



# Treatment characteristics of various sediment components spiked with 2-chlorobiphenyl using reactive activated carbon

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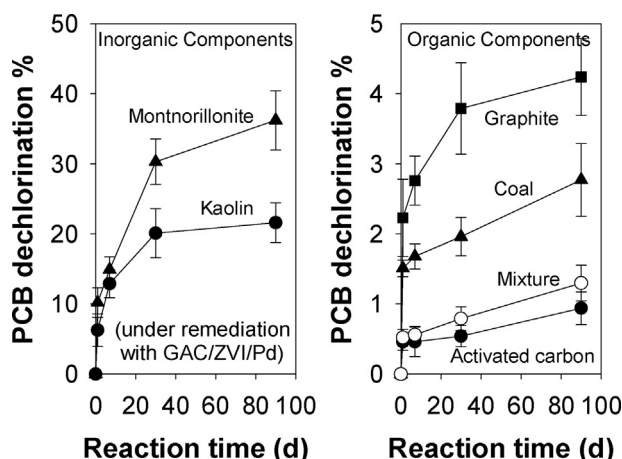
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## HIGHLIGHTS

- Various solid organic and inorganic sediment components were tested.
- Fate and transport of 2-CIBP spiked to the sediment components was fully traced.
- Role of the various components in adsorbing and desorbing 2-CIBP was studied.
- Performance of the most advanced remediation material, RAC was evaluated.
- 2-CIBP spiking was correlated with 2-CIBP desorption and 2-CIBP dechlorination.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Previously, the concept of reactive activated carbon (RAC), where the porous structure of activated carbon (AC) is impregnated with palladized zerovalent iron, has been proposed to be effective to adsorb and dechlorinate polychlorinated biphenyls (PCBs). To explain the low dechlorination of PCBs bound to actual aquatic sediments under remediation with RAC, this study investigated the role of various solid organic and inorganic sediment components in adsorbing and desorbing PCBs. Detailed fate and transport mechanism of 2-chlorinated biphenyl (2-CIBP) spiked to sediment components, including kaolin, montmorillonite (MMT), coal, graphite, AC, and their mixture, was revealed. Adsorption and holding capability of sediment components toward 2-CIBP strongly influenced amount of spiked 2-CIBP, amount of desorbed 2-CIBP, overall dechlorination of 2-CIBP to biphenyl (BP), and eventual partitioning of 2-CIBP and BP to water, sediment component, and RAC. Order of the amount of spiked 2-CIBP to sediment components after drying, following AC > mixture > coal > graphite > kaolin > MMT, was in agreements (in opposite direction) with order of the amount of desorbed 2-CIBP and order of overall 2-CIBP dechlorination. Substantial role of organic components in aquatic sediments for holding 2-CIBP and thus preventing it from dechlorination on RAC was proven.

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## 1. Introduction

Contaminated aqueous sediments are of great concern in the United States [1,2]. Particular interest is given to polychlorinated

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biphenyls (PCBs) due to their chemical persistence, environmental toxicity, and hydrophobic property [3–5]. Capping contaminated sites with clean sand layer has been proposed to isolate sites from direct contact [6]. Sand layer can be further amended with activated carbon (AC) or AC layer can also be added on the top of sand layer, which significantly reduces PCBs level in water [7–10]. Since AC-based approaches do not decompose PCBs, electrochemical dechlorination of PCBs to relatively biodegradable biphenyl (BP) has been also studied using reactive metal particles such as zerovalent iron (ZVI) [6,11,12]. The studies mostly tested aqueous phase PCBs to quickly investigate kinetics and mechanisms of the dechlorination reaction. Treatment of real aquatic sediments contaminated with PCBs using such reactive metals has been rarely reported most probably because PCBs in sediments would be much less available for the reaction at metal surface. PCBs are strongly bound to sediment solids, particularly organic components, and thus they are hard to desorb into water [13].

In order to facilitate desorption of PCBs in sediments to water and then reaction of the desorbed PCBs onto metal surface, the concept of reactive activated carbon (RAC) has been proposed, where the porous structure of granular activated carbon (GAC) is impregnated with palladized ZVI nanoparticles [14]. RAC was able to promptly adsorb PCBs available in water, effectively dechlorinate them to eventually BP, and completely sequester PCBs and reaction intermediates [15–17]. The RAC strategy or similar approaches seemed to work synergistically for removal of many organic and inorganic chemicals and metals, while taking advantages of the two remediation approaches, physical adsorption and chemical dechlorination [18–22]. As one of the most highly contaminated sites with PCBs, Waukegan Harbor sediment (WHS), IL has attracted significant attention [23,24]. Eventually, treatment of WHS by using the RAC strategy was recently reported [25]. The study experimentally revealed desorption of PCBs from WHS, their adsorption and subsequent dechlorination onto RAC, and ensuing partitioning of PCBs and intermediates into water, WHS, and RAC. Although the presence of RAC facilitated PCBs desorption from WHS, the slow desorption of PCBs limited overall performance, resulting in five-order of magnitude lower dechlorination when compared with treatment of aqueous PCBs [16,25].

In order to find scientific reasons for the slow desorption process and thus low dechlorination yield for WHS and presumably for many other aquatic sediments potentially under remediation with such reactive media, this current study investigated the role of various solid sediment components (herein, sediment or component) in adsorbing and desorbing PCBs in the presence of RAC. Considering sediments are a heterogeneous mixture of various solid organic and inorganic components, kaolin, montmorillonite (MMT), coal, graphite, GAC, and even their mixture were selected as sediment components, spiked with 2-chlorinated biphenyl (2-CIBP), and treated using RAC. A systematic lab-scale test was designed in manner of direct mixing and compartment configuration to reveal the fate and transport of 2-CIBP in the treatment environment [25]. Eventually, the capability of sediment components to adsorb and hold 2-CIBP during spiking process was correlated with the desorption trend of 2-CIBP to water and RAC and with its dechlorination onto RAC.

## 2. Experimental

### 2.1. RAC synthesis

Detailed synthesis procedure of RAC was reported previously [14]. Briefly, 2–3 mm size mesoporous GAC (HD3000, Norit Americas Inc.) was used as base material for RAC. The surface area of GAC at 574 m<sup>2</sup>/g was significantly decreased to 358 m<sup>2</sup>/g after in-situ

placement of ZVI/Pd particles via incipient wetness impregnation. The porous structure of GAC was well occupied with Fe at around 14.4% and Pd at around 0.7%. Synthesis and handling of RAC was performed in anaerobic glove box (oxygen < 0.05 mg/L and hydrogen at 3.5%).

### 2.2. Sediment components and PCB spiking

Initially four different solid components were selected; two inorganic components (kaolin and MMT) and two organic components (coal and graphite). GAC used as base material for RAC was also chosen as organic component because it might be interesting to investigate partitioning behavior of 2-CIBP spiked to GAC in the presence of RAC. Such organic components are known to exhibit stronger chemical affinity for PCBs than inorganic components [13]. Lastly, mixture of the sediment components was also prepared. As a result, total 6 individual components were tested in this study. Among the components, mixture was the closest to actual sediments. Kaolin (Sigma-Aldrich), MMT (Sigma-Aldrich), coal (BCR reference, CRM 460), graphite (EC100, Graphite Sales, Inc.) and GAC (HD3000, Norit America, Inc.) were further purified with deionized water several times to remove any impurities. Their properties were characterized including surface area using Tristar 3000 porosimetry analyzer (Micromeritics) and organic carbon content using TOC analyzer with SSM-5000A solid module (Shimadzu).

To spike sediment components with 2-CIBP, 500 mg/L of 2-CIBP solution in acetone (Sigma-Aldrich) was prepared and then 2.4 mL of 2-CIBP solution was transferred to 12 g of each sediment component or 2.5 mL of 2-CIBP solution was transferred to 12.5 g of mixture (2.5 g of each component). Then, 40 mL of acetone was additionally added to mix sediment component and 2-CIBP under rigorous tumbling at 30 rpm for 15 h. After spiking, slurry was dried in an oven at 58 °C for 6 h to remove acetone. Theoretical solid phase concentration of 2-CIBP was 100 mg/kg as target concentration, assuming all 2-CIBP added was left on sediment component without loss. It should be noted that 2-CIBP was transformed only to BP by dechlorination reaction on RAC, which makes it easy to interpret experimental result.

### 2.3. Sacrificial batch test

Most of experimental procedures, from sample preparation to sample analysis, were done in anaerobic glove box or within air-tight bottles. All experiments were based on sacrificial batch. Experimental set up to determine fate and transport of spiked 2-CIBP was categorized into control, direct mixing, and compartment configuration, as precisely described elsewhere [25]. To investigate desorption of spiked 2-CIBP from sediment component to water in the absence of RAC, 0.9 g of sediment component was directly mixed with 22 mL of water (control). Batch reactors were disturbed at 150 rpm in rotary shaker. 2-CIBP would partition into water and sediment component. Additional set was built with RAC, where 0.6 g of RAC was directly mixed with the aqueous sediment component (direct mixing).

Separation of RAC from sediment component, which is not feasible in direct mixing configuration, is essential for understanding partitioning behavior of spiked 2-CIBP between the two heterogeneous materials. To address the need, RAC was physically separated from sediment component (compartment configuration). RAC compartment made of 2 mL vial (Supelco) was filled with 0.6 g of RAC followed by water, and capped with filter paper (Whatman). RAC vial was then inserted to main reactor containing water and sediment component. The filter allows 2-CIBP and BP to move freely between the two compartments but it prevents sediment component and RAC from mixing. As a result, it was possible to

measure 2-CIBP desorbed in water, 2-CIBP left in sediment component, and 2-CIBP transported to RAC. Compartment configuration indirectly mimics concept of reactive cap/barrier.

#### 2.4. Extraction and analysis of PCBs

At a given time schedule of 1, 7, 30, and 90 d, one batch reactor was sacrificially taken for analyzing 2-CIBP and BP and determining their partitioning in water, sediment component, and RAC. Water was separated from solids (i.e., RAC and sediment component). In 4 mL extraction vial, 0.5 mL of water sample was mixed with 1.5 mL hexane (Fisher). To extract 2-CIBP and BP in solid samples, automated Soxhlet showing high extraction efficiency was adopted. A detailed description for 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 [15,17].

### 3. Results and discussion

#### 3.1. Properties of sediment components and their 2-CIBP concentration

Table 1 summarizes the properties of sediment components tested in this study and their 2-CIBP concentration after spiking. Inorganic components such as kaolin and MMT contained negligible amount of organic carbon while organic components such as coal, graphite, and GAC contained significant amount of organic carbon. Graphite was purely composed of organic carbon. They exhibited crystal or amorphous structure and some of them, including kaolin and GAC, showed porous structure. GAC had highest surface area at 474 m<sup>2</sup>/g and pore volume at 0.543 cm<sup>3</sup>/g which might act as effective adsorption sites for PCBs. Kaolin also had relatively high surface area at 18.7 m<sup>2</sup>/g.

Solid phase 2-CIBP concentration in sediment component after spiking is interesting. Considering that target 2-CIBP concentration is 100 mg/kg when all spiked 2-CIBP is left on sediment component, only 59.6 and 50.9% of 2-CIBP was actually spiked into kaolin and MMT, respectively. Since such inorganic components do not show strong chemical affinity for PCBs, significant portion of spiked 2-CIBP seemed to be lost during solvent drying process [26]. Meanwhile, organic components had much higher 2-CIBP concentration. It is known that organic carbon content in sediment components is one of the most important parameters for determining PCBs holding capability of sediment components [13]. 2-CIBP concentration was in order of GAC > mixture > coal > graphite > kaolin > MMT. This trend is supported by a previous study on kinetics and mechanisms of PCB congener sorption to carbonaceous sediment components [27]. Especially GAC, which was proven to exhibit high affinity for PCBs, showed the highest 2-CIBP concentration, equivalent to 92.7% of added 2-CIBP [13,27]. It is believed that GAC adsorbed and held 2-CIBP more effectively and tightly during 2-CIBP spiking process and thus less amount of 2-CIBP was lost during solvent drying process. Mixture of five sediment components exhibited intermediate properties. Even the small amount of GAC in mixture was able to strongly hold 2-CIBP at 81.2%.

#### 3.2. Desorption of 2-CIBP in control

Desorption of 2-CIBP spiked to sediment components was monitored in the absence of RAC (control), as shown in Fig. 1. In cases of inorganic components, 2-CIBP spiked to sediment component was effectively desorbed. Kaolin and MMT showed 16% and 18% of 2-CIBP desorption, respectively. Meanwhile, organic components exhibited very low 2-CIBP desorption. Graphite

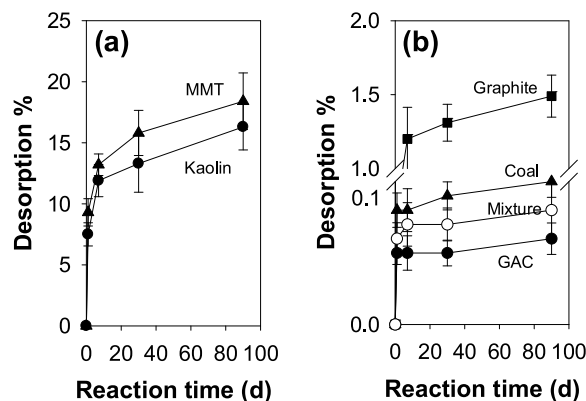


Fig. 1. Desorption of 2-CIBP spiked to sediment components into water in the absence of RAC (control): (a) inorganic components: kaolin and MMT and (b) organic components: coal, graphite, GAC, and mixture. Desorption% was calculated based on the total amount of 2-CIBP desorbed into water out of the total amount of 2-CIBP initially available in sediment component.

showed highest desorption only at 1.5%, while 2-CIBP desorption from coal, GAC, and mixture was negligible at less than 0.1%. Interestingly, order of 2-CIBP desorption, following GAC < mixture < coal < graphite < kaolin < MMT, was in agreement with order of the amount of 2-CIBP spiked to sediment component, following GAC > mixture > coal > graphite > kaolin > MMT.

Desorption results deliver important messages. First, sediment components showing strong adsorption capability towards 2-CIBP desorbed less amount of 2-CIBP into water. As discussed previously, more 2-CIBP was actually spiked to organic components which can strongly hold 2-CIBP. There might be two types of 2-CIBP available on sediment component: one strongly adsorbed or attached onto solid surface during 2-CIBP spiking process and one necessarily simply left over onto solid surface during solvent drying process. Even if sediment components do not have any chemical affinity for PCBs, the second type of 2-CIBP always exists and thus such 2-CIBP might be more subject to immediate desorption. Low desorption of 2-CIBP from organic components can be explained by the first type of 2-CIBP dominant in organic components while the second type of 2-CIBP might be significant in cases of inorganic components and thus desorption of 2-CIBP was high.

Second, in spite of slight difference in 2-CIBP spiking% between inorganic and organic components, i.e., 50.9–59.6% for inorganic and 74.8–92.7% for organic, desorption% showed huge difference, i.e., 16–18% for inorganic and only 1.5% or less than 0.1% for organic. The result implies that organic carbon in sediment components was able to strongly hold spiked 2-CIBP and thus 2-CIBP stayed preferentially in sediment components rather than being desorbed into water. Third, components such as kaolin and MMT released 2-CIBP significantly from the beginning of desorption process and then slowly and continuously released 2-CIBP over 90 d while components such as coal and GAC did not release 2-CIBP continuously over time. Difference in the desorption behaviors might be associated with the types of 2-CIBP available in sediment components as discussed above. Kaolin and MMT could immediately release 2-CIBP simply left over onto their surface and then slowly released 2-CIBP attached onto their surface. Fourth, although inorganic kaolin exhibited significantly high surface area at 18.7 m<sup>2</sup>/g, its surface was not so effective enough to strongly adsorb 2-CIBP, compared to organic coal and graphite with low surface areas only at 2.89 and 2.79 m<sup>2</sup>/g, respectively. Fifth, the behavior of mixture, which partly represents actual sediments, was very similar to that of GAC, implying even the small amount of GAC used in mixture (presumably present in actual sediment) was enough to strongly adsorb and hold spiked 2-CIBP.

**Table 1**  
Physicochemical properties of sediment components and their solid phase 2-CIBP concentration after spiking.

Component	Physicochemical Properties						2-CIBP (mg/Kg) <sup>g</sup>
	f <sub>OC</sub> <sup>a</sup>	Crystal <sup>b</sup>	Porous <sup>c</sup>	S <sub>BET</sub> <sup>d</sup> (m <sup>2</sup> /g)	V <sub>Pore</sub> <sup>e</sup> (cm <sup>3</sup> /g)	PS <sup>f</sup> (nm)	
Kaolin	~0	Crystal	Meso	18.7	0.114	21.9	59.6
MMT	~0	Crystal	Non	5.26	0.018	15.3	50.9
Coal	0.69	Amorphous	Non	2.89	0.011	>15	77.0
Graphite	1.00	Crystal	Non	2.79	0.011	>10	74.8
GAC	0.84	Amorphous	Mes + Micro	474	0.543	<6, 8–40	92.7
Mixture	0.51	–	–	100.7	0.139	–	81.2

<sup>a</sup> f<sub>OC</sub>: organic carbon fraction.  
<sup>b</sup> Even amorphous components have crystallinity at some extent.  
<sup>c</sup> Porous structure (micro: microporous, meso: mesoporous, and non: nonporous).  
<sup>d</sup> BET surface area.  
<sup>e</sup> Pore volume.  
<sup>f</sup> Average pore size.  
<sup>g</sup> Actual solid phase 2-CIBP concentration after spiking and drying (target concentration was 100 mg/Kg), which is equal to sum of 2-CIBP and BP found in all phases at any time since 2-CIBP is transformed only to BP by dechlorination reaction on RAC.

### 3.3. Partitioning and dechlorination in direct mixing

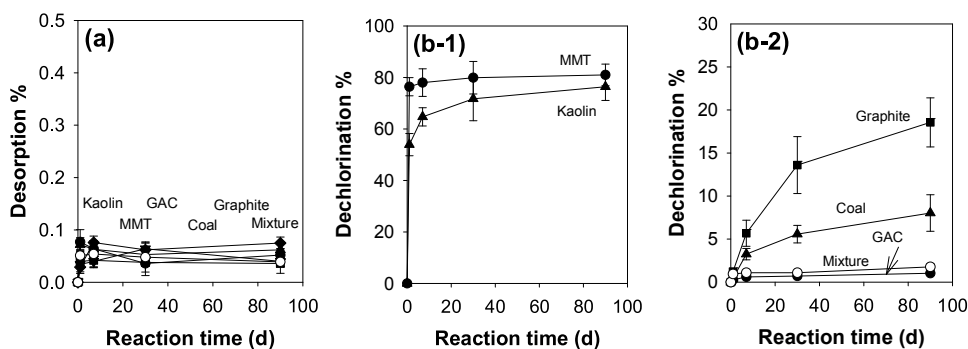
Since 2-CIBP is transformed to only BP by dechlorination reaction at RAC, the initial amount of spiked 2-CIBP to sediment component should always be the same as sum of 2-CIBP and BP in all phases at any time. This makes it easy to interpret and explain partitioning and fraction data. Desorption of spiked 2-CIBP from sediment component, overall dechlorination of 2-CIBP to BP, and eventual partitioning of 2-CIBP and BP in the presence of RAC (direct mixing) were traced, as shown in Fig. 2. Desorption% is shown in Fig. 2(a), which can be used as a general indicator to show how much of 2-CIBP and BP was available and partitioned into water eventually at a given time, but not as a quantitative indicator to show how much of 2-CIBP was totally desorbed from sediment component (because 2-CIBP desorbed and then transported to RAC is unknown). Regardless of sediment components, much less than 0.1% of 2-CIBP and BP was available in water, meaning that most of 2-CIBP and BP stayed adsorbed in sediment component and RAC. In particular, considering that inorganic components released 2-CIBP significantly from the beginning of reaction in the previous control test, it is believed that 2-CIBP, once desorbed and available in water, was immediately adsorbed onto RAC showing high affinity for 2-CIBP (note the raw material for RAC is GAC).

2-CIBP and BP partitioning between sediment component and RAC was not clear in this experimental configuration because the two solid materials were mixed. It is difficult to quantify how much of 2-CIBP was actually desorbed from sediment component to water and transported to RAC, and how much of BP stayed on RAC after dechlorination reaction at RAC and left to sediment component. Overall dechlorination based on 2-CIBP and BP available in water and extracted from mixed solids is shown in Fig. 2(b).

Inorganic components exhibited high dechlorination at 74–80% and even organic components also demonstrated significant dechlorination at up to 18%. The result is interesting because desorption of 2-CIBP shown in Fig. 1 was relatively not significant (e.g., 2-CIBP desorption from graphite and coal was at 1.5% and 0.1%, respectively). Considering that dechlorination reaction should occur only at RAC, it can be concluded that the presence of RAC apparently facilitated 2-CIBP desorption from sediment component to water followed by its transport to RAC. After dechlorination of 2-CIBP, BP also stayed at RAC. The result also implies that the presence of highly adsorptive sediment components such as GAC strongly adsorbed PCBs, held them firmly, and thus inhibited their dechlorination onto RAC, resulting in very low dechlorination of 2-CIBP at less than 1% for GAC. It was reported that chemical treatment of PCBs-contaminated sites should be integrated with enhanced desorption process as a prerequisite [28].

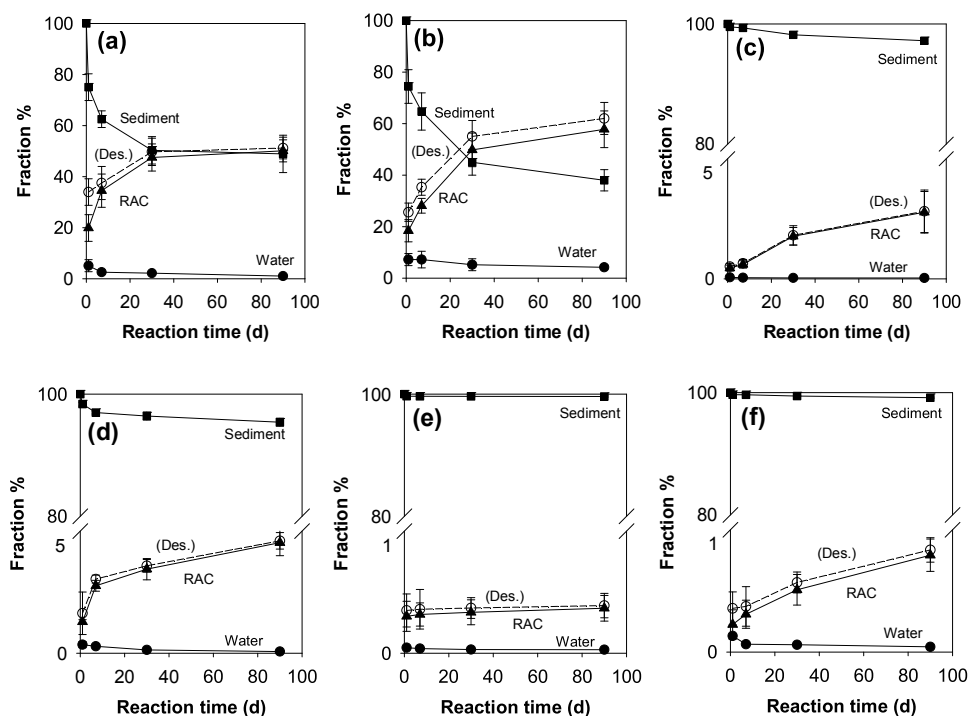
### 3.4. Partitioning and dechlorination in compartment configuration

Compartment configuration was set up to distinguish fraction of 2-CIBP and BP transported to RAC from fraction of 2-CIBP and BP remaining in sediment component and thus to measure total desorption of 2-CIBP and BP from sediment component to water and RAC. Fig. 3 shows partitioning of 2-CIBP and BP to water, sediment component, and RAC. Regardless of sediment components used, 2-CIBP and BP were negligible in water even in this compartment configuration, implying that they either stayed in sediment component or immediately adsorbed onto RAC once desorbed. Compared to the result in Fig. 1 showing desorption of 2-CIBP in the absence of RAC, significant amounts of 2-CIBP and BP were available in RAC.



**Fig. 2.** Desorption and dechlorination of 2-CIBP spiked to sediment components in the presence of RAC under direct mixing: (a) 2-CIBP and BP partitioning (desorption) to water and (b) overall dechlorination of 2-CIBP to BP. Note different scales in Y axis. Along with 2-CIBP and BP partitioned to water, 2-CIBP and BP are also present in the solid phase of mixed sediment component and RAC. Overall dechlorination is determined based on 2-CIBP and BP available in water and extracted from the mixed solid.





**Fig. 3.** Partitioning of 2-CIBP and BP to water, sediment component, and RAC in the presence of RAC under compartment configuration: (a) kaolin, (b) MMT, (c) coal, (d) graphite, (e) GAC, and (f) mixture. (Des.) stands for overall desorption, which is total amount of 2-CIBP and BP in water and RAC. Note different scales and breaks in Y axis to best accommodate data comparison. Since 2-CIBP is transformed to only BP, total amount of 2-CIBP and BP in all phases does not change over time, which makes it easy to interpret and explain partitioning and fraction data.

For kaolin, 16% of 2-CIBP was desorbed in the absence of RAC while almost 50% of 2-CIBP (and BP) was desorbed in the presence of RAC and thus available mostly in RAC and negligibly in water. Reason for putting BP into parentheses above (i.e., (and BP)) is that the amount of BP actually found in RAC is the same as the amount of 2-CIBP transported to and dechlorinated at RAC. As a result, 2-CIBP (not dechlorinated yet) and BP (already dechlorinated) found in RAC can be interpreted as total 2-CIBP transported to RAC. Similar result is also shown for MMT. Even for organic components, desorbed 2-CIBP (and BP) to RAC and water was not negligible. As a result, the presence of RAC even in this compartment configuration significantly facilitated desorption of 2-CIBP and sequestered 2-CIBP and BP by adsorbing them onto RAC.

However, sediment components such as GAC still strongly held spiked 2-CIBP and thus total desorption was very low at 0.40% even in the presence of RAC (but higher than 0.10% in the absence of RAC). In comparison between direct mixing and compartment configuration, the amount of 2-CIBP (and BP) available in RAC for dechlorination reaction is believed to be much less in compartment configuration than direct mixing because of slow mass transport of 2-CIBP in compartment configuration which requires multiple steps composed of desorption of 2-CIBP from sediment component to water, transport of the desorbed 2-CIBP to RAC compartment through filter paper, and then its eventual adsorption to RAC.

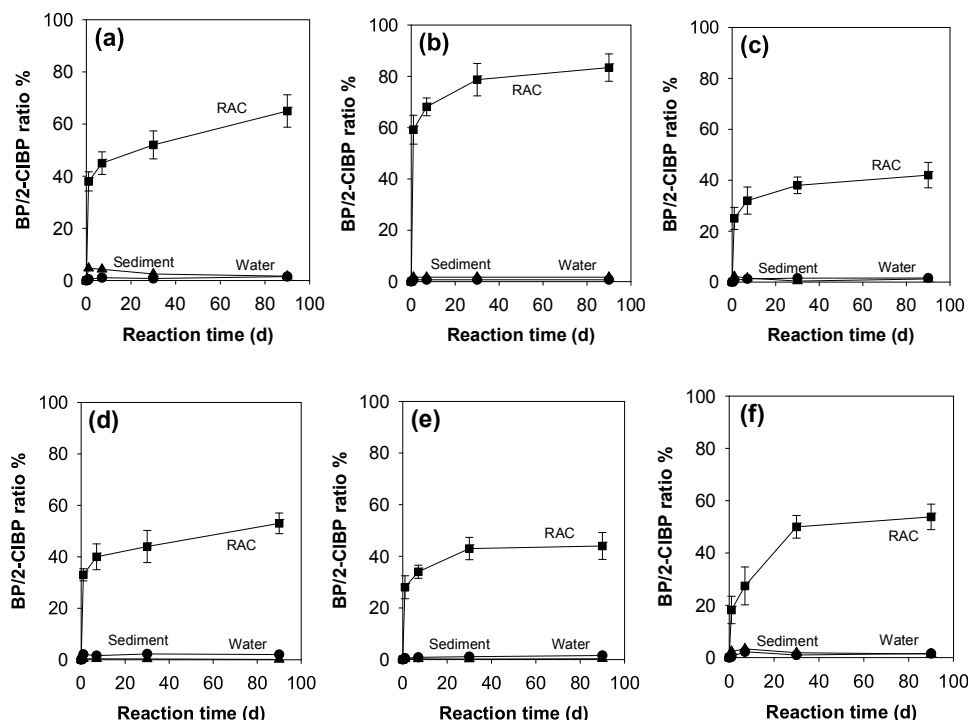
Fig. 4 shows BP/2-CIBP ratio% in each phase of water, sediment component, and RAC. The result indicates where the dechlorination reaction mostly occurred. It should be noted that the result in Fig. 4 does not demonstrate how much of 2-CIBP, as total, was dechlorinated because the result does not incorporate quantitative partitioning of 2-CIBP and BP into water, sediment component, and RAC. BP/2-CIBP ratio in water as well as sediment component was almost zero regardless of sediment components while BP/2-CIBP ratio in RAC was significant at 43% for GAC and up to 82% for MMT. This simply implies dechlorination reaction occurred only at RAC, and BP, once formed, stayed adsorbed at RAC. One thing

which should be investigated later in detail is that inorganic components such as kaolin and MMT showed slightly higher BP/2-CIBP ratio in RAC than organic components. Interestingly, 2-CIBP transported to RAC was effectively dechlorinated in case of MMT and kaolin although significant amounts of 2-CIBP were transported to RAC. Meanwhile, in spite of small amounts of 2-CIBP transported to RAC in cases of organic components, dechlorination of 2-CIBP in RAC seemed to be not so effective.

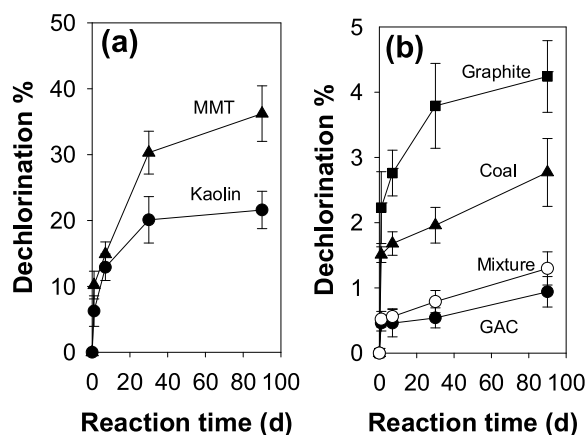
Based on the amount of 2-CIBP and BP in water, sediment component, and RAC and the ratio of BP/2-CIBP in each phase, overall dechlorination in the presence of RAC was determined, as shown in Fig. 5. 2-CIBP dechlorination increased in order of GAC < mixture < coal < graphite < kaolin < MMT, which is good agreement with 2-CIBP desorption trend for sediment components. Overall dechlorination in this compartment configuration was relatively low, compared to dechlorination in direct mixing, as expected based on slow mass transport of 2-CIBP from sediment component to RAC. However, the dechlorination of spiked 2-CIBP to sediment components in this study was much more significant than the dechlorination of PCBs aged in real sediment reported elsewhere [25]. Previously, overall dechlorination efficiency for WHS containing 2.85% of amorphous organic carbon and 0.34% of soot carbon was very low only at 0.5–3.0% in direct mixing and 0.03–0.53% in compartment configuration after 30 d under similar conditions [25]. In spite of their high organic carbon contents, 2-CIBP spiked to and aged in the organic sediment components for at most 1 d was much more mobile and easy to desorb and dechlorinate in the presence of RAC.

#### 4. Conclusion

This study investigated the role of various solid sediment components in adsorbing and desorbing PCBs in order to explain the low dechlorination of PCBs bound and aged to actual aquatic sediments under remediation with RAC. Adsorption and holding capability of



**Fig. 4.** BP/2-CIBP ratio% in each phase of water, sediment component, and RAC under compartment configuration: (a) kaolin, (b) MMT, (c) coal, (d) graphite, (e) GAC, and (f) mixture. BP/2-CIBP ratio % in RAC corresponds to solid phase dechlorination efficiency.



**Fig. 5.** Overall dechlorination of 2-CIBP spiked to sediment components in the presence of RAC under compartment configuration: (a) inorganic components: kaolin and MMT and (b) organic components: coal, graphite, GAC, and mixture.

sediment components toward 2-CIBP strongly influenced amount of spiked 2-CIBP, amount of desorbed 2-CIBP, overall dechlorination of 2-CIBP to BP, and eventual partitioning of 2-CIBP and BP to water, sediment component, and RAC. As a result, order of the amount of spiked 2-CIBP to sediment components after drying, following GAC > mixture > coal > graphite > kaolin > MMT, was in good agreements with order of the amount of 2-CIBP desorbed to water and RAC as well as with order of overall 2-CIBP dechlorination under direct mixing and compartment configuration, following GAC < mixture < coal < graphite < kaolin < MMT. The presence of RAC even in compartment configuration facilitated desorption of 2-CIBP and contributed to complete sequestration of 2-CIBP and BP. This study proved the substantial role of organic components in aquatic sediments for strongly adsorbing and holding PCBs which prevent them from dechlorination on RAC as a heterogeneous reaction medium. 2-CIBP shortly spiked to sediment

components (even with high organic carbon contents) was much more mobile and easy to desorb and dechlorinate than PCBs aged in actual sediments.

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### References

- [1] L.H. Nowell, P.W. Moran, R.J. Gilliom, D.L. Calhoun, C.G. Ingersoll, N.E. Kemble, K.M. Kuivila, P.J. Phillips, Contaminants in stream sediments from seven United States metropolitan areas: part I: distribution in relation to urbanization, *Arch. Environ. Contam. Toxicol.* 64 (2013) 32–51.
- [2] K.D. Daskalakis, T.P. O'Connor, Normalization and elemental sediment contamination in the coastal United States, *Environ. Sci. Technol.* 29 (1995) 470–477.
- [3] M. Dopic, A. Gomez, Review of the current state and main sources of dioxins around the world, *J. Air Waste Manage. Assoc.* 65 (2015) 1033–1049.
- [4] D. Dodoo, D. Essumang, J. Jonathan, J. Bentum, Polychlorinated biphenyls in coastal tropical ecosystems: distribution, fate and risk assessment, *Environ. Res.* 118 (2012) 16–24.
- [5] D.O. Carpenter, Polychlorinated biphenyls (PCBs): routes of exposure and effects on human health, *Rev. Environ. Health* 21 (2006) 1–23.
- [6] S. Agarwal, S.R. Al-Abed, D.D. Dionysiou, In situ technologies for reclamation of PCB-contaminated sediments: current challenges and research thrust areas, *J. Environ. Eng.* 133 (2007) 1075–1078.
- [7] Y.J. Choi, Y.M. Cho, R.G. Luthy, In situ sequestration of hydrophobic organic contaminants in sediments under stagnant contact with activated carbon. 1. Column studies, *Environ. Sci. Technol.* 48 (2014) 1835–1842.
- [8] Y.J. Choi, Y.M. Cho, D. Werner, R.G. Luthy, In situ sequestration of hydrophobic organic contaminants in sediments under stagnant contact with activated carbon. 2. Mass transfer modeling, *Environ. Sci. Technol.* 48 (2014) 1843–1850.
- [9] Y.M. Cho, D. Werner, Y.J. Choi, R.G. Luthy, Long-term monitoring and modeling of the mass transfer of polychlorinated biphenyls in sediment following pilot-scale in-situ amendment with activated carbon, *J. Contam. Hydrol.* 129 (2012) 25–37.
- [10] Y.M. Cho, U. Ghosh, A.J. Kennedy, A. Grossman, G. Ray, J.E. Tomaszewski, D.W. Smithenry, T.S. Bridges, R.G. Luthy, Field application of activated carbon

- amendment for in-situ stabilization of polychlorinated biphenyls in marine sediment, *Environ. Sci. Technol.* 43 (2009) 3815–3823.
- [11] G.P. Fan, Y. Wang, G.D. Fang, X.D. Zhu, D.M. Zhou, Review of chemical and electrokinetic remediation of PCBs contaminated soils and sediments, *Environ. Sci.-Processes Impacts* 9 (2016) 1140–1156.
  - [12] S. Agarwal, S.R. Al-Abed, D.D. Dionysiou, Enhanced corrosion-based Pd/Mg bimetallic systems for dechlorination of PCBs, *Environ. Sci. Technol.* 41 (2007) 3722–3727.
  - [13] M.T. Jonker, A.A. Koelmans, Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations, *Environ. Sci. Technol.* 36 (2002) 3725–3734.
  - [14] H. Choi, S.R. Al-Abed, S. Agarwal, D.D. Dionysiou, Synthesis of reactive nano-Fe/Pd bimetallic system-impregnated activated carbon for the simultaneous adsorption and dechlorination of PCBs, *Chem. Mater.* 20 (2008) 3649–3655.
  - [15] H. Choi, S. Agarwal, S.R. Al-Abed, Adsorption and simultaneous dechlorination of PCBs on GAC/Fe/Pd: mechanistic aspects and reactive capping barrier concept, *Environ. Sci. Technol.* 43 (2009) 488–493.
  - [16] H. Choi, S.R. Al-Abed, S. Agarwal, Effects of aging and oxidation of palladized iron embedded in activated carbon on the dechlorination of 2-chlorobiphenyl, *Environ. Sci. Technol.* 43 (2009) 4137–4142.
  - [17] H. Choi, S.R. Al-Abed, S. Agarwal, Catalytic role of palladium and relative reactivity of substituted chlorines during adsorption and treatment of PCBs on reactive activated carbon, *Environ. Sci. Technol.* 43 (2009) 7510–7515.
  - [18] G.Z. Qu, L.Q. Kou, T.C. Wang, D.L. Liang, S.B. Hu, Evaluation of activated carbon fiber supported nanoscale zero-valent iron for chromium (VI) removal from groundwater in a permeable reactive column, *J. Environ. Manage.* 201 (2017) 378–387.
  - [19] Development of an activated carbon-supported zero-valent iron catalyst (AC-Fe<sup>0</sup>) for enhancing degradation of reactive brilliant orange and reducing iron sludge production, *Environ. Prog. Sustain. Energy* 35 (2016) 949–956.
  - [20] H.H. Tseng, J.G. Su, C. Liang, Synthesis of granular activated carbon/zerovalent iron composites for simultaneous adsorption/dechlorination of trichloroethylene, *J. Hazard. Mater.* 192 (2011) 500–506.
  - [21] J. Yang, L.M. Cao, R. Guo, J.P. Jia, Permeable reactive barrier of surface hydrophobic granular activated carbon coupled with elemental iron for the removal of 2,4-dichlorophenol in water, *J. Hazard. Mater.* 184 (2010) 782–787.
  - [22] H. Choi, S.R. Al-Abed, Effect of reaction environments on the reactivity of PCB (2-chlorobiphenyl) over activated carbon impregnated with palladized iron, *J. Hazard. Mater.* 179 (2010) 869–874.
  - [23] International Joint Commission (IJC), PCB Contaminated Sediment Remediation in Waukegan Harbor, available at <http://www.ijc.org/php/publications/html/cases/waukegan/waukegan.html> (Accessed 30 August 2017).
  - [24] Environmental Protection Agency (EPA), Cleanup of Outboard Marine Corporation/Waukegan Harbor Site, Office of Public Affairs, Chicago, IL, 1988.
  - [25] H. Choi, W. Lawal, S.R. Al-Abed, Desorption, partitioning, and dechlorination characteristics of PCBs in sediments in interaction with reactive activated carbon, *J. Hazard. Mater.* 287 (2015) 118–125.
  - [26] H. Choi, P.A. Nfodzo, W.A. Lawal, S.R. Al-Abed, Y. Seo, Phenomenological and spectroscopic analysis on the effects of sediment ageing and organic carbon on the fate of a PCB congener spiked to sediment, *J. Hazard. Mater.* 239 (2012) 325–332.
  - [27] H. Choi, S.R. Al-Abed, PCB congener sorption to carbonaceous sediment components: macroscopic comparison and characterization of sorption kinetics and mechanism, *J. Hazard. Mater.* 165 (2009) 860–866.
  - [28] A. Rianza-Frutos, J. Quiroga, M. Manzano, Remediation of contaminated soils with PCBs using an integrated treatment: desorption and oxidation, *J. Environ. Eng.* 133 (2007) 541–547.