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Long-term potential of *in situ* chemical reduction for treatment of polychlorinated biphenyls in soils

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HIGHLIGHTS

- Batch studies compared reductive treatment of PCBs in water and soil–water systems.
- Pd-catalyzed degradation of 2-chlorobiphenyl was apparent in aqueous-phase studies.
- For PCBs in soils, results for most treatments were similar to untreated controls.
- Treatments that were successful in water had little impact in soil–water systems.
- In soils, treatment involving desorption agents improved rates to a limited extent.

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ABSTRACT

Polychlorinated biphenyls (PCBs) are well-known for being hydrophobic and persistent in the environment. Although many treatment approaches have been demonstrated to result in degradation of PCBs in water or water/cosolvent systems, few examples exist where such approaches have been applied successfully for PCB degradation in soil–water systems. A possible explanation for the limited treatment of PCBs in soil–water systems is that reactants that are capable of degrading PCBs in the aqueous phase are unlikely to persist long enough to achieve meaningful treatment of slowly-desorbing PCBs associated with the soil phase. To investigate this explanation, laboratory studies were conducted to evaluate chemical reductants, including zero valent metals, palladium (Pd) catalyst, and emulsified zero valent iron (EZVI), for dechlorination of PCBs in the presence and absence of soil. In the absence of soil, Pd-catalyzed treatments (Pd with electrolytic ZVI or iron/aluminum alloy) achieved rapid destruction of a model PCB congener, 2-chlorobiphenyl, with half-lives ranging from 43 to 110 min. For treatment of soils containing Aroclor 1248 at an initial concentration of approximately 1500 mg kg^{-1}, Pd-catalyzed treatments achieved no measurable enhancement over the background PCB depletion rate (i.e., that measured in the untreated control) of 5.3 mg kg^{-1} $week^{-1}$. In the presence of soils, EZVI was the only approach evaluated that resulted in a clear enhancement in PCB dechlorination rates. EZVI achieved PCB concentration reductions of greater than 50% at an average rate of 19 mg kg^{-1} $week^{-1}$. The results suggest that slow PCB desorption limits treatment effectiveness in soils.

1. Introduction

In 1976, the Toxic Substances and Control Act (TSCA) ended commercial production of polychlorinated biphenyls (PCBs) in the United States; world-wide production of PCBs was greatly reduced in 2001 with the Stockholm Convention on Persistent Organic Pollutants. After the cessation of commercial-scale PCB production, global concentrations of PCBs in air, water, and soil have declined (Diamond et al., 2010). Nevertheless, PCBs continue to present environmental and social challenges. Methods that have typically been employed for treatment of PCB-impacted soils and sediments include thermal oxidation (incineration), chemical oxidation, biodegradation, stabilization/sequestration, and thermal desorption. Although capable of reducing environmental risks of

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PCBs under certain circumstances, each of these methods is subject to limitations. For example, thermal and chemical oxidation technologies risk formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (Zhao et al., 2012). Biodegradation of PCBs has been widely studied (e.g., Abramowicz et al., 1993; Wiegel and Wu, 2000; Luo et al., 2008) but is often slow and may result in incomplete dechlorination. Stabilization/sequestration can effectively reduce mobility and bioavailability of PCBs (Cho et al., 2012) but does not ultimately result in removal of PCBs from the environment. Thermal desorption can be effective at reducing total PCB concentrations but requires high temperatures (>200 °C) (Iben et al., 1996; Zhao et al., 2012), which may be cost prohibitive for certain situations and may be challenging to implement in high groundwater flow conditions.

An approach that could overcome these limitations involves *in situ* use of chemical reductants. A recent review addresses the advantages and limitations of several chemical reductants for degradation of PCBs (Wu et al., 2012). Of the extensive list of treatments identified in the review, only eight addressed treatment of PCBs in soil or sediment (Korte et al., 2002; Ehsan et al., 2003; Varanasi et al., 2007; Aresta et al., 2008; Agarwal et al., 2009; He et al., 2009; Liao et al., 2009; Mitoma et al., 2009). Generally, these studies reflect conditions that are unlikely to be applied for *in situ* treatment. Extreme temperature (greater than 300 °C) or pressure (20 MPa at 100 °C) conditions were often required for substantial degradation of PCBs (Varanasi et al., 2007; Aresta et al., 2008; Liao et al., 2009). Although the authors did not always state their envisioned method of implementation, we assume that such conditions are intended primarily for *ex situ* applications. Treatment of PCBs in soils under ambient temperature and pressure conditions utilized reactive media loading rates of 25–250% of the mass of soil treated (He et al., 2009), which may present challenges in terms of cost and deliverability. In addition, several studies addressed the use of surfactants or cosolvents to enhance liquid-phase availability of PCBs (Korte et al., 2002; Agarwal et al., 2009; Mitoma et al., 2009). Under laboratory study conditions, surfactants and cosolvents have been effective in enhancing PCB desorption rates from soil and sediment but have often resulted in limited reaction rates (e.g., Korte et al., 2002; Devor et al., 2008; Agarwal et al., 2009). Information presented by Wu et al. (2012) suggests that few, if any, instances of degradation of PCB in soil–water systems under *in situ* conditions have been achieved.

PCBs are difficult to degrade in soils and sediments for two primary reasons: (1) high chemical stability and (2) high hydrophobicity, which leads to low availability in the aqueous phase. In the presence of soils, equilibrium phase partitioning calculations indicate that the fraction of PCBs in the aqueous phase may range from 0.79% for mono-chlorobiphenyl (CBP) to 0.00023% for deca-CBP (see Supporting Information). Therefore, any treatment applied to the aqueous phase may affect only a very small fraction of the total PCB mass.

The hypothesis addressed by this research is that PCBs present a treatment conundrum, wherein reactive media exist that are capable of degrading persistent compounds such as PCBs, but such reactive media are unlikely to persist long enough under *in situ* conditions to achieve meaningful treatment of PCBs in soils. The objectives of the study include (a) comparing treatment performance of chemical reductants, including zero-valent metals and Pd-catalyst, in water and soil–water systems and (b) evaluating the long-term potential of these chemical reductants to enhance the degradation rates of PCBs in soil–water systems. For treatment of PCBs in the presence of soils, the envisioned implementation approach utilizes soil mixing for delivery of reactive media and stabilizing agents, an approach that has been advanced for remediation of soils impacted with chlorinated aliphatic compounds (Wadley et al., 2005; Olson et al., 2012). Moreover, the studies focus on conditions that conceivably can be implemented *in situ* at contaminated sites.

2. Materials and methods

2.1. Materials

The studies were conducted using soils, groundwater, and field-weathered PCB dense non-aqueous phase liquid (DNAPL) collected from the Outboard Marine Corporation (OMC) Superfund Site, Waukegan, IL. Soil samples consisted of medium-grained, poorly-sorted sand. Groundwater and PCB DNAPL, which consisted of nearly-pure Aroclor 1248, were collected from on-site monitoring wells.

Treatment reagents included 50–200 mesh zero-valent iron (Fe) filings and 40–80 mesh zero-valent magnesium (Mg) obtained from Peerless Metal Powders and Abrasive (Detroit, MI) and Fisher Scientific (Pittsburgh, PA), respectively. OnMaterials (Akron, OH) provided electrolytic Fe (Fe*), metallic iron/aluminum alloy (Fe/Al), and 1% zero-valent palladium (Pd) on alumina (Pd–Al_2O_3). The Fe*, Fe/Al, and Pd–Al_2O_3 were shipped and stored in propylene glycol (PG). Emulsified zero-valent iron (EZVI) was produced following procedures similar to those outlined by Quinn et al. (2005). Materials used to make EZVI included BASF (Evans City, PA) Microspheres 200-plus zero-valent Fe, food-grade corn oil and SPAN-85 surfactant (Sigma–Aldrich, St. Louis, MO). The EZVI was prepared in a kitchen-grade blender by mixing 100 mL of water, 80 mL of corn oil, 3 mL of surfactant, and 20 g of micro-scale Fe. A 10% bentonite slurry mixture was prepared with Black Hills Bond unaltered sodium bentonite (Black Hills Bentonite, Mills, WY) and tap water (City of Fort Collins). All other chemicals used were ACS grade.

2.2. Aqueous study methods

The aqueous-phase study was conducted to validate reactivity of select treatments toward 2-chlorobiphenyl, which was selected as the model PCB congener due to a relatively high solubility ($2.9\ mg\ L^{-1}$). Five treatment sets were included: Fe*, Fe* + Pd, Fe/Al, Fe/Al + Pd, and an untreated control (additional details are provided in Supporting Information); each treatment set was prepared in triplicate. The study was conducted in 60-mL borosilicate glass vials equipped with Mininert® caps. In preparation for the study, the Fe*, Fe/Al, and Pd–Al_2O_3 (all in PG) were transferred into the dry vials under atmospheric conditions. The vials were then placed into an anaerobic chamber, where 50 mL of site groundwater were added. Next, 50 μL of a spiking solution, comprising 2-chlorobiphenyl (Ultra Scientific, North Kingstown, RI) in methanol, were added to obtain an initial concentration of 10 μM. Vials were then rotated in a tumbler at 20 rpm until sampling.

For sample collection, 500 μL of the liquid phase were removed through the Mininert® cap using a 500-μL glass gas-tight syringe. The liquid sample was added to a 2-mL glass vial containing 500 μL of *n*-hexane. The extraction vial was placed on a vortex shaker (Scientific Manufacturing Industries, Bohemia, NY) for 60 s. A portion of the organic phase was then removed for analysis.

2.3. Soils study methods

Soil-phase studies were conducted to evaluate the potential of select reductants to achieve reductive degradation of PCBs under conditions that conceivably can be applied for *in situ* treatment. The treatments applied in the soil-phase study included Fe, Mg, Fe*, Fe* + Pd, Fe/Al, Fe/Al + Pd, EZVI without clay, and EZVI with clay (see Supporting Information for additional details). Two controls