Published in final edited form as:

Environ Sci Technol. 2010 November 1; 44(21): 8209–8215. doi:10.1021/es101003j.

Redox Control and Hydrogen Production in Sediment Caps Using Carbon Cloth Electrodes

Mei Sun¹, Fei Yan³, Ruiling Zhang³, Danny D. Reible³, Gregory V. Lowry^{1,2,*}, and Kelvin B. Gregory^{1,*}

¹ Department of Civil & Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA

² Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA

³ Environmental & Water Resources Engineering, University of Texas, Austin, TX 78712

Abstract

Sediment caps that degrade contaminants can improve their ability to contain contaminants relative to sand and sorbent-amended caps, but few methods to enhance contaminant degradation in sediment caps are available. The objective of this study was to determine if, carbon electrodes emplaced within a sediment cap at poised potential could create a redox gradient and provide electron donor for the potential degradation of contaminants. In a simulated sediment cap overlying sediment from the Anacostia River (Washington, DC), electrochemically induced redox gradients were developed within 3 days and maintained over the period of the test (~100 days). Hydrogen and oxygen were produced by water electrolysis at the electrode surfaces and may serve as electron donor and acceptor for contaminant degradation. Electrochemical and geochemical factors that may influence hydrogen production were studied. Hydrogen production displayed zero order kinetics with ~75% coulombic efficiency and rates were proportional to the applied potential between 2.5V to 5V and not greatly affected by pH. Hydrogen production was promoted by increasing ionic strength and in the presence of natural organic matter. Graphite electrode-stimulated degradation of tetrachlorobenzene in a batch reactor was dependent on applied voltage and production of hydrogen to a concentration above the threshold for biological dechlorination. These findings suggest that electrochemical reactive capping can potentially be used to create “reactive” sediments caps capable of promoting chemical or biological transformations of contaminants within the cap.

Introduction

Contaminated sediments often contain complex mixtures of toxic anthropogenic organic and inorganic contaminants, and are ubiquitous and costly to remediate (1). The high cost and limited effectiveness of dredging (2–4), and slow rates of monitored natural recovery (5), lead to the use of *in situ* sediment caps for abatement of risk from contaminated sediments. In brief, a layer of material (usually sand) is overlain on the sediment to isolate the contaminants from the aquatic ecosystem (2,6). A recent improvement to the basic sand cap, known as amended

*Corresponding authors: K.B. Gregory (kelvin@cmu.edu) 412-268-9811 (phone) 412-268-7813 (fax); G. V. Lowry (glowry@cmu.edu) 412-268-2948 (phone) 412-268-7813 (fax).

Supporting Information: The following supporting information is available free of charge via the Internet at <http://pubs.acs.org>: calculation of coulombic efficiency, method for 1,2,3,5-tetrachlorobenzene (TeCB) measurement, scheme of T-cell and H-cell reactors, comprehensive ORP and pH profile in T-cell experiment, figure describing the initial pH impact on hydrogen production rates, and a figure detailing results for the degradation of TeCB.

capping, employs adsorbents such as activated carbon or apatite in the cap material to sequester contaminants and further retard the movement of contamination from the sediments into the basal trophic levels of the ecosystem (7–9). However, capping does not necessarily provide removal or detoxification, and the risk to human and environmental health may return once the capping material becomes saturated. State-of-the-art caps have also been proposed which include a reactive component for biotic or abiotic contaminant degradation, reducing the time scales for habitat redevelopment (9) and site closure (10).

Reactive caps incorporate engineered components which act to stimulate biotic or abiotic contaminant degradation to reduce toxicity of or mineralize contaminants. For example, 2-chlorobiphenyl is adsorbed and simultaneously dechlorinated by granular activated carbon cap material containing Fe/Pd nanoparticles (11). Additionally, reactive caps may be designed to promote microbial growth and biodegradation of contaminants; Himmelheber *et al.* demonstrated depth-dependent microbial populations which varied with the stratified geochemical redox zones within a sand sediment cap (12). The chemical species in each stratified zone indicated a corresponding biogeochemical process and led to the suggestion that microbial contaminant degradation may be engineered within a reactive sediment cap (13).

Some remediation strategies were developed based on electrochemical technologies. Electrodes may be emplaced in groundwater or sediment for treating contamination with chlorinated solvents and energetic compounds (electrolytic reduction) (14–16), mixed organic/inorganic wastes (Lasagna process) (17), and heavy metals (electrosorption) (18). In these cases the electrodes are used to directly degrade contaminants, sequester heavy metals at the electrode, or collect contaminants by electrokinetic process for further treatment (19). Usually these processes require high voltage or a large number of electrodes, increasing costs (19).

In contrast to other electrode-based remediation approaches, we propose to employ geotextiles with polarized carbon electrodes in the sediment-cap to impose a desired electrical potential gradient to stimulate *biodegradation of contaminants* within the cap, i.e., an electrode biobarrier (Figure 1). In brief, the electrodes are placed perpendicular to contaminant transport through the cap, and polarized at low potentials to accelerate contaminant degradation by, 1) rapidly establishing and maintaining a redox gradient within the cap, which may be varied in real time, and 2) supplying the cap with electron acceptor and electron donor to stimulate microbial growth. As contaminants migrate from the deeper sediments, they will be exposed to the electrode biobarrier maintained by microbial growth and respiration, which is scalable in both magnitude and thickness of the respective reducing and oxidizing zones created by the electrodes. The critical advance in this research is the application of low voltage and low current to large area electrodes to enhance and control appropriate microbial activity in a thin horizontal layer within a cap. Microbial growth can be stimulated by hydrolytic reactions at the anode and cathode producing oxygen and hydrogen, respectively, and by direct microbial respiration of the anode and cathode as electron acceptor and donor, respectively. This approach has enabled the coupling of microbial oxidation of benzene to the respiration of an anode as the electron acceptor (20), or the microbial reduction and precipitation of U(VI) (21) and nitrate reduction (22) to the respiration of the cathode as the electron donor for bacteria. The residence time of contaminants within these zones will, in principle, be controllable in real time by manipulating the applied potential. In this manner, the reactive electrode-stimulated biobarrier may be specifically engineered and adjusted for targeted degradation of contaminants or their mixtures through electrode stimulation of appropriate microbial communities.

An electrode-based biobarrier for reactive sediment capping has the potential to address the unique challenges imposed by the sediment environment. First, biodegradation processes in sediment caps are commonly limited by the availability of either electron donor or electron acceptor, depending on the contaminant. The electrode cap will supply both spatially and

temporally controlled electron donor and acceptor. Secondly, complete mineralization of some contaminants (e.g. PCBs and some chlorinated solvents) only occurs through sequential reduction and oxidation, which may not develop under natural conditions. Through the electrode imposed and microbially maintained redox gradient, residence times through reductive and oxidative conditions for specific contaminant transformation may be engineered. Thirdly, the common observance of contamination in mixtures which degrade or detoxify under disparate redox conditions confounds single-approach remedial or sequestration designs. As before, an electrode stimulated biobarrier, redox gradient may be engineered to address the specific contaminants of concern on a site by site basis.

Here, we describe the deployment of carbon electrodes in a simulated sediment cap orientation for engineering redox gradients to achieve a reactive cap over freshwater sediment from the Anacostia River (Washington DC). Electrodes rapidly establish oxidizing conditions at the anode and reducing conditions at the cathode as well as a gradient between the electrodes, which was maintained for about 100 days. The impact of various geochemical porewater parameters and electrochemical conditions on hydrogen evolution rates from the cathode were examined as well as the potential for electrodes to stimulate degradation of 1,2,3,5-tetrachlorobenzene.

Materials and Methods

Chemicals

Sodium bicarbonate (NaHCO_3), sodium chloride (NaCl), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH) and chloride acid (HCl) were supplied by Fisher Scientific (Pittsburgh, PA). Magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was purchased from ICN Biomedicals Inc (Costa Mesa, CA). Humic acid sodium salt (50–60% as humic acid) was purchased from Acros Organics (Geel, Belgium). Hydrogen standard (1%) and nitrogen were purchased from Butler Gas Products (Pittsburgh, PA).

Engineered Redox Gradient in sediment

Three T-cell reactors evaluate the ability of carbon electrodes to control the redox gradient in a sand cap overlying Anacostia River sediment (Figure S1a). The reactor, as previously described (6), was filled with sieved (2mm) sediment from the Anacostia River. A 14cm $\times$ 7cm woven carbon cloth (BASF Fuel Cell, Inc., Somerset, NJ) was placed on top of the sediment as the cathode. A 2.5-cm layer of sieved (0.425mm) sand (Riccelli Enterprises, Rush NY) was placed over the cathode and a second, identical, carbon cloth on the sand layer as the anode, followed by a 0.5cm sand layer. The sediment and sand layers were saturated with tap water. The electrodes of T-cell 1 and T-cell 2 were connected by copper wire to 4V Extech 382202 DC power supply (Extech Instruments Corp., Waltham, MA). Power to T-cell 1 was continuously applied for ~100 days whereas power to T-cell 2 was removed after 30 days of continuous operation in order to examine the recovery of the sediment cap following stimulation. A third T-cell served as an unpowered control reactor. The potential was continuously applied except during microelectrode pH and Oxidation-Reduction Potential (ORP) measurement. pH was measured by MI-405 pH microelectrode (Microelectrodes Inc, Bedford, New Hampshire) and ORP was measured by Pt microelectrode against Ag/AgCl reference (fabricated as previously described (23)). pH and ORP measurement required 2 and 5 minutes, respectively, to reach equilibrium. Vertical profiles of pH and ORP from the water-sand interface to a depth of 44 mm with 2 mm intervals were acquired and ORP data were converted and reported as versus standard hydrogen electrode (SHE).

Geochemical Impacts on Electron Donor Supply Rate

Experiments to evaluate the impact of environmentally relevant geochemical porewater parameters on H₂ production were carried out in triplicate H-cell reactors (Figure S1b) described previously (22). The two chambers were separated by a cation-exchange membrane (Nafion 117; Electrosynthesis Inc., Lancaster, NY). Electrodes were 12.6cm × 6.25cm carbon cloth as described above. The electrodes were connected to an E3620A DC power supply (Agilent Technologies, Santa Clara CA) via 0.64-cm diameter × 15.2-cm graphite rods (GraphiteStore.com, Inc., Buffalo Grove, IL) by graphite epoxy (377H; Epoxy Technology, Inc., Billerica, MA). The reactors were well stirred at room temperature. Reactors contained 250ml buffer solution and 60ml headspace. Unless specified, the buffer solution contained 20mM NaHCO₃ and 20mM NaCl (supporting electrolyte, conductivity ~4mS/cm). Buffer solution was prepared anoxically and pH adjusted by HCl or NaOH. Identical control experiments using the same tap water as used in the T-cell experiments were also performed to verify comparison and are not presented.

The solution pH in the H-cell was measured using a gel-filled 8mm pH electrode (Fisher Scientific, Pittsburgh, PA). Current was recorded by a Model 2700 digital multimeter (Keithley Instruments, Inc., Cleveland, Ohio). Headspace H₂ concentration was determined using GC/TCD as previously described (24). The H₂ production rate was calculated according to Henry's Law (Supporting Information, Eqn. S1). Coulombic efficiency (CE), an estimation of the fraction of the current captured as hydrogen was calculated as the ratio of measured cumulative hydrogen production (Eqn. S1) to the theoretical hydrogen production calculated by integrating current equivalent with time (Eqn. S2).

Electrode-stimulated degradation of 1,2,3,5- tetra-chlorobenzene

Degradation of 1,2,3,5-tetrachlorobenzene (TeCB) was examined in borosilicate glass, electrochemical reactors (Figure S1(c)). The effective volume of the reactor was 600 ml and 2/3 of the reactor was filled with Anacostia river sediment with approximately 80 percent water content, and spiked with TeCB (Sigma-Aldrich, St. Louis, MO) to achieve the desired initial concentration. Carbon electrodes (6.15-mm diameter × 15.2-cm Alfa Aesar, Ward Hill, MA) were connected to an external power supply and agitated on a shaker table. Control experiments without electrodes were also examined. TeCB concentrations in aqueous phase were analyzed by solid-phase microextraction (SPME) as described elsewhere (25) and in SI.

Results and Discussion

Redox control and pH change in sediment

Poised electrodes emplaced in a sediment cap rapidly established a depth-dependent stratification of redox potential over Anacostia river sediment (Figure 2 shows data in selected days, all the data are shown in Figure S2). A 4V potential was chosen to ensure adequate hydrogen evolution as detailed later. Prior to the application of potential, the ORP at the anode was +270mV and increased with depth through the sand cap to around +350mV at the cathode. The sediment below the cathode became more reduced with depth, a likely result of natural microbial processes (13). After 3 days with applied potential between the electrodes, the ORP in the vicinity of the anode had slightly increased to near +350mV and the ORP in the vicinity of the cathode had decreased sharply to approximately -300mV. The ORP measured in both powered T-cell reactors changed similarly under applied potential, indicating reproducibility; the redox conditions stratified through the sediment cap and developed a relative steady state after approximately one month. T-cell 2 was disconnected from the power supply on day 30 to monitor the ORP during recovery. The depth-dependent stratification of ORP through the sand cap in T-cell 1 continued until day 98. In contrast, ORP stratification in T-cell 2 gradually diminished after the power off (Figure 2b): on day 98, the ORP in the vicinity of the anode

was +240mV and near the cathode, +210mV. Over the course of the experiment, the control T-cell 3 (with imbedded, but unpowered electrodes), remained oxidizing in the vicinity of and between both anode and electrodes (Figure 2c).

A depth dependent stratification of redox conditions in the control reactors was only observed within the sediment. Such gradients develop naturally under the sediment-water interface and are indicative of the microbial oxidation of sediment organic matter coupled to the reduction of terminal electron acceptors in an order which reflects the maximum energy yield for the microbial community (26). By applying a voltage through the electrodes, however, the location and size of the respective oxidation and reduction zones can be controlled.

The pH profile in the sand cap demonstrated a similar, depth-dependent gradient (Figure 2d and 2e). On day 0, the pH between the anode and cathode in all T-cells varied from around 8 at the anode to 6.5 at the cathode. Soon after external power application, the pH gradient through the cap increased sharply: pH in the vicinity of the anode dropped while near the cathode, the pH changed from circumneutral to near pH 11 on approximately day 9. The pH in the control reactor remained relatively steady with time and depth (Figure 2f). The rapid increase of pH near the cathode is the result of the reduction of water-derived protons for H₂ formation and the lack of sufficient buffer capacity in the sand cap to neutralize OH⁻ produced from reduction of water. Following removal of power from T-cell 2 on day 30, the pH began to return to circumneutral, but did not completely recover over the course of the experiment (Figure 2e). The pH change was expected in this system since no buffer was added to balance the buildup of H⁺ and OH⁻ at the electrodes. Under field conditions, such large pH increases would not be expected; since electrolyte flow between electrodes may alleviate accumulation of H⁺ and OH⁻ (27). Additionally, under field conditions, porewater may be buffered by solid and dissolved organic and inorganic phases in the cap and porewater seep may flush excessive H⁺ to the anode to neutralize excessive OH⁻. The addition of modest amounts of a buffering solids in the cap design, e.g. iron carbonate (siderite), could maintain pH if needed.

Hydrogen production rate and coulombic efficiency

The ability to control the redox profile and microbial processes in sediment will depend on the rate of electron donor and acceptor evolution. Although electrolysis of water and proton reduction rates are more efficient when catalyzed by noble metals, for sediment applications, inexpensive electrode material such as carbon is more likely to be employed. H₂ evolution from the carbon electrode displayed zero-order kinetics. At an applied potential of 4V, the electrode surface area normalized rate constant was 5mmol H₂ m⁻² hr⁻¹ (Figure S3a), despite an increase in pH from 7 to 9.5. The zero-order kinetic relationship agrees with a previous report of hydrogen production from carbon-based electrodes (28). Over 24 hours the CE was about 75% (Figure S3b), indicating that 25% of the current flow between the electrodes was not captured as H₂. This was not surprising as O₂ produced at the anode may diffuse through the CEM (29) and consume electrons at the cathode. Additionally, H₂ was detected on the anode side of the H-cell where it would be consumed at the anode. Non-Faradiac current to maintain charge neutrality at the electrodes may also be a source of current which was not captured as electron equivalents in H₂ gas.

Influence of voltage on hydrogen production

The theoretical equilibrium potential necessary for water electrolysis is 1.23V (30). Therefore hydrogen and oxygen accumulation requires a greater potential difference at the electrodes. In addition, overpotentials at the anode and cathode, resulting from activation and mass-transfer resistive losses as well as ohmic loss across the electrolytic cell, must be overcome for H₂ production to proceed. In order to address these concerns, experiments were performed to evaluate H₂ production at various cell potentials using carbon cloth electrodes. When cell

potential was in the range of 2 – 5V, the observed current was between 0.5 – 5mA. H₂ production rate was proportional to the applied cell potential above 2.5V (Figure. 3a). There was no statistically significant difference between H₂ production rate at 2.0 and 2.5V. Since external cell potential is the driving force for electrolysis of water, the increase in H₂ production rate was not surprising. Similar findings with graphite electrodes are reported (29). The relationship between applied potential and H₂ production rate may enable real-time control of electron donor for microbial growth within the sediment cap, creating an impenetrable biobarrier if the contaminant degradation rate is sufficiently high relative to advection and diffusion through the cap (10).

Lower cell potentials produced lower H₂ evolution rates and resulted in smaller pH changes over the course of the experiment (Figure 3b). The pH changes are likely to be less of an issue during field applications, as the required rates of H₂ evolution are will be lower for degradation of contaminants present in low concentrations (e.g. PCBs) and, as described briefly above, migration of sediment porewater containing natural organic matter and alkalinity creates an elevated buffer capacity (31). Nevertheless, the impact of pH on H₂ production rates was examined in the H-cell reactors (Figure S4). H₂ production rate was not significantly affected by initial pH at either 4V or 2.5V applied potential, according to single factor analysis of variance (ANOVA) (p=0.16). This result is consistent with the approximately zero-order kinetics for H₂ production (discussed later) despite the pH increase observed with extended reaction times in Figure 3b. However, the impact of pH on H₂ production as well as the change in pH observed with H₂ production should be verified in field samples under conditions which more closely simulate *in situ*.

Influence of aqueous chemical species on hydrogen production

Many chemical species which may affect rates and efficiencies of the electrolytic cell are present in sediment porewater. Among these, electrolyte concentration, presence of divalent cations, and natural organic matter (NOM) were investigated. In reference to Figure 4a, the “diluted electrolyte” group and “concentrated electrolyte” group simulated freshwater (I=0.044 N) and seawater (I=1.040 N), respectively (32) and addressed the impact of overpotential changes on H₂ production. The rate of H₂ production increased over an order of magnitude from freshwater to seawater-like conditions and is the result of increasing conductivity in the solution, therefore reducing the ohmic resistance. The overall result is higher current at a similar electrode potential, which leads to a higher hydrogen production rate. Additionally, depending on the ionic species, they may adsorb to the electrode and alter the kinetics of the H₂-producing reaction through occupation of reactive sites or formation of mineral precipitates. This finding is analogous to those of Call and Logan (33) where H₂ production in MEC increased with catholyte concentration. In practice, the electrode cap operating in high ionic strength porewater would require less energy to achieve similar delivery rates of electron donor and redox gradients through the cap. The ionic strength and species of the sediment porewater will be site-specific and greatly impact remedial design.

Cations may potentially impact remedial design through their precipitation at the electrode. 5mM of calcium and magnesium salts were evaluated for their impact on H₂ production rates (Figure 4a). H₂ production was not significantly impacted by the addition of Mg²⁺ and slightly enhanced through the addition of Ca²⁺. Precipitation of solids was observed on the bottom of the cathode chamber but not on the electrode material. These results are different from Franz et al. who observed precipitation and deposition on stainless steel plate cathodes and increased resistance across the cell. (34). This difference is likely the result of different electrode materials which may alter the double-layer composition as well as kinetics of precipitation reactions. Should cathode pH effect precipitation reactions the polarity of the electrodes can be periodically reversed to re-dissolve the precipitates (35).

Natural organic matter (NOM) is a major component of sediment porewater and exerts a contribution to conductivity, buffer strength, and reactions at the anode and cathode through electron shuttling, and therefore may be expected to affect electrode reactions. Humic acid was added to a relatively high concentration of 200mg/L (about 32mg carbon/L). The rate of H₂ production increased statistically significantly. The potential reasons for its effect are: (1) contribution to conductivity (by adding 200mg/L humic acid sodium salt, sodium concentration increased about 5mM); (2) humic acid may be adsorbed onto the electrodes and act as electron shuttles (36) or as a donor or acceptor (37). T-test results indicated that except for the “concentrated electrolyte” group, coulombic efficiency in all other groups was not significantly different from the control (Figure 4b).

Electrode-stimulated degradation of TeCB in Sediment

Degradation of TeCB in Anacostia river sediments was briefly examined to verify the potential for contaminant degradation using an electrode-based approach. Although electrochemical degradation of a variety of contaminants is well known, most studies were conducted in sediment-free systems (14,15,27). Figure S5(a) shows that degradation of TeCB was voltage-dependent. An external potential of 4 V stimulated removal of TeCB; approximately 90% over 21 days. Similar removal was not observed in the absence of electrodes or when only 3 V was applied to the system. It is worth noting that TeCB degradation did not occur until the H₂ concentration were above the threshold concentration for biological dechlorination of TeCB (0.4ppm or 16nM) (38). The H₂ concentration did not reach this threshold in the 3V reactor (Figure S5a). While not conclusive, the voltage and H₂-threshold dependence of TeCB removal suggest that degradation may be linked to electrode-stimulated microbial metabolism.

Power supply to the electrodes decreased ORP from +200mV to +70mV (vs. SHE) (Fig. S5b). In addition, the pH change was less than 1 unit and was likely stabilized by the natural capacity for buffering in sediments. Note that the pH change in this experiment is not directly comparable with the T-cell experiments; T-cells were a quiescent incubation. Therefore, neutralizing of excess H⁺ and OH⁻ was limited by diffusion and not expected. Additional studies of the electrode-based approach in sediments are needed for a better understand the pH control and the mechanisms of contaminant transformation.

Implications for Electrochemical Sediment Capping

The results presented here show that simple carbon electrodes can be used to engineer a redox gradient in a sediment cap, produce microbial electron donor, and stimulate contaminant degradation. Successful implementation of electrode-based capping of sediments will meet with a variety of technical and economic challenges which relate to scaling of electrode technology to the field; capital costs for materials and remote power (such as solar) or recurring costs for conventional electricity are just a few. A recent field demonstration of electrode-based treatment of groundwater using an “e-barrier” suggests that electrode technology is cost-comparable with conventional permeable reactive barrier technology (16). Alternatively, the electrochemical capping strategy can be applied in combination with “funnel and gate” treatment (39). In such configuration, the majority of the sediment area is covered by a low permeability cap, and the contaminants can be funneled by hydraulic control to a relatively small area, or “gate”, where electrochemical cap is installed for contaminant degradation.

Electrode-based capping with bio-barriers may enable contaminant degradation and in particular those which require or are enhanced by sequential anaerobic/aerobic treatment, such as contaminant mixtures (e.g. aromatics and chlorinated solvents). Our results show that important environmental variables such as pH, dissolved organic carbon and ionic composition do not greatly affect the rate of H₂ production or coulombic efficiency, suggesting a relatively robust technology under a variety of field conditions, but longer term studies will be necessary

and operating parameters (e.g. applied potential) will likely need to be optimized for specific site conditions. The same electrode material was used for over six months in this study without decrease in H₂ production rate or coulombic efficiency, indicating the potential for long term use. Based on this investigation, further study of electrode-based sediment capping is warranted for determination of construction and operational costs, the potential for pH control under *in situ* flow conditions, the effect of geochemical parameters on contaminant removal rates, and the evolution of microbial communities within an engineered redox gradient to confirm the practicability of this remediation strategy.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank Dr. Guy Sewell (East Central University, Ada, OK) for initial discussions on electrode-based remediation using BioLance technology. The assistance of Dr. XiaoXia Lu during proof of concept experiments is also greatly appreciated. The project described was supported by Award #: 1R01 ES016154-01 from the National Institute of Environmental Health Sciences, National Institute of Health. The content is solely the responsibility of the authors and does not necessarily represent the official views of the NIEHS or the NIH.

References

1. U.S. Environmental Protection Agency. The incidence and severity of sediment contamination in surface waters of the United States, national sediment quality survey. Washington, DC: 2004.
2. Palermo, M.; Maynard, S.; Miller, J.; Reible, D. Guidance for in situ subaqueous capping of contaminated sediments. Great Lakes National Program Office; Chicago: 1998.
3. National Research Council. A risk-management strategy for PCB-contaminated sediments. Washington, D.C: 2001.
4. Reible D, Hayes D, Lue-Hing C, Patterson J, Bhowmik N, Johnson M, Teal J. Comparison of the long-term risks of removal and in situ management of contaminated sediments in the Fox River. *Soil Sediment Contam* 2003;12(3):325–344.
5. U.S. Environmental Protection Agency. EPA's monitored natural attenuation policy. *The Army Lawyer* 1998;308(85)
6. Wang XQ, Thibodeaux LJ, Valsaraj KT, Reible DD. Efficiency of capping contaminated bed sediments in situ. I, laboratory-scale experiments on diffusion-adsorption in the capping layer. *Environ Sci Technol* 1991;25(9):1578–1584.
7. Jacobs PH, Forstner U. Concept of subaqueous capping of contaminated sediments with active barrier systems (ABS) using natural and modified zeolites. *Water Res* 1999;33(9):2083–2087.
8. Knox AS, Paller MH, Reible DD, Ma XM, Petrisor IG. Sequestering agents for active caps - Remediation of metals and organics. *Soil Sediment Contam* 2008;17(5):516–532.
9. McDonough KM, Murphy P, Olsta J, Zhu YW, Reible D, Lowry GV. Development and placement of a sorbent-amended thin layer sediment cap in the Anacostia River. *Soil Sediment Contam* 2007;16(3): 313–322.
10. Murphy P, Marquette A, Reible D, Lowry GV. Predicting the performance of activated carbon-, coke-, and soil-amended thin layer sediment caps. *J Environ Eng* 2006;132(7):787–794.
11. Choi H, Agarwal S, Al-Abed SR. Adsorption and simultaneous dechlorination of PCBs on GAC/Fe/Pd: mechanistic aspects and reactive capping barrier concept. *Environ Sci Technol* 2009;43(2):488–493. [PubMed: 19238984]
12. Himmelheber DW, Thomas SH, Loffler FE, Taillefert M, Hughes JB. Microbial colonization of an in situ sediment cap and correlation to stratified redox zones. *Environ Sci Technol* 2009;43(1):66–74. [PubMed: 19209586]
13. Himmelheber DW, Taillefert M, Pennell KD, Hughes JB. Spatial and temporal evolution of biogeochemical processes following in situ capping of contaminated sediments. *Environ Sci Technol* 2008;42(11):4113–4120. [PubMed: 18589974]

14. Gilbert DM, Sale TC. Sequential electrolytic oxidation and reduction of aqueous phase energetic compounds. *Environ Sci Technol* 2005;39(23):9270–9277. [PubMed: 16382952]
15. Gent DB, Wani AH, Davis JL, Alshawabkeh A. Electrolytic redox and electrochemical generated alkaline hydrolysis of hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX) in sand columns. *Environ Sci Technol* 2009;43(16):6301–6307. [PubMed: 19746729]
16. Sale, T.; Petersen, M.; Gilbert, D. ESTCP Final Report. 2005. Electrically induced redox barriers for treatment of groundwater.
17. Ho SV, Sheridan PW, Athmer CJ, Heitkamp MA, Brackin JM, Weber D, Brodsky PH. Integrated in situ soil remediation technology: the Lasagna process. *Environ Sci Technol* 1995;29(10):2528–2534.
18. Farmer JC, Bahowick SM, Harrar JE, Fix DV, Martinelli RE, Vu AK, Carroll KL. Electrosorption of chromium ions on carbon aerogel electrodes as a means of remediating ground water. *Energy & Fuels* 1997;11(2):337–347.
19. Acar YB, Alshawabkeh AN. Principles of electrokinetic remediation. *Environ Sci Technol* 1993;27(13):2638–2647.
20. Zhang T, Gannon SM, Nevin KP, Franks AE, Lovley DR. Stimulating the anaerobic degradation of aromatic hydrocarbons in contaminated sediments by providing an electrode as the electron acceptor. *Environ Microbiol* 2010;12(4):1011–1020. [PubMed: 20105223]
21. Gregory KB, Lovley DR. Remediation and recovery of uranium from contaminated subsurface environments with electrodes. *Environ Sci Technol* 2005;39(22):8943–8947. [PubMed: 16323798]
22. Gregory KB, Bond DR, Lovley DR. Graphite electrodes as electron donors for anaerobic respiration. *Environ Microbiol* 2004;6(6):596–604. [PubMed: 15142248]
23. Brendel PJ, Luther GWI. Development of a gold amalgam voltammetric microelectrode for the determination of dissolved Fe, Mn, O₂, and S(-II) in porewaters of marine and freshwater sediments. *Environ Sci Technol* 1995;29(3):751–761.
24. Liu Y, Majetich SA, Tilton RD, Sholl DS, Lowry GV. TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties. *Environ Sci Technol* 2005;39(5):1338–1345. [PubMed: 15787375]
25. Mayer P, Vaes WHJ, Wijnker F, Legierse K, Kraaij RH, Tolls J, Hermens JLM. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environ Sci Technol* 2000;34(24):5177–5183.
26. Reimers CE, Tender LM, Fertig S, Wang W. Harvesting energy from the marine sediment-water interface. *Environ Sci Technol* 2001;35(1):192–195. [PubMed: 11352010]
27. Shimomura T, Sanford RA. Reductive dechlorination of tetrachloroethene in a sand reactor using a potentiostat. *J Environ Qual* 2005;34(4):1435–1438. [PubMed: 15998866]
28. Sun M, Sheng GP, Zhang L, Xia CR, Mu ZX, Liu XW, Wang HL, Yu HQ, Qi R, Yu T, Yang M. An MEC-MR-coupled system for biohydrogen production from acetate. *Environ Sci Technol* 2008;42(21):8095–8100. [PubMed: 19031908]
29. Logan BE, Call D, Cheng S, Hamelers HVM, Sleutels THJA, Jeremiasse AW, Rozendal RA. Microbial electrolysis cells for high yield hydrogen gas production from organic matter. *Environ Sci Technol* 2008;42(23):8630–8640. [PubMed: 19192774]
30. Benjamin, MM. Water chemistry. McGraw Hill; 2002. p. 648
31. Khaitan S, Dzombak DA, Lowry GV. Chemistry of the acid neutralization capacity of bauxite residue. *Environ Eng Sci* 2009;26(5):873–881.
32. Holland, HD. The chemistry of the atmosphere and oceans. John Wiley & Sons Inc; New York: 1978. p. 154
33. Call D, Logan BE. Hydrogen production in a single chamber microbial electrolysis cell lacking a membrane. *Environ Sci Technol* 2008;42(9):3401–3406. [PubMed: 18522125]
34. Franz JA, Williams RJ, Flora JRV, Meadows ME, Irwin WG. Electrolytic oxygen generation for subsurface delivery: effects of precipitation at the cathode and an assessment of side reactions. *Water Res* 2002;36(9):2243–2254. [PubMed: 12108717]
35. Petersen MA, Sale TC, Reardon KF. Electrolytic trichloroethene degradation using mixed metal oxide coated titanium mesh electrodes. *Chemosphere* 2007;67(8):1573–1581. [PubMed: 17234239]

36. Kang SH, Choi W. Oxidative degradation of organic compounds using zero-valent iron in the presence of natural organic matter serving as an electron shuttle. *Environ Sci Technol* 2009;43(3):878–883. [PubMed: 19245030]
37. Motheo AJ, Pinhedo L. Electrochemical degradation of humic acid. *Sci Total Environ* 2000;256(1): 67–76. [PubMed: 10898388]
38. Löffler FE, Tiedje JM, Sanford RA. Fraction of electrons consumed in electron acceptor reduction and hydrogen thresholds as indicators of halo-respiratory physiology. *Appl Environ Microbiol* 1999;65(9):4049–4056. [PubMed: 10473415]
39. Reible, DD. Funnel and gate innovations -stabilization and treatment of contaminated sediments; RO1 2007-2010. National Institute Of Environmental Health Sciences; 2007.

Figure 1.

Conceptual model for an electrode-based reactive sediment cap. Through water electrolysis, hydrogen is produced in the cathode to stimulate reductive biodegradation, and oxygen is produced in the anode to stimulate oxidative biodegradation

Figure 2.

Vertical (a, b) ORP and (d, e) pH profiles developed in sediment and cap containing carbon cloth electrodes (T-cell 1 and T-cell 2) imposed to a 4V external voltage. Vertical (c) ORP and (f) pH profiles in control sediment (with electrode unpowered). T-cell 2 showed recovery of ORP and pH towards control after the power is disconnected, while in T-cell 1 ORP and pH

profile developed rapidly after ~25 days and stabilized over ~100 days. Depth zero was the water-sand interface. The horizontal dashed lines indicate the position of electrodes.

Figure 3.

Influence of applied potential on (a) hydrogen production rate and (b) cathode solution pH. All experiments were conducted at an initial pH=7 in 20mM NaHCO₃ and 20mM NaCl solution over 24 hours. Dashed vertical line in (a) shows the equilibrium potential for water electrolysis. When voltage is over 2.5V, increase of voltage causes linear increase of hydrogen production rate and hence greater pH change.

Figure 4.

Influence of aqueous chemical species on (a) hydrogen production rate and (b) Coulombic efficiency. All experiments were conducted at voltage 4V over 24 hours with initial solution pH 7. The chemical composition for each group was: Control: 20mM NaHCO₃ and 20mM NaCl; Diluted electrolyte: 20mM NaHCO₃ and 2mM NaCl; Concentrated electrolyte: 20mM NaHCO₃ and 500mM NaCl; Mg²⁺: 20mM NaHCO₃, 20mM NaCl and 5 mM MgCl₂; Ca²⁺: 20mM NaHCO₃, 20mM NaCl and 5mM CaCl₂; Natural organic matter: 20mM NaHCO₃, 20mM NaCl and 200mg/l humic acid sodium salt. The dashed line showed the average results of control group.