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Enrichment of anaerobic polychlorinated biphenyl dechlorinators from sediment with iron as a hydrogen source

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Abstract

Little is known about anaerobic polychlorinated biphenyl (PCB) dechlorination, although it is believed that some microorganisms are capable of respiring PCBs, gaining energy for growth from PCB dechlorination. If this is the case, the amendment of appropriate electron donors to contaminated sediment should stimulate dechlorination. The effect of elemental iron (Fe^0) addition, an easily amended electron donor, on the microbial dechlorination of the PCB congeners 3,4,5-trichlorobiphenyl (3,4,5-CB) and 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (2,2′,3,4,4′,5,5′-CB) was investigated in microcosms containing estuarine sediment from Baltimore Harbor. Results showed that the addition of 0.1 g Fe^0/g sediment reduced the lag time for removal of doubly flanked *para* chlorines by approximately 100 days. Because Fe^0 is a source of cathodic hydrogen (H_2), the effect of direct H_2 addition to sediment microcosms was also tested. The addition of 0.001 atm H_2 in the headspace generated the same dechlorination activity and reduction in lag time as the addition of 0.1 g Fe^0/g. Higher concentrations of Fe^0 or H_2 increased the lag prior to dechlorination. Additional results showed that an alkaline pH ($\geqslant$7.5), high [Fe^{2+}] (3.3 g/L), or HS^- ($\geqslant$0.1 mg/L total sulfide) inhibited dechlorination. Elevated concentrations of Fe^{2+}, OH^-, and HS^- are products of Fe^0 oxidation or increased microbial activity (methanogenesis, homoacetogenesis, and sulfate reduction), both of which would result from the amendment of large quantities of Fe^0 or H_2 to sediment. This research shows that not only can PCB dechlorination be stimulated through the addition of electron donor, but implies that the dechlorinators are enriched by the continuous addition of low concentrations of H_2, similar to other known dechlorinators, such as the dehalorespirer *Dehalococcoides ethenogenes*. These results suggest that the direct addition of controlled amounts of Fe^0 to sediments may be an effective remediation tool to reduce the lag period prior to dechlorination at PCB-impacted sites. They also suggest that PCB dechlorinators may be enriched using techniques similar to those used with known dehalorespirers.

Keywords: Hydrogen; PCBs; Elemental iron; Bioremediation; Sediment; Anaerobic dechlorination

1. Introduction

Polychlorinated biphenyls (PCBs) were produced in the United States from 1929 to 1977 for many applications, including electrical insulators, coolants in capacitors and transformers, hydraulic fluids, and carbonless copy paper (Abramowicz and Olson, 1995).

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In the mid-1960s, it was discovered that PCBs were accumulating in the environment as a result of their chemical stability and resistance to biological degradation; this led to their eventual ban in the United States in 1979. It has been estimated that 2.1×10^8 kg of PCBs, one-third of the total quantity produced, have been released into the environment as contaminants in soil and river, lake, and ocean sediments (Hutzinger and Verrkamp, 1981). This is of great concern because these compounds act as endocrine disrupters, teratogenic agents, and carcinogens and are distributed throughout the biological food chain via bioaccumulation (Cogliano, 1998).

PCB treatment options are few in number and often prohibitively expensive, leading researchers to investigate the potential for biological dechlorination to serve as an in situ remediation option. Anaerobic dechlorination can attack more highly chlorinated PCBs and has the potential to reduce their toxicity, particularly if *meta* and *para* chlorines are removed (Mohn and Tiedje, 1992). Such dechlorination has been observed at PCB-contaminated sites and also in microcosms containing sediment from non-impacted sites (Wiegel and Wu, 2000). Nevertheless, our current understanding of anaerobic biological PCB dechlorination is limited. Methanogens (Ye et al., 1995) and sulfate reducers (Zwiernik et al., 1998) have been implicated in PCB dechlorination, although no anaerobic PCB-dechlorinating organisms have been isolated. Two uncultured anaerobic PCB dechlorinators (DF-1 and *o*-17) that are phylogenetically related to known dehalorespiring microorganisms have been recently identified using molecular techniques (Cutter et al., 2001; Wu et al., 2002). Little is known, however, about the physiology of PCB dechlorinators in general. Moreover, the varying dechlorination patterns observed in complex PCB mixtures have been attributed to different microbial populations (Wiegel and Wu, 2000), suggesting that different techniques may be required to enrich for varying dechlorination patterns.

Long lag periods before PCB dechlorination begins, ranging from months to years (Wiegel and Wu, 2000), are often observed. This is a significant obstacle to the use of anaerobic bioremediation as sediment clean-up technology. Because of our lack of understanding regarding the identity and physiology of PCB dechlorinators, we are limited in our ability to understand and overcome these long lag periods. The creation of particular environmental conditions, or niches, for the PCB dechlorinators, the low bioavailability of PCBs (i.e., Bedard et al., 1998), and/or competition for electron donor could each contribute to long lag periods.

Hydrogen (H_2) has been reported to be an electron donor for the dechlorination of 2,3,4-trichlorobiphenyl (2,3,4-CB) in Hudson River sediment microcosms (Sokol et al., 1994). Nevertheless, in additional experiments H_2 was observed to be inhibitory to dechlorination (Wu, 1996). More recently, H_2 was shown to serve as an electron donor for a specific PCB-dechlorinator enriched from Charleston Harbor sediment, bacterium DF-1, which removes doubly flanked chlorines from PCB congeners (Wu et al., 2000, 2002). The general role of H_2 in a complex community that includes PCB-dechlorinators is currently unknown, but needs to be clarified if this process is to be understood and then manipulated for sediment remediation. Because of this, the overall goal of this study was to further investigate the apparent physiology of PCB-dechlorinators. Specifically, it was hypothesized that the addition of H_2 generated by the corrosion of elemental iron (Fe^0) would stimulate the microbial reductive dechlorination of PCBs in sediment microcosms if added at the appropriate rate. H_2, which is generated in anaerobic environments as a fermentation product, is maintained at low steady-state concentrations as a result of the catabolic activity of sulfate reducing bacteria and methanogenic archaea. Competition for H_2 may thus contribute to the long lag periods prior to PCB dechlorination observed in the environment and laboratory. The oxidation of Fe^0 to H_2 has an oxidation–reduction potential of 0.44 V, making this chemical reaction (shown below) thermodynamically favorable:

$$Fe^0 + 2H_2O = Fe^2 + 2OH^- + H_2.$$

In addition to providing H_2 in situ to stimulate microbial activity, the production of Fe^{2+} will sequester potentially inhibitory sulfide, an end product of biological sulfate reduction.

Herein we report that Fe^0 reduced the lag period prior to microbial reductive dechlorination of 3,4,5-CB and 2,2′,3,4,4′,5,5′-CB in sediment microcosms. We show that the enrichment of dechlorinators with the ability to remove doubly flanked chlorines resulted from the generation of H_2 via Fe^0 corrosion. The results of these microcosm studies suggest that treatment of PCB-impacted sediments with Fe^0 could serve as part of a tractable and inexpensive biological remediation technology to promote in situ microbial reductive dechlorination. These results also shed light on the physiology of PCB-dechlorinators, which appear to have a high affinity for H_2, much like known dehalorespirers.

2. Materials and methods

2.1. Chemicals

The PCB congeners, 3,4,5-CB and 2,2′,3,4,4′,5,5′-CB (AccuStandard) were dissolved in acetone (HPLC-UV grade) to concentrations of 1–10 mg/mL. Single PCB congeners (99% purity, AccuStandard) used to prepare