

In Situ Remediation of the Trinity River Sediment Contaminated with Polychlorinated Biphenyls

1. Title of Proposal

In Situ Remediation of the Trinity River Sediment Contaminated with Polychlorinated Biphenyls

2. Focus Category

Toxic Substances, Sediments, Treatment

3. Keywords

Polychlorinated Biphenyls, Trinity River, Sediment, In Situ Remediation, Reactive Activated Carbon, Permeable Reactive Barrier, Adsorption, Sequestration, Dechlorination

4. Duration

March 1, 2011 – February 28, 2012

5. Federal Funds Requested

\$5,000

6. Non-Federal (Matching) Funds Pledged

\$10,319

7. Principal Investigator (Graduate Student)

Prince Nfodzo, Ph.D. Student; The University of Texas at Arlington, Department of Civil Engineering, 416 Yates Street, Arlington, TX 76019-0308

8. Co-Principal Investigator (Faculty Advisor)

Hyeok Choi, Assistant Professor; The University of Texas at Arlington, Department of Civil Engineering, 416 Yates Street, Arlington, TX 76019-0308; Email: hchoi@uta.edu, Phone: 817-272-5116

9. Congressional District(s)

TX-006

10. Abstract

Aquatic sediments are often the ultimate receptors of all kinds of contaminants, in particular highly toxic and persistent polychlorinated biphenyls (PCBs). The sediments act as long term sources for the release of PCBs to aquatic environment. Developing effective technologies for cleaning up PCBs-contaminated sites has been one of the highest priorities of USGS, EPA, and DOD. State-level concerns were also issued that fish in the Trinity River located in the North Texas is not safe for people to eat due to the high level of PCBs, and PCBs-contaminated sediment in Hudson River, NY is being moved and disposed to a PCBs-approved landfill in Andrews, TX. Recently, EPA researcher and Dr. Choi have developed an innovative material named reactive activated carbon (RAC) which possesses capability to physically sequester and chemically degrade PCBs, and they have preliminarily tested it for the adsorption and dechlorination of *PCBs exclusively in pure water*. Consequently, this study will, for the first time, explore the treatment capability of the RAC strategy towards *PCBs in actual sediment matrix with heterogeneous nature*, in particular the Trinity's PCBs, in order to propose the RAC cap/barrier concept as a new environmental risk management option for PCBs-contaminated aquatic sediments in US.

11. Statement of Critical Regional Water Problems

According to US EPA, 10% of the sediment underlying the country's surface water is contaminated with toxic pollutants to pose potential risks to fish, wildlife, and humans [1]. In particular, 200,000 tons of probable human carcinogenic and persistent PCBs were released and deposited to aquatic sediments [2]. The sediments act as long term sources for the release of PCBs to aquatic environment. *Based on a state study by the Texas Commission on Environmental Quality (TCEQ), Dallas Morning News reported on*

February 4, 2010 that fish in the Trinity River located in the North Texas will not be safe for people to eat until the levels of PCBs in the river come down by more than half [3]. The article also emphasized that just making a decontamination plan for the Trinity’s PCBs will take two years, and in the end the only answer may be to wait for nature to break down the PCBs for decades (due to their recalcitrant and hydrophobic nature). There is a more historical event. General Electric Co. discharged PCBs into Hudson River, NY for three decades. Now, the company is spending at least 750 million dollars to remediate the contaminated sites [4]. *The remediation strategy is, unfortunately, to dredge the sediment and transport it to a PCBs-approved landfill in Andrews, TX.* The principal mechanism of the strategy is just physical relocation of the contaminated site to elsewhere. What if cleaning up the PCBs could be done in situ without dredging?

12. Nature, Scope, and Objectives of the Research

EPA and others have traditionally installed an adsorptive activated carbon layer to simply cap a contaminated site and thus to sequester PCBs in situ [5–7]. However, PCBs are still in the site after remediation. To develop a more aggressive strategy, EPA researcher and Dr. Choi (my research advisor) recently synthesized an innovative material, named RAC, as shown in Figure 1 [8]. The pores of adsorptive activated carbon are impregnated with reactive Fe/Pd nanoparticles which possess capability to chemically destroy PCBs. As a new environmental risk management option, they proposed the concept of a RAC cap/barrier that sequesters as well as breaks down PCBs in place [9]. After the pioneering work, many other researchers also started adopting the RAC strategy [10, 11]. *For the studies, however, they have used pure aquatic PCBs (i.e., mixture of PCBs and water) to preliminarily elucidate the physical and chemical mechanisms, without considering the complexities of treating PCBs in actual sediment with heterogeneous nature [8–14].* During discussion with Dr. Choi, I realized that there has been no research study demonstrating that the RAC strategy works for actual sediments contaminated with PCBs. In fact, PCBs tend to strongly attach to the solid surfaces in sediment matrix and thus they are less mobile in the aquatic environment [15, 16]. It is easily expected that the PCBs strongly bound to sediment solids (in particular organic carbon components) are not available for the reaction on RAC. This invokes a critical issue on the implementation of the RAC strategy. Consequently, there is a fundamental and applied research need to answer the following questions: i) does RAC system really work for the remediation of actual sediments contaminated with PCBs? and ii) if so, what are the sequence and nature of the reactions during the remediation?

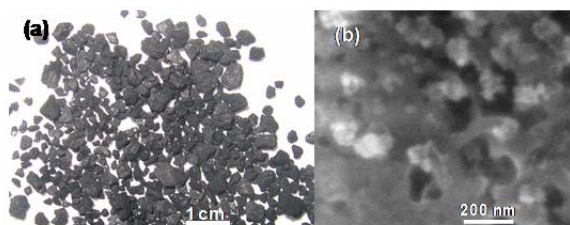
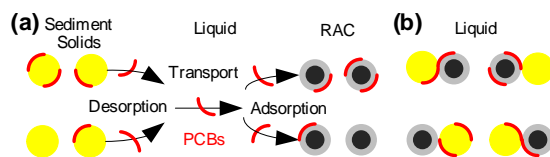


Figure 1. (a) granular RAC typically in size of 2–3 mm and (b) its microscopic cross-section, suggesting that many pores are occupied with Fe/Pd nanoparticles.



Scheme 1. Transport and fate of PCBs bound to solid surfaces in aquatic sediment. For their decomposition, PCBs should be available at the surface of RAC. The transport of PCBs from sediment solids to RAC occurs via (a) pathway I: desorption from sediment solids to the aqueous phase followed by adsorption to RAC and (b) pathway II: direct physical contact of RAC with PCBs bound to sediment solids.

Under Dr. Choi’s supervision, I will investigate how the transport and fate of PCBs bound to sediment matrix sequentially progresses in the presence of highly adsorptive RAC, focusing on the desorption of PCBs from the sediment solids to the aqueous phase, transport of the desorbed PCBs to RAC surface (adsorption), and their subsequent decomposition (note Scheme 1). I am particularly interested in the contact strategy of sediment with RAC: direct mixing or compartment configuration, as demonstrated in Figure 2. This experimental set up is uniquely customized to investigate many important subjects associated with the fate and transport of PCBs. These include: i) to quantify how much of PCBs are desorbed from the sediment solids, present in the aqueous phase, transported (adsorbed) to RAC, and

eventually decomposed, ii) to evaluate which one, between interaction of RAC with free PCBs available in the liquid phase (pathway I) and interaction of RAC with fixed PCBs bound to sediment solids (pathway II), is the dominant route for the PCB transport to RAC, and iii) to investigate whether the presence of highly adsorptive RAC facilitates desorption of PCBs from sediment and thus their adsorption to RAC. Through identifying the species and distribution of PCBs within the liquid, sediment solid, and RAC phases, detailed mechanistic aspects of the underlying reaction during the remediation of actual sediment contaminated with PCBs will be suggested. In collaboration with a research team at EPA (note Section 15), special attention will be given to the Trinity River sediment. Before applying the RAC strategy, I will fully characterize the properties of the sediment, including identification of various PCB congeners (gas chromatograph/mass spectrometer), structural properties of sediment solids (porosimetry analyzer, electron microscope), organic carbon composition (carbon analyzer), pH, and conductivity.

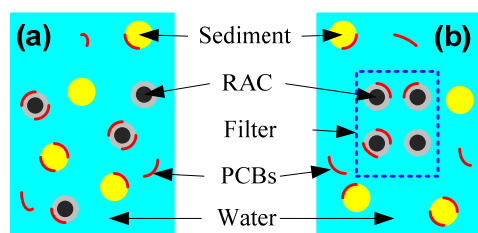


Figure 2. Experimental set up for the treatment of aquatic sediment in configuration of: (a) direct mixing of sediment with RAC and (b) compartment of sediment separated from RAC. PCBs in sediment are partitioned to the water, RAC, and sediment phases. In case of the direct mixing, overall PCBs in the solid mixture of RAC and sediment are measured while in the compartment configuration, PCBs transported to the RAC sector are differentiated from those remaining in the sediment. The compartment configuration conceptually mimics the cap/barrier strategy.

13. Results Expected from this Project

Developing effective technologies for cleaning up PCBs-contaminated sites has been one of the highest priorities of USGS, EPA, and TCEQ (also DOD which is responsible for managing thousands of sites contaminated with toxic organic compounds released by DOD's military activities). This research focuses on a really reactive (not just active) capping material with multiple functions of physical adsorption and chemical decomposition, and targets at truly in situ application, which has been overlooked in previous studies. The RAC strategy can be applicable not only for PCBs but also for other co-existing contaminants (multiple targets) since it has been well established that the Fe/Pd system can decompose many other halogenated compounds and activated carbon can adsorb a variety of toxic organic and inorganic contaminants. This study represents an important first step in a new direction of permeable reactive barrier research to provide effective tools for managing contaminated sediment (in particular superfund sites) in a manner that reduces risk to human health and the environment and gains regulatory acceptance.

14. Qualification and Competence of the PI and Co-PI

Since January 2010, I have been involved in Dr. Choi's projects related to oxidative and reductive decomposition of emerging chemicals of concern, and influenced by his research philosophy emphasizing broad-minded learning and study and inter- and multi-disciplinary nature of modern research. Dr. Choi developed the RAC material and strategy [8, 9, 12–14]. His work has been introduced and highlighted in several news media [17, 18]. All the technologies, principles, and innovative ideas demonstrated in this proposal are solely based on his research experience and my intuition and inspiration.

15. Partnership with Federal Agency

Before joining UT-Arlington, Dr. Choi was a postdoctoral research fellow at the National Risk Management Research Laboratory (NRMRL) of EPA. The study on RAC for PCB cleanup was initiated during his tenure working with Dr. Souhail Al-Abed at the NRMRL. Dr. Choi said that Dr. Al-Abed has already expressed his enthusiasm to continue the collaboration and advance the RAC strategy (in case, directly contact him via al-abed.souhail@epa.gov). Involvement of the national lab in this research is crucial with respect to sediment sampling and supply, PCB analysis, and EPA's expertise. If this exploratory study demonstrates successful outcomes, our research team will formulate a comprehensive academic-federal collaborative research proposal to scale up and implement the RAC strategy.

Key References (Optional Page)

- [1] U.S. Environmental Protection Agency. *EPA's Contaminated Sediment Management Strategy* (EPA-823-R-98-001); Office of Water: Washington, DC, 1998.
- [2] Robertson, L.W.; Hansen, L.G. (eds.) *PCBs: Recent advances in environmental toxicology and health effects*; The University Press of Kentucky, **2001**.
- [3] Loftis, R.L. PCBs make Trinity River fish unsafe for humans, state finds. *Dallas Morning News*. February 4, 2010.
- [4] U.S. Environmental Protection Agency Website at <http://www.epa.gov/hudson>.
- [5] Murphy, P.; Marquette, A.; Reible, D.D.; Lowry, G.V. Predicting the performance of activated carbon-, coke-, and soil-amended thin layer sediment caps. *J. Environ. Eng.* **2006**, *132*, 787–794.
- [6] McDonough, K.M.; Murphy, P.; Olsta, J.; Zhu, Y.; Reible, D. D.; Lowry, G.V. Development and placement of a sorbent-amended thin layer sediment cap in the Anacostia River. *Soil Sediment Contam.* **2007**, *16*, 313–322.
- [7] Werner, D.; Higgins, C.P.; Luthy, R.G. The sequestration of PCBs in Lake Hartwell sediment with activated carbon. *Wat. Res.* **2005**, *39*, 2105–2113.
- [8] Choi, H.; Al-Abed, S.R.; Agarwal, S.; Dionysiou, D.D. Synthesis of reactive nano Fe/Pd bimetallic system-impregnated activated carbon for the simultaneous adsorption and dechlorination of PCBs. *Chem. Mater.* **2008**, *20*, 3649–3655.
- [9] Choi, H.; Agarwal, S.; Al-Abed, S. R. Adsorption and simultaneous dechlorination of PCBs on GAC/Fe/Pd: mechanistic aspects and reactive capping barrier concept. *Environ. Sci. Technol.* **2009**, *43*, 488–493.
- [10] Zhuang, Y.; Ahn, S.; Luthy, R.G. Debromination of Polybrominated diphenyl ethers by nano-iron particles and carbon-supported nano-iron particles at *Symposium on Nanoporous Materials for Environmental Applications, 239th American Chemical Society National Meeting*, March 21-25, 2010, San Francisco, CA.
- [11] Liu, Z.G.; Zhang, F.S. Nano-zerovalent iron contained porous carbons developed from waste biomass for the adsorption and dechlorination of PCBs. *Bioresource Technol.* **2010**, *101*, 2562–2564.
- [12] Choi, H.; Al-Abed, S.R.; Agarwal, S. Effects of ageing and oxidation of palladized iron embedded in activated carbon on the dechlorination of 2-chlorobiphenyl. *Environ. Sci. Technol.* **2009**, *43*, 4137–4142.
- [13] Choi, H.; Al-Abed, S.R.; Agarwal, S. Catalytic role of palladium and relative reactivity of substituted chlorines during trapping and treatment of PCBs on reactive activated carbon. *Environ. Sci. Technol.* **2009**, *43*, 7510–7515.
- [14] Choi, H.; Al-Abed, S.R. Effect of reaction environments PCB reactivity with activated carbon impregnated with palladized iron. *J. Hazard. Mater.* **2010**, *179*, 869–874.
- [15] Choi, H.; Al-Abed, S.R. PCB congener sorption to carbonaceous sediment components: macroscopic comparison and characterization of sorption kinetics and mechanism. *J. Hazard. Mater.* **2009**, *165*, 860–866.
- [16] 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.
- [17] Lubick, L. Cap and degrade: a reactive nanomaterial barrier also serves as a cleanup tool. *Environ. Sci. Technol.* **2009**, *43*, 235.
- [18] Kellyn Betts, Top papers in environmental technology, second runner-up: Stars align for PCB cleanup technology, *Environ. Sci. Technol.* **2009**, *43*, 2201.