IN SITU STABILIZATION OF PERSISTENT ORGANIC CONTAMINANTS IN MARINE SEDIMENTS (CU-1207)

Final Technical Report
Strategic Environmental Research and Development Program
April, 2004

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Final Technical Report

Fiscal Years 2001, 2002, 2003

IN SITU STABILIZATION OF PERSISTENT ORGANIC CONTAMINANTS IN MARINE SEDIMENTS

(CU1207)

Submitted to:

Strategic Environmental Research and Development Program

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CONTENTS

1. Executive Summary 2
2. Organization of the report 5
3. Background 6
4. Research Objectives and Milestones 6
5. Project Accomplishments 7
6. Response to Action Items 11
7. Transition to the field 12
8. Cost estimate of proposed technology 15
9. Relevant Publications 17
10. Relevant Presentations 18
11. Key Project Staff 20
12. Appendices

Appendix I. PCB and PAH Speciation Among Particle Types in Contaminated Harbor Sediments and Effects on PAH Bioavailability, U. Ghosh, J.R. Zimmerman, R.G. Luthy. *Environ Sci Technol.* 37: 3625-3634, 2003.

Appendix II. Microscale Detection of Polychlorinated Biphenyls Using Two-Step Laser Mass Spectrometry. T.B. Mahajan, U. Ghosh, R.N. Zare, and R.G. Luthy.

Appendix III. Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: Physicochemical Tests. J.R. Zimmerman, U.Ghosh, R.G. Luthy, T.S. Bridges, and R.N. Millward. *Environ Sci Technol.* 38: 5458-5464, 2004.

Appendix IV. Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (Neanthes arenaceodentata) and an Amphipod (Leptocheirus plumulusos) R.N. Millward, T.S. Bridges, U. Ghosh, R.G. Luthy, J.R. Zimmerman. *Environ Sci Technol.* 39: 2880-2887. 2005.

Appendix V. Contaminant Exposure Control in Sediments Using Activated Carbon Adsorbent. R.G. Luthy, J.R. Zimmerman, P.M. McLeod, U. Ghosh, R.N. Millward, T.S. Bridges.

Appendix VI. Model Verification of Thermal Programmed Desorption-Mass Spectrometry for Estimation of Release Energy Values for PAHs on Mineral Sorbents. S.I. Nicholl, J.W. Talley, S. Silliman.

Appendix VII. The Effects of Dose and Particle Size on Activated Carbon Treatment to Sequester PCBs and PAHs in Marine Sediments. J.R. Zimmerman, D. Werner, U. Ghosh, R.N. Millward, T.S. Bridges, R.G. Luthy.

Appendix VIII. An overview of field mixing technologies. U. Ghosh, D. Smithenry, R.G. Luthy.

Appendix IX. Unpublished results: a) PCB desorption kinetics from Hunters Point sediments; b) Kinetics of PCB adsorption into carbon; c) Demonstration of PCB mass transfer from sediment to carbon.

1. EXECUTIVE SUMMARY

Effective management of polychlorinated biphenyls (PCBs) in sediments is challenging and expensive. Hydrophobic organic compounds (HOCs) such as PCBs, PAHs, and DDT associate with fine-grained, organic-rich, sediment material. This serves as a contaminant reservoir in shallow estuarine and coastal regions from which fish and bottom-dwelling organisms accumulate toxic compounds passed up the food chain. However, recent work at Stanford University and elsewhere proposes that the bioavailability of hydrophobic organic contaminants depends on how weakly or strongly they are sorbed to sediment organic matter. We find that black carbon particles in a wide variety of sediments act as strong sorbents, which naturally over time tend to concentrate HOCs and make these compounds less available for organisms. Building on these observations, we have tested a new concept for sediment management based on addition of activated carbon to sediment to repartition hydrophobic organic compounds in the sediment, reducing biological uptake and leaching into the overlying water.

Sediment from the inter-tidal zone of South Basin, Hunters Point Naval Shipyard, San Francisco Bay (cover picture), was used in this research. Sampling took place during low tide along approximately 150 yards of shoreline within the inter-tidal zone as shown in Figure 1. Historic shipyard and industrial activities in the adjacent region discharged PCBs, PAHs, and heavy metals into the soil and sediment. Previous sampling at the site has shown high PCB and PAH concentrations and this site currently is under investigation for remedial action. Sediment characterization was carried out for the bulk material and also for size and density separated fractions. The total PCB concentration was 9.9 ±(0.9) mg/kg with predominantly higher chlorinated congeners and resembling Aroclor 1260 in congener distribution. The concentration of 16 EPA priority pollutant PAHs was 8 mg/kg and the total organic carbon (TOC) was 1.7 mg/kg.

The major effort in this study addresses the feasibility of using a coal-derived sorbent (e.g., coke or granular activated carbon) for in-situ stabilization of persistent organic contaminants such as PCBs and PAHs in marine sediments. PCB contaminated Hunters Point sediment was contacted with different sizes and doses of coke and activated carbon for one and six months (Figure 1). Wet, Hunters Point sediment, equivalent to approximately 3.8 kg dry weight, was placed in one

Figure 1. Picture on the left shows collection of sediment samples form the inter-tidal zone at Hunters Point South Basin. Picture on the right shows the setup for mixing experiments where sediment was contacted with coke or activated carbon sorbent for 1-6 months in 1 gallon glass bottles at 2-3 rpm tumbling speed.

gallon glass roller bottles, followed by addition of sorbent and approximately 300 mL of 17 ppt seawater. The glass bottles containing sediment and carbon were rolled at 2-3 rpm. At the end of a contact experiment, the treated and control sediments were harvested for physicochemical, and biological tests for contaminant availability.

Sediment characterization by size and density fraction revealed that the heavier density (>1.8 s.g.) mineral fraction of the sediment comprising sand/silt/clays contributed to 94% of the sediment mass but only 32% of the total PCBs and 11% of the total PAHs. In comparison, the lighter density organic fraction comprising coal/charcoal/coke/wood comprised only 6% of the sediment mass but contained 68% of the PCBs and 89% of the PAHs. This study is the first documented case showing that PCBs are concentrated on the light fraction of sediment solids. Because there is no reason to suspect co-disposal of PCBs and materials that comprise the light density sediment fractions, it appears that over an extended period of time in the field, PCBs slowly transfer onto strongly sorbing carbonaceous particles present in the sediment through a natural sequestration process.

Results from three biological and three physicochemical tests show that PCB availability is reduced significantly when contaminated sediments are treated with activated carbon and mixed for one month. Aqueous equilibrium PCB concentrations were reduced by 86% for GAC-treated sediment relative to untreated. Total PCBs released to semi-permeable membrane devices decreased by 72% for GAC-treated sediment. Treating sediment with activated carbon reduced PCB bioaccumulation by 69% in *Macoma balthica* (clam). As shown in Figure 3 the percent reduction in PCB uptake varied with PCB chlorination level and ranged from 83% for the pentachlorobiphenyls to 47% for the octachlorobiphenyls. The parallel test with coke amendment showed that the addition of coke had no significant impact on PCB bioaccumulation. Similar reductions in PCB bioaccumulation with activated carbon were observed in two other benthic organisms: 83% in *Neanthes arenaceodentata* (worm), and 72% in *Leptocheirus plumulosus* (amphipod). We conclude from these results that addition of activated carbon to PCB contaminated sediment is an effective in-situ stabilization method to reduce contaminant availability to biota and surrounding water. Thus, the application of fresh, high adsorption

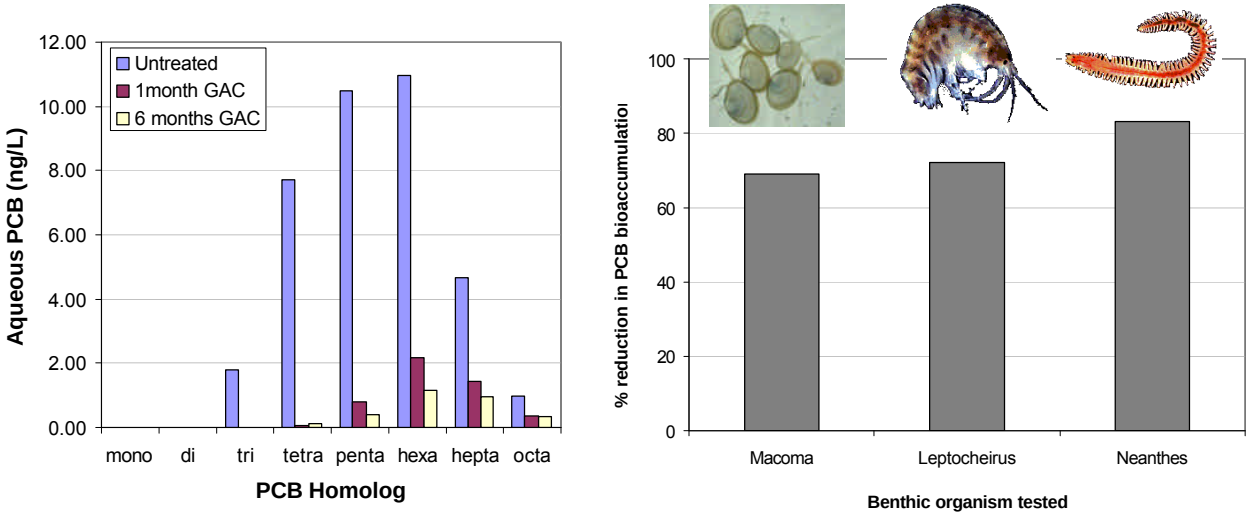

Figure 2. Figure on the left shows reduction of equilibrium aqueous concentrations by PCB homolog after treatment of Hunters Point sediment with activated carbon for 1 month and 6 months. Figure on the right shows reduction of total PCB accumulation in three benthic organisms.

affinity and high surface area activated carbon to sediments in the field will result in the repartitioning of hydrophobic contaminants from the available sediment components to the applied sorbent phase where the contaminants become much less bioavailable due to the strong binding.

We tested the effect of dose on reducing the chemical availability of PCBs and PAHs and the bioavailability of PCBs by contacting sediment with GAC at concentrations of 0.34%, 1.7% and 3.4%, dry mass basis. Our results showed that increasing carbon dose increases the effectiveness of carbon treatment. Adding 3.4% carbon was more effective than adding 1.7%, thus showing that we have likely not reached the optimal dose. A separate experiment using GAC crushed to smaller size (< 75µm) showed that smaller particle diameter GAC was significantly more effective (98% reduction) at reducing aqueous equilibrium concentrations than uncrushed (75–300 µm) (92% reduction).

Coke decreased PAH aqueous equilibrium concentrations by 38-64% depending on coke dose and particle size. Adding coke had a negligible effect on reducing PCB bioaccumulation in benthic organisms, probably due to slow kinetics of PCB diffusion into the particles. The greater effectiveness of GAC compared to coke is attributed to a much greater available surface area and internal porosity, and the ability to bind organic contaminants such as PCBs and PAHs. Results from the physicochemical tests suggest that adding GAC to contaminated field sediment reduces HOC availability to the aqueous phase. The benefit is manifested relatively quickly under optimum contact conditions and improves in effectiveness with contact time.

These results point to a new concept for sediment management based on addition of material like activated carbon to sediment and in situ active treatment to reduce the bioavailability of persistent, hydrophobic organic contaminants. The efficiency of the technology will depend on carbon sorbent type, the effects of different carbon dosages, contact times with sediment, and carbon particle sizes. Prior in situ sediment stabilization efforts include capping with clean sand or geofabric. Problems with these approaches include the long-term efficiency and maintenance of cap integrity during high flow or storm events, physical alteration of indigenous habitat, disruption by organisms that burrow into the caps, and the permanence of the treatment effectiveness. Our approach overcomes these limitations by applying inexpensive and non-toxic coal-derived materials as a sorbent, in combination with in-depth, fundamental investigation of the physicochemical processes involved in the treatment. We anticipate that the addition of granular activated carbon to contaminated sediment is a potentially cost-effective, in situ stabilization technology. A sediment quality criteria for the cleanup of Hunters Point South Basin has not been determined, and therefore actual cost figures for a remedial action is not available. For the purpose of cost comparison in this research we used the effects range median (ER-M) value of close to 200 ppb from the Draft Validation Study Report for Hunters Point. We estimate the cost of in-situ remediation with carbon for a mid-range PCB concentration footprint at Hunters Point South Basin (200 -1000 ppb PCB concentration) to be $ 3.9 million using fresh GAC, and $2.7 million using regenerated carbon. These costs are much smaller than an estimated cost of tens of millions to remove the contaminated sediments in the region, process the sediment, and dispose it in a landfill. Thus, significant cost savings are expected using the proposed in-situ treatment compared to traditional dredging and disposal of sediments.

We have identified several vendors with equipment that can be used to deploy and mix carbon into sediments in the field scale. These equipments are: underwater rototillers used to remove aquatic weeds, and injection systems used traditionally for sediment solidification with cement mortar. Because these equipments are readily available and designed to work in soft sediments, there is little equipment development work required for taking this technology from the bench scale to the pilot scale. Thus, this project is ready for transition into the field through a demonstration project at the pilot scale to test the efficiency of mixing carbon in the field and the effectiveness of activated carbon in reducing PCB bioavailability in the field environment.

2. ORGANIZATION OF THIS REPORT.

This final report is organized into an executive summary followed by an outline of the background and research objectives and milestones of the project. This is followed by a summary of project accomplishments and response to action items. This project has developed a novel remediation approach for PCB-impacted sediments and demonstrated the feasibility at the laboratory-scale. The efforts taken to transition the technology to the field is described in Section 7 and estimated cost of the technology for a field application is provided in Section 8. A list of peer-reviewed papers derived from this research project is presented in Section 9 and a list of technical presentations made is presented in Section 10. Key project staff who made this research possible are presented in Section 11. The research outcomes from the multidisciplinary research team in this project were written up as detailed technical reports that were eventually submitted for publication in peer-reviewed journals. The detailed research reports are presented in Appendices I through IX. We have obtained permission from the American Chemical Society to incorporate the papers published in Environmental Science and Technology into this report.

3. BACKGROUND.

The Department of Defense (DoD) has undertaken the task of cleaning up waste sites resulting from numerous industrial, commercial, training, and weapons testing activities as well as cleaning up and closing military bases for property transfer. The estimated cost of completing the remaining remediation work is over $28 billion [EPA, 1997]. A number of these sites involve contaminated sediments.

Hydrophobic organic compounds such as PAHs and PCBs are important contaminants of concern to the DoD. These contaminants associate with fine grained, organic-rich material in sediment, and are long-lived. Sediment serves as a contaminant reservoir from which fish and bottom-dwelling organisms can accumulate toxic compounds like PCBs that are passed up the food chain. Thus cost-effective and efficient technologies for contaminated sediment management can significantly reduce the defense expenditure on environmental restoration and achieve the DoD environmental security goals and objectives. Of special interest are non-removal, in situ technologies that are aimed at contaminant stabilization. Such in situ technologies are attractive due to their less intrusive nature and significant cost-effectiveness.

Innovative engineering solutions to the problem of persistent organic contaminants in aquatic food webs requires rethinking of the existing remediation paradigm of ``dredge-and-landfill." Our recent discoveries of contaminant sorption and association with highly sorbing natural particles in sediments are opening up new opportunities for revolutionary in situ management strategies. New initiatives by the EPA on incorporating site-specific bioavailability factors in sediment restoration decisions makes innovative, in situ technologies aimed at reducing the biological availability of contaminants in sediments especially attractive. In our current work we are beginning to address this challenge by bringing together researchers from diverse fields to assess benthic biogeochemical processes and biota feeding and contaminant exposure. We are applying this mechanistic knowledge to assess a novel sediment management strategy. We propose that the addition of a low cost sorbent like granular activated carbon (GAC) to sediments may be a cost-effective, in situ management strategy by sorbing organic contaminants and thereby reducing bioavailability and bioaccumulation. Such a management strategy is especially attractive for large areas of low level PCB concentrations. Our management strategy requires mechanistic understanding of linked physical and biological processes and using such information in conceptual and quantitative models to understand the efficacy of the in situ stabilization process.

4. RESEARCH OBJECTIVES AND MILESTONES

This research extends and applies the scientific foundations developed in an award-winning SERDP project by the principal investigators and carries the work forward to the development of a novel and cost effective in-situ containment/stabilization technology for the management of PCB and PAH contaminated marine/estuarine sediments. This work extends to marine sediments and PCBs new research methods on the characterization of PAHs, their association with sediment particles, and their aqueous and biological availability. These techniques are applied to assess in situ stabilization of PCBs and PAHs through the use of low-cost, coal-derived material like coke and activated carbon to sequester persistent organic contaminants. Marine sediments from a Navy site were chosen for laboratory testing and demonstration of

proof of concept for the technology. The major milestones accomplished in the three years of this project are listed below.

Milestones	**Responsible Organization**	**Deadline**
1. Obtain marine sediment samples from a DoD site contaminated with PAHs and PCBs.	Stanford	1/01 Completed
2. Select and obtain samples of coal-derived sorbents to be tested.	Stanford	5/01 Completed
3. Screening tests on toxicity of proposed sorbent materials before and after addition to sediment. (**Go/No-Go**)	WES	9/01 Completed
4. Investigate PAH and PCB distribution among sediment particle types using subparticle scale analytic techniques and bulk separation and analysis.	Stanford	9/01 Completed
5. Develop TPD test protocols for PCBs and perform screening tests with field sediment samples.	WES	9/01 Completed
6. Conduct desorption kinetic studies and estimate aqueous availability of PAHs and PCBs from sediment particle types.	Stanford	9/02 Completed
7. Set up short-term and long-term equilibration tests for assessing the effect of sorbent contact time for bioassay tests; conduct bioaccumulation tests.	WES	9/02 Completed
8. Investigate the phase transfer of PAHs and PCBs from sediment to coal-derived sorbent material. (**Go/No-Go**)	Stanford	9/02 Completed
9. Conduct thermal program desorption tests with separated particles from Hunters Point sediment, and coke particles.	Notre Dame	12/02 Completed
10. Contaminant phase transfer and decrease in availability	Stanford/ UMBC	12/2003 Completed
11. Cost estimate of proposed technology	Stanford/ UMBC	12/2003 Completed
12. Assimilation and technical reports	Stanford UMBC WES Notre Dame	3/2004 Completed

5. PROJECT ACCOMPLISHMENTS:

All project milestones for fiscal years 2001, 2002, and 2003 have been accomplished. The research results are presented as journal articles that have either been submitted for publication or are in working draft forms. The major findings of the research have been outlined in the executive summary. The summaries of the submitted and published journal articles that present the detailed technical outcome of this research are presented in this section. The full papers are presented in the appendices.

1. PCB and PAH Speciation Among Particle Types in Contaminated Harbor Sediments and Effects on PAH Bioavailability. This research provides particle scale understanding of PCB and PAH distribution in sediments obtained from three urban locations in the United States: Hunters Point, CA; Milwaukee Harbor, WI; and Harbor Point, NY. The sediments comprised mineral grains (primarily sand, silt, and clays) and carbonaceous particles (primarily coal, coke, charcoal, pitch, cenospheres, and wood). The carbonaceous sediment fractions were separated from the mineral fractions based on their lower density and were identified by petrographic analysis. In all three sediments carbonaceous particles contributed 5-7% of the total mass and 60-90% of the PCBs and PAHs. The production of carbonaceous particles is not known to be associated with PCB contamination, and it is very unlikely that these particles can be the source of PCBs in the environment. Thus, it appears that carbonaceous particles preferentially accumulate PCBs acting as sorbents in the aqueous environment if PCBs are released directly to the sediment or if deposited as airborne soot particles. Aerobic bioslurry treatment resulted in negligible PAH loss from the carbonaceous coal-derived material in Milwaukee Harbor sediment, but resulted in 80% of the PAHs being removed from carbonaceous particles in Harbor Point sediment. Microscale PAH extraction and analysis revealed that PAHs in Harbor Point sediment were associated mainly with coal tar pitch residue. PAHs present in semi-solid coal tar pitch are more bioavailable than PAHs sorbed on carbonaceous particles such as coal, coke, charcoal, and cenosphere. Results of this study illustrate the importance of understanding particle-scale association of hydrophobic organic contaminants for explaining bioavailability differences among sediments.

2. Microscale Detection of Polychlorinated Biphenyls Using Two-Step Laser Mass Spectrometry. Microprobe two-step laser desorption/laser ionization mass spectrometry (μL^2MS) is used as a new analytical technique for the detection of polychlorinated biphenyls (PCBs). Three standard Aroclor solutions (Aroclor 1232, 1242, and 1262) and three samples of activated carbon spiked with Aroclor 1242 are examined. All the PCBs present in the Aroclor solutions are clearly identified using μL^2MS. The distribution of the peaks follows the relative natural abundances of the carbon and chlorine isotopes. μL^2MS analyses of the spiked particles of activated carbon reveal the presence of PCBs and an abundance of polycyclic aromatic hydrocarbons. The detection limit for PCBs on solid surfaces is determined to be between 1 and 10 ppm. Because the spatial resolution of the μL^2MS instrument varies between 10 and 40 microns, PCB information at the sub-particle scale can be obtained.

3. Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: Physicochemical Tests. The addition of carbon sorbents, i.e., coke and granular activated carbon (GAC), to marine sediments is evaluated as an in situ treatment method to reduce the chemical and biological availability of hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). In this first of a two part series, we report results from physicochemical experiments that assess this concept. PCB- and PAH-contaminated sediment from Hunters Point Naval Shipyard, San Francisco Bay, CA, was contacted with coke and GAC (3.4% by weight) in roller bottles for periods of one and six months. At the end of the contact periods, the sediment was divided for use in physicochemical and biological studies. Sediment treated with GAC showed reductions in aqueous equilibrium PCB and PAH concentrations up to 92% and 80%, respectively, compared to untreated sediment. Treating with GAC reduced PCB and PAH uptake by semi-permeable

membrane devices (SPMD) up to 77% and 83%, respectively. Treating with GAC reduced PCB flux to overlying sediment in quiescent systems up to 89%. Adding coke to contaminated sediment decreased aqueous equilibrium PAH concentrations by 38-64% depending on coke doses and particle sizes. In most other experiments, adding coke did not significantly reduce PCB and PAH availability as measured by these flux or SPMD physicochemical tests. The greater effectiveness of GAC compared to coke is attributed to its greater available surface area and ability to bind organic contaminants such as PCBs and PAHs. Results from the physicochemical tests in this work and from the biological studies described in part 2 suggest that adding a carbon sorbent such as GAC to sediment can reduce HOC availability to the aqueous phase and to biota, thus making it a potentially effective method for in situ treatment of marine sediment contaminated with HOCs.

4. Addition of Granular Activated Carbon (GAC) and Coke to Reduce PCB Bioavailability in Sediments: Bioaccumulation and Toxicity Tests. This work compares the effects of adding coke and granular activated carbon (GAC) on the bioavailability of polychlorinated biphenyls (PCBs) in contaminated sediment. We show that GAC reduces PCB bioaccumulation by a polychaete and amphipod, and PCB concentrations in sediment pore water, by nearly one order of magnitude. Adding coke had a negligible effect on reducing PCB bioaccumulation, probably due to slow kinetics of PCB diffusion into the particles. Regression analyses revealed that reductions in dissolved PCB concentrations in both the pore water and digestive fluids in the presence of GAC correspond to reductions in bioaccumulation. However, the effects of these carbon sources on bioaccumulation were not predicted by the BSAF model, which over-predicted the efficacy of coke and under-predicted the efficacy of GAC. Reductions in congener bioaccumulation were inversely related to congener Kow, suggesting that the efficacy of GAC is controlled by the rate and extent that HOCs are released from sediment into the aqueous phase and/or taken up by GAC. While no acute toxic effects of GAC addition were observed, growth rates were reduced by GAC for the polychaete but not for the amphipod. The study demonstrates that GAC can reduce the surfactancy of polychaete digestive fluids, and suggest that growth impairment might be a result of the strong organic sorptive properties of GAC limiting nutrient availability to the GAC-ingesting polychaete. The study concludes that GAC treatment warrants consideration as an in situ technique for reducing bioavailability of sediment-associated HOCs.

5. Contaminant Exposure Control in Sediments Using Activated Carbon Adsorbent. Innovative engineering solutions to the problem of persistent organic contaminants in aquatic food webs requires rethinking of the existing remediation paradigm of “dredge-and-landfill.” In this research we propose that the addition of a low cost sorbent like granular activated carbon (GAC) to sediments may be a cost-effective, in-situ management strategy by sorbing organic contaminants and thereby reducing bioavailability and bioaccumulation. We used three different physicochemical tests to determine the effectiveness of adding carbon sorbents to sediment to reduce contaminant availability to the aqueous phase. These were aqueous equilibrium PCB and PAH concentration, uptake of PCBs and PAHs by semi-permeable membrane devices (SPMDs), and PCB flux from sediment under quiescent conditions. Adding granular activated carbon (GAC) to sediment significantly reduced PCB and PAH availability to the aqueous phase in all three types of physicochemical tests. To measure the effectiveness of activated carbon in lowering aqueous phase concentrations, we measured equilibrium aqueous PAH concentrations for untreated sediment and sediment treated with activated carbon and contacted for six months.

Reductions in PAH aqueous equilibrium concentrations were 83% for phenanthrene, 94% for fluoranthene, and 88% for pyrene. The other two physicochemical tests gave similar results in reduction of PAH abvailability. Thus, PAH availability in the aqueous phase in contact with sediment or sediment pore water is reduced significantly after contact with activated carbon. The effectiveness of GAC was increased by increasing carbon dose and decreasing carbon particle size.

6. Model Verification of Thermal Programmed Desorption-Mass Spectrometry for Estimation of Release Energy Values for PAHs on Mineral Sorbents. The physical availability of organic compounds in soil and sediment strongly influences their bioavailability and toxicity. Previous work has indicated that physical availability changes throughout the processes of aging and treatment and that it can be linked to the energy required to release the compound from its sorbent matrix, with a higher energy indicating a more tightly bound compound. This study focused on determining release energy values for various mineral geosorbents (glass beads, sand and kaolin) contaminated with a 16 PAH mixture. The sorbents were analyzed using Thermal Program Desorption/Mass Spectrometry (TPD/MS) and the release energy values were calculated from the resulting thermograms utilizing a non-linear fit of the analytical solution to a simplified version of the Polanyi-Wigner equation. This solution method resulted in a series of combinations of values for the pre-exponential factor and release energy (E) that produced desorption rate curves with similar errors when fit to actual data sets. These combinations can be viewed as an error surface, which clearly shows a valley of minimum error values spanning the range of both E and the pre-exponential factor, indicating that this method may not provide a unique set of E and pre-exponential factorvalues and suggesting that the simplified version of the Polanyi-Wigner equation cannot be used to determine release energy based on TPD data alone.

7. The Effects of Dose and Particle Size on Activated Carbon Treatment to Sequester PCBs and PAHs in Marine Sediments. Recent laboratory studies show that mixing activated carbon with contaminated sediment reduces the chemical and biological availability of hydrophobic organic contaminants. In this study we test the effects of varying the activated carbon dose and particle size in reducing the aqueous availability of polychlorinated biphenyls (PCBs) and polycylic aromatic hydrocarbons (PAHs) and the uptake of PCBs by two benthic organisms. We mixed PCB- and PAH-contaminated sediment from Hunters Point Naval Shipyard San Francisco Bay, CA, USA,for one month with activated carbon, at doses of 0.34%, 1.7% and 3.4%, dry mass basis. We found that increasing the carbon dose increased the effectiveness in reducing PCB bioaccumulation. In 56-d uptake tests with the benthic organisms Neanthes arenaceodentata and Leptocheirus plumulosus PCB bioaccumulation was reduced by 93% and 90%, respectively, with 3.4% carbon. Increasing the dose also increased the effectiveness in reducing PCB and PAH aqueous concentrations and uptake by semi-permeable membrane devices and quiescent flux of PCBs to overlying water. Decreasing activated carbon particle size increased treatment effectiveness in reducing PCB aqueous concentration, while larger-sized activated carbon (400–1700~μm) was ineffective with a contact period of one month. We invoke a numerical model based on intraparticle diffusion in sediment and activated carbon particles to help interpret our experimental results. This model was useful in explaining the trends for the effect of activated carbon dose and particle size on PCB aqueous concentrations in well-mixed systems.

6. RESPONSE TO ACTION ITEM:

"In the Final Report, please include discussions of whether an order of magnitude in bioavailability reduction has the potential to affect risk assessment efforts at field sites (e.g., Hunters Point), initial thoughts on means to determine when sufficient carbon has been added, and economics of using activated carbon as opposed to coke or charcoal."

Effect on site risk assessment: The PCB concentration contour map of Hunters Point South Basin prepared by Battelle is reproduced in Figure 3. A final sediment quality criteria for the protection of benthic organisms and water quality has not been established for this site. For the purpose of illustration, we use the effects range–median (ER-M) value of 180 ppb for total PCBs from the Draft Validation Study Report for Hunters Point. The footprint shown in green and light yellow (200 – 1000 ppb), is a relatively low PCB concentration area occupying a large portion of the South Basin. Application of activated carbon to this concentration range footprint for example (with a overall PCB bioavailability and aqueous availability reduction by a factor of 5) will result in lowering the PCB risk for this entire area to that of untreated sediments with a total PCB concentration of less than 200 ppb. Thus, for risk calculations based on exposure through the water pathway or through feeding on benthic organisms, this 200 – 1000 ppb sediment footprint, after amending with carbon, could be considered similar to untreated sediments that have a PCB concentration of 200 ppb or less. New initiatives by the EPA on incorporating site-specific bioavailability factors in sediment restoration decisions makes such innovative, in situ technologies aimed at reducing the biological availability of contaminants in sediments especially attractive.

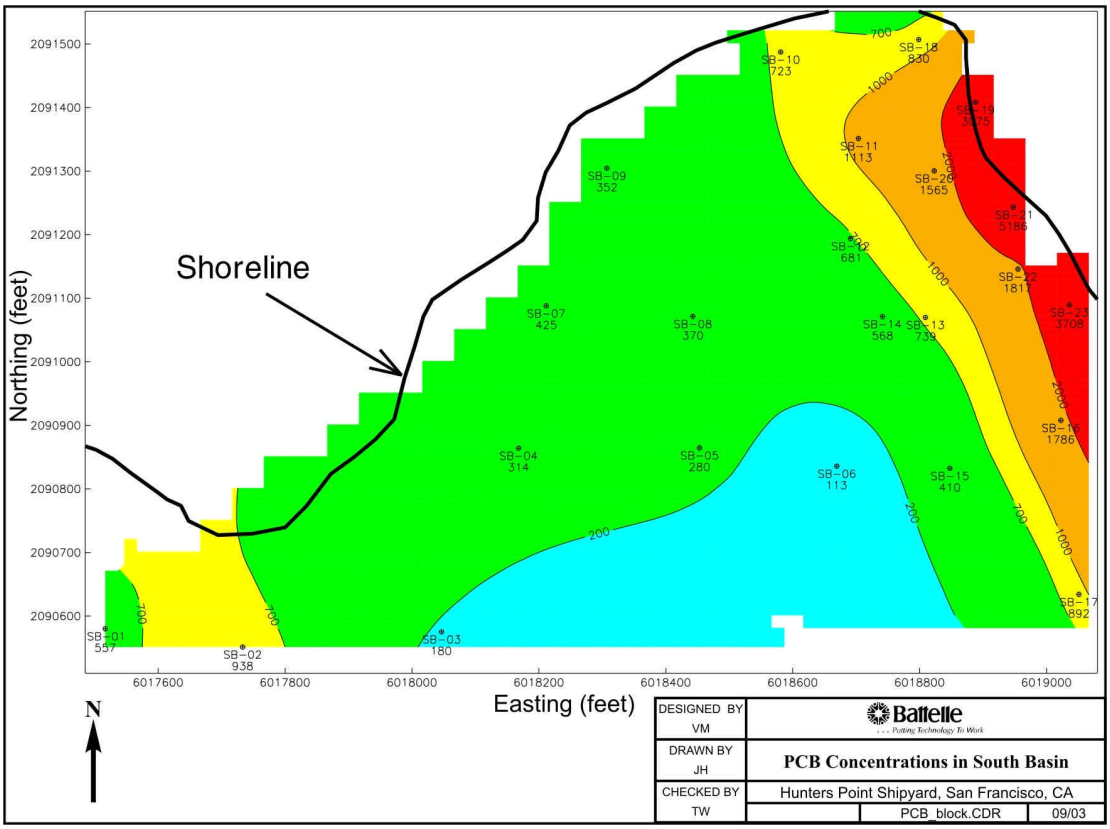

Figure 3. PCB contour map of Hunters Point South Basin, prepared by Battelle.

Means to determine when sufficient carbon has been added: The required dose of carbon for any potential sediment site will have to be assessed through a bench-scale treatability study. Based on our work comparing the effects of carbon addition on three physicochemical tests and three benthic organism bioaccumulation tests, we think a quick assessment of PCB bioavailability reduction is possible through the physicochemical tests. We suggest using the aqueous equilibrium or SPMD measurement for a relatively inexpensive test to monitor changes in PCB bioavailability reduction. Bioaccumulation tests with native organisms will provide the most robust measurement of bioavailability reduction, but these tests are expensive. We also think, that a workable carbon dose for most sediments could be in the range of 0.5x – 2x the total organic carbon present in the sediments.

Economics of coke or charcoal: Our results with Hunters Point sediment showed no change in PCB bioaccumulation in benthic organisms with even as high as 8.5% by weight of coke. We therefore think that coke may not have the necessary sorption capacity to bring about a observable bioavailability reduction especially in the presence of a multitude of other organic compounds in natural sediments. Charcoal may work better than coke, but being very light, and having a tendency to float in water, may cause major resuspension problems. Thus, we have ruled out the use of coke or charcoal for sediment amendment for bioavailability reduction.

7. TRANSITION TO THE FIELD

Work in the last six months of the project has involved identification of field equipment capable of adding carbon to sediments and achieving good mixing of the carbon into the sediments. Several technologies have been identified and are presented in Appendix VII. We have also discussed with contractors the feasibility of performing carbon application in the field. Several of the contractors have expressed their readiness to test equipment in the field through a pilot-scale project. We are presenting a field demonstration project proposal to ESTCP for the 2005 fiscal year competition to transition this technology to the field. The principal focus of the proposed ESTCP project is to demonstrate whether the beneficial results found in the laboratory are observed in the field. The proposed project involves application of granular activated carbon sorbent to contaminated sediment in marked plots using three different technologies by vendors followed by periodic sampling to assess the efficacy of the stabilization process in terms of reducing exposure to biota and to the aqueous phase. Additional work will evaluate particle movement and the maintenance of the integrity of the applied sorbent in the sediment. The field tests are proposed within the tidal flat region of South Basin, in the north/northwest portion of the cove away from possible impacts of any potential on-going PCB releases on the southeast side of the cove. The field work will emphasize PCBs because these are the principal organic contaminants of concern at this site.

We have discussed our technology application in the field with regulators from the SF Bay Regional Water Quality Control Board, and EPA region 9. The response has been very positive with interest in seeing a field demonstration of bioavailability reduction. We also have strong support for technology demonstration from the Navy projects managers for Hunters Point. We are working with the Southwest Division Naval Facilities Engineering Command, San Diego, and their on-site contractor, Battelle, to design a preliminary test of a mixing technology to incorporate GAC into Hunters Point sediment.

Technical Approach and Methodologies. There are three goals of our proposed preliminary field test.

Goal 1) Perform a trial run of GAC application using a contractor's large-scale mixing device and develop protocol for assessing how well the GAC is mixed into the sediment in terms of homogeneity and depth. We have identified a contractor, Aquatic Environments, Inc., with equipment that can be used to deploy and mix carbon into sediments in the field scale. This contractor has a barge-like machine with a rotovator attachment that is typically used to disrupt weed growth in marshy areas. In the preliminary field test, the Aquamog, shown in Figure 4, will be deployed on the water during high tide and allowed to settle onto the sediment surface at low tide. Two types of GAC applications will then be tried. In the first application, GAC will be spread onto the surface of the sediments via a backpack spreader (larger scale options exist) located on the Aquamog and then the rotovator arm will mix the GAC into the sediments. The depth of the mixing can be controlled by the speed and downward pressure of the rotovator. In the second application, carbon will be applied in a one-step process where GAC is sprayed (via a device designed by Aquatic Environments, Inc.) onto the rotovator as it mixes.

To develop a protocol that assesses the depth and homogeneity of the mixed GAC in the sediment, five spatially distributed one-inch diameter sediment core samples in each plot will be taken *before* and *after* GAC treatment to evaluate the degree of carbon mixing with depth. For well-mixed sediment we expect an average total organic carbon (TOC) of 5.1 wt.% (original sediment TOC = 1.7 wt.%) with a small standard deviation among samples within a plot. Since the added GAC and the organic carbon already in the sediment should have different ^{13}C signatures, isotopic analyses on the same core cross sections will also be performed to corroborate the TOC data.

Figure 4. "Aquamog" with rotovator arm.

Goal 2) Validate field sampling techniques that assess aqueous PCB availability and PCB bioaccumulation. These field results will be compared with those obtained from previous lab experiments.

a) PCB bioaccumulation in sediment-dwelling organisms. We will measure PCB bioaccumulation using particle-feeding *Macoma* clams native to San Francisco Bay. These benthic organisms will be placed in mesh-covered containers sunk into the three plots before and after GAC treatment.
b) Assessment of in situ stabilization using physicochemical tests of PCB availability. A combination of field and laboratory physicochemical tests will evaluate the effect of GAC

addition on changes in chemical availability of PCBs in sediment. Semi-permeable membrane devices (SPMDs) will be deployed in the sediment before and after GAC treatment to evaluate the in situ availability of PCBs to biota. A portion of the sediment from the one-inch core samples will be brought to the laboratory and tested for aqueous equilibrium concentration of PCBs.

Goal 3) Validate field sampling techniques for the collection of tidal water and measurement of dissolved and particulate PCBs before and after carbon treatment. A possible concern during sediment treatment with GAC is the mobilization of sediment-bound PCBs due to sediment mixing and resuspension. The purpose of this work is to validate the use of a field sampling technique to monitor changes in water column PCB concentrations during sediment remediation using GAC.

8. COST ESTIMATE OF PROPOSED TECHNOLOGY

Many DoD facilities across the country are challenged with management of sediments contaminated with persistent organic contaminants such as PCBs, PAHs, and DDT. This work addresses the DoD need for cost effective, in-situ remediation technologies for persistent organic contaminants in sediments. The development of this technology for contaminated sediment management offers the potential to significantly reduce expenditures on environmental restoration, as well as gain acceptance by regulators and communities since it does not involve dredging and habitat destruction. The technology may be more acceptable to regulators and other stakeholders than processes that rely on removal and disposal or ex-situ treatment such as incineration.

A study by Battelle showed that a mid-range PCB concentration footprint (0.25 – 1.0 mg/kg) in the South Basin may cover an area of about 90,000 m^2 (Figure 10-14, Hunters Point Validation Study by Battelle). The highest concentration of PCBs in this region was found at 0-4 ft depth. A final sediment quality criteria for the protection of benthic organisms and water quality has not been established for this site. For the purpose of cost comparisons, if we assume that the remediation goal for PCBs is 200 ppb in the sediment, this mid-range PCB footprint area (200 – 1000 ppb) to a depth of 4 ft may need to be removed from the site and disposed in a landfill. The cost of such a removal action may be in the range of several tens of millions of dollars (assuming dredging and disposal cost of $250/$m^3$, a total area of 90,000 m^2, and a contaminated sediment depth of 4 ft). We expect that after in-situ treatment with carbon, the human health and ecological impact of the mid-range footprint area in South Basin will be reduced to that of sediment PCB concentration below 200 ppb. Table 1 shows cost calculations based on the assumption that our selected sediment mixing equipment will cost about the same as an auger dredge commonly used for contaminated sediment remediation. These equipment costs are obtained from estimates presented in the Lower Fox River Feasibility Study report (http://www.dnr.state.wi.us/org/water/wm/lowerfox/rifs/). The cost of in-situ remediation with carbon is estimated to be $ 3.9 million using fresh GAC, and $2.7 million using regenerated carbon. Thus, significant cost savings are expected using the proposed in-situ treatment compared to traditional dredging and disposal of sediments. The actual costs of deploying the GAC in mudflat areas, labor costs, equipment costs, monitoring etc., will have to be confirmed through a pilot demonstration project.

Table 1. Cost estimate for GAC addition to sediments in Hunters Point South Basin area.

SEDIMENT HANDLING COSTS		
Capital costs		
Site Preparation		$20,000
Mobilization - Equipment and silt curtain		$285,000
Cost of fresh carbon (at $2.5/kg)		$2,057,400
Carbon application and mixing		$262,920
(approximation using typical cost for auger dredging; no disposal cost)		
Water quality monitoring during operations		$50,000
Site restoration		$5,000
Direct Capital		$2,680,320
Engineering, Procurement & Construction Management (12% of direct capital)		$321,638
Contractor Overhead/Profit (15%)		$402,048
Total capital cost		$3,404,006
INSTITUTIONAL CONTROLS		
Capital Items:		
Public Education Program		$50,000
O&M Plans		$10,000
Deed Restrictions		$2,500
Engineering, Procurement and Construction Management (12% of direct capital)		$7,500
Present worth of Longer Term Operating Costs (assuming interest rate of 8%)		
Long Term Monitoring (40 years at $10k/year)		119246
Public Education Program (40 years at $15k/year)		178869
Maintaining O&M Plans (40 years at $400/year)		4770
Reporting (40 years at $10k/year)		119246
TOTAL COST (using fresh GAC)		$3,896,137
TOTAL COST (using regenerated GAC)		$2,661,697
Material Handling And Cost Assumptions:		
Sediment area to be treated in square meters	90,000	
Volume of sediment to be treated in cubic meters (top 1 foot)	27,432	
Weight of dry sediment in kg(assuming density of sediment = 1500kg/cum)	41,148,000	
Weight of carbon needed in kg (2% of sediment dry weight)	822,960	
Cost of carbon (assuming $2.5/kg for fresh GAC)	2057400	
Cost of carbon (assuming $1.0/kg for regenerated carbon)	822960	

Sediment handling costs are based on costs reported for sediment dredging using a horizontal auger dredge (Basis for Preliminary Cost Estimates: Sediment Remediation, Fox River, Wisconsin, Little Lake Butte Des Morts, Wisconsin DNR). The cost of mobilizing and operating a horizontal auger dredge is assumed to be similar to a sediment mixing equipment we may use for carbon mixing. Mobilization cost was kept the same. All other operational costs including site preparation, sediment mixing, water quality monitoring, and site restoration was assumed to be one tenth of the costs estimated at the Fox River site which had a 13 times larger volume of sediments to be treated compared to the sediment volume that will be handled at Hunters Point. The cost of institutional controls is assumed to be half that of the Fox River estimate.

9. RELEVANT PUBLICATIONS

1. Microprobe Laser Mass Spectrometry Studies of Polycyclic Aromatic Hydrocarbon Distributions on Harbor Sediments and Coals, J. S. Gillette, U. Ghosh, T. B. Mahjan, R. N. Zare, and R. G. Luthy, *Israel Journal of Chemistry* 41: 105-110. 2001.

2. Microscale Detection of Polychlorinated Biphenyls Using Two-step Laser Mass Spectrometry, Tania B. Mahajan, Upal Ghosh, Richard N. Zare, and Richard G. Luthy, *International Journal of Mass Spectrometry*, R. Graham Cooks Memorial Issue 212: 27-34. 2001.

3. Particle-scale Investigation of PAH Desorption Kinetics and Thermodynamics from Sediments. U. Ghosh, J.W. Talley, R.G. Luthy, *Environmental Science and Technology* 35: 3468-3475. 2001.

4. PCB and PAH Speciation among Particle Types in Contaminated Sediments and Effects on PAH Bioavailability. U. Ghosh, J. Zimmerman, R.G. Luthy. *Environmental Science and Technology* 37: 2209-2217. 2003.

5. Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments. Physicochemical tests. J.R. Zimmerman, U. Ghosh, R.G. Luthy, R.N. Millward, T.S. Bridges. *Environmental Science and Technology* 38: 5458-5464. 2004.

6. Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (Neanthes arenaceodentata) and an Amphipod (Leptocheirus plumulusos). R.N. Millward, T.S. Bridges, U. Ghosh, R.G. Luthy, J.R. Zimmerman. *Environmental Science and Technology*. 39: 2880-2887. 2005.

7. Model Verification of Thermal Programmed Desorption-Mass Spectrometry for Estimation of Release Energy Values for PAHs on Mineral Sorbents. Sara I. Nicholl, Jeffrey W. Talley, Stephan Silliman. *Environmental Toxicology and Chemistry* 23: 2545-2550. 2004.

10. RELEVANT PRESENTATIONS

1. Microscale Investigation of Location and Association of Organic Pollutants in Soils and Sediments. U. Ghosh, R.G. Luthy, Infrared Spectromicroscopy Workshop, Advanced Light Source, Lawrence Berkeley National Laboratory, Oct 15-17, 2001.
2. In Situ Stabilization of Persistent Organic Contaminants in Marine Sediments. Dr. Millward, Ecotoxicology and Ecological Risk Team (ERDC-WES, Vicksburg, MS) on November 27, 2001. Conference paper.
3. In-Situ Stabilization of PCBs and PAHs: Lessons from Natural Processes and New Ideas for Remediation. U. Ghosh, et al. Navy's Risk Assessment Workgroup Meeting, USEPA Region 9, San Francisco, Dec 4, 2001.
4. Sequestration of PCBs and PAHs in Sediments: Lessons from Natural Processes and New Ideas for Restoration. U. Ghosh, et al., Electric Power Research Institute Advisors Meeting, March 13, 2002, San Francisco, CA.
5. Contaminant Exposure Control in Sediments Using Activated Carbon Adsorbent. Richard G. Luthy, John R. Zimmerman, Pamela McLeod, Upal Ghosh, Rod N. Millward, Todd S. Bridges. Paper presented at NIEHS Superfund Basic Research Program, Conference on Bioremediation and Biodegradation, Asilomar Conference Center, Pacific Grove, CA, June 9-12, 2002.
6. PCB Contaminant Distribution Among Sediment Particles and Implications for Bioavailability Control and In Situ Stabilization. Luthy, R. G., Invited Seminar, University of Notre Dame, South Bend, IN, October 4, 2002
7. Bioavailability Control and In-situ Stabilization of Contaminated Sediments using Carbon Sorbents. U. Ghosh, et al. Remediation Technology Development Forum, Sediments Remediation Action Team Meeting, Seattle, WA, October 29-30, 2002.
8. PCB Bioaccumulation from Marine Sediments Following In situ Application of Coal-Derived Particles. Dr. Millward Society of Environmental Toxicology and Chemistry (SETAC) meeting in Salt Lake City, UT on November 19, 2002. Conference paper.
9. Effects of Carbon Substrate on the Bioavailability of Organic Contaminants. McLeod, PB, van den Heuvel-Greve, M, Allen-King, RM, Luoma, SN, Luthy, RG, Stanford, SETAC meeting in Salt Lake City, UT on November 19, 2002. Conference paper.
10. Particles in Sediments: What Can We Learn about Bioavailability and In Situ Stabilization? Luthy, R. G., US/Italy Workshop on Sediment Management Research, National Science Foundation, Washington, DC, December 9-10, 2002. Invited presentation and conference chair.
11. Bioavailability of Contaminants in Soil and Sediment. Luthy, R. G., Tri-Service Ecological Assessment Work Group, SPAWAR System Center, San Diego January 28, 2003
12. Microscale Association of Organic Contaminants to Sediment Particles and Implications for Risk Management. U. Ghosh. Seminar at the Department of Geography and Environmental Engineering, Johns Hopkins University. February 25, 2003.

13. Bioavailability of Contaminants in Soils and Sediments: Processes, Tools, and Applications, Luthy, R. G., Department of Toxic Substances Control, California EPA, April, 4, 2003, Berkeley, CA

14. Organic Sequestration and Bioavailability Control. R.G. Luthy, U. Ghosh, J. R. Zimmerman, P. McLeod, R. Millward, T. Bridges. Plenary presentation, USACE Workshop on Environmental Stability of Chemicals in Sediments, April 8-10, 2003, San Diego, CA

15. In Situ Stabilization of Persistent Organic Compounds in Marine Sediments. Luthy, R. G., U. Ghosh, J. R. Zimmerman, P. McLeod, T.S. Bridges, R. Millward. Hunters Point Shipyard Parcel F Strategy Meeting, Battelle, Navy Sediment Work Group, April 30-May 1, 2003, Boston, MA.

16. In-situ Stabilization of Persistent Organic Contaminants in Sediments. U. Ghosh, R.G. Luthy, J.R. Zimmerman, M. Heuvel-Greve, P. Mcleod, R. Millward, T.S. Brides. A Workshop on In-Situ Contaminated Sediment Capping, EPRI, May 12-14, 2003. Cincinnati, OH.

17. In Situ Stabilization of Persistent Organic Compounds in Marine Sediments. Luthy, R. G., U. Ghosh, J. R. Zimmerman, P. McLeod, T.S. Bridges, R. Millward, Navy/University of California Berkeley Sediment Meeting, Battelle, May 14, 2003, San Francisco, CA.

18. Organic Sequestration and Bioavailability Control. Luthy, R. G., U. Ghosh, J. R. Zimmerman, P. McLeod, R. Millward, T. Bridges. Invited presentation. US EPA Region 9 and San Francisco Bay Regional Water Quality Control Board, Biological Technical Assistance Group, May 21, 2003, Oakland, CA.

19. Organic Contaminants in the Environment: Challenges for the Water/Engineering Community. Luthy, R. G., Invited Presentation, Water and Sustainable Development: Opportunities for the Chemical Sciences, Chemical Sciences Roundtable, National Research Council, Irvine, CA, June 2, 2003

20. In Situ Stabilization of Persistent Organic Contaminants in Sediments. U. Ghosh, J. R. Zimmerman, P. McLeod, R. G. Luthy, R. Millward, T. Bridges. Invited paper. International Association for Great Lakes Research, IAGLR/ILEC 2003 Session on Advances in Assessment and Remediation of Contaminated Sediments, Chicago, June 23, 2003.

21. In-situ Stabilization of Persistent Organic Contaminants in Sediments. U. Ghosh, R.G. Luthy, J.R. Zimmerman, M. Heuvel-Greve, P. Mcleod, R. Millward, T.S. Bridges. Invited paper. In Situ and On-Site Bioremediation, The Seventh International Symposium, Orlando, FL. June 2-5, 2003.

22. PCB Bioavailability Reduction in Sediments Using Activated Carbon: A New Remediation Tool. U. Ghosh. Invited seminar, Chesapeake Biological Laboratory, Solomons, MD, Oct 2, 2003.

23. Contaminant-Sediment Interactions at the Particle-Scale: Implications for Risk Assessment and Remediation. U. Ghosh, Invited speaker. SERDP Annual Symposium: Partners in Environmental Technology Technical Symposium and Workshop, Dec 2, 2003.

24. PAH Distribution Among Organic Matter Types in Contaminated Sediments and Effects on Bioavailability, U. Ghosh, J.R. Zimmerman, L. Hong, and R.G. Luthy. Invited presentation. Natural Gas Technologies II Conference, Phoenix, AZ, Feb 8-11, 2004.

25. In Situ Bioavailability Reduction of PCBs in Sediments: From Bench-scale to Field Demonstration. U. Ghosh, R.G. Luthy, J.R. Zimmerman, M. Heuvel-Greve, P. Mcleod, R. Millward, T.S. Bridges. Remediation Technology Development Forum, Sediment Remediation Action Team Meeting, Baltimore, MD, February 18-19, 2004.
26. In Situ Stabilization of Persistent Organic Contaminants in Sediments Using Activated Carbon. U. Ghosh, R.G. Luthy, J.R. Zimmerman, P. Mcleod, R. Millward, T.S. Bridges. Invited presentation. Technology Benchmarking Workshop for Sediment and Floodplain Remediation. University of Michigan, Ann Arbor, MI, March 25-26, 2004.
27. Microscale association of organic contaminants to sediment particles and implications for environmental risk management. U. Ghosh, Invited seminar, Civil and Environmental Engineering Department, Lehigh University. April 9, 2004.
28. Microscale association of organic contaminants to sediment particles and implications for environmental risk management. U. Ghosh, Invited seminar, Chemistry and Biochemistry Department, University of Maryland College Park. April 16, 2004.

11. KEY PROJECT STAFF

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Appendix I.

Published paper:

PCB and PAH Speciation Among Particle Types in Contaminated Harbor Sediments and Effects on PAH Bioavailability

by

Upal Ghosh, John R. Zimmerman, Richard G. Luthy

Environmental Science and Technology 37: 3625-3634, 2003

Appendix II.

Microscale Detection of Polychlorinated Biphenyls Using Two-Step Laser Mass Spectrometry

by

Tania B. Mahajan[1], Upal Ghosh[2], Richard N. Zare[1], and Richard G. Luthy[2]

Appendix III.

Published paper

Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments. Physicochemical Tests.

by

John R. Zimmerman[1], Upal Ghosh[2], Richard G. Luthy[1], Todd S. Bridges[3], and Rod N. Millward[3].

Environmental Science and Technology 38: 5458-5464, 2004

Appendix IV

Paper in review

Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (Neanthes arenaceodentata) and an Amphipod (Leptocheirus plumulusos).

by

R.N. Millward, T.S. Bridges, U. Ghosh, R.G. Luthy, J.R. Zimmerman,

Environmental Science & Technology, 39: 2880-2887, 2005.

Appendix V.

Contaminant Exposure Control in Sediments Using Activated Carbon Adsorbent

By

Richard G. Luthy, John R. Zimmerman, Pamela McLeod, Upal Ghosh, Rod N. Millward, Todd S. Bridges.

Appendix VI.

Model Verification of Thermal Programmed Desorption-Mass Spectrometry for Estimation of Release Energy Values for PAHs on Mineral Sorbents.

Sara I. Nicholl, Jeffrey W. Talley, Stephan Silliman.

Appendix VII.

The Effects of Dose and Particle Size on Activated Carbon Treatment to Sequester PCBs and PAHs in Marine Sediments.

J.R. Zimmerman, D. Werner, U. Ghosh, R.N. Millward, T.S. Bridges, R.G. Luthy.

Appendix VIII.

Report

An overview of field mixing technologies.

Upal Ghosh, Dennis Smithenry, Richard G. Luthy

Appendix IX.

Unpublished results

a) PCB desorption kinetics from Hunters Point sediments;

b) Kinetics of PCB adsorption into carbon

c) Demonstration of PCB mass transfer from sediment to carbon

Appendix I.

Published paper:

PCB and PAH Speciation Among Particle Types in Contaminated Harbor Sediments and Effects on PAH Bioavailability

by

Upal Ghosh, John R. Zimmerman, Richard G. Luthy

Environmental Science and Technology 37: 3625-3634, 2003

Environ. Sci. Technol. **2003**, *37,* 2209−2217

PCB and PAH Speciation among Particle Types in Contaminated Harbor Sediments and Effects on PAH Bioavailability

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This research provides particle-scale understanding of PCB and PAH distribution in sediments obtained from three urban locations in the United States: Hunters Point, CA; Milwaukee Harbor, WI; and Harbor Point, NY. The sediments comprised mineral grains (primarily sand, silt, and clays) and carbonaceous particles (primarily coal, coke, charcoal, pitch, cenospheres, and wood). The carbonaceous sediment fractions were separated from the mineral fractions based on their lower density and were identified by petrographic analysis. In all three sediments, carbonaceous particles contributed 5−7% of the total mass and 60−90% of the PCBs and PAHs. The production of carbonaceous particles is not known to be associated with PCB contamination, and it is very unlikely that these particles can be the source of PCBs in the environment. Thus, it appears that carbonaceous particles preferentially accumulate PCBs acting as sorbents in the aqueous environment if PCBs are released directly to the sediment or if deposited as airborne soot particles. Aerobic bioslurry treatment resulted in negligible PAH loss from the carbonaceous coal-derived material in Milwaukee Harbor sediment but resulted in 80% of the PAHs being removed from carbonaceous particles in Harbor Point sediment. Microscale PAH extraction and analysis revealed that PAHs in Harbor Point sediment were associated mainly with coal tar pitch residue. PAHs present in semisolid coal tar pitch are more bioavailable than PAHs sorbed on carbonaceous particles such as coal, coke, charcoal, and cenosphere. Results of this study illustrate the importance of understanding particle-scale association of hydrophobic organic contaminants for explaining bioavailability differences among sediments.

Introduction

The management of sediments and the control of sediment contaminants are among the most challenging and complex problems faced by environmental engineers and scientists. Because of the strong binding of hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), sediments serve as a long-term source of the contaminants to water bodies and biota, even long after the original source of contamination has been removed. While recent advances in analytical techniques make it possible to quantify even the smallest amount of anthropogenic contaminants present in sediment, our ability to relate sediment concentrations to water quality, biological availability, and toxicological effects is hindered by inadequate understanding of the binding and release of the contaminants in the sediment. This is due to the inherent heterogeneity of sediment material that defies organic geochemical generalizations based on bulk sediment physicochemical parameters such as total organic carbon content, surface area, and particle size distribution.

PCBs and PAHs sorb to the organic carbon fraction of sediment, and thus organic carbon fraction is taken as a measure of the sorption capacity for regulatory purposes. This enables normalization of the aqueous equilibrium relationship for sediments containing different amounts of organic carbon (*1*). However, a major problem with this approach is that organic carbon in sediment comes in different forms that may have very different sorption capacities for HOCs. For example, in addition to natural materials such as vegetative debris, decayed remains of plants and animals, and humic matter, sediment organic carbon also comprises particles such as coal, coke, charcoal, and soot that are known to have extremely high sorption capacities (*2*−*6*). Figure 1 shows a comparison of reported organic carbon-normalized phenanthrene partition coefficients (K_{oc}) for different sorbents (*5*, *7*−*12*). The K_{oc} values for different organic carbon forms span several orders of magnitude. On the basis of the partition coefficients presented in Figure 1, it is clear that HOCs associated with soot- or coal-type carbon may be orders of magnitude less available in the aqueous phase than HOCs associated with natural organic matter in soils and sediment. Thus, HOCs that end up in the sediment as contaminants may be of more or less concern depending on how weakly or strongly they are sorbed to the sediment organic matter.

Past work indicates the possible importance of soot carbon in sorption processes in sediment (*2*, *6*, *13*, *14*). These studies measured soot carbon in sediment using partial thermal oxidation to remove non-soot organic carbon followed by treatment with acid to remove inorganic carbon and analysis of the remaining carbon. The soot carbon material isolated by partial thermal oxidation does not retain sorbed chemicals for further analysis. However, Gustafsson et al. (*2*) and Bucheli and Gustafsson (*13*) showed that elevated PAH partitioning in sediment samples could be explained on the basis of the soot carbon content and known high PAH sorption capacity of soot. They concluded that sorption of PAHs on a soot-phase carbon in sediments may impact in situ bioavailability of PAHs. Accardi-Dey and Gschwend (*6*) performed PAH sorption studies with the isolated soot carbon and demonstrated that a modified, soot-partitioning inclusive, distribution model can better predict the observed PAH partitioning from sediment. Karapanagioti et al. (*5*) showed that sediments containing coaly particulates exhibited high K_{oc} values and nonlinear isotherms for phenanthrene sorption. Recently Salloum et al. (*12*) studied the sorption of phenanthrene on several aliphatic natural organic matter types (algae, cellulose, collagen, cuticle, lignin, kerogen, and humic acid) and concluded that aliphatic organic matter domains in soils and sediment may also play a significant role in the sorption of HOCs. However, none of these studies directly measured the levels of PAHs on natural organic matter particles, soot, or coal particles in field sediment, and as such, the conclusions are based on inference from equilibrium partitioning

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10.1021/es020833k CCC: $25.00 © 2003 American Chemical Society
Published on Web 04/15/2003

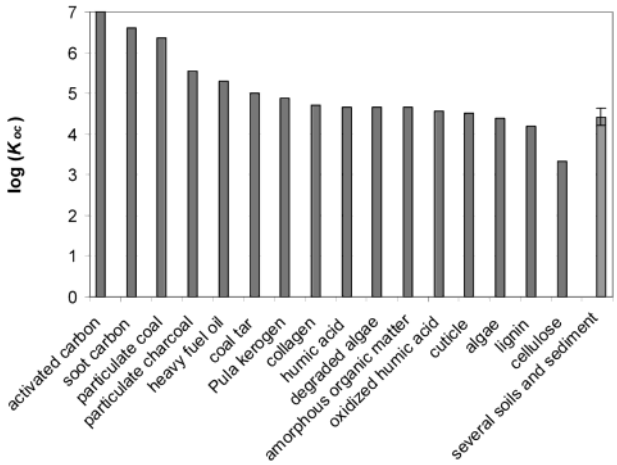


FIGURE 1. Organic carbon-normalized partition coefficient for phenanthrene for different types of organic carbon. Data sources: activated carbon (*7*); soot carbon (*8*); particulate coal, particulate charcoal, and amorphous organic matter (*5*); heavy fuel oil (*9*); several soils and sediments showing average and range (*10, 11*); Pula kerogen, collagen, humic acid, degraded algae, Green River kerogen, oxidized humic acid, cuticle, algae, lignin, and cellulose (*12*); coal tar (*23*).

and not on direct evidence of PAH association. Thus, from these studies it is not clear whether natural organic matter or black carbon in sediments comprise the predominant repository of hydrophobic contaminants such as PCBs and PAHs. In our earlier work, we demonstrated the predominant association of PAHs with coal-derived particles in Milwaukee Harbor sediments (*4*). We found from direct analysis of separated fractions and particle-scale microanalysis that the majority of PAHs in the sediment was associated with coal-derived particles and that these PAHs were strongly bound, not easily desorbable, unavailable for biological treatment, and unavailable for uptake in earthworms (*4, 15, 16*).

The objective of this research is to extend particle-scale understanding of PCB and PAH distributions in sediment by comparing sediments from three different geographical locations and to illustrate the effect of PAH association with particle types on bioslurry treatment. We use three different aged, harbor sediment samples to investigate the importance of carbonaceous particles in the sequestration of PCBs and PAHs. The particulate organic carbon components in the sediments were separated by a density technique that preserves the physical and chemical integrity of the particles. Two of the sediments containing high levels of PAHs were subjected to aerobic bioslurry treatment to investigate PAH bioavailability to microorganisms. Microscale extraction and analysis were carried out to illustrate differences in PAH levels among carbonaceous particle types in sediment and to explain differences in PAH bioavailability.

Materials and Methods

Contaminated sediments often occur near harbors and old industrial establishments. Therefore, we selected three harbor/industrial locations across the country to study the extant distribution of PCBs and PAHs among particle classes. Three sediments used in this study were obtained from the following locations. All sediment samples were stored at 4 °C until used.

(*i*) *Hunters Point, San Francisco Bay, CA.* Sediment samples were collected from the intertidal zone in South Basin near the southern edge of the Hunters Point Naval Shipyard in January 2001 and screened through a 4 mm screen. Sampling took place during low tide along approximately 150 yards of shoreline within the intertidal zone. Historic shipyard and industrial activities in the adjacent region discharged PCBs, PAHs, and heavy metals into the soil and sediment. Operations at the site included a former transformer storage yard, industrial landfills, fuel lines, a scrapyard, and an oil reclamation area. Between 1954 and 1974, nearly 250 gal of PCBs was estimated to have been released in the scrapyard parcel adjoining South Basin (*17*). Other PCB releases may have occurred as well. The Hunters Point South Basin Area is designated as a PCB hotspot in San Francisco Bay (*18*).

(*ii*) *Milwaukee Harbor Confined Disposal Facility* (*CDF*). Sediments in the CDF originated from Milwaukee Harbor during dredging operations to maintain waterway navigability. This 44 acre facility is operated by the Milwaukee Harbor Port Authority. Concerns have been raised about the potential for release of contaminants from such CDF sites and about closure requirements, as discussed by Bowman (*19*). Samples for this work were collected in fall 1996 at a depth of 4 m in the CDF. The sediment was sieved through a 1/4 in. screen in the field.

(*iii*) *Harbor Point Sediment, NY.* This sediment sample was collected in 1999 from a freshwater harbor site located near a former manufactured gas plant in Utica, NY. The sediment was collected using 1−2 ft cores and sieved through 3/8 in. mesh and composited on site. High levels of PAHs in the sediment are thought to have originated from a historic gas manufacturing facility in the vicinity.

Size and Density Separation. Wet sieving was performed to separate the sediment into four size fractions (<63, 63−250, 250−1000, and >1000 μm). The larger size fractions (>63 μm) were composed primarily of sandy grains, carbonaceous particles, and woody material. The lighter carbonaceous particles were washed off from the heavier sand particles by swirling with water in a beaker and draining off the entrained lighter particles, giving two separate fractions that we define as "light" and "heavy". As a final step, a saturated cesium chloride solution with a specific gravity of 1.8 was used to remove the remaining lighter density particles. Materials in the fine fraction (<63 μm) were density-separated using the cesium chloride solution. Five grams of wet sediment and 40 mL of cesium chloride solution were mixed and centrifuged at 2000*g* for 10 min in 50 mL glass centrifuge tubes. Separated particles were washed with water to remove cesium chloride (*4*).

Coal Petrography Analysis. Coal petrography analysis of sediment particles was performed according to ASTM standard methods for coal analysis: D2797 (Preparing Coal Samples for Microscopic Analysis by Reflected Light), D2798 (Microscopic Determination of the Reflectance of Vitrinite in a Polished Specimen of Coal), and D2799 (Microscopic Determination of Volume Percent of Physical Components of Coal).

PCB/PAH Analysis. Soil PCBs and PAHs were extracted following U.S. EPA Method 3550B using 3 volumes of 40 mL each of an acetone−hexane mixture (1:1) and sonicating the slurry for 6 min (pulsing for 15 s on and 15 s off). Pesticide-grade hexane and acetone were used for all extractions. EPA Method 3630C was followed for sample cleanup where the dried and concentrated extracts are passed through a deactivated silica gel column to remove organic interferences and to separate the PCBs and PAHs. PCB congener-specific analysis was performed using a modified EPA Method 8082. An Agilent gas chromatograph (model 6890) with a fused silica capillary column (HP-5, 60 m × 0.25 mm i.d.) and an electron capture detector was used for analysis. PCB standards for calibration were purchased as hexane solutions from Ultra Scientific (North Kingstown, RI) and also obtained from the U.S. EPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, MI. A multi-level calibration table was prepared using a PCB mixture containing 250 μg/L of Aroclor 1232, 180 μg/L of Aroclor 1248 and 180 μg/L of Aroclor 1262 yielding a total PCB concentration

of 610 μg/L (*20*). Concentrations of individual PCB congeners in the mixture were obtained from Mullin (*20*). Two internal standards were used: 2,4,6-trichlorobiphenyl and 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl, which are not present in commercial Aroclor mixtures. Using this protocol, 86 PCB congeners or congener groups could be identified and quantified. With this analytical method, there are some coeluting peaks in the analysis. Where this occurs, coeluting peaks are calibrated as the sum of congeners. PAH analysis was performed using an Agilent gas chromatograph (model 6890) with a fused-silica capillary column (HP-5, 30 m × 0.25 mm i.d.) and a flame ionization detector based on U.S. EPA Method 8100 for PAHs. A standard U.S. EPA mixture of 16 PAH compounds obtained from Ultra Scientific was used for calibration.

Microscale PAH Extraction and Analysis. To investigate differences in PAH abundances among particle types in Harbor Point sediment, a small quantity of lighter density particles in the 250−1000 μm size fraction were manually separated under the microscope into five particle types: wood, coal/coke, charcoal, coal tar pitch, and cenosphere (see Figure S1 in Supporting Information). These particle types were identified by visual observation under a light microscope. The wood and charcoal were identified based on grain structure and color. The cenospheres appeared as black hard rounded shells. Coal appeared as hard, black, and shiny particles, and coke had a porous look. The coal tar pitch was confirmed from its softness under the tweezers and by observing particle melting upon contact with the heated tip of a spatula (see Figure S2 in Supporting Information). Five particles of each kind were weighed and extracted in 1.5 mL glass vials with Teflon-lined caps using a 50:50 mixture of methylene chloride and acetone. The capped vials were placed in a sonicator bath and warmed to 50 °C for 3 min for the extraction. Following three sequential extractions, the solvent was exchanged into cyclohexane and cleaned up in a silica gel microcolumn prepared in a disposable glass pipet. The cleanup procedure was a scaled down version of the standard U.S. EPA Method 3630C. The final extract was concentrated to 150 μL before analysis. Lighter density particles in Milwaukee Harbor sediment were also separated into the two primary components (coal-derived, and wood) and analyzed for PAHs.

Aerobic Bioslurry Experiments. Aerobic slurry reactors using Harbor Point sediment were prepared in separate 4 L glass flasks. A total of 2.4 L of minimal medium was added with 1.33 kg of Harbor Point sediment. The minimal medium contained 0.4 g of K_2HPO_4, 0.317 g of $NaH_2PO_4 \cdot H_2O$, 0.216 g of NH_4Cl, 0.1 g of $MgSO_4$, 1.0 mg of $FeSO_4 \cdot 7H_2O$, and 1.0 mL of trace elemental substances (TES)/L of deionized water, and pH was adjusted to 7.0 with NaOH. TES consisted of 0.15 g of $ZnNO_3 \cdot 6H_2O$, 0.1 g of $MnCl_2 \cdot 4H_2O$, 0.062 g of H_3BO_3, 0.19 g of $CoCl_2 \cdot 6H_2O$, 0.035 g of $CuSO_4 \cdot 5H_2O$, 0.027 g of $NiSO_4 \cdot 6H_2O$, 0.026 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and 5.2 g of EDTA/L of deionized water. Oxygen was supplied to the reactors through an air pump (1.6 L/min). The reactors were homogeneously mixed by Lightnin General Purpose mixer (Rochester, NY) and operated for 60 d at 24 °C. Polyurethane foam traps were used to test for volatilization of PAHs during the bioslurry process. Only naphthalene was detected in the trap and accounted for 0.8% of naphthalene present in the sediment added to the bioslurry reactor.

Light Microscopy Imaging. A Leica WILD M3Z microscope (65−400× magnification) was used for light microscopy imaging of sediment particles. A Kodak DX3900 digital camera was attached to the imaging tube of the microscope to collect pictures.

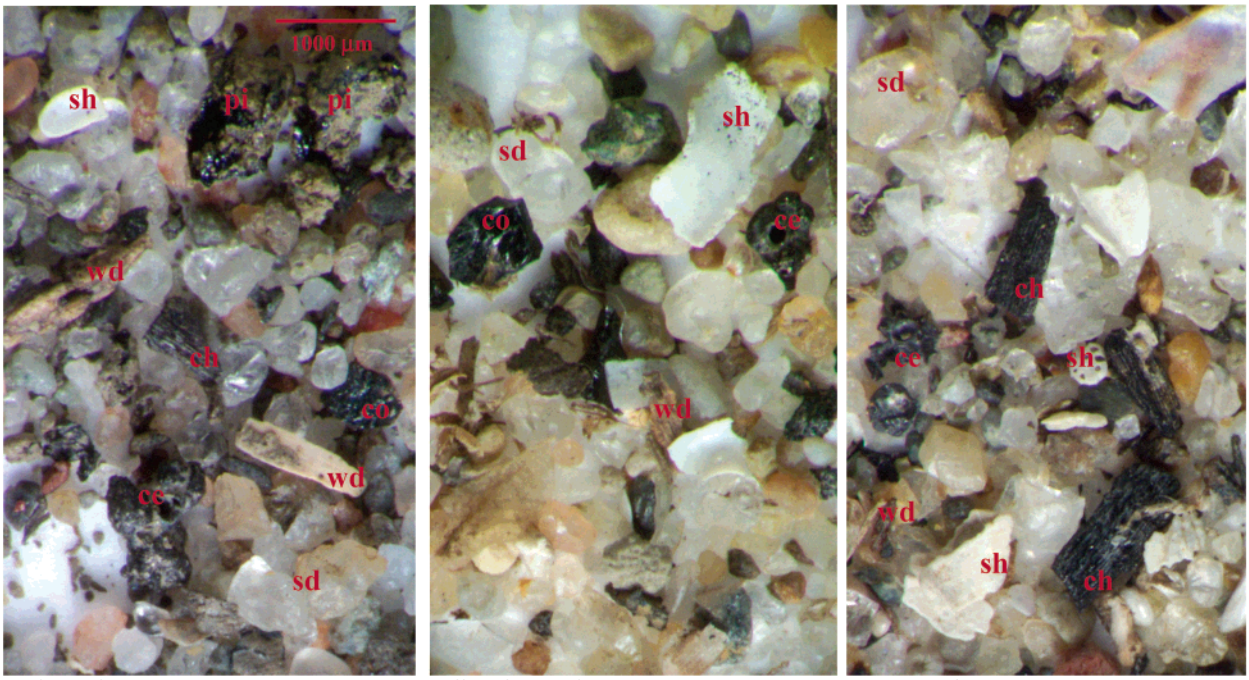
PAH Desorption Study. PAH desorption kinetic studies were conducted using separated lighter fractions. Desorption tests followed previously used procedures (*15*). Tenax beads (0.5 g) and sediment sample (0.2 g) were added to a 12 mL glass vial containing 10 mL of water and continuously mixed in a rotator. Sodium azide (1000 mg/L) was added to the mixture to prevent biological growth. At sampling times, the Tenax beads were harvested by allowing the sediment to settle and the Tenax beads to float up. The Tenax beads were scooped out of the test tube, and fresh Tenax was added. PAHs were extracted from the Tenax beads and analyzed by GC-FID.

Results and Discussion

Sediment Particle Characterization. Sediments from the three locations were separated into four size classes: <63, 63−250, 250−1000, and >1000 μm. Light microscopy illustrates the diversity of particles and identifies prominent particle classes in the sediment samples. As shown in the microscopic image of sediments from the three locations in Figure 2, the 250−1000 μm size sediments comprise mineral grains (primarily sand) and organic particles of various kinds such as wood, charcoal, coal, coke, pitch, and cenosphere. An exact identification of the nature of organic particles was performed through petrographic analysis. Petrographic analysis involves preparation of a polished particle surface followed by visualization under a microscope using normal or polarized light. This technique has been used historically to identify coal maceral structures, rank coals, identify different stages of coal pyrolysis and coke formation, determine coal tar and pitch quality, and identify chars and cenospheres (*21*). Karapanagioti et al. (*5*) used petrographic techniques to identify types of organic matter including coals in different size fractions of aquifer material. In our earlier work, we used similar techniques to identify coal-derived particles in Milwaukee Harbor sediment (*4*).

The various kinds of organic particles identified in the three sediments in this study by petrographic analysis are shown in Figure 3. A striking common feature in the analysis of the three sediments is the abundance of coal and coal-derived particles in all three sediments. Possible sources of coals in these sediments are coal transportation activities in harbors near the sampling locations, historic coal use in the local area, and coal gas manufacturing facilities in the vicinity. All three sediments showed the presence of wood particles. Hunters Point and Harbor Point sediment showed significant presence of lignite and cenospheres. Cenospheres are more or less spherical, porous semicoke or coked particles formed during the rapid heating of unconfined coal (*21*). These particles appear as hollow carbon spheres often broken into pieces in the sediment. A special feature of the Harbor Point sediment was the presence of pitch, a likely residue and waste product from former manufactured gas operations. The Milwaukee Harbor sediment was unique in showing a preponderance of coal-derived particles. The Hunters Point sediment showed significant presence of charcoal, which was not observed in abundance in the other sediment samples. Oil-soot particles were not seen abundantly in the two size fractions that were studied in detail: 63−250 and 250−1000 μm. Oil-soot particles are typically nanometer sized globules, often in grape-like clusters several micons in size. On the basis of the size of oil-soot particles, these may be present in the study sediments in the <63 μm lighter density fraction. In our petrography analysis for Hunters Point sediment, we found an oil-soot cluster in the 63−250 μm size range among more prevelant black carbonaceous particle types described above. Although there were differences in carbonaceous particle types found in the three sediment samples, a common characteristic is the abundance of highly sorbing carbon substrates in all three sediments.

PCB and PAH Concentrations in Sediment. PCB homologue and PAH concentrations in the three sediments are shown in Figures S3 and S4, respectively, in the Supporting Information. Among the three sediments, Hunters Point had



Harbor Point, NY Milwaukee Harbor, WI Hunters Point, CA

FIGURE 2. Light microscopy images of particles in sediment from three locations showing the different geochemical types in the size range of 250−1000 μm. The relevant particle types identified are sd, sand; sh, shell; co, coal; ch, charcoal; pi, coal tar pitch; ce, cenosphere; and wd, wood.

the highest levels of PCBs at 9.9 ± 0.9 mg/kg with predominantly higher chlorinated congeners and resembling Aroclor 1260 in congener distribution. The most abundant PCB homologues were hexa- and heptachlorobiphenyls. The PCB concentrations at this site are approximately 3 orders of magnitude higher than background PCB levels (25 μg/kg) in the sediment in San Francisco Bay (*18*). Total PCB concentration in Milwaukee Harbor sediment was 1 mg/kg with tetra- and pentachlorobiphenyls being the most abundant homologues. Although PCBs were detected in Harbor Point sediment, a detailed study of the PCB distribution in this sediment was not conducted as part of this investigation. Research with Harbor Point sediments focused on PAHs, which were the primary contaminant of concern at this site at 262 ± 25 mg/kg total PAHs. This sediment also appears to be the least weathered based on the relatively higher levels of lower molecular weight PAHs such as phenanthrene. Total PAH concentration in Milwaukee Harbor sediment was 90 ± 7 mg/kg. Hunters Point sediment had the lowest levels of PAHs at 8 mg/kg.

It is well-known that hydrophobic organic compounds such as PCBs and PAHs partition into organic carbon on soils and sediments. However, this partitioning process may vary greatly if the organic carbon present in soils and sediments comprises various forms such as humic matter particles, humic matter sorbed on mineral surfaces, animal and vegetative debris, and products of coal and wood use and combustion. Our earlier work with Milwaukee Harbor sediment showed the importance of coal-derived particles in sorption of PAHs. The following compares the distribution of PCBs and PAHs among particle sizes and density classes for three different sediments.

Sediment Mass Distribution among Particle Classes. The carbonaceous sediment fraction comprising coal, coke, charcoal, pitch, cenospheres, and wood are separable from the mineral fraction based on their lower density. The three sediments were separated into size and density fractions and analyzed for PCBs and PAHs in each fraction. Results of sediment mass distribution by size and density shown in Figure 4 reveal for each size fraction that the lighter density fraction has much smaller mass as compared to the heavier mineral fraction. For all three sediments 5−7% of the total sediment mass is contributed by the lighter density carbonaceous particles. The two freshwater sediment samples, Milwaukee Harbor and Harbor Point, have clay/silt (<63 μm heavy) as the predominant sediment component. The Hunters Point sediment is coarser in grain size with fine and coarse sands comprising the majority of the sediment.

Sediment PCB and PAH Distribution among Particle Classes. PCB and PAH analyses of the lighter and heavier density fractions reveal that the majority of the contaminants are associated with the small quantity of lighter density carbonaceous particles. As shown in Figure 5, the fraction of total PAHs associated with the lighter density carbonaceous particles in Hunters Point, Milwaukee Harbor, and Harbor Point sediments are 89%, 68%, and 62%, respectively. We find that the fraction of total PCBs associated with lighter density carbonaceous particles in Hunters Point and Milwaukee Harbor sediments are 68% and 58%, respectively (Figure 6). Thus, for all three sediments, PAHs and PCBs are predominantly associated with the carbonaceous particles. Earlier work by us for Milwaukee Harbor sediment (*4*) and recent work by Rockne et al. (*22*) for NY/NJ harbor sediments has shown that PAHs can be found predominantly in the lighter density fraction of sediments. As with PAHs, our data for two sediments are the first reporting of the distribution of PCBs among sediment particle density classes.

PAH and PCB analyses by size and density fractions shown in Figures 5 and 6 reveal that except for the fine grained (<63 μm) sediment fraction, for every size fraction, the lighter density material contributes to the majority of PAHs and PCBs in the sediment. For the fine size fraction (<63 μm), in all three sediments the heavier density particles contributed more PCBs and PAHs than the lighter density particles. Possible reasons for the difference with the finest size fraction are the much larger surface area of the finer size fraction and the comparatively larger overall mass of heavy particles in this size fraction. For example, in the case of Harbor Point

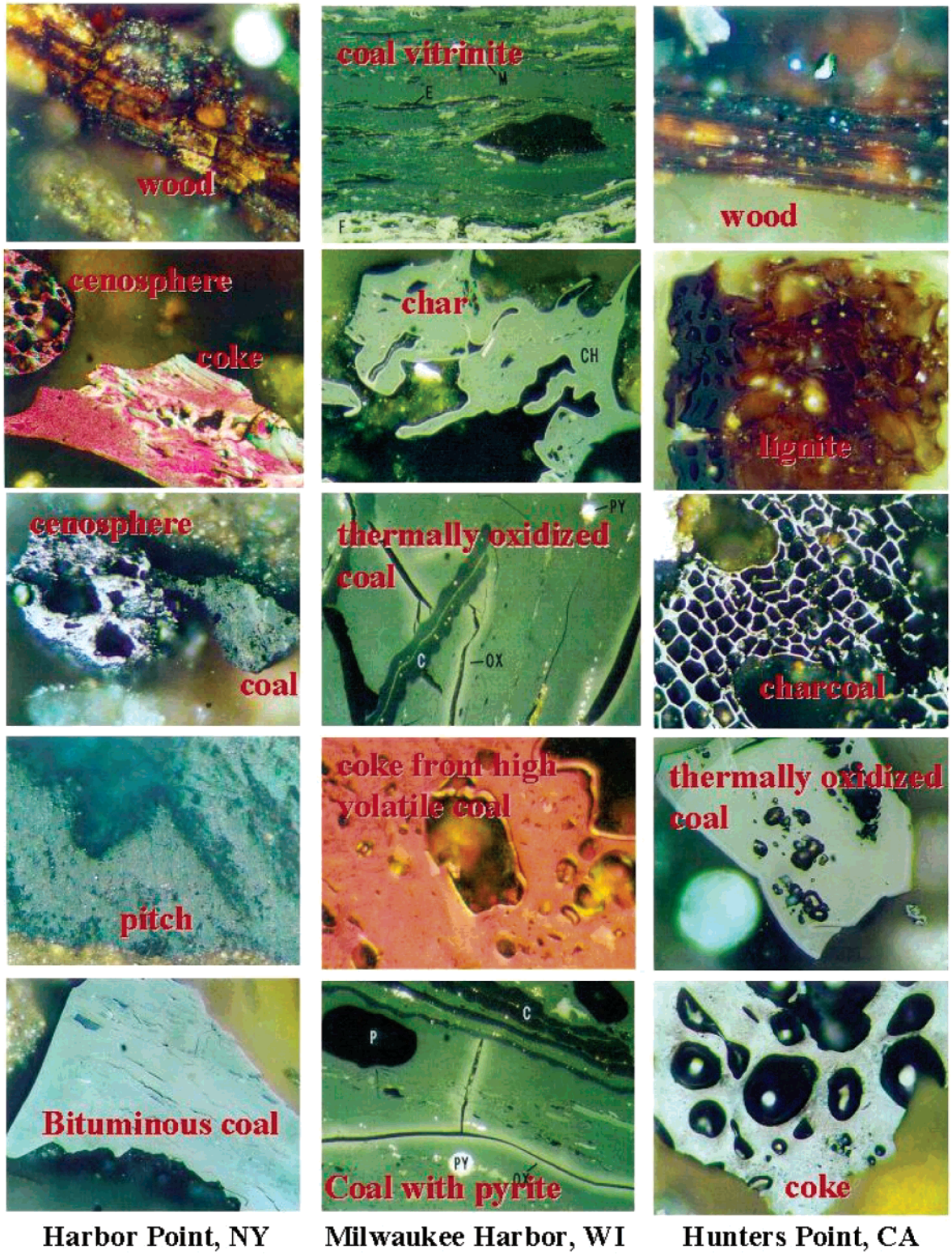


FIGURE 3. Petrographic identification of organic carbon particles in sediment from three locations reveals the presence of coal, partially oxidized coal, coke, lignite, wood, charcoal, cenospheres, char, and pitch. Petrography images shown are under reflected light in oil at 500× magnification.

sediment, only 1% by mass in the <63 μm size fraction comprises light particles.

Implications of PCB Speciation in Carbonaceous Particles. Since combustion and pyrolysis processes are associated with the production of PAHs as a byproduct, there is a possibility that the coal- and combustion-derived particles reach the sediment with PAHs already sorbed to the particles. In our current work, we analyzed PCB distribution in two of the sediments. Results of PCB analysis by sediment density fractions reveal a strikingly similar story wherein the majority of the PCBs are associated with the lighter density carbonaceous particles. Since the production of coal, coke, charcoal, and cenosphere is in no way associated with PCB use, it is unlikely that these particles can be the source of PCBs in the environment. For the <63 μm size light fraction, if airborne soot particles are present, those may have picked up some

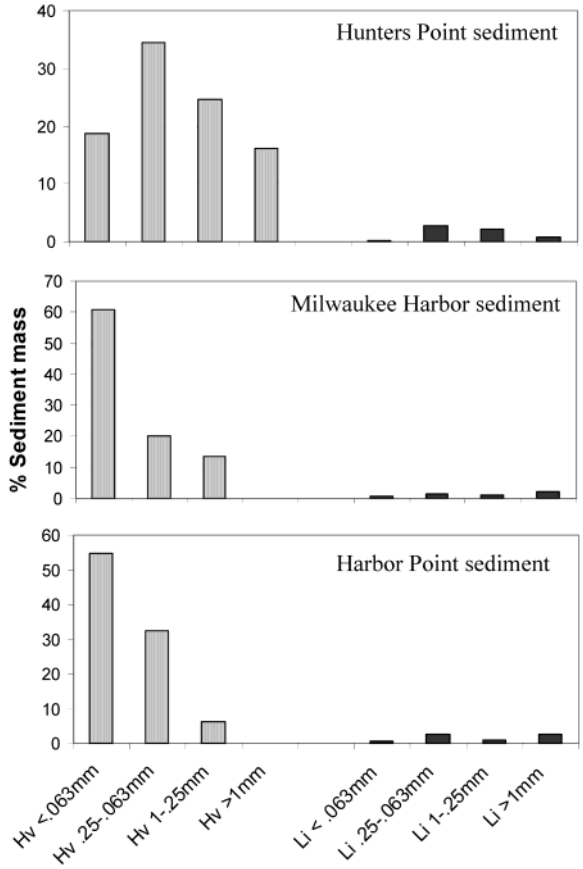


FIGURE 4. Sediment mass distribution by size and density, heavy (Hv) and light (Li), for Hunters Point, CA; Milwaukee Harbor, WI; and Harbor Point, NY, sediments.

of the PCBs from the atmosphere before depositing in the sediment. For the larger sized particles such as coal, coke, and charcoal, it appears that over a long period of time, PCBs in the sediment tend to preferentially accumulate in these carbonaceous particles where they may be strongly bound. Such migration of PCBs and possibly PAHs into a more strongly sorbing matrix has significant implications for assessment of sediment quality criteria and for possible in situ stabilization approaches. For example, addition of sorbent carbonaceous material like activated carbon to the sediment may enhance the sequestration of these hydrophobic compounds in the sediment, making them less available for biological uptake and release into the overlying water.

Effect of PAH Association with Particle Types on Bioavailability. Aerobic bioslurry experiments were carried out using the two sediments that had high levels of PAHs: Milwaukee Harbor (90 mg/kg) and Harbor Point (262 mg/kg). We reported in an earlier study for Milwaukee Harbor sediment that PAH biodegradation was achieved mainly within the <63 μm heavy fraction comprising the clays and silt, for which there was 75% reduction in PAHs (*16*). The coal-derived material from Milwaukee Harbor sediment showed no significant reduction in PAH concentrations during the biotreatment process. Thus PAHs associated with the lighter density fraction of Milwaukee Harbor sediment, which was primarily coal-derived particles, appear to be strongly bound and not available for biological degradation.

A similar aerobic bioslurry treatment study was conducted using Harbor Point sediment to compare with the finding from the Milwaukee Harbor study. As shown in Figure 7, nearly 75% reduction of total PAHs was achieved during 2 months of aerobic bioslurry treatment of Harbor Point

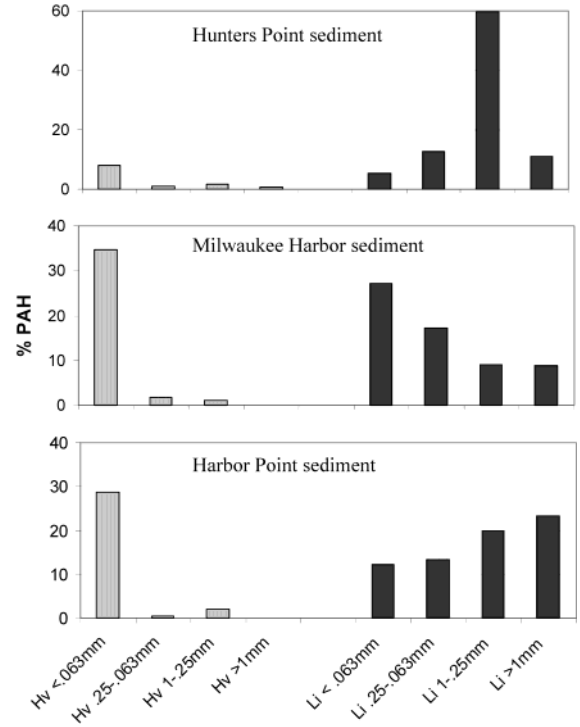


FIGURE 5. Sediment PAH distribution by size and density, heavy (Hv) and light (Li), for the contaminated sediments from urban areas. The lighter density fractions comprise 89%, 68%, and 62% of the total PAHs for Hunters Point, CA; Milwaukee Harbor, WI; and Harbor Point, NY, sediments, respectively.

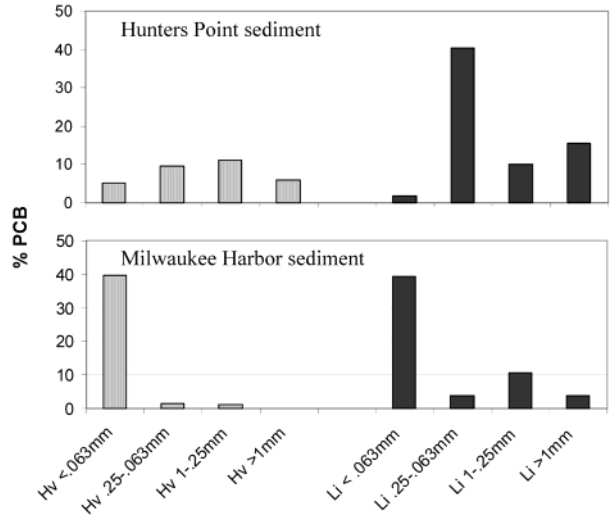


FIGURE 6. PCB distribution in Hunters Point sediment and Milwaukee Harbor sediment by size and density, heavy (Hv) and light (Li). The less dense fractions of the sediment comprise 68% and 58% of the total PCBs for Hunters Point, CA, and Milwaukee Harbor, WI, respectively.

sediment. Greater than 90% reduction was achieved for the low molecular weight PAHs (2−3 ring) and 20−50% reduction was achieved for the high molecular weight PAHs (5−6 rings). PAH analysis by particle size and density revealed that, although reductions of PAHs associated with the heavy sand/silt/clay fractions were high (69%), significant PAH reductions were also achieved for PAHs associated with the lighter density fractions comprising coal, charcoal, char, cenospheres, and coal tar pitch (80%). As shown in Figure 8, the four size classes of the lighter density fraction of Harbor Point sediment underwent significant losses of PAHs during the bioslurry treatment process.

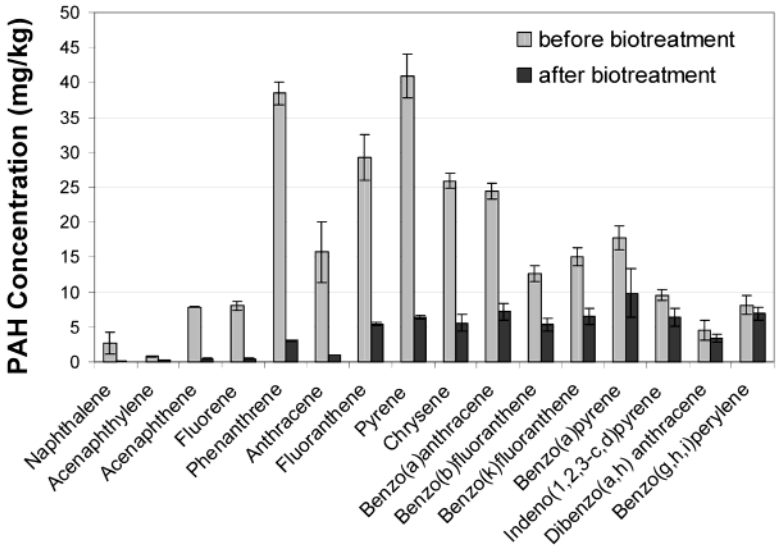


FIGURE 7. Change in PAH concentration during 2 months of aerobic bioslurry treatment of Harbor Point sediment.

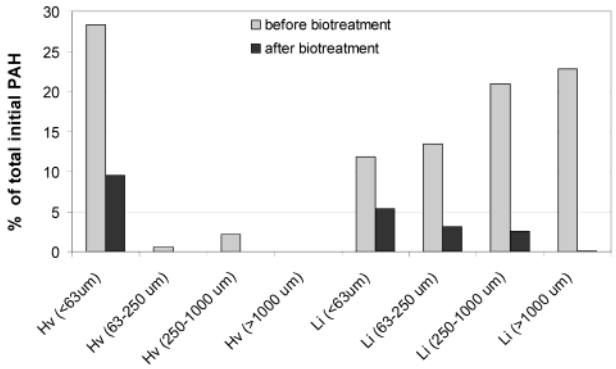


FIGURE 8. PAH loss from Harbor Point sediment for size and density fractions during 2 months of aerobic bioslurry treatment showing losses from heavy (Hv) mineral fractions as well as light (Li) organic particle fractions.

PAH Desorption Kinetics. Abiotic desorption studies using Tenax resin were conducted with two size fractions (63−250 and 250−1000 μm) of the lighter density particles in Milwaukee Harbor and Harbor Point sediments. Results of these desorption studies are shown in Figure 9 where the fraction of PAHs released from the sediment particles after different times of desorption are plotted over a 8−10 day period. For the three most prominent PAHs that were degraded during biotreatment (phenanthrene, fluoranthene, and pyrene), 10−20% of the PAHs are desorbed in Milwaukee Harbor sediment as compared to 40−70% for Harbor Point sediment in the same time period. Thus, mass transfer of PAHs from the lighter density particles is much faster in Harbor Point sediment as compared to that in Milwaukee Harbor sediment. The striking difference in PAH desorption rates in the lighter density fraction of the two sediments explains the differences in extents of PAH biodegradation observed.

Microscale PAH Extraction from Organic Particle Types. Microscale extraction and analysis was performed on the different particle classes in Harbor Point and Milwaukee Harbor sediments to investigate further the association of PAHs with the lighter density carbonaceous particles in these two sediments. Individual particles of the lighter density fraction particles (250−1000 μm) were separated manually using a pair of fine-point tweezers under a microscope. The five types of carbonaceous particles separated out as shown in Figure S1 in the Supporting Information are coal tar pitch, charcoal, cenosphere, coal/coke, and wood (56%, 9%, 18%, 5%, and 12%, respectively, by weight). Coal petrography analysis performed on another set of particles confirmed the presence of these particle types (see Figure 3). Results of

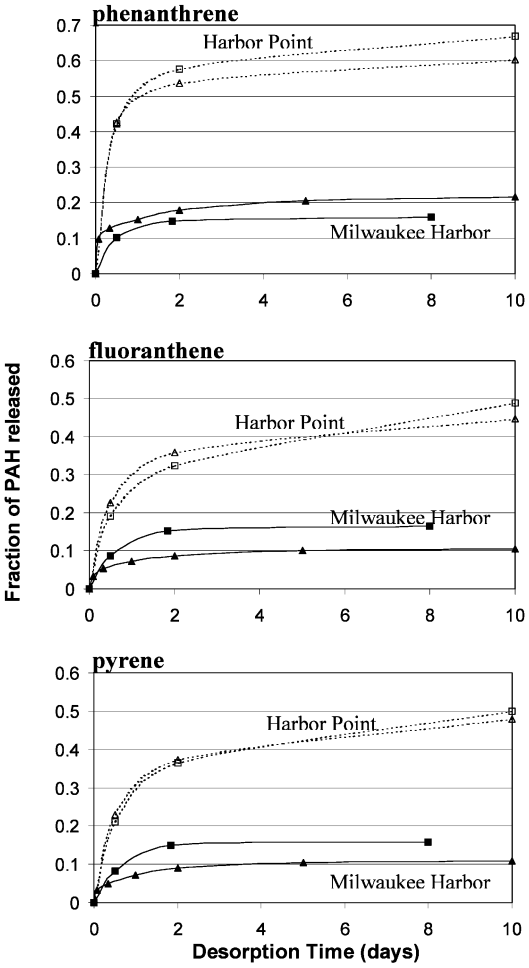


FIGURE 9. Desorption of PAHs from light-density fractions showing faster release of PAHs from Harbor Point sediment as compared to the Milwaukee Harbor sediment. The dashed lines and open symbols represent data for Harbor Point. Full lines and closed symbols represent data for Milwaukee Harbor. Triangles represent particle size 63−250 μm, and squares represent size 250−1000 μm.

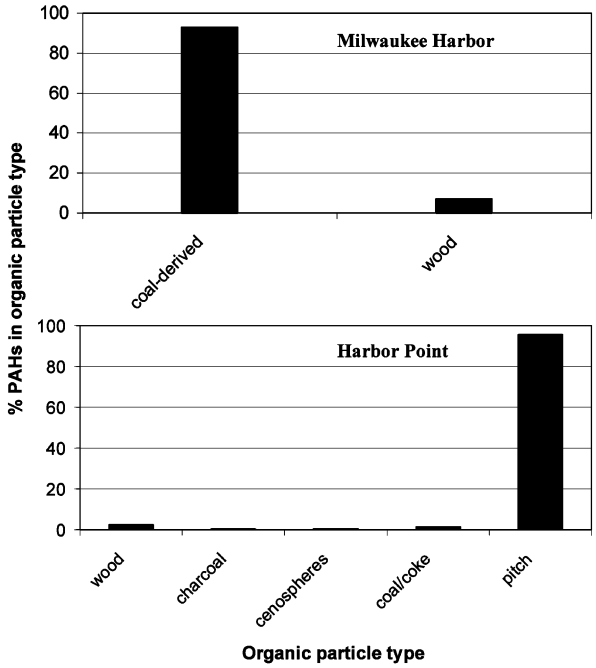


FIGURE 10. Microextraction and analysis of major organic particles classes in the 250−1000-μm size fraction showing the predominance of PAH association with coal-derived particles in Milwaukee Harbor and coal tar pitch particles in Harbor Point sediment.

extraction and microanalysis of carbonaceous particles from Milwaukee Harbor and Harbor Point sediment are shown in Figure 10. For Milwaukee Harbor, coal-derived particles (coal, partially oxidized coal, and coke) contributed 95% of the PAHs in the lighter density fraction (250−1000 μm). In contrast, coal tar pitch particles contributed 96% of the total PAHs in the Harbor Point sediment light density fraction (250−1000 μm). Contributions from the other types of particles amount to the remaining 4% of the PAHs. Although the individual particle separation and microscale PAH analyses were not possible for the smaller size fractions, visual observation under a microscope revealed a similar nature of particle distribution across particle sizes in the lighter density fraction. Thus, for Harbor Point sediment, the predominance of PAHs in the lighter density particles is due to the presence of PAH containing coal tar pitch particles. The implications from these observations are as follows:

PAHs sorbed on coal-derived particles and aged for years in the field (as seen in Milwaukee Harbor sediment) are strongly bound and not available for biodegradation, whereas PAHs associated with semisolid, coal tar pitch (as seen in Harbor Point sediment) are largely bioavailable. In the first case, PAHs are sorbed on highly aromatic, hard, coal-derived particles; in the second case, PAHs are partitioned into a softer coal tar pitch matrix and therefore more easily available for desorption. Our results from abiotic desorption tests show that PAHs desorb much faster when associated with pitch particles as compared to coal/coke particles. Log K_{oc} values for phenanthrene sorption on coals are reported to be 6.3−6.4 (*5*) as compared to a log K_{oc} of 5 for phenanthrene partitioning from coal tars (*23*) (assuming carbon content of coal tar to be 95%). Thus, based on equilibrium partitioning, PAHs associated with coal tar are much more available in the aqueous phase than PAHs sorbed on coals. The semisolid matrix of coal tar pitch may inhibit mass transfer rates but not as much as polymer-like diffusion in coals. Work by Ortiz et al. (*24*) reports solid-phase diffusivities for phenanthrene through solid paraffin in the order of 10^{-10} cm^2/s, which is orders of magnitude higher than estimated diffusivities of PAHs in coal matrix reported by us of 10^{-17} cm^2/s (*15*) and those reported by Karapanagioti et al. (*5*) of 10^{-14} cm^2/s. On the basis of the large differences in equilibrium partitioning and desorption rates between hard coal versus the softer semisolid pitch matrix and the fact that during bioslurry treatment some of the soft coal tar pitch particles may also undergo breakdown, it is not surprising that we see significantly higher extent of biotreatment in Harbor Point sediment as compared to Milwaukee Harbor sediment.

Several recent studies suggest the predominant role of soot carbon or black carbon in the sequestration of PAHs in sediments (*2*, *3*, *6*, *8*, *14*). Most of these studies use two separate observations: high sorption capacity of soot carbon and identification of soot carbon in sediments to infer that PAHs in sediment are actually associated primarily with the soot carbon, as equilibrium conditions would dictate. Nonetheless, there is little direct evidence that soot carbon in sediment indeed contains a major fraction of PAHs. Results of this study illustrate the importance of direct measurements at the particle scale to understand the nature of PCB and PAH distribution in contaminated sediments. We show here that black carbon particles in aged, field sediments may accumulate PCBs. Furthermore, as shown in the case of Harbor Point sediment, even in the presence of black carbon (coal, coke, cenospheres, and charcoal), PAHs may remain primarily associated with original source materials such as coal tar pitch and may be available to microorganisms for biodegradation.

Acknowledgments

We acknowledge funding for this research from the Department of Defense through the Strategic Environmental Research and Development Program (Contract DACA72-01-C-0002) and the Gas Technology Institute (Contract 2863).

Supporting Information Available

Additional light microscopy images of representative organic particle types in Harbor Point sediment and additional data on PCB and PAH distributions in the three sediments. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) *Sediment Quality Criteria for the Protection of Benthic Organisms: Phenanthrene*; U.S. Environmental Protection Agency, Office of Water: Washington, DC, 1993; EPA-882-R-93-014.
(2) Gustafsson, O.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. *Environ. Sci. Technol.* **1997**, 203−209.
(3) Grathwohl, P. *Environ. Sci. Technol.* **1990**, *24*, 1687−1693.
(4) Ghosh, U.; Luthy, R. G.; Gillette, J. S.; Zare, R. N. *Environ Sci Technol.* **2000**, *34*, 1729−1736.
(5) Karapanagioti, H. K.; Kleineidam, S.; Sabatini, D. A.; Grathwohl, P.; Ligouis, B. *Environ. Sci. Technol.* **2000**, *34*, 406−414.
(6) Accardi-Dey, A.; Gschwend, P. M. *Environ. Sci. Technol.* **2002**, *36*, 21−29.
(7) Walters, R. W.; Luthy, R. G. *Environ. Sci. Technol.* **1984**, *18*, 395−403.
(8) Gustafsson, O.; Gschwend, P. M. In *Molecular Markers in Environmental Geochemistry*; Eganhouse, R. P., Ed.; ACS Symposium Series 671; American Chemical Society: Washington, DC, 1997; pp 365−381.
(9) Gaboriau, H.; Saada, S. *Chemosphere* **2001**, *44*, 1633−1639.
(10) Chiou, C. T.; Groddy, S. E. M.; Kile, D. E. *Environ. Sci. Technol.* **1998**, *32*, 264−269.
(11) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241−248.
(12) Salloum, M. J.; Chefetz, B.; Hatcher, P. G. *Environ. Sci. Technol.* **2002**, *36*, 1953−1958.
(13) Bucheli, T. D.; Gustafsson, O. *Environ. Sci. Technol.* **2000**, *34*, 5144−5151.
(14) Schmidt, M. W. I.; Noack, A. G. *Global Biogeochem. Cycles* **2000**, *14*, 777−793.
(15) Ghosh, U.; Talley, J. W.; Luthy, R. G. *Environ. Sci. Technol.* **2001**, *35*, 3468−3475.

(16) Talley, J. W.; Ghosh, U.; Tucker, S. G.; Furey, J. S.; Luthy, R. G. *Environ. Sci. Technol.* **2002**, *36*, 477−483.
(17) *Site Investigation Report for Yosemite Creek, Submitted to City and County of San Francisco Public Utilities Commission*; Arthur D. Little: San Francisco, CA, 2000.
(18) Hetzel, F. *PCBs in San Francisco Bay: Sources and Loadings Progress Report*; California Regional Water Quality Control Board, SF Bay Region: San Francisco, CA, 2000.
(19) Bowman, D. W. *Water Quality '96*, Proceedings of the 11th Seminar, Seattle, WA; U.S. Army Corps of Engineers.
(20) Mullin, M. *PCB Congener Quantification for Lake Michigan Mass Balance Study*; EPA National Health and Environmental Effects Research Laboratory: Grosse Ile, MI, 1994.
(21) Gray, R. J. *Org. Geochem.* **1991**, *17*, 535−555.
(22) Rockne, K. J.; Shor, L. M.; Young, L. Y.; Taghon, G. L.; Kosson, D. S. *Environ. Sci. Technol.* **2002**, *36*, 2636−2644.
(23) Ramaswami, A.; Ghoshal, S.; Luthy, R. G. *Environ. Sci. Technol.* **1997**, *31*, 2268−2276.
(24) Ortiz, E.; Kraatz, M.; Luthy, R. G. *Environ. Sci. Technol.* **1999**, *33*, 235−242.

Received for review July 15, 2002. Revised manuscript received March 11, 2003. Accepted March 12, 2003.

ES020833K

Appendix II.

Microscale Detection of Polychlorinated Biphenyls Using Two-Step Laser Mass Spectrometry

by

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Abstract

Microprobe two-step laser desorption/laser ionization mass spectrometry (μL^2MS) is used as a new analytical technique for the detection of polychlorinated biphenyls (PCBs). Three standard Aroclor solutions (Aroclor 1232, 1242, and 1262) and three samples of activated carbon spiked with Aroclor 1242 are examined. All the PCBs present in the Aroclor solutions are clearly identified using μL^2MS. The distribution of the peaks follows the relative natural abundances of the carbon and chlorine isotopes. μL^2MS analyses of the spiked particles of activated carbon reveal the presence of PCBs and an abundance of polycyclic aromatic hydrocarbons. The detection limit for PCBs on solid surfaces is determined to be between 1 and 10 ppm. Because the spatial resolution of the μL^2MS instrument varies between 10 and 40 microns, PCB information at the sub-particle scale can be obtained.

Keywords: Two-step laser mass spectrometry, polychlorinated biphenyls, microscale characterization.

1. Introduction

Polychlorinated biphenyls (PCBs) have been used widely in industry as heat transfer fluids, hydraulic fluids, solvents, extenders, flame retardants, organic diluents, and dielectric fluids. Such historic use has led to widespread release into the environment. Because PCBs are not easily biodegraded, they accumulate in natural food chains. A recent study of PCBs in butter produced in 23 countries has demonstrated the large-scale transport and bioaccumulation of this persistent organic compound (1). PCBs have been implicated in a number of disease states, from infertility to carcinogenicity (2, 3). Presently, experts cannot agree on approaches to solve the problem of PCB bioaccumulation because of the interplay between complex physical and biological factors. PCBs are highly hydrophobic compounds and tend to bind strongly with soil or sediment particles. Some of the fundamental challenges in managing PCB-contaminated sediments include understanding how PCBs bind to different sediment components, how benthic organisms and particle feeders bioaccumulate PCB contaminants, what are the natural processes governing sediment-particle interactions and dispersion, and how bioavailable are PCBs bound to sediments.

Significant advances in recent decades have helped unravel the complexity of transfer of PCBs among different trophic levels of an ecosystem (4). Nevertheless, a major deficiency in understanding system functioning exists because of a lack of fundamental knowledge of physicochemical and biological complexity at the particle level. Specifically, we lack knowledge of how PCBs bind to different geochemical components of the sediment and how that affects the transfer of PCBs from sediment

particles to the benthic feeders, and from there to higher organisms. Particle-scale availability of PCBs also affects the rates of natural attenuation through microbial processes and sequestration through burial processes. Thus, fundamental knowledge of PCB location and association with soil/sediment particles is key to unraveling the mechanism that governs the release from the sorbed state and accumulation in organisms.

Most PCB analytical techniques available to date, such as US EPA method 8082, rely on solvent extraction and analysis of bulk soil or sediment material (5). These tests do not provide information on the particle-selective behavior of PCB binding. Recent work by Ghosh *et al.* (6) has illustrated the significance of understanding the nature of binding of polycyclic aromatic hydrocarbons (PAHs) to sediment particle classes. Their results showed that sediment from Milwaukee Harbor (USA) comprised two principal particle classes for PAHs, coal-derived and clay/silt, each having much different PAH levels, release rates, and desorption activation energies. PAH sorption on coal-derived particles is associated with slow release rates, and high desorption activation energies, while PAH sorption on clay/silt particles is associated with significant potential biodegradability, relatively fast release rates, and lower desorption activation energies (7). These characteristics are attributed to fundamental differences in the organic matter to which the PAHs are sorbed. Although the majority of the PAHs are found preferentially on coal-derived particles, the PAHs on the clay/silt sediment fraction are more mobile and available, and thus potentially of greater concern. A similar microanalytical tool for *in situ* PCB abundance measurements at the sub-particle scale is therefore vital to understanding the fundamental nature of PCB binding and release from sediment particle classes.

Microprobe two-step laser desorption/laser ionization mass spectrometry (μL^2MS) was used for the *in situ* detection and microscale characterization of PAHs in the work on the Milwaukee Harbor Sediment mentioned above. This technique is highly versatile and powerful. By making minor modifications to the experimental setup it is likely to be ideal for PCB analyses as well. Early, preliminary work on PCB detection was reported in the Ph.D. thesis of Clemett (8); this study extends his effort. In the first step of μL^2MS, the output of a pulsed infrared (IR) laser is focused on the sample. This causes rapid heating in the spot area and thereby releases a plume of neutral molecules. In the second step, the output of a pulsed ultraviolet (UV) laser causes (1+1) resonance-enhanced multiphoton ionization (REMPI) of those desorbed molecules that are able to absorb this radiation and whose ionization potential is less than the energy of two photons at this wavelength. The resulting ions are then mass analyzed in a reflectron time-of-flight (TOF) mass spectrometer. The use of a laser to volatilize neutral molecules and the subsequent laser photoionization enables the *in situ* analysis of samples; and this procedure eliminates the sample preparation, extraction, purification, and separation steps that are involved in other techniques.

In a μL^2MS experiment, sampling occurs from a circular spot of micron dimensions. The surface being analyzed is visualized through a microscope objective that is connected to a video monitor. The exact size of the spot is determined by how tightly the IR laser beam can be focused onto the sample. This, in turn, depends primarily on the wavelength of the IR laser, its spatial beam properties, and the working distance of the microscope objective that is used to focus the beam. Depending on whether a CO_2 or Er:YAG laser is used for desorption, the analysis spot of the current

μL^2MS configuration has a diameter of 40 or 10 μm respectively. By translating the sample under the microscope objective, it should be possible to generate spatial maps of the PCBs on the surface. Because a complete mass spectrum can be obtained from a single analysis spot, spatial maps of all the masses can be acquired simultaneously.

The objectives of the present work are to evaluate whether the μL^2MS technique is capable of identifying PCBs and to assess the utility of μL^2MS for *in situ* microscale detection of PCBs on heterogeneous sediment surfaces.

2. Experimental Section

2.1. Samples

Aroclors 1232, 1242, and 1262 were obtained from Ultra Scientific, USA. The structures and approximate percents of the different PCBs in these samples are given in Table 1. The compositions of Aroclor 1232 and 1262 were determined by using gas chromatography with electron capture detection. Data for Aroclor 1242 was obtained from a study by Fiedler (9). The solutions were prepared in hexane at a concentration of 100 μg/ml. Fifty microliters of each solution was evaporated on a glass plate for μL^2MS analysis. In addition, three samples of activated carbon were spiked with Aroclor 1242 at concentrations of 1, 10, and 100 ppm. This spiking was done by adding the appropriate amounts of Aroclor solution in hexane to the particles, and allowing the solvent to dry overnight.

2.2. mL^{2}MS Technique

The μL^{2}MS instrument has been described in detail elsewhere (10, 11). The sample to be analyzed is placed on a brass platter that is 7 mm in diameter, and introduced into the instrument through a vacuum interlock. The instrument is evacuated to 2 x 10^{-8} torr in five minutes. IR light from either a pulsed CO_2 (Alltech AL 853; 10.6 μm) or an Er:YAG laser (Big Sky Laser 571 A; 2.94 μm) is focused using a Cassegrainian microsocope objective, causing constituent molecules on the sample's surface to be desorbed. The IR laser power is kept low, ~ 2.5 x 10^6 W/cm^2, to avoid plasma formation, minimize decomposition, and ensure the desorption of only neutral species. After an appropriate time delay (25 μs) during which the desorbed molecules move into the extraction region, the output from a pulsed Nd:YAG laser (Spectra Physics DCR11; 212 nm) intersects the gas plume causing only certain compounds to be selectively ionized. The 212 nm light is generated through frequency mixing of the Nd:YAG fundamental at 1.064 μm with the fourth harmonic at 266 nm in a barium borate crystal. The UV laser pulse intensity, ~1.25 x 10^6 W/cm^2, is chosen to maximize parent ion signal while minimizing fragmentation. The ions produced are extracted from the source and injected into the reflectron TOF mass spectrometer using a series of charged plates in a modified Wiley-McLaren geometry (12). A 20 cm^2 active area dual micro-channel plate detector is used in a Chevron configuration to detect the ions. The output of the detector passes through a fast preamplifier (LeCroy VV100BTB) and a timing filter (Ortec 474) and is displayed on a digital oscilloscope (LeCroy 9450). The

resulting signal is averaged in the oscilloscope with subsequent laser shots, and is transferred to a computer.

3. Results and Discussion

3.1. Aroclor Solutions

Figure 1 shows the μL^2MS spectra (50-shot average) of solutions of Aroclor 1232, 1242, and 1262 evaporated on glass plates. The peaks marked correspond to the compounds listed in Table 1. Each PCB in the mixture is isotopically resolved as its parent ion. The PCB compounds have unique mass distributions that differ dramatically from those of PAHs and other compounds. This feature becomes particularly important when complex mixtures are examined because it is likely that other compounds with similar masses to those of the PCBs are present. There are some extra peaks, probably from contaminants, in the spectrum of Aroclor 1242.

Figure 2 presents the spectra predicted for dichloro-, tetrachloro- and heptachloro-biphenyls based on values of the natural abundances of the chlorine and carbon isotopes. These spectra are compared with corresponding μL^2MS spectra. The results indicate that the peak distributions that we obtain experimentally are very similar to the ones expected, implying that the integrity of the isotopic ratios is retained during μL^2MS analyses.

From Figure 1 it is evident that μL^2MS detects all the PCB congeners of one mass in a single peak. In most of the conventional techniques used for PCB analysis, the isomers of a given PCB series are chromatographically separated. For molecules with

large number of isomers, however, the separation effectively lowers the detection sensitivity. μL^2MS does not face a similar problem. In an ideal situation it would be beneficial to use μL^2MS in tandem with some technique that gives clear isomer separation and identification. The complementary information obtained would provide a complete understanding of the PCBs present in the sample.

The prominent PCBs identified in Aroclor 1232, 1242, and 1262 respectively during μL^2MS analysis [Figure 1] are consistent with the information in table 1. μL^2MS is not used to obtain quantitative information on the relative abundances or absolute concentrations of compounds present in a sample. This is because the intensities of μL^2MS peaks are not only a reflection of the concentration of the compound in the sample but also depend on the volatility and the photoionization cross section of the species at a particular laser ionization wavelength. The photoionization cross sections of different PCBs have not been characterized for our instrument as yet.

Some experiments were performed using 266 nm light for photoionization as well. PCBs were identified even at this longer wavelength, but the signal intensity markedly dropped. This signal decrease results from PCB molecules being more readily resonantly photoionized by the more energetic photons at 212 nm.

3.2. Samples of Activated Carbon Spiked with Aroclor 1242

Particles of activated carbon were spiked with Aroclor 1242 to determine the effect of the substrate in μL^2MS analysis of PCBs. Activated carbon was chosen because

it is well known that PCBs bind very strongly to this material, and it is likely that PCBs bind to soils and sediments in a similar manner.

Figure 3 shows the μL^2MS spectrum of activated carbon particles spiked with 10 ppm of Aroclor solution. The spectrum is, once again, a 50-shot average, and the sample was repositioned between laser shots so that desorption occurred from a fresh portion of the surface every time. Two distinct mass envelopes appear, one corresponding to PAHs of lower molecular weight and the other corresponding to the PCBs added. The main PAHs present include naphthalene (128 Da), acenaphthene (154 amu), phenanthrene/anthracene (178 Da), and their alkylated counterparts and the PCBs marked in the spectrum correspond to the ones mentioned in table 1. Although PAHs are not expected to be present in pure activated carbon, this particular sample may have been exposed to laboratory air for an extended period resulting in sorption of some of the volatile PAHs. The presence of PCB peaks in spectra of the activated carbon particles demonstrates the feasibility of using μL^2MS to detect PCBs bound to solid substrates. The PCB peak distribution for this sample differs from that of the Aroclor solution evaporated on a glass plate [Figure 1(b)]. Higher molecular weight PCBs, such as the tetrachloro- and pentachloro- biphenyls, seem to bind more strongly to the solid substrate than ones of lower molecular weight.

In Figure 3 the μL^2MS signal intensity for the PAHs is much greater than that for the PCBs. This difference implies that the instrument is either much more sensitive to PAHs than PCBs, or activated carbon sample is richer in PAHs than PCBs. We routinely use 266 nm of photoionization light for PAHs. It is not surprising that we see these compounds even at 212 nm because it is known that the intermediate excited state of

PAHs, that corresponds to a $\pi \rightarrow \pi^*$ transition, typically has two broad multi-modal distributions in the 210-230 nm and 260-280 nm wavelength ranges. The extinction coefficients for the shorter wavelength transition tend to be larger, and so photoionization at 212 nm offers a greater sensitivity to PAHs. The fact that the shorter wavelength reduces the species selectivity of the ionization event may compromise the ease of μL^2MS spectral analyses in some situations. Fortunately, PCBs have such distinct peak distributions during μL^2MS analysis that we can confidently identify them in complex spectra.

In order to determine the detection sensitivity of the μL^2MS technique, two additional activated carbon samples spiked with 100 and 1 ppm of PCBs were analyzed. For the 100 ppm particles, distinct PCB peaks are present. At 1 ppm, the μL^2MS spectrum still shows the PCB peaks, but the signal/noise ratio drops below the detection limit. Thus, we conclude that the detection limit for our current experimental setup is in the range of 1 to 10 ppm. The uniform decrease in μL^2MS signal as we go from a highly concentrated sample to one with trace amounts of PCBs implies that semi-quantitative analysis of relative PCB abundance on different particles in a sample may be assessed using the μL^2MS technique.

4. Conclusions

The μL^2MS technique is a very powerful and highly versatile microanalytical technique that has successfully been used to study a wide range of compounds such as

polycyclic aromatic hydrocarbons (PAHs) (13-22), fullerenes (8, 23), porphyrins (24), dyes (25, 26), amino acids (27), and polymer additives (28, 29). In this study we extend the capabilities of μL^2MS to detect PCBs.

Using 212 nm light for photoionization, PCBs were identified in the three Aroclor solutions examined. The PCB molecules have distinct signatures in the μL^2MS spectra, which are unique for the PCB compound being examined and differ dramatically from PAHs or other compounds likely to be present in soils and sediments. The results of the experiments in which activated carbon particles were spiked with PCBs indicate that μL^2MS is a feasible technique for PCB detection on solid substrates. Furthermore, the detection sensitivity of the current μL^2MS configuration for PCBs is determined to be between 1 and 10 ppm. With this capability to detect PCBs, future work can be carried out to establish what correlations exist between PCB location on a sediment particle and the type of organic matter present.

Acknowledgments

Funding and technical support for this research was obtained from the Department of Defense through the Strategic Environmental Research and Development Program (Contract number DACA72-01-C-0002).

References

(1) O.I. Kalantzi, R.E. Alcock, P.A. Johnston, D. Santillo, R.L. Stringer, G.O. Thomas, K.C. Jones, Environ. Sci. Technol. 35 (2001) 1013.

(2) United States Environmental Protection Agency, Doc. No. EPA 440/5-90-068, Office of Water: Washington, D. C., 1980.

(3) United States Enviornmental Protection Agency, Doc. No. EPA-823-F-99-019, Office of Water: Washington, D. C., 1999.

(4) J.W. Nichols, C.P. Larsen, M.E. McDonald, G.J. Niemi, G.T. Ankley, Environ. Sci. Technol. 29 (1995) 604.

(5) United States Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Office of Solid Waste: Washington, D. C., 2000.

(6) U. Ghosh, J.S. Gillette, R.G. Luthy, R.N. Zare, Environ. Sci. Technol. 34 (2000) 1729.

(7) J.W. Talley, U. Ghosh, S.G. Tucker, J.S. Furey, R.G. Luthy, Environ. Sci. Technol. (2001) in press.

(8) S.J. Clemett, Ph.D. thesis, Stanford University, Stanford, 1996.

(9) H. Fiedler, Proceedings of the UNEP Regional Awareness Raising Workshop on Persistent Organic Pollutants, Abu Dhabi, United Arab Emirates, 1998.

(10) S.J. Clemett, R.N. Zare, Molecules in Astrophysics: Probes and Processes, Dishoeck, E.F., Ed. ; Leiden, Netherlands, 1997, p. 305.

(11) R. Zenobi, R.N. Zare, Advances in Multiphoton Processes and Spectroscopy, Lin, S. H., Ed.; World Scientific: Singapore, 1991; Vol. 7, p. 1.

(12) W.C. Wiley, I.H. McLaren, Rev. Sci. Instrum. 26 (1955) 1150.

(13) R. Zenobi, J.M. Philippoz, P.R. Buseck, R.N. Zare, Science 246 (1989) 1026.

(14) D.S. McKay, E.K. Gibson, K.L. Thomas-Keprta, H. Vali, C.S. Romanek, S.J. Clemett, X.D.F. Chillier, C.R. Maechling, R.N. Zare, Science 273 (1996) 924.

(15) L.J. Kovalenko, C.R. Maechling, S.J. Clemett, J.M. Phillipoz, R.N. Zare, C.M.O.D. Alexander, Anal. Chem. 64 (1992) 682.

(16) S.J. Clemett, C.R. Maechling, R.N. Zare, P.D. Swan, R.M. Walker, Lunar and Planet. Sci. XXIV (1993) 309.

(17) M.J. Dale, A.C. Jones, S.J.T. Pollard, P.R.R. Langridge-Smith, Analyst 119 (1994) 571.

(18) M.J. Dale, A.C. Jones, S.J.T. Pollard, P.R.R. Langridge-Smith, A.G. Rowley, Environ. Sci. Technol. 27 (1993) 1693.

(19) J.S. Gillette, R.G. Luthy, S.J. Clemett, R.N. Zare, Environ. Sci. Tech. 33 (1999) 1185.

(20) S.M. Hankin, P. John, Anal. Chem. 71 (1999) 1100.

(21) O.P. Haefliger, T.D. Bucheli, R. Zenobi, Environ. Sci. Technol. 34 (2000) 2178.

(22) Q. Zhan, P. Voumard, R. Zenobi, Rapid Commun. Mass Spectrom. 9 (1995) 119.

(23) L. Becker, T.E. Bunch, L.J. Allamandola, Nature 400 (1999) 227.

(24) M.J. Dale, K.F. Costello, A.C. Jones, P.R.R. Langridge-Smith, J. Mass Spectrom. 31 (1996) 590.

(25) M.J. Dale, A.C. Jones, P.R.R. Langridge-Smith, K.F. Costello, P.G. Cummings, Anal. Chem. 65 (1993) 793.

(26) M.J. Dale, Q. Zhan, R. Zenobi, K. Costello, P.R.R. Langridge-Smith, Analytical Methods and Instrumentation 2 (1995) 101.

(27) F. Engelke, J.H. Hahn, W. Henke, R.N. Zare, Anal. Chem. 59 (1987) 909.

(28) Q. Zhan, R. Zenobi, S.J. Wright, P.R.R. Langridge-Smith, Macromolecules 29 (1996) 7865.

(29) S.J. Wright, M.J. Dale, P.R.R. Langridge-Smith, Q. Zhan, R. Zenobi, Anal. Chem. 68 (1996) 3585.

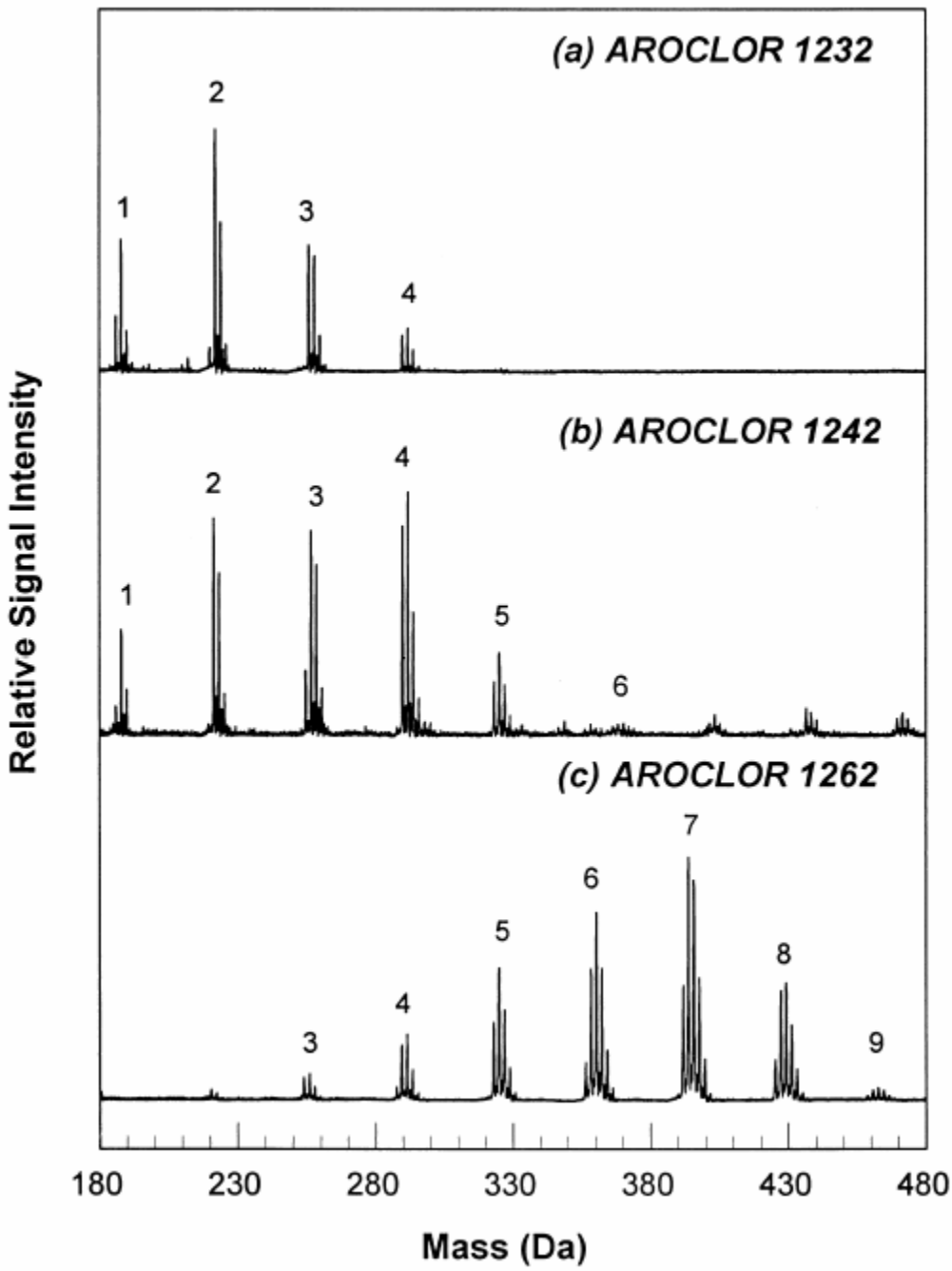


Figure 1. μL^2MS spectra of the PCB mixtures (a) Aroclor 1232 (b) Aroclor 1242 and (c) Arocolor 1262.

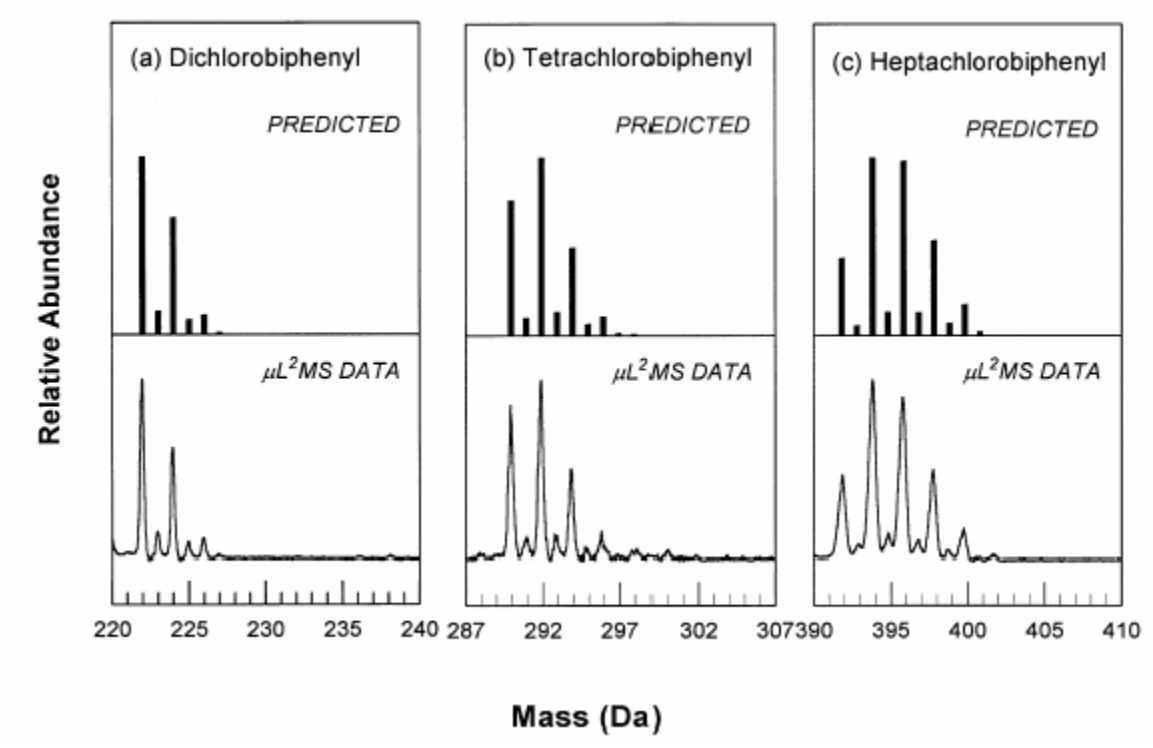


Figure 2. Predicted peak distributions and corresponding μL^2MS spectra of (a) dichlorobiphenyl (b) tetrachlorobiphenyl and (c) heptachlorobiphenyl. The appropriate regions of figure 1 were expanded to depict the experimental data.

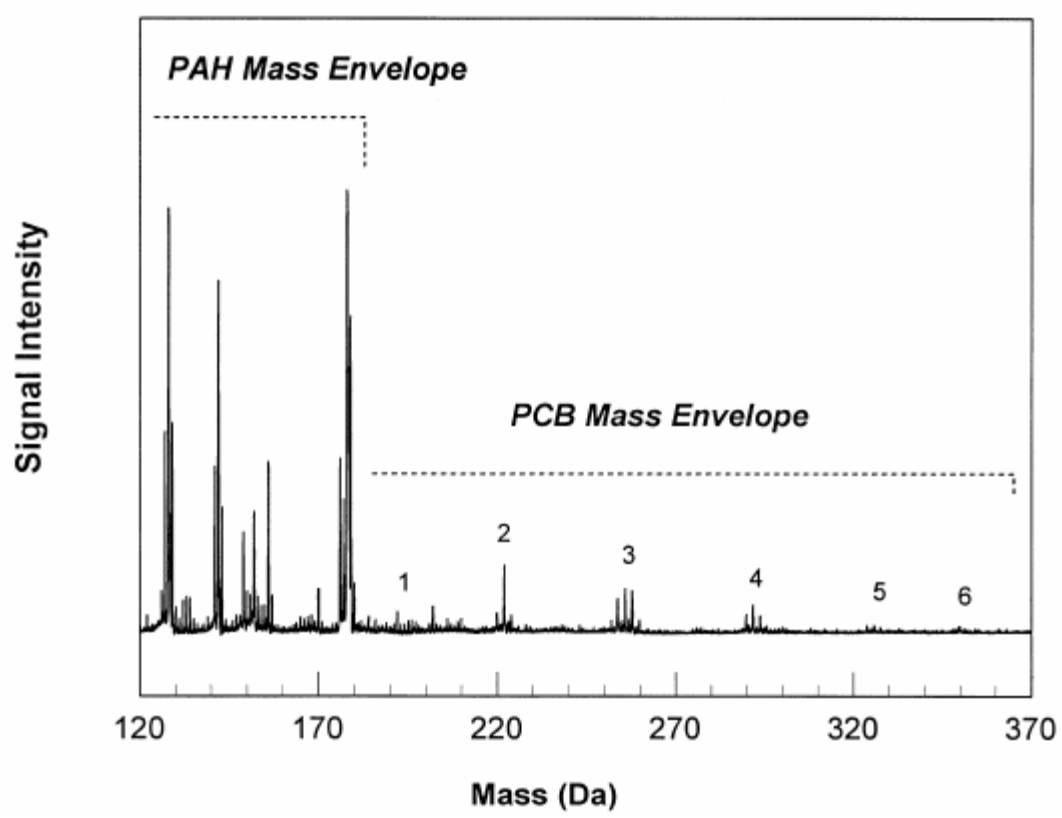
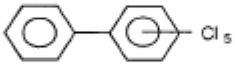
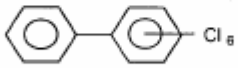
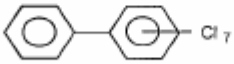
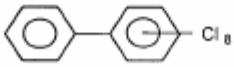


Figure 3. μL^2MS spectrum of activated carbon particles spiked with 10 ppm of Aroclor 1242.

Table 1. Structures of PCBs and composition of commercial aroclor mixtures 1232, 1242, and 1262.

PCB	STRUCTURE	PERCENTAGE IN		
		1232	1242	1262
1. Monochlorobiphenyl		12	3	n.d.
2. Dichlorobiphenyl		28	13	n.d.
3. Trichlorobiphenyl		32	28	n.d.
4. Tetrachlorobiphenyl		24	30	n.d.
5. Pentachlorobiphenyl		4	22	1
6. Hexachlorobiphenyl		n.d.	4	27
7. Heptachlorobiphenyl		n.d.	n.d.	46
8. Octachlorobiphenyl		n.d.	n.d.	23
9. Nonachlorobiphenyl		n.d.	n.d.	3

n.d.: not detected

Appendix III.

Published paper

Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments. Physicochemical Tests.

by

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Environmental Science and Technology 38: 5458-5464, 2004

Environ. Sci. Technol. **2004**, *38,* 5458−5464

Addition of Carbon Sorbents to Reduce PCB and PAH Bioavailability in Marine Sediments: Physicochemical Tests

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The addition of activated carbon as particulate sorbent to the biologically active layer of contaminated sediment is proposed as an in-situ treatment method to reduce the chemical and biological availability of hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). We report results from physicochemical experiments that assess this concept. PCB- and PAH-contaminated sediment from Hunters Point Naval Shipyard, San Francisco Bay, CA, was contacted with coke and activated carbon for periods of 1 and 6 months. Sediment treated with 3.4 wt % activated carbon showed 92% and 84% reductions in aqueous equilibrium PCB and PAH concentrations, 77% and 83% reductions in PCB and PAH uptake by semipermeable membrane devices (SPMD), respectively, and reductions in PCB flux to overlying water in quiescent systems up to 89%. Adding coke to contaminated sediment did not significantly decrease aqueous equilibrium PCB concentrations nor PCB or PAH availability in SPMD measurements. Coke decreased PAH aqueous equilibrium concentrations by 38−64% depending on coke dose and particle size. The greater effectiveness of activated carbon as compared to coke is attributed to its much greater specific surface area and a pore structure favorable for binding contaminants. The results from the physicochemical tests suggest that adding activated carbon to contaminated field sediment reduces HOC availability to the aqueous phase. The benefit is manifested relatively quickly under optimum contact conditions and improves in effectiveness with contact time from 1 to 6 months. Activated carbon application is a potentially attractive method for in-situ, nonremoval treatment of marine sediment contaminated with HOCs.

Introduction

Contamination of marine sediments with hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) is a concern at numerous harbors, estuaries, lakes, and rivers throughout the world. Approximately 10% of the sediment underlying surface waters in the United States poses potential risks to fish and to humans and wildlife that consume fish (*1*). Current approaches to contaminated sediment remediation rely heavily on dredging and disposal. Often this is very expensive and may temporarily increase contaminant exposure as well as destroy wildlife habitat. Furthermore, even when sediments are removed from a site, some contamination inevitably remains, becoming a potential long-term threat for exposure (*2*).

Contaminated sediment management at Hunters Point Naval Shipyard, San Francisco, CA, has been studied for several years (*3*, *4*). A key area of concern is South Basin, a small inlet forming the southwestern border of the former shipyard. The inlet is also where storm sewer outfalls from an industrial area in San Francisco empty into the Bay. The San Francisco Bay Regional Water Quality Control Board reports that Hunters Point sediment contains up to 10.5 mg/kg total PCBs, one of the highest levels anywhere for the estuary (Fred Hetzel, San Francisco Bay Regional Water Quality Control Board, personal communication). Cleaning up contaminated sediment sites such as Hunters Point presents economic, environmental, and technical challenges; thus, innovative solutions are needed to meet sediment management cleanup goals while minimizing costs and environmental impacts. This paper describes results from physicochemical tests to evaluate a newly proposed method for in-situ treatment of HOCs in sediment that is based on addition of particulate carbon sorbent to sediment to achieve repartitioning and sequestering of PCBs and PAHs. This work builds on the discovery of the accumulation and strong binding of PAHs and PCBs in anthropogenic and naturally occurring particulate, black carbonaceous matter already present in sediments, which includes coal and charcoal in Hunters Point sediment (*5*, *6*).

Strong sorption to solids can reduce contaminant bioavailability to organisms. Talley et al. (*7*) found that sediment bioslurry treatment reduced PAH concentrations by 75% in the clay−silt fraction of sediment but did not reduce PAH concentrations in the lighter density, primarily coal-derived sediment fraction. In the same study, earthworms exposed to bioslurry-treated sediment accumulated 75% less PAHs than earthworms exposed to untreated sediment, which indicated that PAHs on the clay−silt sediment fraction were readily available to both microorganisms and to earthworms. Kraaij et al. (*8*) showed that treating contaminated sediment by contacting with Tenax for 48 h reduced both the fraction of readily desorbing PCBs and PAHs and the biota−sediment accumulation factors (BSAFs) in tubifex worms. The authors concluded that the reduction in BSAF values was caused by the Tenax treatment decreasing the rapidly desorbing fraction of PCBs and PAHs. Kosian et al. (*9*) and West et al. (*10*) added Ambersorb 1500 resin, a strong sorbent of hydrophobic organics, to sediment, which reduced PAH body burdens in *Lumbriculus variegatus*. Thus, results from several different studies with sediments and various organisms indicate that strong sorption to solids can reduce contaminant bioavailability.

The objective of this research was to investigate the effect of carbon addition in the form of coke and activated carbon on PCB and PAH availability in sediments. Changes in availability were measured through PCB aqueous flux and through PCB and PAH aqueous equilibrium and uptake in semipermeable membrane devices (SPMDs).

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10.1021/es034992v CCC: $27.50
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Published on Web 09/08/2004

Experimental Methods

Sediment−Sorbent Contact. A composite sample of sediment was obtained from the intertidal region of South Basin, adjacent to the former landfill at Hunters Point (37°43.44′ N, 122°22.62′ W to 37°43.38′ N, 122°22.54′ W). Sediment was screened in the field to remove gravel and debris larger than 4 mm diameter and stored at 4 °C. PCB by congener and PAH (16 Priority Pollutant List PAH) concentrations on sediment solids were measured using sonication with 1:1 hexane:acetone extraction followed by cleanup using silica gel and analysis with GC-ECD and GC-FID, following U.S. EPA Methods 3550B, 3630C, 8082, and 8100, as described by Ghosh et al. (*6*). Sediment total organic carbon (TOC) was measured by combustion in an elemental carbon analyzer (Microanalytical Laboratory, University of Illinois at Urbana−Champaign) following treatment with acid to remove carbonates (*11*). Hunters Point sediment had a TOC content of 1.7%. Coke used in these experiments was 1−2 mm coke breeze obtained from Ispat Inland, Inc., East Chicago, IL, identified as "coke 1881" (Dr. Hardarshan Valia, Ispat Inland Research Department). The coke was ground in a ball mill and sieved to obtain particles in the 63−105 μm (fine) and 105−250 μm (coarse) size ranges. Type TOG activated carbon (75−300 μm), derived from bituminous coal and obtained from Calgon Corporation (Pittsburgh, PA), was boiled in water for 5 min prior to use to remove any air pockets in pores. Wet Hunters Point sediment, equivalent to approximately 3.8 kg dry weight, was placed in 1-gal glass roller bottles, followed by addition of sorbent and approximately 300 mL of 17 ppt seawater. Five different sorbent treatments were set up: fine and coarse coke at two and five times existing sediment TOC content of 1.7% (3.4% and 8.5%) and activated carbon at two times TOC content (3.4%). Controls were set up with no sorbent. Bottles were rolled at approximately 3 rpm for 28 or 180 d (1 or 6 months). At the end of the contact period, wet sediment slurry was placed in amber glass bottles and stored in a cold room at 4 °C. These sorbent doses were selected as a starting point to assess treatment effectiveness. Subsequent work has examined the effect of lesser activated carbon dose and smaller particle size on PCB availability.

Aqueous Equilibrium. Equilibrium distribution of PCBs and PAHs between sediment and aqueous phases was measured by placing approximately 100 g of coke-treated or activated carbon-treated or untreated wet sediment in 1.9-L glass bottles with 17 ppt seawater and 1 g/L sodium azide (practical grade, Mallinckrodt, Paris, KY) to inhibit microbiological growth. The bottles were capped with Teflon-lined caps, shaken, and rotated at approximately 2 rpm on a roller for 14 d, after which the sediment−water mixture was allowed to settle and the supernatant cleared of any floating particles with a Pasteur pipet. Colloids were removed using the flocculation procedure described previously (*12*). PCBs and PAHs were extracted from the aqueous phase using liquid−liquid extraction with hexane. Extract cleanup with silica gel and PCB by congener and PAH (16 Priority Pollutant List PAH) analyses of extracts by GC-ECD and GC-FID from aqueous equilibrium, uptake by SPMD, quiescent flux, and desorption experiments were performed following U.S. EPA Methods 3630C, 8082, and 8100, as described previously (*6*).

SPMDs. SPMDs are a biomimetic tool to assess the chemical and biological availability of PAHs and PCBs in sediment and water (*13*−*17*). SPMDs were used in this work to study the effect of sorbent addition on PCB and PAH release from contaminated sediments. Custom-made SPMDs (EST, St. Joseph, MO) were 100 mm long and filled with 0.1 g of triolein, a component of fish lipid (*18*). Approximately 12 g of wet, untreated, coke-treated or activated carbon-treated sediment was added to 40-mL clear glass vials with 17 ppt seawater and 1 g/L sodium azide, leaving approximately 1 mL of headspace. One SPMD was folded in half and placed in each vial; the vials were sealed with Teflon-lined caps and set on a rotator at approximately 20 rpm for 14 d.

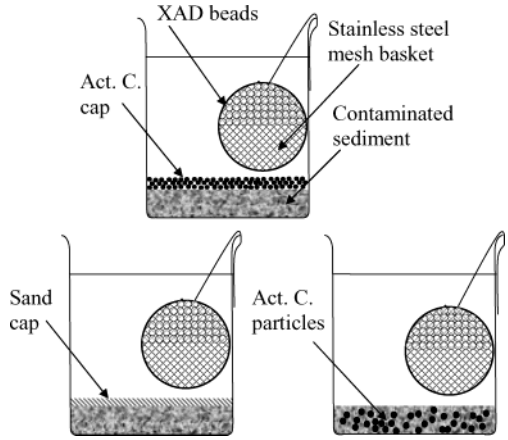

FIGURE 1. Quiescent sediment flux experimental setup with 17 ppt seawater. XAD resin beads are contained in stainless steel baskets suspended above the sediment.

After tumbling, the SPMDs were rinsed with deionized water; swirled for 30 s in 1 N hydrochloric acid (Fisher Scientific, Fair Lawn, NJ); rinsed with deionized water, acetone (pesticide grade, Fisher Scientific, Fair Lawn, NJ), and isopropyl alcohol (Mallinckrodt Baker, Paris, KY); and wiped and air-dried for approximately 30 s. The SPMDs were submerged in hexane and dialyzed at room temperature for 24 h. The dialysate was transferred to a second 250-mL bottle, and the dialysis with fresh hexane was repeated for 8 h. Dialysates were combined with hexane rinse, the total volume was recorded, and aliquots were taken for cleanup and analysis using methods described previously (*6*).

Quiescent Flux. Diffusive PCB flux from contaminated sediment was measured in quiescent systems with Amberlite XAD-4 (XAD) beads (20−60 mesh, Sigma Chemical Co., St. Louis, MO) suspended above the sediment in stainless steel mesh. XAD beads were cleaned using a methanol wash (pesticide grade, Fisher Scientific, Fair Lawn, NJ) and stirring periodically with a glass rod for 15 min; then draining and repeating three times each with methanol, 1:1 hexane: acetone, methanol, and deionized water; and then soaking in deionized water for 12 h. XAD beads were placed in precleaned stainless steel 40 mm diameter wire mesh baskets to about half full, clamped with stainless steel wire, and shaken in deionized water to remove beads smaller than wire mesh openings.

Quiescent sediment systems employed approximately 20 g wet sediment in 250-mL beakers filled to 200 mL with 17 ppt seawater with 1 g/L sodium azide. A schematic of the experiment setup is shown in Figure 1. Four systems were set up: (i) untreated sediment; (ii) sand-capped sediment; (iii) activated carbon-capped sediment; and (iv) carbon-contacted sediment with 3.4 wt % activated carbon. The sediment−water mixtures were allowed to settle for several days and then 2 g of sand or 1 g of activated carbon were sprinkled slowly over the sediment, forming a uniform layer over the undisturbed sediment approximately 2 mm thick. The mass of carbon in the cap was approximately 7% of the whole sediment dry mass. Following addition of the sorbent caps, stainless steel mesh baskets containing the XAD beads were suspended above the sediment or cap and secured to keep the basket in the correct location. Any XAD beads that may have escaped from the basket were removed with a Pasteur pipet. Beakers were then covered with foil and placed in a dark cabinet at room temperature for 35 d. The baskets were removed, and a second set of XAD in baskets was suspended in the beakers for 134 d. XAD beads were extracted

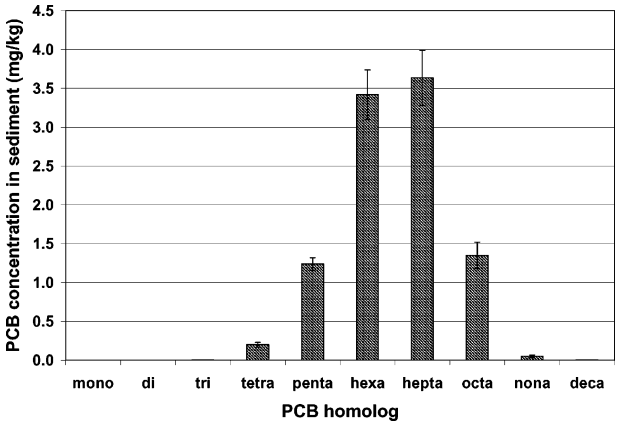

FIGURE 2. PCB concentration by homolog group for a composite sample of Hunters Point sediment. Error bars represent one standard deviation from the mean of three replicates.

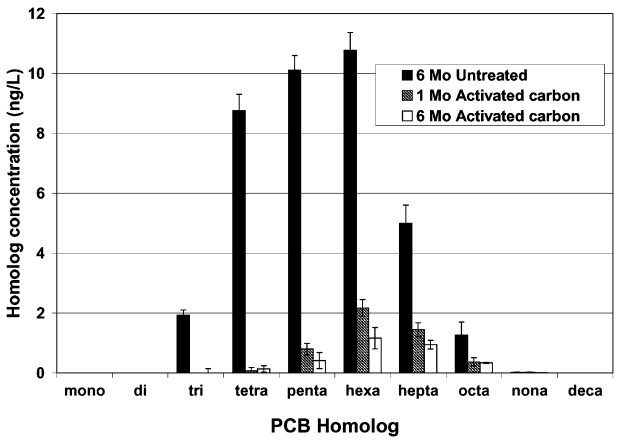

FIGURE 3. Aqueous PCB concentrations for 1- and 6-month contact periods with sediment containing 3.4 wt % activated carbon. Error bars represent one standard deviation from the mean of three replicates.

with 5 mL of 1:1 mixture of hexane:acetone, rotating end over end at approximately 2 rpm for 24 h, and repeating twice with hexane. The combined extracts were dried by adding a few grams of anhydrous sodium sulfate, concentrated to 1 mL, and cleaned and analyzed by the methods described previously (*6*).

PCB Desorption. PCB desorption kinetic studies with untreated Hunters Point sediment followed previously described procedures (*5*). Tenax beads (0.5 g) and sediment sample (5 g) were added to three 12-mL glass vials containing 10 mL of water and continuously mixed in a rotator. Sodium azide (1 g/L) was added to the mixture to prevent biological growth. At sampling times of 0, 1, 2, 3, 6, 14, 30, and 66 d, the Tenax beads were harvested by allowing the sediment to settle and the beads to float up, and then fresh beads were added. PCBs were extracted from the Tenax beads and analyzed by GC-ECD.

Results and Discussion

Reduction in PCB and PAH Aqueous Equilibrium Concentrations with Activated Carbon Addition. The total PCB concentration in composite, intertidal zone sediment samples was 9.9 ± 0.9 mg/kg (*6*). Figure 2 shows the distribution of PCBs by homolog group in Hunters Point sediment. The dominant PCBs in the sediment resemble Aroclor 1260 with hexa- and heptachlorbiphenyl homologs comprising 71% of the total PCBs. Figure 3 compares PCB concentrations by homolog group in the aqueous phase at equilibrium with

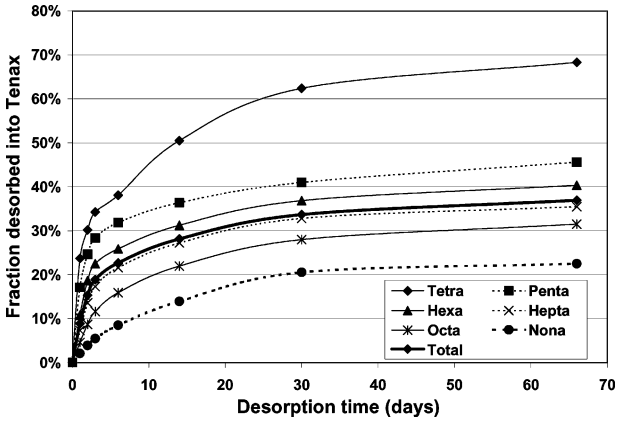

FIGURE 4. PCB desorption rates by homolog group for Hunters Point sediment.

untreated sediment and for sediment treated with 3.4% activated carbon for 1 or 6 months. At equilibrium the total aqueous concentration of PCBs is about 37 ng/L, mainly tetra-, penta-, and hexachlorobiphenyls. Compared to sediment, the aqueous samples show a shift toward lower molecular weight congeners due to their lower hydrophobicity and lesser tendency to sorb to sediment.

For activated carbon-treated sediment, the total aqueous PCB concentrations decreased by 87% and 92% for contact times of 1 and 6 months, respectively. This is a substantial reduction in aqueous PCBs and demonstrates under optimum conditions that activated carbon is a strong sorbent in sediment. With mixing, the effect of adding carbon to sediment on PCB aqueous equilibrium concentration is manifested relatively quickly and is not lost with time. Similar to the results with PCBs, adding activated carbon to sediment reduced aqueous equilibrium total PAH concentrations by 74% and 84% for 1- and 6-month contact periods, respectively.

The effect of activated carbon on lowering aqueous concentrations of PCBs is greatest for tetra- and pentachlorobiphenyl homologs, diminishing for hexa- and heptachlorobiphenyls. This is most likely due to the slower rate of release from sediment and slower rate of uptake by carbon for higher chlorinated PCBs. We measured PCB desorption rates from Hunters Point sediment, and the results in Figure 4 are shown as the fraction of PCBs desorbed by homolog group. These data indicate desorption rate decreases with increasing degree of chlorination. Nearly 70% of the tetrachlorobiphenyls are released over 2 months as compared to about 35% of the heptachlorobiphenyls. This trend is shown also in Figure 5 by comparing the percent reduction in aqueous phase PCBs by homolog versus homolog log K_{ow} values (representative homolog log K_{ow} values from Erickson; *19*). Figures 4 and 5 are suggestive of a relation between the percent concentration reduction in the aqueous phase PCBs from addition of activated carbon and the extent of release of PCBs from the solid. The implications of these desorption results are discussed later in the context of other experimental results.

Effectiveness of Coke versus Activated Carbon in Reducing Aqueous Equilibrium Concentrations. Shown in Figure 6 is a comparison of total aqueous equilibrium concentrations of PCBs for 3.4% activated carbon-treated sediment with that for sediment treated with two size fractions of coke for applications at 3.4% and 8.5 wt % for 1- and 6-month contact periods. Coke has little or no effect on reducing aqueous equilibrium PCB concentrations over 6 months, compared to activated carbon achieving aqueous PCB concentration reductions of 87% and 92% for 1- and 6-month contact periods, respectively.

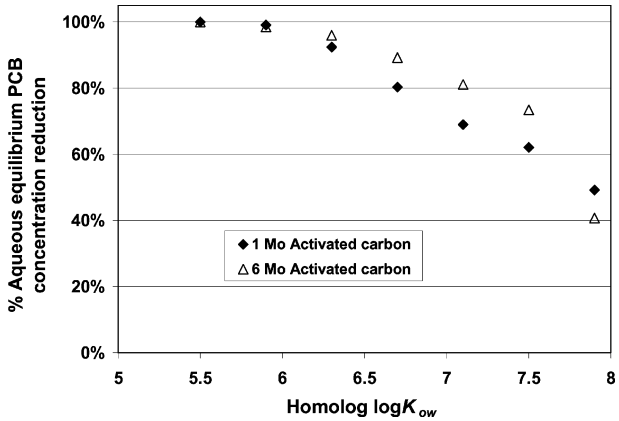

FIGURE 5. Comparison of reduction of PCBs in the aqueous phase by homolog log K_{ow} for sediment treated with 3.4% activated carbon and contacted for 1 and 6 months.

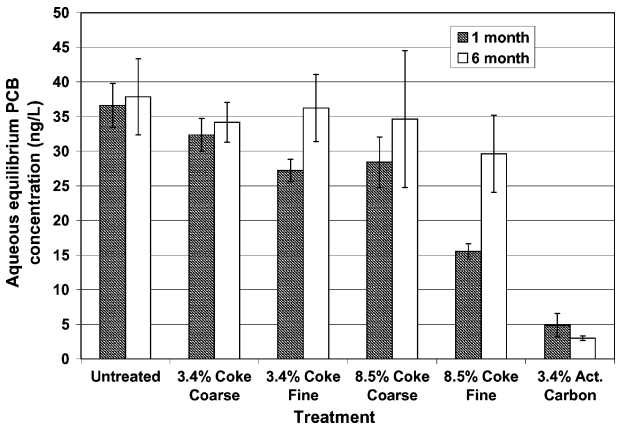

FIGURE 6. Total aqueous PCB concentration in untreated and treated sediment for contact times of 1 and 6 months with 3.4% activated carbon and different doses and sizes of coke particles. Error bars represent one standard deviation from the mean of three replicates.

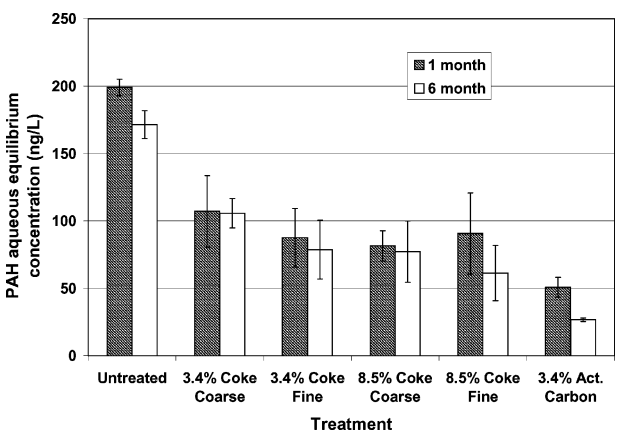

FIGURE 7. Total aqueous PAH concentration in untreated and treated sediment for contact times of 1 and 6 months with 3.4% activated carbon and different doses and sizes of coke particles. Error bars represent one standard deviation from the mean of three replicates.

Figure 7 shows total PAH aqueous equilibrium concentrations for untreated and coke-treated and activated carbon-treated sediment for 1- and 6-month contact periods. Coke reduced aqueous phase PAHs up to 64% over 6 months. The increased effectiveness of coke for reducing aqueous PAH concentrations, as compared to PCBs, is likely due to the stronger sorption of the planar PAH molecules to coke, which bears some structural resemblance to soot. Several studies show elevated PAH organic carbon partition coefficients (K_{oc}) in the presence of soot (*20*−*24*). Soot has been described as "particles of multilayered macro-PAHs" (*22*), and coke is considered to consist of layers of PAH-type molecules (*25*). The elevated partition coefficient values (K_{oc}) observed for PAHs and coplanar PCBs in the presence of soot have been attributed to a combination of the ability of planar molecules to lie flat on the surface of soot particles allowing overlap of π bonds and to a greater extent of pore sorption due to the ability of planar molecules to penetrate soot pores or interlayer spacings (*22*, *24*). Soot has greater porosity and specific surface area as compared to coke, approximately 8−59 m^2/g for soot (*24*) versus 3 m^2/g for our coke samples; the similarity in structural composition could explain why coke reduced PAH aqueous concentrations but did not affect aqueous concentrations of PCBs. A total of 94% of the PCBs measured in Hunters Point sediment are noncoplanar (i.e., containing more than one chlorine atom in ortho positions on the biphenyl rings). We did not see a significant difference in the behavior of coplanar and noncoplanar PCB congeners.

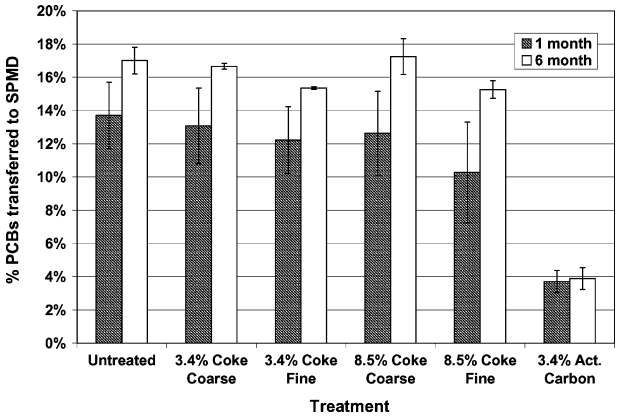

FIGURE 8. PCB uptake by SPMDs for treated and untreated sediment. The data are expressed as percent of total PCBs originally in the solid material transferred to the SPMD. Treatment times are 1 and 6 months with 3.4% activated carbon and different doses and sizes of coke particles. Error bars represent one standard deviation from the mean of three replicates.

Reduction in PCB and PAH Uptake in SPMDs. Figure 8 shows a comparison of total PCB uptake in SPMDs for untreated sediment and sediment contacted with coke or activated carbon for 1 or 6 months. Activated carbon-treatment reduced SPMD uptake by up to 77% and 83% for PCBs and PAHs, respectively. Coke had little or no effect on SPMD uptake of PCBs or PAHs (data not shown), which is likely due to its smaller specific surface area and its pore structure being less favorable for binding HOCs as compared to activated carbon, as discussed above. The PCB homolog distribution for uptake in the SPMDs is similar to that for the sediment with a predominance of hexa- and heptachlorobiphenyl homologs. Ninety-nine percent of total PCBs in the SPMDs are tetra- to octachlorobiphenyl homologs. Similar to our results from aqueous equilibrium experiments, the effectiveness of activated carbon addition in reducing uptake by SPMDs decreased with increasing degree of PCB congener chlorination.

Reduction in PCB Flux from Sediment to Water. The quiescent flux experiments assessed how activated carbon treatment affects PCB flux to overlying water. The tests compared sediment mixed with activated carbon for 1 month with sediment having carbon applied as a cap. Untreated sediment and sediment with a sand layer on top were evaluated as well. The XAD beads maintain a constant driving force for PCB release from sediment by providing an infinite sink for PCBs because of the beads' large sorption capacity and overwhelming affinity for HOCs.

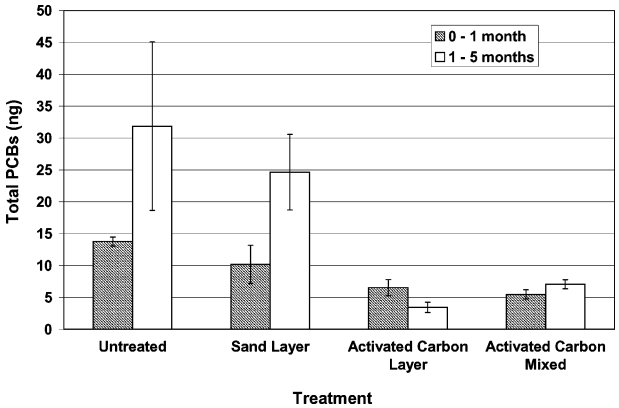

FIGURE 9. Cumulative uptake of PCBs by XAD beads in sequential quiescent flux tests of durations 1 and 4 months. The XAD beads were suspended above the sediments. Error bars represent one standard deviation from the mean of three replicates.

Figure 9 shows the reduction in PCB flux for 1 month (53%) and from 1 to 5 months (89%) for sediment with activated carbon applied as a top layer, compared to untreated sediment. In the case of activated carbon mixed with sediment for 1 month, the PCB flux is reduced by 60% in 1 month and 78% from 1 to 5 months, compared to untreated sediment. The activated carbon treatments are much more effective than a comparable mass of passive sand cap, which reduced PCB flux by 23% relative to untreated sediment over the interval from 1 to 5 months. In systems with either a thin layer of activated carbon or sand on top of the sediment, both act as diffusive barriers to overlying water, but the sand lacks the sorption capacity of carbon, thus hindering PCB diffusion through it to a lesser degree.

Comparison of Untreated Sediment Equilibrium Partitioning with Literature Values. Over limited concentration ranges, the partitioning of HOCs between sediment and water can be described in simple terms according to a solid−water distribution coefficient (K_d) based on the assumption that the partitioning depends primarily upon total organic carbon in the sediment (e.g., ref *26*):

$$\frac{C_s}{C_w} = K_d = f_{oc}K_{oc}$$

where C_s is the contaminant concentration on sediment solids (mg/kg), C_w is the aqueous contaminant concentration (mg/L), K_d is the solid−water distribution coefficient (L/kg), f_{oc} is the fraction of organic carbon in the sediment (−), and K_{oc} is the organic carbon-normalized partition coefficient (L/kg organic carbon). For HOCs, K_{oc} is often correlated with compound octanol−water partition coefficient, K_{ow}. Six expressions for estimating K_{oc} from K_{ow} values are shown in Table 1 in the Supporting Information for data sets that include PCBs. These relationships are discussed below in the context of the aqueous equilibrium experiments performed as part of our study.

K_d and K_{oc} were calculated for PCBs and PAHs in untreated Hunters Point sediment using sediment and aqueous equilibrium concentrations. Tables 2 and 3 in the Supporting Information show average values of log K_{ow} from the literature and measured values of log K_{oc} for PCBs and PAHs, respectively. Values of log K_{ow} for PCB homologs in Table 2 (in the Supporting Information) are representative values reported by Erickson (*19*) from Shiu and Mackay (*27*). Our measured PCB log K_{oc} values and the log K_{oc} correlations presented in Table 3 (in the Supporting Information) are plotted against congener or homolog log K_{ow} values in Figure 10. For the most part, the PCB log K_{oc} values measured in this study are larger and lie outside the range of the various

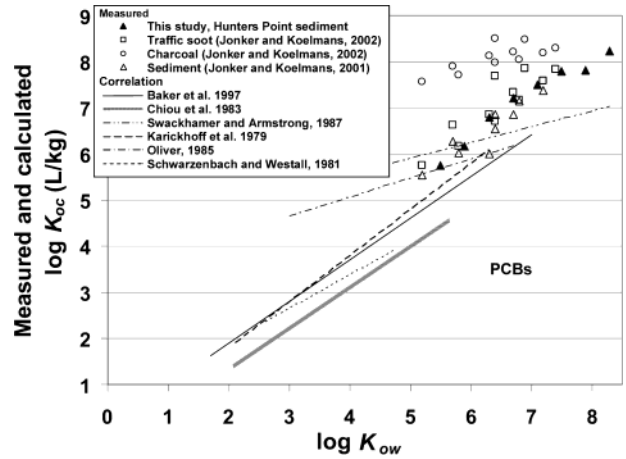

FIGURE 10. Comparison of measured log K_{oc} values for PCB homologs in Hunters Point or Lake Ketelmeer sediment or in soot− or charcoal−water systems with correlations proposed by others for PCBs and other hydrophobic compounds.

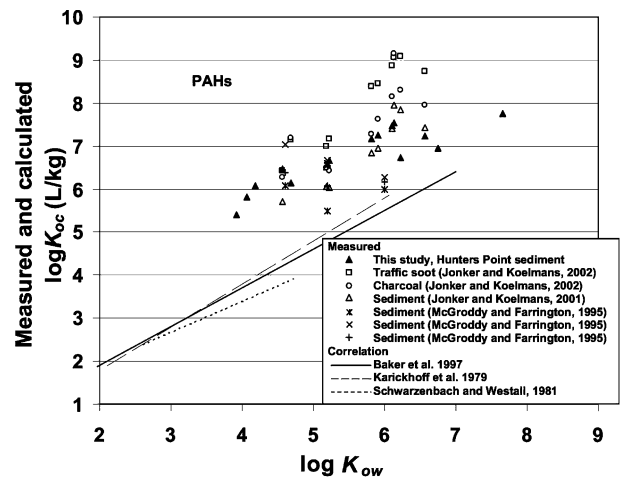

FIGURE 11. Comparison of measured log K_{oc} values for PAH compounds in Hunters Point sediment, Boston Harbor, and Lake Ketelmeer and in soot− or charcoal−water systems with correlations proposed by others for PAHs and other hydrophobic compounds. PAHs were measured at three sites within Boston Harbor, as reported by McGroddy and Farrington (*20*).

correlations. In contrast, log K_{oc} values reported in recent studies with carbon materials such as soot and charcoal (*24*) and with soot-containing sediment (*28*) are closer to our measured values. The larger log K_{oc} values observed for Hunters Point sediment likely result from the presence of anthropogenic black carbon particulate organic matter. Ghosh et al. (*6*) showed that 68% of the PCBs and 89% of the PAHs are associated with particulate organic matter in sediment at the site, which comprises 6% of the total sediment mass. The agreement of our log K_{oc} values with those from other studies where PCB sorption is dominated by soot or charcoal, supports the concept that, given sufficient time, PCBs bind preferentially to charcoal or coal-derived particles, which are present in Hunters Point sediment.

Comparison of results in Figure 11 shows that our measured PAH log K_{oc} values are about 2 orders of magnitude larger than log K_{oc} values predicted from the correlations plotted in the figure. This is likely due to strong binding of PAHs to charcoal and coal-derived materials found in Hunters Point sediment. McGroddy and Farrington (*20*) and Jonker and Koelmans (*28*) measured apparent PAH log K_{oc} values for sediment samples in Boston Harbor, MA, and in Lake Ketelmeer, The Netherlands, respectively. Sediment from

both studies contained soot, which plays an important role in PAH sorption. Jonker and Koelmans (*24*) measured solid−water distribution coefficients for carbon sorbent−water systems (i.e., no sediment), and we calculated log K_{oc} values from those distribution coefficients and normalized their reported values by sorbent percent carbon. As shown in Figure 11, the similarity between log K_{oc} values measured in those three studies (*28*, *24*, *20*), where sorption is dominated by soot or charcoal, and our measured log K_{oc} values supports the concept of the dominance of strong sorption to black carbon particles (e.g., char, charcoal, coke) in Hunters Point sediment.

Comparison of Treated Sediment Equilibrium Partitioning with Literature Values. Aqueous equilibrium contaminant concentrations in water in contact with untreated and activated carbon-treated Hunters Point sediment were used as an indicator of whether adding carbon sorbents decreases PCB and PAH release to the aqueous phase. The greater effectiveness of activated carbon is attributed to a combination of its greater effective surface area (940 vs 3 m^2/g for coke) and its pore size distribution and structure that are favorable for binding contaminants (*24*). Jonker and Koelmans (*24*) measured sorbent−water distribution coefficients for soot and soot-like material and reported activated carbon−water partition coefficients (K_{AC}) ranging from $10^{8.16}$ to $10^{9.87}$ for several tri- to hexachlorobiphenyls in clean water. These values were about 3 orders of magnitude greater than measured values for soots and about 1 order of magnitude greater than for a charcoal. They found that K values for added PCBs correlated well with average pore diameter for soot and soot-like material and proposed that pore sorption dominated PCB binding mechanisms. We calculated K_{AC} values using homolog sediment PCB concentrations in the composite sediment sample (e.g., $C_{s,penta-PCB} = 878\ \mu g/kg$), the fraction of activated carbon in the sediment, $f_{AC} = 0.034$, and aqueous homolog PCB concentrations (e.g., $C_{w,penta-PCB} = 4.1 \times 10^{-4}\ \mu g/L$ for 6-month contact), obtaining log K_{AC} values of 7.6−8.1 for tetra- through nonachlorobiphenyls. Though significantly larger than PCB distribution coefficients for amorphous sediment organic carbon, these values are smaller than those reported by Jonker and Koelmans (*24*) for activated carbon−water systems.

One reason for finding smaller distribution coefficients in this study, compared to those from activated carbon−water systems, is that only about 40% of the total PCBs may be available for mass transfer to carbon due to kinetic limitations. Another factor is the abundance of natural organic matter (NOM) in the sediment, which may reduce the fraction of activated carbon available for binding PCBs by both competing for sorption sites and by blocking entrance to micropores, where the majority of sorption capacity is located. Ebie et al. (*29*) showed that NOM reduced activated carbon sorption capacity of four organic pesticides up to 90% and attributed the reduction to competitive sorption and micropore blockage by NOM. A third possibility is competition among the PCBs and PAHs present in the sediment. Nonlinearity is often evident with sorption to activated carbon, and the total PCB concentration in our aqueous systems is approximately 2 orders of magnitude greater than in Jonker's systems. This could explain the lower K_{AC} value from our work, relative to Jonker's results (*24*).

A comparison of aqueous equilibrium PCB concentrations for samples from 1- and 6-month sediment−activated carbon contact periods indicates that mass transfer limitations are playing an important role for the higher chlorinated PCBs. Tetrachlorobiphenyls do not show a significant change in aqueous phase concentration for sediment−activated carbon contact times of 1 and 6 months. This is likely because release of tetrachlorobiphenyls from sediment is relatively fast as shown in Figure 4, resulting in little additional mass transfer after 1 month. Nonachlorobiphenyls show little change in aqueous concentrations for sediment−activated carbon contact times of 1 or 6 months because only a relatively small amount is released from the sediment and the system may be far from equilibrium. An observable difference in aqueous equilibrium PCB concentrations for sediment−activated carbon contact times of 1 or 6 months was evident for hexachlorobiphenyls. Following an initial fast release from sediment, activated carbon uptake becomes limited as hexachlorobiphenyls diffuse slowly from sediment into activated carbon pores.

Implications. The results from this work demonstrate that adding activated carbon to contaminated sediments can reduce PCB and PAH aqueous equilibrium concentrations, PCB and PAH uptake by SPMDs, and diffusive PCB flux to overlying water. A companion study (*30*) shows that contacting Hunters Point sediment with activated carbon reduces bioaccumulation of PCBs by benthic organisms. Results from the present study and our bioaccumulation work indicate that application of activated carbon to PCB-contaminated sediment can be an effective in-situ stabilization method to reduce contaminant availability to surrounding water and biota. Further work is required to address issues related to the application of activated carbon in the field for in-situ control of PAH and PCB availability in sediments. This includes work to understand the effects of activated carbon dose and particle size and contaminant mass-transfer kinetics with limited mixing. Also, activated carbon deployment and particle dynamics under various hydrodynamic conditions need to be assessed. Each contaminated sediment site will require specific consideration to find an appropriate management strategy and treatment method.

Depending on site conditions, activated carbon could be mixed or injected into sediment, used in conjunction with sand or gravel to hold carbon in place, or used as an "active cap". For the case of Hunters Point sediment, we envision that treatment with activated carbon would involve mixing of the carbon into the upper 0.3−0.5 m of sediment, which comprises the biologically active zone. Hunters Point sediment at South Basin is cohesive, and the site is slightly depositional and protected from extreme hydrodynamic forces. Activated carbon could be mixed into sediment at low tide when the mudflat treatment area is exposed. In this situation, activated carbon treatment may be an attractive, cost-effective alternative to sediment dredging and disposal and possibly at other sites comprising large-volume, low-concentration material or as an adjunct to dredging to manage residuals after more highly contaminated sediments have been removed.

Acknowledgments

Funding for this research was from the Department of Defense through the Strategic Environmental Research and Development Program (Contract DACA72-01-C-0002). Supplemental support was provided by Schlumberger, Ltd.

Supporting Information Available

Three tables and additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) *EPA's Contaminated Sediment Management Strategy*; U.S. Environmental Protection Agency, Office of Water: Washington, DC, 1998; EPA-823-R-98-001.

(2) NRC. *A Risk-Management Strategy for PCB-Contaminated Sediments*; National Research Council Report; National Academy Press: Washington, DC, 2001.

(3) *Phase 1B Ecological Risk Assessment Draft Report, Hunters Point Shipyard, San Francisco, California, Volume 1 − Part 1: Nature and Extent of Contamination*; Department of the Navy, Engineering Field Activity West: September 30, 1996.

(4) *Draft Hunters Point Shipyard Parcel F Validation Study Report, San Francisco Bay, California*; Battelle, Entrix, Inc., and Neptune and Co. prepared for U.S. Navy, Southwest Division NAVFAC: San Diego, CA, April 25, 2002.
(5) Ghosh, U.; Talley, J. W.; Luthy, R. G. *Environ. Sci. Technol.* **2001**, *35*, 3468−3475.
(6) Ghosh, U.; Zimmerman, J. R.; Luthy, R. G. *Environ. Sci. Technol.* **2003**, *37*, 2209−2217.
(7) Talley, J. W.; Ghosh, U.; Tucker, S. G.; Furey, J. S.; Luthy, R. G. *Environ. Sci. Technol.* **2002**, *36*, 477−483.
(8) Kraaij, R.; Seinen, W.; Tolls, J.; Cornelissen, G.; Belfroid, A. C. *Environ. Sci. Technol.* **2002**, *36*, 3525−3529.
(9) Kosian, P. A.; West, C. W.; Pasha, M. S.; Cox, J. S.; Mount, D. R.; Huggett, R. J.; Ankley, G. T. *Environ. Toxicol. Chem.* **1999**, *18*, 201−206.
(10) West, C. W.; Kosian, P. A.; Mount, D. R.; Makynen, E. A.; Pasha, M. S.; Sibley, P. K.; Ankley, G. T. *Environ. Toxicol. Chem.* **2001**, *20*, 1104−1111.
(11) Ball, W. P.; Buehler, C.; Harmon, T. C.; Mackay, D. M.; Roberts, P. V. *J. Contam. Hydrol.* **1990**, *5*, 253−295.
(12) Ghosh, U.; Weber, A. S.; Jensen, J. N.; Smith, J. R. *Environ. Sci. Technol.* **2000**, *34*, 2542−2548.
(13) Echols, K. R.; Gale, R. W.; Schwartz, T. R.; Huckins, J. N.; Williams, L. L.; Meadows, J. C.; Morse, D.; Petty, J. D.; Orazio, C. E.; Tillitt, D. E. *Environ. Sci. Technol.* **2000**, *34*, 4095−4102.
(14) Peven, C. S.; Uhler, A. D.; Querzoli, F. J. *Environ. Toxicol. Chem.* **1996**, *15*, 144−149.
(15) Bennett, E. R.; Metcalfe, T. L.; Metcalfe, C. D. *Chemosphere* **1996**, *33*, 363−375.
(16) Granmo, Å.; Ekelund, R.; Berggren, M.; Brorström-Lundén, E.; Bergqvist, P. A. *Environ. Sci. Technol.* **2000**, *34*, 3323−3329.
(17) Lebo, J. A.; Huckins, J. N.; Petty, J. D.; Cranor, W. L.; Ho, K. T. *Chemosphere* **2003**, *50*, 1309−1317.
(18) Huckins, J. N.; Tubergen, M. W.; Manuweera, G. K. *Chemosphere* **1990**, *20*, 533−552.
(19) Erickson, M. D. *Analytical Chemistry of PCBs*; CRC Lewis Publishers: Boca Raton, FL, 1997.
(20) McGroddy, S. E.; Farrington, J. W. *Environ. Sci. Technol.* **1995**, *29*, 1542−1550.
(21) McGroddy, S. E.; Farrington, J. W.; Gschwend, P. M. *Environ. Sci. Technol.* **1996**, *30*, 172−177.
(22) Gustafsson, Ö.; Gschwend, P. M. In *Molecular Markers in Environmental Geochemistry*; Eganhouse, R. P., Ed.; ACS Symposium Series 671; American Chemical Society: Washington, DC, 1997; pp 365−381.
(23) Gustafsson, Ö.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. *Environ. Sci. Technol.* **1997**, *31*, 203−209.
(24) Jonker, M. T. O.; Koelmans, A. A. *Environ. Sci. Technol.* **2002**, *36*, 3725−3734.
(25) Mantell, C. L. *Carbon and Graphite Handbook*; Interscience Publishers: New York, 1968.
(26) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241−248.
(27) Shiu, W. Y.; Mackay, D. *J. Phys. Chem. Ref. Data* **1986**, *15*, 911−929.
(28) Jonker, M. T. O.; Koelmans, A. A. *Environ. Sci. Technol.* **2001**, *35*, 3742−3748.
(29) Ebie, K.; Li, F. S.; Azuma, Y.; Yuasa, A.; Hagishita, T. *Water Res.* **2001**, *35*, 167−179.
(30) Millward, R. N.; Bridges, T. S.; Ghosh, U.; Zimmerman, J. R.; Luthy, R. G. Submitted for publication.

Received for review September 9, 2003. Revised manuscript received June 25, 2004. Accepted July 14, 2004.

ES034992V

Appendix IV

Paper in review

Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (Neanthes arenaceodentata) and an Amphipod (Leptocheirus plumulusos).

by

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Environmental Science & Technology, 39: 2880-2887, 2005.

Environ. Sci. Technol. **2005**, *39,* 2880−2887

Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (*Neanthes arenaceodentata*) and an Amphipod (*Leptocheirus plumulosus*)

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This work examines the effects of adding coke or activated carbon on the bioavailability of polychlorinated biphenyls (PCBs) in contaminated sediment from South Basin at Hunters Point, San Francisco Bay. We show with 28-day sediment exposure tests that PCB bioaccumulation in a polychaete (*Neanthes arenaceodentata*) is reduced by 82% following 1-month contact of sediment with activated carbon and by 87% following 6-months contact of sediment with activated carbon. PCB bioaccumulation in an amphipod (*Leptocheirus plumulosus*) is reduced by 70% following 1-month contact of sediment with activated carbon and by 75% after 6-months contact of sediment with activated carbon. Adding coke had a negligible effect on reducing PCB bioaccumulation, probably because of the low specific surface area and the slow kinetics of PCB diffusion into the solid coke particles. Reductions in congener bioaccumulation with activated carbon were inversely related to congener K_{ow}, suggesting that the efficacy of activated carbon is controlled by the mass-transfer rate of PCBs from sediment and into activated carbon. We find that reductions in aqueous PCB concentrations in equilibrium with the sediment were similar to reductions in PCB bioaccumulation. While no lethality was observed following activated carbon addition, growth rates were reduced by activated carbon for the polychaete, but not for the amphipod, suggesting the need for further study of the potential impacts of activated carbon on exposed communities. The study suggests that treatment of the biologically active layer of contaminated sediments with activated carbon may be a promising in-situ technique for reducing the bioavailability of sediment-associated PCBs and other hydrophobic organic compounds.

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Introduction

Persistent hydrophobic organic contaminants released into the aqueous environment eventually become associated with sediments, where the contaminants may reside for long periods of time because of the combination of strong sorption and slow degradation. Consequently, such contaminants, including polychlorinated biphenyls (PCBs), remain in riverine and coastal sediments of the United States despite bans or restrictions on their use (*1*). Currently, the most commonly used management options for PCB-contaminated sediments are removal by dredging or in-situ capping (*2*).

Recent work demonstrates the important role of lighter density, black carbonaceous particles in sediments such as soot carbon, coal, coke, and charcoal in reducing contaminant aqueous availability and bioavailability. For example, Jonker and Koelmans (*3*) found that soot and sootlike materials have very high affinities for polycyclic aromatic hydrocarbon (PAHs) and PCBs and that the presence of these materials can lower aqueous concentrations of the contaminants, implying a reduction in the potential uptake by aquatic organisms. Several other studies have similarly demonstrated the role of so-called black carbonaceous particles in reducing contaminant aqueous availability (*4*−*8*). In our earlier work (*9*, *10*), we demonstrate that PAHs associated with coal-derived particles are much less available for biological uptake. These findings suggest that the presence of black carbonaceous particles in sediments naturally reduces contaminant availability. McLeod et al. (*11*) showed in clam particle feeding studies that the absorption efficiency for a tetrachloro-PCB was only 1−2% via ingestion if the PCB was sorbed to activated carbon, compared to about 90% for PCBs sorbed to diatoms.

Building on these recent findings, we propose a novel in-situ remediation technique to reduce PCB bioavailability by repartitioning PCBs onto black carbon sorbents that are mixed into the sediment's biologically active layer to enhance the natural process of contaminant stabilization. Microporous black carbon particles have high affinities for hydrophobic organic contaminants (HOCs), as well as high sorption capacities and slow release rates (*9*, *12*−*14*), making them promising candidates as sorbents for sediment remediation. Activated carbon is particularly suitable, given its sorption capacity for HOCs, accessible microporous structure, and high specific surface area, commonly about 1000 m^2/g. The surface of activated carbon particles is characterized by sites with a variety of potential adsorptive interactions, and this heterogeneity in surface character, and the resulting diversity in potential interaction mechanisms, makes activated carbon suitable as a sorbent for a broad spectrum of HOCs (*15*, *16*).

In related work, we demonstrated that adding activated carbon to PCB-contaminated sediment from Hunters Point Naval Shipyard, San Francisco, CA, decreased PAH and PCB aqueous equilibrium concentrations, PAH and PCB uptake by semipermeable membrane devices (SPMD), and diffusive flux of PCBs from sediment into overlying water (*17*). This paper addresses the effects of addition of either coke or activated carbon to sediment on PCB bioaccumulation by two benthic species, with different feeding strategies and hence different exposure characteristics: the particle-browsing amphipod *Leptocheirus plumulosus* and the bulk-sediment ingesting polychaete *Neanthes arenaceodentata*.

10.1021/es048768x CCC: $30.25

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Published on Web 03/05/2005

This study also addresses the effects of these sorbents on the survival, growth, and reproduction of *L. plumulosus* and the survival and growth of *N. arenaceodentata*.

Experimental Methods

Sediment−Sorbent Contact. Field sediment collection and handling are described in Zimmerman et al. (*17*). Briefly, intertidal sediment was collected from South Basin at Hunters Point, San Francisco Bay, CA, and sieved to remove particles >4 mm. Sediment was amended with either coke or activated carbon, and separate batches were mixed for either 1 or 6 months at approximately 3 rpm on a roller. Activated carbon was 75−300 μm type TOG (Calgon Corp., Pittsburgh, PA) dosed at 3.4% dry weight. Coke was obtained as coke breeze (Ispat Inland, East Chicago, IL) and dosed in two size ranges (fine, 63−105 μm, and coarse, 105−250 μm) and at two concentrations (3.4% or 8.5% dry weight). However, since neither the physicochemical tests (*17*) nor the bioaccumulation tests (present study) revealed significant differences in coke efficacy because of either dose, particle size, or contact time, only the results from the coarse 3.4% coke treatments are presented here. The same activated carbon- or coke-amended sediment, and nonamended sediment, were used in both physicochemical tests (*17*) and biological tests (this paper).

PCB Bioaccumulation and Carbon Sorbent Toxicity. Both bioaccumulation and biological effects of the adsorbent amendment were studied using modified 28-day sediment toxicity protocols for *N. arenaceodentata* (*18*, *19*) and *L. plumulosus* (*19*, *20*). Twenty-five 2-day-old *L. plumulosus* were placed in 1-L beakers containing sediment (100 g dry weight) and c. 725 mL of 20‰ artificial seawater (Forty Fathoms Crystal Sea, Marine Enterprises International, Baltimore, MD). Overlying water was aerated gently and exchanged three times each week. *Leptocheirus plumulosus* were fed Tetramin (Tetra Holdings, Blacksburg, VA, 12 mg per replicate) after each water exchange. In tests with *N. arenaceodentata*, 10 2-week-old worms were placed in 1-L beakers containing sediment (100 g dry weight) and c. 725 mL of 30‰ artificial seawater (Instant Ocean, Aquarium Systems, Mentor, OH). *Neanthes arenaceodentata* were fed twice a week (12 mg per replicate) after each water exchange. After a 28-day exposure, *L. plumulosus* were removed from the sediment and allowed to clear gut contents for 2−4 h. *Neanthes arenaceodentata* were depurated for 12 h in 30‰ artificial seawater, after which any remaining ingested sediment was removed by applying gentle rearward pressure along the digestive tract. Tissues were stored at −80 °C prior to PCB measurement. Tissue PCB concentrations were normalized by lipid content to aid comparison of bioaccumulation by species. To address the effects of congener chlorination on activated carbon effectiveness, PCB congeners were summed by homologue group, and percentage reductions in bioaccumulation by homologue were investigated for each group, using average homologue K_{ow} values from Erikson (*21*).

Potential effects of coke and activated carbon amendments on the organisms were assessed by comparison of the survival, growth rate, and lipid content of both *N. arenaceodentata* and *L. plumulosus*, and juvenile production in *L. plumulosus*, in untreated sediment and sediment with either 3.4% coke or 3.4% activated carbon additions after 1-month contact time. At the termination of the exposure, animals were removed from test sediments by gentle sieving and the survival and wet weight were recorded, *L. plumulosus* juvenile abundances were noted, and the tissues were analyzed for lipid content (see below).

Digestive Fluid Extracts. We assessed the ability of activated carbon to reduce PCB bioavailability from ingested sediment by measuring PCB concentrations extracted from amended and nonamended sediment by a polychaete digestive fluid, using methods based on those of ref *22*. Digestive fluids were taken from the deposit-feeding polychaete *Arenicola brasiliensis* collected near San Francisco in May 2001 and stored at −80 °C until use. Whereas digestive fluids from *N. arenaceodentata* might have been preferable, the small size of this species and the large digestive fluid requirements precluded their use. Digestive fluid was mixed with either wet sediment or wet-activated carbon-amended sediment (1.2 mL digestive fluid to 0.6 g sediment on a dry weight basis) in precleaned screw-capped glass centrifuge tubes. Mixtures were vortexed for 30 s before placement in a culture-tube rotator for 3 h, with additional vortexing every hour. We used 3-h extractions as an estimate of gut passage time for the subadult *N. arenaceodentata* used in these experiments, interpolated from gut passage time data for juvenile (0.5−1 h) and adult (>5 h) *Nereis succinea* (*23*). After vortexing, tubes were then removed and centrifuged at 4000 rpm for 10 min. After centrifugation, 1 mL of supernatant was removed and frozen at −80 °C until analysis. Three replicates were analyzed per sediment, together with one method blank (digestive fluid with no sediment).

TABLE 1. List of 31 Selected PCB Congeners Used to Calculate Total PCBs in Tissues

congener	IUPAC #	congener	IUPAC #
2,2′,4,5′	49	2,2′,3,3′,4,5′,6	175
2,2′,3,4,4′	85	2,2′,3,3′,4,6,6′	176
2,2′,3,5′,6	95	2,2′,3,3′,4,5′,6′	177
2,2′,4,4′,5	99	2,2′,3,3′,5,5′,6	178
2,3,3′,4′,6	110	2,2′,3,4,4′,5,5′	180
2,3′,4,4′,5	118	2,2′,3,4,4′,5,6	183
2,2′,3,3′,4,4′	128	2,2′,3,4,5,5′,6	185
2,2′,3,3′,4,5′	130	2,3,3′,4′,5,5′,6	193
2,2′,3,3′,6,6′	136	2,2′,3,3′,4,4′,5,5′	194
2,2′,3,4,4′,5′	138	2,2′,3,3′,4,4′,5,6	195
2,2′,3,4′,5,5′	146	2,2′,3,3′,4,4′,5,6′	196
2,2′,3,4′,5′,6	149	2,2′,3,3′,4,5,5′,6′	201
2,2′,3,5,5′,6	151	2,2′,3,4,4′,5,5′,6	203
2,2′,3,3′,4,4′,5	170	2,2′,3,3′,4,4′,5,5′,6	206
2,2′,3,3′,4,5,5′	172	2,2′,3,3′,4,5,5′,6,6′	208
2,2′,3,3′,4,5,6′	174		

PCB Analyses. PCB concentrations in tissues and digestive fluids were analyzed using standard EPA methods adapted to use smaller (about 100 mg) wet weights of tissue. Tissue and digestive fluid samples were sonicated using EPA method 3550B with the following modifications: solutes were extracted using a single volume of 10-mL hexane and sonicated at 50% pulse for 6 min using a microtip probe. Samples were cleaned and concentrated using methods based upon EPA 3630C with the exception that extracts were reduced to 40 μL. PCB congeners were analyzed using EPA 8270 and selective-ion monitoring on a Hewlett-Packard 5890 series II gas chromatograph−mass spectrophotometer (GC−MS) with detection limit <0.25 μg/kg wet weight. PCB concentrations in sediments were analyzed using standard method EPA 8270. PCB concentrations in the water phase were analyzed as described by Zimmerman et al. (*17*) with 14-day equilibration followed by colloid removal and hexane extraction.

Total sediment and tissue PCB concentrations refer to the sum of 31 selected congeners listed in Table 1. Congeners were chosen on the basis of occurrence in both tissue and sediment samples at concentrations above method detection limits, and on reproducible absence of peak coelution. Chosen congeners range from the tetra- through nonachloro-biphenyls. Mono- through tri-chloro-biphenyls constituted a very small fraction of total PCBs in the sediment (<1%).

Tissue Lipid Analyses. Lipid was measured using a spectrophotometric assay method modified from van Handel

(*24*). Tissue samples (whole animals) were homogenized in 0.5 mL chloroform:methanol (1:1, v/v), and the solvent was evaporated. Concentrated sulfuric acid (0.2 mL) was added, and the tubes were incubated at 100 °C for 10 min. After cooling, samples were vortexed with 4.8 mL of vanillin reagent (600 mg vanillin (Sigma) dissolved in 100 mL hot deionized water and 400 mL of 85% phosphoric acid (Sigma)). After 5 min, color intensity was analyzed by spectrophotometer at 490 nm against a reagent blank. Lipid content was derived by comparison with a soybean oil (Sigma) standard curve.

Digestive Fluid Surfactancy and Enzyme Activity. The effects of activated carbon on digestive fluid surfactancy and enzyme activity were measured using digestive fluids collected from the benthic deposit-feeding polychaete *Arenicola brasiliensis*. The digestive fluid used was a composite of archived material collected using the methods of ref *25* and stored at −80 °C. Hunters Point sediment and a laboratory reference sediment from Sequim Bay, WA, were freeze-dried and sieved to remove coarse (>500 μm) particles. Dried sediments were either nonamended or amended with 3.4% activated carbon. Sediments were then added to digestive fluids (100 mg dry weight sediment to 600 μL digestive fluid), shaken for 1 h, and centrifuged at 5000 rpm for 10 min. Supernatant was then removed for analyses of surfactancy and enzyme activity.

Digestive fluid surfactancy was assessed by measuring the static contact angle between a 10-μL droplet of digestive fluid and a hydrophobic surface (Parafilm) (*26*). Droplets were placed on Parafilm and the side view image of the droplet was entered into an image analyzer. The tangent was drawn at the droplet−Parafilm intersection, and the angle between this tangent and the base of the droplet was determined. Surfactant activity and micelle stability were investigated over a dilution series by measuring digestive fluid contact angles over a range of artificial seawater dilutions.

Effects of activated carbon on digestive fluid protease, lipase, α-glucosidase, and β-glucosidase enzyme activities were measured using substrate monomers attached to fluorophores via the appropriate bond linkage, such that enzyme activity might be inferred by rate of increase in fluorescence. For protease activities, alanine attached via peptide bond to methylcoumarinyl amide (MCA, Sigma-Aldrich, St. Louis, MO) was used; for lipase activities, palmitate esterified to methylumbelliferone (MUF, Sigma-Aldrich, St. Louis, MO) was used; and for α- and β-glucosidase activities, glucose attached by either α- or β-glucosidase bonds to MUF (Sigma-Aldrich, St. Louis, MO) was used. Methods were similar to those used in ref *26*. For each enzyme analysis, 250 μL digestive fluid supernatant was diluted to 25 mL with 0.1M pH 8 phosphate buffer, and 1 mL was placed in a fluorescence cuvette; 0.1 mL of tagged enzyme substrate (two replicates per enzyme) was added, vortexed, and the ensuing hydrolysis reaction was monitored by measuring the fluorescence (excitation wavelength λ_{ex} = 355 nm, emission wavelength λ_{em} = 440 nm) of the free MCA or MUF as it was cleaved from the conjugate. Slopes of the plots of fluorophore release over time were converted to molar hydrolysis rates after correcting for fluorescence quenching by measuring the fluorescence of 1 μM solutions of unbound MCA or MUF (Sigma-Aldrich, St. Louis, MO) in the same diluted solutions.

Statistics. Lipid-normalized tissue concentrations and biological responses were compared using either one-way analysis of variance (ANOVA, for comparison of variables from both coarse and fine coke treatments with nonamended sediment) or Student's T test (for all pairwise comparisons of tissue concentrations between both activated carbon-amended and nonamended sediment exposures and between 1- and 6-month contact times). Digestive fluid enzyme activities were compared using nonparametric ANOVA on ranks, because of heteroscedacity. Null hypotheses were rejected at the level $P \leq 0.05$. All statistical analyses were performed using SigmaStat 3.0 (SPSS Inc, Chicago, IL).

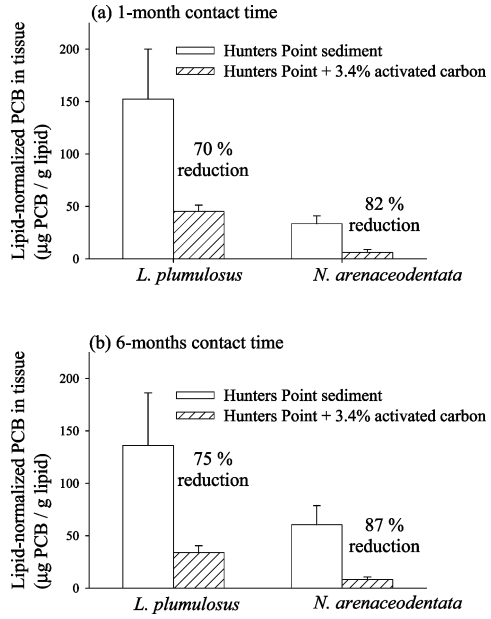

FIGURE 1. Effect of 3.4% dry weight activated carbon addition on lipid-normalized PCB tissue burdens (μg PCB/g lipid) after (a) 1-month contact time and (b) 6-months contact time. Tissue burdens represent the sum of 31 selected congeners listed in Table 1.

Results and Discussion

Effect of Coke and Activated Carbon on PCB Bioavailability in Sediments. The addition of identical proportions of coke and activated carbon resulted in very different effects on PCB bioaccumulation. Addition of 3.4% coke had no significant effect ($P > 0.05$) on PCB bioaccumulation in either *L. plumulosus* or *N. arenaceodentata* (Supplemental Figure S1). Additional data (not presented) showed that the low efficacy of coke was not improved by increasing dosage (from 3.4 to 8.5%) or increasing contact time (from 1 to 6 months) or decreasing particle size range (from 105 to 250 μm to 63−105 μm). Similarly, the previous physicochemical studies demonstrated little or no effect of these coke treatments on aqueous PCB concentrations (*17*).

Activated carbon reduced PCB bioaccumulation following 1-month contact time with sediment by 70% in *L. plumulosus* ($P = 0.003$) and 82% in *N. arenaceodentata* ($P < 0.001$) compared to nonamended sediment as shown in Figure 1a. These decreases in PCB bioaccumulation are of similar magnitude to the decreases observed in aqueous-phase PCBs (87%, Supplemental Figure S2a). These decreases are also similar to reductions in uptake by SPMD (up to 83%) and in the diffusive flux from sediment (up to 89%), using the same activated carbon-amended Hunters Point sediment (*17*). The effects of activated carbon on *A. brasiliensis* digestive fluid solubilization of PCBs were less conclusive, with a statistically insignificant 36% decrease in total PCB solubilization in the treated sediment (Supplemental Figure S2b). Because ingested material can be the primary source for the bioaccumulation of highly hydrophobic contaminants by deposit feeders (*27*), we might expect that activated carbon would decrease both digestive-fluid PCB solubilization and bioaccumulation by similar magnitudes. Since this was not the case, the digestive-fluid solubilization method used in this study was not a good analogue of biological exposure. From Figures 1a and S2 we conclude that activated carbon reduces PCB bioaccumulation through reduced exposure via the aqueous, and possibly the ingested sediment, uptake routes.

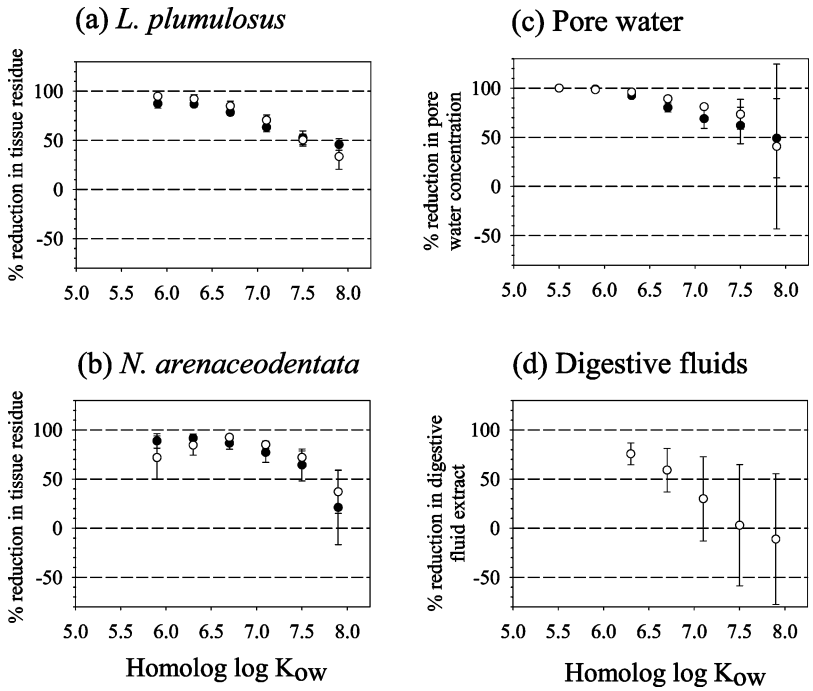

FIGURE 2. Percent reduction in PCB homologues in activated carbon-amended sediment compared to unamended sediment in (a) the amphipod *L. plumulosus*, (b) the polychaete *N. arenaceodentata*, (c) pore water, and (d) polychaete digestive fluid extracts. Closed circles represent 1-month contact time, open circles represent 6-months contact time. Homologue log K_{ow} values; tri = 5.5, tetra = 5.9, penta = 6.3, hexa = 6.7, hepta = 7.1, octa = 7.5, nona = 7.9 (from ref *21*).

The greater effectiveness of activated carbon compared to coke likely results from its higher affinity for hydrophobic organic contaminants and interconnected micropores that yield a higher specific surface area per unit mass compared to coke particles. Jonkers and Koelmans (*28*) reported nearly 2 orders of magnitude higher K_{oc} values for PCB adsorption on activated carbon versus coke. The specific surface area of coke used in our work was 3.2 m^2/g compared to 938 m^2/g for the activated carbon. Coke is somewhat porous, but the pores are largely unconnected voids, thus limiting PCB uptake due to small available specific surface area and extremely slow diffusion through solid coke material.

Increasing sediment−carbon contact time to 6 months resulted in additional, although not statistically significant, improvements in activated carbon effectiveness as shown in Figure 1b, with further reductions of total PCB content in *L. plumulosus* from 70% to 75% and in *N. arenaceodentata* from 82% to 87%. In Zimmerman et al. (*17*), we observed similar incremental improvements in decreasing equilibrium aqueous PCB concentrations from 87 to 92% after increasing sediment−carbon contact time from 1 to 6 months. We conclude under these laboratory-mixing conditions that the benefit of activated carbon is manifested relatively quickly and that the benefit in reducing either bioaccumulation or aqueous concentration is not lost after an additional 5 months of mixing.

PCB tissue concentrations were consistently lower in *N. arenaceodentata* than in *L. plumulosus* (Figure 1). The difference in tissue PCB concentrations between the two organisms may reflect dissimilarities in net rates of bioaccumulation, which might be explained by the 6-fold difference in the wet weight between the two species. Landrum et al. (*29*) demonstrated that a higher organism mass (and by inference higher volume and lower surface-area-to-volume ratio) resulted in lower aqueous uptake rates, presumably because of slower movement of hydrophobic contaminants to the lipid phase.

Relationship between Congener K_{ow} and Activated Carbon Effectiveness. To address the effects of congener chlorination on activated carbon effectiveness, PCB congeners were summed by homologue group and percentage reductions in bioaccumulation were investigated for each group, using homologue K_{ow} values from Erikson (*21*). Reductions in PCB bioaccumulation, PCB aqueous concentrations, and digestive-fluid extractions for activated carbon-treated sediment were inversely related to congener log K_{ow} as shown in Figure 2. This is due to several factors including the greater mass-transfer resistance from sediment and the slower uptake in activated carbon for higher K_{ow} congeners. Evidence for desorption resistance is demonstrated in Zimmerman et al. (*17*), in which higher K_{ow} congeners show slower release rates and a lower fast desorbable fraction compared to congeners with lower K_{ow} values. Under this scenario, a higher proportion of lower K_{ow} congeners would be available for passage to the strongly sorbing activated carbon particles and hence become less bioavailable to organisms. Higher K_{ow} congeners would be more prone to retention in the original sediment and hence maintain a bioavailability similar to that in the nonamended sediment. Further, the rate of internal transport of higher chlorinated PCB congeners in the activated carbon is slower because of chemisorption interaction with the carbon surface (*30*) and sorption-retarded diffusion.

Contacting activated carbon with the sediment for 6 months reduced the bioavailability of PCB congeners with log $K_{ow} < 7$ by more than 75%. The bioavailability of PCB congeners with a log $K_{ow} > 7$ may be reduced to a similar extent over longer time periods. Inferences about desorption resistance and bioavailability have been made in other studies. In a study on PAH bioaccumulation in a sediment-feeding oligochaete (*Ilyodrilus templetoni*), Lu et al. (*31*) found that the prior extraction of a more easily desorbed fraction of phenanthrene from contaminated sediments using 2-propanol reduced subsequent bioaccumulation by 50%. They found for benzo[*a*]pyrene, which has a high log K_{ow} value, that the prior extraction method did not change bioaccumulation significantly. Kraaij et al. (*32*) also found that laboratory-spiked sediment treated with Tenax adsorbent

resin for 48 h removed greater fractions of the lower K_{ow} PAHs and PCBs compared to the higher K_{ow} compounds. They also found that the treatment with Tenax resulted in a greater reduction in PCB and PAH bioaccumulation for the lower K_{ow} compounds compared to the higher K_{ow} compounds.

Effect of Activated Carbon on Biota-Sediment Accumulation Factors. The bioaccumulation potential of sediment-associated organic contaminants can be described using the biota-sediment accumulation factor (BSAF) (*33*):

$$\mathrm{BSAF} = \frac{C_{org}/f_{lipid}}{C_{sed}/f_{oc}} \quad (1)$$

where C_{org} = individual congener or sum of 31 congeners in organism (μg kg^{-1} wet weight tissue); f_{lipid} = lipid content of organism (percent wet weight tissue); C_{sed} = individual congener or sum of 31 congeners in sediment (μg kg^{-1} dry weight sediment); and f_{oc} = total organic carbon content of sediment (percent dry weight sediment).

Although a sediment-organism equilibrium state may not be reached in a short exposure test for many organisms, BSAF values for about a month exposure are widely published for various organisms and sediments and provide a mechanism for comparison of results across different studies. Ranges of BSAF (sum of 31 congeners) from exposure to unamended Hunters Point sediment were 0.87 to 0.88 (*L. plumulosus*) and 0.19 to 0.24 (*N. arenaceodentata*) (Supplemental Table S1). Ankley et al. (*34*) presented BSAF values for total PCBs of 0.87 derived from field-collected oligochaetes and 0.84 from oligochaetes exposed to the field sediment for 30 d in the laboratory, which are similar to our BSAF values for *L. plumulosus*. Calculation of BSAF for selected congeners using 28-d exposures to Hunters Point sediment revealed, for both species, an inverse relationship between BSAF and compound K_{ow} (Supplemental Figure S3), in agreement with field data for high K_{ow} PCB congeners (*34*). Kraaij et al. (*35*) observed tubifex worm BSAF values (for 21−34 days exposure) in the range of 1−4 for laboratory-contaminated sediments for four PCBs and seven PAHs. The BSAF for individual PCBs in this study are generally lower than those reported by Kraaij et al. (*35*). A possible reason could be the predominance of carbonaceous particles such as charcoal in Hunters Point sediment (*10*) that reduces the bioavailability due to stronger binding of the PCBs compared to natural organic carbons.

For coke-amended sediments, the BSAF increased compared to the untreated sediments from 0.88 to 1.89 for *L. plumulosus* and from 0.24 to 0.57 for *N. arenaceodentata*. These trends reflect the increase in f_{oc} by approximately 2.6 times for the coke treatments, without a significant reduction in 28-d PCB bioaccumulation. For activated carbon-amended sediments, the BSAF decreased compared to the unamended sediments, from 0.87 to 0.68 for *L. plumulosus* and from 0.19 to 0.09 for *N. arenaceodentata*. Thus, the added activated carbon acts as a stronger sorbent than the native sediment organic carbon. Although tissue PCB concentrations in both organisms decreased by greater than 70% after treatment with activated carbon, the BSAF did not change to the same extent because the fraction of organic carbon in sediments also increased. These results indicate that BSAFs are affected by the nature of organic carbon responsible for contaminant binding, at least over the exposure periods used in this study. Introduction of activated carbon into the sediment changes the PCB partitioning behavior by out competing the partitioning among the sediment organic carbon and the aqueous and organism lipid phases.

Effect of Activated Carbon on PCB Bioconcentration Factors. The bioaccumulation of hydrophobic organic compounds from sediments has been described as a two-stage process, whereby organics partition from the sediment into either the aqueous phase or digestive fluid and are then available for partitioning from these solubilized phases into the lipid fraction of organisms (*31*). Kraaij et al. (*35*) showed that the bioaccumulation potential might be derived using pore water concentrations and associated bioconcentration factors (BCF) alone. Therefore, we investigated the degree to which the observed decreases in PCB bioaccumulation in the activated carbon-amended sediments might be explained by decreases in PCB concentrations in the aqueous phase. We calculated BCFs for both *N. arenaceodentata* and *L. plumulosus*, using the sum of 14 PCB congeners (listed in Table 2) in organism tissues (C_{org}) and in aqueous phase (C_{aq}) presented in Zimmerman et al. (*17*) for untreated and treated sediment. BCFs were calculated using

TABLE 2. List of 14 Congeners Used to Calculate the Sum of PCBs in Digestive Fluid Extracts and the Aqueous Phase and Bioaccumulation Factors

congener	IUPAC #	congener	IUPAC #
2,2′,4,4′,5	99	2,2′,3,3′,4,5,6′	174
2,2′,4,5,5′	101	2,2′,3,3′,4,5′,6′	177
2,3′,4,4′,5	118	2,2′,3,4,4′,5,5′	180
2,2′,3,3′,6,6′	136	2,2′,3,4,4′,5,6	183
2,2′,3,4′,5,5′	146	2,2′,3,3′,4,4′,5,5′	194
2,2′,3,5,5′,6	151	2,2′,3,3′,4,5,5′,6′	201
2,2′,3,3′,4,5,5′	172	2,2′,3,3′,4,4′,5,5′,6	206

$$\mathrm{BCF} = C_{org}/C_{aq} \quad (2)$$

where C_{aq} = individual congener or sum of 14 selected PCB congeners in water at equilibrium (μg L^{-1}).

Figure 3 presents aqueous BCFs (L/kg) for the two organisms with the untreated and activated carbon-treated Hunters Point sediment (data for Figure 3 shown in supplemental Table S2). For the untreated sediment, BCFs (L/kg) for *N. arenaceodentata* range from 4000−97000, whereas BCFs for *L. plumulosus* range from 53000−476000. For sediment treated with activated carbon, BCF values for individual congeners changed, but the range of BCFs remained about the same (7000−107000 for *N. arenaceodentata* and 61000−530000 for *L. plumulosus*). These results indicate that the relationship between aqueous concentrations and tissue PCB concentrations do not change after treatment with activated carbon. Thus, on the basis of evidence to date, PCB bioaccumulation reduction using activated carbon amendment can be related to aqueous PCB concentrations and congener BCF.

Kraaij et al. (*35*) found that the bioconcentration factors for PCBs in a deposit-feeding tubifex worm did not change after the treatment of sediments with Tenax for 48 h. They also found that the lipid-normalized bioconcentration factors were very similar to the log K_{ow} of the PCB congeners. In our case also we find that the lipid-normalized bioconcentration factors are mostly within an order of magnitude of congener K_{ow} (data not shown). An average bioconcentration factor of 31 200 L/kg for fish was used in developing EPA's ambient water quality criteria for PCBs (*36*), and this value is also used for developing total maximum daily loads for PCBs in natural waters (*37*). Our measured BCF for *N. arenaceodentata* for total PCBs in untreated Hunters Point sediment is 34 000 L/kg and is close to the value used by the EPA for fish. For *L. plumulosus*, we measured 5-fold higher bioaccumulation compared to *N. arenaceodentata* and a corresponding higher bioconcentration factor. Different PCB exposure pathways and different surface area-to-volume ratios for the two organisms could be responsible for the observed differences in bioconcentration factors.

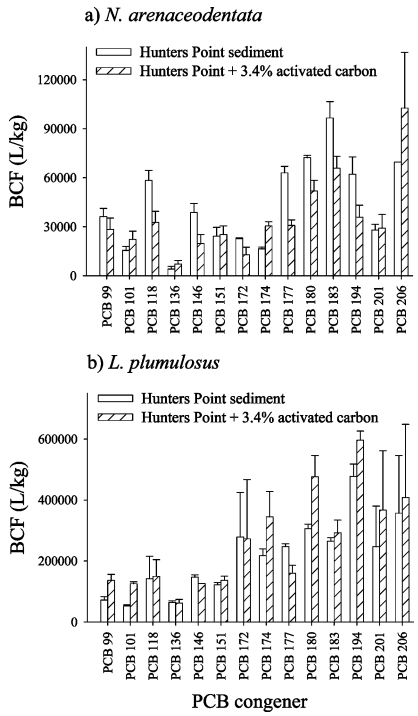

FIGURE 3. PCB bioconcentration factors (BCF) in activated carbon-amended sediment compared to unamended sediment for (a) the amphipod *L. plumulosus* and (b) the polychaete *N. arenaceodentata*.

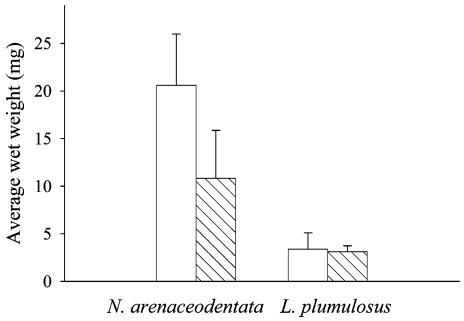

FIGURE 4. Effect of 3.4% activated carbon on 28-d growth in *N. arenaceodentata* and *L. plumulosus*. Open bar represents growth in unamended HP sediment, hatched bar represents growth in HP amended with 3.4% dry weight activated carbon.

Chronic Effects of Activated Carbon on *L. plumulosus* and *N. arenaceodentata*. Exposure to 3.4% activated carbon in sediment resulted in no significant effect on the survival, growth, lipid content, and fecundity in *L. plumulosus* or survival and lipid content in *N. arenaceodentata* (data not shown). However, activated carbon did result in decreased *N. arenaceodentata* wet weight of approximately 50% after 28 d (Figure 4). Direct toxicity of activated carbon is discounted as an explanation for this effect. During our sediment exposure trials, we observed ingestion of activated carbon particles by *N. arenaceodentata*, but not *L. plumulosus*, and it is conceivable that ingested activated carbon affects *N. arenaceodentata* indirectly because of its sorbent properties. Given its affinity for lipids, carbohydrates (*38*), and proteins (*39*), activated carbon could sorb nutrients dissolved in both the aqueous phase and digestive fluid, potentially impairing nutrient uptake. In addition, since the species was observed to ingest activated carbon particles, it is possible that activated carbon might impair digestion through the sorption of enzymes in digestive fluid. To test this concept, we investigated the effects of activated carbon on (a) glucosidase, lipase, and protease enzyme activity in digestive fluid and (b) digestive fluid surfactant activity.

Effect of Activated Carbon on Enzyme Activity and Digestive Fluid Surfactancy. Addition of 3.4% activated carbon to either Hunters Point or control sediment (Sequim Bay, WA) had no significant deleterious effect on protease, lipase, or α- or β-glucosidase activities, as shown in Table 3. This suggests that any sorption of digestive enzymes by activated carbon was not sufficient to decrease the functional efficiency of these key digestive enzymes. Droplet contact angle formed by pure digestive fluid from *A. brasiliensis* was not affected by the contact of the digestive fluid with control sediment. When 3.4% activated-carbon-amended control sediment was contacted with the digestive fluid, the contact angle increased from 28.3° to 34.5° indicating decreased surfactancy. However, digestive fluid contact angles were increased by the same extent in both the unamended and activated-carbon-amended Hunters Point sediment. This indicates that for Hunters Point sediment, there was no change in digestive fluid surfactancy from the addition of activated carbon. High digestive fluid surfactancy is common in deposit-feeding invertebrates (*26*). The role of surfactancy in digestion is not clear; it might be associated with solubilizing food particles, activating and deactivating digestive enzymes, enhancing solubility of lipids, preventing adsorptive loss of enzymes from the gut, and aiding gut lubrication (*26*). While it is possible that activated carbon particles can reduce *A. brasiliensis* digestive fluid surfactancy in some sediments with potential effects on nutrient assimilation, the addition of activated carbon did not contribute to any additional loss of digestive fluid surfactancy in the Hunters Point sediment.

Relevance to the Field. The results from this work and a companion study (*17*) demonstrate that adding activated carbon to contaminated Hunters Point sediment can reduce PCB bioaccumulation in two benthic organisms, *L. plumulosus* and *N. arenaceodentata*, by nearly 1 order of magnitude. Thus, application of activated carbon to the biologically active layer of PCB-contaminated sediment may be an effective in-situ stabilization method to reduce contaminant bioavailability to sediment organisms at the base of the aquatic food web. In-situ bioavailability reduction using carbon amendment may be applicable at sites where bioaccumulation reduction can reduce exposures and consequent risk to acceptable levels.

TABLE 3. Effect of Sediment and Activated Carbon on Enzyme Activities and Digestive Fluid Droplet Contact Angle in Polychaete Digestive Fluid

	protease activity (μM/min)	lipase activity (μM/min)	α-glucosidase activity (μM/ min)	β-glucosidase activity (μM/min)	digestive fluid droplet contact angle (°)
digestive fluid	270 ± 33	20.2 ± 1.3	1.0 ± 0.0	6.0 ± 0.6	27.1
control sediment	116 ± 20	15.2 ± 3.0	0.5 ± 0.2	2.1 ± 0.2	28.3
control sediment + activated carbon	138 ± 8	15.2 ± 2.9	0.6 ± 0.1	2.8 ± 0.8	34.5
Hunters Point sediment	122 ± 45	8.4 ± 0.6	0.4 ± 0.1	0.5 ± 0.0	36.4
Hunters Point + activated carbon	113 ± 14	16.6 ± 11.6	0.2 ± 0.2	2.1 ± 0.6	36.9

Ongoing laboratory work is testing the effects of activated carbon dose and particle size and contaminant mass-transfer kinetics on reducing PCB bioaccumulation in organisms. Additional studies will be required to develop an understanding of both the underlying mechanisms and implications of the effect activated carbon had on the reduced growth of the exposed polychaete. Transitioning this in-situ treatment approach to the field requires testing the effectiveness of mixing activated carbon into contaminated sediment under field conditions where mixing may be less complete and where organism exposure conditions are more variable.

This technology may be applicable at low energy, net depositional, sediment environments where activated carbon loss through resuspension and transport would be minimal. These conditions exist at South Basin, adjacent to Hunters Point, where the cohesive nature of the sediment would further stabilize the added carbon particles. There may be several potential modes of application of activated carbon to sediments. Depending on particular site conditions, the carbon could be incorporated directly into sediments using a large-scale mixing device such as a rotovator or a hollow-stem mixing auger used for soil stabilization. Carbon could also be placed as a layer on the sediments with a clean sand cap and thus act as an active sorptive barrier to contaminant migration from sediments into the water column. Alternatively, carbon could be incorporated into sediments during dredging operations to stabilize the contaminants before disposal. The authors plan to investigate some of these challenges to field transition through a pilot field demonstration project and to evaluate site characteristics that may allow the successful application of this remediation technology.

Acknowledgments

Michael Pound and Ryan Ahlersmeyer from the U.S. Navy and Patty White and Victor Magar from Battelle assisted with site background information and access to the Hunters Point site. We acknowledge the technical assistance of Henry Banks, Michelle Beatty, Maurice Duke, Daniel Farrar, Sarah Kate Hendricks, Jerre Houston, Stetson King, Kyle Landers, Guilherme Lotufo, Cory McNemar, and Leslie Yoo. Don Weston, Larry Mayer, Linda Schick, and Ian Voparil provided methodological assistance and digestive fluids. Funding for this research is from the Department of Defense through the Strategic Environmental Research and Development Program (Contract No. DACA72-01-C-0002).

Supporting Information Available

Three figures and two tables. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) United States Environmental Protection Agency (U.S. EPA). *Incidence and Severity of Sediment Contamination in Surface Waters of the United States, Volume 1: National Sediment Quality Survey*; EPA 823/R-97-006; Washington, DC, 1997.

(2) National Research Council of the National Academies (NRC). *A risk-management strategy for PCB-contaminated sediments*; The National Academy Press: Washington, DC, 2001.

(3) Jonker, M. T. O.; Koelmans, A. A. Extraction of Polycyclic Aromatic Hydrocarbons from Soot and Sediment: Solvent Evaluation and Implications for Sorption Mechanism. *Environ. Sci. Technol.* **2002**, *36*, 3725−3734.

(4) Pickard, S. W.; Yaksich, S. M.; Irvine, K. N.; McFarland, V. A. Bioaccumulation Potential of Sediment-Associated Polychlorinated Biphenyls (PCBs) in Ashtabula Harbor, Ohio. *J. Great Lakes Res.* **2001**, *27*, 44−59.

(5) Bucheli, T. D.; Gustaffson, O. Quantification of the Soot-Water Distribution Coefficient of PAHs Provides Mechanistic Basis for Enhanced Sorption Observations. *Environ. Sci. Technol.* **2000**, *34*, 5144−5151.

(6) Gustaffson, O.; Haghseta, F.; Chan, C.; McFarlane, J.; Gschwend, P. M. Quantification of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and Bioavailability. *Environ. Sci. Technol.* **1997**, *31*, 203−209.

(7) Karapanagioti, H. K.; Kleineidam, S.; Sabatini, D. A.; Grathwohl, P.; Ligouis, B. Impacts of Heterogeneous Organic Matter on Phenanthrene Sorption: Equilibrium and Kinetic Studies with Aquifer Material. *Environ. Sci. Technol.* **2000**, *34*, 406−414.

(8) Song, J.; Peng, P.; Huang, W. Black Carbon and Kerogen in Soils and Sediments. 1. Quantification and Characterization. *Environ. Sci. Technol.* **2002**, *36*, 3960−3967.

(9) Talley, J. W.; Ghosh, U.; Tucker, S. G.; Furey, J. S.; Luthy, R. G. Particle-Scale Understanding of the Bioavailability of PAHs in Sediment. *Environ. Sci. Technol.* **2002**, *36*, 477−483.

(10) Ghosh, U.; Zimmerman, J. R.; Luthy, R. G. PCB and PAH Speciation among Particle Types in Contaminated Harbor Sediments and Effects on PAH Bioavailability. *Environ. Sci. Technol.* **2003**, *37*, 2209−2217.

(11) McLeod, P. B.; van den Heuvel-Greve, M. J.; Allen-King, R. M.; Luoma, S. N.; Luthy, R. G. Effects of Particulate Carbonaceous Matter on the Bioavailability of Benzo[a]pyrene and 2,2′,5,5′-Tetrachlorobiphenyl to the Clam, *Macoma balthica*. *Environ. Sci. Technol.* **2004**, *38*, 4549−4556.

(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*, 1729−1736.

(13) Ghosh, U.; Talley, J. W.; Luthy, R. G. Particle-Scale Investigation of PAH Desorption Kinetics and Thermodynamics from Sediment. *Environ. Sci. Technol.* **2001**, *35*, 3468−3475.

(14) Accardi-Dey, A.; Gschwend, P. M. Reinterpreting Literature Sorption Data Considering Both Absorption into Organic Carbon and Adsorption onto Black Carbon. *Environ. Sci. Technol.* **2003**, *37*, 99−106.

(15) Weber, W. J.; van Vliet, B. M. Synthetic Adsorbents and Activated Carbons for Water Treatment: Overview and Experimental Conditions. *J. Am. Water Works Assoc.* **1981**, *73*, 426−431.

(16) Belfort, G. Selective Adsorption of Organic Homologues onto Activated Carbon from Dilute Aqueous Solutions. Solvophobic Interaction Approach and Correlations of Molar Adsorptivity with Physicochemical Parameters. *Environ. Sci. Technol.* **1979**, *13*, 939−949.

(17) Zimmerman, J. R.; Ghosh, U.; Luthy, R. G.; Bridges, T. S.; Millward. R. N. Addition of Carbon Sorbents to Reduce PCB and PAH Bioavailability in Marine Sediments: Physicochemical Tests. *Environ. Sci. Technol.* **2004**, *38*, 5458−5464.

(18) Bridges, T. S.; Farrar, J. D. The Influence of Worm Age, Duration of Exposure and Endpoint Selection on Bioassay Sensitivity for *Neanthes arenaceodentata* (Annelida: Polychaeta). *Environ. Toxicol. Chem.* **1997**, *16*, 1650−1658.

(19) United States Environmental Protection Agency (U.S. EPA)/ United States Army Corps of Engineers (USACE). *Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S.−Testing Manual*; EPA 823/B-98-004; Washington, DC, 1998.

(20) United States Environmental Protection Agency (U.S. EPA). *Methods for Assessing the Chronic Toxicity of Marine and Estaurine Sediment-associated Contaminants with the Amphipod Leptocheirus plumulosus, First Edition*; EPA 600/R-01-020; Washington, DC, 2001.

(21) Erikson, M. D. *Analytical Chemistry of PCBs*; CRC Lewis: Boca Raton, FL, 1997.

(22) Weston, D. P.; Maruya, K. A. Predicting Bioavailability and Bioaccumulation with In Vitro Digestive Fluid Extraction. *Environ. Toxicol. Chem.* **2002**, *21*, 962−971.

(23) Ahrens, M. J.; Hertz, J.; Lamoureux, E. M.; Lopez, G. R.; McElroy, A. E.; Brownawell, B. J. The Role of Digestive Surfactants in Determining Bioavailability of Sediment-Bound Hydrophobic Organic Contaminants to 2 Deposit-Feeding Polychaetes. *Mar. Ecol.: Prog. Ser.* **2001**. *212*, 145−157.

(24) van Handel, E. Rapid Determination of Total Lipids in Mosquitoes. *J. Am. Mosq. Control Assoc.* **1985**, *1*, 302−304.

(25) Weston, D. P.; Mayer, L. M. Predicting Bioavailability and Bioaccumulation with In Vitro Digestive Fluid Extraction. *Environ. Toxicol. Chem.* **1998**, *17*, 830−840.

(26) Mayer, L. M.; Schick, L. L.; Self, R. F. L.; Jumars, P. A.; Findlay, R. H.; Chen, Z.; Sampson, S. Digestive Environments of Benthic Macroinvertebrate Guts: Enzymes, Surfactants, and Dissolved Organic Matter. *J. Mar. Res.* **1997**, *55*, 785−812.

(27) Weston, D. P.; Penry, D. L.; Gulmann, L. K. The Role of Ingestion as a Route of Contaminant Bioaccumulation in a Deposit-Feeding Polychaete. *Arch. Environ. Contam. Toxicol.* **2000**, *38*, 446−454.

(28) Jonker, M. T. O.; Koelmans, A. A. Sorption of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls to Soot and Soot-like Materials in the Aqueous Environment: Mechanistic Considerations. *Environ. Sci. Technol.* **2002**, *36*, 3725−3734.
(29) Landrum, P. F.; Tigue, E. A.; Kane Driscoll, S.; Gossiaux, D. C.; Van Hoof, P. L.; Gedeon, M. L.; Adler, M. Bioaccumulation of PCB Congeners by Diporeia spp.: Kinetics and Factors Affecting Bioavailability. *J. Great Lakes Res.* **2001**, *27*, 117−133.
(30) Sotelo, J. L.; Ovejero, G.; Delgado, J. A.; Martinez, I. Comparison of Adsorption Equilibrium and Kinetics of Four Chlorinated Organics from Water onto GAC. *Water Res.* **2002**, *36*, 599−608.
(31) Lu, X. X.; Reible, D. D.; Fleeger, J. W. Bioavailability of Desorption-Resistant Phenanthrene to the Oligochaete *Ilyodrilus templetoni*. *Environ. Toxicol. Chem.* **2003**, *22*, 153−160.
(32) Kraaij, R.; Seinen, W.; Tolls, J.; Cornelissen, G.; Belford, A. C. Direct Evidence of Sequestration in Sediments Affecting the Bioavailability of Hydrophobic Organic Chemicals to Benthic Deposit-Feeders. *Environ. Sci. Technol.* **2002**, *36*, 3525−3529.
(33) Boese, B. L.; Lee, H.; Specht, D. T.; Randall, R. C.; Winsor, M. Comparison of Aqueous and Solid Phase Uptake for Hexachlorobenzene in the Tellinid Clam, *Macoma nasuta* (Conrad): A Mass Balance Approach. *Environ. Toxicol. Chem.* **1990**, *9*, 221−231.
(34) Ankley, G. T.; Cook, P. M.; Carlson, A. R.; Call, D. J.; Swenson, J. K.; Corcoran, H. F.; Hoke, R. A. Bioaccumulation of PCB from Sediments by Oligochaetes and Fishes. *Can J. Fish. Aquat. Sci.* **1992**, *49*, 2080−2085.
(35) Kraaij, R.; Mayer, P.; Busser, F. J. M.; Bolscher, M. V. H.; Seinen, W.; Tolls, J. Measured Pore-Water Concentrations Make Equilibrium Partitioning Work-a Data Analysis. *Environ. Sci. Technol.* **2003**, *37*, 268−274.
(36) United States Environmental Protection Agency (U.S. EPA). *Ambient Water Quality Criteria for Polychlorinated Biphenyls*; EPA 440/5-80-068; Washington, DC, 1980.
(37) United States Environmental Protection Agency (U.S. EPA). *Final Total Maximum Daily Load for the Susquehanna River, PCBs*; March 12, 1999; (http://www.epa.gov/owow/tmdl/examples/organics/pa_susquehanna.html); Washington, DC, 2005.
(38) Aitcheson, S. J.; Arnett, J.; Murray, K. R.; Zhang, J. Removal of Aquaculture Therapeutants by Carbon Adsorption 1. Equilibrium Adsorption Behaviour of Single Components. *Aquaculture* **2000**, *183*, 269−284.
(39) Eretsky, E. Studies of the Kinetic Characteristics of HSA Adsorption by Different Types of Activated Carbon Fibres. *Adsorp. Sci. Technol.* **2000**, *18*, 469−475.

Received for review August 6, 2004. Revised manuscript received January 11, 2005. Accepted January 25, 2005.

ES048768X

Appendix V.

Contaminant Exposure Control in Sediments Using Activated Carbon Adsorbent

By

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Contaminant Exposure Control in Sediments Using Activated Carbon Adsorbent

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1 Introduction

Hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are long-lived in sediments and impair water quality by leaching into overlying water, accumulating in sediment-dwelling organisms and aquatic biota, and transferring through the food web to humans and other animals. These persistent compounds are widespread in sediments and pose risks to humans and wildlife and the nation's economy through deterioration of water quality.(*1*) The magnitude of the sediment contamination problem in the US is evidenced by more than 2,100 state advisories issued against consuming fish. This is aggravated by the fact that contaminated sediments are very widespread in extent and traditional cleanup technologies such as dredging and disposal are too expensive and too disruptive of existing ecosystems. In the well-publicized case of PCBs in the Hudson River, the EPA and General Electric cannot agree on whether to dredge or not because of fundamentally different views regarding the links among geochemistry, PCB availability, and bioaccumulation. Experts cannot agree on management strategies because of the lack of understanding of organism exposure at the lower trophic levels and the ability to link sediment physical and geochemical phenomena with biota particle

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feeding behavior, contaminant uptake, and accumulation.

Innovative engineering solutions to the problem of persistent organic contaminants in aquatic food webs requires rethinking of the existing remediation paradigm of "dredge-and-landfill." Our recent discoveries of contaminant sorption and association with highly sorbing natural particles in sediments are opening up new opportunities for revolutionary in-situ management strategies. New initiatives by the EPA on incorporating site-specific bioavailability factors in sediment restoration decisions makes innovative, in-situ technologies aimed at reducing the biological availability of contaminants in sediments especially attractive. In our current work we are beginning to address this challenge by bringing together researchers from diverse fields to assess benthic biogeochemical processes and biota feeding and contaminant exposure. We are applying this mechanistic knowledge to assess a novel sediment management strategy. We propose that the addition of a low cost sorbent like granular activated carbon (GAC) to sediments may be a cost-effective, in-situ management strategy by sorbing organic contaminants and thereby reducing bioavailability and bioaccumulation. Such a management strategy is especially attractive for large areas of low level PCB concentrations. Our management strategy requires mechanistic understanding of linked physical and biological processes and using such information in conceptual and quantitative models to understand the efficacy of the in-situ stabilization process.

2 Background

Hydrophobic organic contaminants, such as PCBs and PAHs, sorb to the organic carbon fraction of sediment, leading researchers to take the sediment organic carbon fraction as a measure of sediment sorption capacity. Thus the equilibrium distribution relationship can be normalized to the organic carbon fraction for different sediments.(*2*) However, a major problem with this approach is the

assumption that all organic carbon in sediment exhibit equal sorption capacity. Grathwohl(*3*) showed that sorption of HOCs is strongly dependent not only on the amount of organic carbon, but the nature of it, as well. Ghosh et al.(*4*) showed that different types of organic carbon can have very different sorption capacities for HOCs. Citing several studies, they present organic carbon-normalized partition coefficient (K_{oc}) values for phenanthrene for a number of different sorbents, including vegetative debris, decayed remains of plants and animals, humic matter and particles such as coal, coke, charcoal and soot. The values span a range of several orders of magnitude. Based on the partition coefficients presented in the paper, it is clear that sorption of HOCs associated with soot- or coal-type carbon may be orders of magnitude stronger than HOCs associated with natural organic matter in soils and sediment. Thus HOCs residing in the sediment may be more or less available, depending on how weakly or strongly they are sorbed to the sediment organic matter.

Previous studies, which have measured the amount of soot carbon in sediment have shown the importance of soot carbon in sorption processes in sediment.(*5–8*) Gustafsson et al.(*5*) and Bucheli and Gustafsson(*7*) showed that elevated PAH partitioning in sediment samples could be explained based on the soot carbon content and known high PAH sorption capacity of soot. They proposed that the sorption of PAHs to a soot-phase carbon in sediments may affect in-situ bioavailability of PAHs. Working with isolated soot carbon Accardi-Dey and Gschwend(*6*) demonstrated that the observed PAH partitioning from sediment can be better predicted by a modified, soot-partitioning inclusive, distribution model. Karapanagioti et al.(*9*) showed that sediments with coaly particulates exhibited strong sorption of phenanthrene.

Ghosh et al.(*10*) demonstrated the predominant association of PAHs with coal-derived particles in Milwaukee Harbor sediments. They found from direct analysis of separated fractions and particle-scale microanalysis that the majority of PAHs in the sediment was associated with coal-derived

particles. In a different study Ghosh et al.(*4*) used three different aged, harbor sediment samples to investigate the importance of carbonaceous particles in the sequestration of PCBs and PAHs. By separating the particulate organic components in the sediments by a density technique that preserves the physical and chemical integrity of the particles they demonstrated that majority of both PAHs and PCBs are associated with a coal-derived particulate organic carbon. They also showed that PAHs associated with natural organic matter and mineral particles in sediments were readily bioavailable and PAHs sorbed on carbonaceous particles in sediments were strongly bound and unavailable for biological treatment or for uptake in earthworms.(*10–12*) Thus, the transfer of PAHs from a more easily available state in sediments to a more strongly sorbed state may result in significant reductions in PAH availability and biological uptake.

A few recent studies have investigated the feasibility of adding sorbents as a sediment manipulation to reduce HOC availability by transfer of the compounds from an easily available state to a strongly sorbed state. Kosian et al.(*13*) tested the effectiveness of adding Ambersorb resin to fluoranthene-spiked sediment in reducing contaminant chemical and biological availability. They found that adding Ambersorb to fluoranthene-spiked sediment significantly reduced pore water concentrations. To test the effectiveness in reducing fluoranthene bioaccumulation, the authors exposed the oligochaete *Lumbriculus variegatus* to Ambersorb-amended and nonamended sediment. Following exposure to the sediments, the authors measured whole-body fluoranthene concentrations, and found that fluoranthene body burdens of the organisms exposed to treated sediment were greatly reduced, compared to those exposed to untreated sediment.

In a second study with Ambersorb, West et al.(*14*) measured concentrations of eight PAHs in pore water of sediment before and after contacting with the resin. They found that contacting sediment with Ambersorb significantly reduced pore water concentrations of the eight PAHs studied.

Adding Ambersorb also significantly reduced PAH body burdens for oligochaetes tested. The authors proposed that adding Ambersorb may be an effective in-situ method for treating some contaminated sediments.

Kraaij et al.(*15*) investigated the relationship between contaminant bioavailability and sequestration using manipulation of PCB- and PAH-contaminated sediment with Tenax. By contacting sediment with Tenax beads for 48 h and removing the Tenax, they reduced the fraction of rapidly desorbing contaminants by factors of 28 and 13 times for PAHs and PCBs, respectively. In addition they calculated BSAF values for tubifex worms exposed to the treated and untreated sediments. Using the two data sets they showed that the relationship between contaminant sequestration, as expressed in terms of the rapidly desorbing fraction, and bioavailability, as expressed as BSAF values, is causal. In other words, a decrease in the rapidly desorbing fraction caused a concomitant reduction in uptake by tubifex worms.

These studies and our earlier work on PAH bioavailability suggest that the transfer of HOCs from a weakly bound state in sediments to a strongly bound state on a sorbent amendment may lead to significant reductions in HOC bioavailability. In this work we investigated the use of activated carbon as an amendment to reduce PAH and PCB bioavailability in contaminated sediment. In this paper we present our results of aqueous availability reduction for selected PAHs and discuss results presented elsewhere(*16*) for PCBs in sediments.

3 Our Research

In this research we examined how the addition of low-cost sorbents, such as coke or granular activated carbon, may sequester contaminants like PAHs and PCBs, thereby reducing contaminant solubility, exposure, and accumulation in sediment dwelling organisms.

3.1 Sediment Contact

We obtained sediment from the intertidal zone of South Basin, adjacent to the landfill at Hunters Point Naval Shipyard. Sediments at the site have some of the highest PCB concentrations of anywhere in San Francisco Bay, up to 10.5 mg/kg. Contaminated sediment was contacted with coke or granular activated carbon (GAC) for one or six months on a roller. The amount of carbon sorbent added was twice the total organic carbon content of sediment (1.7%) Experimental details are described elsewhere.(*16*)

3.2 Physicochemical Tests

Three different physicochemical experiments were used to test the effect of adding carbon sorbents on availability to the aqueous phase. These were PCB and PAH aqueous equilibrium concentration, PCB and PAH uptake by semi-permeable membrane devices (SPMD) and PCB flux from sediment under quiescent conditions.

3.3 Biological Tests

Three invertebrate species, which comprise the base of the food chain, have been used as model organisms for the study of bioavailability of PCBs, *Macoma balthica*, *Neanthes arenaceodentata* and *Leptocheirus plumulosus*. *Neanthes* and *Leptocheirus* are model organisms that have been used extensively for studies with contaminated sediment. The three organisms represent three different feeding mechanisms: *Macoma* is a deposit feeder, *Neanthes* feeds by ingesting sediment, and *Leptocheirus* feeds from the particle surface.

One important task was to show that adding carbon sorbents to sediment does not adversely affect organisms. Survival and growth tests were performed with *Leptocheirus* and *Neanthes*, and

reproduction tests were done with *Leptocheirus* to determine whether any adverse effects accompanied carbon addition.

We measured the absorption efficiency of a PAH and PCB to clams from a variety of particle types including activated carbon, coke, coal, and wood. Bioaccumulation studies with the three organisms were performed by exposing them to carbon-treated and untreated sediment, then analyzing for PCBs in their tissues.

4 Results

4.1 Physicochemical Tests

We used three different physicochemical tests to determine the effectiveness of adding carbon sorbents to sediment to reduce contaminant availability to the aqueous phase. These were aqueous equilibrium PCB and PAH concentration, uptake of PCBs and PAHs by semi-permeable membrane devices (SPMDs), and PCB flux from sediment under quiescent conditions. In our first round of testing, we used coke as an engineered sorbent because coal-derived materials have been found to accumulate PAHs, as in the studies previously discussed. However, tests with coke showed it to have little or no effect on reducing PCB concentrations in water. In contrast, adding granular activated carbon (GAC) to sediment significantly reduced PCB and PAH availability to the aqueous phase in all three types of physicochemical tests.

To measure the effectiveness of activated carbon in lowering aqueous phase concentrations, we measured equilibrium aqueous PAH concentrations for untreated sediment and sediment treated with activated carbon and contacted for six months. Results for the three most abundant PAHs are shown in Figure 1. Reductions in PAH aqueous equilibrium concentrations were 83% for

Figure 1: PAH aqueous equilibrium concentration for GAC-treated and untreated Hunters Point sediment

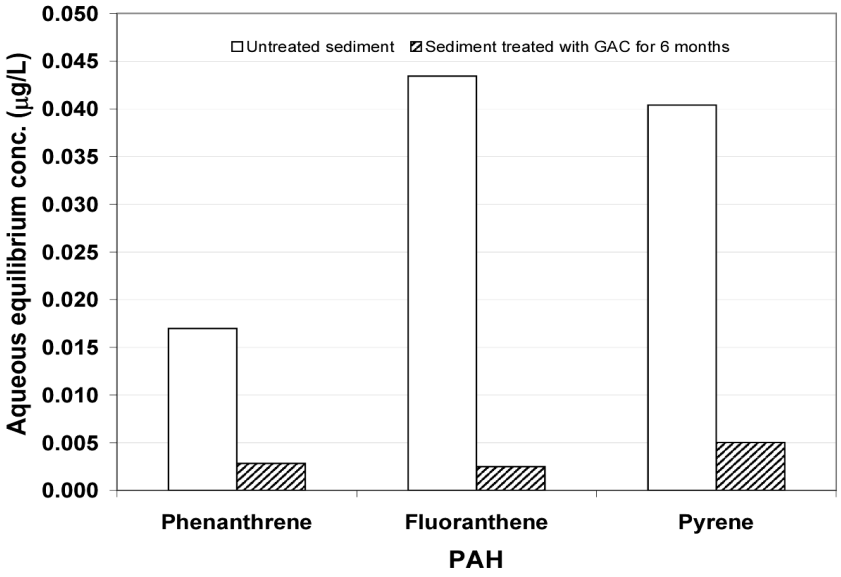


Table 1: LogK_{oc} values for PAHs in sediment.

Compound	Measured, this study logK_{oc}	Measured, apparent(*17*) logK_{oc}
Phenanthrene	6.9	7.03
Fluoranthene	7.4	6.66
Pyrene	7.1	6.61

phenanthrene, 94% for fluoranthene, and 88% for pyrene. Thus, PAH availability in the aqueous phase in contact with sediment or sediment pore water is reduced significantly after contact with activated carbon.

We calculated organic carbon-normalized partition coefficients, K_{oc}, for PAHs in GAC-treated sediment. Values of logK_{oc} for three PAHs are shown in Table 1, along with values measured from other studies with sediment containing strong sorbents such as soot. These values are in agreement with those for PAHs in the soot-impacted sediment.

Results of other physicochemical tests for PAHs and PCBs have been presented elsewhere.(*16*)

4.2 Biological Tests

First, our results showed that adding coke or activated carbon did not adversely affect survival or reproduction either organism. However, *Neanthes* growth was slightly reduced in the sediment treated with activated carbon. The cause of this reduction is currently being investigated. Detailed descriptions of these studies and bioaccumulation studies with *Neanthes* and *Leptocheirus* are found in an article being prepared for publication.(*18*)

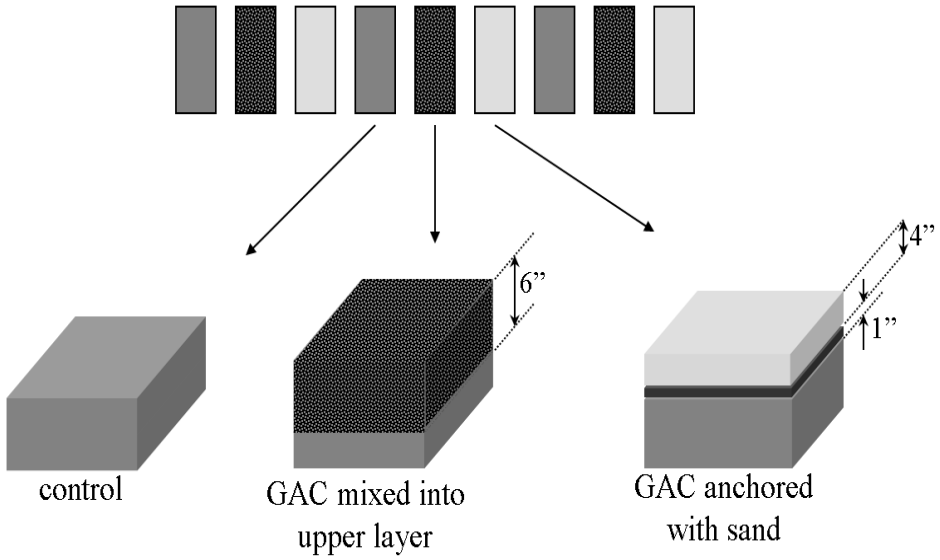
Our results showed that adding coke to sediment had little or no effect on reducing bioaccumulation in any of the organisms. In contrast, contacting GAC with sediment resulted in significantly reduced bioaccumulation in all three organisms, compared to untreated sediment. In addition, the level of reduction in the organisms tracked the levels of reduction shown in the physicochemical tests.

In controlled particle feeding tests with radiolabeled compounds, we determined that the absorption efficiency of a PAH and a PCB to clams was highly dependent upon the particle type to which the compounds were bound. The low absorption efficiency of compounds bound to activated carbon supports the use of activated carbon to lower the bioavailability of PAHs and PCBs in contaminated sediment. Bioaccumulation tests with clams exposed to carbon-treated and untreated sediment showed that activated carbon amendment significantly lowers the bioavailability of PCBs to clams, whereas coke is ineffective.

5 Ongoing Studies

Our results showing that adding activated carbon to sediment can reduce contaminant availability to the aqueous phase and reduce bioaccumulation in three different organisms, provide encouragement

Figure 2: GAC field demonstration methods using replicated control and treatment plots



to pursue this novel technology on a larger scale. This will be pursued in a proposed field scale implementation of GAC application to sediment. The laboratory experiments so far have been performed under ideal conditions and ensured that sediment and carbon were well-mixed. In our pilot scale field experiment we will test the effectiveness under conditions where mixing will be less complete than in the lab. A schematic of our proposed test plots are shown in Figure 2. These tests plots will be placed in South Basin, adjacent to Hunters Point Naval Shipyard, near the location where sediment samples were obtained for our laboratory studies.

An array of physicochemical and biological uptake studies will be performed. Physicochemical tests will be similar to those completed previously, with treated and untreated sediment from the field evaluated in the lab to determine the effects on contaminant release from sediment. In addition SPMDs and solid phase microextraction (SPME) devices will be evaluated as potential in-situ methods for measuring reduction in contaminant availability to the aqueous phase.

We will measure PCB bioaccumulation using particle-feeding organisms native to San Francisco

Bay, the clam *Macoma* and the worm *Nephtys* or *Nereis*. The benthic organisms will be placed in enclosed containers sunk into both treated and control plots. At intervals during the study, we will deploy organisms and characterize organism survival and 28-day PCB bioaccumulation. In-situ biological exposure trials are particularly pertinent to the present study, which aims to 1) demonstrate whether the benefits of carbon addition found in laboratory tests are observed in the field, 2) quantify effects of deployment and temporal variables on environmental PCB exposure, and 3) assess the stability of GAC particles in sediment.

The maintenance of the integrity of the sorbent added to the sediment is important for in-situ stabilization. A principal concern is that since GAC particles are lighter than sediments, activated carbon particles (sp. grav. = 1.4) may be more easily resuspended and preferentially transported by ambient currents from the site. Our demonstration project will evaluate under field conditions the movement of sediment and sorbent activated carbon particles in the treated plots under two deployment scenarios. This will include monitoring of water currents, bulk sediment resuspension at different heights above the bed, relative transport of carbon particles, and the size distribution and nature of suspended particulates.

We will conduct particle resuspension tests as a function of bottom shear in two laboratory-scale setups using sediment from the field and granular activated carbon of different sizes using a vibrating grid mechanism and a water flume. Results from these experiments will allow us to better understand the physical stability of the added sorbent in the field.

6 Active Capping of Contaminated Sediment

Activated carbon can also be deployed in the field along with coarse sand forming a "sorptive cap" to retard contaminant migration and bioavailability. In this case, the activated carbon can be mixed

in the sand to enhance the sorptive property of the cap. Sorptive capping technology can offer a great advantage over standard sand capping by enabling capture and stabilization of mobilized contaminants in the strongly sorbing activated carbon. Such an application mode minimizes the possibility of resuspension of the lighter density carbon and also gains greatly from the wealth of field deployment experience from decades of standard sand capping applications. A typical field application of a sorptive cap may involve mixing activated carbon with in-place contaminated sediments followed by the application of a sorptive cap and a coarse sand/gravel armor. A great benefit of an activated carbon amended sorbent cap is that even if the cap integrity is compromised in the field over a long period of time, repartitioning of the PCBs to a strongly sorbed form in the activated carbon would minimize availability to the aqueous phase and biota. This is unlike regular sand caps where a structural breakdown of the cap results in the release of contaminants to the overlying water and exposure of the biota to the contaminant.

For in-situ management of contaminated sediments, it is critical to evaluate potential pathways by which contaminants might pose ecological or human health risks, and to minimize, or eliminate exposure by these pathways. The governing contaminant transport mechanisms within an amended cap need to be understood under field hydraulic conditions to assess the long-term effectiveness and cost-benefit of the approach. For example, the enhanced retardation of contaminants in the sorptive cap may allow the use of much smaller thickness of cap material.

7 Conclusion

Our laboratory studies demonstrate that persistent organic contaminants, such as PCBs and PAHs, can be effectively sequestered by contacting contaminated sediment with granular activated carbon. This has been demonstrated using three different physicochemical parameters: aqueous equilibrium

concentration, uptake by SPMDs, and flux from sediment under quiescent conditions. Our biological uptake studies also show the effectiveness of reducing bioaccumulation in a clam, an amphipod, and a worm. This combination of results from physicochemical and biological studies provides encouragement for pursuing further application of the in-situ sediment treatment technology. Our proposed pilot scale field demonstrations will be used to measure the effectiveness of this treatment method under less ideal, more realistic conditions. The field demonstration will also address critical issues related to GAC particle and/or sand cap stability under actual field conditions.

Acknowledgements

Funding for this research is from the Department of Defense through the Strategic Environmental Research and Development Program (Contract No. DACA72-01-C-0002) and from Stanford University through the Bio-X Program.

References

1. NRC, *Contaminated Sediments in Ports and Waterways: Cleanup Strategies and Technologies;* National Research Council Report; National Academy Press: Washington, D.C., 1997.

2. Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979,** *13,* 241–248.

3. Grathwohl, P. *Environ. Sci. Technol.* **1990,** *24,* 1687–1693.

4. Ghosh, U.; Zimmerman, J. R.; Luthy, R. G. *Environ. Sci. Technol.* **2003,** *37,* 2209–2217.

5. Gustafsson, O.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. *Environ. Sci. Technol.* **1997,** *31,* 203–209.

6. Dey, A.; Gschwend, P. *Environ. Sci. Technol.* **2002,** *36,* 21–29.

7. Bucheli, T.; Gustafsson, O. *Environ. Sci. Technol.* **2000,** *34,* 5144–5151.

8. Schmidt, M.; Noack, A. *Global Biogeochem. Cycles* **2000,** *14,* 777-793.

9. Karapanagioti, H.; Kleineidam, S.; Sabatini, D.; Grathwohl, P.; Ligouis, B. *Environ. Sci. Technol.* **2000,** *34,* 406–414.

10. Ghosh, U.; Gillette, J.; Luthy, R.; Zare, R. *Environ. Sci. Technol.* **2000,** *34,* 1729–1736.

11. Ghosh, U.; Talley, J.; Luthy, R. *Environ. Sci. Technol.* **2001,** *35,* 3468–3475.

12. Talley, J.; Ghosh, U.; Tucker, S.; Furey, J.; Luthy, R. *Environ. Sci. Technol.* **2002,** *36,* 477–483.

13. Kosian, P.; West, C.; Pasha, M.; Cox, J.; Mount, D.; Huggett, R.; Ankley, G. *Environ. Toxicol. Chem.* **1999,** *18,* 201–206.

14. West, C.; Kosian, P.; Mount, D.; Makynen, E.; Pasha, M.; Sibley, P.; Ankley, G. *Environ. Toxicol. Chem.* **2001,** *20,* 1104–1111.

15. Kraaij, R.; Seinen, W.; Stolls, J.; Cornelissen, G.; Belfroid, A. *Environ. Sci. Technol.* **2002,** *36,* 3525–3529.

16. Zimmerman, J. R.; Ghosh, U.; Luthy, R. G.; Millward, R. N.; Bridges, T. S., submitted for publication in *Environ. Sci. Technol.*

17. McGroddy, S.; Farrington, J. *Environ. Sci. Technol.* **1995,** *29,* 1542–1550.

18. Millward, R. N.; Bridges, T. S.; Luthy, R. G.; Ghosh, U.; Zimmerman, J. R. Unpublished data.

Appendix VI.

Model Verification of Thermal Programmed Desorption-Mass Spectrometry for Estimation of Release Energy Values for PAHs on Mineral Sorbents.

Sara I. Nicholl, Jeffrey W. Talley, Stephan Silliman.

Abstract

The physical availability of organic compounds in soil and sediment strongly influences their bioavailability and toxicity. Previous work has indicated that physical availability changes throughout the processes of aging and treatment and that it can be linked to the energy required to release the compound from its sorbent matrix, with a higher energy indicating a more tightly bound compound. This study focused on determining release energy values for various mineral geosorbents (glass beads, sand and kaolin) contaminated with a 16 PAH mixture. The sorbents were analyzed using Thermal Program Desorption/Mass Spectrometry (TPD/MS) and the release energy values were calculated from the resulting thermograms utilizing a non-linear fit of the analytical solution to a simplified version of the Polanyi-Wigner equation. This solution method resulted in a series of combinations of values for the pre-exponential factor (ν) and release energy (E) that produced desorption rate curves with similar errors when fit to actual data sets. These combinations can be viewed as an error surface, which clearly shows a valley of minimum error values spanning the range of both E and ν indicating that this method may not provide a unique set of E and ν values and suggesting that the simplified version of the Polanyi-Wigner equation cannot be used to determine release energy based on TPD data alone.

Keywords: thermal programmed desorption, PAHs, release energy, Polanyi-Wigner equation

Introduction

The remediation of soils and sediments contaminated with PAHs often results in residuals that exceed clean up standards. This has lead to an interest in determining if these residuals are actually available for uptake by plants and organisms, and thus pose a threat to human health and the environment. Research has found that PAH concentrations found by exhaustive extraction methods may not be indicative of the concentrations available to microorganisms [1] [2] and that the availability of PAHs tends to decrease with aging and treatment [3] [4]. This has lead to interest in the sorption and desorption behavior of PAHs and how it relates to physical availability.

Sorption and diffusion phenomena control the physical availability of PAHs for partitioning into the aqueous phase and, in turn, uptake by microorganisms. This physical availability can be assessed semi-quantitatively using release energy, with higher energy values indicating a more tightly bound compound. This release energy value depends on the type of compound as well as the characteristics of the sorbent. For this work, release energy can be thought of as the total energy required to release the compound from its sorbent, including the energy required for desorption from and diffusion through the sorbent matrix. Thus, it does not represent what is often called the activation energy of desorption (or desorption activation energy) in surface science and catalysis literature.

Release energy values can be calculated from TPD thermograms using several methods that fall into two general approaches, integral and differential. The integral approach relates desorption parameters to bulk peak characteristics such as half-widths and peak desorption temperatures. This approach is useful when the parameters are independent of coverage. The differential method utilizes Arrhenius plots from one or more thermograms and can be applied to

parameters that are coverage dependent. Specifically, Talley et al., used diffusion based desorption models and fit the activation energy parameter to TPD thermograms and found energy values ranging from 35-140 kJ/mol depending on the type of sorbent [5][6]. Yang et al., ran TPD at different temperature ramp rates and used the relationship between peak temperature and ramp rate (based on a method developed by Cvetanovic for first order desorption from homogenous surfaces [7]) to calculate desorption activation energies of nonchloro-dioxins on a variety of sorbents [8] [9].

Cornelissen et al., performed desorption studies at several temperatures and utilized the relationship between the activation enthalpy for slow desorption and the slow desorption rate constant to calculate desorption activation energies of several chlorobenzenes, polychlorinated biphenyls (PCBs) and PAHs. He found fairly constant energy values for lab and field contaminated sediments for all studied compounds (60-70 kJ/mol) [10]. It should be noted that these values represent only desorption activation energy and may not be directly comparable to release energy values found by Talley et al.

This work seeks to build upon the work of Talley et al. to determine if a non-linear fit method can be used to calculate release energy values from known contaminants on simple geosorbents. The current method fits the analytical solution to a simplified version of the Polanyi-Wigner equation to TPD thermograms by varying E and ν and determining the total squared error between the model and data. An error surface is generated to determine if a unique solution can be found within experimental variations. The work utilizes specific mineral sorbents to eliminate the complications associated with polymer diffusion (the early release of compounds from high carbon sorbents due to a heat induced change in the sorbent) found by Talley et al.[5].

Materials and Methods

Materials

The mineral sorbents used in this study were glass beads (1.0 mm nominal diameter), standard Ottawa sand, and kaolin from Fisher Scientific. The PAH standard was prepared from a TCL Polynuclear Aromatic Hydrocarbon mix containing 2000 μg/mL each of 16 PAHs (listed in Table 1) in a solution of 50:50 methylene chloride and benzene from Sigma-Aldrich. An internal standard was prepared from a 200 μg/mL indeno(1, 2, 3-c, d)pyrene solution in methanol from Sigma-Aldrich. The methylene chloride used was HPLC-GC/MS grade.

Instrumentation

This work utilizes thermal program desorption mass spectrometry (TPD-MS) with a direct insertion probe. The instrument setup includes a Thermo Finnigan Polaris Q mass spectrometer and a Thermo Finnigan Direct Insertion Probe (DIP) with a glass sample vial. Schematics of the TPD-MS used in this work are shown in Figure 1. This configuration allows a sample to be inserted directly into the MS, allowing for a better transfer of desorbed compounds and increased sensitivity.

The sample vials are cylindrical with an inside diameter of 1.0 mm and a 10 mm length. The sample is emplaced in a vial and weighed. The probe holding the vial is then inserted into the MS and the temperature is increased at a predetermined linear rate. Within each sample run, the raw ion count detected by the MS is proportional to the molecular flux in the ion volume and is thus proportional to the desorption rate of PAHs from the sample. Since PAHs typically produce molecular ions with very little fragmentation, multiple compounds can be analyzed simultaneously, provided they have different molecular weights.

Spiking procedure

Half a gram of each solid sample was saturated with methylene chloride to make a slurry. 25 μL of a 1 to 5 dilution of the 2000 μg/mL 16 PAH mixture was added to the slurry to create a 20 ppm concentration of each PAH, corresponding to 320 ppm total PAHs. The slurry was shaken continuously for 15 minutes, followed by 5 minute shaking once an hour for 4 hours. The samples were shaken to prevent loss of solid or PAH mixture on stir bars. Between shaking times, the slurry was allowed to evaporate in the ambient air inside a fume hood. Kaolin was allowed to dry for a slightly longer time as the slurry did not evaporate as quickly due to the kaolin's fine powdery nature. Samples were run within two days of spiking as initial results indicated the possibility of changes in some thermograms if samples were allowed to age for more than two days.

TPD method

For this study, three temperature ramp rates (10°/min, 20°/min, and 30°/min) were used for each sorbent tested. These temperature ramp rates were chosen based on machine limitations (ramp rates from 10 to 100°/min in 10° increments) and previous work conducted by Talley et al., which found consistent results using a 10°/min temperature ramp rate. For all temperature rates, a final temperature of 400°C and a hold time of 900 seconds were used. The maximum temperature of 400°C was chosen to ensure desorption was as complete as possible (for heavier weight PAHs) while limiting organic sample pyrolysis [5].

As recommend by Talley et al. [5], all sample vials were generally filled to approximately 1/8 capacity to limit interparticle-diffusional influences. Due to its lower density, kaolin sample vials were filled with slightly greater volume. Internal standards (40 ppm

indeno(1, 2, 3-c, d)pyrene on glass beads) were run at the beginning and end of each day to verify that the instrument was functioning properly.

Data processing and normalization

The raw TPD data was first transformed into thermograms for each PAH mass homolog using Polaris Q Xcalibur software that allows for the selection of specific mass to charge (m/z) values. The mass spectra of individual mass homologs were also checked with the NIST Mass Spectral Search Program (1998) to ensure that they represented the expected PAHs. The mass homolog thermograms were then normalized by dividing each intensity value by the total area under the curve, resulting in a normalized curve with a total area of one.

Release energy value calculation methods

The starting point for the determination of the kinetic parameters order (n), desorption activation energy (E), and the pre-exponential factor (ν) from a TPD thermogram is the desorption rate equation. Typically the Polanyi-Wigner equation [11] is used to model the rate of thermal desorption from a surface [12].

$$\frac{d\theta}{dT} = -\nu(\theta)\, \theta^{n}\, e^{-E(\theta)/RT} \qquad (1)$$

where ν is the pre-exponential factor (sec^{-1}), E is the desorption activation energy (J/mol), T is temperature (K), and R is the universal gas constant (J/mol-K), θ is the adsorbate coverage, and n is the desorption order. When E and ν are assumed to be coverage independent, the rate of temperature increase is constant, and coverage is assumed to correspond to concentration, the Polanyi-Wigner equation simplifies to equation 2.

$$\frac{dC}{dT} = -\frac{\nu}{\beta}\, Ce^{-E/RT} \qquad (2)$$

where β is the temperature ramp rate (K/sec). In order to build upon the method developed by Talley et al. [5], equation 2 was utilized for all further calculations.

For this work, equation 2 was first solved analytically for C (as opposed to numerically for dC as done by Talley et al.), giving equation 3:

$$C = C_o \exp\left[k_1\left(T_o e^{-k2/To} - T e^{-k2/T}\right) + k_1 k_2 \left(Ei\,(k_2/T) - Ei\,(k_2/T_o) \right) \right] \qquad (3)$$

where C is concentration, C_o is initial concentration, T is the temperature (K), T_o is initial temperature, $k_1 = \nu/\beta$, $k_2 = E/R$, and Ei is the exponential integral. For all model calculations, the initial concentration was set to one to correspond with the TPD data that was normalized to a total concentration of one. The derivative with respect to temperature (dC/dT) was then calculated numerically for any given combination of E and ν values. The derivative with respect to temperature was calculated as opposed to simply the change in concentration (dC) because, for a TPD spectrum, the intensity is proportional to the desorption rate [13]. Additionally, using the desorption rate ensures that the analytical solution does not depend on the temperature increment chosen for input into the model. The entire analytical model was then programmed into Matlab for user ease.

For application to the TPD data, E ranged from 20 kJ/mol to 140 kJ/mol to encompass the range of values found by Talley et al. for similar mineral sorbents [6] and ν ranged from 10^2 to 10^{16} to include the values calculated from experimental data [13]. The model was then applied to thermograms of individual mass homologs. The total squared error between the model and the data was calculated for each combination of E and ν and an error surface was generated to study how the error varied with each combination and determine if there was a unique set of E and ν values that resulted in a minimum error.

Results

In order to determine if the analytical solution behaved as expected, the model was run with E = 60 kJ/mol, $\nu = 10^6$ sec-^{1} and $\beta = 10^o$/min and concentration versus time and desorption rate versus time were plotted. These values for E and ν were chosen because they represented the midrange for both parameters and gave a full curve in the experimental temperature range. As expected, the concentration begins at one and decreases exponentially to zero over the course of the desorption process and dC/dT resembles a TPD thermogram with a total area of one, as shown in Figure 2. The effects of separately varying E and ν were also studied and it was found that when E was increased, the desorption rate curve shifted to the right, decreased in magnitude and became wider. Increasing ν shifted the desorption curve to the left, increased its magnitude and caused it to become more narrow, illustrated in Figure 3. This agrees with the compensation effect observed in many other studies, namely as E rises or falls, ν changes in the same direction resulting in the term $\nu\, e^{-E/RT}$ remaining relatively constant [14] [15] [16].

When the analytical model was applied to TPD data for glass beads, sand and kaolin, the results for each of the geosorbents were very similar. For this reason, the results will focus on glass beads mass homolog 228 and note any differences found for sand or kaolin, also mass homolog 228.

For E ranging from 20 kJ/mol to 140 kJ/mol and a ν range of 10^2 to 10^{16} sec^{-1}, the error surfaces for each of the temperature ramp rates (10°/min, 20°/min and 30°/min) are very similar in shape with the magnitude of the error decreasing with increasing temperature ramp rate. The error surface reveals a clear valley that, when viewed from above, shows a nearly linear relationship between E and ν for minimum error values, shown in Figure 4. This valley has a lumpy bottom for glass beads, leading to many combinations of E and ν that give similar error

values. It should be noted that even though there are local minima for the glass beads results, the difference between the values is not substantial enough to overcome the variation between replicate TPD runs. For the sand and kaolin, the valley has a smooth bottom, making the determination of even local error minimums impossible. The planes on either side of the valley/peak area occur because the model curves for those combinations of E and ν become flat lines for the experimental temperature range of 303 K to 773 K, leading to a constant error.

The error results were studied at smaller E and ν intervals around areas of low error to determine if the problem was resolution. This simply resulted in the identification of several model curves with very close error values, as shown in Figure 5.

Discussion

The analytical model does not provide a unique set of E and ν values when fit to actual TPD thermograms. Rather, it provides a series of pairs of values that result in similar total error when compared to TPD data. This makes it difficult to determine a distinct release energy value for any of the PAH mass homologs on any of the studied geosorbents, indicating that this method cannot be used by itself to calculate release energy values. There may also be further problems concerning both the assumption of coverage independence of E and ν and the Polanyi-Wigner equation's neglect of the simultaneous process of adsorption.

It has been found that for desorption from single crystal surfaces, E and ν vary strongly with surface coverage, often due to the adsorbate lateral interactions that can lead to multiple binding sites [15]. Zhdanov found changes in E exceeding approximately 40 kJ/mol (10 kcal/mol) and variation in ν of three or more orders of magnitude [17]. Seebauer also found changes in ν of up to six orders of magnitude and noted the importance of determining the coverage dependence ofν, especially for systems with higher coverage [14]. It has also been

noted recently that typical treatment of TPD data using the Polanyi-Wigner approach (which is based on the absolute rate theory and assumes equilibrium between adsorbing species and the substrate [18]) eliminates the adsorption term from the adsorption rate equation and may thus be missing the simultaneous presence of adsorption and desorption [19]. This may be impacting the interpretation of TPD data. Both of these issues suggest that, especially for geosorbent systems that are more complex than metal catalyst-gas systems, approaches that do not address coverage dependence or the presence of adsorption may not be used alone to determine release energy values.

Future work is needed to evaluate both the differential approach (if the required temperature ramp ranges and/or coverage variations can be achieved experimentally) and the statistical rate theory (SRT) approach to calculate E and ν. The differential or Arrhenius approach uses only the initial portion of the TPD thermogram where E and ν are relatively constant and may thus be used to provide an estimate of these desorption parameters. The equations developed using SRT have been found to predict TPD spectra for several metal-gas systems and appear to explicitly include all the necessary coverage and temperature dependence of the desorption parameters [18] so they may also be applicable to well characterized geosorbent systems.

Conclusions

The analytical solution to the simplified Polanyi-Wigner equation has been used to calculate release energy values of PAHs from several geosorbents. This method results in a series of combinations of E and ν values that produce desorption rate curves with similar errors when compared to real TPD data sets. These combinations of E and ν values can be viewed as an error surface, which contains a valley of minimum errors. This valley spans the range of E

and ν values, indicating that this method alone cannot be used to determine a unique set of E and ν values.

This approach and its results are important for two main reasons. First, the modeling approach is important because it allows for a global view of the non-linear fit and reveals the difficulty in determining a best fit solution, whereas, on a smaller scale it might seem that a true minimum model error had been found and a unique set of E and ν values determined. Second, the results suggest that the simplified version of the Polanyi-Wigner equation is not adequate for calculating desorption parameters from TPD thermograms and indicate that, as suggested in many reviews of TPD methods, the coverage dependence of both E and ν must be addressed. Therefore, future work will focus on determining if differential methods and the SRT approach can be used to estimate E and ν for similar geosorbent systems and then be applied to carbon containing materials and real soils and sediments. Future work will also seek to ascertain if exact release energy values can be calculated for sorbent systems that may not be as easily characterized as the metal catalyst-gas systems that have been used to develop most of the calculation techniques.

Acknowledgement

We would like to thank the Department of Defense (DOD) Strategic Environmental Research Development Program (SERDP) and the United States Army Engineer Research Center (ERDC), Waterways Experiment Station (WES) for their support of this work.

References

1. Alexander, M. 2000. Aging, Bioavailability, and Overestimation of Risk from Environmental Pollutants. *Environ. Sci. Technol*.; *(Critical Review)* 34(20): 4259-4265.
2. Kelsey, J. W.; Kottler, B. D.; Alexander, M. 1997. Selective Chemical Extractants To Predict Bioavailability of Soil-Aged Organic Chemicals. *Environ. Sci. Technol*. 31(1): 214-217.
3. Paul B. Hatzinger, Martin Alexander. 1995. Effect of Aging of Chemicals in Soil on Their Biodegradability and Extractability. *Environ. Sci. Technol.* 29(2): 537-545.
4. Tang, J.; Carroquino, M. J.; Robertson, B. K.; Alexander, M. 1998. Combined Effect of Sequestration and Bioremediation in Reducing the Bioavailability of Polycyclic Aromatic Hydrocarbons in Soil. *Environ. Sci. Technol*. 32(22): 3586-3590.
5. Ghosh, U.; Talley, J. W.; Luthy, R. G. 2001. Particle-Scale Investigation of PAH Desorption Kinetics and Thermodynamics from Sediment. *Environ. Sci. Technol.* 35(17): 3468-3475.
6. Talley, J., Ghosh, U., Furey, J., Tucker, S., Luthy, R. *Environmental Engineering Science*, in review.
7. Cvetanovic, R.J., Amenomiya, Y. 1972. A Temperature Programmed Desorption Technique for Investigation of Practical Catalysts. *Catal. Rev.* 6:21-85.
8. Long, R. Q.; Yang, R. T. 2001. Carbon Nanotubes as Superior Sorbent for Dioxin Removal. *J. Am. Chem. Soc.* 123(9): 2058-2059.
9. Yang, R. T.; Long, R. Q.; Padin, J.; Takahashi, A.; Takahashi, T. 1999. Adsorbents for Dioxins: A New Technique for Sorbent Screening for Low-Volatile Organics. *Ind. Eng. Chem. Res.* 38(7): 2726-2731.

10. Cornelissen, G.; van Noort, P. C. M.; Parsons, J. R.; Govers, H. A. J. 1997. Temperature Dependence of Slow Adsorption and Desorption Kinetics of Organic Compounds in Sediments. *Environ. Sci. Technol.* 31(2): 454-460.

11. Polanyi, M., Wigner E. 1928. *Zeitschrift fur Physikalische Chemie.* 139: 439.

12. Miller, J.B., Siddiqui, H.R., Gates, S.M., Russell, J.N., Yates, J.T. 1987. Extraction of Kinetic Parameters in Temperature Programmed Desorption: A Comparison of Methods. *J. Chem. Phys.* 87(11):6725-6732.

13. Hubbard, Arthur. 1995. *Surface Imaging and Visualization.* CRC Press, New York, New York, USA.

14. Seebauer, E.G., Kong, A.C.F., Schmidt, L.D. 1988. The Coverage Dependence of the Pre-exponential Factor for Desorption. *Surface Science*. 193:417-436.

15. Guo, X., Yates, J. 1989. Dependence of Effective Desorption Kinetic Parameters on Surface Coverage and Adsorption Temperature: CO on Pd(111). *J. Chem. Phys.* 90(11):6761-6766.

16. Adamson, Arthur W., Gast, Alice P. 1997. *Physical Chemistry of Surfaces.* John Wiley & Sons, Inc., New York, New York, USA.

17. Zhdanov, V.P. 1991. Arrhenius Parameters for Rate Processes on Solid Surfaces. *Surface Science Reports.* 12:183-242.

18. Elliot, J.A., Ward, C.A. 1997. Temperature Programmed Desorption: A Statistical Rate Theory Approach. *J. Chem. Phys.* 106(13):5677-5684.

19. Rudzinski, W.; Borowiecki, T.; Panczyk, T.; Dominko, A. 2000. Theory of Thermodesorption from Energetically Heterogeneous Surfaces: Combined Effects of Surface Heterogeneity, Readsorption, and Interactions between the Adsorbed Molecules**.** *Langmuir* 16(21): 8037-8049.

Table 1 PAH Mass Homologs

Mass Homolog	Compound
128	naphthalene
152	acenaphthylene
154	acenaphthene
166	fluorene
178	phenanthrene, anthracene
202	fluoranthene, pyrene
228	benzo(a)anthracene, chrysene
252	benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene
276	benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene
278	dibenzo(a,h)anthracene

Figure Legends

Figure 1. Schematic of thermal program desorption mass spectrometer with direct insertion probe with sample crucible placed inside.

Figure 2 – Analytical model for E = 60 kJ/mol, $\nu = 10^6$ sec^{-1}, $\beta = 10^o$/min. a) Normalized Concentration versus temperature, b) Desorption Rate versus temperature.

Figure 3 - Analytical model variation of E andν, $\beta = 10^o$/min. a) $\nu = 10^6$ sec^{-1}, E varied, illustrates shift towards the right with increasing E, b) E = 60 kJ/mol, ν varied, illustrates shift towards the left with increasingν.

Figure 4 – Glass beads mass homolog 228, $\beta = 10^o$/min, E = 30-130 kJ/mol (the range has been limited due to Matlab plotting limitations, error values between 20-30 kJ/mol and 130-140 kJ/mol were greater than those between 30-130 kJ/mol), $\nu = 10^2 – 10^{16}$ sec^{-1}. a) Error surface full view showing error valley, b) Error surface top view showing linear trend in error with E and ν, c) Error surface side view showing bottom of error valley. E in kJ/mol and ν in sec^{-1}.

Figure 5 - Three analytical model results show similar curves and error values when fit to TPD thermogram for glass beads mass homolog 228, $\beta = 10^o$/min. Error for curve 1, 2 and 3 is $2.91E^{-3}$, $2.12E^{-3}$ and $3.19E^{-3}$, respectively.

Figure 1

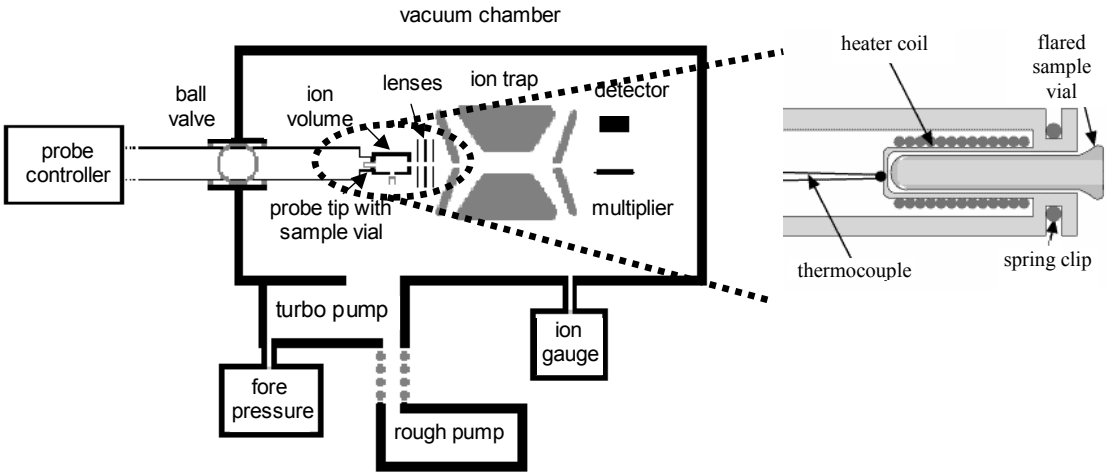
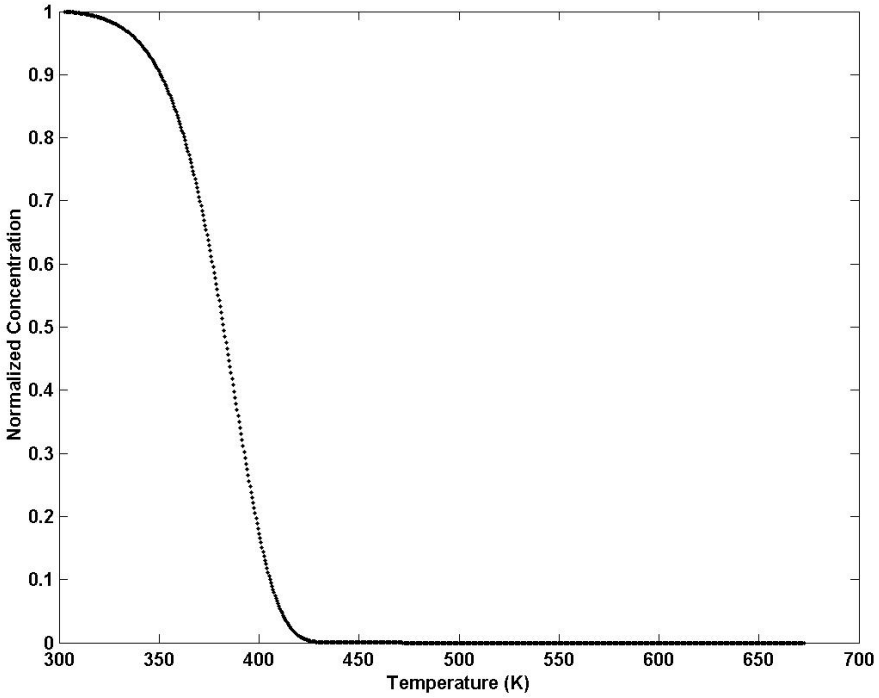

vacuum chamber
ball valve
ion volume
lenses
ion trap
detector
probe controller
probe tip with sample vial
multiplier
turbo pump
ion gauge
fore pressure
rough pump
heater coil
flared sample vial
thermocouple
spring clip

Figure 2

a)


Normalized Concentration
Temperature (K)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
300
350
400
450
500
550
600
650
700

b)

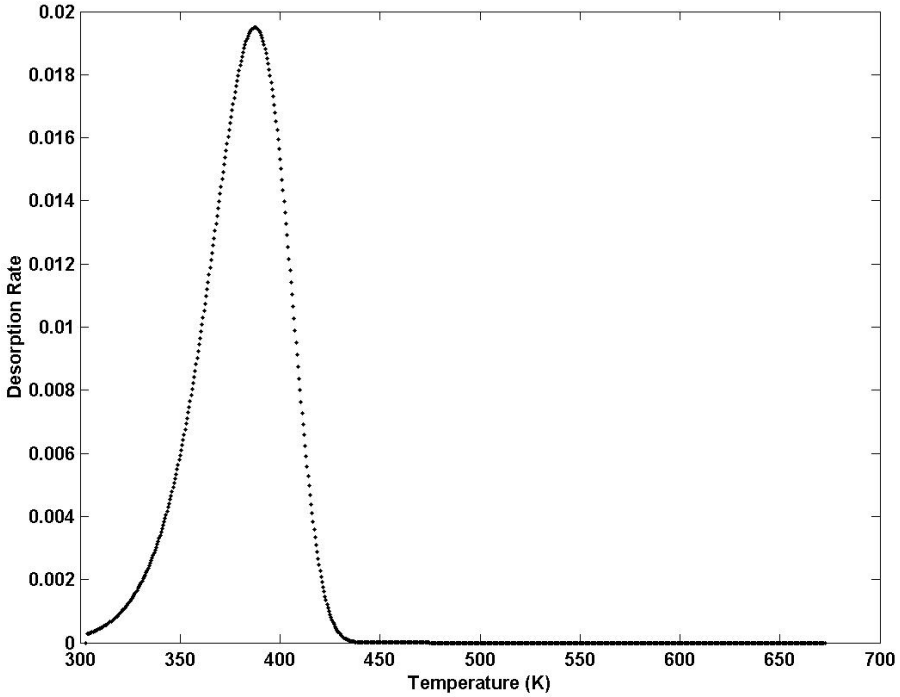
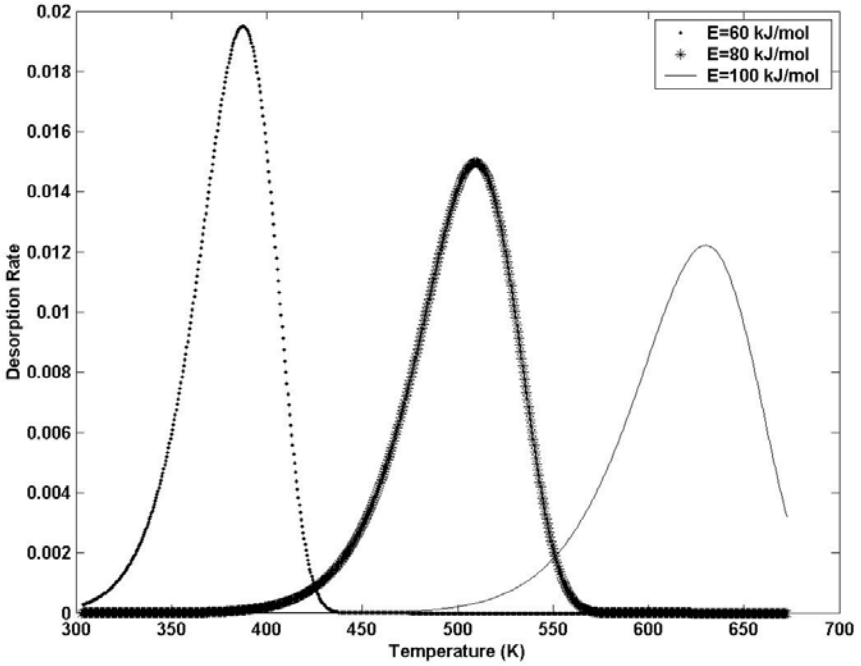

Desorption Rate
Temperature (K)
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
0.018
0.02
300
350
400
450
500
550
600
650
700

Figure 3

a)


E=60 kJ/mol
E=80 kJ/mol
E=100 kJ/mol
Desorption Rate
Temperature (K)
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
300
350
400
450
500
550
600
650
700

b)

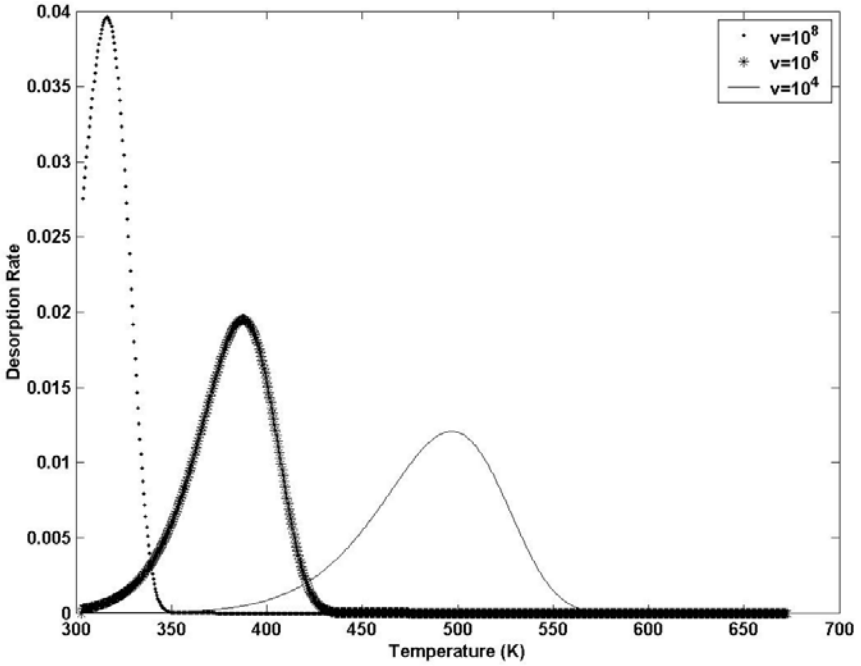
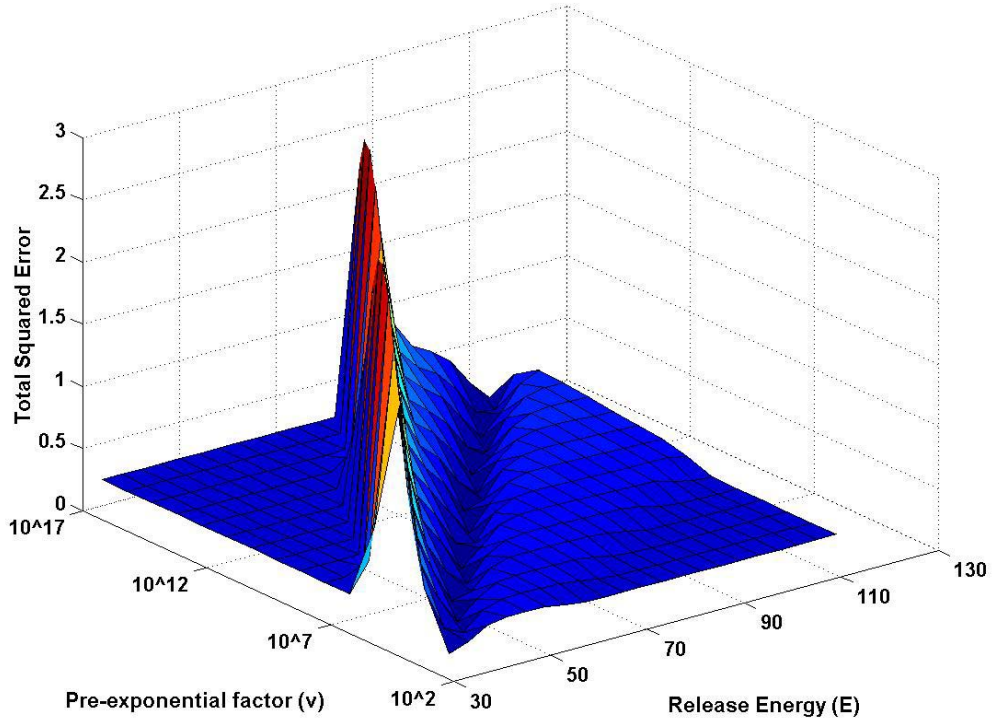
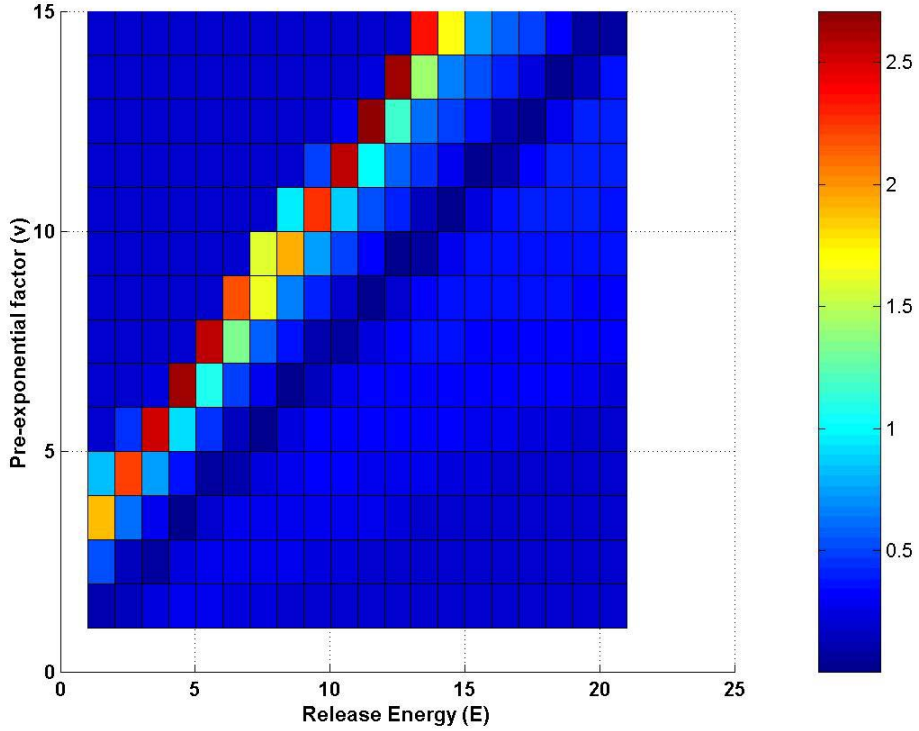

v=10^8
v=10^6
v=10^4
Desorption Rate
Temperature (K)
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
300
350
400
450
500
550
600
650
700

Figure 4

a)


Total Squared Error
3
2.5
2
1.5
1
0.5
0
10^17
10^12
10^7
10^2
Pre-exponential factor (v)
30
50
70
90
110
130
Release Energy (E)

b)


Pre-exponential factor (v)
15
10
5
0
0
5
10
15
20
25
Release Energy (E)
2.5
2
1.5
1
0.5

c)

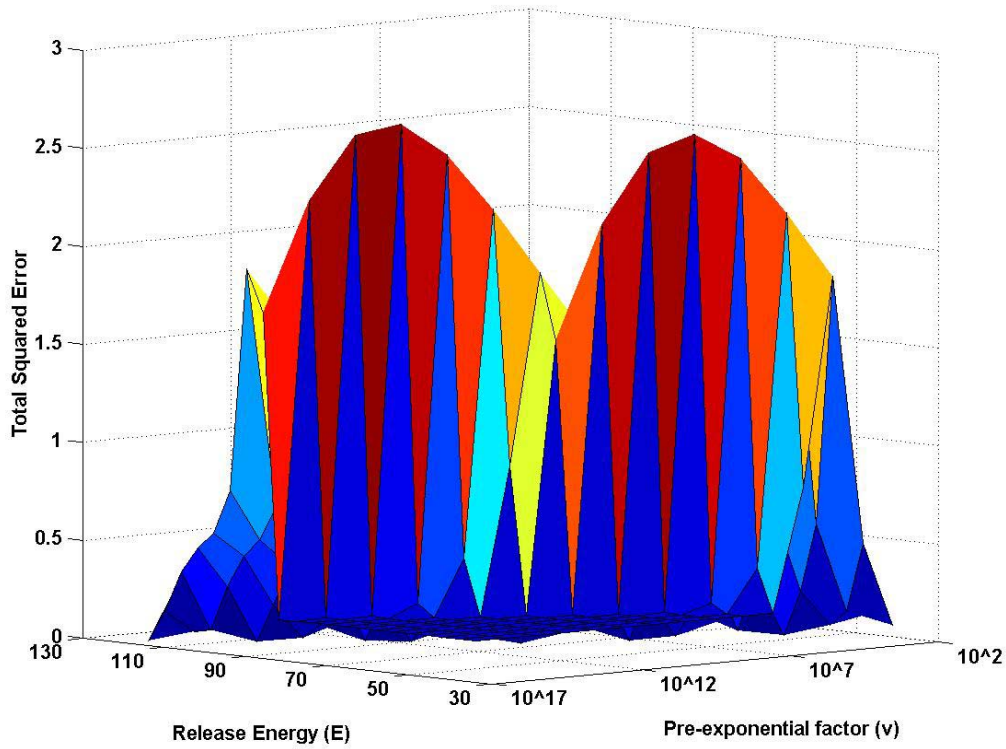
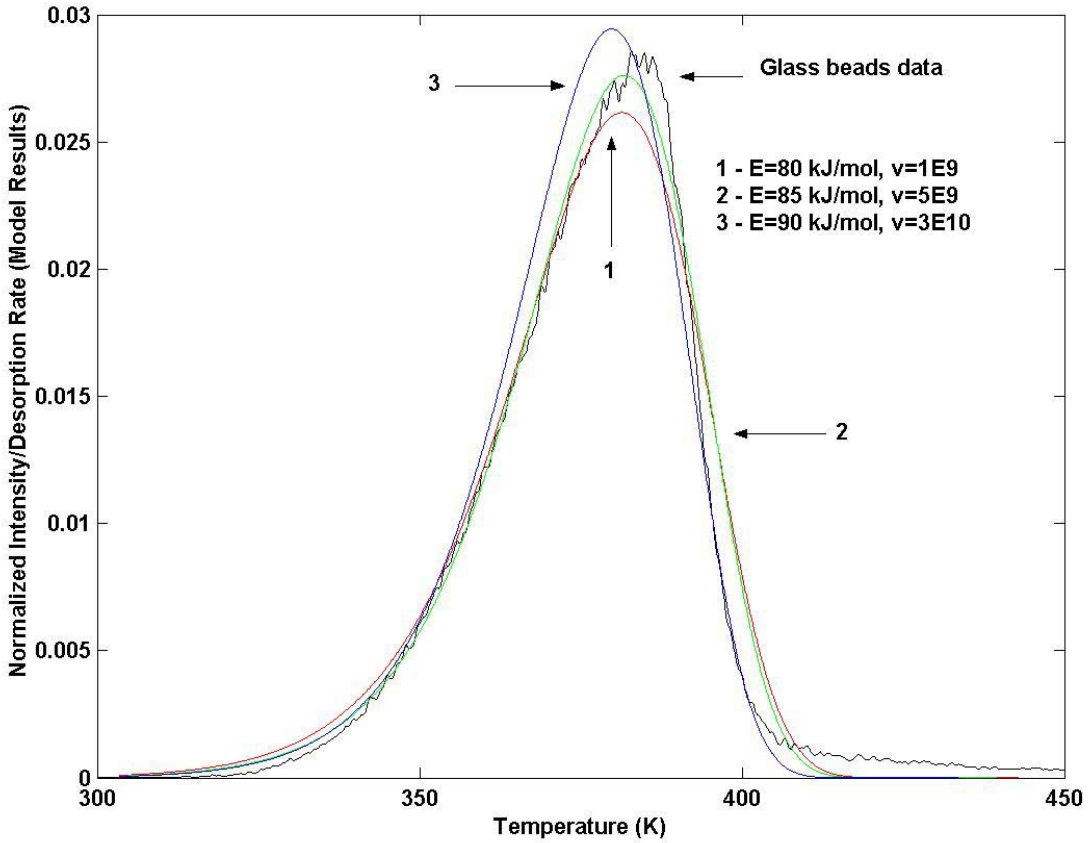

Total Squared Error
3
2.5
2
1.5
1
0.5
0
130
110
90
70
50
30
Release Energy (E)
10^17
10^12
10^7
10^2
Pre-exponential factor (v)

Figure 5


0.03
0.025
0.02
0.015
0.01
0.005
0
300
350
400
450
Temperature (K)
Normalized Intensity/Desorption Rate (Model Results)
Glass beads data
1 - E=80 kJ/mol, v=1E9
2 - E=85 kJ/mol, v=5E9
3 - E=90 kJ/mol, v=3E10
1
2
3

Appendix VII.

The Effects of Dose and Particle Size on Activated Carbon Treatment to Sequester PCBs and PAHs in Marine Sediments.

J.R. Zimmerman, D. Werner, U. Ghosh, R.N. Millward, T.S. Bridges, R.G. Luthy.

ABSTRACT

Recent laboratory studies show that mixing activated carbon with contaminated sediment reduces the chemical and biological availability of hydrophobic organic contaminants. In this study we test the effects of varying the activated carbon dose and particle size in reducing the aqueous availability of polychlorinated biphenyls (PCBs) and polycylic aromatic hydrocarbons (PAHs) and the uptake of PCBs by two benthic organisms. We mixed PCB- and PAH-contaminated sediment from Hunters Point Naval Shipyard San Francisco Bay, CA, USA, for one month with activated carbon, at doses of 0.34%, 1.7% and 3.4%, dry mass basis. We found that increasing the carbon dose increased the effectiveness in reducing PCB bioaccumulation. In 56-d uptake tests with the benthic organisms *Neanthes arenaceodentata* and *Leptocheirus plumulosus* PCB bioaccumulation was reduced by 93% and 90%, respectively, with 3.4% carbon. Increasing the dose also increased the effectiveness in reducing PCB and PAH aqueous concentrations and uptake by semi-permeable membrane devices and quiescent flux of PCBs to overlying water. Decreasing activated carbon particle size increased treatment effectiveness in reducing PCB aqueous concentration, while larger-sized activated carbon (400–1700 μm) was ineffective with a contact period of one month. We invoke a numerical model based on intraparticle diffusion in sediment and activated carbon particles to help interpret our experimental results. This model was useful in explaining the trends for the effect of activated carbon dose and particle size on PCB aqueous concentrations in well-mixed systems.

INTRODUCTION

Several studies have investigated the possibility of adding carbonaceous sorbents to sediment to reduce the bioavailability of hydrophobic organic contaminants. Kosian et al. [1] showed that mixing Ambersorb 1500 resin with spiked sediment reduced fluoranthene pore water concentrations and bioaccumulation by the oligochaete *Lumbriculus variegatus*. West et al. [2] found that contacting Ambersorb resin with contaminated field sediment reduced PAH pore water concentrations and body burdens in *L. variegatus*. Lebo et al. [3] showed that organic contaminant bioavailability was reduced to a much greater degree by Ambersorb and coconut charcoal that was finely ground compared to the same sorbents left whole (coarse). This group also used low-density polyethylene membranes and semi permeable membrane devices (SPMDs) to remove contaminants from spiked sediments and found that contaminants were removed to a much greater degree by LDPE membranes, which had a factor of 21 greater surface area than SPMDs of comparable mass [4].

Our recent work showed that mixing 3.4% activated carbon for one month with contaminated sediment from Hunters Point, San Francisco Bay, CA, USA, reduced the bioaccumulation of polychlorinated biphenyls (PCBs) in *Neanthes arenaceodentata* (worm) and *Leptocheirus plumulosus* (amphipod) by 82% and 70%, respectively, and *Macoma balthica* (clam) by 69% to 78% [unpublished data R.G. Luthy, Stanford University, Stanford, CA, USA] relative to untreated sediment in 28-d bioaccumulation tests. Six-months contact time of activated carbon with sediment showed further benefit in reduced PCB bioaccumulation by *N. arenaceodentata* and *L. plumulosus* in 28-d tests by achieving 87% and 75%, reductions respectively. Physicochemical tests with the same activated carbon-treated and untreated sediment showed 92% and 83% reductions in aqueous equilibrium PCB and polycyclic aromatic hydrocarbon (PAH) concentrations, reductions in PCB and PAH uptake by semi-permeable membrane devices (SPMD) of 77% and 83%, respectively, and reductions in PCB flux to overlying water in quiescent systems up to 89% [5]. Controlled, particle-feeding studies confirmed very low assimilation efficiency by *M. balthica* for benzo(a)pyrene and 22'55'-tetrachlorobiphenyl spiked onto powdered activated carbon compared to other forms of particulate organic matter [6].

In the present study we continue to explore the effects of activated carbon addition on reducing bioavailability of persistent organic contaminants through investigation of how the dose of activated carbon affects the reduction in PCB bioaccumulation and the availability of PCBs and PAHs to the aqueous phase. In addition, we study the effects of varying activated carbon particle size on reducing aqueous PCB concentrations and employ a numerical model to help interpret the results.

EXPERIMENTAL METHODS

Physicochemical tests

Activated carbon. We used two activated carbon types in this study, TOG and F400, whose properties are summarized in **Table 1**. Total carbon measurements of the activated carbons were performed by Huffman Labs (Golden, CO, USA). Other parameters were based on manufacturer specifications. Activated carbon was boiled in water for 5 minutes prior to use to remove any air pockets in pores.

Sediment-carbon contact: Test series 1–variable activated carbon dose. A composite sediment sample was obtained from the intertidal region in South Basin, adjacent to the former landfill at Hunters Point Naval Shipyard, San Francisco Bay, CA, as described previously [7]. We measured 9.9±0.9 mg/kg total PCBs in a composite sample from the site. Total PAH concentration for this sediment was 8±1 mg/kg [7]. Wet Hunters Point sediment, equivalent to approximately 3.8 kg dry mass, was placed in one gallon glass roller bottles, followed by addition of activated carbon and approximately 300 mL of seawater at 17 parts per thousand (‰) salinity. Four different treatments were set up: untreated sediment and sediment with TOG carbon added at 0.2, 1.0, and 2.0 times the existing sediment total organic carbon content of 1.7% (0.34%, 1.7% and 3.4%, dry mass basis). Bottles were rolled at approximately 3 rpm for 28 d. At the end of the contact period, wet sediment was shipped to the Environmental Research and Development Center, Vicksburg, MS, USA for bioaccumulation tests. Approximately 250 g of each sediment was placed in amber glass bottles and stored in a cold room at 4ºC for use in physicochemical tests.

Sediment-carbon contact: Test series 2–variable activated carbon particle size. Contact experiments were set up with TOG and F400 activated carbon to test the effects of variable activated carbon particle size in reducing aqueous availability. Coarse (uncrushed) TOG (75–300 μm) carbon was used as a baseline for the degree of reduction in aqueous availability. We crushed and sieved a portion of the TOG carbon to obtain a fraction <75 μm, which we refer to as "TOG fine." Carbon type F400 (size range 400–1700 μm), is much larger than TOG (75–300 μm). To assess differences in treatment effectiveness due to particle size rather than differences in the carbon characteristics (e.g., porosity, specific surface area), we crushed and sieved F400 carbon to 75 – 250 μm, which is within the same particle size range as TOG. The uncrushed F400 is referred to as "F400 granular," and the crushed F400 is referred to as "F400 coarse." A total of five different treatments were set up: untreated sediment (control) and sediment contacted with TOG coarse, TOG fine, F400 granular, and F400 coarse activated carbon, all at 3.4%, dry mass basis.

Approximately 18 g wet sediment was added to 20 mL glass vials, followed by TOG or F400 carbon and a small amount of 17‰ seawater with 1g/L sodium azide, leaving approximately 1 mL headspace, and sealed with Teflon-lined caps. The vials were rotated end over end at 18 rpm for 28d. At the end of the contact period, sediment/carbon slurries were transferred to 780 mL glass centrifuge tubes for aqueous PCB concentration measurements. Previous tests with 75-300 mm TOG carbon showed further improvement in aqueous concentration reduction with contact period of 6 months for well-mixed systems.

Semi-Permeable Membrane Device (SPMD). The SPMDs are a biomimetic tool used to assess the chemical and biological availability of hydrophobic organic contaminants in sediment and water [8-11]. In this work SPMDs were used to study the effect of activated carbon on reducing the aqueous availability of PCBs and PAHs. Our experimental method followed that described previously [5]. Untreated sediment and sediment contacted with 0.34%, 1.7%, and 3.4% TOG carbon from Test 1 was placed in 40 mL vials, followed by 17‰ seawater with 1g/L sodium azide, leaving approximately 1 mL headspace. The mass of wet sediment used in each vial averaged 11.8 ± 0.4 g. The vials were rotated end over end at approximately 18 rpm for 14 d. SPMDs were then removed from vials, cleaned with 1 N hydrochloric acid, rinsed with deionized water, acetone and isopropyl alcohol and air dried, and then dialyzed with hexane to extract PCBs and PAHs.

Quiescent flux. Diffusive PCB flux from contaminated sediment was measured in quiescent systems with untreated sediment and sediment contacted with 0.34%, 1.7%, and 3.4% TOG carbon from Test 1. The experimental procedure followed that described previously [5], wherein sediment was added to 250 mL beakers, followed by 17‰ seawater with 1g/L sodium azide. Water and sediment were stirred, then solids were allowed to settle and stainless steel mesh baskets filled with XAD resin beads were suspended above the sediment. The beakers were covered and placed in a dark cabinet for 36 d. At the end of the quiescent flux period, the baskets were removed from the beakers without disturbing the sediment, and the XAD beads were removed and extracted with 1:1hexane:acetone, then hexane. Extracts were concentrated, cleaned and analyzed for PCBs as described below. Stainless steel baskets with clean XAD beads were placed in the beakers for another flux period of 131 d (four months), after which PCBs were extracted and analyzed as in the 36-d flux experiment.

Aqueous concentration: Test series 1–variable activated carbon dose. Equilibrium aqueous PCB and PAH concentrations were measured for untreated sediment and sediment contacted with 0.34%, 1.7%, and 3.4% TOG carbon from Test 1. Approximately 100 g of treated or untreated sediment was added to 1.9 L bottles with 17‰ seawater and 1 g/L sodium azide and then rotated on a bottle roller at approximately 3 rpm for 14 d. At the end of this period the bottles were removed from the roller and the solids allowed to settle and clear supernatant transferred to 780 mL centrifuge bottles. 2.5 mL of 0.1 M alum solution and 0.8 mL of 1 N NaOH were then added to each centrifuge bottle and shaken gently to promote flocculation and then centrifuged at 700 *g* for 15 min [5]. Supernatant was transferred to a separatory funnel and extracted three times with hexane using a modified version of U.S. EPA SW 846 Method 3510 [12]. The combined extracts were dried with anhydrous sodium sulfate and concentrated to approximately 40 mL using a rotary evaporator and then 1 mL using nitrogen blowdown. The 1 mL sample was cleaned and analyzed for PCBs and PAHs using the methods described below.

Aqueous concentration: Test series 2–variable activated carbon particle size. For Test 2, approximately 30 g of untreated or TOG- or F400-treated wet sediment was placed in 780 mL glass bottles with 17‰ seawater and 1g/L sodium azide. The bottles were rotated at approximately 3

rpm on a roller for 14 d then centrifuged at 700 g for 15 min. Colloid removal by flocculation, extraction and cleanup, and PCB measurements followed the procedures described above for Test 1.

PCB and PAH analysis. Hexane extracts from aqueous equilibrium, SPMD dialysis, and quiescent flux experiments were cleaned using silica gel and analyzed for PCBs by congener and PAHs (16 Priority Pollutant List PAHs) by gas chromatography-electron capture detection (GC-ECD) and gas chromatography-flame ionization detection (GC-FID), respectively, following U.S. EPA SW-846 Methods 3630C, 8082 and 8100 [12], as described by Ghosh et al. [7].

Biological Tests

PCB bioaccumulation. PCB bioaccumulation in *N. arenaceodentata* and *L. plumulosus* was studied using 56-d sediment toxicity protocols, following methods described elsewhere [unpublished data R.G. Luthy, Stanford University, Stanford, CA, USA]. Twenty-five 2-d old *L. plumulosus* were placed in 1 L beakers containing wet sediment (approximately 100 g dry weight) and 725 mL of 20‰ artificial seawater. Overlying water was aerated gently, with 50% water exchange three times each week. *Leptocheirus plumulosus* were fed after each 50% water change. In tests with *N. arenaceodentata*, ten 2-wk old worms were placed in 1 L beakers containing sediment and 725 mL of 30‰ artificial seawater. *Neanthes arenaceodentata* were fed twice a week after each water exchange.

Prior to PCB body burden analysis, *L. plumulosus* were removed from the sediment and allowed to clear gut contents for 2–4 hr. The mean gut passage time for *L. plumulosus* is about 1.5 hr [13] with about 3hr sufficient for most amphipods to clear their guts [14]. *Neanthes arenaceodentata* were allowed to clear their gut contents overnight in 30‰ artificial seawater, after which all remaining ingested sediment was removed by applying gentle rearward pressure along the digestive tract.

PCB analyses. PCB tissue concentrations were analyzed using a procedure based on standard U.S. EPA methods but adapted to utilize smaller (≤100 mg) wet weights of tissue [unpublished data R.G. Luthy, Stanford University, Stanford, CA, USA]. Tissue samples were extracted, cleaned,

concentrated and analyzed using modified versions of U.S. EPA SW-846 Methods 3550B, 3630C and 8270 [12] for 31 PCB congeners present in both tissue and sediment above detection limits.

Numerical mass transfer model

A mass transfer model was developed to simulate contaminant desorption from sediment and uptake by activated carbon in mixed systems. A numerical scheme described by Wu and Gschwend [15] was adapted to simulate the intraparticle diffusive release of contaminants from two sediment domains, comprising low density, carbonaceous sediment particles and high density, mineral sediment particles, and the diffusive uptake by activated carbon particles. Wu and Gschwend [15] used a numerical model to investigate the effect of particle size distributions on sorption dynamics, thus facilitating the necessary adaptations for our model, which also distinguishes between different particle types. The governing equation for sorption-retarded intraparticle diffusion in radial coordinates is:

$$\frac{\partial S(r)}{\partial t} = D_{eff}\left[\frac{\partial^2 S(r)}{\partial r^2} + \frac{2}{r}\frac{\partial S(r)}{\partial r}\right] \qquad 1$$

where *S(r)* is the total local volumetric concentration varying as a function of radial distance, *r*, from the center of light or heavy sediment particles or activated carbon particles, and *t* is time. For the sediment particles we obtain apparent diffusive release rates from desorption data presented in our earlier work [5]. For activated carbon, we estimate D_{eff} according to [15].

$$D_{eff} = \frac{D_m n^2}{(1-n)\, r_s K_p + n} \qquad 2$$

where D_m is the aqueous solution molecular diffusivity, K_p is the equilibrium sorption partition coefficient, n is the particle porosity, and r_s is the dry solid density. The change in aqueous phase PCB concentration is given by

$$\frac{dC}{dt} = -\frac{V_h}{V}\frac{d}{dt}\left[\frac{3}{R_h^{\,3}}\int_0^{R_h} r^2 S_h(r)dr\right] - \frac{V_l}{V}\frac{d}{dt}\left[\frac{3}{R_l^{\,3}}\int_0^{R_l} r^2 S_l(r)dr\right] - \frac{V_{AC}}{V}\frac{d}{dt}\left[\frac{3}{R_{AC}^{\,3}}\int_0^{R_{AC}} r^2 S_{AC}(r)dr\right] \qquad 3$$

where V_h, V_l and V_{AC} are the total volumes of the heavy and light sediment particles and the activated carbon particles, *V* is the volume of the solution, *C* is the aqueous PCB concentration, and R_h, R_l and R_{AC} are the radii of the heavy and light sediment particles and the activated carbon particles.

The simulated contaminant concentration on the external surface of each particle type is assumed to be in linear partitioning equilibrium with the external aqueous phase, which is well-mixed. Linear partitioning is assumed because we are examining change in aqueous concentration at low levels over a concentration range spanning less than about two orders of magnitude. For each time step the algorithm calculates the amount of contaminant diffusing out of the two sediment domains and into the activated carbon based on the concentration gradients within the particles. Using a mass balance, these fluxes determine the concentration change in the bulk aqueous phase.

The model requires a total of 16 input parameters to simulate the mass transfer of a PCB congener in sediment/activated carbon contact experiments. These parameters were obtained for 22'455'-PCB (PCB101) and 23'44'5-PCB (PCB118) from experimental and literature data. For the sediment domains linear partitioning coefficients and apparent diffusive release rates (D_{eff}/R^2) were derived from experimental data for PCB distribution between light and heavy sediment particles comprising two sorption domains with different rates of PCB release [7]. For activated carbon, the linear partitioning coefficients were taken from Jonker and Koelmans [16], and apparent diffusivities were estimated using equation 2, above. For the different activated carbon particle sizes, the radius was taken as half the value of the geometric mean of the upper and lower limits of the particle diameters. This is a reasonable choice for a first approximation if the particle size distribution is confined to a narrow range [15]. Particle size ranges and corresponding radii for use in model simulations are shown in **Tables 2 and 3**. For powdered TOG carbon (< 75 μm), the lower limit was estimated as 25 μm because the majority of these particles were larger than this. PCBs 101 and 118 were chosen for the numerical modeling because they were found in measurable quantities in Hunters Point sediment and in the aqueous phase in equilibrium experiments and measured K_{AC} values were available for both (log K_p=9.18 (L/kg carbon) for PCB101 and log K_p=9.45 for PCB 118) [16]. A more complete description of the model, including the input parameters used and the validity of the model assumptions, is available elsewhere [D. Werner, School of Civil Engineering and Geosciences, University of Newcastle upon Tyne, UK].

RESULTS AND DISCUSSION

<u>Physicochemical and bioaccumulation tests: Test series1–variable activated carbon dose.</u>

Figures 1a and 1b show the total PCB and total PAH aqueous concentrations for untreated sediment and sediment contacted with 0.34%, 1.7%, and 3.4% 75–300 μm TOG carbon for one month. The figures show a definite dose response in that increasing the carbon dose decreases the aqueous concentration of both PCBs and PAHs. In the case of PCBs the aqueous concentrations are gradually reduced by 44%, 74%, and 87%, with increasing dose. There is an 81% reduction in aqueous PAHs with 1.7% carbon and no statistically significant change with further increase in carbon dose to 3.4%. The reductions of the aqueous concentrations vary for the individual PCB and PAH compounds. For both PCBs and PAHs, aqueous concentrations of the less hydrophobic compounds are reduced to a greater extent than that for the more hydrophobic compounds. This trend is illustrated for the PCB homologs in **Figure 2**. For the highest dose of carbon, tetrachlorobiphenyl aqueous concentration is reduced by 99% compared to 76% for heptachlorobiphenyls. Lebo et al. [3] found for PAH-spiked sediments that activated carbon addition reduced the bioavailability of naphthalene more than that for phenanthrene. Thus, the repartitioning of the PCBs from sediment to activated carbon appears to be faster for the lower chlorinated and less hydrophobic congeners compared to the higher chlorinated and more hydrophobic congeners. In our previous work using only the highest dose of carbon we showed that with longer time, there is further reduction of aqueous equilibrium PCB concentrations for the hexa and heptachlorobiphenyls [5]. Thus, the aqueous concentration reduction differences among homolog groups may be a matter of slower mass transfer kinetics.

Figure 3 shows the effect of carbon dose on the PCB homolog mass uptake in SPMDs. The uptake of PCBs by SPMD is reduced by 17%, 45% and 73% with increasing activated carbon dose. For SPMD uptake also, the carbon treatment is more effective for the lower chlorinated PCBs than the higher chlorinated PCBs for the 1-month contact time test. The uptake of tetrachlorobiphenyls in SPMD is reduced by 91% for the highest carbon dose compared to 56% for heptachlorobiphenyls with the same carbon dose. The effect of activated carbon dose on PAH uptake by SPMD is shown in **Figure 4**. Although aqueous PAH concentration was not affected significantly by increasing the activated carbon dose from 1.7% to 3.4%, the uptake in SPMDs was decreased further. **Figure 5** shows similar trends for quiescent flux experiments, for which the release of PCBs to overlying water is reduced to a greater degree with increasing activated carbon dose. The same trend of

reducing PCB aqueous flux with increasing carbon dose is seen for the first one month and also for the period between 1-5 months.

The results of 56-d PCB bioaccumulation tests using *N. arenaceodentata* and *L. plumulosus* are shown in **Figure 6**. Both species exhibit a clear dose response in decreasing PCB body burdens with increasing activated carbon additions. For *N. arenaceodentata* statistically significant reductions in PCB uptake of 87% and 93% were observed for the 1.7% and 3.4% dose of activated carbon. For *L. plumulosus* statistically significant reductions in PCB uptake of 73%, 77% and 90% were observed for activated carbon doses of 0.34%, 1.7%, and 3.4% respectively.

We conclude from both physicochemical and bioaccumulation tests using sediment contacted with varying activated carbon doses that increasing the carbon dose increased treatment effectiveness, as evidenced by reductions in aqueous PCB and PAH concentration, PCB and PAH uptake by SPMD, PCB quiescent flux, and PCB bioaccumulation by a worm and an amphipod. Figures 1 through 6 show that the percent reduction achieved among the various tests approaches approximately 90% for a carbon dose of 3.4%. For most of the tests, there was a decrease in contaminant availability as the dose increased from 1.7% to 3.4%. However, for PAHs, the reduction in aqueous concentration and uptake by SPMDs did not decrease as much as for PCBs as dose increased from 1.7% to 3.4%. Based on these results, it appears that there may be different dose responses for different compound classes, which would depend on the distribution of specific contaminants in the sediment and their association among sediment particle types. For consideration of application of activated carbon at any particular contaminated sediment site, it is likely that a series of tests similar to those shown here would be needed to determine an appropriate dose for a desired endpoint within a specified time period.

<u>Physicochemical tests: Test series 2–variable activated carbon particle size</u>. **Figure 7** shows the effect of activated carbon particle size in reducing PCB aqueous equilibrium concentrations. Crushing TOG carbon to approximately 25–75 μm diameter increased the reduction in aqueous PCB concentrations from 82% to 97%. No significant decrease in aqueous PCB concentrations resulted from contacting sediment with granular F400 carbon. However, crushing F400 particles to 75–250 μm resulted in a 67% reduction in aqueous PCB concentration. Analysis of these data to

assess the behavior of individual congeners showed that aqueous PCB concentrations for the granular F400 treatment were reduced only for some of the lowest molecular weight PCB congeners. For the case of Hunters Point sediment and the higher molecular weight congeners present, these activated carbon particle size tests establish an upper bound for the carbon particle size that manifests a beneficial effect under optimal mixing conditions in short term tests.
At Hunters Point the distribution of PCB congeners is weighted toward higher molecular weight PCBs [7], and as explained below, the mass transfer to activated carbon for higher molecular weight PCBs is slow in comparison to lower molecular weight congeners. Activated carbon as large as granular F400 may be effective with other sediments where the distribution of congeners is dominated by lower molecular weight congeners.

Numerical model results. We used numerical modeling to help understand the PCB mass transfer rates and mechanisms occurring in our contact experiments. The model simulates the mass transfer of PCBs as a two step process–-desorption from two domains of sediment particles followed by adsorption on activated carbon. By modifying input parameters with respect to carbon dose and particle size we estimated how changing activated carbon dose or particle size affects the aqueous concentrations of PCBs101 (22'455'-PCB) and 118 (23'44'5-PCB).

Table 2 shows results from model simulations for PCBs 101 and 118 using different doses of 75-300 μm diameter activated carbon treatment doses. Measured values of relative aqueous concentration ($C_{aq,treated}/C_{aq,untreated}$) for 28-d contact are also shown. Comparison of results in Table 2 shows the following. First, the model predicts lesser reduction in aqueous phase concentrations for PCB 118. Second, the model predicts that increasing activated carbon dose decreases aqueous PCB concentration. In both cases, the trend predicted by the model is in agreement with the experimental results. That is, the model predicts greater activated carbon sorption of PCB101 and increasing sorption with increasing carbon dose. However, the relative aqueous concentration values predicted from modeling are consistently lower than the measured relative concentration values by a factor of 3–5 for PCB101 and a factor of 2–3 for PCB118.

Results from modeling the effects of variable activated carbon particle size are presented in Table 3. This shows aqueous PCB101 concentrations are consistently reduced to a greater degree than

PCB118, as was the case in the variable dose experiments. Also, decreasing activated carbon particle size significantly increases the effectiveness in reducing aqueous PCB concentrations. Similar to the modeling results from the variable dose simulations, the model overpredicts the effectiveness of the activated carbon in reducing aqueous PCB concentrations. In this case, the model overpredicts the effectiveness by a factor of 2–6 for TOG carbon, and by a factor of 7–17 for F400 carbon.

We envision PCBs desorbing from sediment particles into the bulk water and then sorbing to the outermost portion of the activated carbon particles. PCBs then diffuse slowly toward the carbon particle center, which may occur over a period of months to years for the more highly chlorinated PCBs. Diffusion of PCBs out of the sediment and into the activated carbon pores is retarded by the strong sorption to the pore walls and is slower for more hydrophobic, higher molecular weight PCB congeners as compared to lower molecular weight, less hydrophobic, congeners. The model predicts slower mass transfer of the higher molecular weight congeners from the sediment into the carbon. This is a consequence of several mass transfer steps for the PCBs moving from the sediment into the carbon, any of which could cause the slow uptake of higher molecular weight PCBs including the aqueous concentrations of the different congeners.

The increased effectiveness of activated carbon treatment with decreasing particle size is clearly evident from Table 3. However, the models are less consistent with regard to predicting the increase in effectiveness of activated carbon due to decreasing particle size than it is for predicting the effect of increasing dose. This is likely due in small part to differences between the physical properties of TOG and F400 carbon. A more probable reason for disagreement between modeled and measured aqueous concentrations is the values taken for the activated carbon/water partition coefficient, K_{AC}. The values we used in modeling were obtained from Jonker and Koelmans [16], who measured K_{AC} for systems comprising activated carbon and clean water. In contrast, for our systems K_{AC} may actually be substantially lower due to competition from other adsorbents such as humic materials and other PCBs and PAHs, or due to pore blockage. The modeling showed that by decreasing the K_{AC} value by a factor of 4–270 (median 24) from that reported by Jonker and Koelmans [16] for clean water led to significantly better agreement between modeled and measured aqueous PCB concentrations.

Another probable reason for disagreement between the numerical model and experimental results is the use of equation 2 for the estimation of the diffusivity in activated carbon. In highly microporous solids like activated carbon the effective diffusivity, D_{eff}, is further reduced due to constricted diffusion in narrow pores [17]. Multiplying the right-hand side of equation 2 by a constrictivity factor, K_r, of 0.002–0.25 (median 0.04) also leads to significantly better agreement between model and experimental results.

Thus the numerical mass transfer model is capable of qualitatively reproducing the effect of sediment-PCB association and activated carbon uptake on aqueous PCB concentrations for well-mixed systems, but systematically overestimates the actual reduction in PCB aqueous concentration. Sediment-impacted values of K_{AC} for activated carbon contacted with fine sediments from Hunters Point and measured values of D_{eff} from kinetic uptake studies may provide more accurate parameter values and improve agreement between measured and modeled concentrations.

In conclusion, we found that varying the dose of activated carbon mixed with contaminated sediment strongly affects the degree of reduction in aqueous PCB and PAH concentrations, PCB and PAH uptake by SPMDs, and PCB quiescent flux to overlying water. PCB bioaccumulation by *N. arenaceodentata* and *L. plumulosus* showed a definite dose response, with greater reduction in biouptake with increasing activated carbon dose, up to 93% and 90%, respectively, with 3.4% carbon. The effect of the carbon doses on aqueous concentration or uptake by SPMD was not as pronounced for PAHs as for PCBs. Our short-term experiments clearly showed the importance of activated carbon particle size, corroborating the results shown by others [3, 4] on greater reduction in contaminant availability with increased sorbent external surface area. Our data also suggest that there is an upper limit to the activated carbon particle size that can be effectively applied with this sediment. We compared measured versus modeled aqueous PCB concentrations and conclude that determining K_{AC} and D_{eff} values for activated carbon contacted with sediment will likely improve agreement between measured and modeled values in mixed systems.

ACKNOWLEDGEMENT

Funding for this research is from the Department of Defense through the Strategic Environmental Research and Development Program (Contract No. DACA72-01-C-0002). Supplemental support was provided by Schlumberger, Ltd. John R. Zimmerman is with Environ Corp., Arlington, VA, USA. David Werner was previously a post doctoral researcher in the department of Civil and Environmental Engineering, Stanford University. He received support from the Swiss National Science Foundation, Grant 81EL68477.

1. Kosian PA, West CW, Pasha MS, Cox JS, Mount DR, Huggett RJ, Ankley GT. 1999. Use of nonpolar resin for reduction of fluoranthene bioavailability in sediment. *Environ Toxicol Chem* 18:201-206.

2. West CW, Kosian PA, Mount DR, Makynen EA, Pasha MS, Sibley PK, Ankley GT. 2001. Amendment of sediments with a carbonaceous resin reduces bioavailability of polycyclic aromatic hydrocarbons. *Environ Toxicol Chem* 20:1104-1111.

3. Lebo JA, Huckins JN, Petty JD, Cranor WL, Ho KT. 2003. Comparisons of coarse and fine versions of two carbons for reducing the bioavailabilities of sediment-bound hydrophobic organic contaminants. *Chemosphere* 50:1309-1317.

4. Lebo JA, Huckins JN, Petty JD, Ho KT, Stern EA. 2000. Selective removal of organic contaminants from sediments: a methodology for toxicity identification evaluations (TIEs). *Chemosphere* 40:811-819.

5. Zimmerman JR, Ghosh U, Millward RN, Bridges TS, Luthy RG. 2004. Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments. Physicochemical tests. *Environ Sci Technol* 38:5458-5464.

6. McLeod PB, van den Heuvel-Greve MJ, Allen-King RM, Luoma SN, Luthy RG. 2004. Effects of particulate carbonaceous matter on the bioavailability of benzo[a]pyrene and 2,2',5,5'-tetrachlorobiphenyl to the clam *Macoma balthica*. *Environ Sci Technol* 38:4549-4556.

7. Ghosh U, Zimmerman JR, Luthy RG. 2003. PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability. *Environ Sci Technol* 37:2209-2217.

8. Echols KR, Gale RW, Schwartz TR, Huckins JN, Williams LL, Meadows JC, Morse D, Petty JD, Orazio CE, Tillitt DE. 2000. Comparing polychlorinated biphenyl concentrations and patterns in the Saginaw River using sediment, caged fish, and semipermeable membrane devices. *Environ Sci Technol* 34:4095-4102.

9. Peven CS, Uhler AD, Querzoli FJ. 1996. Caged mussels and semipermeable membrane devices as indicators of organic contaminant uptake in Dorchester and Duxbury Bays, Massachusetts. *Environ Toxicol Chem* 15:144-149.

10. Bennett ER, Metcalfe TL, Metcalfe CD. 1996. Semi-permeable membrane devices (SPMDs) for monitoring organic contaminants in Otonabee River, Ontario. *Chemosphere* 33:363–375.

11. Granmo Å, Ekelund R, Berggren M, Brorström-Lundén E, Bergqvist PA. 2000. Temporal trend of organochlorine marine pollution indicated by concentrations in mussels, semipermeable membrane devices, and sediment. *Environ Sci Technol* 34:3323–3329.

12. U.S. EPA, SW-846 On-Line. Test methods for Evaluating Solid Wastes: Physical/Chemical Methods. U. S. Environmental Protection Agency, Office of Solid Waste. (http://www.epa.gov/epaoswer/hazwaste/test/main.htm)

13. Schlekat CE, Decko AW, and Chandler GT. 1999. Dietary Assimilation of cadmium associated with bacterial exopolymer sediment coatings by the estuarine amphipod Leptecheirus plumulosus: Effect of Cd concentration and salinity. *Mar Ecol Prog Ser* 183:205-216.

14. Schlekat CE, Decko AW, and Chandler GT. 2000. Bioavailability of particle-associated silver, cadmium, abd zinc to the estuarine amphipod Leptocheirus plumulosus through dietary ingestion. *Limnol Ocean* 45: 11-21.

15. Wu SC, Gschwend PM. 1988. Numerical modeling of sorption kinetics of organic-compounds to soil and sediment particles. *Water Resour Res* 24:1373–1383.

16. Jonker MTO, Koelmans AA. 2002. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations. *Environ Sci Technol* 36:3725–3734.

17. Ball WP, Buehler C, Harmon TC, Mackay DM, Roberts PV. 1990. Characterization of a Sandy Aquifer Material at the Grain Scale. *J Contam Hydrol* 5:253–295.

Table 1: Summary of activated carbon properties

	TOG	F400
Particle diameter (μm)	75–300	420–1700
Solid density (g/mL solid)	1.96	1.80
Carbon source	Coal	Coal
Percent elemental carbon	87%	89%
Specific surface area (m^2/g)	938	1,100
Porosity (volume void/total particle volume)	0.55	0.59
Manufacturer	Calgon	Calgon

Table 2: Results of numerical modeling of the aqueous concentration of polychlorinated biphenyls for an activated carbon dose of 3.4% dry mass basis and 28-d contact. $C_{aq,meas}/C_{aq,mod}$ is the ratio of the measured aqueous concentration to the aqueous concentration obtained from modeling. R_{AC} is the geometric mean activated carbon particle radius used in model simulations.

	TOG Carbon			$C_{aq,treated}/C_{aq,untreated}$		$C_{aq,meas}/C_{aq,mod}$
PCB	Dose (%)	Dia (μm)	R_{AC} (μm)	Measured	Modeled	Comparison
101	3.4	75–300	75	0.086	0.019	4.6
118	3.4	75–300	75	0.11	0.033	3.3
101	1.7	75–300	75	0.15	0.037	4
118	1.7	75–300	75	0.2	0.064	3.1
101	0.34	75–300	75	0.54	0.17	3.2
118	0.34	75–300	75	0.68	0.26	2.6

Table 3: Results of numerical modeling of the effect of activated carbon particle size on the aqueous concentration of polychlorinated biphenyls for 3.4% total carbon mass and 28-d contact. Note a: Not available.

	Activated carbon			$C_{aq,treated}/C_{aq,untreated}$		$C_{aq,meas}/C_{aq,mod}$
PCB	Type	Dia (μm)	R_{AC} (μm)	Measured	Modeled	Comparison
101	F400 granular	420–1700	420	NA[a]	0.085	NA
118	F400 granular	420–1700	420	1	0.14	7
101	F400 coarse	75–250	68	0.24	0.015	17
118	F400 coarse	75–250	68	0.25	0.026	10
101	TOG coarse	75–300	75	0.12	0.019	6.4
118	TOG coarse	75–300	75	0.17	0.033	5.2
101	TOG fine	25–75	22	0.013	0.0057	2.3
118	TOG fine	25–75	22	0.02	0.01	2.0

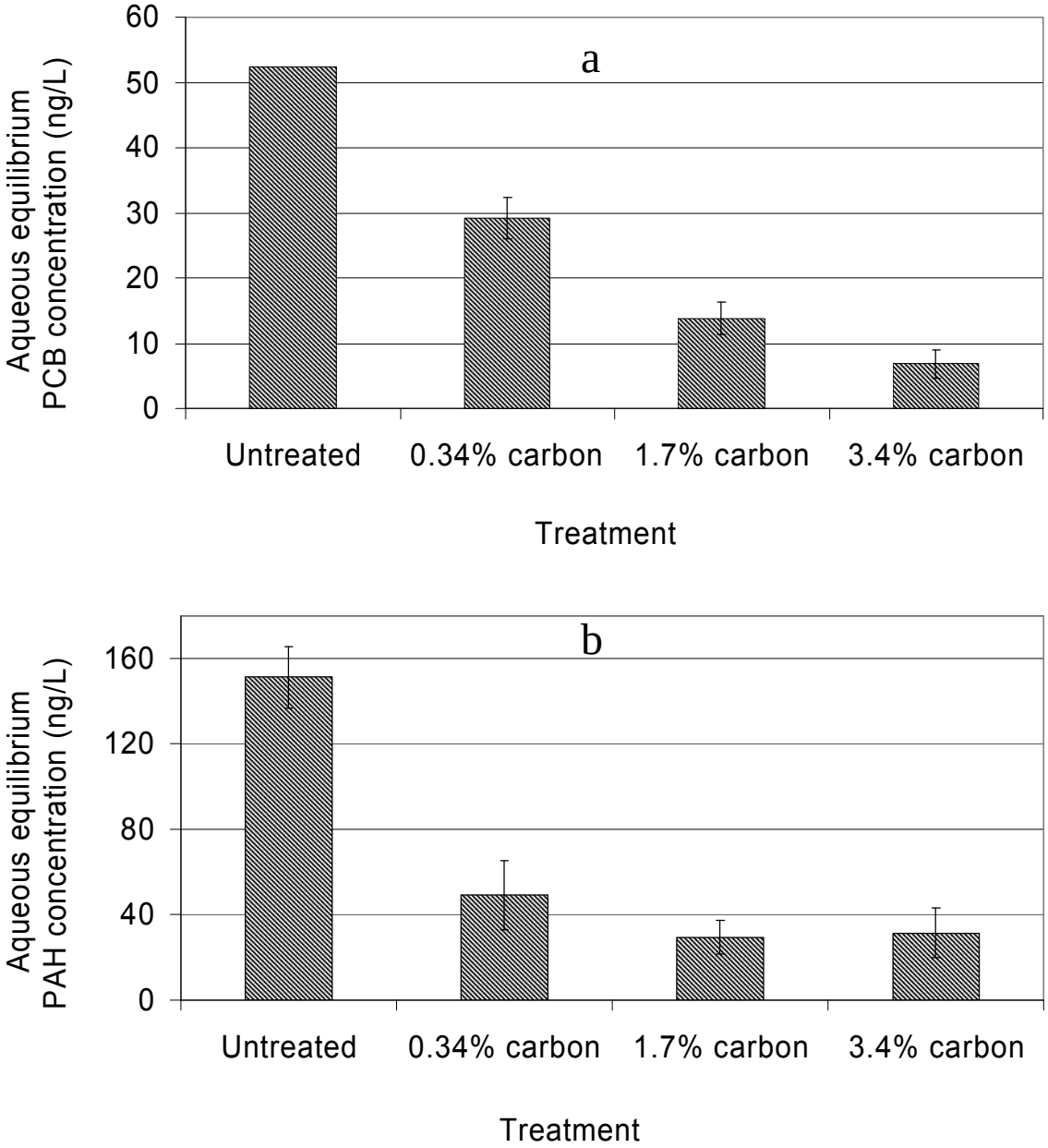


Figure 1. Aqueous PCB (a) and PAH (b) concentrations for Hunters Point sediment contacted with varying doses of activated carbon for one month. The activated carbon is coarse (75–300 μm) type TOG.

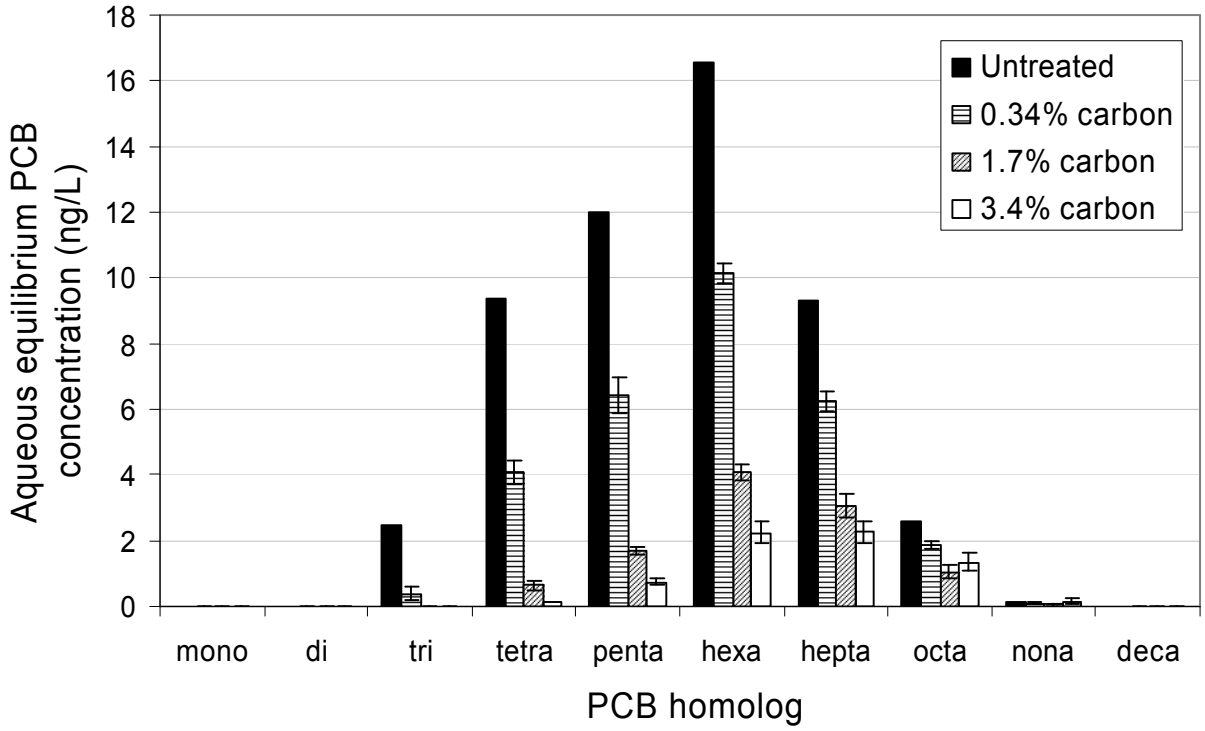


Figure 2. Aqueous PCB homolog concentrations for Hunters Point sediment contacted with varying doses of activated carbon for one month. The activated carbon is coarse (75–300 μm) type TOG.

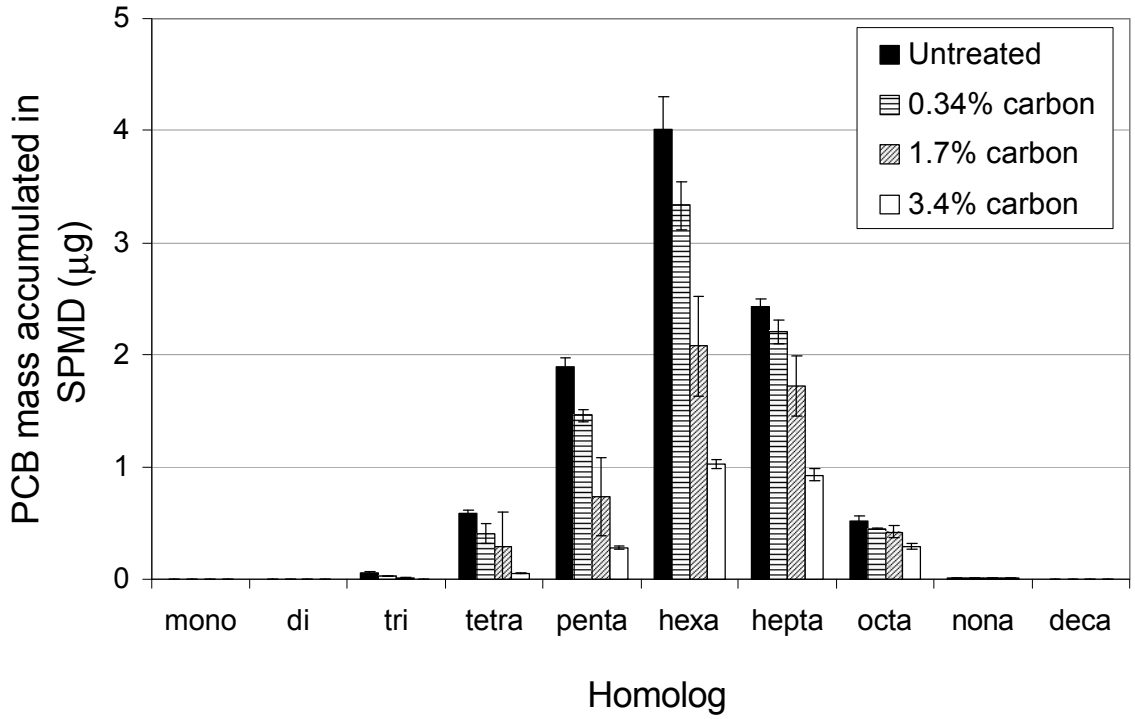


Figure 3. PCB mass uptake by SPMDs for Hunters Point sediment contacted for one month with varying doses of activated carbon. The activated carbon is coarse (75–300 µm) type TOG.

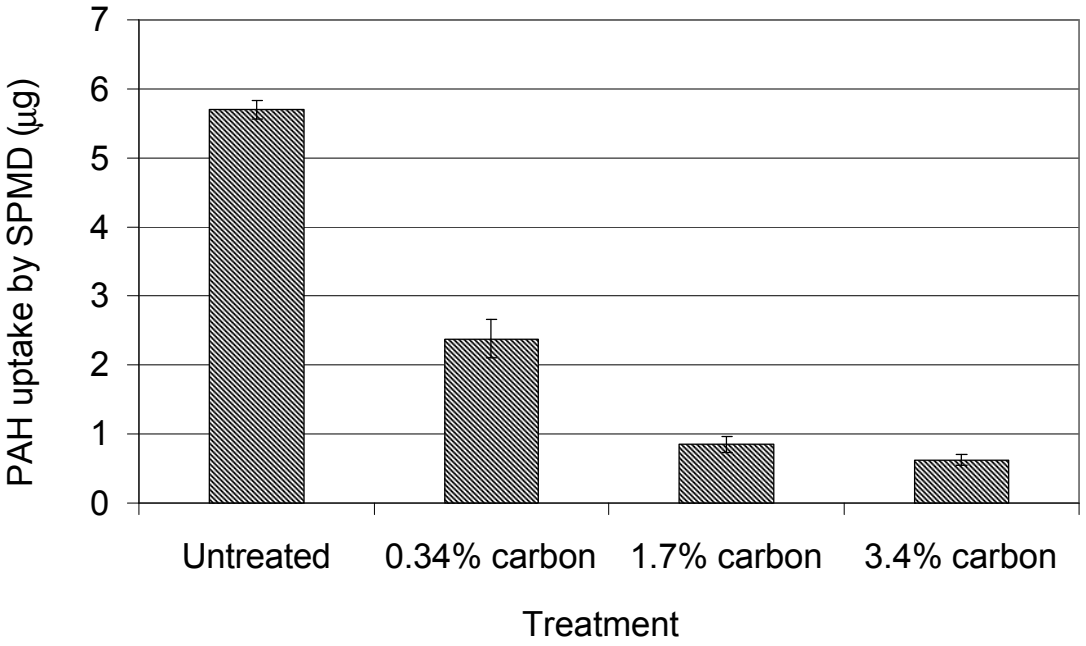


Figure 4. PAH uptake by SPMDs for Hunters Point sediment contacted for one month with varying doses of activated carbon. The activated carbon is coarse (75–300 µm) type TOG.

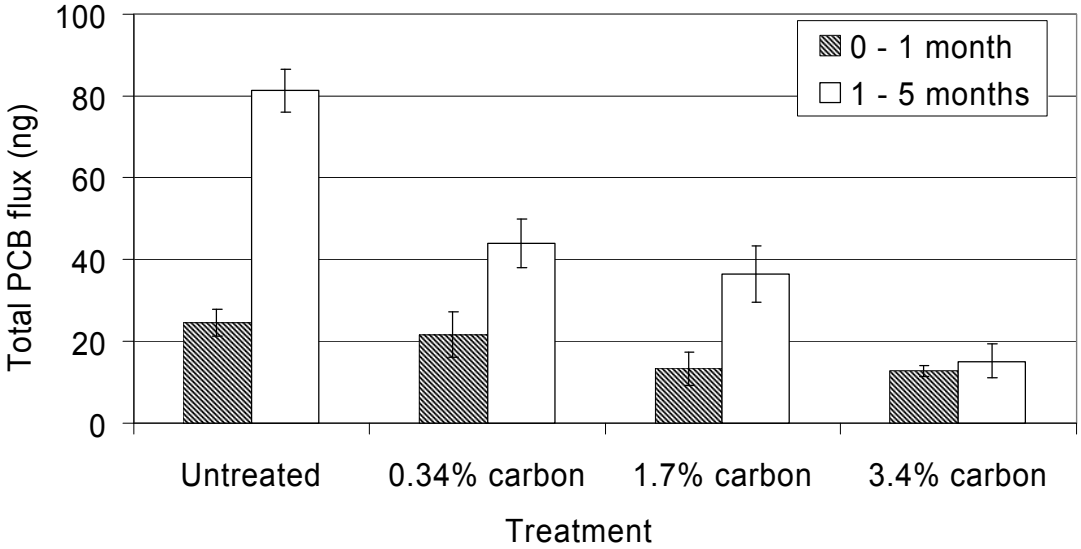


Figure 5. Uptake of PCBs by XAD beads suspended above Hunters Point sediment contacted with varying doses of type TOG (75–300 μm) activated carbon for one month.

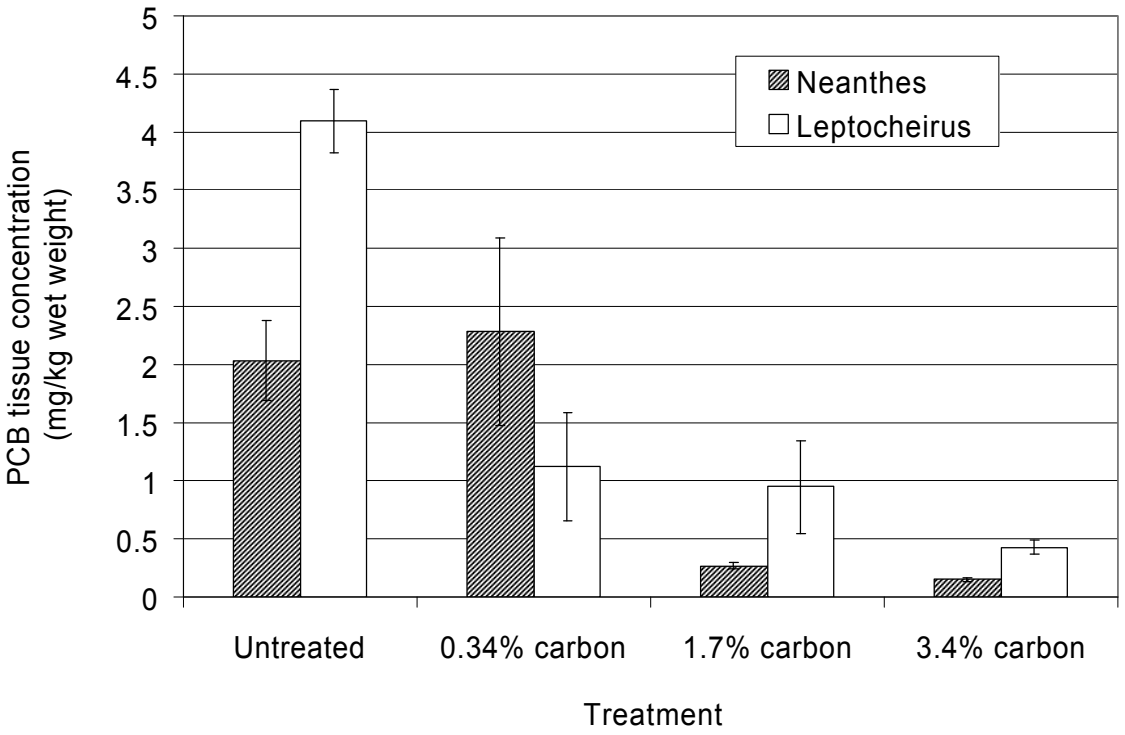


Figure 6. PCB bioaccumulation by *N. arenaceodentata* and *L. plumulosus* during 56-d exposure tests. Sediment was contacted for one month with varying doses of 75–300 μm type TOG carbon prior to the bioaccumulation tests.

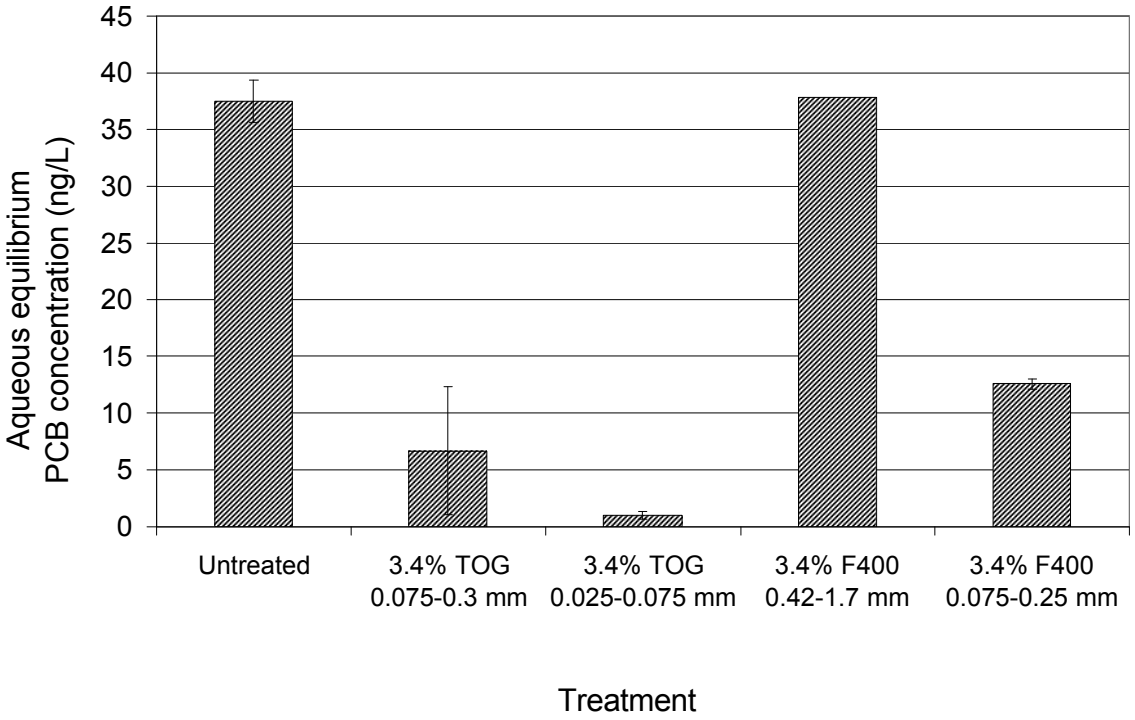


Figure 7. Aqueous PCB concentrations for Hunters Point sediment contacted with varying sizes of TOG and F400 carbon for one month.

Appendix VIII.

Report

An overview of field mixing technologies.

Upal Ghosh, Dennis Smithenry, Richard G. Luthy

MIXING EQUIPMENT AND TOOLS FOR POSSIBLE USE IN BLENDING ACTIVATED CARBON TO SEDIMENT IN THE FIELD

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The application of activated carbon to a large area of contaminated sediments, and providing adequate mixing to facilitate good mass transfer of contaminants is a challenging but not insurmountable engineering problem. Shown on the right is a picture of the gently sloping inter-tidal zone in Hunters Point South Basin that is the proposed demonstration site for a ESTCP project. We have looked into the literature and consulted with several vendors to learn from similar engineering applications involving soil and sediment mixing. We have found five basic categories of equipment that can be used for mixing viscous slurries after adding an amendment:

1. Tools used in agriculture for seed/fertilizer application and mixing into soil. These equipments (eg. rakes and disks) typically are tractor mounted and can cover large areas. Although designed primarily for soil applications, some of these technologies can be adapted for wet sediment conditions. The big advantage of these equipments is the widespread availability across the country and also relatively low cost. Golder Associates have adapted these equipments for the delivery of nitrate to sediments in their Limnofix technology. Cost estimates for the sediment application is available from large-scale trials of the Limnofix technology. Golder Associates have adapted agricultural equipment for their Limnofix treatment technology for sediments where they add nitrate to sediments as an alternate electron acceptor for the degradation of hydrocarbon contaminants. They use a 'chisel plow' to deliver the nitrate below the sediment surface and to till the surface during application. They have also used this technique for submerged sediments by attaching the 'chisel plow' to a crane mounted on a barge. For our application, delivering the carbon slurry through the small orifice of the chisel may be tricky and we may need to lay out the carbon first before plowing. *(Picture was provided by Brian Senefelder of Golder Associates)*

2. Tools used in the chemical stabilization/solidification industry. Such treatments are carried out to enhance the geotechnical properties of soil or sediment before building or bridge construction, or for the purpose of stabilization of a hazardous waste. In these operations a stabilization/solidification agent such as cement or fly-ash is amended to soil or sediment and mixed to create a uniform paste that solidifies over time. These are typically large-scale operations and a good mixing of the amendment with the soil/sediment is required. Depth of application in these treatments can reach several meters. Due to the long history of these applications, cost figures are available. The top figure shows the use of backhoes in a large soil mixing application. Figure below shows the use of an auger device for soil mixing. Source of the two figures below: Conner J.R. (1993). Chemical Fixation and Solidification of Hazardous Wastes, Van Nostrand Reinhold.

Williams Environmental Services, has used an injection system for sediment solidification with cement mortar (figure on the right). In these operations a stabilization/solidification agent such as cement or fly-ash is applied by injecting a slurry and mixing to create a uniform paste that solidifies over time. In a recent application at a superfund site (Koppers Co, Ashley River), Williams Environmental Services used this technology for in-situ solidification of one acre of marine sediments contaminated with creosote, pentachlorophenol, and copper-chromated-arsenate. For our purposes, a GAC slurry may be pumped and mixed into sediment using the injector arm with the machine located near shore. For larger scale operations, the injector arm could be mounted on a marsh excavator or on a barge for greater portability over soft or submerged sediments.

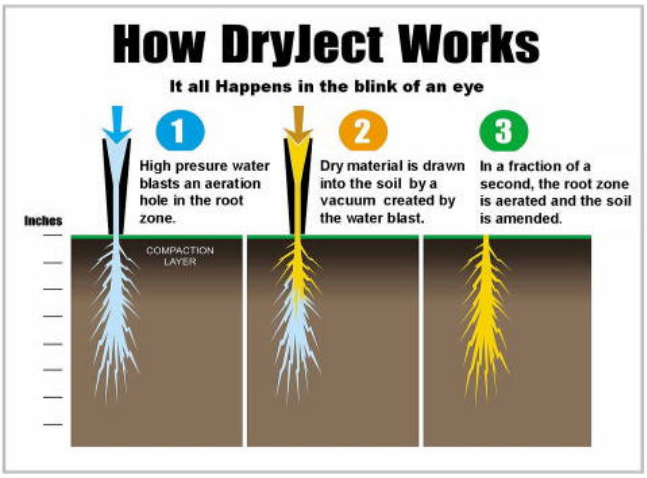
3. Tools used for underwater weeding operations. Underwater rototillers may be suitable for applications where the contaminated sediment is sub-tidal. These tools are barge mounted and can work in shallow water depths. Cost per acre of treatment is low for shallow depths of tilling. Rototilling (underwater rotary hoeing) is a mechanical option for weed control and can be used in water depths of between 1.5 and 4 m. The underwater rototillers are designed to dig into the sediments to uproot the weeds. The depth of sediment penetration affects the results. Deep rototilling (to ca. 3–5 cm sediment depth) is more costly ($5000/ha) but provides a greater duration of control (1–2 years), while shallow rototilling (blades set at surface of sediment) is more rapid and less costly ($1000–2000/ha) but provides only about six months control. These equipment may be used for carbon mixing in sub-tidal sediments. One would probably need to deploy silt screens to enclose the area of application and prevent sediment relocation during such a disruptive underwater application.
(From: National Institute of Water & Atmospheric Research Limited, New Zealand)
http://www.niwa.cri.nz/rc/prog/aquaticplants/weedman/control

"Costs for a private contractor to harvest plants, remove obstacles, rototill, and collect and dispose of plants range from $1,500 to $2,000 per acre." *From: Washington State Department of Ecology. (http://www.ecy.wa.gov/programs/wq/plants/management/aqua027.html)*

Aquatic Environments, Inc., has a barge-like machine (see figure below) with a rotovator attachment that is typically used to disrupt weed growth in marshy areas. The Aquamog may be deployed on the water during high tide and rested on the sediment at low tide. Then GAC can be spread onto the surface of the sediments via a backpack spreader (larger scale options exist) located on the Aquamog. Next the rotovator arm can mix the GAC into the sediments, with the depth of the mixing controlled by the speed and downward pressure of the rotovator.

4. Solids injection into the ground using a high pressure water jet.

High pressure water jet has been used to aerate lawns and golf courses and to introduce sand into the ground. The Dryject technology uses a high pressure water jet to create a 6-8 inch hole in the ground and pull in sand that fills up the hole. This technology may be used to introduce granular activated carbon into soils or sediments. The equipment drive mechanism will need modifications for deployment in soft sediments. (Figures below are from www.dryject.com)



5. Portable tools used in the industry to mix batches of thick pastes and slurries.
Portable/stand mountable mixing devices are used in industry for batch mixing of viscous slurries such as food processing and solids blending. These mid-range mixing devices are designed for batches of tens of gallons and may be suitable for small pilot-scale studies where plot-size is too small for the mobilization of the above large-scale equipments. These tools are available with electric or pneumatic drives. The pneumatic drives are preferable for safety considerations under wet sediment environments. Pneumatically driven portable mixers of the type shown below are used widely in the food processing industry and also to mix paints, cement, and other industrial materials. The mixing head is typically 4-6 inches in diameter and can be operated at low rpm and high torque for viscous materials.

(Figures from http://www.csunitec.com/)

Appendix IX.

Unpublished results

a) PCB desorption kinetics from Hunters Point sediments;

b) Kinetics of PCB adsorption into carbon

c) Demonstration of PCB mass transfer from sediment to carbon

UNPUBLISHED DATA REPORTS

a) PCB desorption kinetics from Hunters Point sediments. The maximum rate of desorption of PCBs from three samples of sediment from Hunters Point were measured using the Tenax resin desorption technique. The Tenax desorption method is described in the paper presented in Appendix I. The three sediment samples tested are named: "Old HP" referring to the sediments used for most of the carbon amendment experiment and which came from close to the shore and near the landfill. Two other sediment samples collected in 2002 named HP#4 and HP #3 are progressively farther away from the landfill and into the bay. Total PCB concentrations in these three sediments are 9.9 mg/kg for "Old HP", 0.7 mg/kg for "HP#4", and 0.3 mg/kg for "HP#3". As shown in the figure below, a fraction of each PCB homolog is desorbed readily within the first few days followed by a slow release of the more tightly bound PCBs. The fraction desorbed readily may be the more bioavailable fraction, and transfer of this bioavailable fraction into the added carbon sorbent leads to an enhanced reduction of overall bioavailability. Another important observation from these data is that the fraction of available PCBs increase with decreasing PCB concentration. The organic matter type responsible for PCB binding for areas further into the bay may be different.

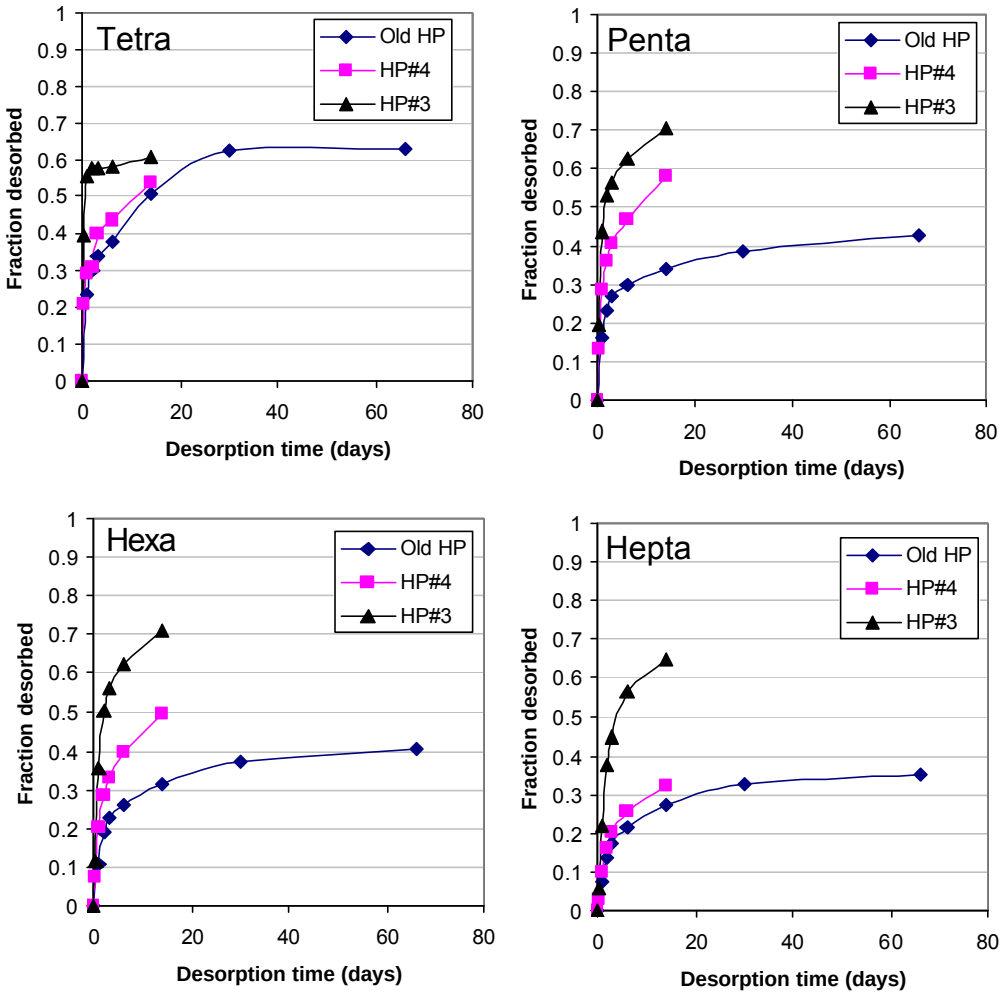


Figure 1. PCB desorption kinetics for three sediment samples collected from Hunters Point.

b) Kinetics of PCB adsorption into carbon

To better understand mass transfer rate limitation in the process of PCB transfer from sediment to activated carbon, we independently measured the rates of PCB desorption from sediment into water and the rates of PCB adsorption from water into activated carbon. As shown in the figure below, the initial rates of adsorption of PCBs into carbon are rapid, taking place within the first hour compared to the desorption rates that take place in the order of hundreds of hours. Thus, we expect the initial mass transfer of PCBs from sediment into the carbon to be controlled by the rates of desorption from the sediment. However, over time, as the easily accessible outer surfaces of the carbon are occupied, the rates of adsorption can slow down significantly leading to a situation where the mass transfer is limited by slow diffusion into the carbon interior. Thus, particle size of carbon may have a big impact on rates of mass transfer in the long run. Also, the initial rates of PCB adsorption into carbon seem to be independent of PCB chlorination level. The rates of PCB desorption are a strong function of PCB chlorination level.

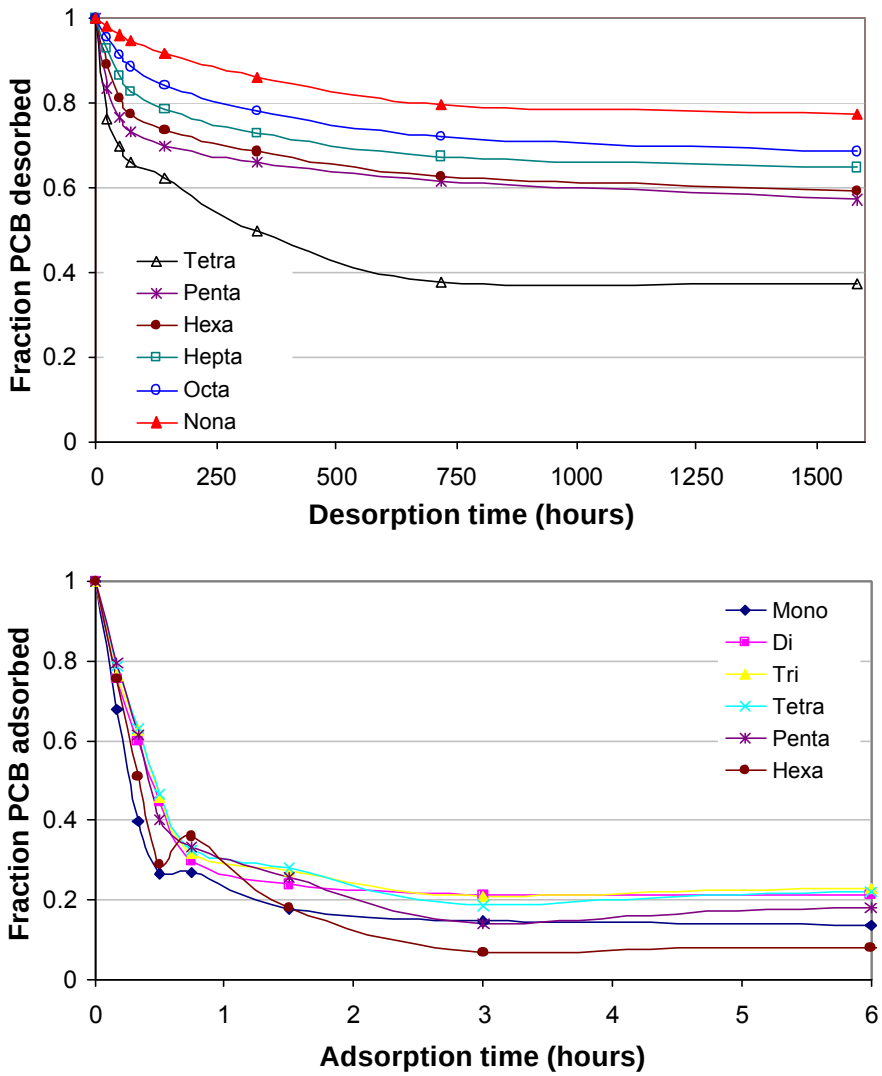


Figure 2. Comparison of rates of desorption of PCBs from Hunters Point sediment with the measured initial rates of adsorption of PCBs into carbon.

c) Demonstration of PCB mass transfer from sediment to carbon.

The demonstration of PCB mass transfer from sediment into the added activated carbon is complicated by the fact that it is very difficult to separate the added carbon from the bulk sediment. Hunters Point sediment naturally contains carbonaceous particles like coke and charcoal that have size and densities equivalent to the activated carbon we are using. To overcome this obstacle, we used a novel activated carbon that has ferromagnetic properties due to magnetite embedded in the particles. Use of this magnetic activated carbon (MAC) allowed us to separate the carbon by magnetic separation after addition to the sediment and measure the remaining PCBs in the sediment after contact with the MAC. Results shown below indicate a loss of 45% of total PCBs from the sediment after contact with the MAC for 1 week. We confirm through these measurements that when field sediments are mixed with activated carbon, PCBs repartition from the sediment into the added activated carbon.

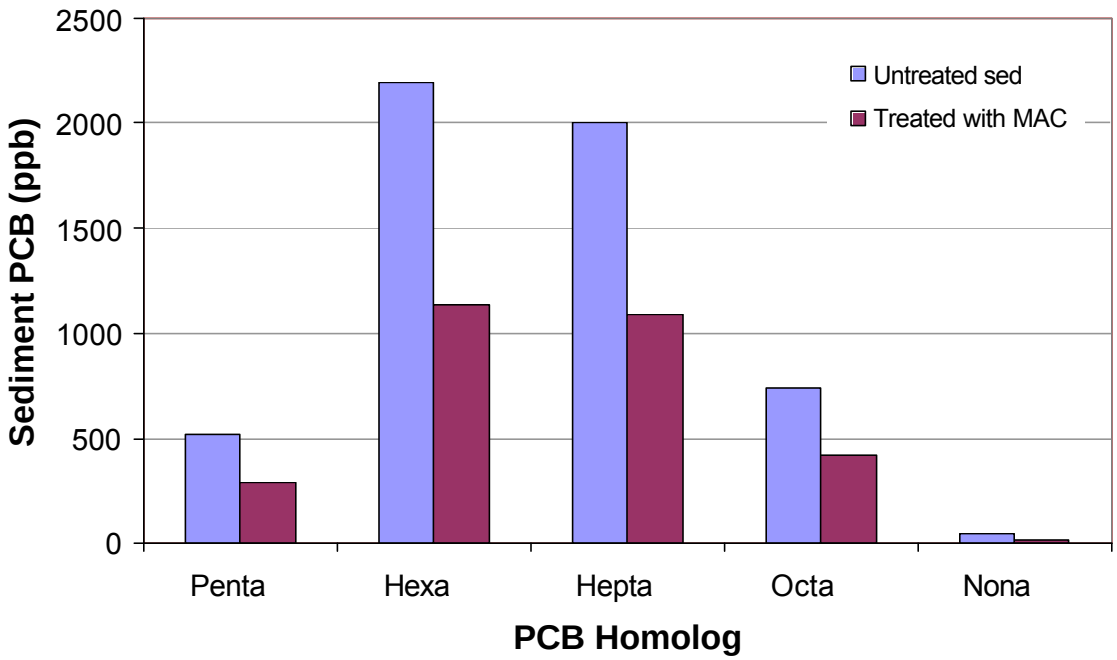


Figure 3. PCB concentration by homolog in hunters point sediment before and after contact with magnetic activated carbon and removal of the carbon from the sediment.