental media to which the sorbents are exposed. The principle of the approach is such that the polymeric sorbents concentrate the target contaminants into a small sorbent volume or membrane which can be extracted, analyzed, and related back to the exposure concentration. The first attempt of using a passive sampling method was in the late 1980s, where solid phase microextraction (SPME) was used in the direct transfer of analytes into the gas chromatograph that resulted in rapid separation times particularly for high molecular weight (HMW) compounds [48, 49]. Subsequently, the passive sampling method has been developed using different sorbents and successfully applied for the analysis of environmental, food, pharmaceutical and forensic samples [36, 47, 50-54].

Other polymer sorbents or membranes employed for passive sampling include semipermeable membrane, polyurethane foam (PUF), XAD-2, PDMS, PE and POM. These polymers exhibit strong sorption of hydrophobic contaminants and are different in geometry [47, 55]. Any of these passive sorbents or samplers can be calibrated, utilized, explored and customized depending on the stakeholders' study objective, contaminants of interest and site conditions.

2.4.2. Choice of passive samplers' sorbents

2.4.2.1. Semipermeable membrane devices

Semipermeable membrane devices (SPMD) are device using a non-porous low-density polyethylene membrane that contains a thin film of synthetic lipid triolein (1,2,3 tri[cis-9-octadecenoyl] glycerol) as shown in Figure 2.3. The SPMD is usually designed by the U.S Geological Survey (USGS) for sampling organic contaminants in surface water and air [56]. Huckin et al [57] used SPMD and noted its ability to measure time-averaged concentrations and estimate bioavailability and bioconcentration factors of organics such as PCBs in aquatic environments. Studies employing SPMD were used to measure gaseous concentrations of PAHs and the result was similar to gaseous concentration measured by the conventional HVAS [58]. As an air sampler, the SPMD has been suggested to sample particulates but the process is not well understood. Disadvantages resulting from the use of SPMD include elaborate analytical cleanup, and complication in data interpretations resulting from the leaking of membrane over time and two sampling phases, that is triolein and membrane [36].

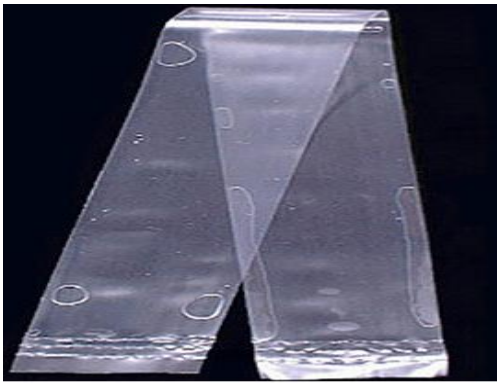


Figure 2.3. Semipermeable devices.

2.4.2.2. XAD-2 resins

This passive sampler utilizes resin, a styrene-divinyl benzene copolymer as the sampling membrane. Until now, XAD-2 resin has been deployed as a passive sampler in air and water. The resin is placed in a container (Figure 2.4) and then positioned under a protective shelter. Initial calibration and implementation of XAD-2 for air sampling was performed by Wania et al [59], where persistent organic contaminants such as hexachlorbenzene was monitored. Later applications of XAD-2 resin in air were conducted to in investigating local and regional patterns of PCBS and PAHs [60, 61]. Some applications in water include the use of XAD-2 to remove organics from water during mutagenicity studies [62].

Figure 2.4. XAD-2 resin placed in a glass tube.

2.4.2.3. Polyurethane foams

The polyurethane foams (PUF) are similar to those used in high volume air sampler (HVAS). PUF are polymers containing the group -NHCOO- and formed as a result of the reactions between diisocyanate and a glycol (Figure 2.5). They typically have a density of 0.0213 g/cm^3, surface area of 365 cm^2 and volume of 207 cm^3 [36]. PUFs have been applied as passive samplers in a number of studies, particularly as air samplers [63-65]. They were first categorized as a passive sampler in 2002 by Shoieb and Harner [66] to monitor PCBs in air. A number of other sorbents are employed as passive air samplers, however, PUF is recognized as the most commonly used passive air sampler primarily as a result of its ease of use and applicability for a wide range of organic contaminants [55].

Figure 2.5. Polyurethane foam.

2.4.2.4. Polyethylene

Polyethylene (PE) is one of the most commonly used sorbent and can be high density or low density sorbent type. For passive sampling application, the most commonly used sorbent is the low density polyethylene (LDPE). LDPE is partially a crystalline (~65%) solid with a density in the range of 0.91-0.94 g/cm^3. LDPE has a chemical structure of (-CHCH-)$_n$, where n is the number of the repeating unit. Polyethylene is chemically inert and does not dissolve in any solvent at room temperature but slightly swells when exposed to solvents at higher temperatures [67]. The LDPE is a flat sheet (Figure 2.6) and comes in varying thicknesses that can be customized to intended use. LDPE has been used as passive sampler in air and water. As an air sampler, it is usually deployed as a SPMD [68] or directly as a flat sheet usually protected against ultraviolent rays and rainfall during deployment with a dome [69]. LDPE is popular and used as an equilibrium sampler for assessing porewater or freely dissolved concentrations in sediment [41] and water systems [70, 71].

Figure 2.6. Polyethylene sheet.

2.4.2.5. Polydimethylsiloxane

Polydimethylsiloxane or PDMS belongs to a group of silicon-based polymers and is the most used silicone-based polymer. It is available in various geometries and popular for its unusual rheological (flow) properties. PDMS has a chemical structure of $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$ where n refers to the number of repeating monomer "$[Si(CH_3)_2O]$" unit. PDMS can be in the form of an optical fiber which is coated on a cylindrical glass core (Figure 2.7), and has a good surface to volume ratio. As a passive sampler, PDMS has been successfully used to sample air [72, 73], water [74] and sediment [33, 39] as reported in a number of studies.

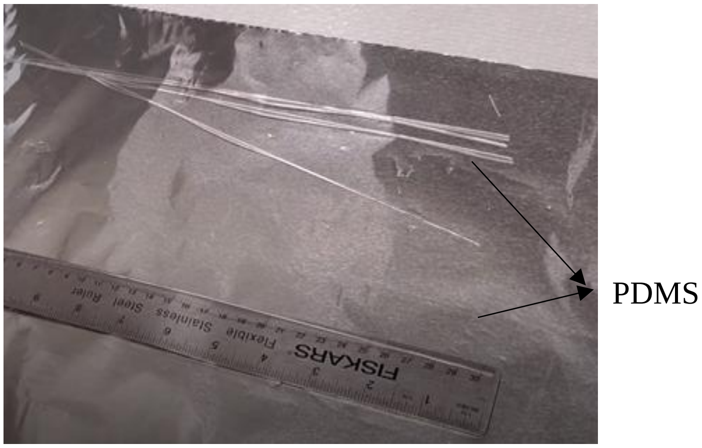


Figure 2.7. Polydimethylsiloxane fiber.

2.4.2.6. Polyoxymethylene

Polyoxymethylene (POM) is a polymer also known as acetal or polyformaldehyde. POM is a partially crystalline (~75%) high-molecular-weight polymer, and has a high impact strength, stiffness and yield stress higher than other crystalline polymers (Figure 2.8). POM is known to be insoluble in common solvents at room temperature, intrinsically opaque white, and can be easily processed or cut without wear. Pure formaldehyde (99.9% CH_2O) is polymerized in the presence of solvent, high pressure, and temperature to obtain POM with a density range of 1.41-1.42 g/cm^3. POM has a large surface area to volume ratio. All these characteristics make POM attractive for engineering applications such as being used for automobile parts, as a replacement for metal and for environmental passive sampling [67]. As a passive sampler, application has been mostly for sampling sediment [43, 75] and aquatic systems[76]. Also, POM was recently employed as a passive air sampler [77] in our research.

Figure 2.8. Polyoxymethylene sampler.

2.5. Theory of passive sampling

The contaminants sorbed on the passive samplers are translated at equilibrium to environmental concentrations, referred to as air concentrations in ambient air and freely dissolved concentrations in sediment and water medias as depicted in Equation 2.2.

$$C_{Env,target} = \frac{C_{polymer,eq}}{K_{P-Env}} \tag{2.2}$$

where $C_{Env,target}$ is the environmental target concentration, $C_{polymer,eq}$ is the contaminant concentration sorbed on polymeric passive sampler and K_{P-Env} is the partition coefficients between passive sampler and the exposed environmental media. Partition coefficients differ for individual polymers and are a function of the intrinsic properties of the polymer sorbent, the physicochemical properties of the contaminants and the environmental site conditions. Passive sampling can be deployed in situ or ex situ. *In* situ involves the deployment of passive samplers at the field. While *ex* situ is the deployment of the passive sampler under laboratory conditions.

Prior to the use of a passive sampler, the partition coefficients of the passive sampler to the media of interest should be determined and the uptake kinetics of the HOCs on the sampler understood. These can be assessed in a number of ways including the equilibrium sampling approach [47]. This study focuses on the equilibrium sampling methods which can be established using the time series exposure, utilizing multiple thicknesses of samplers and the use of performance reference compounds (PRCs). Non-equilibrium sampling can be corrected with the use of PRCs and multiple thicknesses of a passive sampler, particularly during in-situ sampling where uptake of contaminants can take multiple weeks or months before equilibrium is achieved.

2.5.1. Time series exposure

Passive samplers can be deployed at different time stamps until a uniform concentration is obtained. In time series exposure, the uptake of contaminant is measured over a time period until uniform concentration is attained. This uniform concentration is defined as equilibrium concentration and for simplicity, can be fitted to a first order equation to obtain or estimate other parameters needed for understanding contaminants' uptake. Several studies have utilized this approach in the determination of equilibrium conditions and correction of non-equilibrium sampling of freely dissolved concentrations in air, water or sediment systems [52, 77].

2.5.2. Multiple polymer thicknesses

Equilibrium can also be assessed by the deployment of multiple thicknesses of a sampler during in situ or ex situ studies. The achievement of the same concentration of contaminants on polymers of different thicknesses confirm the attainment of equilibrium.

Maenpaa et al [78] utilized this approach to determine equilibrium partitioning concentrations in lipids.

2.5.3. Performance Reference Compounds (PRCs)

In this method, equilibrium can be assessed using performance reference compounds known as PRCs. Traditionally, PRCs are compounds that are not usually present in the environment and are preloaded on the passive samplers before *in* situ or *ex* situ deployments. The loss of PRCs loaded on a passive sampler reflects the degree of approach to equilibrium of target compounds i.e. the rate of desorption of PRCs from a passive sampler is equal to the rate of adsorption of target compounds on a passive sampler. This principle assumes a linear relationship as shown in Figure 2.9.

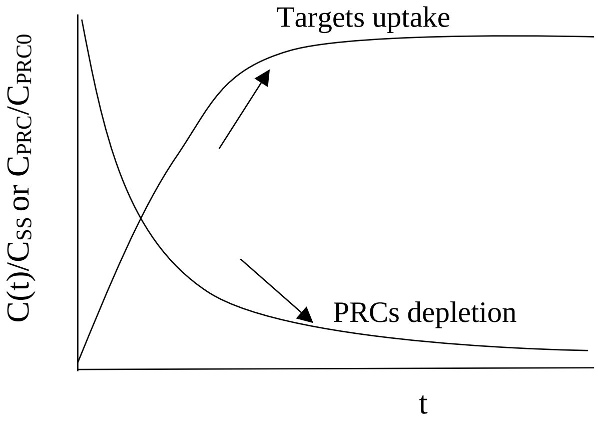


Figure 2.9. Schematics of the uptake of target contaminants and release of PRCs.

Generally, the initial amount of PRCs loaded on a sampler is known, and when deployed, approaches zero concentration as it approaches equilibrium; and the remaining amount of PRCs can be estimated after retrieval. Therefore, the steady state condition can be modelled by Equation (2.3).

$$fss, PRC = \frac{C_{deployment} - C_{retrieval}}{C_{deployment}} \tag{2.3}$$

and the target compounds can be described by,

$$C_{Env,\ target\_corr} = \frac{C_{Env,\ target}}{fss} \tag{2.4}$$

where fss is defined as the fractional steady state , $C_{deployment}$ is the concentration of PRCs before deployment, $C_{retrieval}$ is the concentration measured after retrieval, $C_{Env,\ target\_corr}$ is the corrected concentration of targets contaminants and $C_{Env,target}$ is the equivalent environmental concentration obtained from Equation 2.2.

2.6. Summary

This chapter discussed and reviewed the contaminants of interest, in this case, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Efficient characterization of the risks posed by these pollutants is important for stakeholders in the aspect of decision making, regulations, site cleanups and remediation technology, among others. Passive sampling has been recognized as a technology capable for assessing contaminants' concentrations, estimating risks and exposure to human health. Passive samplers estimate the true concentrations present in air, water or sediment unlike the conventional method of sampling.

In subsequent chapters, passive sampling techniques are explored based on existing understanding. Development of a passive sampling technique using POM sampler was explored as an air sampler under laboratory conditions, and the capacity of the POM sampler was also assessed at a site. Standardization studies were conducted with a number of other stakeholders for the purpose of increasing commercial availability, public use, and decision and regulation making.

References

1. Johnson, G. W.; Quensen III, J. F.; Chiarenzelli, J. R.; Hamilton, M. C., Polychlorinated biphenyls. In *Environmental forensics*, Elsevier: 1964; pp 187-225.
2. BIPHENYLS, P., TOXICOLOGICAL PROFILE FOR POLYCHLORINATED BIPHENYLS (PCBs). 2000.
3. NOAA What are PCBs? https://oceanservice.noaa.gov/facts/pcbs.html 2020.
4. EPA Polychlorinated Biphenyls (PCBs). *https://www.epa.gov/pcbs/learn-about-polychlorinated-biphenyls-pcbs 2020.*
5. Lee, B.-K., Sources, distribution and toxicity of polyaromatic hydrocarbons (PAHs) in particulate matter. In *Air pollution*, IntechOpen: 2010.
6. Pyrene, N. R. C. C. o.; Analogues, S., *Polycyclic aromatic hydrocarbons: evaluation of sources and effects*. National Academies Press: 1983.
7. Mumtaz, M.; George, J.; Gold, K.; Cibulas, W.; DeRosa, C., ATSDR evaluation of health effects of chemicals. IV. Polycyclic aromatic hydrocarbons (PAHs): understanding a complex problem. *Toxicology and industrial health* 1996, *12*, (6), 742-971.
8. Maliszewska-Kordybach, B., Persistent organic contaminants in the environment: PAHs as a case study. In *Bioavailability of organic xenobiotics in the environment*, Springer: 1999; pp 3-34.
9. Emsbo-Mattingly, S. D.; Litman, E., Polycyclic aromatic hydrocarbon homolog and isomer fingerprinting. In *Standard Handbook Oil Spill Environmental Forensics*, Elsevier: 2016; pp 255-312.
10. ATSDR, A., Toxicological profile for polycyclic aromatic hydrocarbons. In Agency for Toxic Substances and Disease Registry Atlanta, GA: 1995.
11. EPA, Ü., Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. *Development* 1993, 1-28.
12. USEPA Substance Details - Polycyclic organic matter - 16-PAH. https://iaspub.epa.gov/sor_internet/registry/substreg/substance/details.do?displayPopup=&id=6012 2020.
13. Council, N. R., *A risk-management strategy for PCB-contaminated sediments*. National Academies Press: 2001.
14. Ross, G., The public health implications of polychlorinated biphenyls (PCBs) in the environment. *Ecotoxicology and environmental safety* 2004, *59*, (3), 275-291.
15. Zani, C.; Toninelli, G.; Filisetti, B.; Donato, F., Polychlorinated biphenyls and cancer: an epidemiological assessment. *Journal of Environmental Science and Health, Part C* 2013, *31*, (2), 99-144.

16. Engel, S. M.; Wolff, M. S., Causal inference considerations for endocrine disruptor research in children's health. *Annual review of public health* 2013, *34*, 139-158.

17. Golden, R.; Doull, J.; Waddell, W.; Mandel, J., Potential human cancer risks from exposure to PCBs: a tale of two evaluations. *Critical reviews in toxicology* 2003, *33*, (5), 543-580.

18. Ritchie, J. M.; Vial, S. L.; Fuortes, L. J.; Robertson, L. W.; Guo, H.; Reedy, V. E.; Smith, E. M., Comparison of proposed frameworks for grouping polychlorinated biphenyl congener data applied to a case–control pilot study of prostate cancer. *Environmental research* 2005, *98*, (1), 104-113.

19. Dai, Q.; Min, X.; Weng, M., A review of polychlorinated biphenyls (PCBs) pollution in indoor air environment. *Journal of the Air & Waste Management Association* 2016, *66*, (10), 941-950.

20. Dybing, E.; Schwarze, P. E.; Nafstad, P.; Victorin, K.; Penning, T. M., Polycyclic aromatic hydrocarbons in ambient air and cancer. 2013.

21. EPA, U., Polycyclic aromatic hydrocarbons (PAHs)-EPA fact sheet. *Washington DC: National Center for Environmental Assessment, office of Research and Development* 2008.

22. Kim, K.-H.; Jahan, S. A.; Kabir, E.; Brown, R. J., A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environment international* 2013, *60*, 71-80.

23. Qiu, L.; Leng, S.; Wang, Z.; Dai, Y.; Zheng, Y.; Wang, Z., Path analysis of biomarkers of exposure and early biological effects among coke-oven workers exposed to polycyclic aromatic hydrocarbons. *Cancer Epidemiology and Prevention Biomarkers* 2007, *16*, (6), 1193-1199.

24. Huang, Y.; Guo, J.; Lv, N.; Li, S.; Wu, Y.; Bai, R.; Shen, J.; Chen, G.; Zhang, D., Associations of urinary polycyclic aromatic hydrocarbons with age at natural menopause in US women aged 35–65, NHANES 2003–2012. *Environmental pollution* 2018, *243*, 1878-1886.

25. Kaushik, C.; Haritash, A., Polycyclic aromatic hydrocarbons (PAHs) and environmental health. *Our earth* 2006, *3*, (3), 1-7.

26. Myers, M. S.; Johnson, L. L.; Collier, T. K., Establishing the causal relationship between polycyclic aromatic hydrocarbon (PAH) exposure and hepatic neoplasms and neoplasia-related liver lesions in English sole (Pleuronectes vetulus). *Human and Ecological Risk Assessment* 2003, *9*, (1), 67-94.

27. ASTDR Polychlorinated Biphenyls (PCBs) Toxicity. What Standards and Regulations Exist for PCB Exposure? https://www.atsdr.cdc.gov/csem/csem.asp?csem=30&po=8 2018.

28. ATSDR, A. Polycyclic Aromatic Hydrocarbons (PAHs). What are the Standards and Regulations for PAHs Exposure? https://www.atsdr.cdc.gov/csem/csem.asp?csem=13&po=8 2013.

29. Reible, D. D., *Processes, assessment and remediation of contaminated sediments*. Springer: 2014.

30. Program, N. R. C. C. t. R. R. M. i. t. D. s. E. R.; Program, N. R. C. C. t. R. R. M. i. t. D. s. E. R., *Building consensus through risk assessment and management of the Department of Energy's environmental remediation program*. National Academies: 1994.

31. Council, N. R., *Science and decisions: advancing risk assessment*. National Academies Press: 2009.

32. Burgess, R. M.; Driscoll, S. B. K.; Maynard, M.; Ozretich, R. J.; Mount, D. R.; Reiley, M. C., *Equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Procedures for the determination of the freely dissolved interstitial water concentrations of nonionic organics*. United States Environmental Protection Agency, Office of Research and …: 2012.

33. Lampert, D. J.; Lu, X.; Reible, D. D., Long-term PAH monitoring results from the Anacostia River active capping demonstration using polydimethylsiloxane (PDMS) fibers. *Environmental Science: Processes & Impacts* 2013*, 15*, (3), 554-562.

34. DiToro DM, Zarba CS, Hansen DJ, Berry WJ, Swartz RC, Cowan CE, Pavlou SP, Allen HE, Thomas NA, Paquin PR. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equlibrium partitioning. Environ Toxicol Chem 10*:*1541–1583.

35. Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental organic chemistry*. John Wiley & Sons: 2016.

36. Greenwood, R.; Mills, G.; Vrana, B., *Passive sampling techniques in environmental monitoring*. Elsevier: 2007.

37. Ghosh, U.; Gillette, J. S.; Luthy, R. G.; Zare, R. N., Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles. *Environ Sci Technol* 2000, *34*, (9), 1729-1736.

38. Edmunds, W. M.; Bath, A. H., Centrifuge extraction and chemical analysis of interstitial waters. *Environ Sci Technol* 1976, *10*, (5), 467-472.

39. Thomas, C.; Lampert, D.; Reible, D., Remedy performance monitoring at contaminated sediment sites using profiling solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers. *Environmental Science: Processes & Impacts* 2014, *16*, (3), 445-452.

40. Lu, X.; Skwarski, A.; Drake, B.; Reible, D. D., Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. *Environmental Toxicology and Chemistry* 2011, *30,* (5), 1109-1116.

41. Fernandez, L. A.; MacFarlane, J. K.; Tcaciuc, A. P.; Gschwend, P. M., Measurement of freely dissolved PAH concentrations in sediment beds using

passive sampling with low-density polyethylene strips. *Environ Sci Technol* 2009, *43*, (5), 1430-1436.

42. Devault, D. A.; Gourlay-Francé, C., Pore water contribution to in-situ sampling of polycyclic aromatic hydrocarbons in sediment using low density polyethylene. *Revista Internacional de Contaminación Ambiental* 2017, *33*, 23-32.

43. Oen, A. M.; Janssen, E. M.; Cornelissen, G.; Breedveld, G. D.; Eek, E.; Luthy, R. G., In situ measurement of PCB pore water concentration profiles in activated carbon-amended sediment using passive samplers. *Environ Sci Technol* 2011, *45*, (9), 4053-4059.

44. Beckingham, B.; Ghosh, U., Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field. *Chemosphere* 2013, *91*, (10), 1401-1407.

45. Arp, H. P.; Hale, S. E.; Elmquist Krusa, M.; Cornelissen, G.; Grabanski, C. B.; Miller, D. J.; Hawthorne, S. B., Review of polyoxymethylene passive sampling methods for quantifying freely dissolved porewater concentrations of hydrophobic organic contaminants. *Environ Toxicol Chem* 2015, *34*, (4), 710-20.

46. Chapman, P. M.; Wang, F.; Germano, J. D.; Batley, G., Pore water testing and analysis: the good, the bad, and the ugly. *Marine Pollution Bulletin* 2002, *44*, (5), 359-366.

47. Ghosh, U.; Kane Driscoll, S.; Burgess, R. M.; Jonker, M. T.; Reible, D.; Gobas, F.; Choi, Y.; Apitz, S. E.; Maruya, K. A.; Gala, W. R., Passive sampling methods for contaminated sediments: practical guidance for selection, calibration, and implementation. *Integrated environmental assessment and management* 2014, *10*, (2), 210-223.

48. Arthur, C. L.; Pawliszyn, J., Solid phase microextraction with thermal desorption using fused silica optical fibers. *Analytical chemistry* 1990, *62*, (19), 2145-2148.

49. Lord, H.; Pawliszyn, J., Evolution of solid-phase microextraction technology. *Journal of Chromatography A* 2000, *885*, (1-2), 153-193.

50. De Santis, F.; Allegrini, I.; Fazio, M.; Pasella, D.; Piredda, R., Development of a passive sampling technique for the determination of nitrogen dioxide and sulphur dioxide in ambient air. *Analytica Chimica Acta* 1997, *346*, (1), 127-134.

51. Lydy, M. J.; Landrum, P. F.; Oen, A. M.; Allinson, M.; Smedes, F.; Harwood, A. D.; Li, H.; Maruya, K. A.; Liu, J., Passive sampling methods for contaminated sediments: State of the science for organic contaminants. *Integrated environmental assessment and management* 2014, *10*, (2), 167-178.

52. Hawthorne, S. B.; Jonker, M. T.; van der Heijden, S. A.; Grabanski, C. B.; Azzolina, N. A.; Miller, D. J., Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Analytical chemistry* 2011, *83*, (17), 6754-6761.

53. Dhodapkar, R. S.; Gandhi, K. N., Pharmaceuticals and personal care products in aquatic environment: chemicals of emerging concern? In *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, Elsevier: 2019; pp 63-85.

54. Tucca, F.; Moya, H.; Barra, R., Ethylene vinyl acetate polymer as a tool for passive sampling monitoring of hydrophobic chemicals in the salmon farm industry. *Marine pollution bulletin* 2014, *88*, (1-2), 174-179.

55. Melymuk, L.; Bohlin-Nizzetto, P.; Prokeš, R.; Kukučka, P.; Klánová, J., Sampling artifacts in active air sampling of semivolatile organic contaminants: Comparing theoretical and measured artifacts and evaluating implications for monitoring networks. *Environmental Pollution* 2016, *217*, 97-106.

56. Alvarez, D. A., Guidelines for the use of the semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) in environmental monitoring studies. *US Geological Survey, Techniques and Methods* 2010, *1*, 28.

57. Huckins, J. N.; Tubergen, M. W.; Manuweera, G. K., Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavaiiability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* 1990, *20*, (5), 533-552.

58. Zhu, X.; Zhou, C.; Henkelmann, B.; Wang, Z.; Ma, X.; Pfister, G.; Schramm, K.-W.; Chen, J.; Ni, Y.; Wang, W., Monitoring of PAHs profiles in the urban air of Dalian, China with active high-volume sampler and semipermeable membrane devices. *Polycyclic Aromatic Compounds* 2013, *33*, (3), 265-288.

59. Wania, F.; Shen, L.; Lei, Y. D.; Teixeira, C.; Muir, D. C., Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere. *Environ Sci Technol* 2003, *37*, (7), 1352-1359.

60. Barthel, P.; Thuens, S.; Shunthirasingham, C.; Westgate, J. N.; Wania, F.; Radke, M., Application of XAD-resin based passive air samplers to assess local (roadside) and regional patterns of persistent organic pollutants. *Environmental pollution* 2012, *166*, 218-225.

61. Schummer, C.; Tuduri, L.; Briand, O.; Appenzeller, B. M.; Millet, M., Application of XAD-2 resin-based passive samplers and SPME–GC–MS/MS analysis for the monitoring of spatial and temporal variations of atmospheric pesticides in Luxembourg. *Environmental pollution* 2012, *170*, 88-94.

62. Daignault, S.; Noot, D.; Williams, D.; Huck, P., A review of the use of XAD resins to concentrate organic compounds in water. *Water research* 1988, *22*, (7), 803-813.

63. Esen, F., Development of a passive sampling device using polyurethane foam (PUF) to measure polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) near landfills. *Environmental Forensics* 2013, *14*, (1), 1-8.

64. Herkert, N. J.; Spak, S. N.; Smith, A.; Schuster, J. K.; Harner, T.; Martinez, A.; Hornbuckle, K. C., Calibration and evaluation of PUF-PAS sampling rates across the Global Atmospheric Passive Sampling (GAPS) network. *Environmental Science: Processes & Impacts* 2018, *20*, (1), 210-219.

65. Genualdi, S.; Lee, S. C.; Shoeib, M.; Gawor, A.; Ahrens, L.; Harner, T., Global pilot study of legacy and emerging persistent organic pollutants using sorbent-impregnated polyurethane foam disk passive air samplers. *Environ Sci Technol* 2010, *44*, (14), 5534-5539.

66. Shoeib, M.; Harner, T., Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ Sci Technol* 2002, *36*, (19), 4142-4151.

67. Billmeyer, F. W.; Billmeyer, F. W., *Textbook of polymer science*. Wiley New York: 1984; Vol. 19842.

68. Ockenden, W. A.; Corrigan, B. P.; Howsam, M.; Jones, K. C., Further developments in the use of semipermeable membrane devices as passive air samplers: Application to PCBs. *Environ Sci Technol* 2001, *35*, (22), 4536-4543.

69. Meire, R. O.; Khairy, M.; Targino, A. C.; Galvão, P. M. A.; Torres, J. P. M.; Malm, O.; Lohmann, R., Use of passive samplers to detect organochlorine pesticides in air and water at wetland mountain region sites (S-SE Brazil). *Chemosphere* 2016, *144*, 2175-2182.

70. Bao, L. J.; Xu, S. P.; Liang, Y.; Zeng, E. Y., Development of a low-density polyethylene-containing passive sampler for measuring dissolved hydrophobic organic compounds in open waters. *Environmental toxicology and chemistry* 2012, *31*, (5), 1012-1018.

71. Adams, R. G.; Lohmann, R.; Fernandez, L. A.; MacFarlane, J. K.; Gschwend, P. M., Polyethylene devices: Passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. *Environ Sci Technol* 2007, *41*, (4), 1317-1323.

72. Okeme, J. O.; Saini, A.; Yang, C.; Zhu, J.; Smedes, F.; Klánová, J.; Diamond, M. L., Calibration of polydimethylsiloxane and XAD-pocket passive air samplers (PAS) for measuring gas-and particle-phase SVOCs. *Atmos. Enviro.* 2016, *143*, 202-208.

73. Okeme, J. O.; Yang, C.; Abdollahi, A.; Dhal, S.; Harris, S. A.; Jantunen, L. M.; Tsirlin, D.; Diamond, M. L., Passive air sampling of flame retardants and plasticizers in Canadian homes using PDMS, XAD-coated PDMS and PUF samplers. *Environmental pollution* 2018, *239*, 109-117.

74. DiFilippo, E. L.; Eganhouse, R. P., Assessment of PDMS-water partition coefficients: implications for passive environmental sampling of hydrophobic organic compounds. *Environ Sci Technol* 2010, *44*, (18), 6917-6925.

75. Cornelissen, G.; Pettersen, A.; Broman, D.; Mayer, P.; Breedveld, G. D., Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations. *Environmental Toxicology and Chemistry: An International Journal* 2008, *27*, (3), 499-508.

76. Perron, M. M.; Burgess, R. M.; Suuberg, E. M.; Cantwell, M. G.; Pennell, K. G., Performance of passive samplers for monitoring estuarine water column concentrations: 1. Contaminants of concern. *Environmental toxicology and chemistry* 2013, *32*, (10), 2182-2189.

77. Odetayo, A. A.; Reible, D. D.; Acevedo-Mackey, D.; Price, C.; Thai, L., Development of polyoxymethylene passive sampler for assessing air concentrations of PCBs at a confined disposal facility (CDF). *Environmental Pollution* 2020, 114720.

78. Mäenpää, K.; Leppänen, M. T.; Reichenberg, F.; Figueiredo, K.; Mayer, P., Equilibrium sampling of persistent and bioaccumulative compounds in soil and sediment: Comparison of two approaches to determine equilibrium partitioning concentrations in lipids. *Environ Sci Technol* 2011, *45*, (3), 1041-1047.

Chapter 3

Research Methodologies

3.1. Overview of the Study Area

The study area (Figure 3.1) is a Confined Disposal Facility (CDF) located in East Chicago, Lake County towards the southwest shore of Lake Michigan, and at the property of former Energy Cooperative, Inc (ECI) site. The CDF is approximately 2,000 feet west of the Indiana Harbor Canal and about 17 miles southeast of downtown Chicago, Illinois. The CDF site is surrounded at the south by the Lake George Canal, north by Cline Avenue, east by Indianapolis Boulevard and at the west by Amoco Oil Company Refinery (Figure 3.1). The CDF is structured with control systems that allows the disposal and management of dredged materials in a manner protective of human health and the environment. These control systems include

- A slurry wall system around the CDF boundary at the west, north and the east.
- An installed anchor wall made of steel along the southern boundary and the Lake George Canal.
- An installed groundwater gradient control system that include 96 extraction wells, 40 monitoring wells, two water level indicators, 14 groundwater piezometers and clay dike walls to separate the two cells.

Three (3) sampling studies were conducted at the Indiana Harbor and Canal, Confined disposal facility (IHC-CDF) for sediment, water and air samples. Sediment, water and air samples collected from the IHC-CDF were transported in an ice chest to

Reible Research Lab in Texas Tech University. Supplementary information about the CDF and sampling are discussed in subsequent chapters of this dissertation.

Figure 3.1. The study map showing the IHC-CDF with the expanded view showing adjacent industries, the POM samplers (red), High volume air samplers (red circles) and the discharge locations of dredged materials into the CDF (purple circles) in East Chicago.

3.2. Reagents and Materials

All solvents utilized were of optima grade quality and were purchased from Fisher Scientific (Hampton, NH, U.S.A.) and/or VWR Chemicals BDH (Radnor, PE, U.S.A.). Calibration and working standards for PCBs and PAHs were purchased from chemical companies such as AccuStandard (New Haven, CT., USA), Ultra Scientific Analytical solution (USA) and Cambridge Isotope laboratories, Inc. (Tewksbury, MA, USA). The de-ionized water used for the experiment was provided by GenPure Pro UV, Thermo Scientific (USA).

During sediment extraction process, diatomaceous earth (Thermo Scientific) was prepared and mixed with sediment samples, anhydrous sodium sulfate (BDH Analytical, USA) were prepared by drying at 550 ^{o} C in a muffle furnace for 2 hours. Florisil (EMD chemicals, USA) was heated in a glass container loosely covered with aluminum foil in an oven at 130 ^{o}C overnight and then cooled in a desiccator. Copper powder (Spectrum, USA) is treated with 0.5 N nitric acid three times, followed by the addition of de-ionized water to remove the nitric acid and neutralize the pH, then acetone is added to remove the water. The copper powder is oven dried at 105 ^{o}C for 5-10 minutes. Sodium Azide 100 mg/L + 0.01 M calcium chloride solution was prepared and spiked into the sediment slurry to prevent microorganism activities. Cleaned glass wares were solvent-washed before use, other materials used in this study include aluminum rod, septum, parafilm, tweezers, scissors, and ceramic cutter.

Two kinds of polymer fibers used during the air and water sampling study are the POM strips (76 µm thickness) obtained from CS Hyde Company (Lake Villa, USA) and PDMS fibers of different coating thickness purchased from Polymicro Technologies (Phoenix, USA) respectively.

3.3. Analytical Instrument

Qualitative and quantitative analysis were carried out on a number of analytical instruments depending on the type of contaminants and samples. Analytical equipment used include High Performance Liquid Chromatography (HPLC) (Agilent technologies 1260 infinity, (Santa Clara, CA, USA)), Gas Chromatography Mass Spectrometer (GC-MS), and Gas Chromatography – Triple quad Mass Spectrometer (GC-TQMS). Samples designated for HPLC are in acetonitrile and samples designated for GC-ECD, GC-MS and GC-TQMS are mostly in hexane and alternatively in acetonitrile.

3.3.1. High Performance Liquid Chromatography (HPLC)

The HPLC is an Agilent product used for PAHs separation equipped with an ultraviolent-diode array (1260 DAD VL+) and fluorescence detector (1260 FLD spectra). And operated with an excitation wavelength of 430nm and a Phenomenex Luna 5µ C18 column (250 x 4.6mm) (Torrance, CA, USA) under an isocratic condition. The flow rate was 1.0 mL/min. The acetonitrile-water mixture (7:3, v/v) was used as a mobile phase. For sample analysis, EPA method was used.

3.3.2. Gas Chromatography– Mass Spectrometer (GC-MS)

The GC-MS is a low sensitivity Agilent technologies 6890 GC coupled with 5973 MSD and equipped with a HP-5 60m x .32 mm, 0.25micron column (Agilent, USA) and operated with under the splitless mode, inlet temperature of 270 ^{o}C, flowrate of 0.8 ml/min, oven temperature of 50 ^{o} C, injection volume of 1 µL with runtime of ~43 mins. PAH analysis was performed using modified EPA method 8270/1625A. Individual PAHs analyzed, the retention time and analysis parameters are included in Appendix A.

3.3.3. Gas Chromatography– Triple quad Mass Spectrometer (GC-TQMS)

High sensitivity analyte determination was achieved using an Agilent Technologies 7890 GC coupled with 7000 MS/MS, equipped with a HP-5 60m x .32 mm, 0.25micron column (Agilent, USA) and operated with under the splitless mode, inlet temperature of 280 ^{o} C, flowrate of 1.2 ml/min, oven temperature of 80 ^{o} C, and injection volume of 1 µL with runtime of ~57 mins. For sample analysis, EPA method 8270/1668C was used for PCB and EPA method 1625A for PAHs. Individual PCB congener analyzed, the retention time and analysis parameters are included in Appendix A.

3.4. Sediment characterization

Sediment samples were dried, and moisture content determined by drying over night at 105^{o} C. Organic content in sediment samples were determined using a TOC analyzer (Elemental, USA). Homogenized sediment samples were spiked with surrogate compounds, seven (7) C^{13} labelled PCB congeners 28, 52, 101, 138, 153, 180 and 209 in the case of PCB analysis, and four (4) deuterated PAHs namely d-fluoranthene, d-chrysene, d-benzo[b]fluoranthene and d-dibenzo(a,h)anthracene for PAH analysis. Samples were extracted with Accelerated Solvent Extraction (ASE 350, Dionex) with a hexane/acetone (3:1, v/v) at 100^{o} C for PCBs analysis and dichloromethane/hexane (4:1, v/v) for PAHs analysis. Individual sample extracts from ASE (~60 mL) were concentrated using Rocket evaporator (Genevac) to a volume of 1-2 mL and cleaned using solid phase extraction (sodium sulphate/florisil for PCBs and silica gel/activated alumina for PAHs). The eluate is desulphurized using copper powder and then concentrated to a final volume of 1 mL. Finally, the resulting eluates were analyzed for PCB congeners and PAH compounds (more details in Appendix A).

3.5. Water sampling

Water samples were collected in 17th November 2016, 7th November 2017 and 19th June 2018, however Liquid-Liquid extraction could not be used in the measurement of the HOCs during the analysis of the first water samples (from 2016) due to the presence of dissolved organic content in the water. Hence, water samples were analyzed for total suspended solids (TSS). A known volume of water sample was passed through a 0.45 um filter paper using a pump. The wet filter was then dried to a constant mass at 50^{o} C for a period of 24 hours.

3.6. Porewater sampling

Porewater concentration was assessed using PDMS fibers and performed by inserting the PDMS in sediment samples. The sediment samples are dosed with 100 mg/L Sodium Azide solution and homogenously mixed before PDMS fibers are deployed for a minimum of 28 days. The obtained porewater water concentration in addition to the bulk sediment concentration was used to determine sediment-water partition coefficient for individual compound.

3.7. Air sampling

Air sampling was performed using passive techniques, specifically using POM sheets. An initial study of the most appropriate passive samplers was conducted using POM and PDMS with the latter showing promising results by providing longer average concentration (details in Appendix A). Hence, Field sampling was conducted using POM samplers at 10 different locations at the IHC-CDF with three (3) separate field efforts conducted on the 7th November 2017, 19th June 2018 and 10th October 2018. Detailed descriptions and individual analytes are discussed in detail in later chapters.

3.8. Quality Assurance and Quality Control (QAQC)

Solvent blanks were included for every 10-sample analysis on the analytical instrument. QAQC samples for chemical analysis include initial calibration, second source standard checks and continuous verification checks, all of which should meet the accepted criterion set for analytical method and/or instrument. A linearity of (≥ 0.995) with a minimum of five (5) point initial calibration (ICAL) and/or a percent relative standard deviation (% RSD) of ≤ 20% for each analyte. Method detection limit (MDL) on analytical instrument was determined with a ratio ≥ 3:1 signal to noise. Practical quantification level (PQL) was determined as the lowest calibration point with an RSD ≤ 20%. For most analysis, samples were analyzed in either duplicates or triplicates (n = 2 or 3) and analyte recovery were assessed using surrogate compounds with acceptance criteria range of 65% - 135%.

Chapter 4

Development of polyoxymethylene passive sampler for assessing air concentrations of PCBs at a confined disposal facility (CDF)

Adesewa A. Odetayo[a], Danny D. Reible[a*], Damarys Acevedo-Mackey[b], Cynthia Price[b], Le Thai[c]

[a] Department of Civil, Environmental and Construction Engineering, Texas Tech University, 911 Boston Avenue, Lubbock. Texas 79409. U.S.A

[b] U. S Army Engineer Research and Development Center, 3909 Halls Ferry Rd., Vicksburg, Mississippi. 39180. U.S.A.

[c] U. S Army Corps of Engineers, Chicago District.

Citation

Odetayo, A. A., Reible, D. D., Acevedo-Mackey, D., Price, C., & Thai, L. (2020). Development of polyoxymethylene passive sampler for assessing air concentrations of PCBs at a confined disposal facility (CDF). *Environmental Pollution*, 114720.

Abstract

In this study, 76 µm polyoxymethylene (POM) strips were evaluated as a passive air sampler (PAS) for monitoring the volatile emissions from dredged material placed in confined disposal facilities (CDF). Laboratory evaluations were used to assess the uptake kinetics, average equilibrium time, and estimate the POM-air partition coefficients (K_{POM-A}) of 16 PCB congeners. The uptake kinetics defined the effective averaging time for air sampling and ranged from about a week for dichlorobiphenyls to 2 weeks or more for tetra- and pentachlorobiphenyls at ~20°C under internal mass transfer resistance control which was applicable for Log $K_{POM-A} < 8$. The measured Log K_{POM-A} for PCBs ranged from 5.65 – 9.34 and exhibited an average deviation of 0.19 log unit from the theoretical value of K_{POM-W}/K_{AW}. The PAS approach was then tested with a preliminary field application (n=17) at a CDF allowing equilibration over 42 days. The field application focused on lower congener PCBs as a result of the estimated increase in K_{POM-A} and longer uptake times expected at the low ambient temperatures during the field study (average of 3.5°C). Total PCB air concentrations around the CDF averaged 0.32 ng/m^3 and varied according to proximity to placement of the dredged materials and predominant wind directions. Average PAS concentration of low congener number PCBs (15, 18, 20/28, 31) were compared to available high volume air sampler (HVAS) measurements. The PAS concentrations were within 20% of HVAS in the dominant north and south directions and showed similar trends as east and west HVAS samplers although PAS concentrations were as much as an order of magnitude below the west HVAS.

Keywords: Passive sampling, polyoxymethylene (POM), PCBs, air sampling, CDF.

4.1. Introduction

Aquatic sediment is typically the ultimate sink for hydrophobic organic contaminants (HOCs) from past industrial activities [1, 2]. Approximately 900 million cubic meters of contaminated sediment are present in U.S surface waters which can pose risks to aquatic organisms and human health [3]. Due to navigation requirements or as a remedial approach, these sediments are often dredged and relocated to a confined disposal facility (CDF) for storage, treatment or disposal [4-6].

CDFs contain ponded waters with suspended contaminated solids as well as porewater from dewatering sediment giving rise to concerns for volatile losses and airborne exposures. Volatile and low solubility compounds such as polychlorinated biphenyls (PCBs) and low molecular weight polycyclic aromatic hydrocarbons (PAHs) may be of particular concern from old industrial harbor sediments being placed within a CDF [7-9]. Active monitoring of airborne contaminants around a CDF is a common means to assess the risks of volatile HOCs and to identify the need for and effectiveness of mitigation approaches [8]. Commonly, high-volume air samplers (HVAS) are used to monitor volatile emissions of both particulate bound and vapor contaminants.

The HVAS uses a pump to trap air through a module that consists of a fiber filter where particulates species are retained and an absorbent where gaseous species are retained. HVAS are typically used to measure short-term (e.g. 24 hour) averages from discrete locations and require multiple analyses to determine regional, time-averaged exposure [10-12]. Usually, dredging activities are ongoing for weeks or longer and longer-term averages are more relevant to long-term risks [11, 13]. The objective of the current work is to evaluate passive sampling as an alternative that can reduce the number of analyses by averaging air concentrations over time as is inherent in the slow uptake and equilibrium of HOCs in a passive sampling media. The study is designed to identify a passive sampler media than can provide sensitive measurement of common HOCs including PCBs and PAHs and appropriate equilibration time to provide a longer-term average air concentration.

Passive sampling techniques has increasingly been adopted for air sampling using a variety of sorbent materials and based on the physicochemical properties of a number of contaminants. Passive air sampler sorbents have included XAD-2 [14, 15], semipermeable membrane devices (SPMDs) using low density polyethylene [16, 17], polyurethane foams (PUF) [18-21], polyethylene [22] and polydimethylsiloxane [23-26]. XAD-2 and PUF are samplers that have often been used to monitor semi-volatile compounds but are sensitive to sampling rates (which suggests the influence of external mass transfer resistances) and have been viewed as semi-quantitative [27].

Passive sampling using polymeric sorbents such as polymethylsiloxane (PDMS), polyethylene (PE) and polyoxymethylene (POM) have gained popularity in assessing freely dissolved contaminants concentrations in water [28-30] and sediment [31-37]. These have not been used extensively for air passive sampling but due to a combination of available geometries (thickness) and intrinsic diffusion rates typically exhibit equilibration times in the order of PDMS<PE<POM[38]. Uptake in POM, which is commercially available only in relatively thick layers (≥76 µm), may be limited by internal diffusion rates slowing uptake and limiting the influence of atmospheric conditions such as wind speed or mass transfer in air. PDMS-air exchange of PAHs have been shown to have kinetics of uptake and release that are too rapid for time-averaged air passive sampling, particularly for low molecular weight PAHs [39]. Polyethylene has been used in some cases [22, 26, 40] and provides somewhat slower kinetics than PDMS [32, 38, 41, 42] but is typically used in relatively thin layers (e.g. 25 µm).

Since our goal is to provide longer time-average sampling, POM was chosen as the polymer sorbent and a standard commercially available thickness of 76 µm was employed to balance relatively rapid uptake of low molecular weight contaminants (such as naphthalene) with relatively slow uptake of higher molecular weight contaminants that are still volatile (e.g. PCB congeners 1-100). Similar to their use in water sampling, the concentration of contaminants accumulated on POM, $C_{POM,eq}$ as a result of exposure to a concentration in air, C_A, is related to the air-polymer partition coefficient, K_{POM-A}, as depicted in equation 4.1.

$$C_{POM,eq} = K_{POM-A} * C_A \tag{4.1}$$

The current study focuses on PCBs and aims to i) assess the uptake and equilibrium time of PCBs on POM from air; ii) establish the POM-air partition coefficients to allow estimates of equilibrium air concentrations; and finally iii) assess the performance of the POM air sampler in a preliminary field application at a CDF including a comparison between the measured concentrations using PAS and that measured using HVAS.

4.2. Materials and Methods

4.2.1. Reagent, Material and Instrument

Methanol, dichloromethane, hexane, and acetone solvents of optima grade quality were purchased from Fisher Scientific (Hampton, NH. USA). Parent PCB standards of all congeners in isooctane for calibration were acquired from AccuStandard (USA). A series of C^{13}PCBs were also acquired from the same source for use as performance reference compounds but these compounds were not successfully loaded uniformly into the POM and were abandoned. Sodium Azide 100 mg/L + 0.01 M calcium chloride solution was prepared and spiked into the sediment slurry employed in laboratory experiments to prevent any degradation of contaminants of interest. All glassware and tools were washed and solvent-rinsed before use.

4.2.2. Sediment and Water PCB measurements

The sediment employed in laboratory slurry experiments was collected from a CDF in the midwestern United States. This same CDF was employed for preliminary field measurements. The bulk solid PCB concentration was measured by using EPA method 3545A for sample preparation, and final extracts analyzed on GC-TQ/MS using EPA method 1668c. Water concentrations were measured in the laboratory slurries as outlined below.

4.2.3. Polymeric samplers

The polymeric samplers used for air sampling in this study were 76 µm thick POM sheets. Polydimethylsiloxane fiber (PDMS ~34 µm layer on a 500 µm glass core, 0.5 µL PDMS/cm) was used to measure water slurry concentrations. The polymeric materials were purchased from CS Hyde Company, Lake Villa, USA (POM) and Polymicro Technologies, Phoenix, USA (PDMS). Prior to deployment and use, POM was segmented into masses of 20 mg ± 0.1 mg and 200 mg ± 0.1 mg for laboratory and field studies respectively, and PDMS fiber were segmented into 5 cm lengths. The polymers were then cleaned through extraction with solvents, twice with hexane, dichloromethane, and methanol sequentially for 30 minutes each, and finally rinsed with de-ionized water (GenPure Pro UV, Thermo Scientific, USA). The cleaned polymeric samplers were left to dry in a fume hood.

4.2.4. Laboratory Experiments

A series of laboratory experiments were conducted to evaluate kinetics and equilibrium uptake into the POM using PCB contained in a sediment from a midwestern harbor CDF. The contaminated sediment contained 14 mg/kg PCBs ($\sum_{124}$PCBs) and were exposed to a POM sampler in the airspace of a closed vessel at laboratory temperatures (~20 ^{o} C) (selected PCB congener concentrations in SI). POM strips were prepared (20 mg ± 0.1 mg) and then exposed to the headspace of a sediment slurry in 120 mL amber jars. Each jar contained approximately 22 g of sediment dosed with 100 mg/L + 0.01 M calcium chloride solution to make a 40 mL slurry. PDMS was added to the slurry phase for water concentration measurements. After setup, the caps were taped with parafilm to prevent volatile losses of contaminants of concern, then agitated using a one-directional mechanical shaker at 45 rpm to keep sediment suspended in the slurry without contacting the POM strip. Individual jars were sacrificed at 1, 3, 7, 14 and 28 days. After retrieval at the end of each sampling period, the polymers were cleaned using Kim-wipes wetted with de-ionized water. Extraction of the POM sampler was performed using a mixture of Hexane: Acetone (1:1, v/v) and the PDMS fiber was extracted with hexane. The extracts were vortexed after an extraction period of 24 hours and spiked with internal standards before analysis. 16 PCB congeners (1-10, 19, 33, 52, 101, 153, and 180) that were likely to be present (based on chemical analysis of the sediment samples) were analyzed and quantified. The mixing of the water and the resulting air movement were expected to minimize fluid side (external) resistances to uptake for both the POM (from the air headspace) and the PDMS (from water). PDMS uptake from the slurry water achieved equilibrium within 3 days for all congeners measured. POM uptake kinetics are much slower and discussed in more detail below.

4.2.5. Preliminary deployment of POM Air samplers (PAS) at the CDF site

The location chosen for this study is a 90 acre CDF in the midwestern United States oriented along a north-south axis and surrounded by active industrial activity as well as a nearby community that includes commercial, industrial and residential activities. The CDF is constantly ponded with water to reduce direct volatile losses of contaminants from dredged material and equipped with a groundwater gradient control system, slurry cutoff walls, and clay dikes to control subsurface migration. The CDF contains two (2) cells separated by a dike and dredged materials are periodically placed into one or both cells during dredging operations in a nearby harbor. POM PAS were deployed between Nov 7, 2017 and Dec 19, 2017. Dredged materials had been placed in the west cell but active dredging had ceased just prior to the start of the sampling effort. HVAS and weather stations were located around the perimeter of the CDF at four locations (south, east, west and the north). A total of ten (10) PAS were deployed at different locations including nine (9) PAS around the perimeter of the CDF and along the centerline of the CDF (north (N), south (S), east (E), west (W), northwest (NW), center (C), northeast (NE), southwest (SW), and southeast (SE) and one (1) in the direction of the administrative offices at the CDF (AD). PAS were deployed close to but not immediately adjacent to the HVAS stations. This was not expected to pose a problem for comparing exposures north and south since these stations were along the axis of the CDF (long fetch) and in dominant wind directions. The east and west sampling stations, perpendicular to the primary axis of the CDF, however, were observed to be sensitive to wind direction and placement of the dredged material (Figure 4.1). East and west samplers also had the widest separation between the locations of the HVAS and the PAS.

For the deployment, the POM strips (200 ± 0.1 mg) were transported on ice at 4^{o}C to the field and assembled onsite. The PAS was retrieved after 42 days, processed in the field including a rinse and wipe to remove any adhered particulates and extracted with methanol solvent into a 2 mL vial. All vials were labelled and transported at 4 ^{o} C to the laboratory where they were stored at -17 ^{o} C until analysis. A second extraction into acetone/hexane was performed to ensure complete extraction of the PCBs using methanol. Prior to analysis, the extracts were exchanged into hexane for analysis. 52 PCB congeners were present above practical quantification limits during extract analysis.

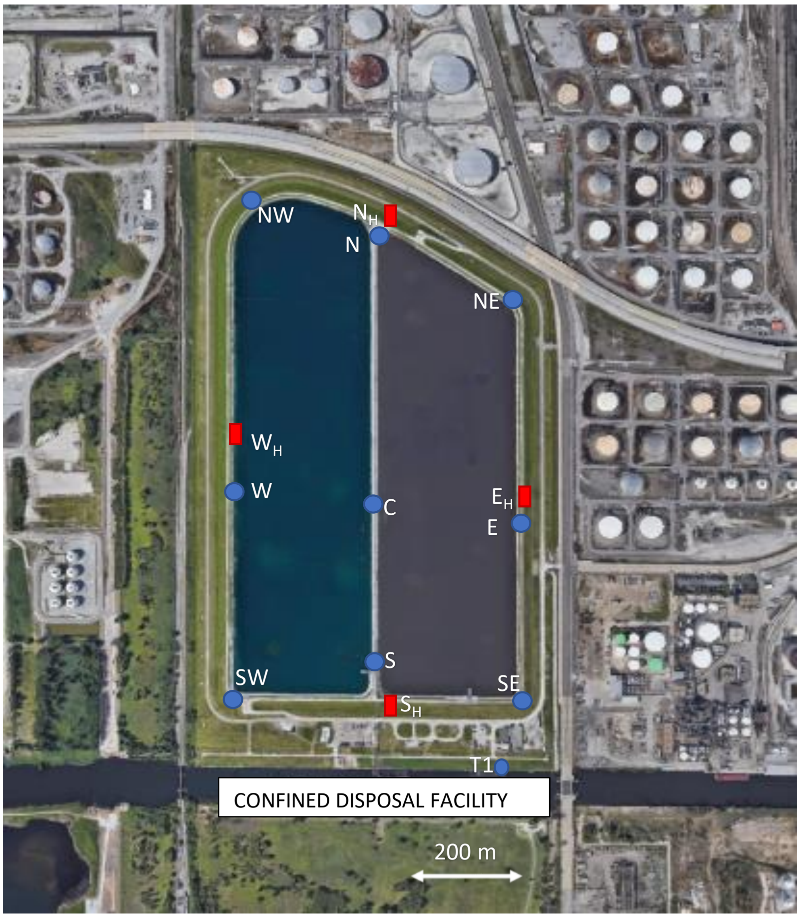


Figure 4.1. Overhead picture of the CDF and the surrounding industrial areas showing the 10 locations for PAS with 9 location around the perimeter of the CDF and a location AD near the administration office, and 4 locations for HVAS at the four cardinal directions namely S_H, E_H, N_H and W_H.

4.2.6. Meteorological data at the CDF

Four weather stations (wind speed, direction and temperature) were located south, east, west and north of the CDF. The weather data from the four weather stations were consolidated using WRPLOT View-Version 8.0.2 (Lakes Environmental, USA) to determine the frequency distribution of the wind speed and direction during the period of deployment at the CDF (Data in SI). The weather condition indicated that the wind was predominantly from the south with a westerly component and with minimal winds from the east. The air temperature ranged from -5^{o} C to 12^{o} C with an average of 3.5 ± 1.5 °C. The average wind speed measured at a height of 10 meters was 4.6 ± 2.7 m/s.

4.2.7. Instrument analysis and Quality control

Sample analysis was performed using a Gas Chromatography-Triple Quad/Mass Spectrophotometer (GC-TQ/MS) (Agilent technologies 7890 GC with 7000 MS/MS) with modified EPA method 1668c for PCBs. The GC-TQ/MS was set up to quantify 131 PCB congeners (124 parent and 7 C^{13} labeled congeners) although the laboratory experiments focused only on 16 PCB congeners. All extracts from POM samplers were analyzed in triplicate (n= 3) during the laboratory study and either in duplicates or triplicates (n=2 or 3) during the field study. Method and sample blanks were analyzed for each batch of samples and showed no interference with measured air concentrations. All data below the practical quantification limit (PQL) of the lowest calibration point were excluded. PQL was determined as the lowest calibration point with a RSD of ≤ 20%. Calibration curves were linear with $R^2 \geq 0.999$ and relative standard deviations of ≤ 20% deviation over the calibration range. The HVAS were operated as part of normal operations at the CDF. HVAS data for PCB congeners 15, 18, 20/28 and 31 during the preliminary deployment were collected and are publicly available from the U.S Army Corps of Engineers [43]. These specific congeners were selected for reporting by the USACE because they were commonly observed in contaminated dredged material placed in the CDF. The HVAS pulls about 300 m^3 ambient air at a flowrate of approximately 200-280 L/min through a glass fiber filter combined with PUF/XAD-2 sorbent media over a 24 hour period. The filter and sorbent were extracted together and the reported HVAS data represents a combined concentration of vapor and particulate PCBs in air.

4.3. Results and discussion

4.3.1. Dissolved PCB concentrations in laboratory slurries

The dissolved PCB concentration ($C_{W,\mathrm{eq}}$) in sediment slurries was measured using the polydimethylsiloxane (PDMS) passive samplers during the laboratory experiments. The porewater concentration ranged from 0.003 – 67 ng/L for the 16 PCB congeners monitored during this experiment (Table S1). The measured C_W and bulk sediment concentration was used to estimate the slurry sediment-water partition coefficients (K_d) (details in SI). The measured K_d correlated with octanol-water partition coefficients (K_{OW}) [44] (R^2= 0.94) (Figure S1) and gave organic carbon normalized K_{oc}'s and K_d's approximately 1 log unit above literature values [45-47], presumably as a result of partitioning to black carbon and weathered sediment phases.

No independent measurements of air concentration in the laboratory vessels were attempted. Instead, the air concentration, $C_{A,eq}$ can be expressed as a function of POM-air partition coefficients from equation 1 or from air-water equilibrium using the measured water concentration from equation 4.2.

$$C_{A,eq} = K_{AW} * C_{w,eq} \tag{4.2}$$

K_{AW} is the air-water partition coefficient (Henry's Constant) and, $C_{w,\mathrm{eq}}$ is the concentration in water at equilibrium. K_{AW} is expected to be known with greater accuracy than $K_{POM\text{-}A}$ and thus the air concentration defined by equation 4.2 will be referred to as the laboratory "measured" concentration while the air concentration defined by equation 4.1 will be referred to as the "estimated" concentration and compared.

At equilibrium in the three phase system (air, water, POM), $C_{POM,eq}$ can also be expressed as a function of polymer-water partition coefficients as shown in equation 4.3

$$C_{POM,eq} = K_{POM-W} * C_{w,eq} \tag{4.3}$$

$K_{POM\text{-}W}$ is defined as the partition coefficient between polyoxymethylene and water. The combination of equations 4.2 and 4.3 suggests that the POM-Air partition coefficient ($K_{POM\text{-}A}$) can be related to the POM-water partition coefficient ($K_{POM\text{-}W}$) [48] and air-water partition coefficient (K_{AW}) [49] as shown in the relationship in equation 4.4

$$K_{POM-A} = \frac{K_{POM-W}}{K_{AW}} \tag{4.4}$$

Thus the equilibrium air concentration can be estimated from Equation 1 using the observed POM concentrations divided by $K_{POM\text{-}A}$ from Equation 4.4 (the "theoretical" air concentration) or estimated directly by the measured water concentration times K_{AW} ("measured" air concentration). The measured Log $K_{POM\text{-}A}$ for selected PCBs ranged from 5.65 – 9.34 log units as shown in Table S2. The measured Log $K_{POM\text{-}A}$ deviation from the theoretical Log $K_{POM\text{-}A}$ ranged between 0.1 – 1 log units but the average deviation was 0.19 log units and the correlation coefficient (R^2) between the two estimates was 0.85.

A comparison of the two approaches to the estimation of $K_{POM\text{-}A}$ is shown in Figure 4.1. A two-tail student t-test indicates no significant difference exists between the air concentrations estimates. The uncertainty in the measurement of POM-water coefficient has previously been estimated to be in the range of 0.15- 0.5 log units [34-36, 50] and could be as high as ± 1 log units [30, 35] for individual PCB congeners. A factor of 2 (0.3 log units) is generally considered to be the typical accuracy of individual estimates of $K_{POM\text{-}W}$ [32] and is shown in the broken lines of Figure 4.2. Applying this error estimate to $K_{POM\text{-}A}$ assumes that the error in K_{AW} is negligible.

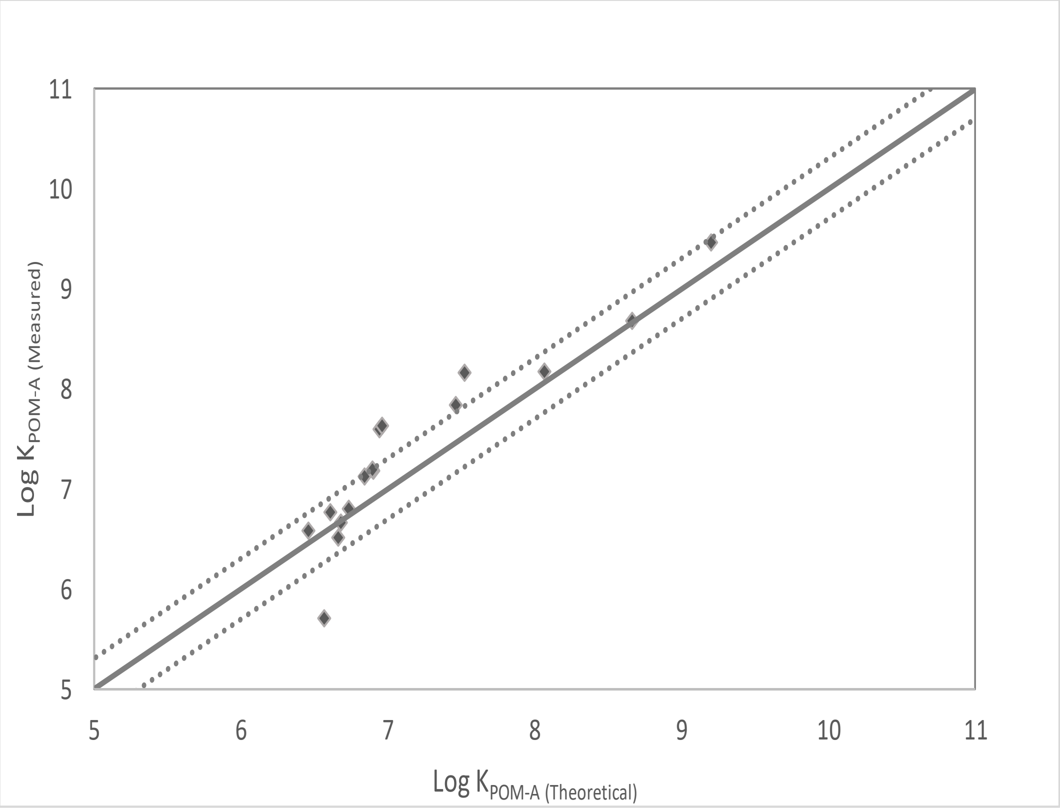


Figure 4.2. Comparison of $K_{POM\text{-}A}$ estimated from the equation 4.4 (theoretical) versus that estimated from the measured POM and water concentrations (using equations 4.1 and 4.2). The dotted lines represent a factor of 2 around the prediction of $K_{POM\text{-}A}$ for individual congeners (0.3 log units) around the 1:1 (thick line).

The measured $K_{POM\text{-}A}$ can also be directly correlated with the octanol-air partition coefficient, K_{OA} [51, 52] to obtain a prediction model as shown in Figure 3. To predict the $K_{POM\text{-}A}$ of an unknown PCB compound at ~20°C, equation 4.5 can be utilized.

$$Log\ K_{POM-A} = 0.73\ Log\ K_{OA} + 1.4 \qquad \mathrm{R}^2 = 0.85,\ \ \mathrm{n} = 16 \qquad (4.5)$$

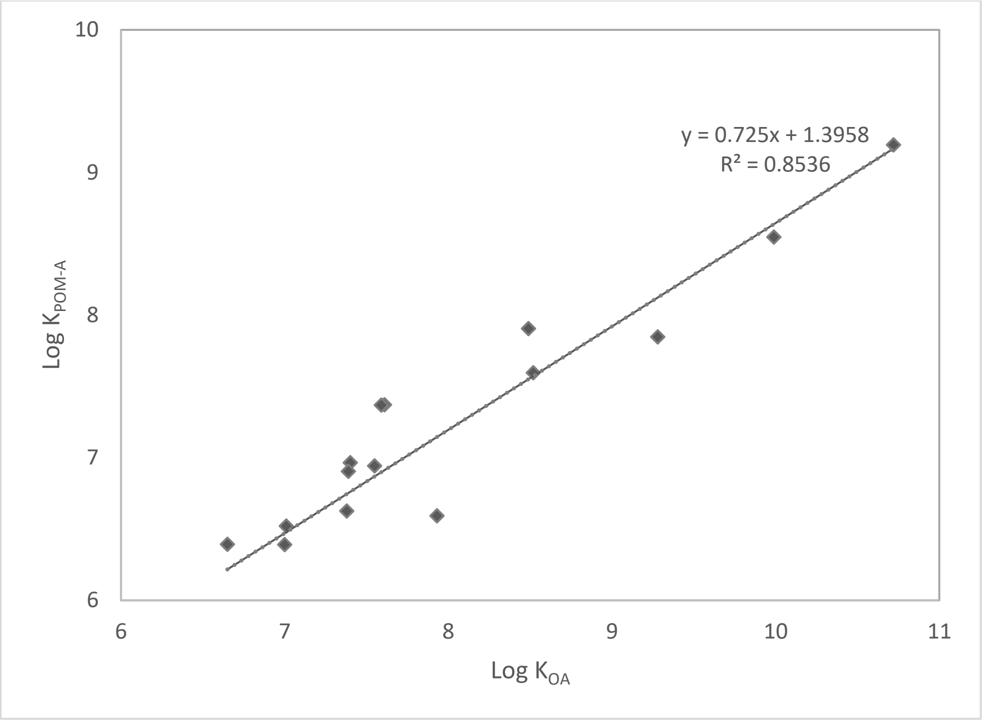


Figure 4.3. Plot of log $K_{POM\text{-}A}$ for selected PCBs as a function of log Koa [10, 52].

4.3.2. Uptake kinetics and equilibrium on POM sampler

Figure 4.4 shows the uptake kinetics of 6 PCB congeners (4, 10, 19, 33, 52, and 101) onto POM from air in the laboratory experiments. At laboratory temperatures of approximately 20 °C, the low congener number (LCN) PCBs (dichlorobiphenyls and PCB 19) reached steady state in approximately 7-10 days while the high congener number (HCN) PCBs (PCB 33 and larger) required 14-28 days. PCB 101 uptake was slowing after 14 days although it may not have been at steady state even at 28 days. Uptake on PCB 153 and PCB 180 were also measured but these congeners showed little apparent time dependence and very low concentrations, indicating that much longer exposures would be required to measure air concentrations. However, these compounds are unlikely to evaporate at significant levels to the air above the CDF due to their strong sorption onto the solids at the bottom of the impoundment. This was reflected in the low concentrations of PCBs in the sediment slurries with more than 80% of the water concentration associated with PCB 53 and lighter. The evaporative flux should be approximately proportional to the water concentration of the PCBs. The uptake of contaminants on POM as a function of time can be fitted to a first order model shown in equation 4.6.

$$C_{POM} = C_{POM,eq} * \left(1 - e^{-\frac{t}{\tau}}\right) \tag{4.6}$$

where C_{POM} is the concentration on the POM sampler at any time, τ is the characteristic time for uptake, and $C_{POM,eq}$ is the concentration on the POM sampler at equilibrium. The time to steady state was taken as approximately 3τ (95% of steady state).

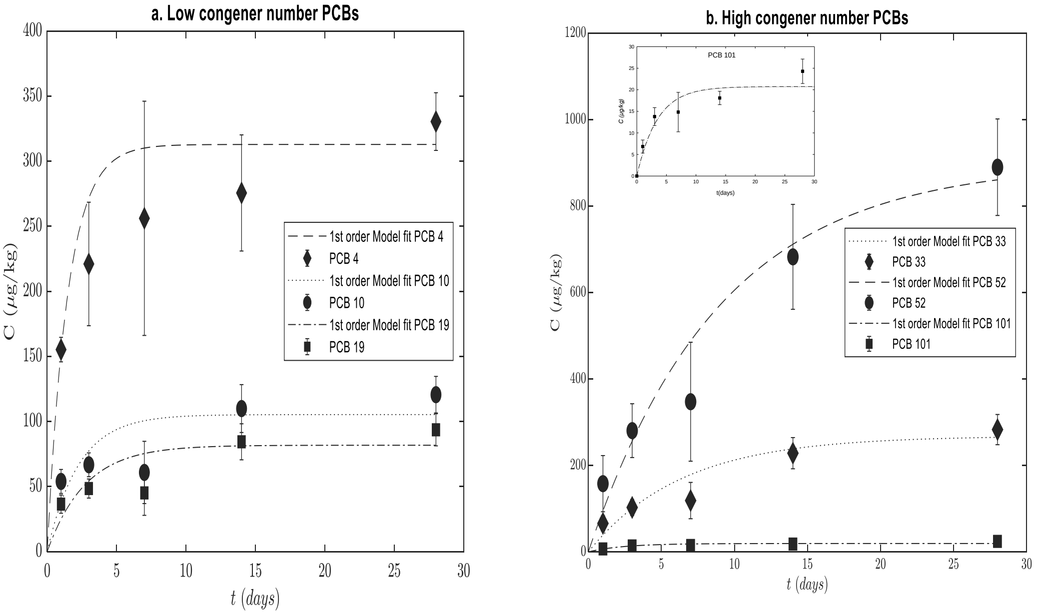


Figure 4.4. Mass uptake on the POM (µg/kg) versus time (days) of a) LCN; b) HCN PCB congeners on POM sampler.

The time to steady state was compared with $K_{POM\text{-}A}$. Compounds with Log $K_{POM\text{-}A}$ of <6.75 required 14 days or less, 6.75-7.25 required 14-30 days and 7.5-8 required 35-50 days.

External (air) resistances could lead to further increases in time to steady state beyond that estimated from the laboratory experiments. The overall uptake resistance can be estimated from a form of two film theory,

$$F = KC_{\infty} = k_A(C_{\infty} - C_{POM}) = \frac{\mathcal{D}}{\delta/2} K_{POM-A} C_{POM} \tag{4.7}$$

$$\frac{1}{K} = \frac{1}{k_A} + \frac{\delta}{2K_{POM-A}\mathcal{D}} \tag{4.8}$$

Where internal resistance controls when $K_{POM-A} \leq \frac{k_A \delta}{2\mathcal{D}}$

Here K represents an overall mass transfer coefficient, and k_A is an air-side mass transfer coefficient, $\mathcal{D}$ is the diffusion coefficient in the POM and δ is the total thickness of POM. For k_A in the atmosphere of the order of 10^3 cm/hr [53], and $\mathcal{D} \sim 10^{-15} m^2 / s$ [31, 54, 55] for a mid-range PCB, $K_{POM-A} \leq 10^8$ is expected to be controlled by internal POM resistances. Compounds with $K_{POM-A} >> 10^8$ would be expected to result in significantly slower uptake due to the increasing importance of external mass transfer resistances.

During the low temperatures of the field experiments (average of 3.5°C) the Log K_{POM-A} of the target compounds was estimated to increase. At the average temperature of 3.5 °C, K_{POM-W} and K_{AW} required correction in order to estimate K_{POM-A} by Equation 4.4. Of these partitioning coefficients, K_{AW} is the most temperature dependent with minor influences on K_{POM-W} and diffusion coefficients in the POM over typical ambient temperature ranges. K_{POM-A} was estimated from K_{POM-W} and K_{AW}. These parameters were estimated at reference temperature (25°C) from Hawthorne, Miller and Grabanski [48] and Dunnivant, Elzerman, Jurs and Hasan [49] respectively for individual PCB congeners. The internal energy of phase transfer (ΔU_{PCB}/KJ/mole) from polymer to water and air to water for the contaminants of interest were estimated from Lohmann [26] and Li, et al. [56], respectively. A van't Hoff relationship was used to correct K_{POM-A} to the average temperature measured during the field sampling. The Log K_{POM-A} was estimated to increase to between 7.3 and 8 for the target low congener number PCBs suggesting that an exposure of 30-50 days would be required to achieve steady state assuming internal diffusion control based on the time to steady state of similar K_{POM-A} compounds in the laboratory study. Log K_{POM-A}, for example, increased from 6.57 to 7.33 for PCB 4 and from 6.73 to 7.53 for PCB 19. The field sampling was continued for 42 days and assumed to achieve equilibrium for all of the LCN PCBs. Midrange (e.g. PCB 101) and HCN PCBs would be expected to exhibit slow uptake kinetics and be influenced by external mass transfer resistances at the lower temperature and would not likely achieve steady state uptake over the 42 days.

4.3.3. Air concentration of PCB congeners at the CDF

The total air concentration for the PCB congeners (sum of all 52 detected congeners from total of 131 scanned) measured approximately 0.32 ng/m^3 (n = 17) across all 10 locations over the 42 day sampling period. Although the HCN PCBs were likely not equilibrated with the POM, the contribution of these congeners to evaporative losses from the CDF would be expected to be small compared to the LCN PCBs due to their higher partition coefficients and therefore much lower water column concentrations. The air concentration of the PCB congeners measured by the PAS showed some variability across the 10 locations, as depicted in Figure 4.5 with locations AD, S, N, NW, and C exhibiting higher (~factor of 3) concentrations compared to other locations.

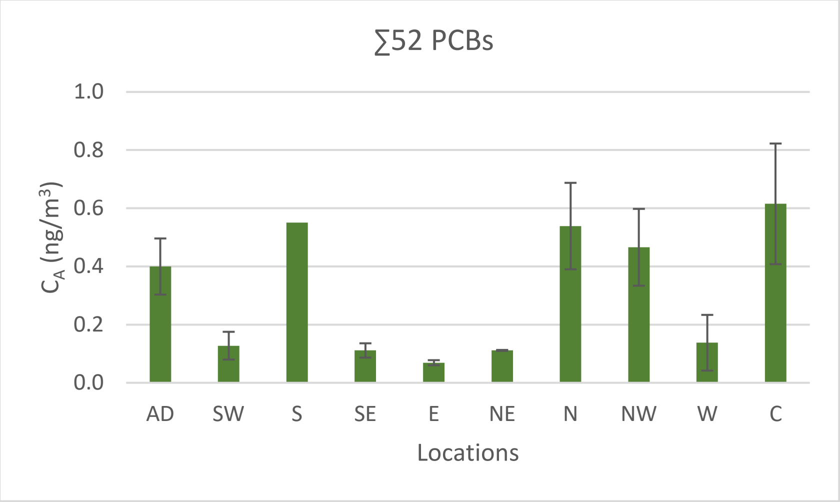


Figure 4.5. Sum of atmospheric PCBs at PAS location.

The high concentrations measured at locations S, N, and C suggests the influence of proximity of PAS to the location of placement of dredged sediment and the dominant wind directions (Figure S3). These locations are located downwind of relatively long fetches of the CDF, likely increasing air concentrations due to greater evaporation and reducing the influence of small changes in wind direction.

4.3.4. Comparison between PAS and HVAS of PCB congeners 15, 18, 20/28 and 31

The PCB congeners 15, 18, 20/28, and 31 were measured both by PAS and HVAS and could be compared. These LCN PCBs exhibit relatively high vapor pressure, are present in high concentrations in the CDF impoundment and would be expected to dominate the air concentrations as well as achieve equilibrium over the 42 day sampling period. The HVAS measurements were 24 hour averages every 7 days and the average of 6 weeks of samples were compared to the PAS measurements. The result of the comparison (Table 4.1) showed that the average PAS air concentrations of the LCN PCBs when compared to the closest HVAS location were within 20% at the north and south locations and not statistically different ($p<0.05$). The north and south locations are expected to be the major locations influenced by activities at the CDF based on the wind directions and proximity to placed dredged materials (Figure 4.1). The north and south sampling locations were also oriented along the primary axis of the CDF and less sensitive to any physical separation between the HVAS and PAS sampling equipment. Larger differences (as much as a factor of 10 difference) in absolute air concentrations were observed between PAS and HVAS at the east and west locations. The east and west HVAS locations were not co-located with the PAS and these directions were also expected to be the most sensitive to wind direction and the placement location of the dredged material due to the small distance between the source areas and the samplers. The HVAS and PAS concentrations were still well correlated at all locations, that is, proportional with high correlation coefficient, despite being significantly different in absolute magnitude at the east and west locations. That is, the PAS and HVAS showed similar trends despite being quantitatively different at the east and west locations.

Table 4.1. Comparison between PAS and HVAS for PCBs 15, 18, 20/28, 31 (mean ± S.D)

Locations	**Samplers**	**PCB Congeners (pg/m^3)**				**P value**	**R^2**
		PCB 15	**PCB 18**	**PCB 20/28**	**PCB 31**		
South	PAS	23.6	70.4	57.2	48		
	HVAS	14.5±9.12	69.5±52.1	48.1±23.2	44.5±20.2	0.001	0.998
East	PAS	4.83±1.05	9.03±3.17	8.12±2.62	8.01±2.12		
	HVAS	11.2±2.09	36.4±29.9	30.8±13.9	28.2±11.9	0.004	0.991
North	PAS	20.8±5.17	67.6±8.85	56.8±8.84	48.5±13.2		
	HVAS	27.7±13.9	104±105	91.6±64.4	86.6±63.7	0.032	0.937
West	PAS	6.51±2.72	17.2±11.5	14.4±7.45	12.5±8.29		
	HVAS	37.4±19.4	184±156	148 ±73.1	138±65.7	0.039	0.923

Unlike HVAS, which measures PCB congeners in both the gaseous and particulate phase, PAS, as a partitioning sorbent, would measure only the gaseous

PCBs. Some particulates may attach to the POM although these are removed as much as possible by rinsing and wiping prior to analysis. Note that evaporation occurs from the dissolved phase and thus volatile losses from a stagnant pond would not be expected to be associated with particulate or aerosol phases immediately adjacent to that pond. Thus, the use of PAS may be more selective at identifying the contributions to airborne PCBs due to evaporative losses from the CDF than the HVAS which may be influenced by particulate associated PCBs from other sources.

4.4. Conclusions

PAS compared to HVAS techniques are easier to deploy, economical in terms of analytical cost due to the reduced number of samples required [10, 12], and provide long time averaged air concentrations of PCB congeners (>30 days at temperatures < 5°C although 7-35 days for LCN PCBs at temperatures >20 °C)). The polyoxymethylene is a suitable passive air sampler for long-term monitoring of contaminants in the air because of its slow uptake and slow desorption kinetics. The POM sampler will also only measure partitioning contaminants rather than particulate associated contaminants and thus may be a more sensitive indicator of evaporative losses from the CDF. Limiting the usefulness of POM samplers, however, is the variation in uptake time as a function of hydrophobicity of the sorbate and the sensitivity to temperature of exposure. These effects are apparently common to all passive air samplers but the POM appears to have the advantage, at least for more volatile compounds, of an uptake time controlled by internal diffusion and therefore independent of air flow and sampling rate.

Acknowledgements

We wish to acknowledge the funding and field support from the U.S Army Engineer Research and Development Center, Vicksburg Mississippi and the U.S Army of Corps of Engineers, Chicago District.

References

1. Perelo, L. W., In situ and bioremediation of organic pollutants in aquatic sediments. *J. Hazard. Mater.* 2010, *177*, (1-3), 81-89.

2. USEPA Superfund Contaminated Sediments. https://www.epa.gov/superfund/superfund-contaminated-sediments (June 27, 2019).

3. SERDP-ESTCP Management of Contaminated Sediments. *https://www.serdp-estcp.org/News-and-Events/Blog/Management-of-Contaminated-Sediments* (June 27, 2019).

4. Calmano, W.; Weilershaus, S.; Förstner, U., Dredging of contaminated sediments in the Weser estuary: Chemical forms of some heavy metals. *Environ. Technol.* 1982, *3*, (1-11), 199-208.

5. Palermo, M. R.; Wilson, J. In *Corps of Engineers Role In Contaminated Sediment Management And Remediation*, American Bar Association, Section of Environment, Energy, and Resources, New Orleans, LA, 2000; New Orleans, LA, 2000.

6. Palermo, M. R.; Schroeder, P. R.; Estes, T. J.; Francingues, N. R. *Technical guidelines for environmental dredging of contaminated sediments*; ENGINEER RESEARCH AND DEVELOPMENT CENTER VICKSBURG MS ENVIRONMENTAL LAB: 2008.

7. USACE *Conceptual CDF design for inner Harbor Navigation canal lock replacement project.*; 2008.

8. Bridges, T. S.; Gustavson, K. E.; Schroeder, P.; Ells, S. J.; Hayes, D.; Nadeau, S. C.; Palermo, M. R.; Patmont, C., Dredging processes and remedy effectiveness: Relationship to the 4 Rs of environmental dredging. *Integrated environmental assessment and management* 2010, *6*, (4), 619-630.

9. Price, C., et al. *Prediction of volatile losses from contaminated exposed sediments*; 1999.

10. Harner, T.; Bartkow, M.; Holoubek, I.; Klanova, J.; Wania, F.; Gioia, R.; Moeckel, C.; Sweetman, A. J.; Jones, K. C., Passive air sampling for persistent organic pollutants: Introductory remarks to the special issue. *Environ. Pollut.* 2006, *144*, (2), 361-364.

11. USACE IHC CDF Air Quality Monitoring. https://www.lrc.usace.army.mil/Missions/Civil-Works-Projects/Indiana-Harbor/Air-Quality-Monitoring/.

12. Greenwood, R.; Mills, G.; Vrana, B., *Passive sampling techniques in environmental monitoring*. Elsevier: 2007.

13. Miller, J., Great Lakes Confined Disposal Facilities. *Buffalo NY: USACE/USEPA* 2003.

14. Baek, S.-Y.; Choi, S.-D.; Chang, Y.-S., Three-year atmospheric monitoring of organochlorine pesticides and polychlorinated biphenyls in polar regions and

the South Pacific. *Environmental science & technology* 2011, *45*, (10), 4475-4482.

15. Wania, F.; Shen, L.; Lei, Y. D.; Teixeira, C.; Muir, D. C., Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere. *Environmental science & technology* 2003, *37*, (7), 1352-1359.

16. Lohmann, R.; Corrigan, B. P.; Howsam, M.; Jones, K. C.; Ockenden, W. A., Further developments in the use of semipermeable membrane devices (SPMDs) as passive air samplers for persistent organic pollutants: field application in a spatial survey of PCDD/Fs and PAHs. *Environ. Sci. Technol.* 2001, *35*, (12), 2576-2582.

17. Ockenden, W. A.; Corrigan, B. P.; Howsam, M.; Jones, K. C., Further developments in the use of semipermeable membrane devices as passive air samplers: Application to PCBs. *Environ. Sci. Technol.* 2001, *35*, (22), 4536-4543.

18. Ahrens, L.; Harner, T.; Shoeib, M., Temporal variations of cyclic and linear volatile methylsiloxanes in the atmosphere using passive samplers and high-volume air samplers. *Environmental science & technology* 2014, *48*, (16), 9374-9381.

19. Chaemfa, C.; Barber, J. L.; Kim, K.-S.; Harner, T.; Jones, K. C., Further studies on the uptake of persistent organic pollutants (POPs) by polyurethane foam disk passive air samplers. *Atmospheric Environment* 2009, *43*, (25), 3843-3849.

20. Persoon, C.; Hornbuckle, K. C., Calculation of passive sampling rates from both native PCBs and depuration compounds in indoor and outdoor environments. *Chemosphere* 2009, *74*, (7), 917-923.

21. Strandberg, B.; Julander, A.; Sjöström, M.; Lewné, M.; Akdeva, H. K.; Bigert, C., Evaluation of polyurethane foam passive air sampler (PUF) as a tool for occupational PAH measurements. *Chemosphere* 2018, *190*, 35-42.

22. Khairy, M. A.; Lohmann, R., Field calibration of low density polyethylene passive samplers for gaseous POPs. *Environ. Sci.: Process. Impacts* 2014, *16*, (3), 414-421.

23. Okeme, J. O.; Yang, C.; Abdollahi, A.; Dhal, S.; Harris, S. A.; Jantunen, L. M.; Tsirlin, D.; Diamond, M. L., Passive air sampling of flame retardants and plasticizers in Canadian homes using PDMS, XAD-coated PDMS and PUF samplers. *Environ. Pollut.* 2018, *239*, 109-117.

24. Okeme, J. O.; Saini, A.; Yang, C.; Zhu, J.; Smedes, F.; Klánová, J.; Diamond, M. L., Calibration of polydimethylsiloxane and XAD-pocket passive air samplers (PAS) for measuring gas-and particle-phase SVOCs. *Atmos. Environ.* 2016, *143*, 202-208.

25. Tromp, P. C.; Beeltje, H.; Okeme, J. O.; Vermeulen, R.; Pronk, A.; Diamond, M. L., Calibration of polydimethylsiloxane and polyurethane foam passive air samplers for measuring semi volatile organic compounds using a novel exposure chamber design. *Chemosphere* 2019, *227*, 435-443.

26. Lohmann, R., Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environmental science & technology* 2011, *46*, (2), 606-618.

27. Melymuk, L.; Bohlin, P.; Sáňka, O. e.; Pozo, K.; Klánová, J., Current challenges in air sampling of semivolatile organic contaminants: sampling artifacts and their influence on data comparability. *Environ. Sci. Technol.* 2014, *48*, (24), 14077-14091.

28. Ouyang, G.; Zhao, W.; Bragg, L.; Qin, Z.; Alaee, M.; Pawliszyn, J., Time-weighted average water sampling in Lake Ontario with solid-phase microextraction passive samplers. *Environ. Sci. Technol.* 2007, *41*, (11), 4026-4031.

29. Belles, A.; Mamindy-Pajany, Y.; Alary, C., Simulation of aromatic polycyclic hydrocarbons remobilization from a river sediment using laboratory experiments supported by passive sampling techniques. *Environ. Sci. Pollut. R.* 2016, *23*, (3), 2426-2436.

30. Perron, M. M.; Burgess, R. M.; Suuberg, E. M.; Cantwell, M. G.; Pennell, K. G., Performance of passive samplers for monitoring estuarine water column concentrations: 1. Contaminants of concern. *Environ. Toxicol. Chem.* 2013, *32*, (10), 2182-2189.

31. Lampert, D. J.; Sarchet, W. V.; Reible, D. D., Assessing the effectiveness of thin-layer sand caps for contaminated sediment management through passive sampling. *Environmental science & technology* 2011, *45*, (19), 8437-8443.

32. Ghosh, U.; Driscoll, S. K.; Burgess, R. M.; Jonker, M. T. O.; Reible, D.; Gobas, F.; Choi, Y.; Apitz, S. E.; Maruya, K. A.; Gala, W. R.; Mortimer, M., Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. *Integrated Environmental Assessment and Management* 2014, *10*, 210-223.

33. Arp, H. P. H.; Hale, S. E.; Kruså, M. E.; Cornelissen, G.; Grabanski, C. B.; Miller, D. J.; Hawthorne, S. B., Review of polyoxymethylene passive sampling methods for quantifying freely dissolved porewater concentrations of hydrophobic organic contaminants. *Environ. Toxicol. Chem.* 2015, *34*, (4), 710-720.

34. Beckingham, B.; Ghosh, U., Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field. *Chemosphere* 2013, *91*, (10), 1401-1407.

35. Cornelissen, G.; Arp, H. P. H.; Pettersen, A.; Hauge, A.; Breedveld, G. D., Assessing PAH and PCB emissions from the relocation of harbour sediments using equilibrium passive samplers. *Chemosphere* 2008, *72*, (10), 1581-1587.

36. Oen, A. M.; Janssen, E. M.; Cornelissen, G.; Breedveld, G. D.; Eek, E.; Luthy, R. G., In situ measurement of PCB pore water concentration profiles in activated carbon-amended sediment using passive samplers. *Environ. Sci. Technol.* 2011, *45*, (9), 4053-4059.

37. Jonker, M. T.; Koelmans, A. A., Polyoxymethylene solid phase extraction as a partitioning method for hydrophobic organic chemicals in sediment and soot. *Environ. Sci. Technol.* 2001, *35*, (18), 3742-3748.

38. Lampert, D.; Thomas, C.; Reible, D., Internal and external transport significance for predicting contaminant uptake rates in passive samplers. *Chemosphere* 2015, *119*, 910-916.

39. Thomas, C. L.; Reible, D. D., Modeling compound loss from polydimethylsiloxane passive samplers. *J. Chromatogr. A* 2015, *2*, (4), 611-624.

40. Apell, J. N.; Gschwend, P. M., The atmosphere as a source/sink of polychlorinated biphenyls to/from the Lower Duwamish Waterway Superfund site. *Environ. Pollut.* 2017, *227*, 263-270.

41. Endo, S.; Hale, S. E.; Goss, K.-U.; Arp, H. P. H., Equilibrium partition coefficients of diverse polar and nonpolar organic compounds to polyoxymethylene (POM) passive sampling devices. *Environ. Sci. Technol.* 2011, *45*, (23), 10124-10132.

42. Nam, G.-U.; Bonifacio, R. G.; Kwon, J.-H.; Hong, Y., Kinetics and equilibrium partitioning of dissolved BTEX in PDMS and POM sheets. *Environ. Sci. Pollut. R.* 2016, *23*, (18), 18901-18910.

43. USACE, High volume air sampler Data. 2018.

44. Hawker, D. W.; Connell, D. W., Octanol-water partition coefficients of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* 1988, *22*, (4), 382-387.

45. Karickhoff, S. W.; Brown, D. S.; Scott, T. A., Sorption of hydrophobic pollutants on natural sediments. *Water Res.* 1979, *13*, (3), 241-248.

46. Baker, J. R.; Mihelcic, J. R.; Luehrs, D. C.; Hickey, J. P., Evaluation of estimation methods for organic carbon normalized sorption coefficients. *Water environment research* 1997, *69*, (2), 136-145.

47. Hansen, B. G.; Paya-Perez, A. B.; Rahman, M.; Larsen, B. R., QSARs for Kow and Koc of PCB congeners: a critical examination of data, assumptions and statistical approaches. *Chemosphere* 1999, *39*, (13), 2209-2228.

48. Hawthorne, S. B.; Miller, D. J.; Grabanski, C. B., Measuring low picogram per liter concentrations of freely dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. *Anal. Chem.* 2009, *81*, (22), 9472-9480.

49. Dunnivant, F. M.; Elzerman, A. W.; Jurs, P. C.; Hasan, M. N., Quantitative structure-property relationships for aqueous solubilities and Henry's law constants of polychlorinated biphenyls. *Environ. Sci. Technol.* 1992, *26*, (8), 1567-1573.

50. Hale, S.; Kwon, S.; Ghosh, U.; Werner, D., Polychlorinated biphenyl sorption to activated carbon and the attenuation caused by sediment. *Global NEST J.* 2010, *12*, (3), 318-326.

51. Brunner, S.; Hornung, E.; Santl, H.; Wolff, E.; Piringer, O. G.; Altschuh, J.; Brueggemann, R., Henry's law constants for polychlorinated biphenyls: Experimental determination and structure-property relationships. *Environ. Sci. Technol.* 1990, *24*, (11), 1751-1754.

52. Harner, T.; Bidleman, T. F., Measurements of octanol− air partition coefficients for polychlorinated biphenyls. *J. Chem. Eng. Data* 1996, *41*, (4), 895-899.

53. Valsaraj, K.; Thibodeaux, L.; Reible, D., Modeling air emissions from contaminated sediment dredged materials. *ASTM Special Technical Publication* 1995, *1293*, 227-238.

54. Ahn, S.; Werner, D.; Karapanagioti, H. K.; McGlothlin, D. R.; Zare, R. N.; Luthy, R. G., Phenanthrene and pyrene sorption and intraparticle diffusion in polyoxymethylene, coke, and activated carbon. *Environ. Sci. Technol.* 2005, *39*, (17), 6516-6526.

55. Rusina, T. P.; Smedes, F.; Klanova, J.; Booij, K.; Holoubek, I., Polymer selection for passive sampling: A comparison of critical properties. *Chemosphere* 2007, *68*, (7), 1344-1351.

56. Li, N.; Wania, F.; Lei, Y. D.; Daly, G. L., A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls. *Journal of physical and chemical reference data* 2003, *32*, (4), 1545-1590.

Supplementary Information

For Chapter 4. Development of polyoxymethylene passive sampler for assessing air concentrations of PCBs at a confined disposal facility (CDF)

S1. Supporting information for vaporization experiment

Equilibrium concentrations in sediment, water and air

The steady state concentrations of PCB congeners measured during the vaporization experiment is shown in Table S1. Cw was estimated using the PDMS-water partition coefficients ($K_{PDMS\text{-}W}$) from [1] as shown by equation S2 and steady state concentration on PDMS (Cp). Estimated Partition coefficients are tabulated in Table S2.

$$K_{PDMS-w} = \frac{C_P}{C_w} \tag{S1}$$

$$\log K_{PDMS-w} = 0.725 \log kow + 0.479 \tag{S2}$$

Table S1. Measured parameters using passive samplers during laboratory experiment

PCB Congeners	Bulk Sediment Concentration (ug/kg)	Concentration in Slurry water (ng/L) C_W	Concentration in air (ng/m^3) C_A	Concentration on POM ($Cp,_{eq}$) (µg/kg)
1	10.89	0.738	9.08	22.5
2	22.08	0.949	11.1	27.5
3	4.76	0.783	8.79	29.1
4	874.3	66.8	900.5	287.4
10	65.08	1.569	27.3	115.3
9	15.79	0.195	2.6	23.8
7	15.79	0.191	2.96	23.8
6	79.32	0.986	13.3	116.3
8	447.4	2.203	27.1	638.8
5	470.3	2.732	26.7	626.1
19	85.56	1.251	22.8	89.0
33	254.9	0.733	7.2	282.8
52	536.8	0.839	11.1	889.7
101	73.09	0.035	0.346	24.3
153	90.40	0.010	0.068	24.1
180	82.61	0.003	0.014	21.5

Air concentration estimated by $C_A = K_{AW}C_W$.

Table S2. Partition coefficients of PCB congeners

PCB congeners	Log $K_{POM\text{-}W}$ [a]	(-) Log K_{AW} [b]	log $K_{POM\text{-}A}$ [c]	log $K_{POM\text{-}A}$ [d]
1	4.55	1.91	6.46	6.58
2	4.73	1.93	6.66	6.51
3	4.73	1.95	6.68	6.65
4	4.70	1.87	6.57	5.71
10	4.85	1.76	6.61	6.76
9	5.02	1.88	6.90	7.18
7	5.03	1.81	6.84	7.12
6	5.02	1.87	6.89	7.18
8	5.03	1.91	6.94	7.59
5	4.95	2.01	6.96	7.63
19	4.99	1.74	6.73	6.80
33	5.45	2.01	7.46	7.83
52	5.64	1.88	7.52	8.16
101	6.07	2.00	8.07	8.17
153	6.49	2.17	8.66	8.67
180	6.84	2.36	9.20	9.46

a The POM-water partitions from [2]

b The air-water partition coefficients from [3]

c POM-air partition coefficients derived from the ratio of a:b

d POM-air partition coefficients estimated using the measured POM concentration and air concentration shown in Table S1.

Table S3. Properties of sediment sample

Sediment properties	mean ± S.D
Sediment Concentration, ∑PCBs (mg/kg)	14.04 ± 1.40
Moisture content (%)	68.28 ± 0.86
Total Organic Carbon (%)	11.92 ± 0.37
Black Carbon (%)	1.68 ± 0.15

S2 Sediment-water partition coefficients

The sediment sample was analyzed prior to the vaporization study to determine the bulk PCB concentration, moisture content and organic content as shown in Table S3. The dissolved PCB concentration (Cw) was assessed using the polydimethylsiloxane (PDMS) passive sampler (Table S1) during the vaporization experiment. The sediment-water partition coefficients for individual PCB congeners were obtained using the measured sediment concentration (Ws) and dissolved PCB concentrations (Cw) as shown in Table S1. Figure S1 shows the comparison between the measured K_d (Equation S3) and the theoretical K_d (s) using [4] depicted by Equation S4, [5] and [6]. These theoretical K_d (s) are modelled based upon organic-carbon partition coefficient (Koc).

$$K_d = \frac{Ws}{C_{pw}} \tag{S3}$$

$$K_d = 0.61 * koc * foc \tag{S4}$$

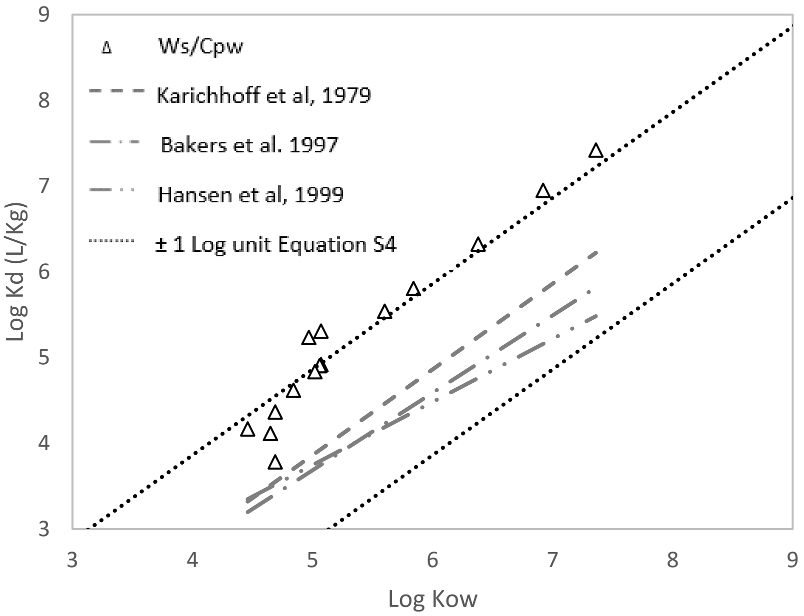


Figure S1. Comparison of sediment-water partition coefficient (K_D) with +/- 1 log units about Equation S4. The citation references in the legend are Karickhoff, Brown and Scott [4], Baker [5] and Hansen, Paya-Perez, Rahman and Larsen [6].

The log difference between the experimental K_d and the theoretical K_d(s) were between 0.2-1.6 log unit. It is common that site sediment-water partition coefficients are larger than theoretical methods due to the presence of strongly sorbing carbon phases (i.e. “black” carbon). The plot of experimental K_d against K_{ow} [7] shows a good correlation with a prediction model as shown in Equation S5, indicating that there is a strong relationship between the physicochemical properties of the studied PCB congeners and the experimental measurements of Ws and Cw in this study.

$$Log\ K_d = 1.15\ Log\ Kow - 0.98 \qquad ;\ R^2 = 0.94,\ n = 16 \qquad \text{(S5)}$$

S3. Additional information on the field application

The surrogate recoveries (Table S4) ranged from 70 – 110 % at the ten (10) sampled locations for PAS. Air concentration were not corrected for surrogate recovery.

The POM air sampler (PAS) was deployed at the CDF and held in place at each end of a pair of grids with clips and zip-ties (Figure S2a). The grids were attached to the sampling device which consisted of a fence post and a stainless-steel dome attached to the fence post it (Figure S2b**)**. The dome was intended to protect the sampler from UV radiation, wind, and precipitation. Figure S3 shows the predominant wind direction collated from the onsite weather stations during the period of deployment.

The partition coefficients ($K_{POM\text{-}w}$ and K_{AW}) were individually corrected for temperature using the Van't Hoff relationship depicted in Equation S6.

$$\ln \mathrm{K}_2 = \ln \mathrm{K}_1 + \frac{\Delta \mathrm{U}_{\mathrm{PCB}}}{\mathrm{R}}\left(\frac{1}{\mathrm{T}_1} - \frac{1}{\mathrm{T}_2}\right) \qquad (S6)$$

where $K_{2,}$ K_1 represents the partition coefficients ($K_{POM\text{-}W}$ and K_{AW}) at measured (T_2) and reference temperature (T_1) in kelvin respectively (Table S5). ΔU is the enthalpy of the respective phase change for individual PCBs and R is the gas constant. Polyoxymethylene-water ($K_{POM\text{-}W}$) and air-water (K_{AW}) partition coefficients for PCB congeners were taken from Hawthorne et al, 2009 and Dunnivant et al, 2000 respectively. The enthalpy of the phase change (ΔU_{PCB}/KJ/mole) [8] from air to water for the contaminants were estimated using Equation S7. The enthalpy of phase change between POM and water was assumed to be -10KJ/mole [9].

$$\Delta U_{\frac{a}{w}} = 0.085 \pm 0.007 * MW - 1 * n_{orthoCl} + 32.7 \pm 1.6, \qquad R^2 = 0.955 \qquad (S7)$$

where MW is the molecular weight of the PCB congeners and n-ortho Cl depicts the number of ortho-positioned chlorine atom. Table S6 shows the resulting air concentration using corrected Log $K_{POM\text{-}A.}$

Table S4. Surrogate recoveries from the field application analysis

Surrogates (%)				
Locations	d*-Fluoranthene	d*- Chrysene	d*-BbF	d*-DBA
AD	104.57 ± 9.19	101.56 ± 8.02	90.00 ± 6.67	85.66 ± 4.51
SW	114.88 ± 11.11	105.32 ± 7.33	97.89 ± 9.08	92.15 ± 8.66
S	113.5 ± 0.00	112.76 ± 0.00	100.48 ± 0.00	93.75 ± 0.00
SE	105.83 ± 15.64	113.13 ± 42.86	103.2 ± 31.67	89.84 ± 14.13
E	92.86 ± 1.56	92.70 ± 6.67	81.64 ± 1.54	75.33 ± 3.15
NE	85.73 ± 10.25	98.18 ± 37.14	86.75 ± 21.98	70.75 ± 13.14
N	87.40 ± 16.35	93.1 ± 6.67	87.47 ± 4.30	73.83 ± 13.33
NW	89.97 ± 7.43	83.39 ± 5.03	78.9 ± 6.09	67.73 ± 12.18
W	95.87 ± 9.52	109.58 ± 33.76	98.05 ± 21.20	78.51 ± 5.44
C	115.34 ± 10.62	117.48 ± 35.54	106.94 ± 25.03	108.04 ± 20.84

where d* is Deuterated
BbF is benzo(b)fluoranthene
DBA is dibenz(a,h) anthracene

The surrogates compounds used in this study were the deuterated fluoranthrene, chrysene, benzo(b)fluoranthene, and dibenz(a,h) anthracene. These surrogates were used because C13 PCBs was the PRC loaded on the PAS. Another reason for selecting these compounds was because the analysis was focused on both PCB congeners and PAHs (PAHs is not the focus in this present paper).

Figure S2. POM air sampler and POM support grid beneath the sampler protective dome.

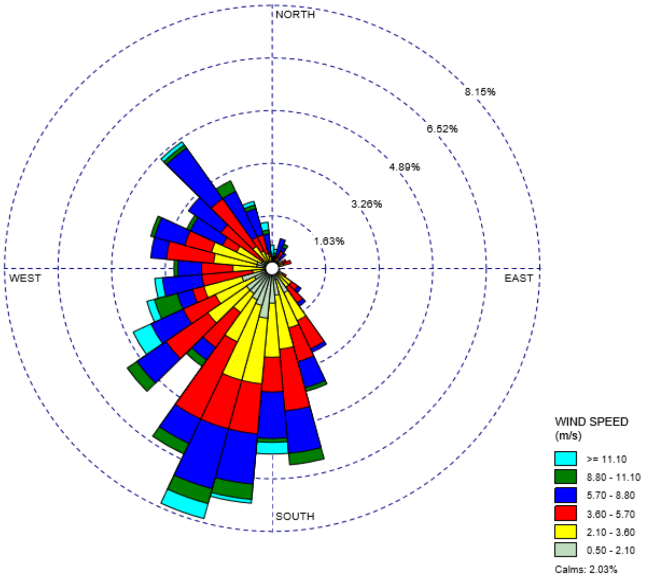


Figure S3. Wind direction during the period of deployment.

Table S5. Partition coefficients (K_{POM-W} and K_{AW}) at reference and measured temperatures for the PCB congeners

PCB congeners	(-Log) K_{AW}[a]	Log K_{POM-W}[a]	(-Log) K_{AW}[b]	Log K_{POM-W}[b]	PCB congeners	(-Log) K_{AW}[a]	Log K_{POM-W}[a]	(-Log) K_{AW}[b]	Log K_{POM-W}[b]
4	1.87	4.70	2.55	4.79	**90**	1.92	6.05	2.72	6.14
6	1.87	5.02	2.56	5.11	**101**	2.00	6.07	2.79	6.15
8	1.91	5.03	2.60	5.12	**99**	1.99	6.07	2.79	6.16
5	2.01	4.95	2.70	5.04	**119**	1.90	6.22	2.69	6.31
19	1.74	4.99	2.45	5.08	**87**	2.12	6.00	2.92	6.08
11	1.93	5.20	2.63	5.28	**115**	2.00	6.15	2.79	6.24
18	1.88	5.16	2.60	5.25	**110**	2.10	6.15	2.89	6.23
17	1.82	5.17	2.53	5.26	**77**	2.38	6.05	3.16	6.14
15	2.04	5.21	2.74	5.30	**82**	2.22	5.92	3.02	6.01
32	1.80	5.32	2.51	5.41	**151**	1.94	6.27	2.76	6.36
16	1.99	5.10	2.71	5.19	**149**	2.01	6.30	2.84	6.38
26	1.91	5.50	2.64	5.59	**118**	2.29	6.35	3.10	6.44
25	1.89	5.50	2.62	5.59	**153**	2.17	6.49	3.01	6.58
31	1.95	5.50	2.68	5.59	**132**	2.08	6.22	2.90	6.31
28	1.93	5.50	2.66	5.59	**105**	2.39	6.28	3.20	6.37
20	2.05	5.43	2.78	5.51					
22	2.11	5.43	2.84	5.52					
45	1.84	5.39	2.58	5.48					
46	1.86	5.39	2.60	5.48					
52	1.88	5.64	2.64	5.73					
47	1.82	5.65	2.58	5.74					
48	1.91	5.59	2.66	5.68					
44	2.03	5.57	2.78	5.66					
42	1.98	5.58	2.74	5.66					
37	2.21	5.63	2.95	5.72					
71	1.89	5.75	2.65	5.84					
41	2.00	5.52	2.76	5.61					
64	1.95	5.73	2.71	5.81					
40	2.13	5.50	2.88	5.59					
74	2.06	5.92	2.83	6.01					
70	2.08	5.92	2.85	6.01					
66	2.08	5.92	2.85	6.01					
93	1.86	5.80	2.64	5.89					
56	2.21	5.85	2.98	5.94					
60	2.20	5.85	2.97	5.94					
92	1.97	6.04	2.77	6.13					
84	1.99	5.80	2.77	5.89					

Where a depicts partition coefficient at reference temperature (20-25°C) and

b depicts partition coefficients corrected at measured temperature.

K_{POM-W} and K_{AW} was taken from Hawthorne et al, 2009 and Dunnivant et al, 2000 respectively.

Table S6. Estimated Log K_{POM-A} at field temperature (3.5°C) and measured air concentrations of PCB congeners during field deployment (Averages ± Standard deviation)

PCB congener	K_{POM-A}	Ca (ng/m^3)
4	7.33	0.060±0.031
6	7.68	0.007±0.000
8	7.72	0.011±0.006
5	7.74	0.011±0.003
19	7.53	0.010±0.000
11	7.91	0.004±0.000
18	7.85	0.038±0.027
17	7.79	0.019±0.012
15	8.04	0.013±0.008
32	7.92	0.014±0.006
16	7.90	0.017±0.007
26	8.23	0.006±0.003
25	8.21	0.004±0.001
31	8.27	0.027±0.018
28	8.26	0.027±0.019
20	8.30	0.005±0.002
22	8.36	0.008±0.005
45	8.06	0.006±0.003
46	8.08	0.002±0.001
52	8.37	0.014±0.008
47	8.31	0.005±0.003
48	8.34	0.004±0.002
44	8.44	0.012±0.007
42	8.40	0.005±0.003
37	8.67	0.004±0.002
71	8.49	0.003±0.001
41	8.37	0.005±0.003
64	8.52	0.003±0.002
40	8.47	0.003±0.001
74	8.84	0.002±0.001
70	8.87	0.005±0.003
66	8.86	0.004±0.002
93	8.53	0.002±0.000
56	8.92	0.001±0.001
60	8.92	0.001±0.001
92	8.90	0.000
84	8.66	0.001±0.000
PCB congener	**Kpom-a**	**Ca (ng/m^3)**
90	8.86	0.001±0.000
101	8.95	0.001±0.000
99	8.95	0.001±0.000
119	9.01	0.000
87	9.00	0.001±0.000
115	9.04	0.000
110	9.13	0.001±0.000
77	9.30	0.000
82	9.03	0.000
151	9.12	0.000
149	9.22	0.000
118	9.54	0.000
153	9.59	0.000
132	9.22	0.000
105	9.57	0.000

References

1. Ghosh, U.; Kane Driscoll, S.; Burgess, R. M.; Jonker, M. T.; Reible, D.; Gobas, F.; Choi, Y.; Apitz, S. E.; Maruya, K. A.; Gala, W. R., Passive sampling methods for contaminated sediments: practical guidance for selection, calibration, and implementation. *Integr. Environ. Assess.* 2014, *10*, (2), 210-223.

2. Hawthorne, S. B.; Miller, D. J.; Grabanski, C. B., Measuring low picogram per liter concentrations of freely dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. *Anal. Chem.* 2009, *81*, (22), 9472-9480.

3. Dunnivant, F. M.; Elzerman, A. W.; Jurs, P. C.; Hasan, M. N., Quantitative structure-property relationships for aqueous solubilities and Henry's law constants of polychlorinated biphenyls. *Environ. Sci. Technol.* 1992, *26*, (8), 1567-1573.

4. Karickhoff, S. W.; Brown, D. S.; Scott, T. A., Sorption of hydrophobic pollutants on natural sediments. *Water Res.* 1979, *13*, (3), 241-248.

5. Baker, J. R., Evaluation of estimation methods for organic carbon normalized sorption coefficients. *Water Environ. Res.* 1997, *69*, (2), 136-145.

6. Hansen, B. G.; Paya-Perez, A. B.; Rahman, M.; Larsen, B. R., QSARs for Kow and Koc of PCB congeners: a critical examination of data, assumptions and statistical approaches. *Chemosphere* 1999, *39*, (13), 2209-2228.

7. Hawker, D. W.; Connell, D. W., Octanol-water partition coefficients of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* 1988, *22*, (4), 382-387.

8. Li, N.; Wania, F.; Lei, Y. D.; Daly, G. L., A comprehensive and critical compilation, evaluation, and selection of physical–chemical property data for selected polychlorinated biphenyls. *J. Phys. Chem. Ref. data* 2003, *32*, (4), 1545-1590.

9. Lohmann, R., Critical review of low-density polyethylene’s partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environ. Sci. Technol.* 2012, *46*, (2), 606-618.

Chapter 5

Application of polyoxymethylene passive air sampler to monitor hydrophobic organics in air around a confined disposal facility

Adesewa A. Odetayo[a], Danny D. Reible[a], Damarys Acevedo-Mackey[b], Cynthia Price[b],
Le Thai[c]

[a] Department of Civil, Environmental and Construction Engineering, Texas Tech University, 911 Boston Avenue, Lubbock. Texas 79409. U.S.A

[b] U. S Army Engineer Research and Development Center, 3909 Halls Ferry Rd. Vicksburg, Mississippi. 39180. U.S.A.

[c] U. S Army Corps of Engineers, Chicago District.

Citation

Odetayo, A. A., Reible, D. D., Acevedo-Mackey, D., Price, C., & Thai, L. "Application of polyoxymethylene passive air sampler to monitor hydrophobic organics in air around a confined disposal facility. *Chemosphere.*

Abstract

Volatile losses of hydrophobic organic contaminants from a confined disposal facility (CDF) containing dredged contaminated sediments is of substantial concern to surrounding communities. A partitioning passive sampling approach using polyoxymethylene (POM) was applied to measure long-term average (weeks to months) air concentrations resulting from evaporation at a CDF. Measurements at 10 locations surrounding the CDF using the POM air samplers indicated that the highest concentrations of ΣPCBs~13 ng/m^3 and ΣPAHs ~ 65 ng/m^3 were measured during an active dredge material placement period when the average temperature was 23 ^{o} C. The measurements were dominated by the more volatile, lower molecular weight compounds of each type. Partitioning to the POM during the post dredge material placement period with average temperature of 5 ^{o} C was corrected for temperature and the measured ∑PCBs and ∑PAHs were ~3 ng/m^3 and 45 ng/m^3 respectively. The partitioning passive sampling measurements agreed well with the available weekly 24-hour high-volume air samples (HVAS) averaged over the POM equilibration time for lower congener number PCBs (15, 18, 20/28 and 31) and naphthalene but were as much as 10 times lower than HVAS for high molecular weight PAHs. The difference was likely the result of the greater association of these PAHs with particulates and sources other than evaporation from the CDF. The POM air sampler achieved the goal of providing a long-term average air concentration without having to collect, analyze and average multiple HVAS samples although the technique is largely limited to the lower molecular weight PAHs and PCBs and different equilibration times for different compounds complicate its use and analysis.

Keywords. Confined disposal facility; Passive air sampling; Air concentration; PCBs; PAHs; POM air sampler.

5.1. Introduction

Globally, aquatic habitats are threatened due to historical contamination from industrial and municipal effluents [1]. These effluents were often contaminated with hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs) and polycyclic aromatic compounds (PAHs) and which preferentially sorb onto the sediment [2, 3]. These HOCs can pose significant risks to aquatic organisms, human health and the environment[4]. Navigational and environmental dredging leads to the requirement for disposal of millions of cubic yards of contaminated sediment containing HOCs, some of which end up in confined disposal facilities (CDFs) [5-7], an engineered structure primarily designed to contain the sediment solids [8, 9]. However, the lower molecular weights (LMW) 2 and 3 ring PAHs and low congener number (LCN) 1- 4 Chlorine PCBs have relatively low sediment-water partition coefficients and high air-water partition coefficients leading to higher impounded water concentrations in a CDF and greater volatilization [10-12]. Effective management of a CDF includes assessing and managing these volatile emissions [8, 13, 14]. High volume air samplers (HVAS) are sometimes used to monitor air concentrations [15, 16]. However, HVAS samplers collect short-term average air concentrations, typically 24 hours, and averages of a number of costly sample analyses are required to assess long-term average air exposures to the surrounding community [17, 18].

Passive air sampling has become increasingly common, with the most commonly deployed samplers for semi-volatile contaminants being polyurethane foam (PUF) [18-20] and XAD-2 [21, 22]. However, it has been shown that these commonly used passive samplers are semi-quantitative and sensitive to sampling rates [23]. Other passive air samplers include semipermeable membrane devices (SPMDs) using low density polyethylene (LDPE) [24-26], polydimethylsiloxane (PDMS) (Okeme et al., 2016a; Okeme et al., 2016b; [27], and most recently, polyoxymethylene (POM) [28]. In general, passive sampling may provide an alternative to the collection of separate short term concentrations, in that passive samplers absorb contaminants over time and a single analysis may provide a relatively long-term average due to the kinetics of uptake on the sampler. In this study, we employ a passive air sampler using polyoxymethylene (POM) to estimate long-term (weeks to months) average air concentrations of HOCs due to evaporation from a CDF during and after a period of active dredged material placement.

POM as a passive sampler is popular for aquatic and sediment sampling, and exhibit longer equilibration time when compared to its counterparts, LDPE and PDMS [29, 30]. POM unique characteristics was explored as an air sampler and investigated in Odetayo, et al. [28] by assessing the dynamics and equilibrium uptake of the contaminants of interest in laboratory studies including measurement of POM-air partition coefficients ($K_{POM\text{-}A}$). POM was attractive because it provides relatively slow uptake kinetics (and therefore long averaging times) compared to other common passive sampler materials and would also better retain low molecular weight volatile compounds, for example compared to PDMS [31]. As discussed below, sorption of hydrophobic contaminants such as PCBs in POM is also limited by internal diffusional resistances under atmospheric conditions, making the sampler relatively insensitive to wind speed. Uptake into 76 µm thick POM at laboratory temperatures required an equilibration time under 7 days for LMW PAHs but 3-5 weeks for di-, tri- and tetrachlorobiphenyls as a result of slow internal diffusion in the POM [28]. Thus using POM as an air sampler would provide a long-term (weeks) average concentration for these compounds at similar temperatures.

The kinetics of uptake between the POM and air are assumed to follow an exponential or first order equation and dependent on an overall fluid mass transfer coefficient k_o according to the following (basis in Supplementary Information, SI),

$$C_{POM} = C_A K_{POM-A}\left(1 - exp^{\frac{-2k_o t}{K_{POM-A}\delta}}\right) \qquad (5.1)$$

where C_{POM} is the amount of contaminants on POM, C_A is the air concentration, $K_{POM\text{-}A}$ is the POM-air partition coefficients, δ (cm) is the POM volume to area ratio (half-thickness) and k_o (cm/hr) is the overall mass transfer coefficient. Contaminant uptake on passive samplers can be influenced, in general, by both internal and external resistances [29, 32-34]. If external mass transfer resistances are characterized by k_A (cm/hr), the air side mass transfer coefficient and $\mathcal{D}$ (cm^2/hr) describes internal diffusion in the POM of thickness δ exposed on both sides, the overall mass transfer coefficient can be written;

$$\frac{1}{k_o} \approx \frac{1}{k_A} + \frac{\delta}{2K_{POM-A}\mathcal{D}} \qquad (5.2)$$

Initially, air-side resistances must control uptake but as the POM approaches equilibrium, the internal resistance term dominates. For 76 µm POM sampling in air, sorption of HOCs with log $K_{POM\text{-}A} < 10^8$ (cm^3/cm^3) are primarily influenced by diffusional mass transfer resistances within the POM since k_A is of the order of 10^3 cm/hr [35] and $\mathcal{D}$ is of the order of 10^{-8} cm^2 /hr [36]. The uptake rate is dependent upon temperature due to temperature effects on both POM diffusivity and $K_{POM\text{-}A}$. Sorption of HOCs with $K_{POM\text{-}A}$ $> 10^8$ are likely to be influenced by external mass transfer resistances increasing the time to steady state and increasing the sensitivity of the rate of approach to equilibration under atmospheric conditions.

The objective of the current study is to evaluate the performance of POM in assessing the air concentration of PCB congeners and PAHs during different atmospheric conditions (warm summer conditions to cool fall/winter conditions) and operational state of a CDF (active dredged material placement and post-placement). As part of that evaluation, the POM measurements will be compared to simultaneous HVAS measurements conducted and reported by the US Army Corps of Engineers (USACE).

5.2. Materials and Methods

5.2.1. Materials

Dichloromethane, hexane, methanol and acetone solvents of optima grade quality were purchased from Fisher Scientific (Hampton, NH. USA). Parent PCB and PAHs standards as well as ^{13}C labelled PCBs and deuterated PAHs were purchased from AccuStandard (USA) and Ultra Scientific Analytical Solution (USA) respectively. POM 76 µm in thickness was purchased from CS Hyde Company (Lake Villa, USA). Prior to field deployment, the POM sheet was segmented into masses of 200 mg ± 0.1 mg (~19

cm^2) and pre-extracted twice with hexane, dichloromethane, and methanol sequentially for 30 minutes each to remove any adsorbed contaminants, and finally rinsed with de-ionized water (GenPure Pro UV, Thermo Scientific, USA). The cleaned polymeric samplers were then dried under the fume hood. All glass ware, scissors, and POM supports were washed and solvent-rinsed before use. The POM samplers were also preloaded with performance reference compounds (PRCs) of ^{13}C labelled PCB (28/52/101/138/153/180/209) in a methanol: water (20:80, v/v) solution for 45 days. The PRCs were designed to indicate reversible release and uptake kinetics of similar compounds to confirm equilibration over the deployment period.

5.2.2. Deployment and retrieval of POM Air samplers

The POM air samplers were deployed in triplicate at ten (10) different locations at a CDF (Figure 5.1) at the southern end of Lake Michigan in the Great Lakes of the United States with sampling locations around the perimeter and center of the CDF namely SW, S, and SE on the southern boundary, NW, N and NE on the northern boundary and E and W centered on the east and west side respectively. Location C was along the center dike of the facility along with dredged material discharge locations. During deployment, the POM was supported on a grid beneath a protective half-dome to protect the sampler from UV radiation and rain following the description in Odetayo, et al. [28]. Samplers were first placed during a period of active dredge material placement into the west cell. The samplers were retrieved only at the end of the deployment period of 113 days between June 19, 2018 and Oct 10, 2018 when the average temperature was approximately ~ 23 ^{o} C Additional samplers were placed for 62 days from Oct 10, 2018 to Dec 12, 2018 when the average temperature was ~ 5 ^{o} C and there was no active placement of dredged material. High volume air samplers (HVAS) and weather stations have been located around the perimeter of the CDF by USACE at locations S_H to the south, E_H to the east, N_H to the north and W_H to the west (Figure 5.1). The HVAS locations were near but not co-located with POM samples S, E, N and W, respectively.

Figure 5.1. Overhead photograph of CDF and adjacent industrial facilities. POM sampling locations are denoted by circles, HVAS sampling locations by rectangles and dredged material discharge locations by D1 through D4.

5.2.3. Sample Analysis

Upon retrieval, the POM air samples were processed and extracted using 2 mL of acetone: hexane (1:1, v/v) solvent with four deuterated PAHs to evaluate spike recovery during subsequent processing. The samples were concentrated to 100 µL and analyzed for 124 PCBs and 16 PAHs using EPA method 1668C and 8270D respectively, on gas chromatograph- triple quadrupole mass spectrometer (GC-TQ/MS) (Agilent technologies 7890 GC coupled with 7000 MS/MS). The average recovery of the deuterated PAHs were observed to be 90 ± 16 % for d10-fluoranthene, 96 ± 22 % for d12-Chrysene, 83 ± 16 % for d12-benzo[b]fluoranthene and 86 ± 24 % for d14-dibenzo[a,h]anthracene. The measured concentrations were not corrected for surrogate recoveries. During the analysis of the samples from the active dredge material placement (ADMP) and post dredge material placement (PDMP) sampling periods, 97 PCB congeners and 106 PCB congeners, respectively, were present above the quantification limit. The limit of quantification (LOQ) was determined from the lowest calibration concentration with a deviation of ≤ 20% from the calibration curve. This translates to different LOQs for target contaminants in air depending upon the K_{POM-A} of the contaminant and equivalent air concentration detection limits are shown in the SI. Lower detection limits could be achieved by increasing the mass of POM or decreasing the final extract volume. All priority PAHs were detected except anthracene during the two sampling periods.

All method and sample blanks (after every 10 samples) showed no concentrations of significance relative (< ~5%) to measured air concentration. Calibration curves were linear with $R^2 \geq 0.999$ and relative standard deviations of ≤ 20% deviation over the calibration range. Calibration checks of known concentration were included with every tenth sample to confirm stability of the calibration.

HVAS were operated by USACE as part of normal operations at the CDF. Data for PCB congeners (15, 18, 20/28 and 31) and PAHs (naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, fluoranthene and pyrene) during the deployment periods were collected and are publicly available from the U.S. Army Corps of Engineers [37]. These specific congeners and PAHs were selected for reporting by the USACE because they were commonly observed in contaminated dredged material placed in the CDF. USACE utilizes a HVAS that pulls ambient air through a glass fiber filter combined with PUF/XAD-2 sorbent cartridge at a flowrate of approximately 200-280 L/min to obtain a total sample volume of $\geq 300 m^3$ over a 24 hour period. The HVAS data is expected to represent a combined concentration of particulate and non-particulate associated contaminant concentrations in air.

5.2.4. Kinetics and equilibrium sorption onto POM air sampler

The kinetics and equilibrium uptake for selected PCBs onto POM were studied in stirred vessels in the laboratory [28]. The equilibrium uptake onto POM was consistent (average deviation 0.19 log unit) with the theoretical estimate based upon three phase equilibrium of POM, air, and water of

$$K_{POM-A} = \frac{K_{POM-W}}{K_{AW}} \tag{5.3}$$

where K_{POM-W} is the POM water partition coefficient estimated from Hawthorne, et al. [38, 39], and K_{AW} is the air-water partition coefficient (Henry's constant) for the compound estimated from Dunnivant, et al. [40] and Williams, et al. [41].

The time required to achieve steady state at laboratory temperatures (~20°C) varied from about a week for PCB 10 to about four (4) weeks for PCB 33 with longer times required for PCBs [28] with 4 or more chlorines. It was estimated that internal mass transfer resistances controlled uptake in stirred vessels in the lab and, as noted above, would control uptake in the field as long as $K_{POM-A} \leq 10^8$. Note that the time to steady state (τ_{ss}) at these temperatures is short for mono- to tetrachlorobiphenyl PCBs relative to the 113 days exposure time at similar temperatures during the active dredge material disposal period. Thus, the concentration measured by the POM for these congeners likely represents an equilibration over a period shorter than the total deployment. The PRCs preloaded into the POM were analyzed in an effort to confirm that the samples collected at the end of the exposure period would have sufficient time to achieve equilibrium. The ^{13}C-hexachlorobiphenyls PCB 138 and PCB 153 showed essentially complete loss from the POM (87-98% and 74-91% respectively) suggesting that equilibrium was achieved for these congeners over the period of exposure. This suggests that lower chlorinated PCBs should also be equilibrated, but the results for ^{13}C 28, 52 and 101 were highly variable over the two deployments. Challenges with PRCs on POM including high variability, apparent irreversible desorption, and difficulty achieving pre-equilibration have been noted previously [42-44]. Alternative approaches such as using different area to volume ratio samplers or placing samplers for different time periods could have been used to confirm equilibration times [29]. The latter approach would have been especially useful but was not easily implemented due to the requirements for multiple trips to the site.

5.2.5. Temperature correction of POM-Air partition coefficient

The kinetics of uptake onto the POM was a strong function of the POM-Air partition coefficient and thus the changes in K_{POM-A} with temperature needs to be accounted for. K_{POM-A} at temperatures other than 20-25°C was estimated using the van't Hoff relationship.

$$Log\ K_{T_2} = log\ K_{298} + \frac{\Delta U}{2.303R}\left(\frac{1}{T_{298}} - \frac{1}{T_2}\right) \tag{5.4}$$

Here K_{T_2} represent the partition coefficients to be corrected at temperatures other than 298K, the enthalpy of the respective phase change (ΔU KJ/mole) for individual PCBs and PAHs were taken from Li, et al. [45] and Beyer, et al. [46] respectively following the description in Odetayo, et al. [28] (more details in SI) and R is the gas constant (J/Kmole).

A correlation between the K_{POM-A} and the required τ_{ss} was developed from the laboratory data at 20-22°C of Odetayo, et al. [28] since both laboratory and field conditions were expected to be controlled by internal diffusion for compounds up to $K_{POM-A} \approx 10^8$.

This correlation was used to estimate approximate τ_{ss} for other target compounds and at other temperatures by using temperature corrected K_{POM-A}. Although the diffusivity in POM is also a function of temperature, its effect is relatively minor compared to the effect on K_{POM-A}. A decrease in ambient temperature of 20°C would be expected to lower diffusivity in the POM by 50% or less but the K_{POM-A} increases by approximately 0.75 log units, a factor of 5 over the same range of temperature (see Table 2 below). Thus decreases in temperature during the cooler second deployment can significantly increase the τ_{ss}. The τ_{ss} from Figure 5.2 was used to confirm expectations of equilibration for particular compounds over the sampling period as well as to estimate the equilibration or averaging time for comparing measured concentrations to HVAS air samples.

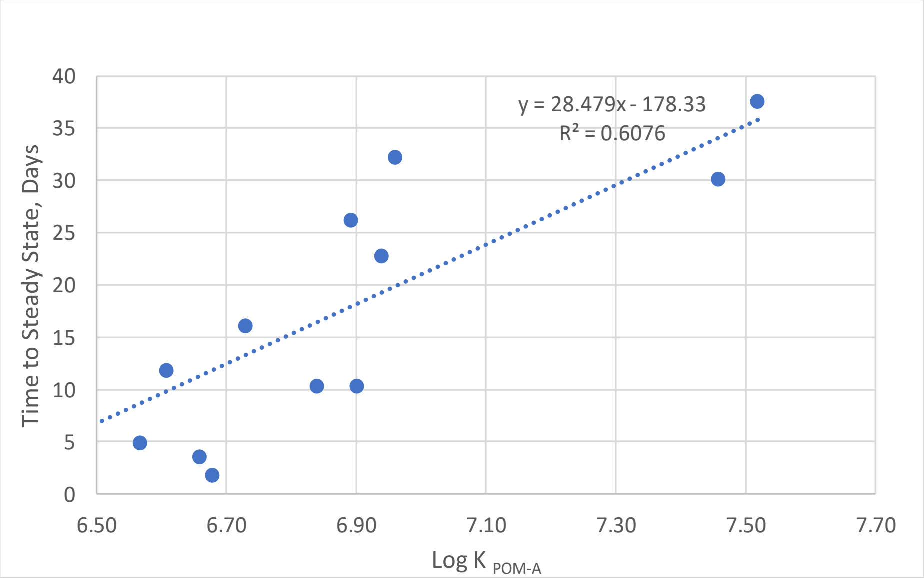


Figure 5.2. Correlation of time to steady state (τ_{SS}) to the POM-Air partition coefficients (K_{POM-A}) at 20°C. Shown on the Figure are estimated time from laboratory kinetic uptake experimental fits to Equation 1 with 12 PCB congeners from PCB 1 to 52 [28].

5.2.6. Meteorological data

There were total of four (4) weather stations located at the south, east, west and north of the CDF. The weather data from the four weather stations were consolidated using WRPLOT View-Version 8.0.2 (Lakes Environmental, USA) (details in SI) which shows the frequency distribution of the occurrences of wind during the period of deployment at the CDF. The air temperature was an average of 23 ± 5.4 ^{o}C standard deviation during the summer ADMP deployment and 4.7 ± 6.0 ^{o}C standard deviation during the fall and early winter PDMP deployment. The $K_{POM\text{-}A}$ was corrected for temperature as outlined above for the PDMP period. The average wind speed measured at a height of 10 meters was 3.9 ± 2.1 m/s during the ADMP deployment and 4.1 ± 2.3 m/s during the PDMP deployment. The distribution of wind speeds and directions during each sampling event are shown via wind roses in Figures S1 and S3.

5.3. Results and discussion of results

5.3.1. Air concentrations of HOCs derived from POM

Table 5.1 shows some of the NOAA and WHO PCB congeners, chosen for their environmental significance and abundance [47, 48], their estimated POM-Air partition coefficient, time to steady state from Figure 5.2 (or averaging time) and observed air concentration as measured by POM during the active dredge material placement period (ADMP) and post-dredge material placement period (PDMP). Air concentrations of other measured PCB congeners are available in the supplementary information. Table 5.2 shows the same information for the priority PAHs. In the first event, the temperature averaged 23 °C and no temperature correction was applied to K_{POM-A}. The kinetics of uptake for compounds with $K_{POM-A} \leq 10^8$ (that is internal resistance controlled) would be expected to be essentially identical to that observed in the laboratory, that is, less than 7 days for LMW PAHs, 7-38 days for the di- tri- and tetrachlorobiphenyl congener PCBs and mid-range PAHs, and longer for the higher molecular weight (HMW) compounds and higher congener number (HCN) PCBs as shown in Tables 5.1 and 5.2. This suggests that measured concentration over the 113 day period during the ADMP event, actually only represented uptake over the last few weeks of the exposure time depending upon the compound.

In the second PDMP event, the average temperature was under 5 °C requiring correction of K_{POM-A} and the estimated time to steady state from the correlation of Figure 2 was 7-28 days for LMW PAHs, 25-56 days for LCN PCBs and much longer for HMW compounds (Tables 5.1 and 5.2). The compounds with Log $K_{POM-A} > 8$ would also be expected to exhibit both internal and external mass transfer resistances, further slowing uptake. Due to the limited partitioning to water and low volatility of these HMW compounds, however, air concentrations were expected to be dominated by the lower molecular weight compounds with Log $K_{POM-A} \leq 8$.

Table 5.1. Partition coefficients, Time to steady state (**τ_{ss}**) and measured concentration, C_A, for PCBs averaged over all CDF sampling locations during deployment periods

	Deployment periods					
	ADMP			PDMP		
PCB Congeners	**Log K_{POM-A} (T=23°C)**	τ_{ss} **(days)**	**C_A (ng/m^3)**	**Log K_{POM-A} (T=5°C)**	τ_{ss} **(days)**	**C_A (ng/m^3)**
2	6.66	11	0.11 ± 0.01	7.36	31	0.01 ± 0.002
5	6.96	20	0.06 ± 0.03	7.68	40	0.04 ± 0.01
8	6.94	19	0.17 ± 0.05	7.66	40	0.02 ± 0.004
18	7.05	22	0.91 ± 0.35	7.79	44	0.10 ± 0.03
28	7.44	33	0.55 ± 0.24	8.20	55	0.05 ± 0.02
52	7.52	36	0.39 ± 0.16	8.31	58	0.02 ± 0.01
44	7.59	38	0.36 ± 0.15	8.38	60	0.02 ± 0.01
66	8.01	50	0.19 ± 0.06	8.8	72*	9.4e-3 ± 3.3e-3
101	8.06	51	0.03 ± 0.01	8.89	75*	4.9e-4 ± 3.3e-4
77	8.43	62	0.14 ± 0.01	9.24	85*	1.3e-2 ± 2.2e-3
118	8.64	68	4.5e-3 ± 6.7e-4	9.47	91*	8.2e-4 ± 1.8e-4
153	8.67	68	8.6e-3 ± 2.1e-3	9.52	93*	3.4e-4 ± 3.8e-5
138	8.7	69	2.9e-3 ± 8.2e-4	9.56	94*	1.5e-4 ± 3.7e-5
169	9.46	91	5.8e-4 ± 1.3e-4	10.35	116*	2.9e-4 ± 3.8e-5
187	8.77	72	2.4e-3 ± 6.4e-4	9.66	97*	1.1e-4 ± 2.6e-5

Note: Complete list of analyzed PCB congeners are in the supplementary data. K_{POM-A} **(v/v,** m^3/m^3) and **τ_{ss}** is the estimated time to steady state. Asterisked **τ_{ss}** are longer than the deployment period.

Table 5.2. Partition coefficients, Time to steady state (τ_{ss}) and measured concentration (C_A) for PAHs averaged around all CDF sampling locations during deployment periods

	Deployment periods					
	ADMP			PDMP		
PAHs	**Log K_{POM-A}**	τ_{ss} **(days)**	**C_A (ng/m^3)**	**Log K_{POM-A}**	τ_{ss} **(days)**	**C_A (ng/m^3)**
Naphthalene	4.92	<7	43.8 ± 27.5	5.67	<7	39.9 ± 11.2
Acenaphthylene	6.00	<7	1.43 ± 0.14	6.85	17	0.24 ± 0.03
Acenaphthene	5.84	<7	5.34 ± 0.67	6.69	12	0.84 ± 0.16
Fluorene	6.24	<7	5.02 ± 1.03	7.11	24	1.86 ± 0.36
Phenanthrene	7.05	23	8.57 ± 2.12	7.92	47	1.62 ± 0.3
Fluoranthene	8.19	55	0.27 ± 0.06	9.12	81*	0.03 ± 0.01
Pyrene	8.04	51	0.33 ± 0.09	8.83	73*	0.08 ± 0.01
Benz(a)anthracene	8.53	65	0.95 ± 0.22	9.56	94*	0.11 ± 0.03
Chrysene	8.93	76	0.02 ± 0.01	10.41	118*	1.9e-3 ± 5.7e-4
Benzo(b)fluoranthene	10.41	118*	6.6e-4 ± 3.1e-4	11.31	144*	3.2e-4 ± 1.1e-4
Benzo(k)fluoranthene	10.39	118*	1.5e-4 ± 4.6e-5	11.29	143*	6.9e-5 ± 2.5e-5
Benzo(a)pyrene	10.53	122*	6.8e-4 ± 1.3e-4	11.18	140*	3.2e-4 ± 5.9e-4
Indeno(123-cd)pyrene	11.07	137*	3.9e-5 ± 1e-5	11.97	163*	1.8e-5 ± 3.5e-6
Dibenzo(ah)anthracene	11.25	142*	4.4e-5 ± 8.7e-6	12.15	168*	2.3e-5 ± 5.5e-6
Benzo(ghi)perylene	11.09	138*	1.1e-4 ± 2.1e-5	11.99	163*	4.4e-5 ± 1.5e-5

Note: K_{POM-A} **(v/v,** m^3/m^3) and **τ_{ss}** is the estimated time to steady state. Asterisked **τ_{ss}** are longer than the deployment period.

5.3.1.1. Active Dredged Material Placement (ADMP) Period

During the summer ADMP, the POM measured air concentration of $\sum_{97}$PCBs and $\sum_{15}$PAHs averaged 12.9 ± 2.44 ng/m^3 and 65.7 ± 27.9 ng/m^3, respectively, across the sampling locations. For the compounds with $K_{POM\text{-}A} \leq 10^8$, average air concentration was 11.1 ± 2.27 ng/m^3 for PCBs, accounting for 80 % of the $\sum_{97}$PCBs and 64.1 ± 27.8 ng/m^3 for PAHs, or 98 % of the $\sum_{15}$PAHs (Figure 5.3). Naphthalene air concentration averaged 43.8 ng/m^3 or 67 % of the measured Σ_{15}PAHs, phenanthrene was 8.57 ng/m^3, acenaphthene and acenaphthylene were individually about 5 ng/m^3 with the rest of the PAHs less than 1 ng/m^3 as shown in Table 5.2. The individual PCB congeners were typically less than 1 ng/m^3 except at the north sampling location closest to the dredged material placement (details in SI). PCB congener 18 exhibited the highest concentration with 1.5 ng/m^3 at that location and averaged 0.94 ng/m^3 across the site. Other significant congeners were PCB 20+28 (co-elutants) and PCB 31 with an average of 0.64 and 0.78 ng/m^3, respectively. As shown in Figure 5.3, $\sum_{97}$PCB, and as well as individual PCB congeners (details in SI), were highest in the northern sample location (N) and lowest to the west (W). Wind rose information (SI) shows that the winds throughout the ADMP were either northerly or southerly consistent with summer lake and land breezes associated with the nearby Great Lake. The $\sum_{15}$PAHs and individual PAHs (Figure 5.3 and Figure S6) showed a peak concentration in the west sampler or other locations inconsistent with the predominant wind direction and primary dredged material placement location. This may reflect the influence of sources other than CDF as noted by the variety of potential PAH sources surrounding the site (combustion sources, roadways, fuel storage and processing) as shown in Figure 5.1.

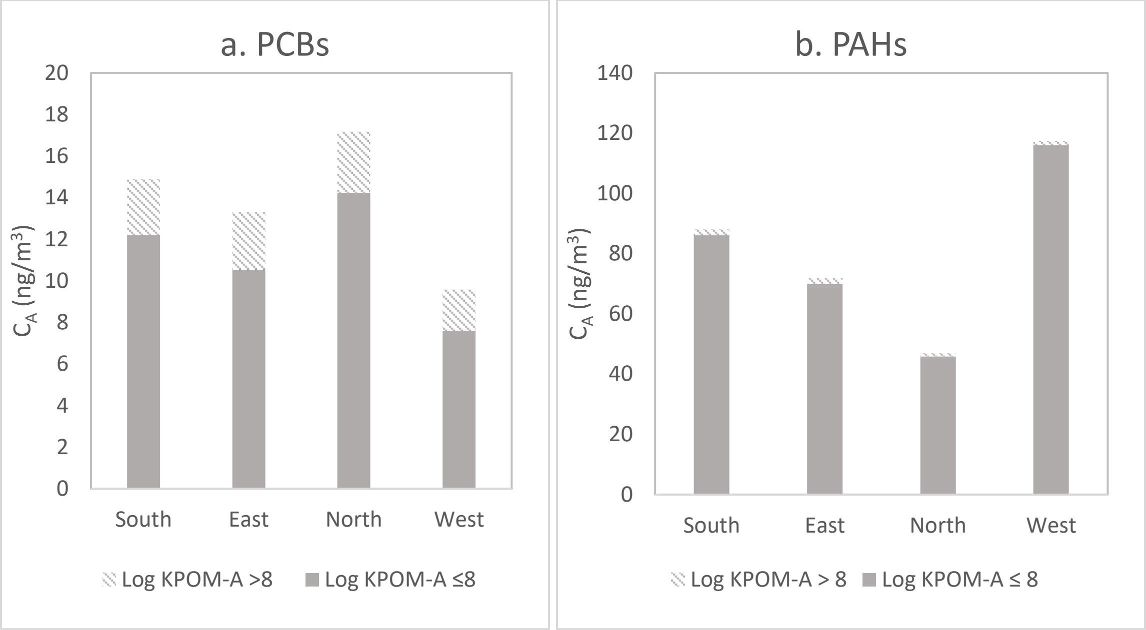


Figure 5.3. Distribution of air concentrations across sampled locations for a) PCBs and b) PAHs during active dredge material placement (ADMP) deployment showing proportion of less than and greater than Log K_{POM-A} =8.

5.3.1.2. Post Dredged Material Placement Period

Due to the lower temperature during the PDMP, the target compounds would be expected to have signifcantly longer equilibration times due to the increases in K_{POM-A} . PCB 18 was expected to require 44 days for equilibration on POM, thus requiring most of the 62 day exposure time to equilibrate. This can be compared to 22 days estimated during the previous warm weather sampling event for PCB 18. Several of the trichlorobiphenyls had an estimated K_{POM-A} such that some influence of external resistances might be expected. PCB 28, for example, had a temperature corrected log K_{POM-A} of 8.20, 0.7 log unit higher than estimated during the ADMP. Tetrachlorobiphenyls and more chlorinated PCBs would be unlikely to achieve equilibration during the PDMP sampling period.

During the PDMP, 106 PCBs were detected by POM and their sum ($\sum_{106}$PCBs) averaged 2.6 ± 0.3 ng/m^3 over the sampled locations, while the sum of PAHs ($\sum_{15}$PAHs) averaged 44.7 ± 11.9 ng/m^3 (Table 5.2). The mono- to trichlorobiphenyl PCB concentrations accounted for 81% of the $\sum_{106}$PCBs although compounds with Log K_{POM-A} ≤ 8 was only 39% of the total. The much lower total PCB concentrations during this period was consistent with the lower temperatures and lower compound volatility. PCB 18 decreased by a factor of ~10 to an air concentration of 0.12 ng/m^3 and again the northern sampling location showed the highest concentration for individual and $\sum_{106}$PCBs, although concentrations around the CDF were much more uniform than during the summer ADMP sampling due to lower and more variable wind speeds and directions during the sampling. The distribution of PCBs at the N, E, S and W sampling locations are shown in Figure 5.4.

Naphthalene was the dominant PAH with an average of 40 ng/m^3, accounting for 89 % of the Σ_{15}PAHs (Table 5.2 and Figure S4). All the 2 or 3 ring PAHs had $K_{POM-A} < 10^8$ during this deployment period and totaled 99 % of the measured $\sum_{15}$PAHs (Table 5.2). Unlike PCBs, PAHs were not dramatically lower in concentration during the PDMP period. Σ_{15}PAHs were approximately 2/3 of the concentration observed during the ADMP period. This again may suggest that PAHs were significantly influenced by other sources not linked to ambient temperature and evaporation from the CDF.

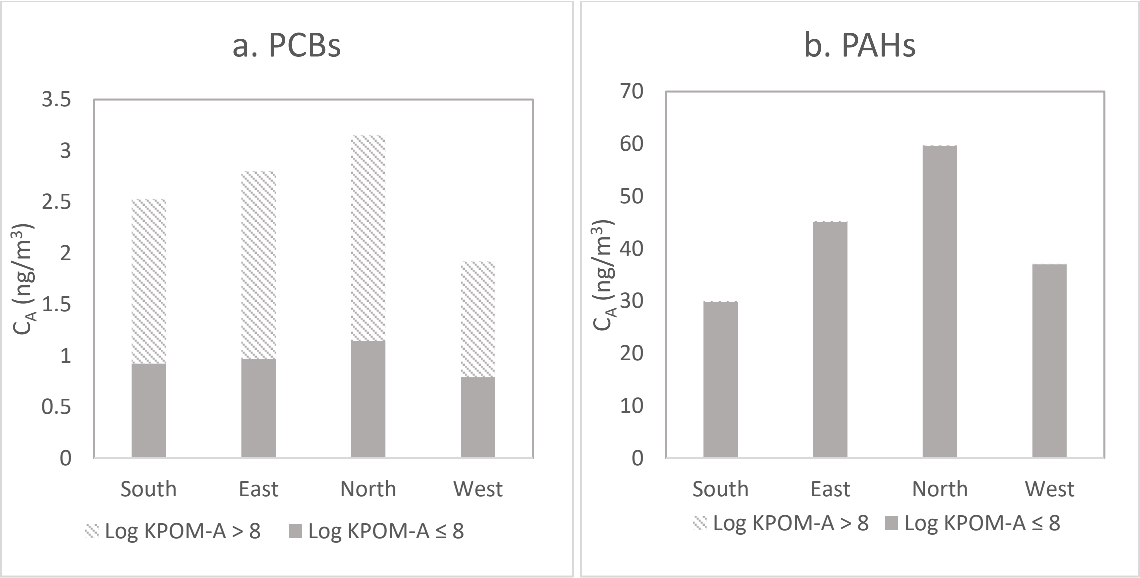


Figure 5.4. Distribution of air concentrations across sampled locations for a) PCBs and b) PAHs during post dredge material placement (PDMP) deployment showing proportion of less than and greater than Log K_{POM-A} =8.

5.3.2. Comparison between POM and HVAS

The measured air concentration on POM was compared to the air concentration measured using the USACE reported HVAS concentrations during the ADMP and PDMP deployments periods as shown in Figure 5.5. Four HVAS were located near the N, E, S and W, and POM locations on the CDF (Figure 5.1). The HVAS included both particulate and vapor phase concentrations. Since any particulates were rinsed/wiped off the POM measurements reflect only vapor phase concentrations. This provides a degree of selectivity for the desired evaporative emissions from the CDF since the evaporative flux is a vapor flux. Nearby PAH sources such as combustion sources would be expected to contribute particulate bound PAHs that would not be measured by the POM. The vast majority of di- and trichlorobiphenyls and 3 ring and smaller PAHs have been observed in vapor form around Chicago but as much as 90% of the high molecular weight PAHs (4+ rings) are particulate bound [49, 50].

HVAS measurements for only select compounds were reported by USACE including PCBs 15, 20/28 and 31 and 2-4 ring PAHs, namely, naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, fluoranthene and pyrene. HVAS data for PCB 18 was not reported by USACE during the ADMP and PDMP due to unspecified quality assurance problems.

HVAS measurements over the time to steady state ($\boldsymbol{\tau_{ss}}$) for each compound were averaged to compare to the passive sampling measurements. This assumes that once per week HVAS samples adequately represented the weekly average air concentration. For example, the estimated τ_{ss} for PCB 15 during the ADMP sampling was 28 days (Table S2) and thus compared to the average of the four HVAS samples collected over the final 4 weeks of the sampling period. Naphthalene was expected to equilibrate in under a week and was thus compared to the single HVAS sample collected in the week prior to collection of the samplers. Note that PCB 31 co-eluted with congeners 21 and 53 during the POM air concentration analysis but PCB 31 is expected to be the dominant congener based upon its production and prevalence [51-53]. It was therefore assumed that 100% of the co-eluting peak was congener 31 for the purposes of comparison to the HVAS measurements.

As shown in Figure 5.5 the concentration of PCBs in air as measured using POM was generally within a factor of 2 of that measured by HVAS for PCB 18, 20/28, 31 and naphthalene although some larger deviations (up to a factor of ~4) were noted for PCB 15. For PAHs, good agreement was found between POM and HVAS for the 2 ring naphthalene but HVAS showed much higher concentrations of the 3 and 4 ring PAHs than were observed in POM. The increasingly large difference with higher MW PAHs is consistent with the likely increasing proportion of these PAHs on particulates that are not measured by the POM but also likely indicating the effect of sources other than evaporation from the CDF. The PCBs and naphthalene were likely dominated by vapor phase contaminants and evaporation from the CDF.

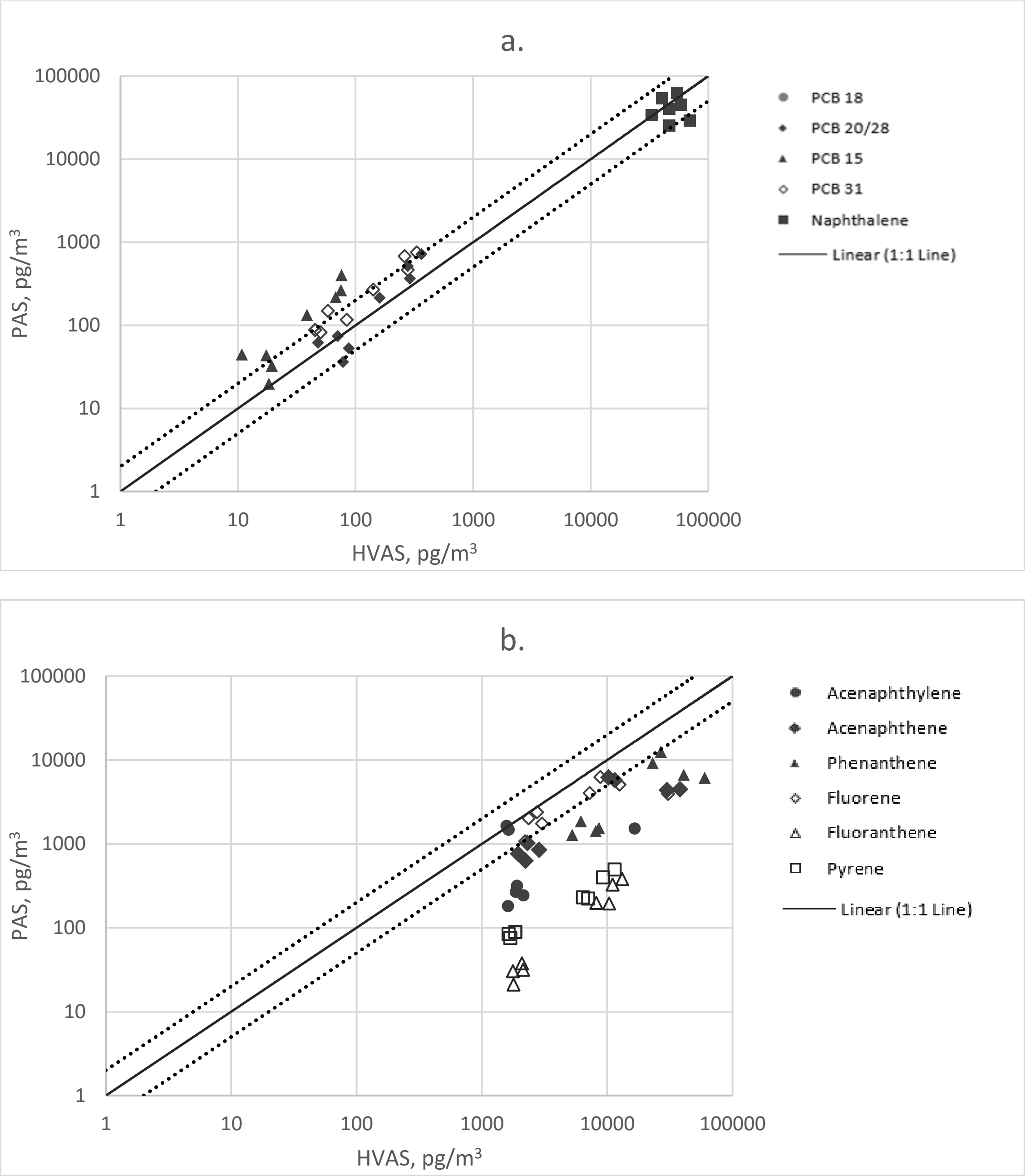


Figure 5.5. Comparison of individual measurements of PCBs and PAHs for HVAS and POM. The broken lines represent +/- a factor of 2 from 1:1 line. Symbols in a) indicate naphthalene and LCN PCBs (which good correspondence was observed between POM and HVAS) and symbols in b) which represents higher molecular weight PAHs (where POM underestimated HVAS measurements presumably due to particulate association of these constituents).

The effect of PAH sources was also explored using diagnostic ratios (Table 5.3). While the use of diagnostic ratios of the priority PAHs is generally not a definitive indicator, they can provide an additional information to contributing sources [54, 55]. Because diagnostic ratios compare compounds of similar physical properties, they are also relatively insensitive to phase changes and partial equilibration. The ratio of fluoranthene to the sum of fluoranthene and pyrene (Flu/Flu+Pyr), chrysene to the sum of chrysene and benzo(a)anthracene (BaA/ BaA+Chry), and Indeno(123-cd)pyrene to the sum of Indeno(123-cd)pyrene and Benzo(ghi)perylene (InD/ InD+BghiP) are shown in Table 5.3. The ratios of Flu/(Flu+Pyr) were within the range of 0.4-0.5, BaA/ (BaA+Chry) was greater than 0.35, and InD/ (InD+BghiP) was within the range of 0.2-0.5 suggesting fuel combustion emission sources [56]. This is consistent with the influence of nearby urban vehicle emissions and emissions from nearby industrial sources and supportive of the preceding conclusions that other sources, including particulate sources, contributed to the PAH concentrations measured.

Table 5.3. Diagnostic test for PAHs air concentration

Deployments	Flu/ (Flu+pyr)	BaA/ BaA+Chry	InD/ InD+BghiP
ADMP	0.442	0.979	0.266
PDMP	0.284	0.982	0.293

where Flu – Fluoranthrene; Pyr- Pyrene; Chry-Chrysene; BaA- benzo(a)anthracene; InD- Indeno(123-cd)pyrene; and Bghip-Benzo(ghi)perylene (interpretation in text).

5.3.3. Evaporative fluxes

USACE operation of the CDF places limits on both nearby air concentrations and the flux of PCBs and PAHs from the facility. Fluxes could be used to estimate concentrations farther from the CDF through an air dispersion model. Original efforts were directed toward estimating evaporative flux by measuring concentrations in the CDF impoundment and then employing mass transfer models [35]. The concentrations in the impoundment were likely variable in time and space, however, requiring extensive sampling to define an average. An estimate was made based upon suspended sediment and a single measurement of PCB and PAH concentration in that sediment and estimated partitioning to the CDF impounded waters (described in SI). This was judged to be of limited accuracy due to the lack of more extensive sampling of the impoundment.

An alternative approach is to estimate the evaporative flux on the basis of its consistency with the observed long-term average air concentration around the CDF measured via POM. Because the POM measurement points are immediately adjacent to the source area and a long-term average is desired, the relationship between average evaporative flux and on-site air concentration was estimated using a simple near-source box model (derived in SI). The relationship between on-site air concentration and CDF emission flux can be estimated by,

$$N_A = \left[\frac{0.22Hln(3.7H)}{L}\right] UC_A \tag{5.5}$$

where N_A is the emission flux (ng/m^2 /s) across the CDF (assumed uniform across the CDF). L (m) is the distance or fetch across the CDF in the direction of the wind, H (m) is the height over which the contaminant is mixed above the ground and dependent upon the aerodynamic roughness and fetch, and U is the wind speed (m/s) at the standard meteorological measurement height of 10 m. Under neutral atmospheric conditions, which may be viewed as an *average* condition, L and H are related as described by Pasquill [57].

$$\frac{L}{z_0} = 6.25\left[\frac{H}{z_0} * ln\frac{H}{z_0} - 1.58\frac{H}{z_0} + 1.58\right] \tag{5.6}$$

Under the assumption of an aerodynamic roughness of the order of 0.1 m (open area with occasional buildings and/or trees which is approximately the conditions around the CDF), the bracketed term in equation 5.5 for air concentration is 24 ± 1 for fetch L between 30 and 1000m, as detailed in the SI. Therefore, the emission flux ($ng/m^2/s$) from the CDF can be estimated from measured air concentrations using $N_A \sim C_A*U/24$. This simple relationship under these conditions is the result of a balance between the growth in the local contaminant mixing height, H, with fetch L, and the evaporative flux leading to a nearly constant air concentration within the breathing zone on and immediately adjacent to the CDF. Taking the average concentration of 0.905 ng/m^3 for PCB 18, the congener present at the highest concentration during the ADMP period, the average emission flux is estimated to be 0.15 $ng/m^2/s$.

The calculated total PCB and PAH fluxes consistent with the observed air concentrations are included in Table 5.4 where they are also compared to the total PCB and PAH flux estimated via a mass transfer model. As noted earlier, the water concentrations on which the mass transfer model is based represent estimated partitioning from a single suspended solids measurement and thus unlikely to adequately characterize the actual evaporative flux. The flux consistent with the measured air concentration is likely a better estimate of the actual flux from the CDF except when influenced by other sources such as for the PAHs. The estimated flux could be used to estimate air concentrations further away from the CDF using an air dispersion model but this is not discussed here.

Table 5.4. Comparison of evaporative flux estimated from a mass transfer model to that estimated by consistency with air concentrations, Equation (5.5)

	PCB Evaporative Flux, ng·m^{-2}·s^{-1}		PAH Evaporative Flux, ng·m^{-2}·s^{-1}	
Period	Equation (5.5)	MT Model (SI)	Equation (5.5)	MT Model (SI)
ADMP	2.08	0.110	10.59	2.85
PDMP	0.44	0.107	7.69	2.10

5.4. Conclusions

The POM air sampler allowed the measurement of air concentration averaged over the equilibration time for the sampler. The POM air sampler achieved the objectives of this study in that a single concentration measurement could replace the averaging of multiple measurements by conventional sampling such as HVAS. As a partitioning sampler, the POM can only measure air phase concentrations although that is helpful for limiting measurements to evaporative emissions. The air concentrations of high molecular weight PAHs measured by POM are significantly below the total air concentration due to the association of these PAHs with particulates and the presence of a sources other than evaporation from the CDF. The equilibration time is a function of the hydrophobicity of the compound complicating the interpretation of average concentrations and for $Log\ K_{POM-A} > 8$ influenced or controlled by external resistances, resulting in uncertain achievement of equilibration of those compounds. For low molecular weight compounds for which equilibration is controlled by internal diffusional resistances, however, the equilibration is independent of wind speed and atmospheric conditions other than temperature. Because of the importance of equilibration time in interpreting the results, a time series of measurements would generally be preferred to measure air concentrations of a wider range of compounds as well as quantify equilibration time under field conditions. In general, estimated air concentrations during the active dredged material placement period was higher than the post dredge material period. The air sampling also suggests that other sources controls the air concentrations of many HOCs, particularly high molecular weight PAHs.

Acknowledgement

We wish to acknowledge field support and financial support under contract W912HZ-17-2-0019 provided by the U.S Army Engineer Research and Development Center, Vicksburg Mississippi and the U.S Army of Corps of Engineers, Chicago District.

References

1. Janine, C.; Reckendorf, F., Effects of Sediment on the Aquatic Environment: Potential NRCS Actions to Improve Aquatic Habitat -Working Paper No. 6. In August, 1995 ed.; 1995.
2. Schmutz, S.; Sendzimir, J., *Riverine ecosystem management*. Springer International Publishing Switzerland: 2018.
3. Council, N. R., *A risk-management strategy for PCB-contaminated sediments*. National Academies Press: 2001.
4. USEPA Sediments - Risk Assessment. https://clu-in.org/issues/default.focus/sec/Sediments/cat/Risk_Assessment/ (June 5, 2020),
5. Schrader, M. H. *Implementing Regional Sediment Management (RSM): Policy Guidance and Authorities Pertinent to Improving the Use of Dredged Sediments*; ERDC Vicksburg United States: 2019.
6. Bailey, P.; Estes, T.; Bourne, S.; Sekoni, T.; Price, D. *Introduction to Using Native Plant Community on Dredge Material Placement Areas*; US Army Engineer Research and Development Center CEERD-IS-L Vicksburg United …: 2017.
7. Szimanski, D. M.; McQueen, A. D.; Suedel, B. C. *Realizing Multiple Benefits in US Army Corps of Engineers (USACE) Baltimore District Dredging Projects through Application of Engineering With Nature (R) Principles*; ERDC Vicksburg United States: 2019.
8. Bridges, T. S.; Gustavson, K. E.; Schroeder, P.; Ells, S. J.; Hayes, D.; Nadeau, S. C.; Palermo, M. R.; Patmont, C., Dredging processes and remedy effectiveness: Relationship to the 4 Rs of environmental dredging. *Integrated environmental assessment and management* 2010, *6*, (4), 619-630.
9. Palermo, M. R.; Wilson, J. R. In *Corps of Engineers Role In Contaminated Sediment Management And Remediation*, Proceedings, American Bar Association, Section of Environment, Energy, and Resources, Panel on Contaminated Sediments: Science, Law, and Politics, 8th Section Fall Meeting, New Orleans, LA, 2000; 2000.
10. Popek, E. P., *Sampling and analysis of environmental chemical pollutants: a complete guide*. Elsevier: 2017.
11. EPA, U. S., Technical Overview of Volatile Organic Compounds. 2017.
12. Ciganek, M.; Neca, J., Chemical characterization of volatile organic compounds on animal farms. *Vet. Med-Czech* 2008, *53*, (12), 641-651.

13. Palermo, M. R.; Schroeder, P. R.; Estes, T. J.; Francingues, N. R. *Technical guidelines for environmental dredging of contaminated sediments*; ENGINEER RESEARCH AND DEVELOPMENT CENTER VICKSBURG MS ENVIRONMENTAL LAB: 2008.

14. Maglio, C.; Scully, B., Confined Disposal Facility Improved Weir Designs. 2016.

15. Thibodeaux, L. J.; Ravikrishna, R.; Valsarag, K. T., *Volatilization Rates from Dredged Material and Soils: A Literature Review with Application to Indiana Harbor and Canal*. Gordon A. and Mary Cain Department of Chemical Engineering & South and …: 2002.

16. Thibodeaux, L. J.; Valsaraj, K. T.; Ravikrishna, R.; Fountain, K.; Price, C. L. *Investigations of the Controlling Factors for Air Emissions Associated With the Dredging of Indiana Harbor and Canal (IHC) and CDF Operations*; ENGINEER RESEARCH AND DEVELOPMENT CENTER VICKSBURG MS ENVIRONMENTAL LAB: 2008.

17. Greenwood, R.; Mills, G.; Vrana, B., *Passive sampling techniques in environmental monitoring*. Elsevier: 2007.

18. Persoon, C.; Hornbuckle, K. C., Calculation of passive sampling rates from both native PCBs and depuration compounds in indoor and outdoor environments. *Chemosphere* 2009, *74,* (7), 917-923.

19. Herkert, N. J.; Spak, S. N.; Smith, A.; Schuster, J. K.; Harner, T.; Martinez, A.; Hornbuckle, K. C., Calibration and evaluation of PUF-PAS sampling rates across the Global Atmospheric Passive Sampling (GAPS) network. *Environ. Sci.: Process. Impacts* 2018, *20,* (1), 210-219.

20. Ahrens, L.; Harner, T.; Shoeib, M., Temporal variations of cyclic and linear volatile methylsiloxanes in the atmosphere using passive samplers and high-volume air samplers. *Environmental science & technology* 2014, *48,* (16), 9374-9381.

21. Baek, S.-Y.; Choi, S.-D.; Chang, Y.-S., Three-year atmospheric monitoring of organochlorine pesticides and polychlorinated biphenyls in polar regions and the South Pacific. *Environmental science & technology* 2011, *45,* (10), 4475-4482.

22. Wania, F.; Shen, L.; Lei, Y. D.; Teixeira, C.; Muir, D. C., Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere. *Environmental science & technology* 2003, *37,* (7), 1352-1359.

23. Melymuk, L.; Bohlin, P.; Sáňka, O. e.; Pozo, K.; Klánová, J., Current challenges in air sampling of semivolatile organic contaminants: sampling artifacts and their

influence on data comparability. *Environ. Sci. Technol.* 2014, *48*, (24), 14077-14091.

24. Bartkow, M. E.; Huckins, J. N.; Müller, J. F., Field-based evaluation of semipermeable membrane devices (SPMDs) as passive air samplers of polyaromatic hydrocarbons (PAHs). *Atmos. Environ.* 2004, *38*, (35), 5983-5990.
25. Zhu, X.; Zhou, C.; Henkelmann, B.; Wang, Z.; Ma, X.; Pfister, G.; Schramm, K.-W.; Chen, J.; Ni, Y.; Wang, W., Monitoring of PAHs profiles in the urban air of Dalian, China with active high-volume sampler and semipermeable membrane devices. *Polycyclic Aromatic Compounds* 2013, *33*, (3), 265-288.
26. Khairy, M. A.; Lohmann, R., Field validation of polyethylene passive air samplers for parent and alkylated PAHs in Alexandria, Egypt. *Environmental science & technology* 2012, *46*, (7), 3990-3998.
27. Tromp, P. C.; Beeltje, H.; Okeme, J. O.; Vermeulen, R.; Pronk, A.; Diamond, M. L., Calibration of polydimethylsiloxane and polyurethane foam passive air samplers for measuring semi volatile organic compounds using a novel exposure chamber design. *Chemosphere* 2019, *227*, 435-443.
28. Odetayo, A. A.; Reible, D. D.; Acevedo-Mackey, D.; Price, C.; Thaic, L., Development of polyoxymethylene passive sampler for assessing air concentrations of PCBs at a confined disposal facility (CDF). *Environ. Pollut.* 2020, 114720.
29. Lampert, D.; Thomas, C.; Reible, D., Internal and external transport significance for predicting contaminant uptake rates in passive samplers. *Chemosphere* 2015, *119*, 910-916.
30. Nam, G.-U.; Bonifacio, R. G.; Kwon, J.-H.; Hong, Y., Kinetics and equilibrium partitioning of dissolved BTEX in PDMS and POM sheets. *Environ. Sci. Pollut. R.* 2016, *23*, (18), 18901-18910.
31. Thomas, C.; Reible, D. D., Modeling Compound Loss from Polydimethylsiloxane Passive Samplers. *Chromatography* 2015, *2*, (4), 611-624.
32. Hong, L.; Luthy, R. G., Uptake of PAHs into polyoxymethylene and application to oil-soot (lampblack)-impacted soil samples. *Chemosphere* 2008, *72*, (2), 272-281.
33. Francisco, A. P.; Harner, T.; Eng, A., Measurement of polyurethane foam–air partition coefficients for semivolatile organic compounds as a function of temperature: Application to passive air sampler monitoring. *Chemosphere* 2017, *174*, 638-642.

34. Tcaciuc, A. P.; Apell, J. N.; Gschwend, P. M., Modeling the transport of organic chemicals between polyethylene passive samplers and water in finite and infinite bath conditions. *Environ. Toxicol. Chem.* 2015, *34*, (12), 2739-2749.

35. Thibodeaux, L. J.; Mackay, D., *Handbook of chemical mass transport in the environment*. CRC Press: 2010.

36. Rusina, T. P.; Smedes, F.; Klanova, J., Diffusion coefficients of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in polydimethylsiloxane and low-density polyethylene polymers. *J. Appl. Polym.* 2010, *116*, (3), 1803-1810.

37. USACE, High volume air sampler Data. 2018.

38. Hawthorne, S. B.; Jonker, M. T.; van der Heijden, S. A.; Grabanski, C. B.; Azzolina, N. A.; Miller, D. J., Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Anal. Chem.* 2011, *83*, (17), 6754-6761.

39. Hawthorne, S. B.; Miller, D. J.; Grabanski, C. B., Measuring low picogram per liter concentrations of freely dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. *Anal. Chem.* 2009, *81*, (22), 9472-9480.

40. Dunnivant, F. M.; Elzerman, A. W.; Jurs, P. C.; Hasan, M. N., Quantitative structure-property relationships for aqueous solubilities and Henry's law constants of polychlorinated biphenyls. *Environ. Sci. Technol.* 1992, *26*, (8), 1567-1573.

41. Williams, A. J.; Grulke, C. M.; Edwards, J.; McEachran, A. D.; Mansouri, K.; Baker, N. C.; Patlewicz, G.; Shah, I.; Wambaugh, J. F.; Judson, R. S.; Richard, A. M., The CompTox Chemistry Dashboard: a community data resource for environmental chemistry. *J. Cheminformatics* 2017, *9*, (1), 61.

42. Fernandez, L. A.; Lao, W.; Maruya, K. A.; Burgess, R. M., Calculating the diffusive flux of persistent organic pollutants between sediments and the water column on the Palos Verdes Shelf Superfund Site using polymeric passive samplers. *Environmental science & technology* 2014, *48*, (7), 3925-3934.

43. Oen, A. M.; Janssen, E. M.; Cornelissen, G.; Breedveld, G. D.; Eek, E.; Luthy, R. G., In situ measurement of PCB pore water concentration profiles in activated carbon-amended sediment using passive samplers. *Environ. Sci. Technol.* 2011, *45*, (9), 4053-4059.

44. Perron, M. M.; Burgess, R. M.; Suuberg, E. M.; Cantwell, M. G.; Pennell, K. G., Performance of passive samplers for monitoring estuarine water column concentrations: 1. Contaminants of concern. *Environ. Toxicol. Chem.* 2013, *32*, (10), 2182-2189.

45. Li, N.; Wania, F.; Lei, Y. D.; Daly, G. L., A comprehensive and critical compilation, evaluation, and selection of physical–chemical property data for selected polychlorinated biphenyls. *J. Phys. Chem. Ref. data* 2003, *32,* (4), 1545-1590.

46. Beyer, A.; Wania, F.; Gouin, T.; Mackay, D.; Matthies, M., Selecting internally consistent physicochemical properties of organic compounds. *Environ. Toxicol. Chem.* 2002, *21*, (5), 941-953.

47. Deshpande, A. D., Contaminant levels in muscle of four species of recreational fish from the New York Bight apex. 2000.

48. Faroon, O. M.; Samuel Keith, L.; Smith-Simon, C.; De Rosa, C. T.; Organization, W. H., *Polychlorinated biphenyls: human health aspects*. World Health Organization: 2003.

49. Odabasi, M.; Vardar, N.; Sofuoglu, A.; Tasdemir, Y.; Holsen, T. M., Polycyclic aromatic hydrocarbons (PAHs) in Chicago air. *Science of the Total Environment* 1999, *227*, (1), 57-67.

50. Harner, T.; Bidleman, T. F., Octanol− air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air. *Environ. Sci. Technol.* 1998, *32*, (10), 1494-1502.

51. Hughes, A. S.; VanBriesen, J. M.; Small, M. J., Impacts of PCB analytical interpretation uncertainties on dechlorination assessment and remedial decisions. *Chemosphere* 2015, *133*, 61-67.

52. Frame, G. M., A collaborative study of 209 PCB congeners and 6 Aroclors on 20 different HRGC columns 2. Semi-quantitative Aroclor congener distributions. *Fresen. J. Anal. Chem.* 1997, *357*, (6), 714-722.

53. Robertson, L. W.; Hansen, L. G., *PCBs: recent advances in environmental toxicology and health effects*. University Press of Kentucky: 2015.

54. Huang, L.; Chernyak, S. M.; Batterman, S. A., PAHs (polycyclic aromatic hydrocarbons), nitro-PAHs, and hopane and sterane biomarkers in sediments of southern Lake Michigan, USA. *Sci. Total. Environ.* 2014, *487*, 173-186.

55. Katsoyiannis, A.; Sweetman, A. J.; Jones, K. C., PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. *Environ. Sci. Technol.* 2011, *45*, (20), 8897-8906.

56. Tobiszewski, M. In *Application of diagnostic ratios of PAHs to characterize the pollution emission sources*, 2014 Proceedings of the 5th International Conference on Environmental Science and Technology, 2014; 2014.

57. Pasquill, F., The dispersion of material in the atmospheric boundary layer—the basis for generalization. In *Lectures on air pollution and environmental impact analyses*, Springer: 1982; pp 1-34.

Supplementary Information

For Chapter 5. Application of polyoxymethylene passive air sampler to monitor hydrophobic organics in air around a confined disposal facility

S1. Supplementary Data

Data Analysis

The air concentration, C_A, was calculated using the sorbed concentration on PAS and the POM-air partition coefficient ($K_{POM\text{-}A}$) as depicted in equation S1.

$$C_A = \frac{C_{POM}}{K_{POM-A}} \tag{S1}$$

where C_{POM} is the concentration measured in POM (ug/kg) at equilibrium. The POM concentration was determined from analysis of the extract and conversion of the extract concentration to equivalent concentration on the POM. $K_{POM\text{-}A}$ was estimated theoretically by the ratio of the POM-water partition coefficient ($K_{POM\text{-}w}$) and the air-water partition coefficient (K_{AW}) for the individual compound, following the description in Odetayo, et al. [1]. Values of $K_{POM\text{-}w}$ and K_{AW} were estimated using established partition coefficient correlations [2-5] with octanol-water partition coefficients [6, 7] for PCBs and PAHs.

Information and data used for temperature effects correction during the post dredging material placement (PDMP) are shown in Table S1 for PCBs and PAHs.

The uptake of hydrophobic organic contaminants (HOCs) from the vapor phase onto POM can be related to a simple mass transfer model relating the average concentration in the POM to a linear driving force model using an overall mass transfer coefficient, k_0, and the difference between the concentration in the surrounding air and the concentration in air that would be in equilibrium with the POM. At equilibrium this difference is 0 and is at a maximum at initial exposure of fresh POM to the contaminated air. The rate of change is given as follows;

$$\frac{d<C_{POM}>}{dt} = \frac{2K_o}{\partial}\left(C_A - \frac{<\mathrm{C}_{\mathrm{POM}}>}{K_{POM-A}}\right) \qquad (S2)$$

Here <C_{POM}> is the average concentration in the POM, k_o is the overall mass transfer (cm/hr), K_{POM-A} is the POM-Air partition coefficient, and ∂ is the POM volume to area ratio (half-thickness). Analytically solving equation S2 give a first order equation of the form of equation 1 in manuscript where the average concentration in POM is simply denoted as C_{POM} which is the measured mass of contaminant in the POM divided by its total volume.

Table S1. Parameters used in the estimation POM-air partition coefficients

Air Temperature, ° K	277.7
Water Temperature, ° K	283.7
ΔU_{PCBi}, KJ/mole	-10 [8]
ΔU_{PAHsi}, KJ/mole	-25 [9]
$Log\ K_{POM-W,ref}$	$PCBs: 0.791 * Log\ K_{OW} + 1.02$ [3] $PAHs: 0.839 * Log\ K_{OW} + 0.314$ [2]
$\Delta U_{a/w}$	$\Delta U_{a/w}$, PCBs $= 0.085 \pm 0.007 * Mw - 1 * n_{orthoCl} + 32.7 \pm 1.6 = 49.66 \frac{KJ}{mole}$ [10] $\Delta U_{a/w}$, PAHs ± 16.5 [11]
Henry constant (Kaw)	$K_{AW,\ PCBi}$ ± 3.7, [4] $K_{AW,\ PAHi,}$ [5]
K_{OW}	$K_{OW,PCBs}$; [6] $K_{OW,\ PAHs}$; [7]
Other Parameters	R=8.314 J/Kmole

S2. Supplemental Information on POM Sampling

Figure S1 shows wind conditions during the active dredged material placement period. Figure S2 shows the average air concentrations of PCBs and PAHs during this period. Figures S3 and S4 show the corresponding data for the post-dredged material placement program. For both deployment periods, the PCB distribution was defined by homolog groups of the same number of chlorine atoms while the PAH distribution was categorized by the number of rings. The limit of quantification (LOQ) for PCBs and PAHs was determined in solvent extracts from the lowest calibration concentration with less than 20% RSD from the calibration. This was 0.08 μg/L for PCBs and 0.2 μg/L for PAHs. These were converted to a limit of quantification for each compound in air based upon the compounds K_{POM-A}, the 200 mg of POM (thickness - 76 μm, area approximately 19 cm^2 and density - 1.41 g/ml) in each sample and final solvent extract volume of 100 μL. The limit of quantification in air for each compound are shown in Tables S2 and S3 with the actual average air concentration detected.

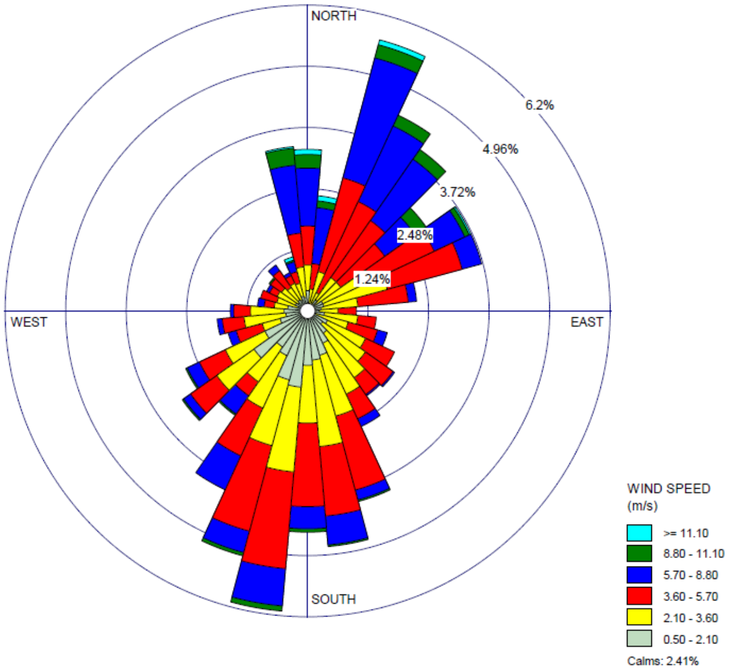


Figure S3. Windrose during active dredging deployment period.

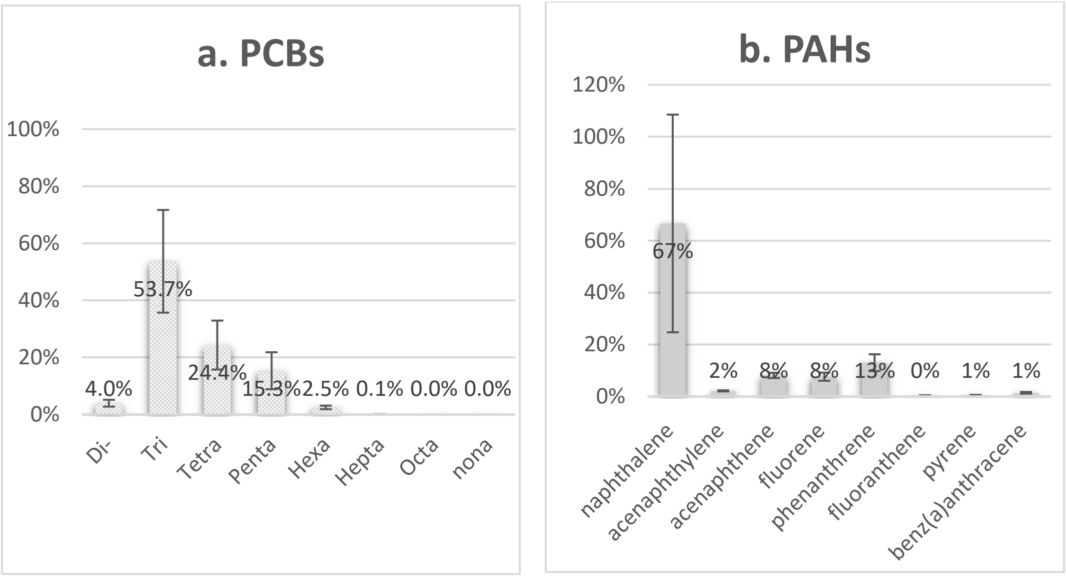


Figure S4. PCBs Homolog and PAHs distribution during active dredging material placement (ADMP) period.

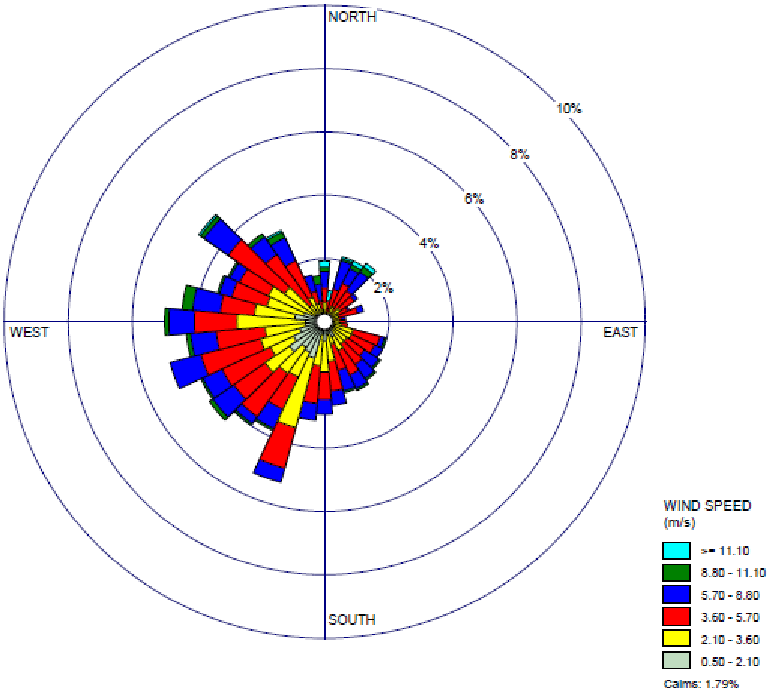


Figure S5. Windrose during Post dredging deployment period.

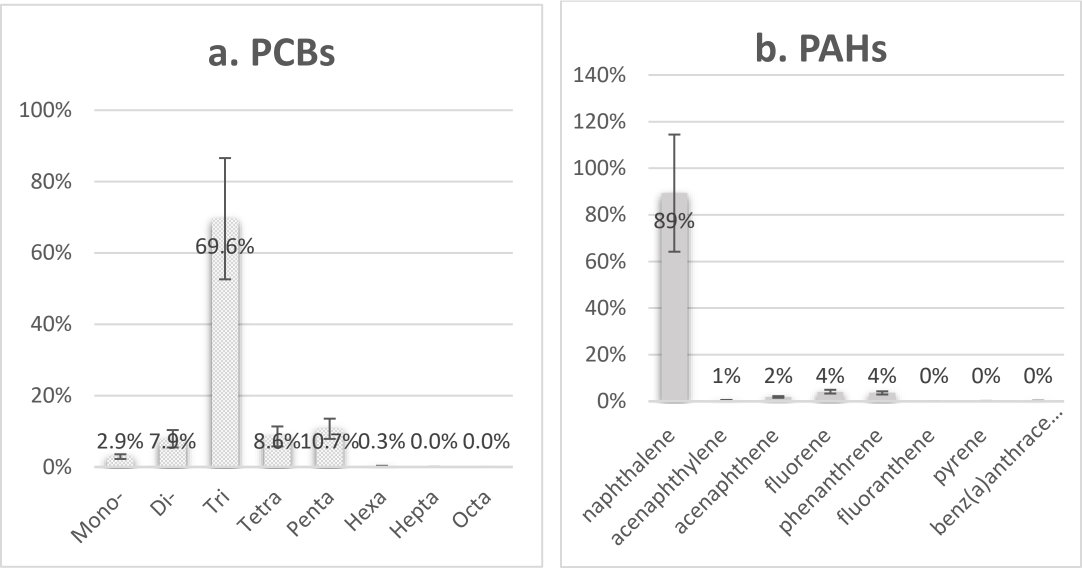


Figure S6. PCB homolog and 15 PAHs distribution during Post dredging material placement (PDMP) periods.

Table S2. PAS measured air concentration for individual PCB congeners during active dredging and post dredging periods including the limit of quantification (LOQ) for individual periods. Estimated from a practical quantification limit of 0.08 µg/L in solvent extracts

PCBs	Deployment Periods					
	Active Dredging			Post Dredging		
	τ_{ss} (days)	LOQ (pg/m^3)	C_A (pg/m^3)	τ_{ss} (days)	LOQ (pg/m^3)	C_A (pg/m^3)
1	6	38.9	ND	25	8.06	51.0 ± 15.3
2	11	24.6	106 ± 6.22	31	4.94	11.1 ± 1.67
3	12	23.6	ND	32	4.74	10.7 ± 1.12
10	10	27.7	ND	30	5.44	46.3 ± 9.05
7	16	16.2	ND	37	3.09	12.4 ± 2.05
9	18	14.2	ND	39	2.69	10.8 ± 1.79
6	18	14.3	ND	39	2.73	22.5 ± 7.43
8	19	13.1	173 ± 52.4	40	2.48	16.6 ± 3.98
5	20	12.3	62.5 ±32.7	40	2.34	43.7 ± 11.9
19	13	20.8	242 ±103	34	3.85	117 ± 24.1
30	20	12.6	115 ±30.1	41	2.25	49.2 ± 13.6
11	24	8.52	109 ±18.1	45	1.57	11.4 ± 9.1
18	22	10.1	905 ± 347	44	1.81	99.0 ± 26.2
17	21	11.6	316 ± 80.8	42	2.08	200 ± 53.6
15	28	6.35	298 ± 130	49	1.17	32.4 ± 10.3
24	25	8.04	260 ± 93.8	46	1.44	75.3 ± 22.3
27	24	8.87	275 ± 94.8	45	1.59	75.4 ± 30.9
16	24	9.17	141 ± 80.1	45	1.65	24.4 ± 7.53
32	24	8.59	176 ± 51.9	46	1.54	60.0 ± 17.1
34	28	6.19	632 ± 207	50	1.08	141 ± 58
29	31	4.85	359 ± 135	53	0.84	95.0 ± 27.7
26	33	4.37	432 ± 172	54	0.76	52.2 ± 25
25	32	4.56	198 ± 74.9	54	0.79	94.0 ± 28.8
31+50	34	3.95	770 ± 258	56	0.69	99.7 ± 22.5
28	33	4.12	545 ± 239	55	0.72	49.6 ± 20.8
20	35	3.93	20.5 ± 3.34	56	0.76	28.2 ± 4.43
21+33+53	34	3.76	234 ± 38.2	56	0.66	323 ± 50.9
22	36	3.25	220 ± 75.1	58	0.57	38.6 ± 10.8
45	28	6.60	93.7 ± 44.1	50	1.12	5.27 ± 2.15

46	28	6.31	45.7 ± 26.7	50	1.07	9.37 ± 2.38
69	35	3.72	22.5 ± 4.27	57	0.61	6.23 ± 0.8
52	36	3.38	388 ± 162	58	0.56	24.4 ± 8.35
47	34	3.83	171 ± 70.4	57	0.63	9.7 ± 3.42
48	35	3.57	105 ± 33.3	58	0.59	5.51 ± 2.03
65	36	3.43	98.8 ± 13.8	58	0.57	14.7 ± 3.12
44	38	2.87	355 ± 154	60	0.47	17.6 ± 7.09
42	37	3.13	195 ± 75.7	59	0.52	14.6 ± 3.59
37	45	1.64	850 ± 145	67	0.28	107 ± 15.2
71	39	2.58	110 ± 39.9	62	0.42	6.72 ± 1.81
41	36	3.40	225 ± 88.6	58	0.56	13.1 ± 4.36
64	40	2.36	154 ± 60.7	63	0.39	9.38 ± 2.72
40	39	2.69	64.4 ± 31.9	61	0.44	3.93 ± 1.62
67	48	1.28	9.93 ± 3.54	71	0.205	ND
74	49	1.18	146 ± 47.3	72	0.19	11.0 ± 2.33
61	44	1.75	ND	67	0.28	4.58 ± 1.12
70	50	1.11	251 ± 91.5	72	0.18	5.07 ± 1.6
76	46	1.49	ND	69	0.24	7.08 ± 3.5
66	50	1.11	192 ± 62	72	0.18	9.4 ± 3.31
93+95	42	2.50	623 ± 325	63	0.39	151 ± 49.7
56	51	0.98	201 ± 45.2	74	0.16	5.6 ± 2.45
60	51	0.99	156 ± 34.5	74	0.16	14.6 ± 8.83
92	50	1.09	11.7 ± 3.6	73	0.164	ND
84	43	1.85	47.7 ± 18.9	66	0.29	1.5 ± 0.75
90	49	1.21	31.3 ± 12	72	0.18	0.47 ± 0.28
101	51	0.97	25.6 ± 9.62	75	0.15	0.49 ± 0.33
113	51	0.96	ND	75	0.15	3.82 ± 1.14
99	51	0.97	26.1 ± 5.09	75	0.15	3.52 ± 1.01
119	53	0.85	513 ± 154	76	0.13	34.0 ± 6.48
83	50	1.04	420 ± 227	74	0.16	57.2 ± 8.59
87	53	0.86	57.7 ± 18.3	76	0.13	3.49 ± 1.12
81	58	0.59	21.2 ± 3.27	81	0.09	6.42 ± 3.38
115	54	0.80	27.4 ± 9.64	77	0.12	0.11 ± 0.09
110	56	0.65	56.7 ± 17.6	80	0.10	2.92 ± 0.45
77	62	0.42	138 ± 10.1	85	0.07	12.9 ± 2.2
82	54	0.80	47.6 ± 15.2	77	0.12	8.98 ± 1.76
151	55	0.70	4.92 ± 1.5	79	0.100	ND

135+144	56	0.66	3.6 ± 0.69	80	0.09	0.11 ± 0.04
147	54	0.78	1.93 ± 1.02	78	0.11	0.14 ± 0.05
107	64	0.35	15.4 ± 2.13	88	0.05	2.44 ± 0.39
123	64	0.36	9.3 ± 2.39	87	0.05	1.61 ± 0.28
149	58	0.55	17.8 ± 3.88	82	0.08	0.07 ± 0.04
118	68	0.26	4.54 ± 0.67	91	0.04	0.82 ± 0.18
134	56	0.67	ND	80	0.10	0.47 ± 0.14
114	64	0.35	40.9 ± 8.32	88	0.05	12.4 ± 2.18
131	56	0.67	ND	80	0.09	0.5 ± 0.09
146	66	0.29	2.55 ± 0.44	91	0.04	0.1 ± 0.03
153	68	0.24	8.61 ± 2.07	93	0.03	0.34 ± 0.04
132	58	0.56	2.84 ± 1.3	82	0.08	0.3 ± 0.11
105	69	0.24	13.9 ± 3.48	92	0.04	0.84 ± 0.15
141	66	0.31	3.56 ± 0.56	90	0.04	0.21 ± 0.05
179	58	0.58	ND	83	0.08	0.04 ± 0.00
138	69	0.23	2.89 ± 0.82	94	0.03	0.15 ± 0.04
163	70	0.22	3.38 ± 0.78	94	0.03	0.26 ± 0.05
158	71	0.20	5.4 ± 1.27	95	0.03	0.28 ± 0.03
178	70	0.21	ND	95	0.03	ND
126	76	0.13	7.76 ± 2.31	101	0.02	0.55 ± 0.11
187	72	0.19	2.4 ± 0.64	97	0.02	0.03 ± 0.00
183	72	0.18	ND	97	0.02	ND
128+167	76	0.21	259 ± 65.9	101	0.03	2.2 ± 0.77
174	72	0.18	1.28 ± 0.24	98	0.02	ND
177	72	0.18	ND	97	0.02	0.1 ± 0.02
171	82	0.18	1.27 ± 0.57	97	0.02	0.03 ± 0.01
156	82	0.08	4.75 ± 0.67	107	0.01	0.87 ± 0.23
157	83	0.08	0.63 ± 0.16	107	0.01	0.35 ± 0.12
173	69	0.23	ND	95	0.03	0.23 ± 0.07
172	82	0.08	0.38 ± 0.25	107	0.01	0.08 ± 0.03
180	84	0.07	ND	109	0.01	0.11 ± 0.03
193	84	0.07	0.91 ± 0.12	110	0.01	0.09 ± 0.02
191	85	0.06	0.4 ± 0.09	111	0.01	0.08 ± 0.03
169	91	0.04	0.58 ± 0.13	116	0.01	0.29 ± 0.04
190	85	0.06	8.07	111	0.01	ND
198	85	0.06	0.26 ± 0.08	111	0.01	ND
203	87	0.05	0.36 ± 0.14	113	0.01	0.15 ± 0.04

189	97	0.02	0.32 ± 0.07	123	0.00	0.11 ± 0.03
195	87	0.05	0.44 ± 0.1	113	6.6E-03	ND
194	99	0.02	0.1 ± 0.04	126	2.3E-03	ND
205	101	0.02	0.1 ± 0.03	127	2.1E-03	ND
206	103	0.02	0.1 ± 0.02	130	1.7E-03	ND

Note: ND indicates non-detects or below the LOQ

Σ_{97}PCBs and Σ_{106}PCB congeners were measured during active dredge material placement (ADMP) and post dredge material placement (PDMP) periods.

Table S3. Limit of quantification (LOQ) during PAHs analysis at individual deployment period. Estimated from a practical quantification limit of 0.2 µg/L in solvent extracts

PAHs	LOQ (ng/m^3)	
	ADMP	PDMP
naphthalene	3.39	0.60
acenaphthylene	0.28	0.04
acenaphthene	0.40	0.06
fluorene	0.16	0.02
phenanthrene	0.02	3.4E-03
fluoranthene	1.8E-03	2.2E-04
pyrene	2.6E-03	4.2E-04
benz(a)anthracene	8.3E-04	7.7E-05
chrysene	3.3E-04	1.1E-05
benzo(b)fluoranthene	1.1E-05	1.4E-06
benzo(k)fluoranthene	1.2E-05	1.4E-06
benzo(a)pyrene	8.3E-06	1.8E-06
indeno(123-cd)pyrene	2.4E-06	3.0E-07
dibenzo(ah)anthracene	1.6E-06	2.0E-07
benzo(ghi)perylene	2.3E-06	2.9E-07

Table S4. PCBs and PAHs concentrations (averages ± S.D) using POM across deployment periods

	Deployment period			
	ADMP (ng/m^3)		PDMP (ng/m^3)	
Locations	**PCBs**	**PAHs**	**PCBs**	**PAHs**
T1	13.1 ± 2.21	35.6 ± 0.92	2.14 ± 0.38	30.2 ± 7.52
SW	10.1 ± 1.62	91.3 ± 11.4	2.62 ± 0.31	38.9 ± 20.5
S	14.9 ± 2.51	88.1 ± 12.9	2.43 ± 0.38	30.0 ± 3.62
SE	9.87 ± 1.08	34.2 ± 5.72	2.33 ± 0.52	44.8 ± 10.1
E	13.3 ± 1.6	71.9 ± 12.2	2.71 ± 0.66	45.4 ± 3.10
NE	11.3 ± 1.49	30 ± 6.71	2.55 ± 0.23	49.5 ± 16.9
N	17.2 ± 2.91	46.9 ± 11.0	3.02 ± 0.45	59.8 ± 5.95
NW	14.0 ± 2.66	83.3 ± 17.1	2.07 ± 0.42	69.7 ± 16.4
W	9.58 ± 1.44	117 ± 24.5	2.55 ± 0.26	37.2 ± 5.34
C	15.2 ± 0.47	58.2 ± 12.7	3.15 ± 0.63	41.5 ± 8.45

Note: S, SW and SE are locations at the southern boundary of the CDF, NW,N and NE are sampling locations at the northern boundary of the CDF, E,W, and C are the sampling location at the east, west and center of the CDF respectively. PCB measurements shows lesser variability across the 10 sampled locations when compared to PAHs measurement during the two deployment periods.

Table S5. Comparison of air concentration (average ± S.D) of PCB congeners and PAHs (ng/m^3)

HOCs	Deployment periods			
	Active dredging		**Post dredging**	
	PAS	HVAS	PAS	HVAS
PCB 15	0.36 ± 0.14	0.06 ± 0.02	0.04 ± 0.001	0.02 ± 0.003
PCB 18	0.94 ± 0.41	NA	0.1 ± 0.01	NA
PCB 20/28	0.66 ± 0.26	0.27 ± 0.07	0.09 ± 0.02	0.07 ± 0.02
PCB 31	0.77 ± 0.19	0.25 ± 0.07	0.11 ± 0.03	0.06 ± 0.02
Naphthalene	59.4 ± 26.4	64.6 ± 8.56	38.5 ± 10.4	41.9 ± 5.67
Acenaphthene	5.19 ± 0.79	22.5 ± 11.9	0.82 ± 0.14	2.34 ± 0.33
Acenaphthylene	1.48 ± 0.14	4.95 ± 6.76	0.25 ± 0.05	1.89 ± 0.18
Fluorene	4.82 ± 0.93	14.8 ± 9.35	1.81 ± 0.48	2.59 ± 0.32
Phenanthrene	8.61 ± 2.50	45.0 ± 7.30	1.52 ± 0.21	7.03 ± 1.36
Pyrene	0.34 ± 0.12	6.62 ± 1.90	0.07 ± 0.02	1.29 ± 0.75
Fluoranthene	0.27 ± 0.08	9.22 ± 1.37	0.03 ± 0.01	1.94 ± 0.17

Note: NA indicates measurements are yet to be analyzed or rejected for quality control reasons.

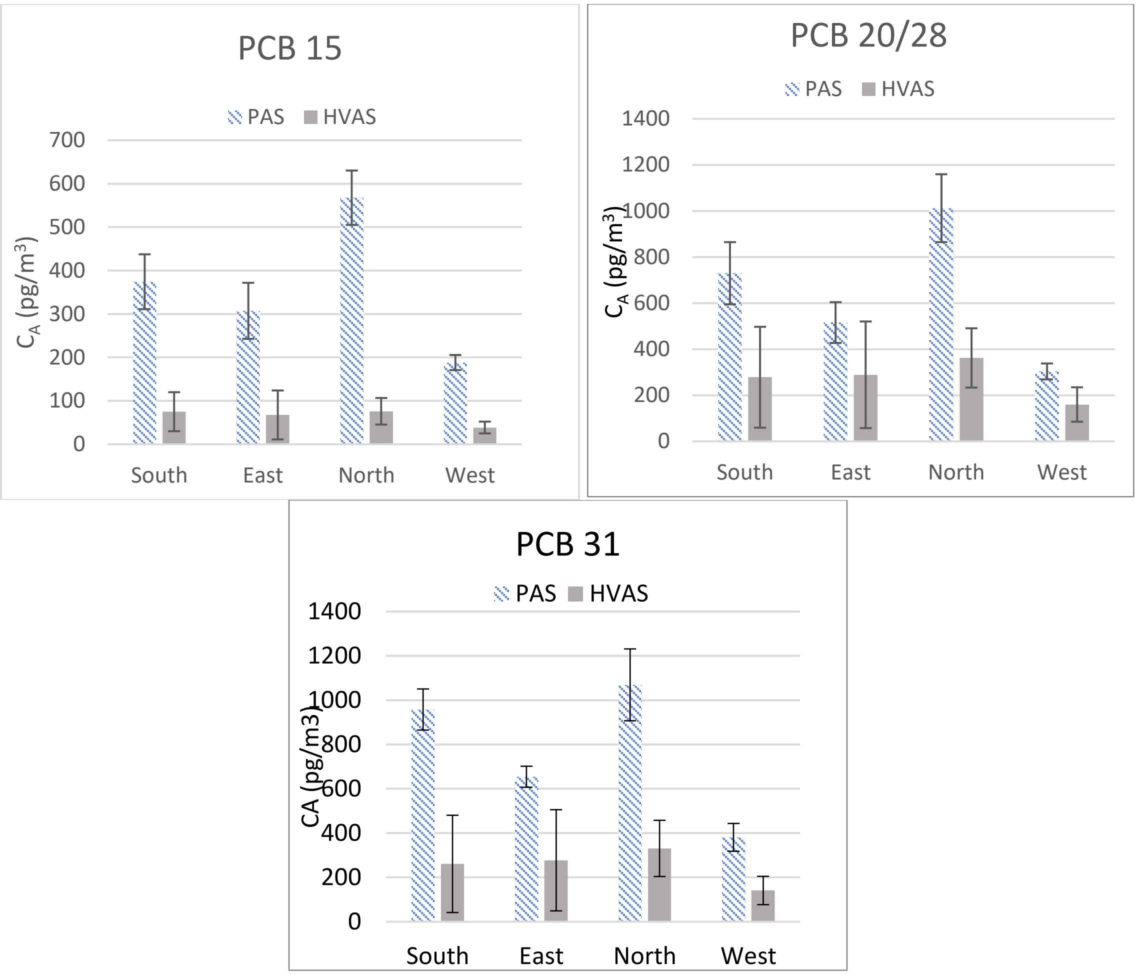


Figure S5. Distribution of PCB congeners across location for PAS and HVAS during active dredging material placement (ADMP) periods.

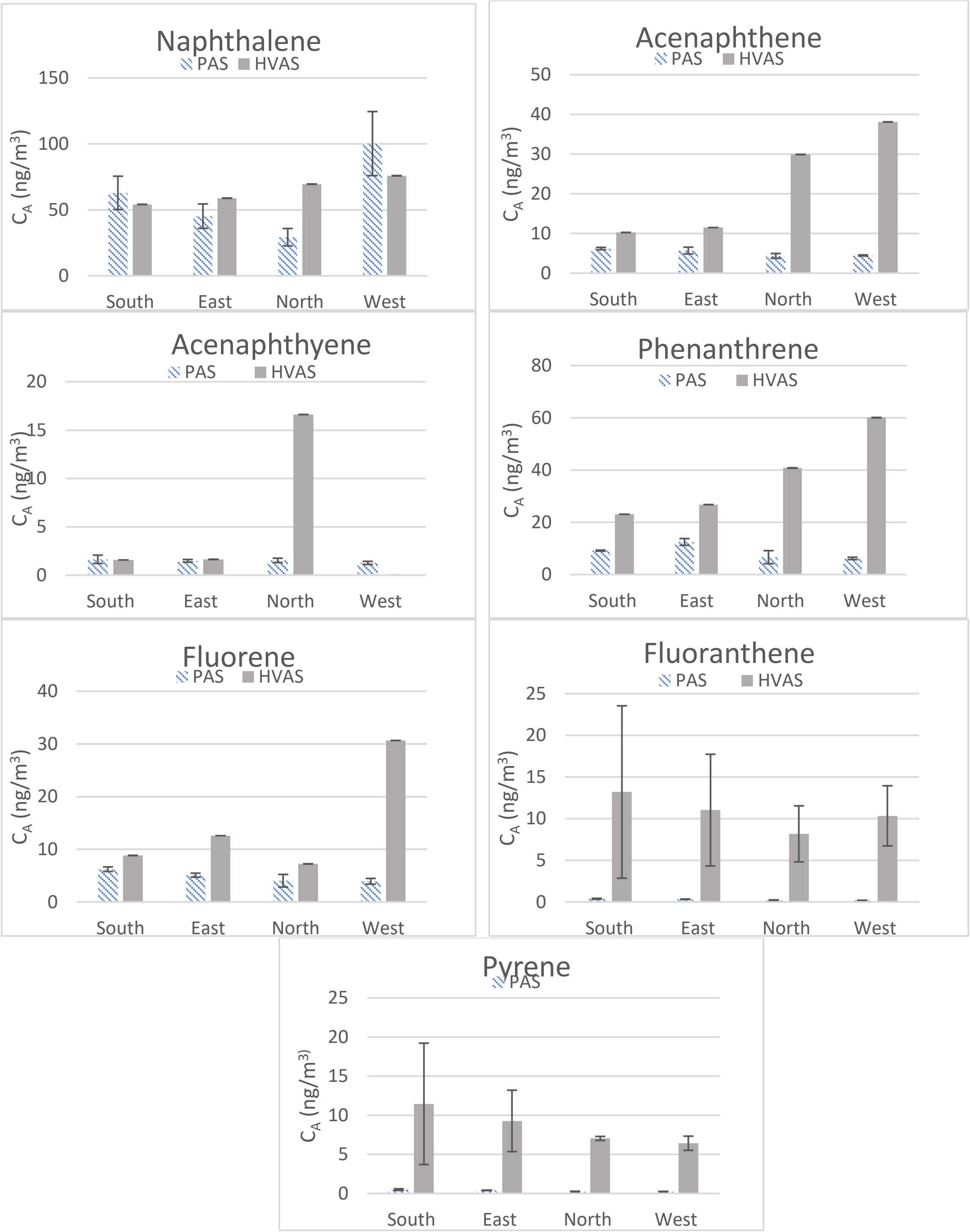


Figure S6. Distribution of uptake of PAHs per location on PAS and HVAS during Active dredging material placement (ADMP) periods.

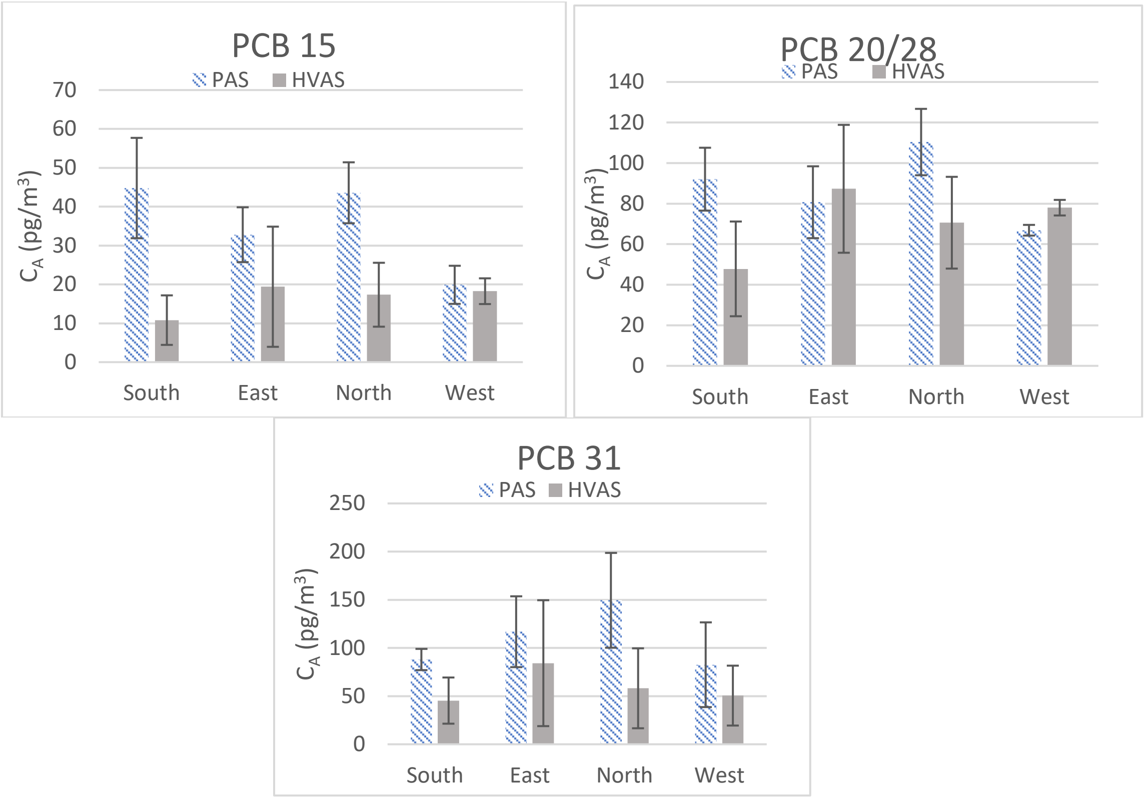


Figure S7. Distribution of uptake of PCB congeners per location on PAS and HVAS during Post dredging material placement (PDMP) periods.

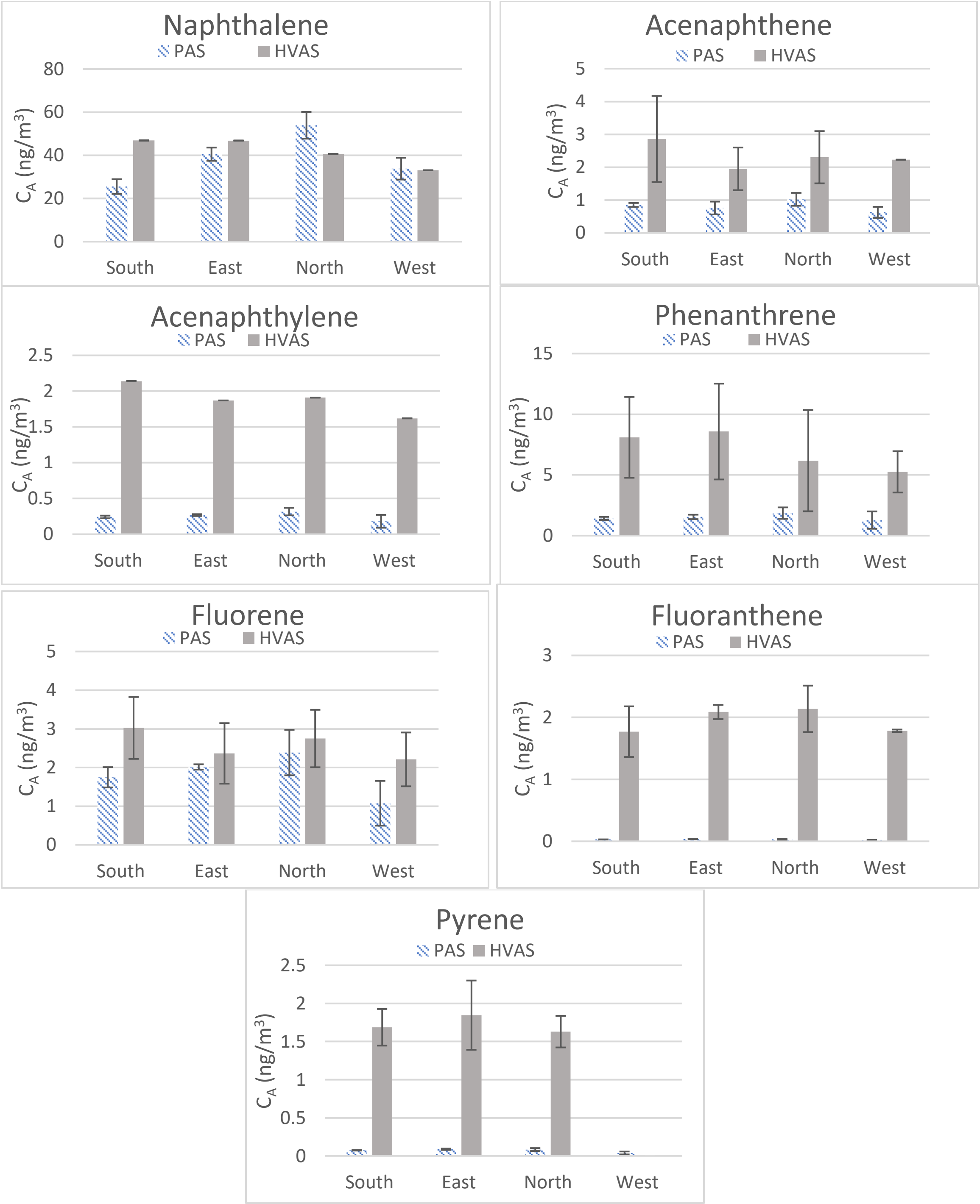


Figure S8. Distribution of uptake of PAHs per location on PAS and HVAS during Post dredging material placement (PDMP) periods.

S3. Derivation of Box Model for Emission flux

Estimation of the atmospheric concentrations on or near the source area may be of interest to estimate exposure to on-site workers or at immediately adjacent receptor locations. Often a long-term average concentration may be of interest rather than a concentration under a specific set of meteorological conditions and at a particular location. In such situations, it may be sufficient to employ average meteorological conditions and a "box" model which averages the pollutant concentration over depth. A mass balance over the box suggests that the concentration at any position x downwind from the upwind edge of the source area (the impoundment) is given by

$$C_A = \frac{N_A * L * W}{H * W * < U >} \qquad \text{(S3)}$$

Here, N_A is the emission flux (ng/m^{2}s) from a source of length L and width W. H is the height over which the contaminant is approximately well-mixed and <U> is the height averaged wind velocity. Under neutral conditions, or conditions under which surface heating or cooling does not significantly influence atmospheric turbulence, the wind velocity as a function of height can be written,

$$u = \frac{u_*}{k} ln\left(\frac{z}{z_0}\right) \qquad \text{(S4)}$$

where z_0 is the effective aerodynamic roughness height and 6 is Von Karman's constant (0.4). Integrating the velocity profile (Equation S4) over a height, H, gives

$$< U >= \frac{u_*}{k} ln\left(\frac{H}{ez_0}\right) \tag{S5}$$

Using the velocity at the normal meteorological measuring height of 10 m, U_{10}, u_* can be written

$$u_* = k\frac{U_{10}}{ln\left(\frac{10}{z_0}\right)} \tag{S6}$$

Substituting into Equation (S3)

$$C_A = \frac{N_A * L * ln\left(\frac{10}{z_0}\right)}{H * U_{10} * ln\left(\frac{H}{ez_0}\right)} \tag{S7}$$

Also under neutral conditions [12] showed that the vertical extent of the dispersing pollutant is defined by the implicit formula,

$$\frac{L}{z_0} = 6.25\left[\frac{H}{z_0} * ln\frac{H}{z_0} - 1.58\frac{H}{z_0} + 1.58\right] \tag{S8}$$

The neutral atmospheric condition under which Equations S4 and S5 are valid typically occur in mid-morning and late afternoon, under overcast conditions day or night, and during high wind conditions. It is also intermediate between the conditions observed in the middle of the night or afternoon when surface heating or cooling most influence atmospheric turbulence. Thus neutral conditions represent, in this sense, an "average" condition over the course of the day. Use of these equations requires specification of the aerodynamic roughness height which is typically 10-30 times smaller than the physical roughness height. In an area with open terrain and occasional buildings, often typical of a landfill or impoundment area, a reasonable estimate of aerodynamic roughness might be about 0.1m. Using this estimate of the aerodynamic roughness, Equation S7 becomes;

$$C_A = \left[\frac{L}{0.22Hln(3.7H)}\right]\frac{N_A}{U_{10}} \qquad (S9)$$

where U is the wind velocity measured at the standard meteorological measurement height of 10 m. Subject to the assumption of neutral conditions and a roughness of 0.1m, the bracketed term is essentially constant and equal to 24 (+/- 1) for L between 30 and 1000 m. The air concentration is thus independent of distance from the upwind edge of the source, i.e. independent of L. That is, under these conditions, the growth in mixed layer height is approximately balanced by the release of additional contaminant as L increases. Since this occurs under neutral atmospheric conditions, which represents an average condition in the sense outlined above, the estimate of $C=24\ N_A/U_{10}$ represents a useful long term average concentration on or immediately adjacent to an impoundment or landfill source. Accurate short term predictions of downwind concentrations, however, requires an alternative approach, for example that of Chitgopekar, et al. [13].

S4. Flux estimation by mass transfer model

The flux of PCBs or PAHs across the CDF impoundment –air surface was estimated using a mass transfer model with equation (S10),

$$Flux = K_{wa}(C_w - C_{w*}) = K_{wa}\left(C_w - \frac{C_{POM}}{HK_{POM-A}}\right) \qquad (S10)$$

And K_{wa} estimated as;

$$K_{wa} = \frac{1}{\frac{1}{k_w} - \frac{1}{Hk_a}} \qquad (S11)$$

where K_{wa} is the water-air transfer coefficients (cm/s), K_w is the water transfer coefficient (cm/s) and K_a is the air transfer coefficient (cm/s). The term "$\frac{C_{POM}}{K_{POM-A}}$" is the air concentration and, the $K_w$and K_a for the individual HOC are estimated using the expressions in Figure S9. H is the Henry law constant corrected for air and water temperatures for individual HOC (PCB congeners or PAHs)

$$K_{a,HOC} = K_{a,H_20} * \left(\frac{D_{a,HOC}}{D_{a,H_20}}\right)^{0.67} \left\{ \begin{array}{l} D_{a,HOC} = \dfrac{10^{-3} T^{1.75} (\frac{1}{M_a} + \frac{1}{M_{HOC}})}{P\ (V_a^{\frac{1}{3}} + V_{HOC}{}^{1/3})^2} \\[2em] k_{a,H_20} = 0.2\ U_{10} + 0.3 \\[2em] D_{a,H_20} = \dfrac{10^{-3} T^{1.75} (\frac{1}{M_a} + \frac{1}{M_{H_2O}})}{P\ (V_a^{\frac{1}{3}} + V_{H_2O}{}^{1/3})^2} \end{array} \right.$$

$$k_{w,HOC} = k_{w,CO_2} * \left(\frac{S_{C,HOC}}{S_{C,CO_2}}\right)^{-0.67} \left\{ \begin{array}{l} S_{w,HOC} = \dfrac{\mu_w}{D_w} \\[2em] k_{w,CO_2} = (0.79 * U_{10} - 2.68) * 10^{-3} \\[2em] S_{w,CO_2} = \dfrac{\mu_w}{D_w} \end{array} \right.$$

Figure S9. Expressions for estimating transfer coefficients for individual HOC.

No direct in situ measurement of water concentrations were measured, so an estimated dissolved concentrations (C_w) were estimated using equation (S12)

$$C_w = \frac{TS*W_S}{1+TS*K_D} \tag{S12}$$

TS is defined as the total suspended solids ~ 69 mg/L, W_S is the solid concentrations and K_D is the sediment –water partition coefficient obtained from ex-situ sediment-water concentration measurement. The analytical procedure for the measurement of solid and water concentrations which follows the description in Odetayo, et al. [1], Table S5 and S6 shows the resulting C_w and flux for the PCBs and PAHs during the two deployment periods.

Definition of terms.

K_{wa} – the air-water transfer coefficient in cm/s [14]

K_w – the water transfer coefficient in cm/s [14]

K_a – the air transfer coefficient in cm/s [14]

Da, H_20 – Diffusivity of water in air (cm^2/s) [14, 15]

Da, HOC - Diffusivity of HOC in air (cm^2/s) [14, 15]

T – Temperature (K)

Ma – Molecular mass of air (g/mole)

M_{HOC}- Molecular mass of individual HOC (g/mole)

Va – Molar volume of air (cm^3/mole) [5]

V_{HOC} – Molar volume of air (cm^3/mole) [5]

P- is the pressure (atm).

U_{10} – wind speed at 10m Height (m/s)

$S_{C, HOC}$ – Schmidt number in water for HOC [14]

$S_{C, CO2}$ – Schmidt number in water for CO_2 [14]

D_w, $C0_2$ – Diffusivity of CO_2 in water (cm^2/s) [14, 16]

D_w, HOC – Diffusivity of HOC in water (cm^2/s) [14, 16]

μ_w, $C0_2$ – kinematic viscosity of CO2 in water (cm^2/s)

μ_w, HOC – kinematic viscosity of HOC in water (cm^2/s)

H – Dimensionless Henry law constant corrected for air and water temperatures.

C_w – water concentrations in ng/L

C_{POM} – concentration on POM in ng/g

K_{POM-A} – POM-air partition coefficients (v/v, m^3/m^3)

Table S6. Water concentration and mass transfer flux estimates for PCB congeners

PCB Congener	**ADMP**			**PDMP**	
	Cw(pg/L)	Flux ($pg/m^2.s$)		Cw(pg/L)	Flux ($pg/m^2.s$)
1	ND	ND		ND	ND
2	0.03	0.06		0.03	0.06
3	ND	ND		0.09	0.19
4	ND	ND		ND	ND
10	ND	ND		0.18	0.39
7	ND	ND		0.01	0.03
9	ND	ND		0.01	0.03
6	ND	ND		0.79	1.66
8	1.51	3.34		1.51	3.15
5	1.47	3.22		1.47	2.98
19	0.45	0.99		0.45	0.95
30	ND	ND		ND	ND
11	0.01	0.03		0.01	0.03
18	5.95	12.88		5.95	12.13
17	2.34	5.10		2.34	4.85
15	0.88	1.92		0.88	1.76
24	0.13	0.29		0.13	0.27
27	0.11	0.25		0.11	0.24
16	1.86	3.98		1.86	3.69
32	1.27	2.76		1.27	2.63
34	0.07	0.16		0.07	0.15
29	0.10	0.22		0.10	0.21
26	0.97	2.09		0.97	1.95
25	0.96	2.08		0.96	1.96
31+50	3.76	8.09		3.76	7.68
28	3.24	6.99		3.24	6.52

20	0.05	0.11		0.05	0.10
21+33+53	0.55	1.18		0.55	1.10
22	1.13	2.38		1.13	2.14
45	1.12	2.38		1.12	2.25
46	0.48	1.01		0.48	0.95
69	1.78	3.81		1.78	3.66
52	3.29	6.96		3.29	6.52
47	1.09	2.32		1.09	2.19
48	0.75	1.58		0.75	1.47
65	ND	ND		ND	ND
44	3.60	7.50		3.60	6.85
42	1.36	2.86		1.36	2.63
37	0.63	1.31		0.63	1.15
71	0.71	1.49		0.71	3.43
41	1.79	3.74		1.79	1.89
64	0.97	2.04		0.97	1.54
40	0.84	1.72		0.84	0.72
67	0.04	0.09		ND	ND
74	0.39	0.80		0.39	0.72
61	ND	ND		0.54	1.03
70	1.14	2.36		1.14	2.13
76	ND	ND		0.67	1.27
66	0.88	1.82		0.88	1.64
93+95	0.37	0.77		0.37	0.72
56	0.52	1.06		0.52	0.92
60	0.51	1.03		0.51	0.90
92	0.08	0.17		ND	ND
84	0.27	0.55		0.27	0.51
90	0.23	0.48		0.23	0.44
101	0.19	0.39		0.19	0.36
113	ND	ND		ND	ND
99	0.17	0.35		0.17	0.32
119	0.09	0.18		0.09	0.17
83	0.14	0.29		0.14	0.26
87	0.32	0.64		0.32	0.57
81	0.01	0.03		0.01	0.02
115	0.12	0.25		0.12	0.23
110	0.37	0.75		0.37	0.67
77	0.13	0.26		0.13	0.21
82	0.16	0.31		0.16	0.27
151	2.3E-02	0.05		ND	ND
135+144	7.8E-03	0.02		0.01	0.01
147	1.7E-03	3.5E-03		0.00	0.00

107	1.5E-02	2.9E-02		0.01	0.03
123	5.3E-03	1.1E-02		0.01	0.01
149	7.0E-02	1.4E-01		0.07	0.13
118	1.2E-01	2.3E-01		0.12	0.20
134	ND	ND		3.6E-03	0.01
114	9.9E-03	2.0E-02		9.9E-03	0.02
131	ND	ND		ND	ND
146	5.5E-03	1.1E-02		5.5E-03	9.5E-03
153	4.2E-02	8.2E-02		4.2E-02	7.1E-02
132	3.5E-02	7.0E-02		3.5E-02	6.2E-02
105	9.6E-02	1.8E-01		9.6E-02	1.5E-01
141	1.3E-02	2.5E-02		1.3E-02	2.2E-02
179	ND	ND		7.6E-03	1.4E-02
138	2.8E-02	5.3E-02		2.8E-02	4.5E-02
163	1.9E-02	3.7E-02		1.9E-02	3.2E-02
158	2.5E-03	4.9E-03		2.5E-03	4.3E-03
178	ND	ND		1.1E-03	1.8E-03
126	2.6E-03	4.8E-03		2.6E-03	3.7E-03
187	7.7E-03	1.5E-02		7.7E-03	1.3E-02
183	ND	ND		3.6E-03	6.2E-03
128+167	6.5E-03	1.2E-02		6.5E-03	9.8E-03
174	7.6E-03	1.5E-02		7.6E-03	1.3E-02
177	ND	ND		4.8E-03	7.8E-03
171	2.0E-03	3.8E-03		2.0E-03	3.3E-03
156	3.1E-03	5.8E-03		3.1E-03	4.5E-03
157	5.0E-04	9.2E-04		5.0E-04	7.1E-04
173	ND	ND		1.8E-05	3.0E-05
172	7.1E-04	1.3E-03		7.1E-04	1.1E-03
180	ND	ND		1.1E-02	1.6E-02
193	3.6E-04	6.9E-04		3.6E-04	5.7E-04
191	1.2E-04	2.2E-04		1.2E-04	1.9E-04
169	4.8E-03	8.5E-03		ND	ND
190	8.0E-04	1.5E-03		8.0E-04	1.2E-03
198	1.3E-03	2.4E-03		ND	ND
203	5.9E-04	1.1E-03		5.9E-04	9.0E-04
189	1.2E-04	2.1E-04		1.2E-04	1.5E-04
195	5.2E-04	9.5E-04		ND	ND
194	9.9E-04	1.7E-03		ND	ND
205	3.9E-05	7.0E-05		ND	ND
206	1.9E-04	3.4E-04		ND	ND
Sum		**110**			**106**

Table S7. Water concentration and mass transfer flux estimates for PAHs compounds

		ADMP		PMDP
PAHs	Cw(ng/L)	Flux (ng/m2.s)		Flux (ng/m2.s)
naphthalene	176	0.46		0.44
acenaphthylene	105	0.25		0.21
acenaphthene	192	0.46		0.42
fluorene	136	0.30		0.25
phenanthrene	353	0.66		0.45
fluoranthene	252	0.25		0.10
pyrene	325	0.38		0.19
benz(a)anthracene	46.1	0.05		0.02
chrysene	70.1	0.05		0.01
benzo(b)fluoranthene	5.77	6.4E-04		1.9E-04
benzo(k)fluoranthene	8.04	7.9E-04		2.3E-04
benzo(a)pyrene	13.1	1.0E-03		4.0E-04
indeno(123-cd)pyrene	1.29	7.6E-05		2.1E-05
dibenzo(ah)anthracene	0.18	1.3E-05		3.8E-06
benzo(ghi)perylene	2.37	1.3E-04		3.7E-05
Sum		**2.85**		**2.10**

References

1. Odetayo, A. A.; Reible, D. D.; Acevedo-Mackey, D.; Price, C.; Thaic, L., Development of polyoxymethylene passive sampler for assessing air concentrations of PCBs at a confined disposal facility (CDF). *Environ. Pollut.* 2020, 114720.
2. Hawthorne, S. B.; Jonker, M. T.; van der Heijden, S. A.; Grabanski, C. B.; Azzolina, N. A.; Miller, D. J., Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Anal. Chem.* 2011, *83*, (17), 6754-6761.
3. Hawthorne, S. B.; Miller, D. J.; Grabanski, C. B., Measuring low picogram per liter concentrations of freely dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. *Anal. Chem.* 2009, *81*, (22), 9472-9480.
4. Dunnivant, F. M.; Elzerman, A. W.; Jurs, P. C.; Hasan, M. N., Quantitative structure-property relationships for aqueous solubilities and Henry's law constants of polychlorinated biphenyls. *Environ. Sci. Technol.* 1992, *26*, (8), 1567-1573.
5. Williams, A. J.; Grulke, C. M.; Edwards, J.; McEachran, A. D.; Mansouri, K.; Baker, N. C.; Patlewicz, G.; Shah, I.; Wambaugh, J. F.; Judson, R. S.; Richard, A. M., The CompTox Chemistry Dashboard: a community data resource for environmental chemistry. *J. Cheminformatics* 2017, *9*, (1), 61.
6. Hawker, D. W.; Connell, D. W., Octanol-water partition coefficients of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* 1988, *22*, (4), 382-387.
7. SPARC-Calculator, Physicochemical properties of compounds. 2010.
8. Lohmann, R., Critical review of low-density polyethylene’s partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environ. Sci. Technol.* 2012, *46*, (2), 606-618.
9. Lei, Y. D.; Wania, F.; Shiu, W. Y.; Boocock, D. G., HPLC-based method for estimating the temperature dependence of n-octanol− water partition coefficients. *J. Chem. Eng. Data* 2000, *45*, (5), 738-742.
10. Li, N.; Wania, F.; Lei, Y. D.; Daly, G. L., A comprehensive and critical compilation, evaluation, and selection of physical–chemical property data for selected polychlorinated biphenyls. *J. Phys. Chem. Ref. data* 2003, *32*, (4), 1545-1590.

11. Beyer, A.; Wania, F.; Gouin, T.; Mackay, D.; Matthies, M., Selecting internally consistent physicochemical properties of organic compounds. *Environ. Toxicol. Chem.* 2002, *21*, (5), 941-953.
12. Pasquill, F., The dispersion of material in the atmospheric boundary layer—the basis for generalization. In *Lectures on air pollution and environmental impact analyses*, Springer: 1982; pp 1-34.
13. Chitgopekar, N.; Reible, D.; Thibodeaux, L., Modeling short range air dispersion from area sources of non-buoyant toxics. *J. Air Waste Manage.* 1990, *8*.
14. Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental organic chemistry*. John Wiley & Sons: 2016.
15. Hayduk, W.; Laudie, H., Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions. *AIChE Journal* 1974, *20*, (3), 611-615.
16. Fuller, E. N.; Schettler, P. D.; Giddings, J. C., New method for prediction of binary gas-phase diffusion coefficients. *Ind. Eng. Chem. Res.* 1966, *58*, (5), 18-27.

Chapter 6

Standardization of polydimethylsiloxane (PDMS) for measuring freely dissolved hydrophobic organic contaminants (HOCs) in sediment porewater

Adesewa Odetayo[a], Magdalena Rakowska[a], Danny Reible[a], Mandy Michalsen[b], Al Kennedy[b], Kristen Kerns[c], Michelle Aylward[c], Robert Burgess[d], Mark Mills[d], Matt Lambert[d], Philip Gschwend[e], John MacFarlane[e], Upal Ghosh[f], Mandar Bokare[f] & Songjing Yan[f] Mingta Lin[g]

[a] Department of Civil, Environmental and Construction Engineering, Texas Tech University, 911 Boston Avenue, Lubbock. Texas 79409. U.S.A

[b] U.S. Army Engineer Research Development Center,

[c] U. S Army Corps of Engineers, Seattle District,

[d] U.S. Environmental Protection Agency,

[e] Department of Civil and Environmental Engineering Massachusetts Institute of Technology

[f] Department of Chemical, Biochemical and Environmental Engineering, University of Maryland, Baltimore County,

[g] Pyron Environmental Inc.,

Citation

Michalsen Mandy; Reible, Danny, **Aribidara Adesewa**, Ghosh Upal; Bokare, Mandar;Gschwend, Philip; MacFarlane, John; Lin, Mingta. “Standardizing Polymeric Sampling for Measuring Freely-Dissolved Organic Contaminants in Sediment Porewater” Technical Report, Accession Number, AD1084245.

Abstract

Passive polymeric samplers such as polyethylene (PE) and polydimethylsiloxane (PDMS) are an alternative to conventional methods for sampling sediment porewater while minimizing disturbance of the sediment. The lack of standardized methods and commercial availability to support polymeric samplers for environmental monitoring purposes has been a barrier to technology transfer and polymeric sampler use. This study demonstrates the use of standardized polymeric sampler procedures using PDMS for quantifying C_{free} in contaminated sediment porewater. This was achieved through a phased evaluation among multiple participating public- and private-sector analytical laboratories. Phase 1 involved participating laboratories using verified and acceptable instrumentation to analyze PRC compounds extracted from PDMS fibers. During phase 2, individual laboratories independently prepare and load PDMS fibers with PRCs. The PRCs loaded PDMS from phase 2 was then inserted in sediment to measure porewater or C_{free} concentrations during phase 3. In a 4th phase of the project, standardized methods were communicated to the public and end users.

The results of the inter-laboratory study using PDMS to measure freely dissolved concentrations in sediment porewater indicated that the objectives of the research study were achieved based on desired accuracies of ±30% and ±50% for targets and performance reference compounds (PRCs) respectively, and precisions of $\leq$ 20% for both targets and PRCs. In general, the achieved success rate for desired accuracies and precisions ranged from 71 – 100% of the participating labs depending on sensitivity group during phase 1.

During phase 2, solvent variations in PRCs loading solutions among participating laboratories led to a deviation from the desired ±50% accuracy for certain PRC compounds. Once the use of appropriate solvents was addressed, all laboratories achieved the desired accuracies and precisions for the PRCs. The results for phase 3 mostly showed that participating laboratories measured porewater concentrations of native PCBs and PAHs within a factor of 2.

6.1. Introduction

Hydrophobic organic contaminants (HOCs), which include polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are pollutants that have high affinity for the organic carbon phase and owing to their strong hydrophobic nature, preferentially adhere to sediment [1, 2]. As a result, these HOCs can persist in the sediment media for years, where their fate and distribution in the environment are closely regulated by sorption and bioavailability [3, 4]. Early efforts toward predicting HOCs' bioavailability, recognized that freely dissolved ($C_{free)}$ and natural organic matter associated concentrations are better indicators of the HOCs fate and distribution in the environment than the bulk sediment concentrations [3, 5].

The measured C_{free} of contaminants have a direct relationship to bioaccumulation in sediment-dwelling organisms and the eventual bio-uptake into the food-chain [6]. In recent years, passive polymeric samplers such as polydimethylsiloxane (PDMS) have been employed as an alternative to alum flocculation and centrifugation [7] in measuring C_{free} of HOCs in the sediment or aquatic environments[8-14]. PDMS fibers are used to assess organic contaminants in the environment by diffusion processes. The HOCs diffuse from the environmental media (sediment, water or air) and sorb on the polymeric fiber. The uptake amount on PDMS fiber is then used to estimate the C_{free} of HOCs which can be translated to implications to the environment [15].

Studies have indicated that passive samplers such as PDMS can be used to assess bioavailability and eventual assessment of exposure and risks to humans [16-18]. However, historically the passive sampling approach is mostly considered an academic tool and its acceptance by the public is limited due to the lack of standardized methods and commercial availability [6, 15, 19]. For increased applications and regulatory decision making, the need to standardize the passive PDMS methodology is crucial. This study aims to demonstrate procedures required in the use of the passive PDMS method through phased inter-laboratory comparison. The results of this study are expected to eliminate the limitations of transfer barriers of the passive sampling technology, hence increasing PDMS use and commercial availability, and promote regulatory acceptance.

6.1.1. Objectives

The project objectives are;

1. Develop a standardized methodology for the preparation and analysis of polydimethylsiloxane (PDMS) sampler, and these would be achieved as follows;
    a) Preparation of PDMS samplers, including loading of performance reference compounds (PRCs).
    b) Deployment of PDMS in ex-situ application, i.e., exposing the sampler to sediment in the laboratory.
    c) Extraction of PDMS fiber and perform chemical analysis of the extracts.
    d) Interpret the results and translate to the concentration of the freely dissolved organic contaminant present in the sediment porewater.

2. Collaboration with government and commercial laboratories to finalize the standardized PDMS methodology and validate the methodology through phased inter-laboratory comparison.
3. Document the methods and results in a guidance document prepared based on EPA SW846 guidelines. In addition, prepare instructional videos and webinars via online platforms.

6.2. Materials and Methods

6.2.1. Polydimethylsiloxane (PDMS) sampler

The PDMS used was purchased from Polymicro Technologies (Phoenix, USA). The core diameter of the PDMS coating was 575 µm and the dimension without coating was 500 µm. The PDMS fiber was prewashed and extracted twice sequentially with dichloromethane, hexane and methanol. Individual solvent washing procedure was for a period of 30 minutes each. After the solvent wash, the fibers were then cleaned twice with De-ionized water for a period of 30 minutes for each wash. The fibers were thereafter left to dry under the fumehood and after drying, they were stored in a solvent cleaned dried vessel prior to use and deployment.

6.2.2. Reagents and Chemicals

Dichloromethane, methanol and hexane of optima grade quality were purchased from Fisher Scientific (Hampton, NH, USA.). Performance reference compounds (PRCs) used were the C13 labelled polychlorinated biphenyls (PCBs) and polycyclic aromatic compounds (PAH) as listed in Table 6.1 and were purchased from Cambridge Isotope laboratories, Inc. (Tewksbury, MA, USA). 20 PCB congeners and 16 priority PAHs were studied. The PCB target compounds are the 18 congeners recognized by the National oceanic and atmospheric administration (NOAA) and in addition PCB congeners 126 and 169. The PCB congeners and the 16 priority PAHs were purchased from Accustandard (New Haven, Cincinnati. USA). These NOAA PCBs include 2,4'-Dichlorobiphenyl (PCB 8), 2,2',5-Trichlorobiphenyl (PCB 18), 2,4,4'-Trichlorobiphenyl (PCB 28), 2,2',3,5'-Tetrachlorobiphenyl (PCB 44), 2,2',5,5'-Tetrachlorobiphenyl (PCB 52), 2,3',4,4'-Tetrachlorobiphenyl (PCB 66), 3,3',4,4'-Tetrachlorobiphenyl (PCB 77), 2,2',4,5,5'-Pentachlorobiphenyl (PCB 101), 2,3,3',4,4'-Pentachlorobiphenyl (PCB 105), 2,3',4,4',5-Pentachlorobiphenyl (PCB 118), 2,2',3,3',4,4'-Hexachlorobiphenyl (PCB 128), 2,2',3,4,4',5'-Hexachlorobiphenyl (PCB 138), 2,2',4,4',5,5'-Hexachlorobiphenyl (PCB 153), 2,2',3,3',4,4',5-Heptachlorobiphenyl (PCB 170), 2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB 180), 2,2',3,4',5,5',6-Heptachlorobiphenyl (PCB 187), 2,2',3,3',4,4',5,6-Octachlorobiphenyl (PCB 195), 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (PCB 206) and the 16 priority PAHs; Naphthalene, Acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benz(a)anthracene, Benzo(b)fluoranthene, benzo(k)fluoranthene, Benzo(s)pyrene, Indeno(1,2,3 –cd)pyrene, benzo(ghi)perylene, and dibenz(a,h)anthracene.

Table 6.1. Analytical methods and performance reference compounds

Target Contaminant Measured by Polymeric Sampler	Analytical Method	PRCs
PAHs	High or Low Sensitivity	13C6-phenanthrene
		13C6-fluoranthene
		13C6-chrysene
		13C6-indeno(1,2,3-cd)pyrene
PCBs	Low Sensitivity	13C-labelled PCB congener 37
		13C-labelled PCB congener 47
		13C-labelled PCB congener 54
		13C-labelled PCB congener 111
		13C-labelled PCB congener 138
		13C-labelled PCB congener 178
	High Sensitivity	13C-labelled PCB congener 28
		13C-labelled PCB congener 47
		13C-labelled PCB congener 70
		13C-labelled PCB congener 80
		13C-labelled PCB congener 111
		13C-labelled PCB congener 141
		13C-labelled PCB congener 182

6.2.3. Study Approach

The approach adopted in this study includes designing and developing plans and methodologies to achieve the desired set objectives of standardizing the polydimethylsiloxane (PDMS) as a regulatory decision-making tool. The project will progress through phases with standard operating procedures (SOPs) developed for each phase of the project. This is to set a suitable basis for comparison among participating laboratories.

6.2.3.1. Phase 1

The first step in this phase involved verifying acceptable instrumentation and analytical capabilities among the laboratories. This was achieved by preparing surrogate standards that were shipped to participating laboratories. Next, instrumentation methods were unified and agreement on the acceptable and quantifiable PRCs were identified based on instrument sensitivity. And finally, the PRC preloaded PDMS fibers were sent to the participating laboratories to extract and analyze. Individual laboratories were expected to achieve an accuracy of ±30 % of the known concentration and a precision of ± 20 % relative standard deviation (R.S.D). Once all requirements were met, the project proceeded to the second phase.

6.2.3.2. Phase 2

During this phase, each participating laboratory was tasked with the responsibility of independently preparing and loading PDMS fibers with PRCs. First, the fibers were pre-extracted with solvents, dried and shipped the cleaned fibers to all participating labs. Once received, the labs individually prepared the loading solution for the PDMS fibers. PDMS fibers were added to the solution and agitated for a minimum of 28 days. The results of the PRC analysis must achieve an accuracy within ± 50 % of target PRC concentration and a precision of ± 20 % relative standard deviation (R.S.D). Once all requirements were met, the third phase of the project would commerce.

6.2.3.3. Phase 3

This phase involved deploying the PRC preloaded PDMS for ex-situ application and estimating the freely dissolved target contaminants in sediment porewater. Sediment with known physicochemical properties were sent to all participating laboratories and the standardized PDMS sampling procedure was utilized to measure target PAHs and PCBs in sediment porewater. The PDMS samplers were deployed in the sediment, and both active and passive sampling were conducted. Active sampling involved placing the sediment containing PDMS samplers on a roller in order to achieve homogeneous mixing of the sediment. The passive sampling involves no shaking of the sediment containing the PDMS fibers. After a minimum of 28 days, the PDMS fibers from both active and passive sampling were retrieved, cleaned, extracted and analyzed.

6.2.3.4. Phase 4

The standardized methods were communicated to the public through videos, workshops, and webinars. The progress of this study has been presented in conferences, workshops and as a technical report [20].

6.2.4. Analytical Instruments and Participatory team

6.2.4.1. Analytical Instrument

Based on analytical sensitivities, the participatory team was categorized into the high sensitivity and low sensitivity groups. The high sensitivity group used the EPA Method 1668C – High Resolution Gas Chromatography/High Sensitivity Mass

Spectrometry (HRGC/HSMS) for PCB analysis and EPA Method 1625/8270D – High Resolution Gas Chromatography/Mass Spectrometry (HRGC/MS) for PAHs analysis. The low sensitivity group used Modified EPA Method SW8270D – High Resolution Gas Chromatography/Low Sensitivity Mass Spectrometry (HRGC/LSMS) for PCB analysis and the Modified EPA Method SW8270D – Gas Chromatography/Mass Spectrometry for PAHs analysis.

6.2.4.2. Participatory teams

The laboratories that participated in this study in no particular order include: Texas Tech University (TTU), Test America (TAL), AXYS SGS, Battelle Memorial Institute, Analytical Resource incorporated (ARI), Vista, ALS, University of Maryland, Baltimore (UMARY) and Massachusetts Institute of Technology (MIT). TAL, AXYS-SGS, and UMARY used the high sensitivity EPA Method 1668C for PCB analysis. While, Battelle, ARI, and ALS used the low sensitivity EPA method 8270D for PCB analysis. TTU and MIT analyzed PCBs using both high and low sensitivity analytical methods. All participating laboratories achieved PAHs analysis using either a combination of EPA method 1625/8270D or EPA method 8270D. To obscure laboratory identity, participating labs are grouped numerically from Lab 1 through Lab 8 except for TTU.

6.2.5. Data Analysis

The analytical results from all the phases for the commercial laboratories were subjected to a stage four (4) full data validation process. This involved determining any notable procedural or quality control deviations from the standardized analytical methods and laboratories' SOPs procedures. Data comparability assessment were conducted based on sensitivity, accuracy and precision for all the participating (both commercial and university) laboratories. Success rates for laboratories were determined using the desired percent (%) accuracies and precisions for target compounds and PRCs.

6.2.5.1. Sensitivity

Sensitivity was evaluated with the method reporting limits (MRLs) or Practical Quantitation Limits (PQLs) that a laboratory can achieve given a sample matrix under the laboratory's standard operation. In some cases where the commercial laboratories did not report sample-specific MRLs, the lowest-point of the initial calibration standard was used for this comparison.

6.2.5.2. Accuracy

This was determined by comparing the analytical results to the target concentrations for each participating laboratory by back-calculating from the amounts and concentrations of their spiking solutions, following SOPs provided by TTU. A criterion of ±50% for PRCs; a PRC value outside 50-150% of the respective target concentration is considered as an outlier. According to EPA Method 1668C, labeled compounds such as PRCs must meet this standard, whereas target unlabeled congeners are held to a ±30% standard.

6.2.5.3. Precision

The precision was determined by the relative percent difference (RFD) if only duplicate measurements were compared and percent relative standard deviation (RSD) if more than duplicate measurements were compared. RFD is the percent of the difference of the duplicate measurements divided by the average of the duplicate values. While, RSD is the percent of the standard deviation divided by the mean of a group of data. According to EPA Method 1668C, Method 8270D, and Method 1625C, replicate analysis precision within a laboratory is evaluated by comparing the %RSD value for replicate analyses to the ≤20% criterion.

6.3. Results and Discussion of results

6.3.1. Phase 1A - Check standard inter-laboratory comparison

Data comparability was performed on the results of the analysis conducted by all participating laboratories based on their analytical methodologies. Concentrations of 5 ng/ml for the high sensitivity group was targeted for both PCBs and PAHs. For the low sensitivity group, concentration of 50 ng/ml for PCB congeners and 100 ng/ml for the PAHs were targeted. Inter-laboratory comparison was performed after a stage 4 (full) data validation on the data packages indicated no procedural and quality control issues were found.

6.3.1.1. PCBs - High sensitivity group

For this analytical group, four (4) laboratories including TTU used this analytical methodology as shown in Figure 6.1. In comparison to TTU, only Labs 1, 7 and 8 achieved the desired accuracies for both target PCBs and PCB PRCs. Lab 2 achieved a - 32 % for PCB 44. Lab 6 achieved the ± 50% for all the PCB PRCs and ± 30% for most of the target PCB congeners except for PCBs 128 and 138, where - 36 % and - 32 % were measured respectively. For all the laboratories, the measured % RSD were significantly less than 20 % indicating an excellent precision among the labs.

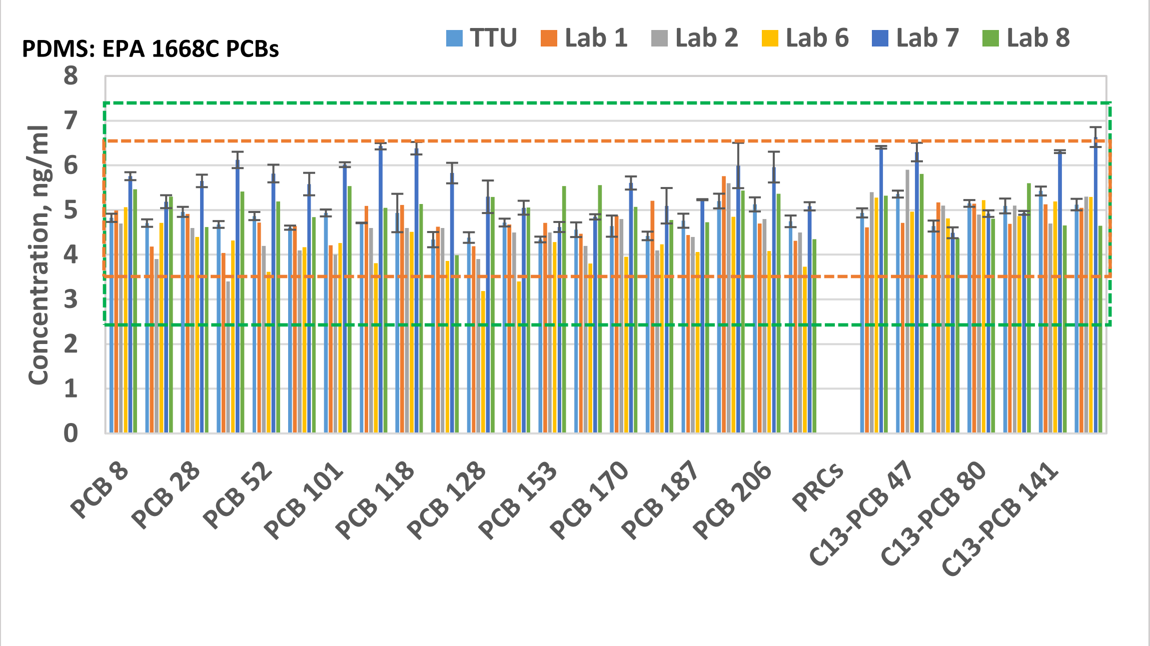


Figure 6.1. The orange line represent accuracy within ± 30% accuracy for the target PCB congeners and the green line represents accuracy within ± 50% accuracy for the PCB PRCs using EPA method 1668C.

6.3.1.2. PCBs - Low sensitivity group

The result of the comparison showed that all the five (5) Labs compared well with TTU in both PCB targets and PRCs in terms of accuracy except for Lab 3 that recorded an exceedance of +33% for PCB 8 (Figure 6.2).

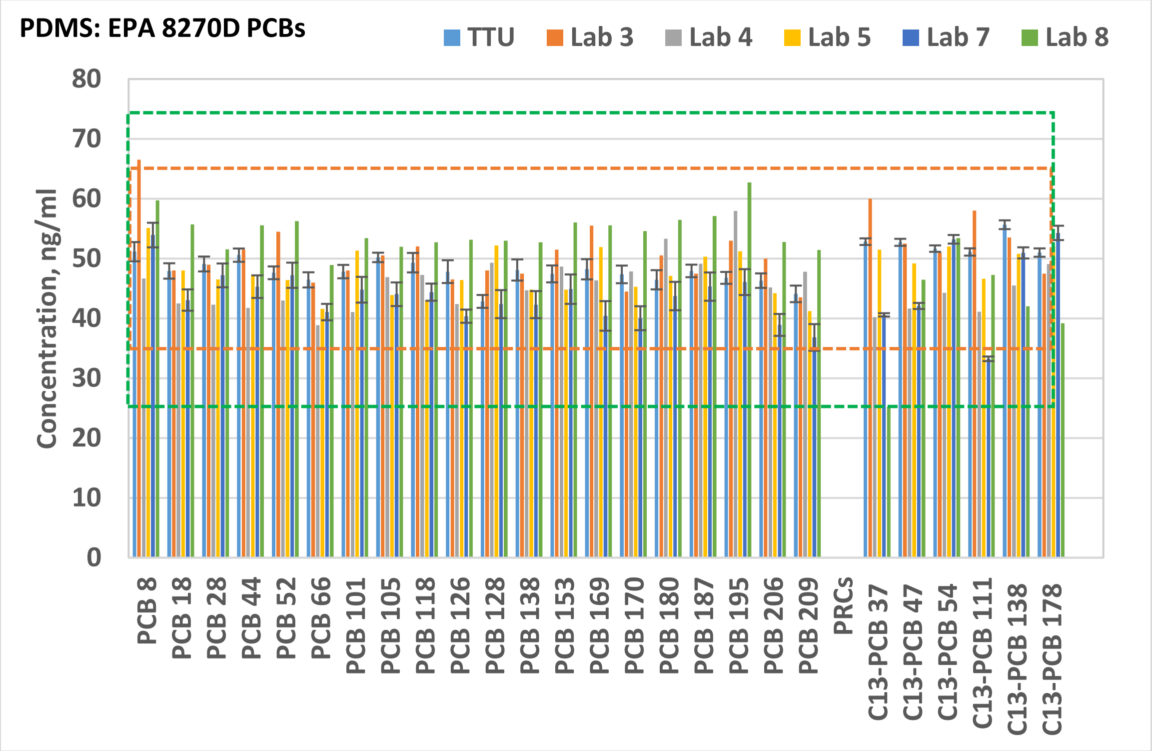


Figure 6.2. The orange line represent accuracy within ± 30% accuracy for the target PCB congeners and the green line represents accuracy within ± 50% accuracy for the PCB PRCs using EPA method 8270D.

6.3.1.3. PAHs

Similar PAH PRCs were used by all participating labs for all analytical methodologies, that is, both high or low sensitivity group used same PRCs. Hence, the result of the comparison as indicated in Figure 6.3 compared among participating labs were in relative concentrations. The results indicated that all participating laboratories compared well with TTU on both target PAHs compounds and PRCs except for Lab 3 that recorded a -38 % and -32 % for dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene respectively. Lab 7 recorded +38% exceedance in naphthalene, and Lab 8 that recorded a -91% for C13 indeno[1,2,3-cd]pyrene. A very low % RSD values was recorded for all laboratories except for Lab 8. Lab 8 had challenge resolving C13 indeno[1,2,3-cd]pyrene in their analytical procedure because sufficient m/z distinction was not achieved for the low resolution GC/MS analysis.

In summary, 100 % achievement rate was recorded for all of the labs for PCB PRCs and PCB natives analysis using EPA method 8270D, and PCB PRCs using EPA method 1668C. 71 % was achieved for PCB natives using EPA method 1668C, 90 % and 80 % for PAH PRCs and PAH natives respectively using either EPA method 1625B/8270D or 8270D (Table S1).

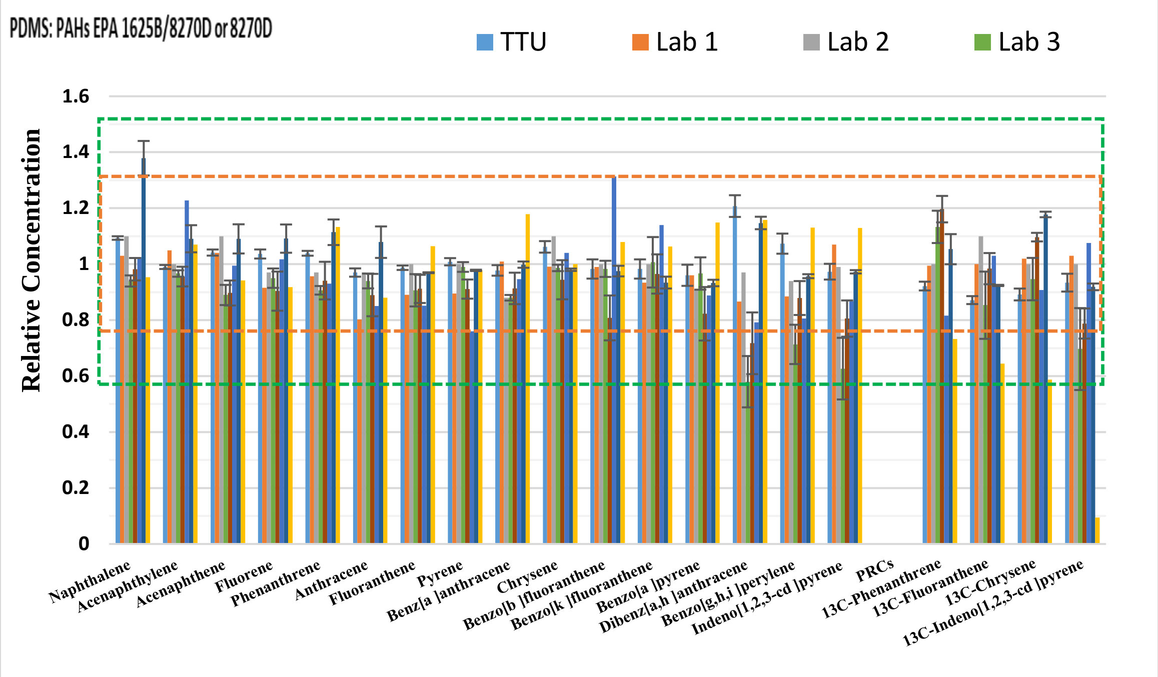


Figure 6.3. The orange line represent accuracy within ± 30% accuracy for the target PAHs compounds and the green line represents accuracy within ± 50% accuracy for the PAH PRCs using EPA method 1625B/8270D or 8270D. Relative concentration is defined as the ratio of the reported (measured) concentration to the target concentration.

6.3.2. Phase 1B- Inter-laboratory comparison of the PRC concentration extracted from PDMS fiber

This phase involved laboratories to analyze the PRC loaded PDMS prepared by TTU. The targets concentrations differ depending on analytical methodologies. High sensitivity PCB and PAHs PRC target concentration was 1579 ng/ml and 790 ng/ml, and low sensitivity PCBs and PAHs PRC target a concentration of 7896 ng/ml individually. Here, relative concentration was used in the comparison between participatory laboratories (Figure S1). For the high sensitivity PCB PRC group, the result of the comparison indicated that all labs achieved the target concentration of 1579 ng/ml and the results were within the ± 50 % accuracy and ± 20 % precision. In the low sensitivity PCB PRC group, all the laboratories compared well with TTU in achieving the target concentration of 7896 ng/ml with accuracy within ± 50 % as shown in Figure S1 and % RSD was within ± 20 %. For the PAH PRCs, TTU analyzed samples in both high and low sensibility group, the result indicated all Labs achieved the target concentration of 7896 ng/ml (Figure S1) with precision within the ± 20 % requirement, except for Lab 4 that achieved a 42 % accuracy (that is, < 50 %) for C13-indeno[1,2,3-cd]pyrene.

The summary of the result for all analytical group are shown in Table 6.2, 100 % achievement rate was observed for PCB PRCs for both EPA methods 8270D and 1668C. While, 89 % achievement rate was achieved for PAH PRCs using either EPA method 1625B/8270D or 8270D.

Table 6.2. Summary of phases 1B and phase 2 for participating laboratories

Phase 1B					
Method	**Analyte**	**Total Labs Performing**	**Achieve**	**Fail**	**% Achieve**
EPA 1668C	**PCB PRCs**	**5**	**5**	**0**	**100%**
EPA 8270D	**PCB PRCs**	**4**	**4**	**0**	**100%**
EPA 1625B/8270D or EPA 8270D	**PAH PRCs**	**9**	**8**	**1**	**89%**

Phase 2					
Method	**Analyte**	**Total Labs Performing**	**Target Range**		**%Achieve**
			Achieve	**Exceed**	
EPA 1668C	**PCB PRCs**	**3**	**3**	**0**	**100%**
EPA 8270D	**PCB PRCs**	**4**	**3**	**1**	**75%**
EPA 1625B/8270D or EPA 8270D	**PAH PRCs**	**6**	**2**	**4**	**33%**

6.3.3. Phase 2- Inter-laboratory comparison of individually loaded PRC concentration

In this phase, each participating laboratory individually loaded the PDMS fibers with PCBs and PAHs PRCs. The required target concentration for the analytical methodologies was 1184 ng/ml of PDMS, however, Lab 4 was the only lab that deviated from the target concentration of 1184 ng/ml and loaded 5922 ng/ml for both PCBs and PAHs PRCs. Hence, relative concentrations were employed for effective inter-laboratory comparison as shown in Figure S4. The result for the high sensitivity PCB group showed that the two laboratories compared well with the result from TTU. The accuracy was within ± 50 % and all laboratory replicate analysis was within ± 20 % as per the precision criteria.

For the low sensitivity PCB group, four (4) laboratories including TTU analyzed the PCBs PRCs loaded PDMS and achieved required accuracy and precision criteria except,

- Lab 4: Observed < 50% in C13-PCBs (54, 111, 138, and 178).
- Lab 5: Observed < 50% in C13-PCB 37.

For the PAH PRCs, five (5) laboratories participated in the loading of the PRCs on the PDMS. All but Lab 1, 2 and 4 did meet the required accuracy criteria of ± 50 %, a deviation from the accuracy criteria was observed as follows (Figure S4);

- Lab 1 and Lab 2: Observed < 50% in C13-phenanthrene.
- Lab 4: Observed < 50% in C13-phenanthrene and C13-indeno[1,2,3-cd]pyrene.

It was noted that the accuracy criteria between the commercial laboratories and TTU was not met for all the PRCs. However, the precision criteria of ± 20 % required for replicate analysis was met for all the low sensitivity commercial laboratories. In summary as shown in Table 2, 75 % and 100 % pass rates were achieved for PCB PRCs using EPA method 8270D and 1668C respectively. While, 33 % pass rate was achieved for PAH PRCs.

The result from phase 2 indicated low recovery of the target concentrations was achieved particularly for the PAHs PRC. Therefore, investigation into the parameters employed by individual laboratory was conducted. These parameters include solvents used in the working standards, fraction of original solvent (that is, nonane) in which the standards were purchased, and the corresponding analysis reported by each laboratory as shown in Table S3.

The result of the investigation suggests that the low analytes recovery recorded by most of the participating laboratories could have a direct relationship to the final nonane fraction in PRC loading solution and the solvents employed in the preparation of the working standard.

Therefore, the standard operating procedure (SOP) on the loading of PRCs on the PDMS was reviewed with specific instructions on using compatible solvents when preparing working standards to be used in the spiking of the PRC loading solution. Also, the labs should be mindful of the final nonane fraction in the PRC loading solution.

Specifically, acetone was noted to be a suitable solvent for making the working standard and discussed in detail in the next section.

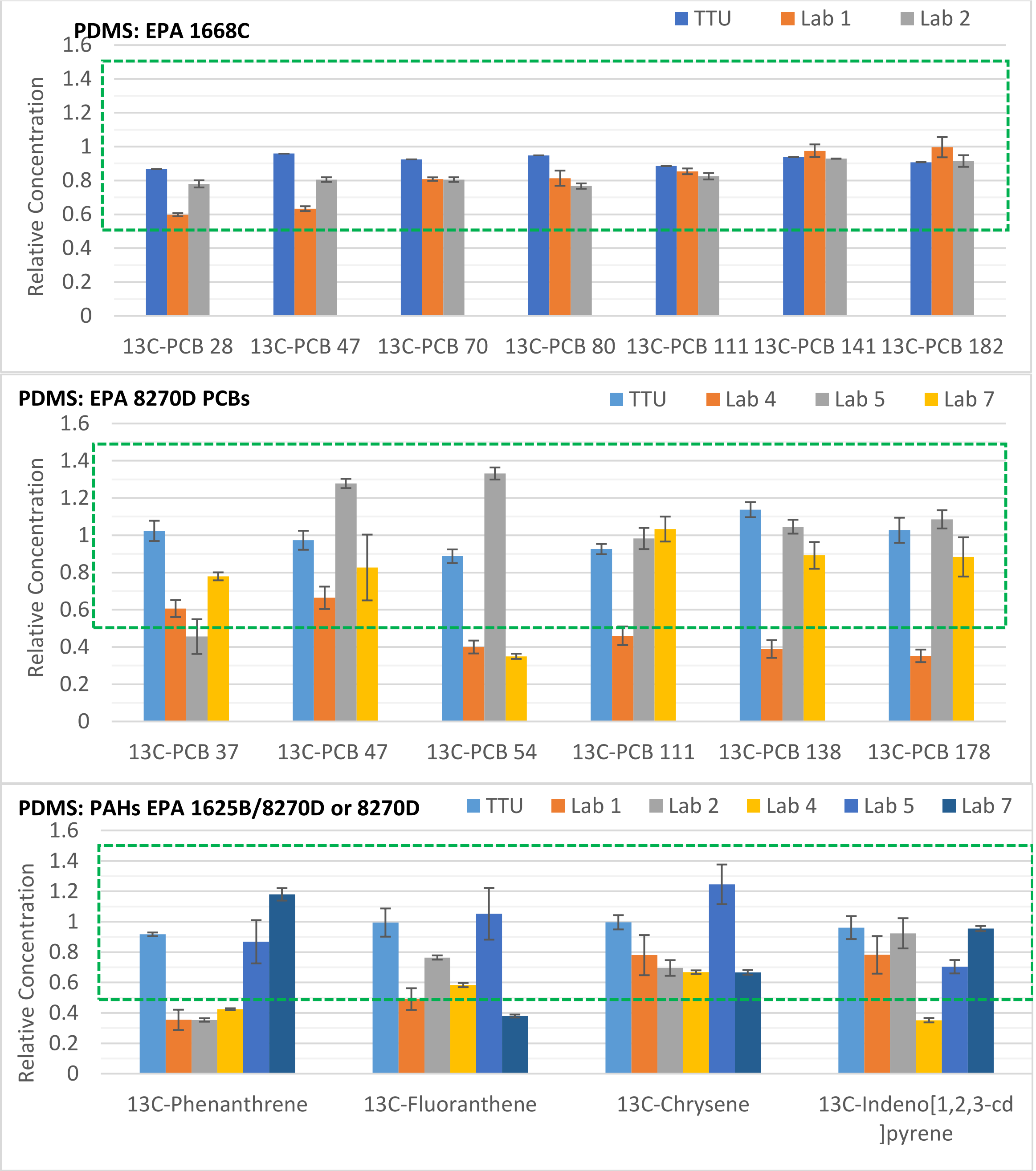


Figure 6.4. Concentrations in relative units (Creported/Cknown). The green line represents accuracy within ± 50% accuracy for the High/Low sensitivity C13-PCBs and C13-PAHs for phase 2.

Table 6.3. Parameters employed by participating laboratories during Phase 2

Phase 2				
Analytical Method	**Labs**	**Nonane fraction in working standard**	**Solvent for working standard**	**Achieve Target concentrations precision and accuracy?**
EPA 1668C	TTU	0.07	Acetone	Yes!
	Lab 1	0.4	Toluene, Acetone	Yes!
	Lab 2	0.5	Acetone	Yes!
EPA 8270D	TTU	0.07	Acetone	
	Lab 4	0.1	Methanol, Ethanol	No! Only C13-PCBs 37 & 47 within range
	Lab 5	0.42	Acetone	No! All achieve target except C13-PCB 37
	Lab 7	0.06	Hexane	No! All achieve target except C13-PCB 54
EPA 1625B/8270D or EPA 8270D	TTU	0.03	Acetone	Yes!
	Lab 1	0.1	Acetone, Hexane	No! All achieve target except C13-PHE & FLUO.
	Lab 2	0.1	Acetone	No! All achieve target except C13-PHE.
	Lab 4	0.04	Methanol, Ethanol	No! All achieve target except C13-PHE & INDENO (c,d -) PYR.
	Lab 5	0.1	Acetone	Yes!
	Lab 7	0.03	Hexane	No! All achieve target except C13 - FLUO

N.B: Yes, if precision and accuracy are achieved and No, if either only accuracy or precision was achieved. Although, all measurements were within the precision of ±20%.

6.3.4. Phase 2 revised - Inter-laboratory PRC loading comparison

This involves a repeat of the loading of the PDMS fibers with PRCs using the revised SOP. The required target concentrations differ depending on the analytical approach. The high sensitivity group targeted a PCB PRCs loading of 474 ng/ml of PDMS, the low sensitivity group targeted a PCB PRCs loading of 790 ng/ml for all laboratories except for Lab 4 that targets a loading of 1579 ng/ml of PDMS. The laboratories targeted a PAH PRCs loading of 15792 ng/ml except for Lab 4 that targeted a loading of 39480 ng/ml of PDMS. Hence, relative concentration was also employed for effective inter-laboratory comparison.

6.3.4.1. High sensitivity group

Using the revised SOP, the two commercial laboratories compared well with the result from TTU. The accuracy was within ± 50 % and all laboratory replicate analysis was within ± 20 % as per the precision criteria for EPA method 1668C (Figure 6.5).

6.3.4.2. Low sensitivity group

Three (3) laboratories prepared and analyzed the PCB PRCs loaded PDMS and all compared well with TTU in terms of ± 50 % accuracy and precision criteria (Figure 6.5) except for Lab 5 that observed < 50% accuracy for C13 PCB 138 and C13 PCB 178 as shown in Figure 6.5.

6.3.4.3. PAHs

Six (6) laboratories including TTU prepared and analyzed PAH PRCs and all measurement were withing the precision and accuracy requirements.

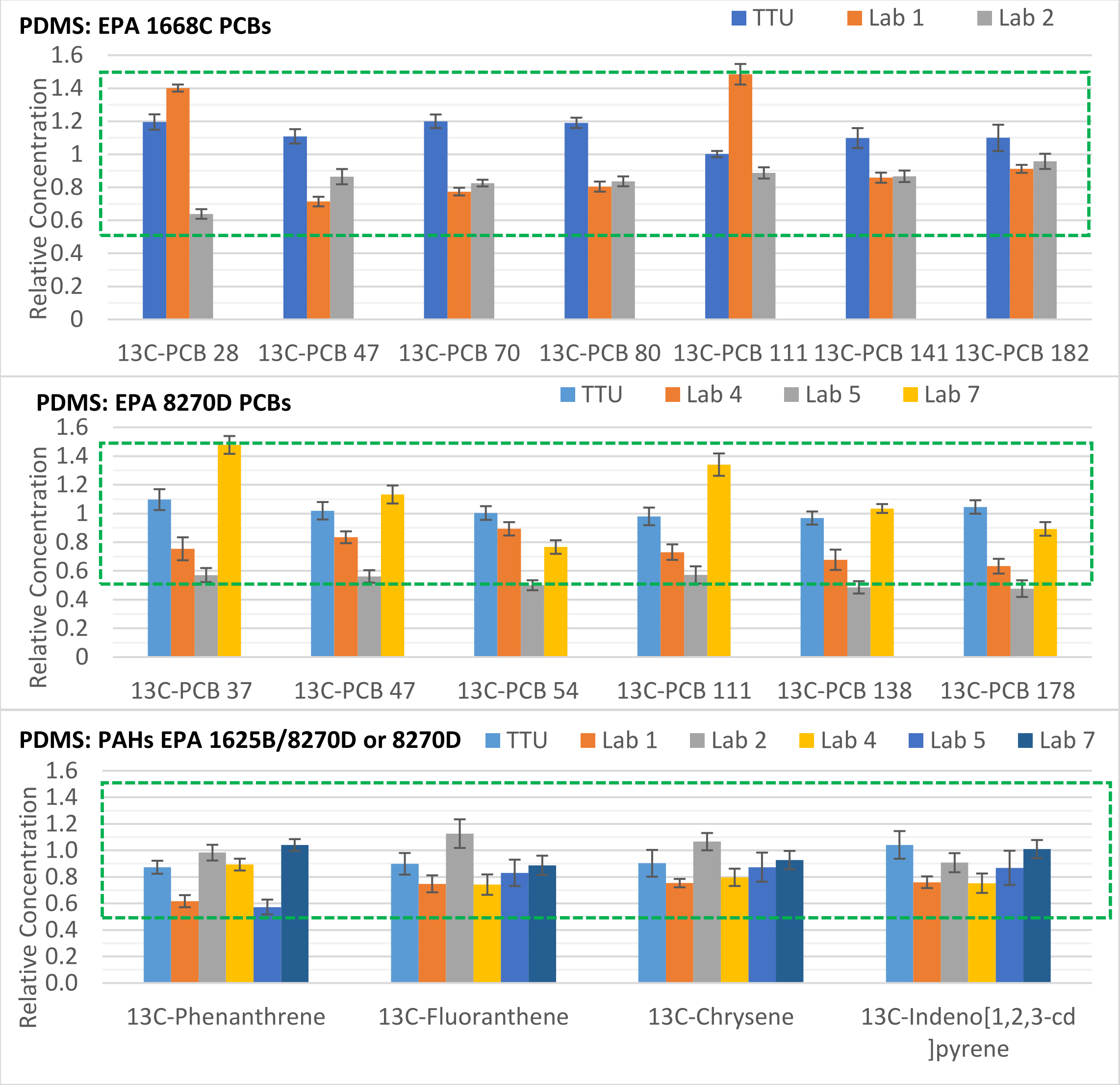


Figure 6.5. Concentrations in relative units (Creported/Cknown). The green line represents accuracy within ± 50% accuracy for the High/Low sensitivity C13-PCBs and C13-PAHs for phase 3.

6.3.5. Phase 3 -Inter-laboratory porewater comparison using PDMS fibers

The phase involves the exposure of the preloaded PDMS from phase 2 to a sediment of known physicochemical properties. The sediment used was from the Indiana Harbor

Canal, Confined Disposal Facility (IHC-CDF) and the sediment properties were analyzed as shown in Table S2. The PRC preloaded PDMS fibers were inserted into sediment samples of known physicochemical properties in the laboratory. Prior to deployment, sediment samples were removed from the cold room where they were preserved, placed in room temperature, and then homogenized. Static and active sampling of PDMS fibers were conducted. Static sampling involved a no-shaking scenario, the sediment containing the fibers are placed undisturbed in the Lab. The active sampling involves the placement of the sediment containing the PDMS fiber on a 1D-shaker or roller throughout the deployment period. After specified number of days (at least 28 days), the PDMS fibers were analyzed for native 20 PCB congeners, 16 priority PAHs and PRC analytes for both the static and active sampling scenarios. The concentrations on the PDMS fibers are then converted to environmental porewater concentrations as discussed in the next subsections. The porewater concentrations were corrected for PRCs using the information in Chapter 2, section 2.5.3 (more details in the supplementary section).

6.3.5.1. High sensitivity PCB congeners

Comparison among the Labs as shown on Figure 6.6 indicated that Lab 1 compared well within a factor of 2 with TTU for both static and active sampling, while Lab 2 showed concentration within a factor of 5 to 10 with TTU concentrations. PCB congeners 126 and 169 are non-detect for all participatory laboratories except for TTU, that detected PCB 126.

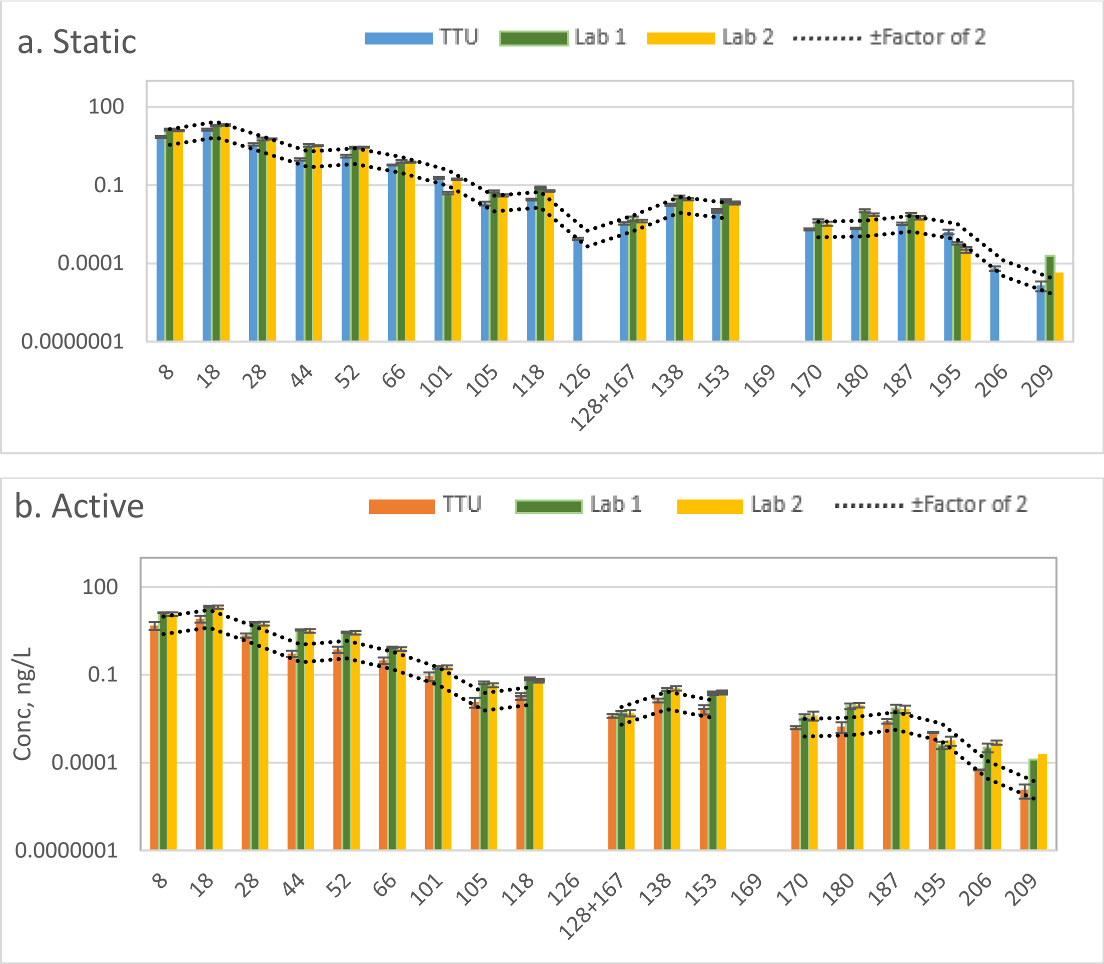


Figure 6.6. Porewater concentrations in Log units for High sensitivity PCB group for a) Static sampling and b.) Active sampling. Dashed lines represent ± factor of 2 for individual congener using TTU porewater concentration as the baseline concentration.

6.3.5.2. Low sensitivity PCB congeners

Figure 6.7 shows the result of the porewater concentrations for the participating Labs. All Labs compared within a ± factor of 2 with TTU, with PCB 126 and 169 undetected for most labs.

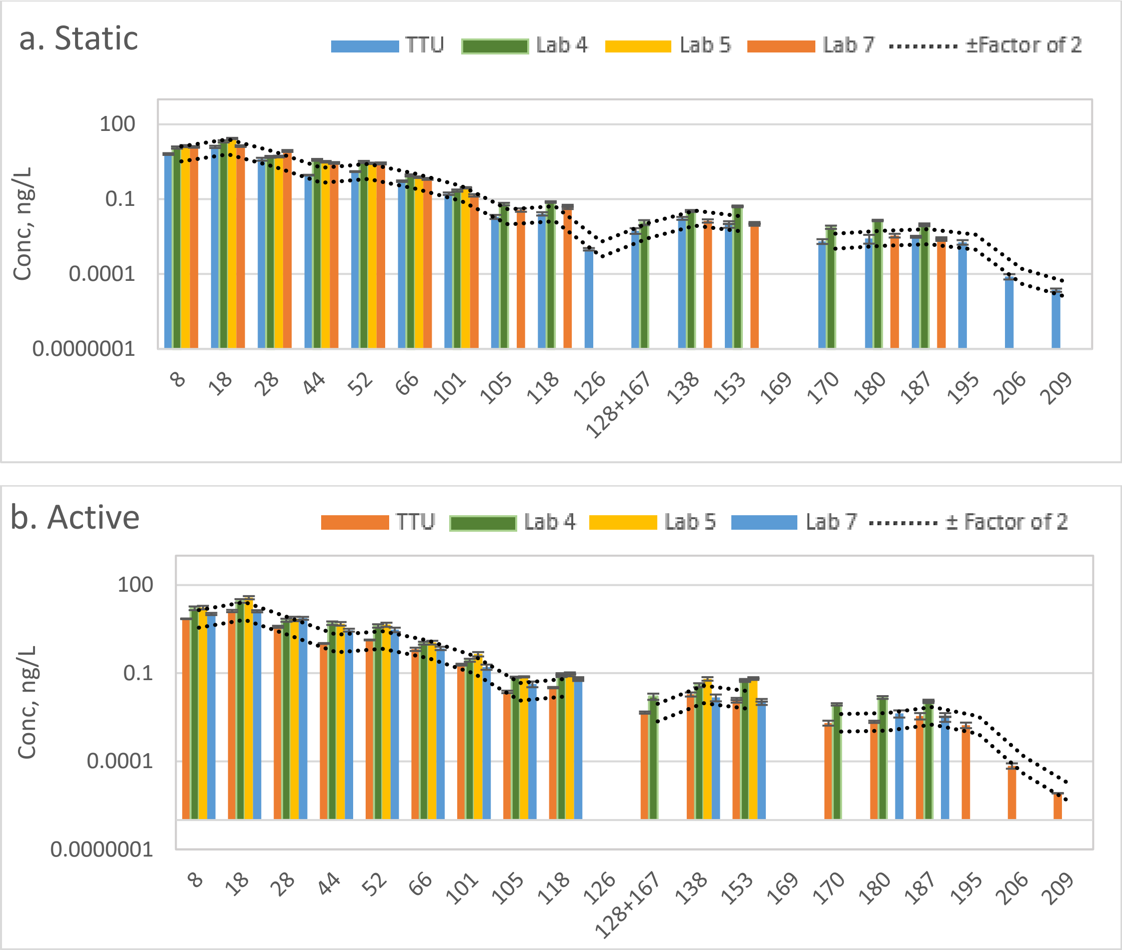


Figure 6.7. Porewater concentrations in Log units for Low sensitivity PCB group for a) Static sampling and b.) Active sampling. Dashed lines represent ± factor of 2 for individual congener using TTU porewater concentration as the baseline concentration.

6.3.5.3. High/Low sensitivity PAHs

Figure 6.8 shows the PAH porewater concentration for the 16 priority PAHs. For the static sampling, all the participating labs compared within a factor of 2 with TTU for detected PAH compounds except for Lab 2 for mostly the High molecular weight (HMW) PAHs namely benzo(k)fluoranthene, benzo(a) pyrene, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene and a non-detect for dibenzo(ah)anthracene. Lab 4 indicated a non-detect for dibenzo(ah)anthracene and Lab 5, a non-detect for benzo(b)fluoranthene, benzo(k)fluoranthene benzo(a) pyrene, indeno(1,2,3-cd)pyrene, dibenzo(ah)anthracene and benzo(ghi)perylene.

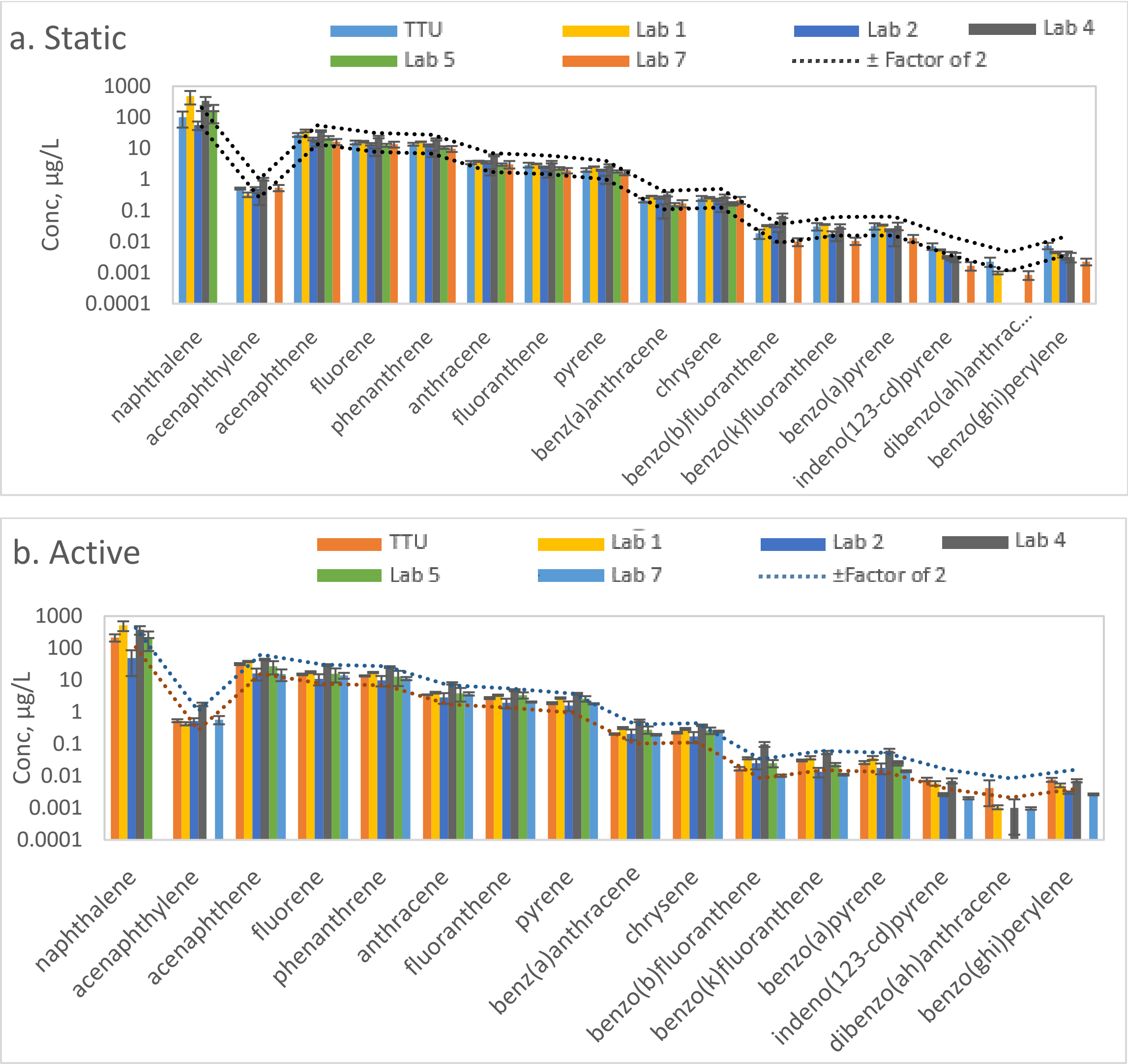


Figure 6.8. Porewater concentrations in Log units for PAHs for a) Static sampling and b.) Active sampling. Dashed lines represent ± factor of 2 for individual PAH compounds using TTU porewater concentration as the baseline concentration.

6.4. Lessons learned and Implications

6.4.1. Solvent types and proportion

During phase 2 of this study, the inter-laboratory comparison indicated that some results deviated from the required accuracy criteria of ± 50% for some select PRCs, although all laboratories recorded the required precision level of ± 20% (Figure 6.4). An in-depth investigation conducted suggested that the underlying factors and reasons for the observed accuracy deviations from the target concentrations among commercial laboratories was as a results of i.) the kind of solvents employed during the preparation of the PRC loading solutions, and ii.) the final fraction of nonane in the working standard. In the case of the former, it should be noted that in the preparation of the PRC loading solution, an intermediate working standard prepared from the main stock solutions, are prepared to be spiked into a known volume of methanol: water (20:80, v/v) solution. However, the result of the in-depth investigation indicated that across laboratories, different types of solvents were employed in the preparation of this intermediate working standard. Hence, the composition of the loading solution differs across laboratories. In the latter case, it should be noted that all of the stock standards purchased during this study was in nonane solution. Nonane is a clear, colorless, flammable solvent with a sharp odor. It is a nonpolar solvent, insoluble in water (a polar solvent), but soluble in nonpolar solvents such as hexane and slightly polar solvents such as acetone. These properties of nonane are essential when considering the solvents to employ in the preparation of a working standard.

The effect of the type of solvent used in the preparation of the working standard and the proportion used for spiking or preparation of the loading solution as shown in Table 6.3 and differs across participatory labs. It was noted that some of the labs (except those that used acetone) recorded phase separation in the working standard, while, most of the laboratories that used acetone as the intermediate solvent achieved recovery of most of the analytes within ± 50 % accuracy. Lab 4 in the low sensitivity group used methanol: ethanol (1:1, v/v) and experienced low PRC recovery in PCB PRCs (54, 111, 138 and 178) as shown in Table 6.3. Although with the use of acetone as an intermediate working solvent, less loading of C13 PCB 37 and C13 phenanthrene was experienced by Lab 5 and Lab 2 (Figure 6.4) respectively, there is uncertainty if high nonane ratio led to the variation from target concentration for these laboratories.

Additionally, most of the commercial laboratories that used solvents other than acetone observed phase separation in either or both working standard and the loading solution during the phase 2. The corrective measure involves strict adoption of the standard operating procedures inclusive of the recommended solvents. The revised phase 2 adopted the corrective measures, and a much-improved accuracies were achieved with the exception of lab 5 recording < 50% in C13 PCB 138 and PCB 178. Targeting a concentration is useful, however, a much important factor to consider during the preparation and use of a passive sampler, is a consistent and measurable initial concentration (C0) for the PRCs of interest.

6.4.2. Delamination of PDMS

The delamination of the PDMS fiber was observed during the revised phase 2 PRC loading process by one of the participating Labs. Hexane solvent was employed in the preparation of the working standards for both PCB PRCs and PAH PRCs, but this problem was observed only in the PAH PRC loading solution. Typically, this delamination process is observed only during the final extraction with hexane prior to analysis of the PDMS fiber, and never at the PRC loading step or process. Consequently, past and current preparation of the PRC loading solution using working standards in hexane were investigated, and the result suggested that hexane concentrations were high enough that some phase separation occurred. That is, free hexane was present in the loading solution and led to delamination (i.e. the peeling of PDMS core from the glass) (Table 6.4). It was observed that the highest concentration of hexane ever used in earlier studies was ~26 % of solubility (Table 6.4). However, for the participating laboratory in question, the hexane used in the PAH PRCs loading solution was more than 100 % of its solubility. Thereby, raising the question of how much of hexane solvent is safe to use in the preparation of intermediate working standards (a subject of further study).

The result of this investigation further supported earlier SOP revision, which advised the use of acetone as the most suitable intermediate solvent due to its compatibility with solvents used both in working standards and loading solutions.

Table 6.4. Amount of Hexane in PRC loading solution investigation

Phase 3		
Labs	Hexane solubility in PRC loading solution	Observation in PDMS
TTU	25.53%	NA
Lab 7, PCB PRCs	138.82%	NA
Lab 7, PAH PRCs	296.69%	Delamination

NA indicates no observation of delamination was observed in PDMS fiber.

6.5. Summary and Conclusions

The study so far was able to achieve part of its objectives and progressed through phases. First, the instrumentation and analytical capabilities of all the laboratories were verified by quantifying the calibration check standards that were sent by TTU. In addition, a select suite of C13 PCBs and C13 PAHs that was acceptable to all parties involved was identified. And then, pre-loaded PDMS fibers were sent to the laboratories for quantification. Secondly, individual laboratories then demonstrated the ability to load PDMS fibers with the selected C13 compounds. Thirdly, laboratories then use a standardized approach to load the PDMS fibers with PRC compounds and the ex-situ deployment into a sediment with known physicochemical properties. The next step of this study is to compare the porewater concentration obtained from the PDMS fibers with porewater obtained from other passive samplers and the conventional techniques (direct extraction and air-bridge). This is to evaluate and validate the capability of the PDMS fibers to measure environmental porewater concentrations.

In conclusion, all the participating laboratories were able to achieve the objectives of the project during the completed phases (1-3a) based on sensitivity and precision from phase 1 through phase 3. Accuracies measurement based on inter-laboratory comparisons, resulted in some deviations from the target concentrations particularly for some of the C13 compounds. That is, < 50% accuracies were measured by some participating labs for C13 PCBs (37, 54, 111, 138, 178) and C13 PAHs (phenanthrene and indeno[1,2,3-cd]pyrene) as a result of variation in solvent types and proportions. These concerns were addressed and improvement in the PRC loading solution was observed.

References

1. Pan, B.; Ning, P.; Xing, B., Part IV—sorption of hydrophobic organic contaminants. *Environmental Science and Pollution Research* 2008, *15*, (7), 554-564.

2. Luthy, R. G. In *Organic contaminants in the environment: challenges for the water/environmental engineering community*, Water and sustainable development: opportunities for the chemical sciences–a workshop report to the chemical sciences roundtable, 2004; 2004; p 40.

3. Di Toro, D. M.; Zarba, C. S.; Hansen, D. J.; Berry, W. J.; Swartz, R. C.; Cowan, C. E.; Pavlou, S. P.; Allen, H. E.; Thomas, N. A.; Paquin, P. R., Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry: An International Journal* 1991, *10*, (12), 1541-1583.

4. Cui, X.; Mayer, P.; Gan, J., Methods to assess bioavailability of hydrophobic organic contaminants: principles, operations, and limitations. *Environmental Pollution* 2013, *172*, 223-234.

5. Cornelissen, G.; Breedveld, G. D.; Næs, K.; Oen, A. M.; Ruus, A., Bioaccumulation of native polycyclic aromatic hydrocarbons from sediment by a polychaete and a gastropod: Freely dissolved concentrations and activated carbon amendment. *Environmental Toxicology and Chemistry: An International Journal* 2006, *25*, (9), 2349-2355.

6. Lydy, M. J.; Landrum, P. F.; Oen, A. M.; Allinson, M.; Smedes, F.; Harwood, A. D.; Li, H.; Maruya, K. A.; Liu, J., Passive sampling methods for contaminated sediments: State of the science for organic contaminants. *Integrated environmental assessment and management* 2014, *10*, (2), 167-178.

7. Carr, R. S.; Nipper, M. A., *Porewater toxicity testing: biological, chemical, and ecological considerations*. SETAC Foundation for: 2003.

8. Tomaszewski, J. E.; Luthy, R. G., Field deployment of polyethylene devices to measure PCB concentrations in pore water of contaminated sediment. *Environ Sci Technol* 2008, *42*, (16), 6086-6091.

9. Arp, H. P.; Hale, S. E.; Elmquist Krusa, M.; Cornelissen, G.; Grabanski, C. B.; Miller, D. J.; Hawthorne, S. B., Review of polyoxymethylene passive sampling methods for quantifying freely dissolved porewater concentrations of hydrophobic organic contaminants. *Environ Toxicol Chem* 2015, *34*, (4), 710-20.

10. Enell, A.; Lundstedt, S.; Arp, H. P.; Josefsson, S.; Cornelissen, G.; Wik, O.; Berggren Kleja, D., Combining Leaching and Passive Sampling To Measure the Mobility and Distribution between Porewater, DOC, and Colloids of Native Oxy-PAHs, N-PACs, and PAHs in Historically Contaminated Soil. *Environ Sci Technol* 2016, *50*, (21), 11797-11805.

11. Jalalizadeh, M.; Ghosh, U., In Situ Passive Sampling of Sediment Porewater Enhanced by Periodic Vibration. *Environ Sci Technol* 2016, *50*, (16), 8741-9.

12. Jalalizadeh, M.; Ghosh, U., Analysis of Measurement Errors in Passive Sampling of Porewater PCB Concentrations under Static and Periodically Vibrated Conditions. *Environ Sci Technol* 2017, *51*, (12), 7018-7027.

13. Sanders, J. P.; Andrade, N. A.; Ghosh, U., Evaluation of passive sampling polymers and nonequilibrium adjustment methods in a multiyear surveillance of sediment porewater PCBs. *Environ Toxicol Chem* 2018, *37*, (9), 2487-2495.

14. Reible, D. D., *Processes, assessment and remediation of contaminated sediments*. Springer: 2014.

15. Ghosh, U.; Kane Driscoll, S.; Burgess, R. M.; Jonker, M. T.; Reible, D.; Gobas, F.; Choi, Y.; Apitz, S. E.; Maruya, K. A.; Gala, W. R., Passive sampling methods for contaminated sediments: practical guidance for selection, calibration, and implementation. *Integrated environmental assessment and management* 2014, *10*, (2), 210-223.

16. Lu, X.; Skwarski, A.; Drake, B.; Reible, D. D., Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. *Environmental Toxicology and Chemistry* 2011, *30*, (5), 1109-1116.

17. Thomas, C.; Lampert, D.; Reible, D., Remedy performance monitoring at contaminated sediment sites using profiling solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers. *Environmental Science: Processes & Impacts* 2014, *16*, (3), 445-452.

18. Lu, X. X.; Hong, Y.; Reible, D. D., Assessing bioavailability of hydrophobic organic compounds and metals in sediments using freely available porewater concentrations. In *Processes, Assessment and Remediation of Contaminated Sediments*, Springer: 2014; pp 177-196.

19. Cornelissen, G.; Arp, H. P. H.; Pettersen, A.; Hauge, A.; Breedveld, G. D., Assessing PAH and PCB emissions from the relocation of harbour sediments using equilibrium passive samplers. *Chemosphere* 2008, *72*, (10), 1581-1587.

20. Michalsen, M.; Reible, D. A., Adesewa;Ghosh,Upal; Bokare,Mandar; Gschwend,Philip; MacFarlane,John; Lin,Mingta Standardizing Polymeric Sampling for Measuring Freely-Dissolved Organic Contaminants in Sediment Porewater. https://apps.dtic.mil/sti/pdfs/AD1084245.pdf 2018.

Supplementary Information

For Chapter 6. Standardization of polydimethylsiloxane (PDMS) for measuring freely dissolved hydrophobic organic contaminants (HOCs) in sediment porewater.

S1. More detail for Phase 1

Table S1. Summary of comparison for Phase 1A

Method	Analyte	Total Labs Performing	Pass	Fail	Pass Rate
EPA 1668C	PCB Natives	7	5	2	71%
	PCB PRCs	7	7	0	100%
EPA 8270D	PCB Natives	6	6	0	100%
	PCB PRCs	6	6	0	100%
EPA 1625B/8270D or EPA 8270D	PAH Natives	10	8	2	80%
	PAH PRCs	10	9	1	90%

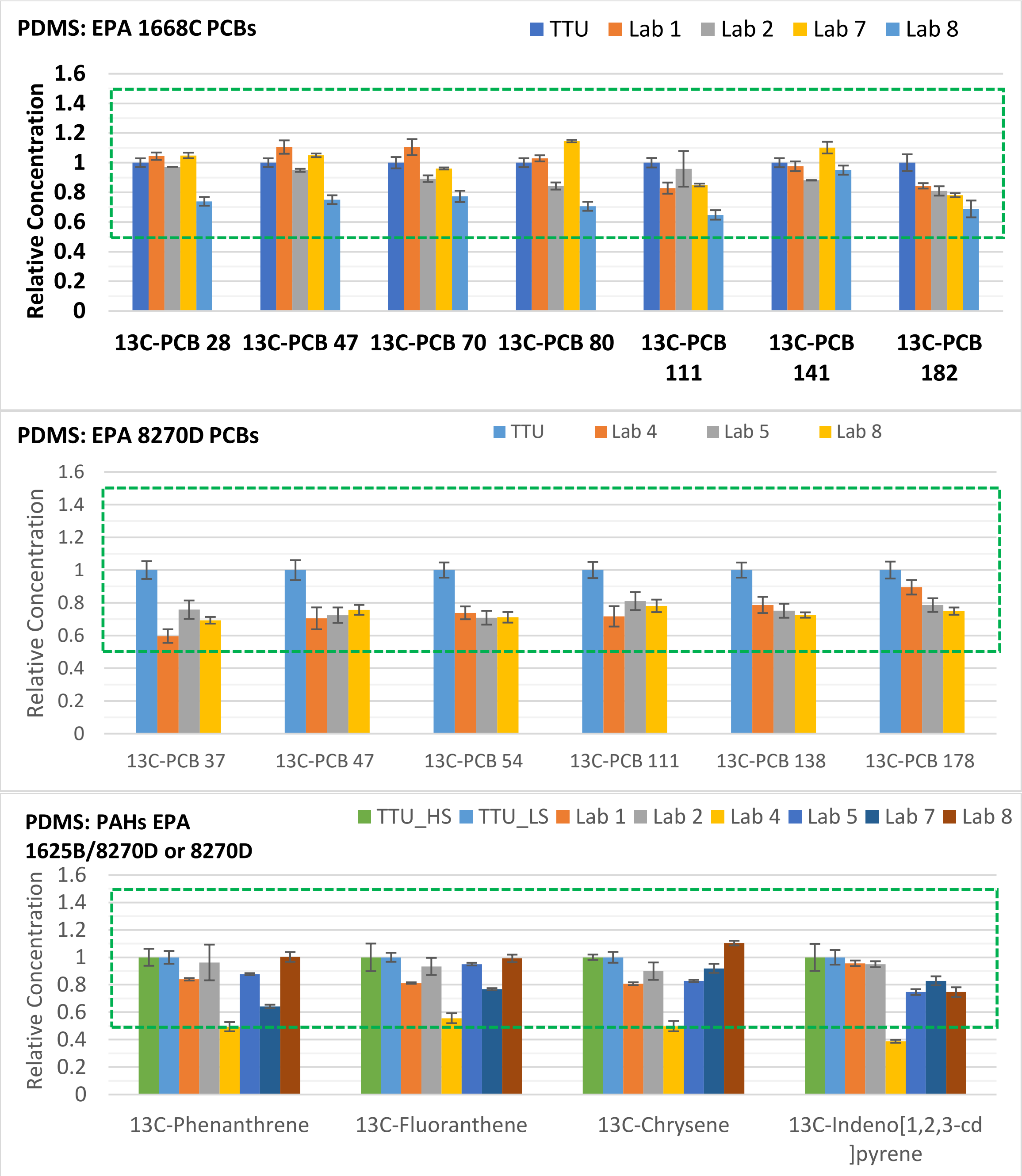
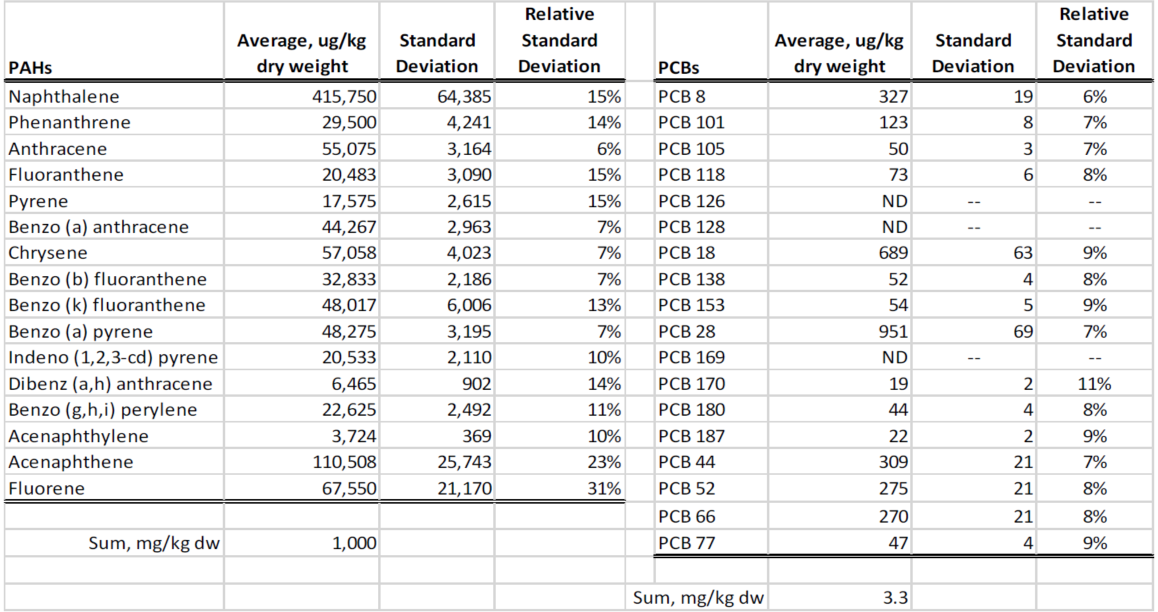


Figure S1. Concentrations in relative units (Creported/Ctarget). The green line represents accuracy within ± 50% accuracy for the high/low sensitivity PCB PRCs and PAH PRCs for phase 1B.

Table S2. Concentration of PAHs and PCBs in IHC-CDF bulk sediment



PAHs	Average, ug/kg dry weight	Standard Deviation	Relative Standard Deviation		PCBs	Average, ug/kg dry weight	Standard Deviation	Relative Standard Deviation
Naphthalene	415,750	64,385	15%		PCB 8	327	19	6%
Phenanthrene	29,500	4,241	14%		PCB 101	123	8	7%
Anthracene	55,075	3,164	6%		PCB 105	50	3	7%
Fluoranthene	20,483	3,090	15%		PCB 118	73	6	8%
Pyrene	17,575	2,615	15%		PCB 126	ND	--	--
Benzo (a) anthracene	44,267	2,963	7%		PCB 128	ND	--	--
Chrysene	57,058	4,023	7%		PCB 18	689	63	9%
Benzo (b) fluoranthene	32,833	2,186	7%		PCB 138	52	4	8%
Benzo (k) fluoranthene	48,017	6,006	13%		PCB 153	54	5	9%
Benzo (a) pyrene	48,275	3,195	7%		PCB 28	951	69	7%
Indeno (1,2,3-cd) pyrene	20,533	2,110	10%		PCB 169	ND	--	--
Dibenz (a,h) anthracene	6,465	902	14%		PCB 170	19	2	11%
Benzo (g,h,i) perylene	22,625	2,492	11%		PCB 180	44	4	8%
Acenaphthylene	3,724	369	10%		PCB 187	22	2	9%
Acenaphthene	110,508	25,743	23%		PCB 44	309	21	7%
Fluorene	67,550	21,170	31%		PCB 52	275	21	8%
					PCB 66	270	21	8%
Sum, mg/kg dw	1,000				PCB 77	47	4	9%
					Sum, mg/kg dw	3.3		

S2. Additional Information for Phase 3B - Fractional Approach to Steady State (fss) for all participatory Labs

The factional Approach to Steady State (fss) PRC fss was estimated from known initial (C0) and final (after deployment) PRCs concentrations as indicated by Equation S1.

$$fss, PRC = \frac{C_{PRC0} - C_{PRCfinal}}{C_{PRC0}} \tag{S1}$$

The fss for target compounds are then either intra or extrapolated as a function of log K_{OW} using the cylindrical model developed by Shen and Reible [1]. Figures S3-S8 shows the measured fss for PRCs and the intra/extrapolated fss for native compounds (PCB congeners and PAHs) for all participatory laboratories.

S2.1. FSS for TTU High Resolution

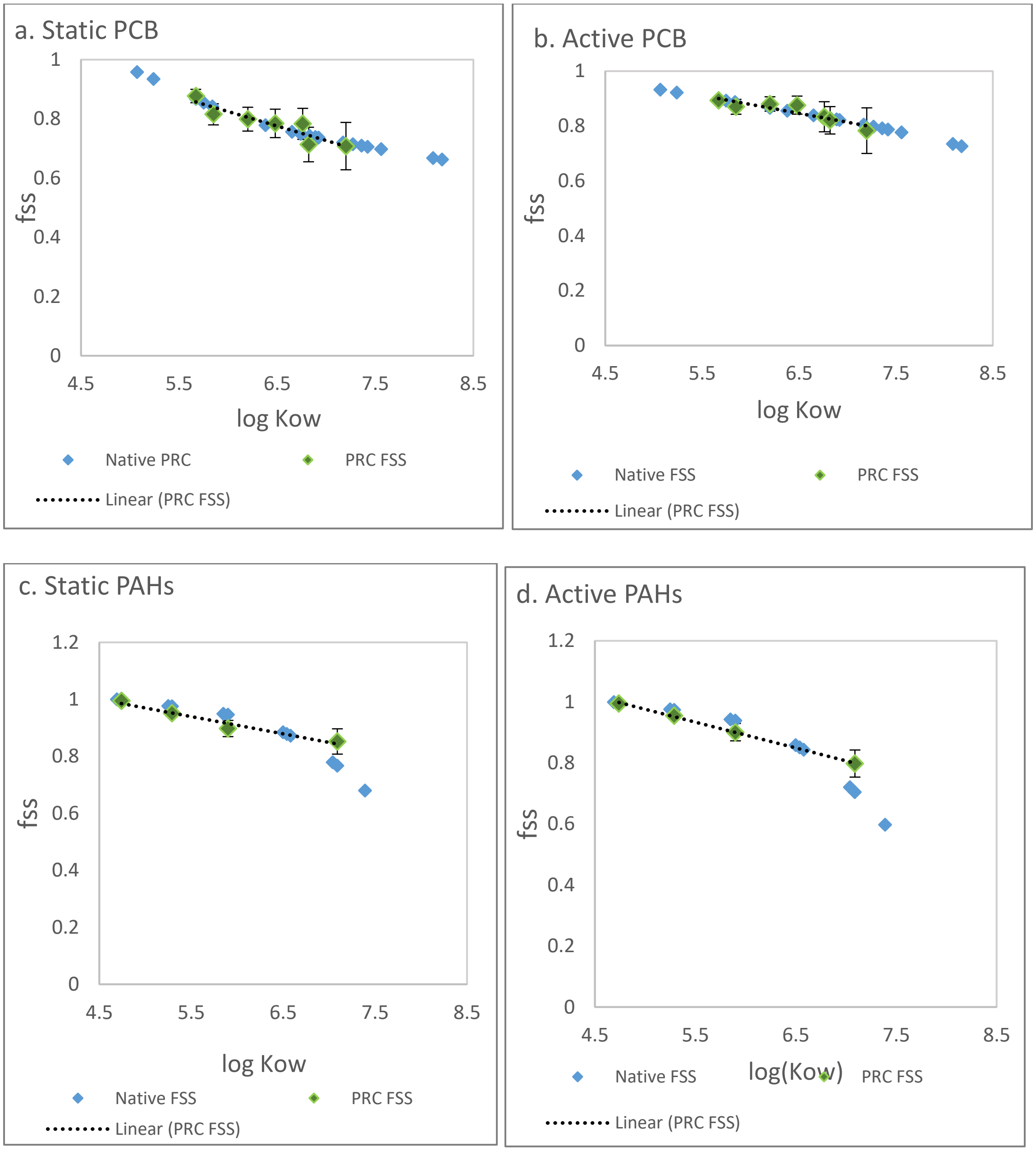


Figure S3. TTU High Resolution FSS for a) PCB static, b) PCB active, c) PAH static and d) PAH active.

S2.2. FSS for TTU Low Resolution

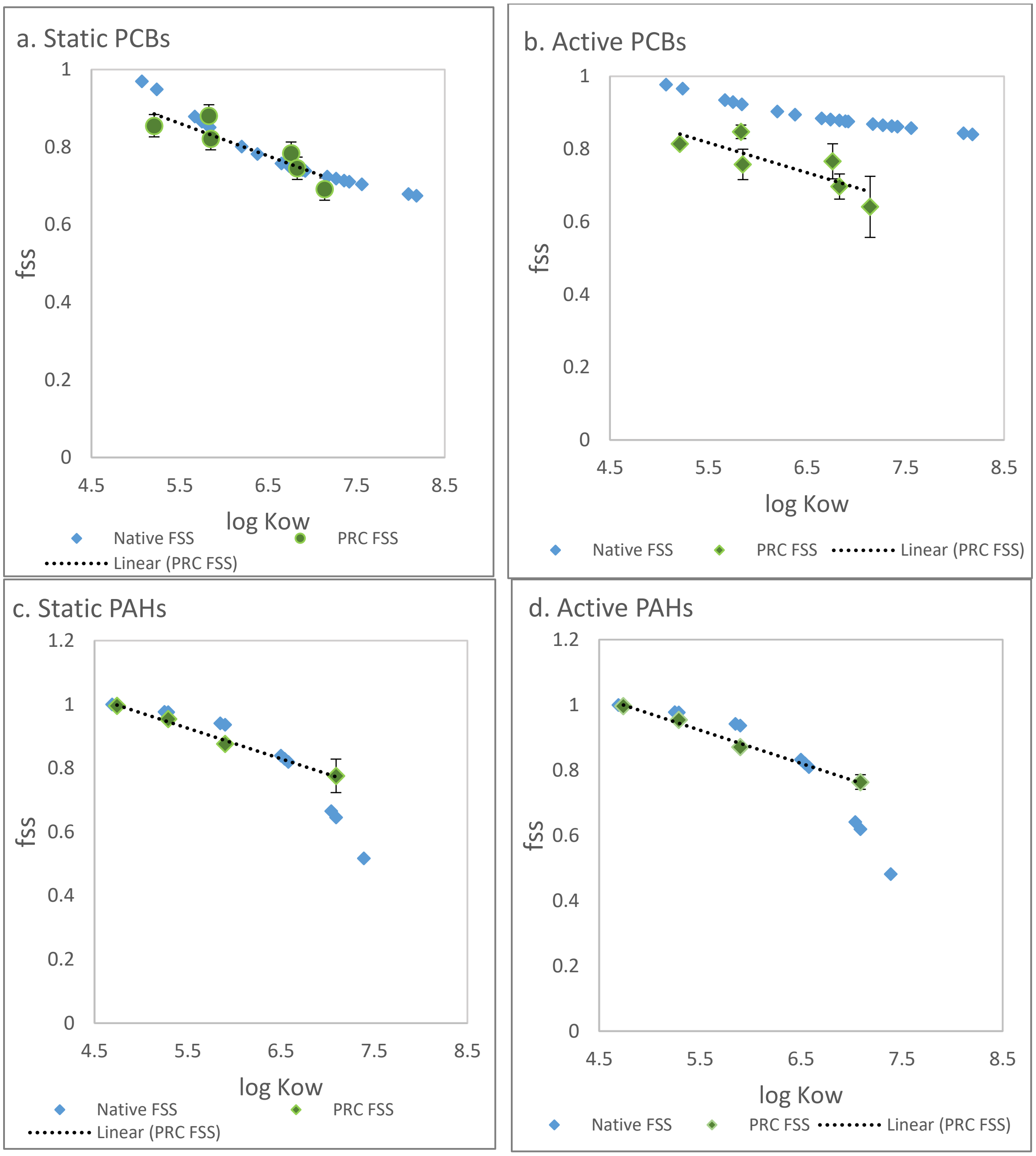


Figure S4. TTU Low Resolution FSS for a) PCB static, b) PCB active, c) PAH static and d) PAH active.

S2.3. FSS for Lab 1

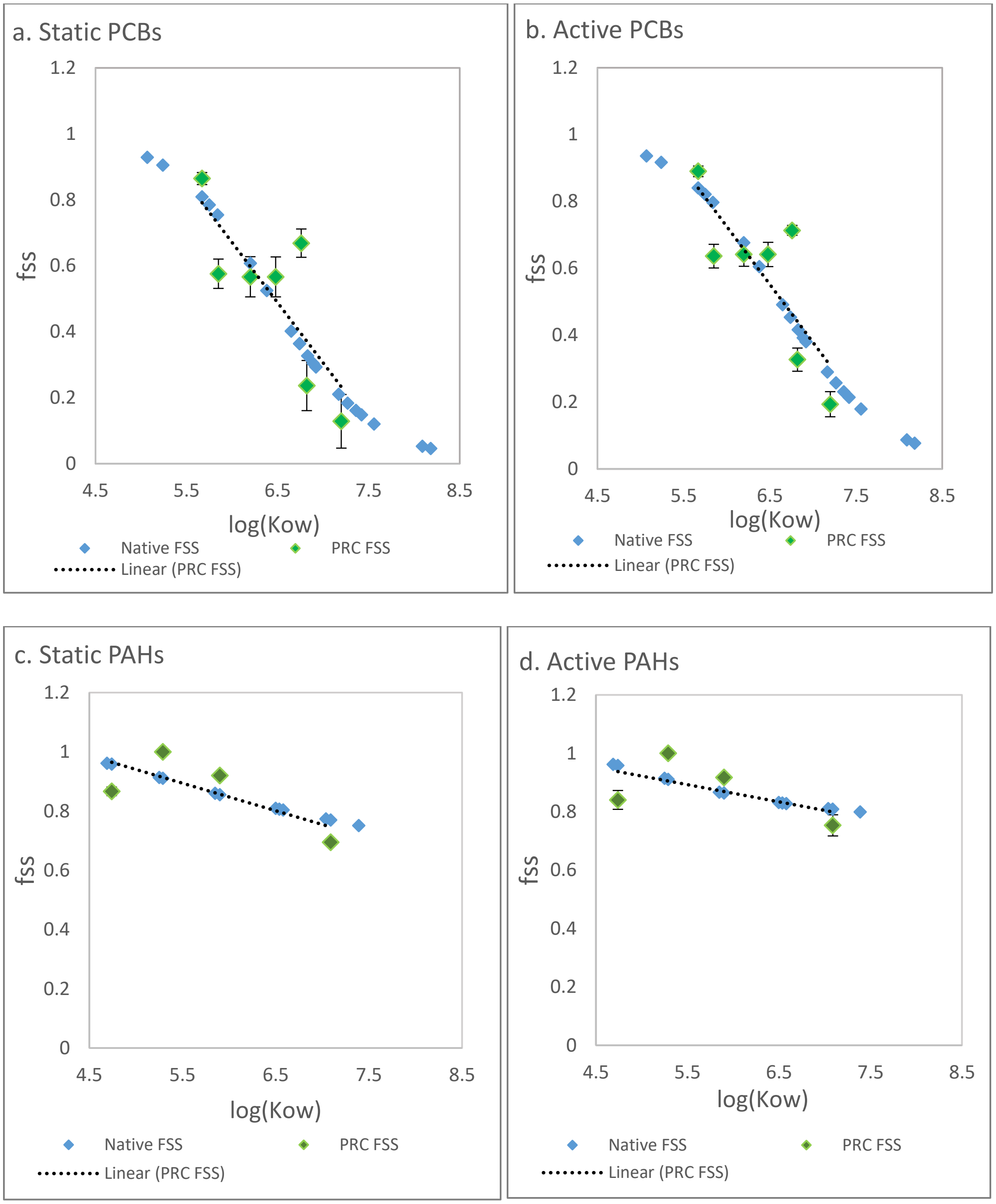


Figure S5. Lab 1 FSS for a) PCB static, b) PCB active, c) PAH static and d) PAH active.

S2.4. FSS for Lab 2

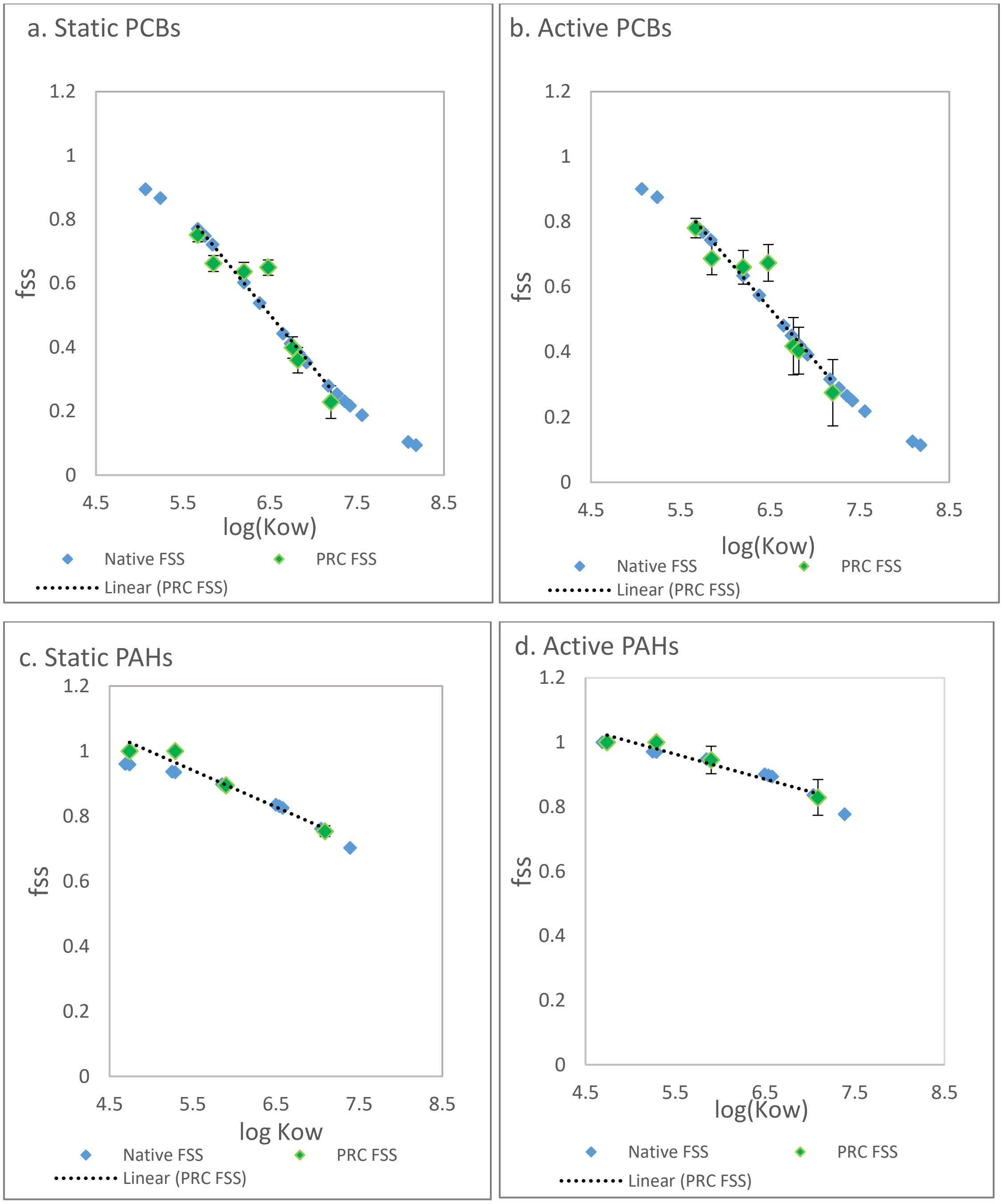


Figure S6. Lab 2 FSS for a) PCB static, b) PCB active, c) PAH static and d) PAH active.

S2.5. FSS for Lab 4

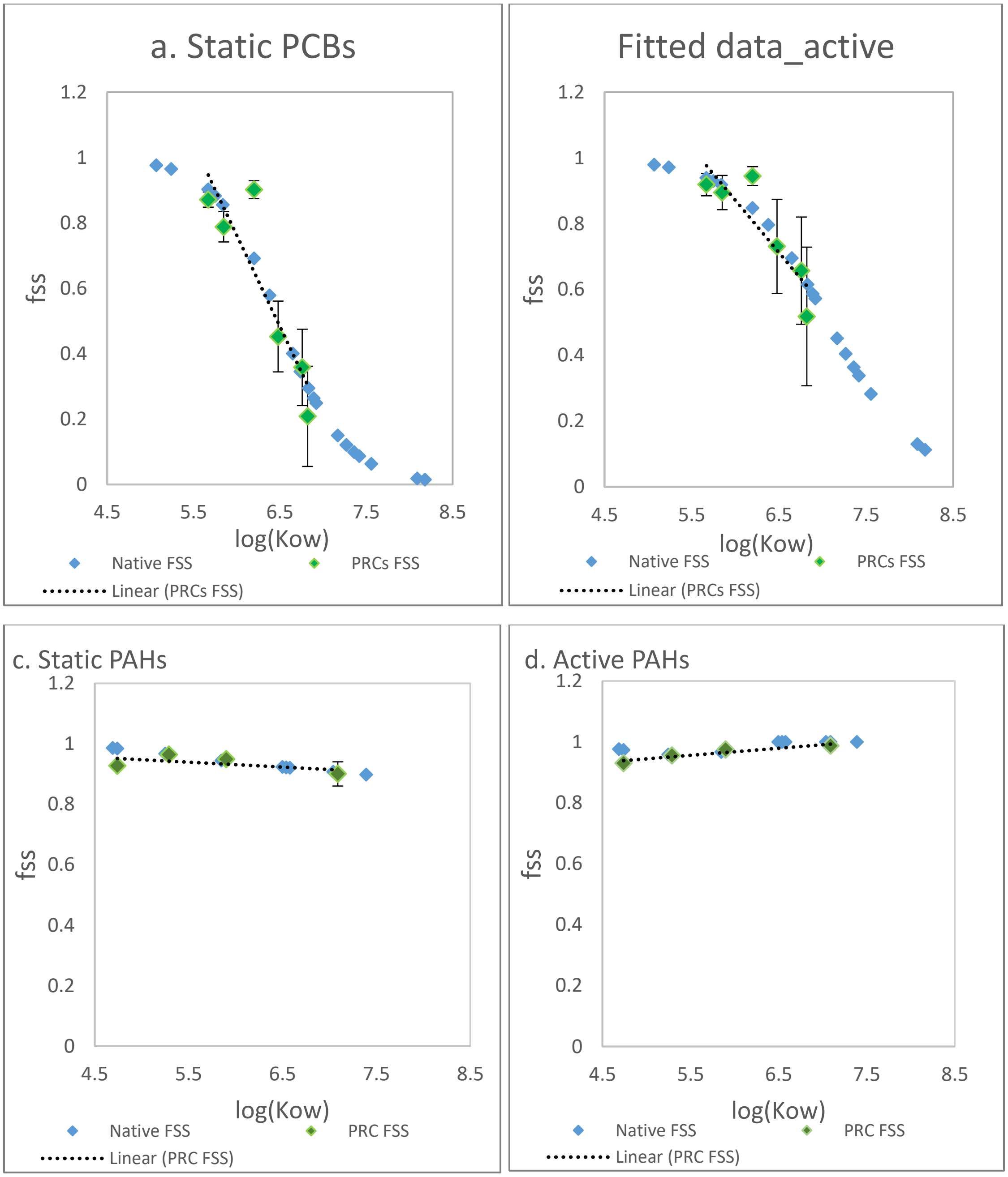


Figure S7. Lab 4 FSS for a) PCB static, b) PCB active, c) PAH static and d) PAH active.

S2.6. FSS for Lab 5

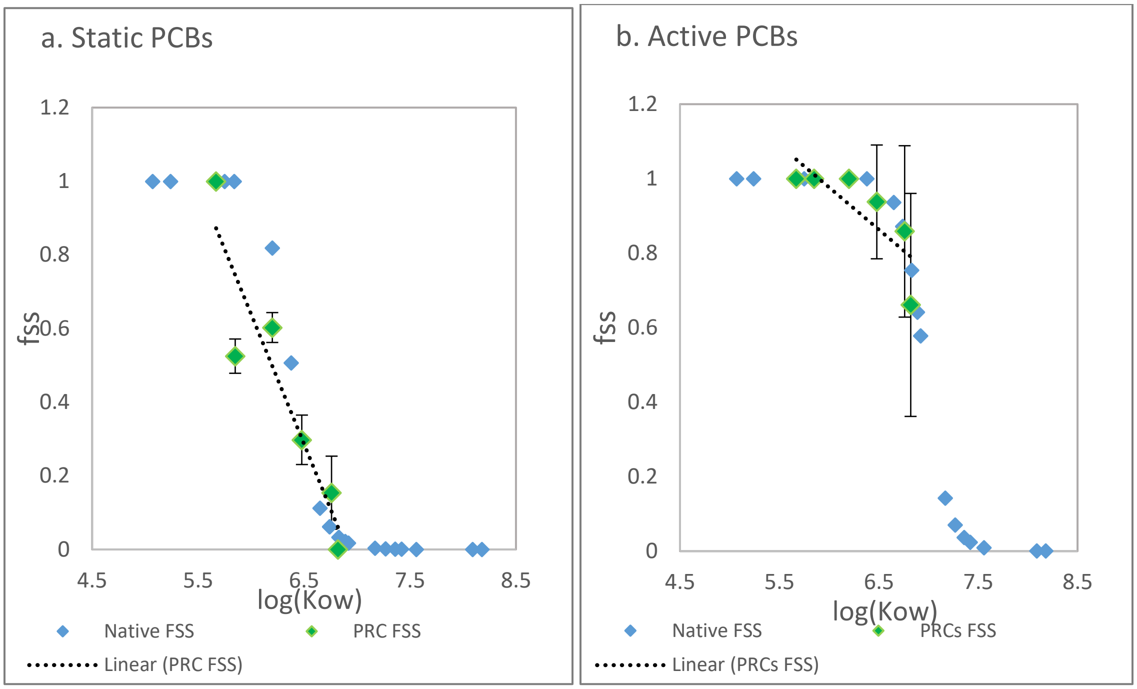


Figure S8. Lab 5 FSS for a) PCB static, and b) PCB active. PAH PRC was detected for only C13 phenanthrene and non-detect for the HMW PAHs, hence 100% Equilibration was assumed for all native.

S2.6. FSS for Lab 7

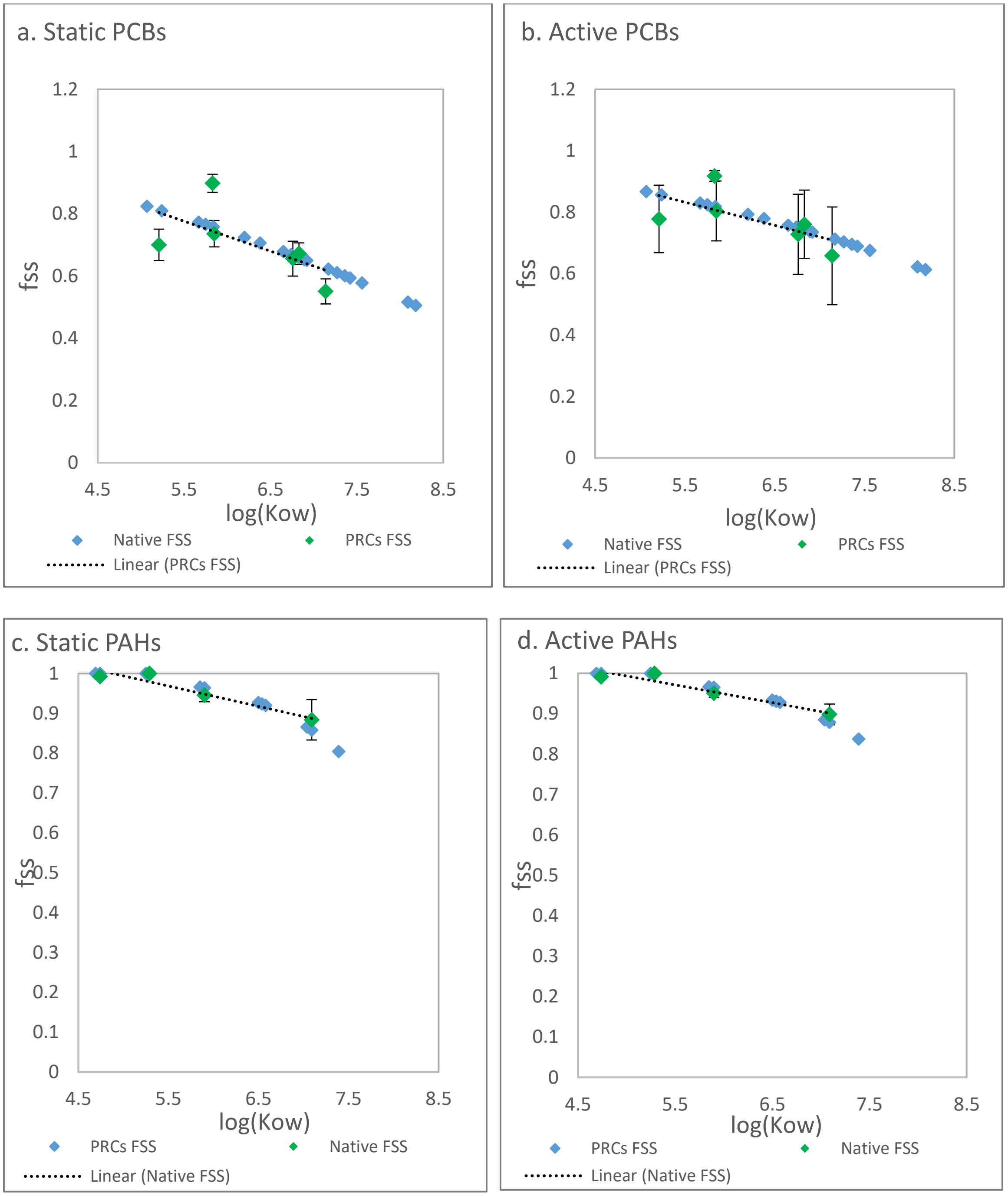


Figure S9. Lab 7 FSS for a) PCB static, b) PCB active, c) PAH static and d) PAH active.

References.

1. Shen, Xiaolong, and Danny Reible. “An analytical model for the fate and transport of performance reference compounds and target compounds around cylindrical passive samplers.” *Chemosphere* 232 (2019): 489-495.

Chapter 7

Conclusions and Recommendations

7.1. Research Objectives

In this dissertation, passive sampling techniques were demonstrated in assessing atmospheric and dissolved concentrations of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in ambient air and sediment.

This dissertation:

1. Developed polyoxymethylene as a passive air sampler (PAS) for measuring air concentrations, demonstrated PAS advantages over conventional high-volume air sampler (HVAS) particularly in providing long time average air concentrations and finally, compared air concentration obtained using PAS to air concentration obtained using HVAS.
2. Evaluated and demonstrated the application of PAS to measure air concentration through multiple field applications.
3. Prepared standard operating procedures (SOPs) for participatory laboratories to adopt and demonstrate reproducibility, precision, and accuracy in the measurement of freely dissolved contaminants in sediment pore water.

The objectives above were achieved through a set of laboratory and field sampling studies performed at the Indiana Harbor and Canal, Confined Disposal Facility (CDF), East Chicago.

7.2. Research Conclusions

This research presents passive sampling techniques for the measurement of volatile emissions from a CDF and freely dissolved concentrations from sediment porewater using POM and PDMS, respectively. In this dissertation, passive sampling techniques using polyoxymethylene (POM) was developed and evaluated as an air sampler for PCBs and PAHs at a confined disposal facility. The results showed that POM can be an alternative air sampler suitable for providing long term average concentrations of HOCs due to its slow uptake and slow desorption kinetics. The use of POM may be limited to low congener PCBs and low molecular PAHs with low octanol-water or POM-air partition coefficients (K_{OW} or $K_{POM\text{-}A}$) due to the assumption of air side controlling uptake. Evaluation of PAS as a function of CDF activities showed that dredged material placement influenced particularly, air concentrations of PCBs and illustrates that measurements are likely due to evaporation. While for PAHs, air concentrations were influenced by external sources other than the CDF. PAS only measures gaseous bound compounds, thus indicating that POM may be a more sensitive indicator of evaporative emissions from the CDF. POM sampler achieved the aim of providing a long-term average air concentration without having to collect and analyze multiple HVAS samples.

This research also involves the standardization of laboratory passive sampling methods for sampling of sediment porewater. The study progressed through a phased inter-laboratory evaluation while developing a standard operating procedure (SOP). Success rate criteria were defined such that participating laboratories achieve accuracies of ±30% and

±50% for targets and PRCs respectively, and precisions of ≤ 20% for both targets and PRCs. For phase 1, success rate recorded was in the range between 71 % to 100 % depending on sensitivity groups. During phase 2, all the laboratories (100 % success rate) were able to achieve the desired ±50% accuracy and 20% precision for PRCs using the revised SOP that addressed the limitation posed by solvents variations. The results for phase 3 showed that measured porewater concentrations among participating labs were mostly with a factor of 2. Several lessons were learnt during the study including the role of solvents in the preparation of PRC loading and extraction of compounds from PDMS.

7.3. Recommendations

Passive sampling technology is still a relatively new method and hence not enough studies are available in addressing some of the challenges observed during the deployment of passive samplers. Hence, further studies are encouraged to address some of these challenges encountered during this research. These issues include,

1. *Limited understanding of the PRCs* – particularly in the case of POM, the rate of uptake of target compounds is observed to be faster compared to the depletion of PRCs from POM, this is an area that requires further study. Understanding the depletion rate of PRCs from POM will improve the understanding of contaminants relative to their uptake and equilibrium partitioning to POM.
2. *Extent to equilibration* – POM samplers are deployed at the field for different exposure durations. However, time to equilibration on POM differs for individual HOCs based

on correlation parameters developed using the time series lab experiment. Hence, it is uncertain if equilibrium was reached in the field particularly for HMW HOCs. Since the PRCs were not useful in addressing this, we recommend the use of additional non-equilibrium correction methods such as the time series deployment at the field of study if it is allowed or deployment of multiple thicknesses of POM.

3. *Influence of windspeed and ambient temperature* – further experimental work can be conducted to understand and validate the influence of different windspeeds and temperatures other than 20 ^{o}C on the uptake of HOCs on the POM air sampler.
4. *Impacts of solvents during PRC loading* – to achieve uniform loading of PRCs on PDMS and to avoid the delamination of PDMS, we recommend the strict use of acetone during the PRC loading preparation. In addition, we recommend proper shaking mechanism of 100-130 rpm through the loading duration of a minimum of 28 days.

Appendices

Appendix A. More information on Analytical Instrument, Sediment and water characterization

A1. More Information on Analytical Instrument

Analytical Instrument used for PCB analysis was Gas Chromatography– Triple quad Mass Spectrometer (GC-TQMS) and for PAHs analysis, both Gas Chromatography Mass Spectrometer (GC-MS) and GC-TQMS was used. The information are shown on Tables A1 and A2.

A2. Sediment and water characterization

Apart from the air sampling in the field during the 2 years (2017-2018), sediment and water samples were also collected from the Indiana Harbor Canal, Confined Disposal Facility (CDF) and characterized. Sediment and water samples were collected in 2017 at both the west and east cells of the CDF, and in 2018, samples were collected at the barge before placement in the CDF.

A2.1 Sediment characterization

For the sediment samples, the bulk concentration of PCBs, PAHs, total organic content (TOC), and black carbon (BC) were analyzed as summarized in Table A3.

A2.2 Water Analysis

For the water samples as shown in Table A4, TSS was performed. The water samples were homogenized before analyzing for TSS. A known volume of water sample was passed through 0.45 µm filter paper using a pump. The wet filter was then dried to a constant mass at 50 ^{o} C for 24 hours. In estimating for PCB congeners and PAHs contaminants in the water samples, the model in Reible, 1999[1] was used as shown in Equation A1,

$$C_{w*} = \frac{TSS * Ws}{1 + TSS * TOC * Koc} \tag{A1}$$

where TSS is the measured total suspended solids, Ws is the PCBs or PAHs concentration in the sediment, TOC is the total organic content in the sediment sample and K_{OC} is the soil organic carbon-based partitioning coefficients. This estimation assumes that the water is equilibrated with the suspended solids and that the partitioning coefficient between the sediment and water is defined by the fraction organic carbon and the organic carbon-based partitioning coefficient. Typically, this will overestimate water concentrations. Hence polydimethylsiloxane (PDMS) was used to estimate truly dissolved concentration as discussed in the next section. During the 2017 sampling event, the average TSS concentration was 131.5 ± 25.8 mg/L for the west cell and 4.2 ± 1.6 mg/L for the east cell. The concentration was higher for the samples collected in the west cell due to active placement sediment placement when the samples were collected. For 2018 sampling event, the average TSS concentration measured in the samples was 68.70 ± 17.5 mg/L.

A2.3. Truly Dissolved concentration

The truly dissolved concentration (C_{W*}) was estimated using Equation A1 using K_d (K_{OC}*F_{OC}) correlation as shown in Figure A1-A3 from the relationship between solid concentration (W_S) to porewater concentration (C_{PW}) from equation A2. The C_{PW} was obtained using polydimethylsiloxane (PDMS) fiber inserted ex situ in the sediment sample obtained at the CDF during 2017 and 2018 sampling. The PDMS exposure was for a period of 28 days for some compounds. The corresponding C_{W*} was used in the estimati0n of flux at the CDF.

$$K_d = \frac{W_S}{C_{PW}} \tag{A2}$$

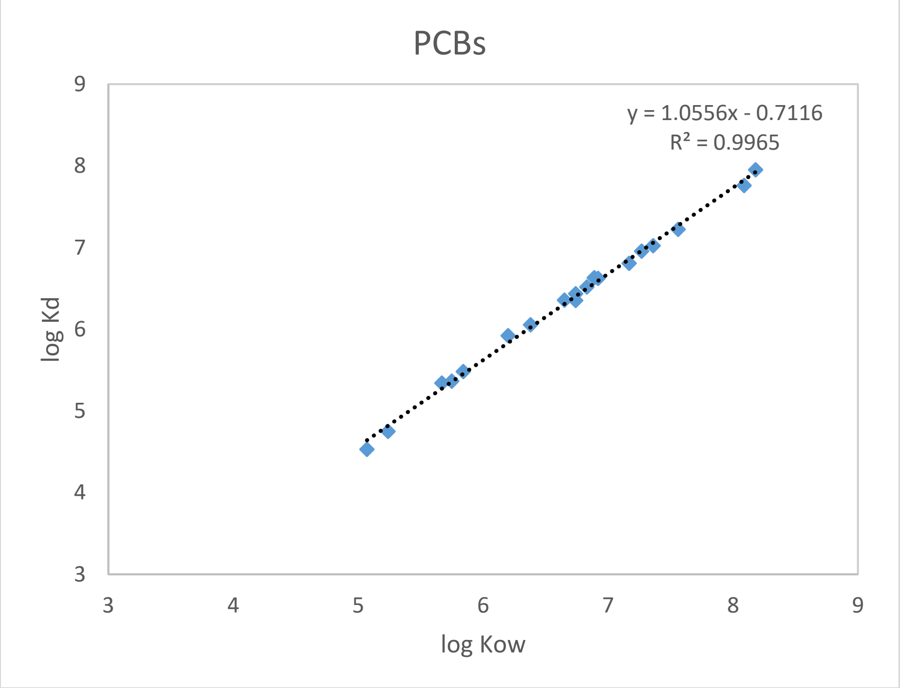


Figure A1. Relationship between log Kd with log Kow for 2017 sampling.

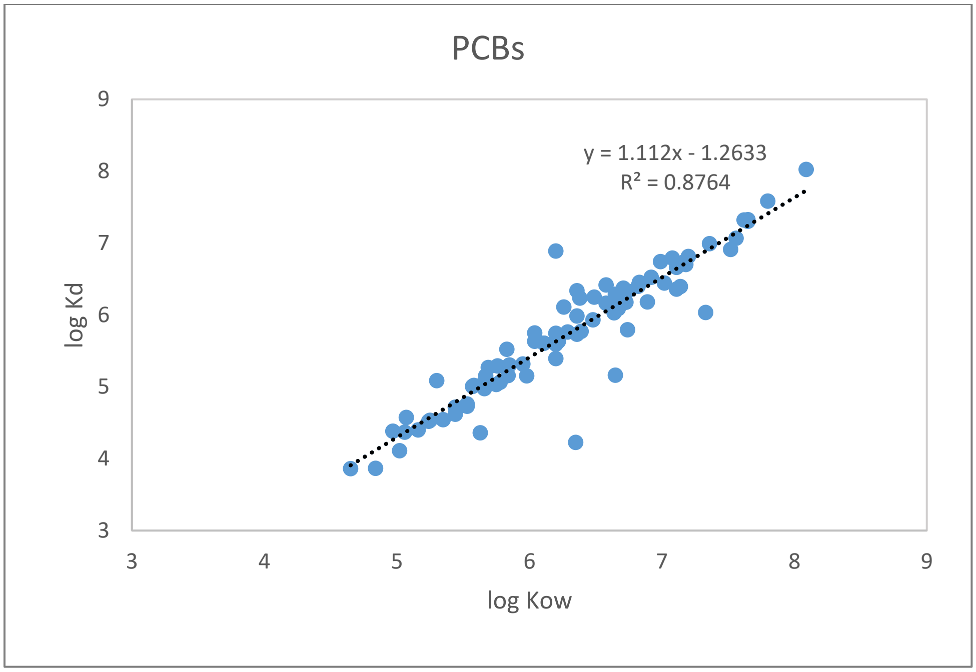


Figure A2. Relationship between log Kd with log Kow for 2018 sampling for PCBs.

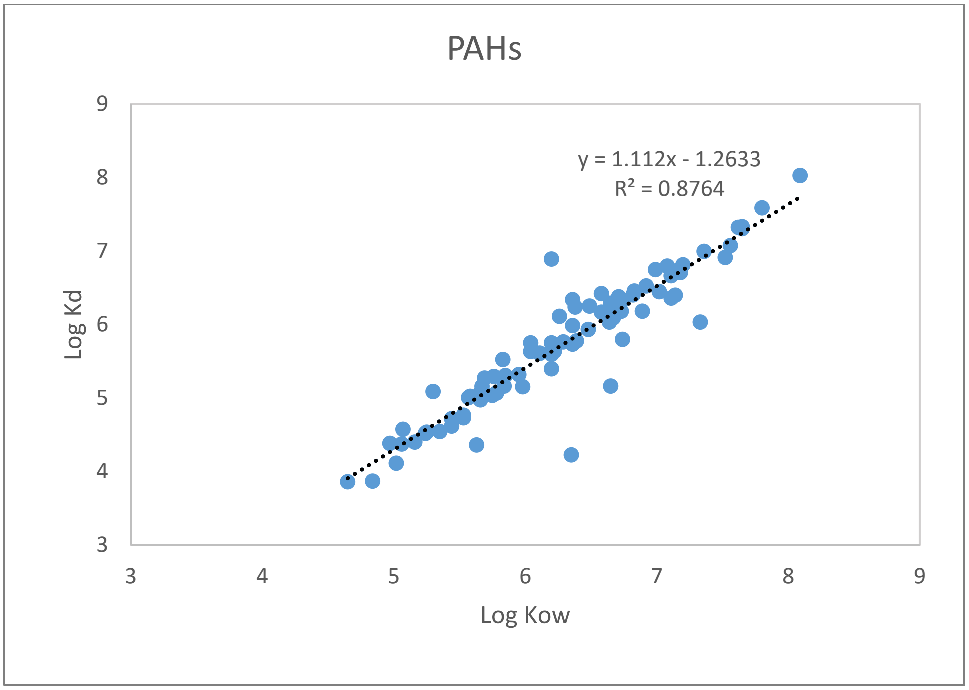
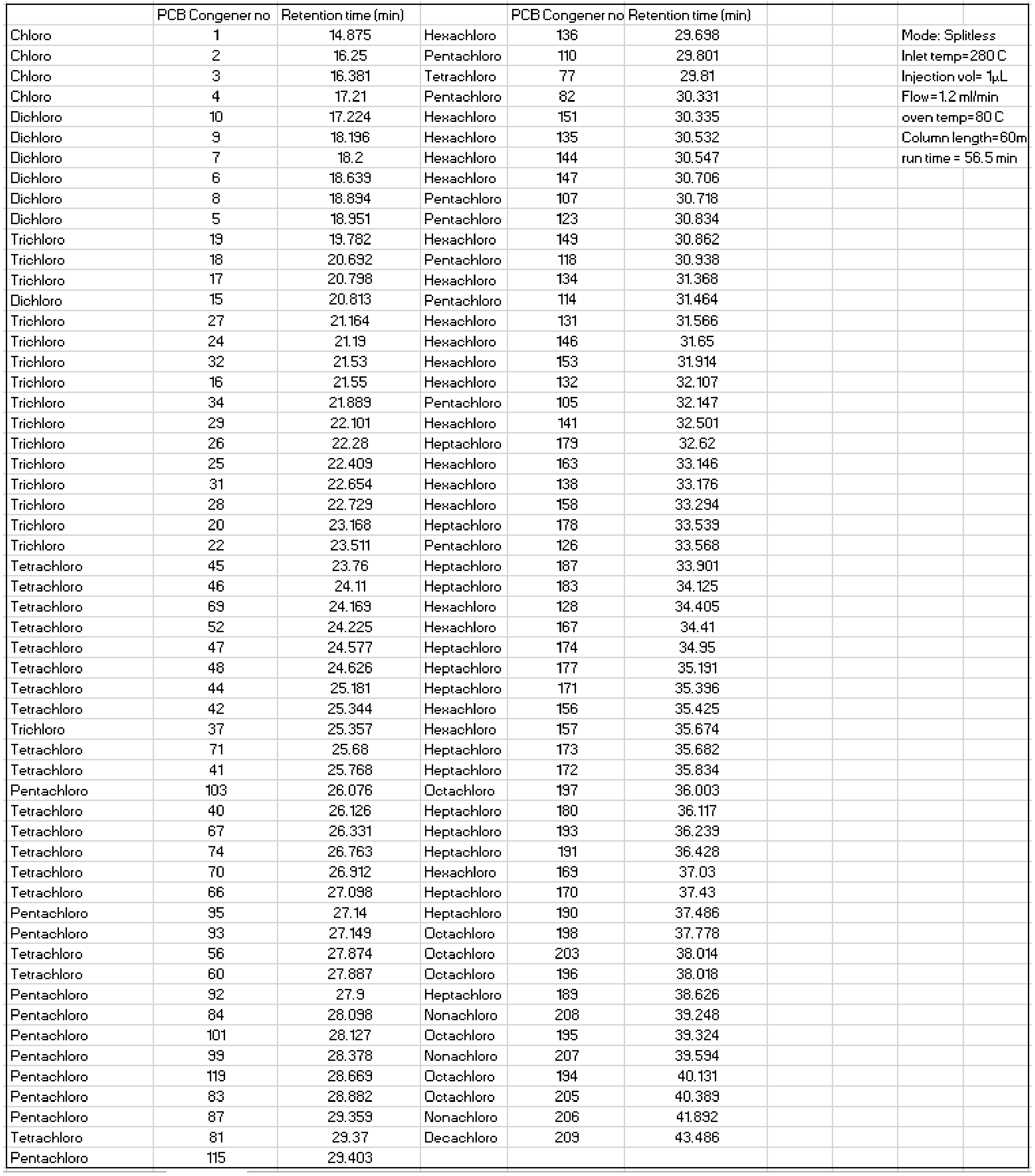


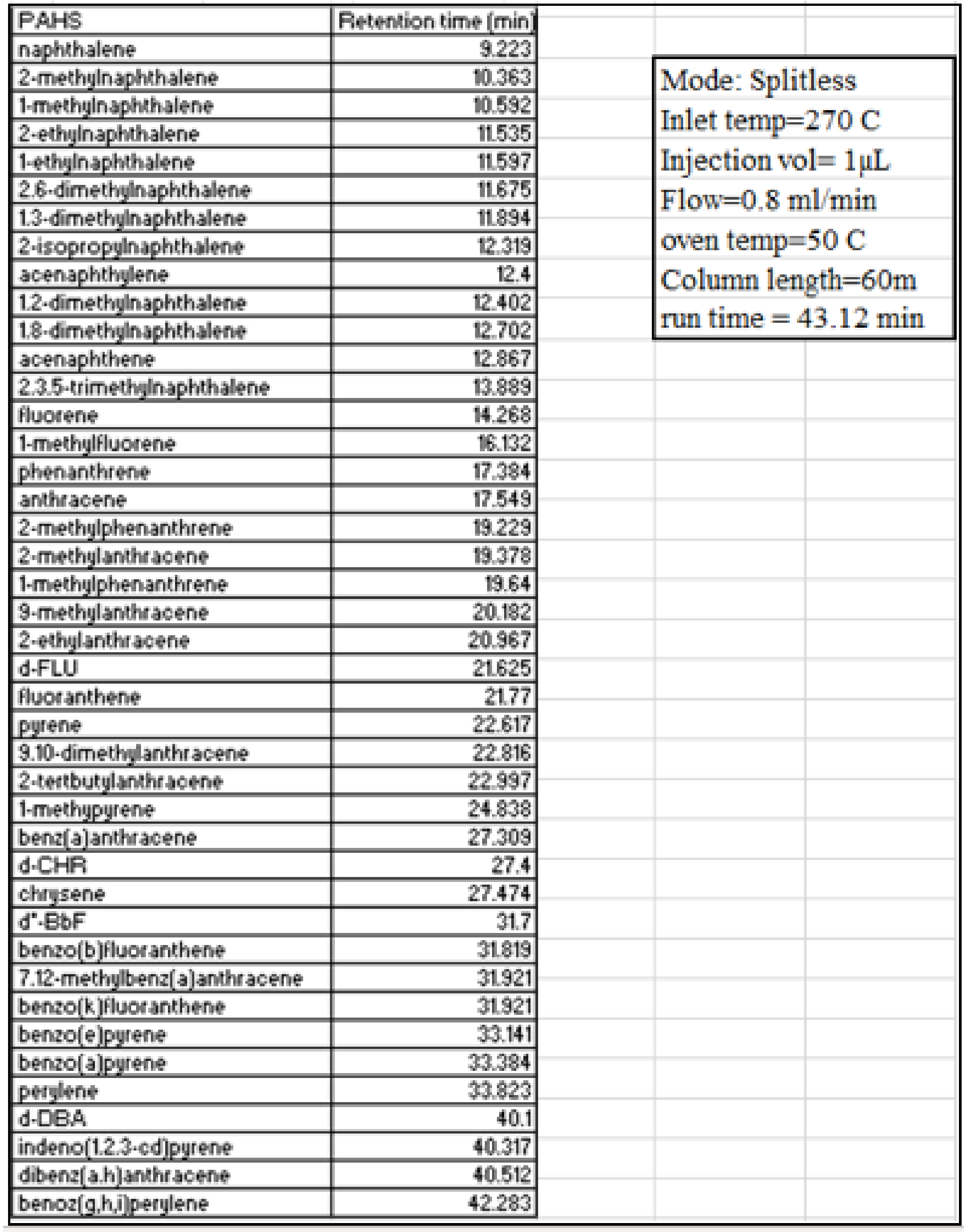
Figure A3. Relationship between log Kd with log Kow for 2018 sampling for PAHs.

Table A1. Individual identified PCB congeners and retention times



	PCB Congener no	Retention time (min)		PCB Congener no	Retention time (min)	
Chloro	1	14.875	Hexachloro	136	29.698	Mode: Splitless
Chloro	2	16.25	Pentachloro	110	29.801	Inlet temp=280 C
Chloro	3	16.381	Tetrachloro	77	29.81	Injection vol= 1µL
Chloro	4	17.21	Pentachloro	82	30.331	Flow=1.2 ml/min
Dichloro	10	17.224	Hexachloro	151	30.335	oven temp=80 C
Dichloro	9	18.196	Hexachloro	135	30.532	Column length=60m
Dichloro	7	18.2	Hexachloro	144	30.547	run time = 56.5 min
Dichloro	6	18.639	Hexachloro	147	30.706	
Dichloro	8	18.894	Pentachloro	107	30.718	
Dichloro	5	18.951	Pentachloro	123	30.834	
Trichloro	19	19.782	Hexachloro	149	30.862	
Trichloro	18	20.692	Pentachloro	118	30.938	
Trichloro	17	20.798	Hexachloro	134	31.368	
Dichloro	15	20.813	Pentachloro	114	31.464	
Trichloro	27	21.164	Hexachloro	131	31.566	
Trichloro	24	21.19	Hexachloro	146	31.65	
Trichloro	32	21.53	Hexachloro	153	31.914	
Trichloro	16	21.55	Hexachloro	132	32.107	
Trichloro	34	21.889	Pentachloro	105	32.147	
Trichloro	29	22.101	Hexachloro	141	32.501	
Trichloro	26	22.28	Heptachloro	179	32.62	
Trichloro	25	22.409	Hexachloro	163	33.146	
Trichloro	31	22.654	Hexachloro	138	33.176	
Trichloro	28	22.729	Hexachloro	158	33.294	
Trichloro	20	23.168	Heptachloro	178	33.539	
Trichloro	22	23.511	Pentachloro	126	33.568	
Tetrachloro	45	23.76	Heptachloro	187	33.901	
Tetrachloro	46	24.11	Heptachloro	183	34.125	
Tetrachloro	69	24.169	Hexachloro	128	34.405	
Tetrachloro	52	24.225	Hexachloro	167	34.41	
Tetrachloro	47	24.577	Heptachloro	174	34.95	
Tetrachloro	48	24.626	Heptachloro	177	35.191	
Tetrachloro	44	25.181	Heptachloro	171	35.396	
Tetrachloro	42	25.344	Hexachloro	156	35.425	
Trichloro	37	25.357	Hexachloro	157	35.674	
Tetrachloro	71	25.68	Heptachloro	173	35.682	
Tetrachloro	41	25.768	Heptachloro	172	35.834	
Pentachloro	103	26.076	Octachloro	197	36.003	
Tetrachloro	40	26.126	Heptachloro	180	36.117	
Tetrachloro	67	26.331	Heptachloro	193	36.239	
Tetrachloro	74	26.763	Heptachloro	191	36.428	
Tetrachloro	70	26.912	Hexachloro	169	37.03	
Tetrachloro	66	27.098	Heptachloro	170	37.43	
Pentachloro	95	27.14	Heptachloro	190	37.486	
Pentachloro	93	27.149	Octachloro	198	37.778	
Tetrachloro	56	27.874	Octachloro	203	38.014	
Tetrachloro	60	27.887	Octachloro	196	38.018	
Pentachloro	92	27.9	Heptachloro	189	38.626	
Pentachloro	84	28.098	Nonachloro	208	39.248	
Pentachloro	101	28.127	Octachloro	195	39.324	
Pentachloro	99	28.378	Nonachloro	207	39.594	
Pentachloro	119	28.669	Octachloro	194	40.131	
Pentachloro	83	28.882	Octachloro	205	40.389	
Pentachloro	87	29.359	Nonachloro	206	41.892	
Tetrachloro	81	29.37	Decachloro	209	43.486	
Pentachloro	115	29.403				

Table A2. Individual Identified PAHs compounds and retention times



PAHS	Retention time (min)
naphthalene	9.223
2-methylnaphthalene	10.363
1-methylnaphthalene	10.592
2-ethylnaphthalene	11.535
1-ethylnaphthalene	11.597
2.6-dimethylnaphthalene	11.675
1.3-dimethylnaphthalene	11.894
2-isopropylnaphthalene	12.319
acenaphthylene	12.4
1.2-dimethylnaphthalene	12.402
1.8-dimethylnaphthalene	12.702
acenaphthene	12.867
2.3.5-trimethylnaphthalene	13.889
fluorene	14.268
1-methylfluorene	16.132
phenanthrene	17.384
anthracene	17.549
2-methylphenanthrene	19.229
2-methylanthracene	19.378
1-methylphenanthrene	19.64
9-methylanthracene	20.182
2-ethylanthracene	20.967
d-FLU	21.625
fluoranthene	21.77
pyrene	22.617
9.10-dimethylanthracene	22.816
2-tertbutylanthracene	22.997
1-methypyrene	24.838
benz(a)anthracene	27.309
d-CHR	27.4
chrysene	27.474
d*-BbF	31.7
benzo(b)fluoranthene	31.819
7.12-methylbenz(a)anthracene	31.921
benzo(k)fluoranthene	31.921
benzo(e)pyrene	33.141
benzo(a)pyrene	33.384
perylene	33.823
d-DBA	40.1
indeno(1.2.3-cd)pyrene	40.317
dibenz(a.h)anthracene	40.512
benoz(g,h,i)perylene	42.283

Mode: Splitless
Inlet temp=270 C
Injection vol= 1µL
Flow=0.8 ml/min
oven temp=50 C
Column length=60m
run time = 43.12 min

Table A3: Summary of sediment properties and contaminant concentrations in the sediment sample

Sediment properties and contaminant concentrations	2017 (n=6)		2018 (n=4)
	West	East	Barge sample
∑16 PAH (mg/kg)	606.71±78.24	93.23±2.82	209.58±32.12
∑118 PCB congeners (mg/kg)	36.02±4.04	12.08±2.43	10.30 ± 4.11
Moisture content (%)	67.27±0.21	72.12±0.82	67.52±0.002
Total organic content (%)	13.14±0.21	8.71±0.33	12.61±0.05
Black carbon (%)	0.86±0.34	0.61±0.1	0.243±0.09

Table A4: Summary of truly dissolved concentration and total suspended solid in water samples

Concentrations	2017		2018
	West	East	Barge sample
C_{PW}*, ∑16 PAH (µg/L)	11.8	0.3	1.85
C_{PW}*, ∑PCB congeners (µg/L)	0.14	0.02	0.05
TSS (mg/L)	131.5 ± 25.8	4.2 ± 1.6	68.70 ± 17.5

Note that C_{PW}* was obtained using PDMS fiber deployed 204x situ in sediment samples.

Appendix B. Additional information on Air Sampling

B1. Initial Study of the uptake and time of equilibration on Polymeric samplers

A laboratory study was conducted to determine the appropriate passive polymeric sampler to be deployed as an air sampler. Two polymeric samplers namely polydimethylsiloxane (PDMS ~ 34 µm) and polyoxymethylene (POM 76 µm) were deployed to the vapor space of an aqueous solution inoculated with naphthalene, phenanthrene and pyrene in a 250 mL amber vessel. Before the exposure study, passive polymers were segmented such that PDMS fiber were cut into dimensions of 5 cm and POM sheet into mass of 20mg ± 0.1 mg, pre-extracted using the hexane, dichloromethane, methanol, and deionized water, respectively.

The sorption and uptake rate of the 3 PAHs (naphthalene, phenanthrene and pyrene) on both PDMS and POM are shown in Figure B1. For PDMS, these PAHs typically reached a peak sorbed concentration within 3 days and then decreased. For POM, the kinetics were slower (e.g. two weeks of exposure was required to attain a maximum concentration for pyrene) and there was no sign of a decreasing sorbed concentration at longer times. The results likely reflect the faster kinetics of uptake on the PDMS and the decreasing concentration over time in the aqueous solutions due to the volatilization and desorption of the PAHs. The decrease in aqueous solution concentration was reflected directly on the PDMS due to its faster kinetics of sorption and desorption. POM was slower to sorb the PAHs but also slow to release the PAHs as the aqueous concentration decreased and thus showed no decrease over the period of the experiment. The result from this experiment, did indicate that subsequent work should focus on POM.

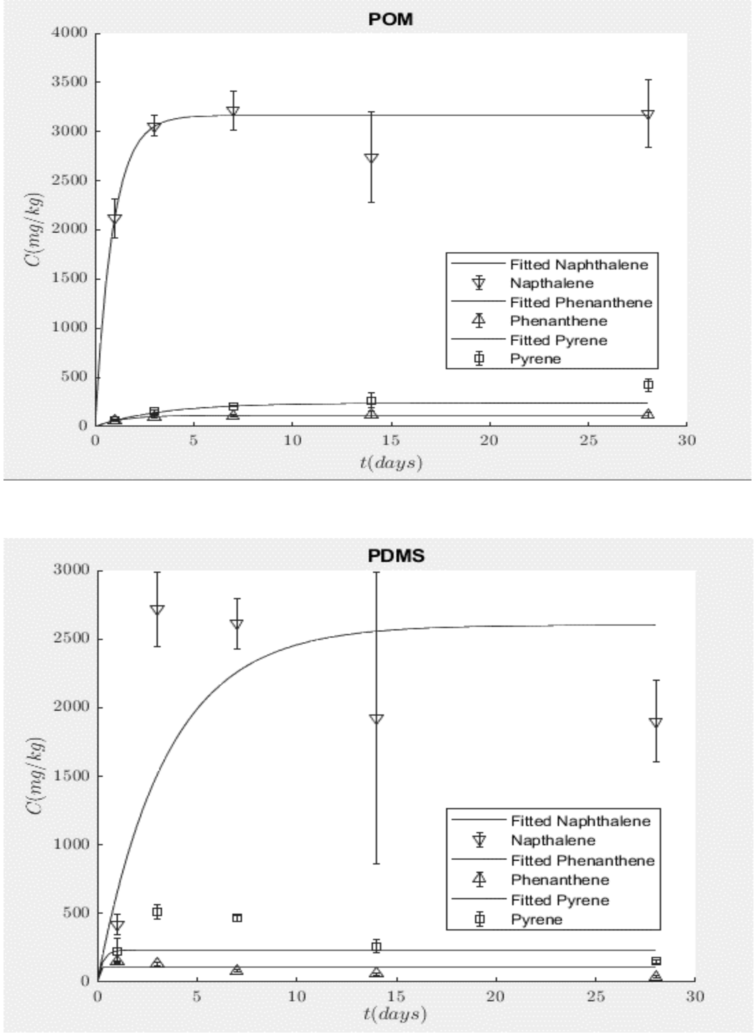


Figure B1. Comparison of uptake and averaging time of PAHs between polyoxymethylene (POM) and polydimethylsiloxane (PDMS). The solid line indicated Fitted 1st order model of the individual PAHs.

B2. Estimated Sample Averaging time for POM for selected compounds

The sample averaging time for POM was applied in the estimating long term HVAS concentration for the purpose of comparison between the two air sampling methods. Table B1 shows the averaging time for individual compounds compared for the three deployment periods.

Table B1. Estimated Sample Averaging time for POM, in days

	Periods		
PCB Congeners	1	2	3
PCB-20/28	42	35	56
PCB-15	42	28	49
PCB-18	42	21	42
PCB-28	42	35	56
PCB-31	42	35	56
PAHs			
Acenaphthene		7	14
Acenaphthylene		7	14
Fluoranthene	42	56	62
Fluorene		7	21
Naphthalene		7	7
Phenanthrene	42	24	56
Pyrene	42	49	62

References

1. Reible, D.D. Fundamental of Environmental Engineering, Lewis Publishers, 1999.