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Long-term monitoring and modeling of the mass transfer of polychlorinated biphenyls in sediment following pilot-scale *in-situ* amendment with activated carbon

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ABSTRACT

The results of five years of post-treatment monitoring following *in-situ* activated carbon (AC) placement for stabilization of polychlorinated biphenyls (PCBs) at an inter-tidal mudflat adjacent to Hunters Point Shipyard, San Francisco Bay, CA, USA are reported in this paper. After five years, AC levels of the sediment cores were comparable to those at earlier sampling times. Passive sampler uptake validated the benefit of the AC amendment with a strong local sorbent dose–response relationship. The PCB uptakes in passive samplers decreased up to 73% with a 3.7 dry wt.% AC dose after five years, confirming the temporal enhancement of the amendment benefit from a 19% reduction with a 4.4% dose observed within one month. The long-term effectiveness of AC, the local AC dose response, the impact of fouling by NOM, the spatial heterogeneity of AC incorporation, and the effects of advective sediment pore-water movement are discussed with the aid of a PCB mass transfer model. Modeling and experimental results indicated that the homogeneous incorporation of AC in the sediment will significantly accelerate the benefit of the treatment.

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1. Introduction

In-situ treatment of sediment with activated carbon (AC) is currently being investigated as a promising approach to complement conventional sediment remedial strategies for sites impacted by hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and dichlorodiphenyltrichloroethane (DDT) (Ghosh et al., 2011). AC is a very strong sorbent material due to its high micro-porosity that depletes HOCs from sediment particles and the aqueous phase, subsequently reducing the exposure to benthic organisms. The concept has been successfully verified in the laboratory via a series of physicochemical studies (Werner et al., 2005; Zimmerman et al., 2004, 2005) and biological assays with various benthic organisms including clams, amphipods, marine worms, and mussels (Cornelissen et al., 2006; Janssen et al., 2009;

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McLeod et al., 2004, 2007a, 2007b; Millward et al., 2005; Sun and Ghosh, 2007). These laboratory results encourage field trials of the technology, from which the feasibility of placing activated carbon in sediment has been demonstrated for various field conditions with a range of engineering techniques (Ghosh et al., 2011). Knowledge gained through field trials can identify practical issues of implementation and monitoring, as well as address potential concerns about long-term stability and ecosystem effects, and the impacts of heterogeneous AC distribution on performance. The field site adjacent to Hunters Point Shipyard, San Francisco Bay, CA, USA, is the best studied field trial to date, where about 3 dry wt.% of AC was incorporated into a 30 cm sediment layer on an inter-tidal mudflat using two commercially available mechanical mixing devices (Cho et al., 2007, 2009). This field trial showed the benefits of field-deployed AC such as reduced uptakes of PCBs into benthic organisms and passive samplers, and diminished releases to pore-water (Cho et al., 2007, 2009; Janssen et al., 2009; Tomaszewski et al., 2008). Furthermore, the field trial investigated sediment re-suspension



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and benthic community health, finding no significant adverse impacts from the AC amendment (Cho et al., 2007, 2009).

Although major advances have been made, significant gaps remain between the current understanding of the AC amendment technology and the level of engineering know-how necessary for widespread implementation as a remedial alternative. First, we should investigate the long-term stability of the AC placement in sediment under various field conditions. Secondly, the long-term benefit of AC amendment to reduce the bioavailability of contaminants should be evaluated. The US Navy's Feasibility Study for sediment cleanup at Hunters Point notes that the effectiveness and implementability of AC as an *in-situ* treatment shows potential but the technology rating is moderate to low because of limited experience and questions about the long-term effectiveness (US. Navy et al., 2008). Thirdly, additional field conditions that can affect the effectiveness of AC amendment should be identified and investigated. Especially, the impact of natural organic matter (NOM) on AC performance should be further investigated, since several researchers have demonstrated a decrease in the AC sorbent strength in the presence of NOM in laboratory trials (Koelmans et al., 2009; To et al., 2008). Fourthly, we need to gain a better understanding of the technologies for uniformly placing AC in the field. Lastly, further assessments of any adverse impacts of AC amendment should be carefully evaluated. For example, possible negative effects of AC on benthic organisms were observed in laboratory studies (Jonker et al., 2009), although no detrimental effects have been observed in the published field studies (Cho et al., 2009; Janssen et al., 2011).

In this paper, we address the first three points in the above list and present for the first time long-term monitoring results of up to five years post-placement for the two pilot-scale field trials of AC amendment conducted at Hunters Point (Cho et al., 2007, 2009). A mass transfer model was developed to support the experimental evaluations and explain the behavior of HOCs in AC-amended sediment under field conditions and further to predict the long-term effectiveness of field-deployed AC. The stability of AC placement and the long-term effectiveness of AC amendment, and field conditions that affect the performance of AC amendment are discussed. Among possible influences of field conditions, the impact by NOM fouling, the spatial heterogeneity of AC, and advective sediment porewater movement are assessed with the aid of the model.

2. Methods

2.1. Site description

Test sites were located at an inter-tidal mudflat adjacent to Hunters Point Shipyard, CA, USA (Fig. 1A and B), wherein



Fig. 1. Schematic of (A) San Francisco Bay; (B) Hunters Point Naval Shipyard and South Basin; and (C) four test plots (A–B and C–D). The two plots indicated by shading (Plots A and D) were treated by mixing the sediment with AC to a nominal 30-cm depth. Plot B served as an unmixed control plot for Plot A, and Plot C served as a mixed control plot for Plot D.

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