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Short communication

Degradation of trichloroethene in water by electron supplementation

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Abstract

Trichloroethene (TCE) is a common and recalcitrant contaminant in groundwater. Microbially catalyzed reductive dechlorination is a dominant pathway for TCE degradation, in which substrates and electron donors are essential. In this study, extraneous electron supplementation was attempted to enhance reductive dechlorination of TCE and its derivatives. Reactors were established with groundwater containing TCE, and a 6-V battery was used to supply an average current of 29 μA of dc power to feed electrons to the microcosms. We measured 80–90% depletion of TCE within 70 d in reactors (both sterile and non-sterile) containing 300–400 μg TCE/l and from 97 to 98% depletion in microcosms containing 10 mg TCE/l. No intermediate products such as dichloroethylene or vinyl chloride were detected during this study. Results demonstrate that electron-supplemented degradation of TCE appears to be an abiotic process that is unassociated with microbial populations or indigenous redox conditions. No apparent accumulation of TCE daughter products were observed and overall efficiency of this electroremediation process was calculated to be 6.9 g TCE degraded/kW h. This efficiency would make electron supplementation an attractive alternative to the substrate-amended biological reductive dechlorination of TCE.

Keywords: Electroremediation; Electron supplementation; Reductive dechlorination; TCE; Trichloroethene

1. Introduction

Trichloroethene (TCE) is a common degreasing agent used by industries and the military. Due to its high density, weak adsorption to soils, and low water solubility, TCE tends to accumulate in the subsurface environment, including groundwater and sediments, where it poses a major threat to environmental and human health [1]. TCE is also recalcitrant to conventional treatment methods, making it one of the most challenging pollutants in the environment. Degradation of TCE has been identified to be associated with multiple anaerobic pathways [2–3], such as sulfate reduction [4–10] and methanogenesis [11–14]. Reductive dechlorination is the major pathway responsible for TCE removal; however, the daughter compounds from TCE dechlorination, including dichloroethenes (DCEs) and vinyl chloride (VC), have been shown to accumulate following incomplete reductive dechlorination of TCE [15–17]. This accumulation was dominantly observed when sulfate-reducing and methanogenic conditions prevail and where insufficient hydrogen (electron donor) is present to sustain complete reductive dechlorination of TCE [14,16].

Electrochemical mechanisms have been investigated to promote denitrification by supplying electrons to reduce nitrate [18–23]. In these studies, the electrolysis of water produced hydrogen gas at the cathode (1), and the process was balanced by electron production at the anode (2), as follows:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (1)$$

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \qquad (2)$$

Similar studies were conducted for dechlorination reactions [24–27] in which highly reducing conditions were generated at the cathodes in an electrochemical system, which promoted degradation of chlorinated organics such as chloroform [28]

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and 2,6-dichlorophenol [29]. Degradation of tetrachloroethene (perchloroethene or PCE) and TCE has been observed using a potentiostat and sand reactor [26], yet research in direct electron supplementation to groundwater is lacking. The objective of this study was to investigate electron supplementation as a direct method to achieve abiotic reductive dechlorination of TCE in groundwater.

2. Experimental

2.1. Analytical methods

Electrical current was calculated with measured values of voltage and resistance. Water pH was measured with an Orion® Thermo model 720A + pH meter equipped with an Orion® Ag/AgCl combination electrode. Conductivity was measured with an Orion® Thermo model 150A + conductivity meter equipped with an Orion® conductivity cell. Chloride, nitrate, and sulfate were measured with a DIONEX DX-100 Ion Chromatograph (Sunnyvale, CA) equipped with a 4 mm × 250 mm IonPac AS14 anion exchange column. TCE, DCE, and VC were analyzed with a gas chromatograph–mass spectrometer (GC–MS) equipped with a purge-and-trap system.

2.2. Groundwater

The TCE-contaminated groundwater was collected from F.E. Warren Air Force Base (Cheyenne, WY, USA). A portion of groundwater was sterilized by autoclaving at 200 °C and 15 psi for 2 h. The concentration of TCE was adjusted to 300–400 μg/l or 10–11 mg/l (depending on the experiment) after sterilization to compensate for volatilization of TCE during heating.

2.3. Reactors

Reactors were established with amber glass bottles sealed with Teflon®-coated lids. The anodes and cathodes were made from graphite and connected to a 6-V battery that provided an initial current of 42 μA. Non-sterilized TCE-contaminated groundwater was added to one set of bottles and another set of bottles contained sterilized TCE-contaminated groundwater. A third set of microcosms contained sterilized TCE-contaminated groundwater but the electrical circuit was cut to serve as control. In a separate experiment, both the original and sterilized TCE-contaminated groundwater was amended with additional TCE to concentrations of 10–11 mg/l. Two separate sets of reactors containing the non-sterilized and sterilized groundwater were established and connected to the battery. Voltage and resistance were monitored throughout the study by using a GB Instruments GMT-18A multimeter. Current was calculated from the voltage and resistance values ($I = V/R$) and the power being delivered to the reactors was calculated from resistance and current ($P = I^2R$). Conductivity, pH, chloride, TCE, DCE, and VC were also monitored throughout the study. Reactors were incubated for 40–70 d, depending on different treatments.

3. Results and discussion

3.1. Baseline analysis of groundwater

Baseline groundwater conductivity, ORP, and pH were 606 μS/cm, 2.6 mV, and 7.25, respectively. The concentrations of chloride, nitrate, and sulfate were 17.5, 30.3, and 28.6 mg/l, respectively. The ammonium and iron concentrations were 84.9 mg/l and 11.4 μg/l, respectively. Concentrations of calcium, magnesium, potassium, and sodium were 2700, 46.3, 12.2, and 6000 μg/l, respectively. The concentrations of TCE and DCE in the freshly collected groundwater samples were 5.15 and 0.21 mg/l, respectively; however, DCE was not detected when stored groundwater samples were used to establish the microcosm study.

3.2. Reactor study

The current passing through each reactor decreased over the duration of the study from 42 to 12 μA as resistance increased and the average current was 29 μA. Conductivity decreased from 1209 to 864 μS/cm in reactors with live medium and electrodes and from 426 to 343 μS/cm in reactors containing sterilized media and electrodes. The decline in conductivity was probably attributed to the movement of electrolytes towards the electrodes, although this is to be confirmed in future studies. Even though resistance increased during the experiment, decreasing TCE concentrations indicate that sufficient current was available for TCE degradation throughout the study (Fig. 1). Conductivity did not change in the reactors with sterilized medium and no electrodes.

In the reactors containing electrodes and live medium, the concentration of TCE decreased by 90% (from 318 down to 33 μg/l), and TCE decreased by 88% (from 403 down to 49 μg/l) in the reactors containing electrodes and sterile medium (Fig. 1). The patterns of TCE degradation varied in different treatments, therefore no regression of rate patterns were conducted. Conversely, concentrations of TCE in reactors containing sterile medium and disconnected electrodes only

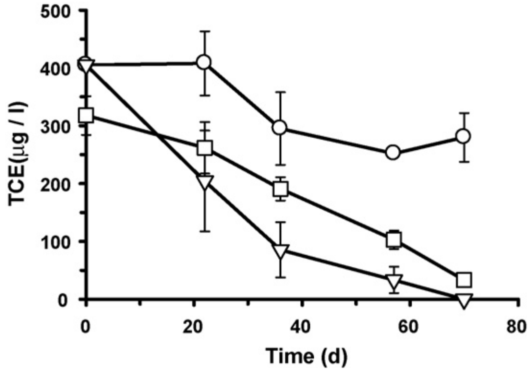

Fig. 1. Degradation of TCE in reactors spiked with 300–400 μg TCE/l containing sterile medium with disconnected electrodes (○), sterile medium with electrodes (▽), or un-sterilized (live) medium with electrodes (□). Microcosms with electrodes received 42 μA throughout the experiment. Error bars are ±S.E. of the mean ($n = 3$).

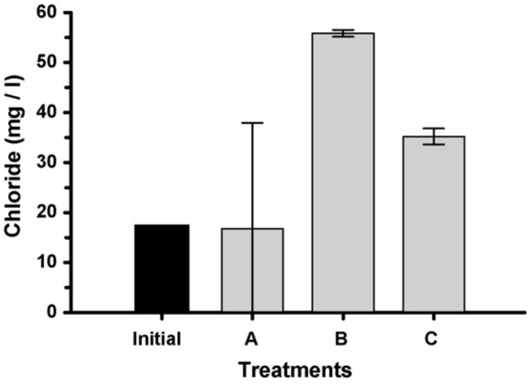

Fig. 2. Initial chloride concentration on d 0 (dark bar) and final chloride concentrations on d 70 (gray bars) in reactors spiked with 300–400 μg TCE/l containing sterile medium with disconnected electrodes (A), sterile medium with electrodes (B), or un-sterilized (live) medium with electrodes (C). Reactors with electrodes received 42 μA throughout the experiment. Error bars on gray bars are ±S.E. of the mean ($n = 3$; $n = 1$ for the initial chloride measurement).

decreased by 35%, suggesting electrical current played a key role in TCE degradation in the reactors. Stored samples (non-sterile, no electrode) were tested and biological degradation of TCE was confirmed (data not included). Chloride concentrations increased in both sets of reactors with electrodes and not in the reactors with disconnected electrodes (Fig. 2). This confirms that TCE degradation in the reactors was achieved through a reductive mechanism. Supplementing electrons to TCE-contaminated groundwater apparently can facilitate TCE reductive degradation. TCE degradation rates between reactors containing live and sterile media were comparable, indicating TCE degradation was probably dominated by abiotic reactions.

In reactors containing elevated concentrations of TCE (10–11 mg/l) and sterile or live media, TCE concentrations decreased by 98 and 97% (from 10.5 down to 0.2 mg/l and from 11.2 down to 0.3 mg/l), respectively (Fig. 3). These similar degradation rates support the previous observation from reactors containing lower concentrations of TCE that the degradation occurs through electrochemically mediated reductive dechlorination.

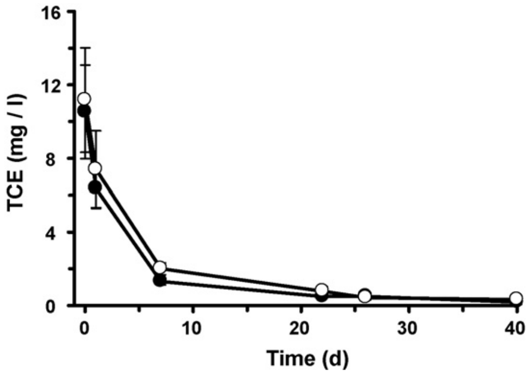

Fig. 3. Degradation of TCE in reactors spiked with 10–11 mg TCE/l containing sterile medium (●) or un-sterilized (live) medium (○). All reactors contained electrodes and received 42 μA throughout the experiment. Error bars are ±S.E. of the mean ($n = 3$).

No DCE or VC was detected during TCE degradation in the reactors. Although the mechanisms of TCE degradation under abiotic, reductive dechlorinating conditions are unknown, the non-detection of these compounds does not exclude the possibility that DCE, VC, and ethene were present for a short time and not monitored by the sampling intervals.

The pH in our experiments decreased by as much as 2.6 units in the reactors with electrodes, which suggests that a proton reservoir was created between the electrodes. Normally, Reactions (1) and (2) would occur concurrently and increase pH. This occurs as cations and anions migrate towards the cathode and anode, respectively, and inhibit redox reactions and increase resistance [27]. This migration of ions results in a decrease in cathodic potential, which accelerates Reaction (1) and creates alkaline conditions that could disrupt biological and chemical processes [30]. Ultimately, this increase in pH can potentially limit the breakdown of TCE. The observed pH decrease in our experiments may be a result of the reduction of TCE and other electron acceptors such as sulfate and nitrate, which would decrease the quantity of electrons flowing to the cathode, thus, producing less alkalinity and a higher concentration of protons in the reactors.

On average, the reactors with electrodes degraded 6.9 g TCE/kW h. Essentially, little power is required to degrade TCE at elevated concentrations or levels commonly detected in the field. In addition, no intermediate products were observed in the reactors throughout this study.

4. Conclusion

Results demonstrate that degradation of TCE by electron supplementation appears to be an abiotic process that is not associated with microbial populations or indigenous redox conditions. Furthermore, electrons supplied by a battery may reduce TCE completely without the involvement of microorganisms or observable accumulation of daughter compounds. The overall efficiency of this electroremediation was calculated to be 6.9 g TCE degraded/kW h. Though the pathway is unknown, the effectiveness and efficiency of electron supplementation in degrading TCE offers an attractive alternative to the substrate-amended biological reductive dechlorination of TCE.

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