

# REPORT

## **Title**

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

## **Project Number**

2011TX400B

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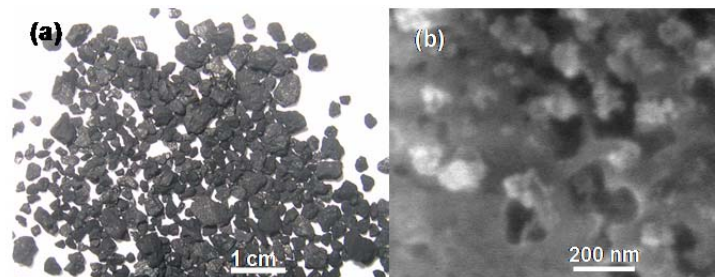
## **Abstract**

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 slow 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 concern was also issued that fish in the Trinity River located in North Texas is not safe for people to eat due to the high level of PCBs. Recently, EPA researcher and Dr. Choi have developed an innovative material, reactive activated carbon (RAC), which possesses capability to physically sequester and chemically degrade PCBs, and they have preliminarily tested RAC strategy for the adsorption and dechlorination of PCBs exclusively in pure water. In this present study, we explored the capability of the RAC to treat PCBs in an actual sediment matrix, i.e., PCB-contaminated sediment from the Trinity River in North Texas in order to propose the RAC cap/barrier concept as a new environmental risk management option for PCBs-contaminated aquatic sediments in US.

## **Problem and Research Objectives**

According to US EPA, 10% of the sediment underlying the country's surface water is contaminated with toxic pollutants that 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 slow release of PCBs to aquatic environment. Based on a state study by the Texas Commission on Environmental Quality (TCEQ), the Dallas Morning News reported on February 4, 2010 that fish in the Trinity River located in 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 river's PCBs will take two years, and in the end the only answer may be to wait for nature to break down the PCBs which can take decades (due to their recalcitrant and hydrophobic nature). It is also reported that General Electric Co. discharged PCBs into Hudson River, NY for three decades, and the company is now spending over 750 million dollars to remediate the contaminated sites [4]. Unfortunately, the remediation strategy being used is to dredge the sediment and transport it to a PCBs-approved landfill in Andrews, TX. The principal mechanism of this strategy is just physical relocation of the contaminated site to elsewhere. What if cleaning up the PCBs could be done in situ without dredging?

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 recently synthesized an innovative material, named RAC, as shown in Figure 1 [8]. The pores of



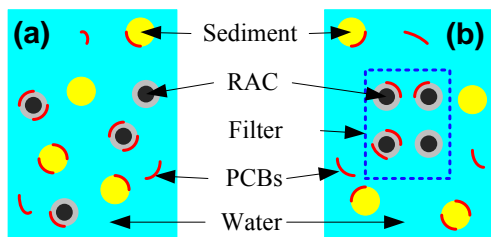
**Figure 1. (a) granular RAC typically in size of 2–3 mm and (b) its microscopic cross-section, suggesting that many pores are occupied with Fe/Pd nanoparticles.**

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]. 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?

## **Materials/Methodology**

### *Synthesis of Reactive Activated Carbon*

The detailed synthesis procedure and route of RAC containing around 14.4% Fe and 0.7% Pd (weight base) was reported previously [8]. Briefly, iron was incorporated into mesoporous GAC (HD 3000, Norit Americas Inc.) in 2–3 mm size *via* an incipient wetness impregnation method.  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  of 22.8 g was melted at 55–60 °C, mixed with 10 g of GAC, and then dried at 60–70 °C using an infrared ramp for 2 h. The GAC/ $\text{Fe}(\text{NO}_3)_3$  composite was further calcined in a furnace at 300 °C for 4 h to transform  $\text{Fe}(\text{NO}_3)_3$  to  $\text{Fe}_2\text{O}_3$  and sieved using a #20 to remove unincorporated  $\text{Fe}_2\text{O}_3$  particles. In order to reduce  $\text{Fe}_2\text{O}_3$  to zerovalent Fe (ZVI,  $\text{Fe}^0$ ), 1.6 g  $\text{NaBH}_4$  dissolved in 20 mL water was added to 4 g GAC/ $\text{Fe}_2\text{O}_3$  suspension in 50 mL of methanol/water (30/70 v/v) at pH 6.5. Then GAC/ZVI was recovered and washed with methanol to remove free ZVI and other impurities, and then dried at room temperature. For Pd doping, the GAC/ZVI was mixed with 75 mg of palladium acetate ( $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ ) dissolved in 20 mL methanol. Then GAC/ZVI/Pd, denoted as RAC composite, was recovered, washed, and dried again. Samples at the end of each procedure were sieved with a #20 sieve to remove grains smaller than 0.85 mm.



**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.

### *Trinity River Sediment (TRS)*

PCB-contaminated sediment was obtained from the West Fork Trinity River at Beach Street, Fort Worth, TX (Station ID 10938). The sample (Trinity River Sediment. TRS) was dried at 105 °C in an oven for 1 d, and ground into fine powder. A set of batch reactors were built with 1 g of RAC, where TRS was directly mixed with RAC in 10 mL water at a RAC:sediment ratio of 1:3 (by weight) to implement the direct mixing configuration shown in Fig. 2(a). To facilitate desorption of PCBs from TRS, 10% acetone or 1% Triton X-100 surfactant was also used. PCBs are possibly partitioned to the liquid, solid WHS, and solid RAC phases. However, this direct mixing configuration makes it difficult to separate RAC from WHS.

### *Waukegan Harbor Sediment (WHS)*

Since we found the level of PCBs in TRS was very low, another sediment heavily contaminated with PCBs was tested in a similar way. Sediment in Waukegan Harbor (Waukegan, IL), one of Superfund sites, was taken and denoted as Waukegan Harbor Sediment (WHS). In a vial, 1.8 g of WHS was mixed with 22 mL of water. A set of batch reactors were built with RAC, where 0.6 g of RAC was directly mixed with WHS. To facilitate desorption of PCBs, 1% of acetone or 1% Triton X-100 surfactant was also used. The direct mixing was further modified to investigate RAC loading effect. The ratio of RAC/WHS at 1:3 was incremented to 1:1, 2:1, and 4:1.

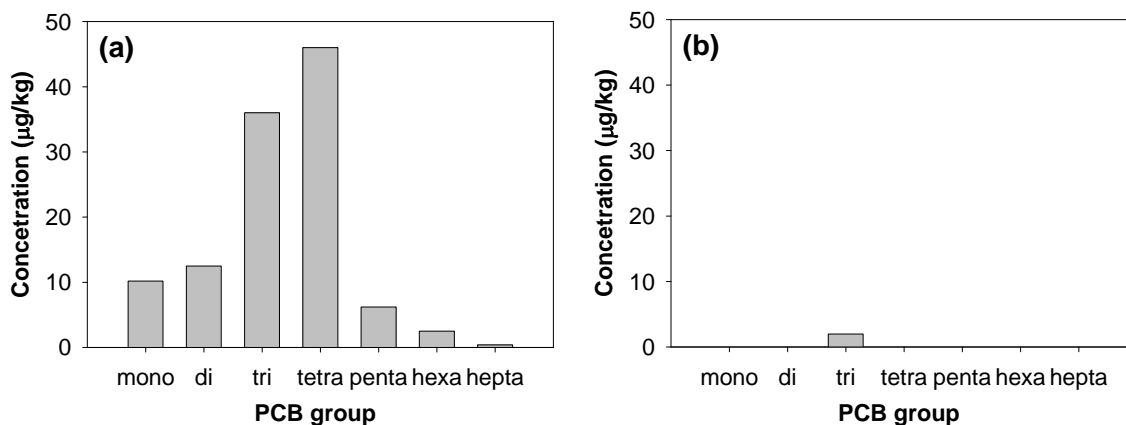
### *Analysis of PCBs and Reaction Intermediates*

The batch reactors were tumbled at 90 rpm in a rotary shaker for up to 100 d. One reactor was sacrificed in each sampling event for extraction and measurement of PCBs in the liquid, WHS, and RAC phases. A detailed description for the extraction (hexane extraction for liquid and automated Soxhlet for solid, EPA Method 3541) and measurement (HP 6890 gas chromatograph/HP 5973 mass spectrometer, EPA Method 8082) of PCBs was reported elsewhere [8, 9]. The detection limit of each PCB congener was at around 2 µg/L.

## **Principal Findings**

### *PCB Congeners Distribution in TRS*

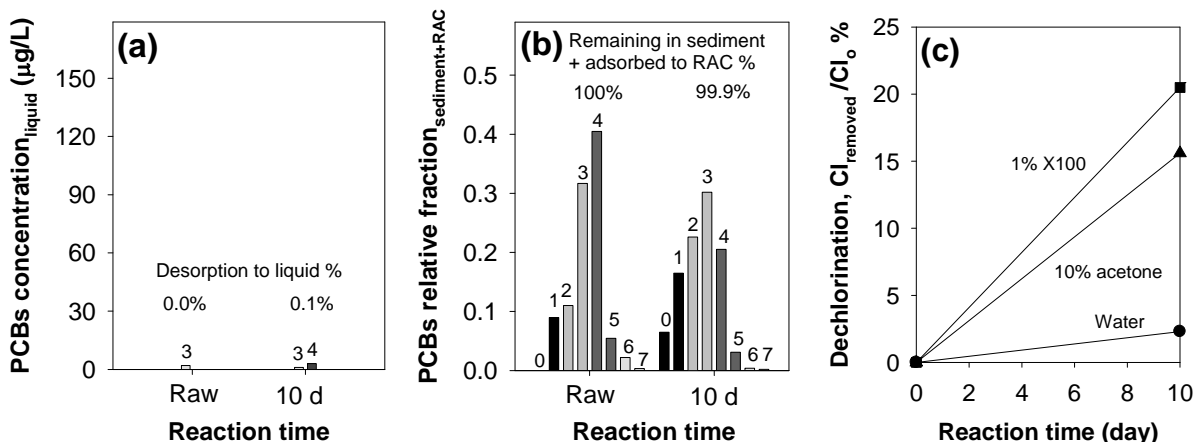
The concentration of PCBs in TRS is shown in Fig. 3(a). TRS was mildly contaminated with PCBs at 113.6 µg/kg. Tetrachlorinated and trichlorinated biphenyls were dominant. The degree of chlorination of PCBs is 3.3. Meanwhile, after mixing TRS with pure water, PCBs desorbed to water were monitored, as shown in Fig. 3(b). No significant amounts of PCBs were desorbed (even 2 µg/kg of trichlorinated biphenyls is close to the detection limit of GC/MS used), implying that PCBs were strongly bound to TRS solid matrix, as expected.



**Figure 3.** PCB congener distribution in (a) solid matrix and (b) supernatant of Trinity River Sediment (TRS).

#### Adsorption and Dechlorination of PCBs in TRS

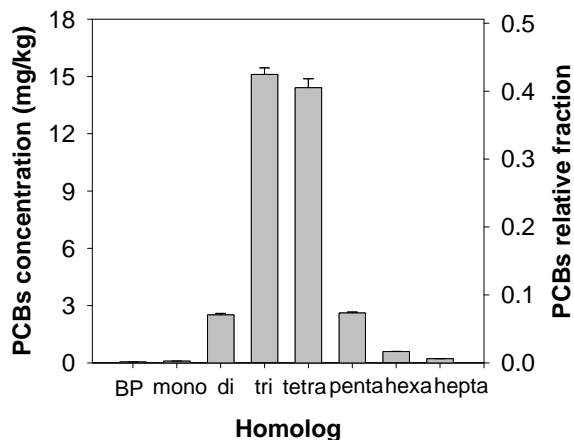
Results on mixing of TRS with RAC are summarized in Fig. 4. Partitioning of PCBs to the liquid phase was negligible (Fig. 4(a)). The result suggests addition of RAC was effective to completely sequester PCBs available in the liquid phase. As shown in Fig. 4(b), changes in the relative PCBs fraction in the solid phase were the most significantly noticeable under 1% Triton X-100 condition. The fraction of higher chlorinated congeners decreased while that of lower chlorinated congeners somewhat increased. Trichlorinated biphenyls accumulated while tetrachlorinated biphenyls exhausted. Biphenyls (no chlorines) were detected. Overall chlorine removal efficiency is presented in Fig. 4(c). The efficiency increased in order of 1% Triton X-100 > 10% acetone > water. Even in cases of water and acetone showing no apparent PCBs partitioning to the liquid phase, desorption of PCBs to the liquid phase is believed to occur, and thus the instantaneously desorbed PCBs are immediately re-adsorbed to RAC and dechlorinated.



**Figure 4.** Desorption and adsorption/dechlorination of PCBs in TRS mixed with RAC: (a) PCBs desorbed to 1% Triton X-100, (b) relative fraction of PCBs remaining in the mixture of WHS and RAC after desorption to 1% Triton X-100, and (c) overall dechlorination efficiency based on chlorine removal under various solvent conditions.

### PCB Congeners Distribution in WHS

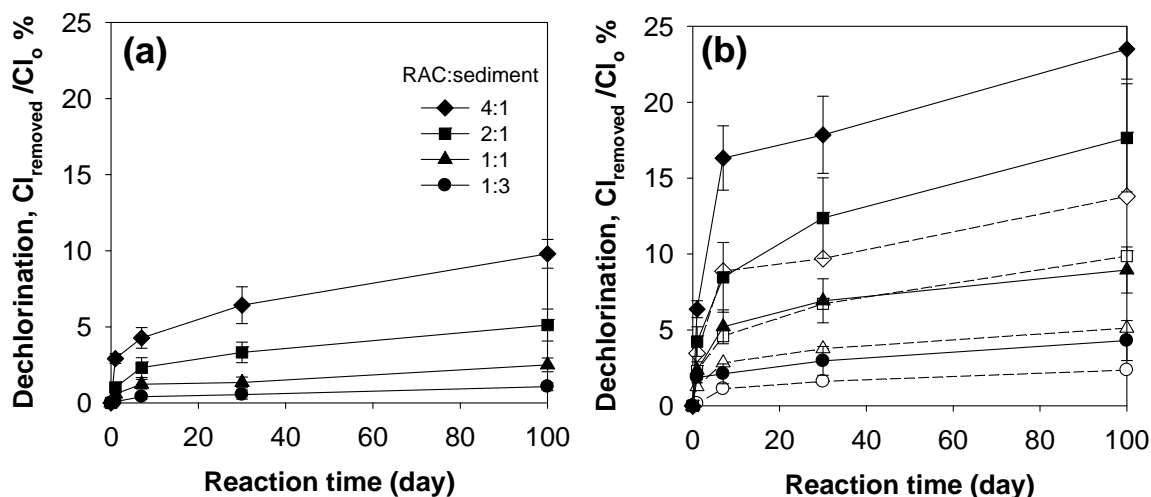
Since the total concentration of PCBs in TRS was too low at 113.6  $\mu\text{g}/\text{kg}$ , we had a difficulty to accurately quantify the dechlorination efficiency and thus we decided to test more practical sediment samples containing much higher level of PCBs. The concentration of PCBs in WHS is shown in Fig. 5. WHS was heavily contaminated with PCBs at 35.6 mg/kg. Trichlorinated and tetrachlorinated biphenyls were dominant. The degree of chlorination of PCBs is 3.6. Meanwhile, after mixing WHS with pure water, no PCBs were desorbed to water, implying that PCBs were strongly bound to WHS matrix.



**Figure 5.** PCB congener distribution in Waukegan Harbor Sediment (WHS). No PCBs were found in the liquid phase.

### Adsorption and Dechlorination of PCBs in WHS

PCBs were negligibly detected in water and even in 1% acetone and 1% Triton X-100 surfactant after 100 d mixing. However, certain amount of PCBs might have been desorbed from WHS to the aqueous phase, but immediately partitioned to RAC and dechlorinated. The dechlorination of PCBs in WHS mixed with RAC at various RAC/WHS ratios is shown in Fig. 6.



**Figure 6.** Overall dechlorination of PCBs in WHS mixed with RAC at RAC/WHS ratio from 1:3 to 4:1 in (a) water and (b) 1% Triton X-100 (solid) and 1% acetone (vacant).

The efficiency increased in order of 1% Triton X-100 > 1% acetone > water. The ratio of RAC/WHS was incremented to evaluate RAC dose-dechlorination response. The efficiency increased with increasing RAC dose. In case of RAC/WHS ratio at 4 under 1% Triton X-100, approximately 24% of chlorines of the PCBs in WHS were removed after 100 d.

### Significance

Remediation of soil and sediments contaminated with PCBs remains a scientific and technical challenge. In order to overcome the short-comings of current remediation strategies for contaminated sediments, our effort has been given to the development of RAC strategy. Trinity River Sediment and Waukegan Harbor Sediment contaminated with PCBs were effectively treated on RAC impregnated with palladized iron particles. During the treatment, we proved that the electrochemical dechlorination of PCBs and the physical adsorption and sequestration of PCBs and their reaction intermediates can be simultaneously achieved with the hybrid RAC composite. Based on the results, the concept of a “reactive” cap/barrier composed of RAC pellets contained between thin geo-textile membranes can be proposed. We envision that the concept of RAC cap/barrier will be an effective option for the environmental risk management of PCBs-contaminated sites. Results from this study will therefore be of interest to chemists and engineers working for remediating environmentally contaminated sites with PCBs or other chlorinated compounds.

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