



Case study: Electrochemical Geo-Oxidation (ECGO) treatment of Massachusetts New Bedford Harbor sediment PCBs

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ABSTRACT

An electrochemical remediation technology, referred to as Electrochemical Geo-Oxidation (ECGO) was tested in field to assess its potential to treat polychlorinated biphenyls (PCBs) contaminated sediments from New Bedford Harbor (NBH), Massachusetts. The primary objective was to evaluate the effectiveness of ECGO for reducing PCB levels under the anaerobic conditions typical of saturated and submerged sediments. The ECGO treatment of aerated and un-aerated (anaerobic) samples of the NBH sediments began on November, 2003 and lasted over four-years until early July, 2008. During 2003–2006 seven sampling events occurred, and the last sampling was done on March, 2010, about 20 months after the treatment power was turned off on July 12, 2008. Full PCB congener analyses (EPA 22 1668A) and partial PCB scans (EPA Method 8082) were performed on samples collected from the ECGO test cells and the control cell. At the end of the first 30-month period, the sample analyses indicated about 30% reduction in total PCB levels in un-aerated ECGO test cell compared to the control. The eighth and final sampling in March 2010 showed that total PCBs had been greatly reduced in the un-aerated test cell, from about 40,000 $\mu\text{g/kg}$ (ppb) to 200 $\mu\text{g/kg}$ (ppb). Conversely, PCB levels in sediments contained in the aerated ECGO test cell remained relatively unchanged compared to the pre-test level and control. This represented a greater than 90% reduction in total PCBs relative to the 2003 starting levels and the control sample average. The final results indicated that ECGO was effective at degrading PCBs in a reducing environment.

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1. Introduction

In most field situations, the contaminants, particularly the organics and immiscible liquids, are found adsorbed onto soil particle surfaces, iron-oxide coatings, soil colloids and natural organic matter. Most of these contaminants are retained in clay interstices as complex molecular compounds, or in the form of immobile precipitates and products in soil pore throats and pore-pockets that “lace” the vadose and the saturated zones. This exacerbates clean-up efforts as the available technologies, such as in-situ bioremediation, chemical treatment or the traditional pump-and-treat method may not be able to treat the entire site effectively in low permeability soils. Electrochemical treatments, when designed to

properly address the site-specific features, can potentially reduce the subsurface pollution by transporting and/or transforming contaminants, or enhance resource recovery by extracting trapped materials (i.e., heavy metals, oils and petroleum) which may not be extractable by other means. Such applications of electrochemically and electrokinetically (EK) assisted in-situ remediation has been shown viable and versatile for most soils and most contaminant types, particularly for low permeability clayey deposits containing soluble compounds [1–15].

Although the field-scale applications of the electrokinetic and electrochemical remediation have been conducted at variety of scales over the years [16–27], the technology has not yet advanced to a commonly-accepted commercial status, still facing unique engineering challenges. These challenges stem mainly from short- and long-term side effects, such as temporally and spatially changing process parameters including pH, voltage gradient, pore water pressure, migrating front of high ion concentration; electrolysis gases generated at the electrodes; or other redox reactions

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[8,21,28–34].

Although some of these effects can have distinct consequences on EK assisted mass transport, they have also been shown to aid in degradation and/or extraction of some of the persistent substances [35,36]. For example, electrokinetically assisted mass displacement have been demonstrated as a stand-alone technique for oil transport and recovery from geological media including soils, sediments and rock formations [37–46]. Other innovative use of electrokinetics and electrochemistry for in-situ clean-up of soils and sediments involves electrodialysis which manages the electrode reaction products [3,4,47–54].

Transport and extraction of both the inorganic and organic substances from soil pores frequently involve the addition of one or more chemical reagents to the system [48,55–59]. Similarly, electrochemical transformations do take place in contaminated systems either through intervention of redox active compounds or by microbial activity [60–64]. There are chemical destruction (oxidation) methods using ozone or Fenton's reagents (hydrogen peroxide and catalysts) to transform contaminants to their benign components in soils and sediments [65–67]. In these applications most of the transformations take place in the bulk fluid, and the clay-electrolyte interfaces do not contribute to the process directly except for ion exchange and sorption reactions. Electrically assisted in-situ transformation of the contaminants to their benign forms through beneficial electrochemical reactions in the pore fluid has been explored in the past. It has been shown that fast electrochemical oxidation of chlorinated solvents, such as TCE, can be achieved near the electrodes subsequently reducing the contaminant concentration in soils during electrokinetic treatment [68–70]. Good results have been shown for naphthalene transformation under high current (10 mA) in which 75% of the initial concentration (25 m/L) was transformed after only 4.5 h of processing [71]. Similar results were obtained with benzene [72], where nearly 100% of the initial mass was transformed at 5–10 mA application after 100 h.

Laboratory evidence also shows that low direct electric current can contribute to the success of desired transformation reactions by lowering the energy for the redox reactions to occur. This enhancement of transformation reactions is attributed to the double-layer polarization of the clay surfaces leading to Faradaic processes under the applied electric field [1,73,74]. Experimental evidence was provided in effectiveness of low direct current on separation and demulsification processes in oily sediments or sludges [46,75–78]. In these electrically assisted transformations, optimization factors include varying electric field direction and intensity [34], applying a sinusoidal electric field with pulses and a polarity reversal [74,76,78] and increasing the magnitude of the potential gradient [79].

As discussed by Rahner et al. [80], and Röhrs et al. [81], electrochemical reactions can be induced on or near soil particles if the particles possess films with electronic conducting properties, or act as 'micro-conductors'. The wet soil can act as a 'diluted' electrochemical solid bed reactor. The ECGO technology takes advantage of this phenomenon, as it assists electrochemical transformations near the diffuse-double layer (DDL) films of the clay particles or other conducting particles in contaminated wet soil matrices. The process has shown promise as a cost-effective and rapid remediation option, and has been used in Europe to treat over 50 sites contaminated with industrial organic contaminants including PAHs, chlorinated hydrocarbons and other organic materials [23]. However, the use of the technology for the in-situ treatment of saturated sediments, which are typically found in anoxic environments, has had limited application. ECGO uses low voltage and both direct and alternating amperage (DC/AC) applied in a proprietary

sequence to induce reduction–oxidation reactions on soil solid surfaces at the micro-scale. In essence, the method advocates that each sediment particle acts as a micro-capacitor that charges and discharges in a cyclic fashion. Even though low voltage and amperage are used, the energy burst on discharge at the micro-scale is intense, theoretically resulting in transformation of most organic contaminants to carbon dioxide and water near the conducting particle surface.

This paper provides first a theoretical overview of electrically induced redox reactions at the micro-scale which constitutes the premise of ECGO, and then presents the results of a more than four-year duration ECGO treatment case of PCB contaminated sediments.

2. Background

2.1. DDL processes in clay-electrolyte systems under externally applied potential

Flow of electric current through a network of clay-electrolyte system occurs in different phases simultaneously: in the bulk liquid (the electrolyte in the pores), on the surface of the solid (clay particles), and in the interface layer(s) between the solid and the liquid. Flow of current can be achieved by ionic conduction through the liquid phase and electronic conduction through the solid and the interface layer(s). The electronic conduction along the interface layer(s) takes place by charge transfer. In the classical treatise of electrokinetic phenomenon of colloidal systems [82,83], it is this interface, known as the diffused double layer (DDL) which plays a critical role in the coupling between the ion motion and the fluid flow. The DDL intrinsically connects the solid and the liquid phase, and mediates the relative motion of charges between the liquid and solid phases [84].

In electrochemical systems the analysis of mass transport by diffusion and migration under chemical and electrical potential gradients in dilute solutions are described by the Nernst-Planck and the Poisson's (PNP) equations [85,86]. Since the ions themselves contribute to the local electric potential, Poisson's equation that relates the electrostatic potential to local ion concentrations describe this effect, as given in Equation [1].

$$-\epsilon_s \nabla^2 \Phi = \rho = \sum_i z_i F c_i \quad [1]$$

where, c_i , z_i are the concentration, and the charge number of a single species i , respectively, and F is the Faraday's constant (a mole of charge); Φ is the electrostatic potential; ϵ_s the permittivity of the solvent, and ρ the volume charge density.

For many electrochemical systems the local electroneutrality condition is used, which sets the left-hand side of the Poisson's equation [Eq. (1)] to zero for zero charge density [$\rho = 0$]. The mathematical implication is then that the electrical potential satisfies the Laplace equation [$\nabla^2 \Phi = 0$] hence uniform concentration distribution and uniform conductivity within an electrochemical cell. However, the electroneutrality assumption does not hold true at the DDL interface because of charge accumulation and concentration gradients that occur in this region. Chu [87] showed that the electroneutrality condition can be satisfied when the DDL thickness is small compared to the electrical field length (i.e., approximated as pore diameter), and the charge density in the DDL is small compared to total ion concentration in bulk solution. Electroneutrality can be achieved only by Faradaic reactions as the charge

density in DDL approaches to total ion concentration in bulk solution [87–89].

The interactions of an electrode surface with its surrounding bulk solution can explain the necessity of Faradaic reactions for electroneutrality. Fig. 1 shows a charged electrode surface with fully developed electric double layer (DDL), where the oxidants with positive charge diffuse toward the negatively charged electrode, subsequently accept electrons from the electrode at the OHP interface and become the reductants and diffuse towards the bulk solution. IHP and OHP are the Inner and the Outer Helmholtz planes, respectively. An equivalent circuit representing each physical component at the interface and in the bulk solution is also shown. Here, C_{ddl} is the double layer capacitor and R_p is the polarization resistor representing the electrochemical processes in the region between IHP-OHP; the diffusion-controlled impedance, Z_W or Warburg resistor represents the processes in the diffused layer, and R_b is the bulk solution resistance. Similarly, Fig. 2 depicts a schematic of a clay particle with negative surface charge with a fully developed DDL, where the capacitor and the diffuse layer structure mimics that of an electrode-electrolyte interface as shown in Fig. 1. Under equilibrium, the electroneutrality of the particle is satisfied by the specifically adsorbed ions and those that move in and out of the diffused layer from the surrounding bulk solution. When a clay-electrolyte system is subjected to an external electric potential, the capacitor and resistor structure of its DDL can be activated similar to that of an electrode surface. As a result, electron transport occurs across the OHP of the clay particle producing a “zone of redox reaction” in its vicinity, as shown in Fig. 2.

The electrified clay particle can be considered behaving like a micro-electrode whose redox contribution may be controlled by the applied electric field as depicted for a clay surface in Fig. 3. In such a system, as the donated (or accepted) electrons pass across the DDL into and out of the bulk fluid, available species are converted into others via oxidation-reduction reactions. Three interface planes occur within the DDL: the IHP and the OHP with constant set locations of x_1 and x_2 , respectively; and third is the plane of shear where the electrokinetic (zeta) potential is measured and often assumed to coincide with OHP plane. The IHP is the outer limit of the specifically adsorbed water, molecules with dipoles and

other species. The OHP is the plane that defines the outer limit of the compact Stern layer, the layer of positively charged ions that are condensed on the clay particle surface. In this model, known as the Gouy–Chapman–Stern–Grahme (GCSG) model, the diffuse part of the double layer starts at the location of the OHP plane [82].

When an external electric field is applied to a clay-electrolyte system of high ionic concentration in the bulk solution (high C_{eq}), given the incompatibility between the conductivity of the two conducting layers in the mixture, that is: 1) the DDL with low conductivity (σ_s), and 2) the surrounding electrolyte solution (bulk solution or pore fluid) with high conductivity (σ_b), a large electric potential difference is induced across the DDL. This results in compression of the DDL, rendering it a “capacitor”. It is assumed in here that the compression of DDL occurs in the diffused section, resulting in a higher charge density than before, whereas the charge density of the compact Stern layer (IHP \Rightarrow OHP) remains same. Owing to the compression of the diffused layer, the potential distribution shifts, lowering the electrokinetic potential at the shear plane, or OHP. This shift also results in increased electric field intensity between IHP and OHP, as depicted by the steeper slope of the potential drop in Fig. 3. It is well known that the capacitance of a dielectric, such as a DDL, decreases with increasing electrical field intensity [84,90]. This comes about by physical compaction of the mass in the diffuse layer, by strong orientation of the dipoles, and the polarization of charges in the compact layer [91,92]. Chu [87] models this behavior where Faradaic reactions maintain electroneutrality as the charge density of the interface increase.

The increased electric field intensity followed by the decrease in the capacitance of the compact layer between IHP-OHP (Stern layer) causes electrons transfer across OHP towards the solution, giving rise to a “cathodic” current, hence a cathodic reaction in the diffuse layer and its vicinity. Under large electrical field intensity, to maintain the current flow, the electrodes adapt a new potential, differing from equilibrium by the “over-potential”, η [84]. Hence, as the DDL compress or expand, charges migrate across OHP and redox reactions take place whereby the over-potential is overcome and the Nernstian equilibrium is restored.

Describing the DDL act as a micro-capacitor, as shown in Fig. 3, the Nernstian equilibrium potential, $\Phi_{d(eq)}$ is the equilibrium potential at OHP plane in the absence of an applied electric field; Φ_o is the electrostatic potential on clay surface or the IHP plane, and η is the over-potential that drives the current for redox reactions. Then according to GCSG model [82]:

$$1/C_{ddl} = 1/C_i + 1/C_d \quad [2]$$

where, C_i and C_d are the capacitance of the compact (IHP \Rightarrow OHP), and the diffuse layers, respectively. Except when Φ_d and/or the ionic concentration are very small, C_d is normally so very large that the integral capacitance, C_{ddl} is essentially equivalent to C_i . The potential difference, $\Delta\Phi$ across the entire diffuse double layer can then be written as:

$$\Delta\Phi = q_i/C_{ddl} + \Phi_{d(eq)} \quad [3]$$

$$q_m + q_i + q_d = 0 \quad [4]$$

where, q_i is the charge under IHP \Rightarrow OHP, and q_d is the charge under the diffuse layer, and q_m is the surface charge of the clay. The q_i is the majority of the charge that counters the surface charge of the clay particle, q_m . Under the assumptions of constant surface charge and electrical neutrality, $(q_i + q_d)$ remain constant, hence the total potential difference $\Delta\Phi$ across the DDL is constant. Any change in the shear plane (OHP) potential brings about a change in the

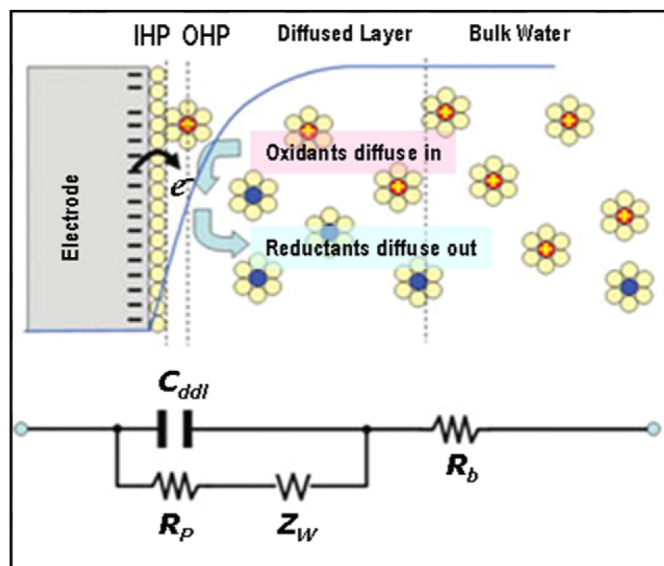


Fig. 1. Schematic of a DDL interface of an electrode surface with equivalent circuit representation in the usual Grahame notation; C_{ddl} ; R_p ; Z_W ; R_b (Park and Yoo, 2003).

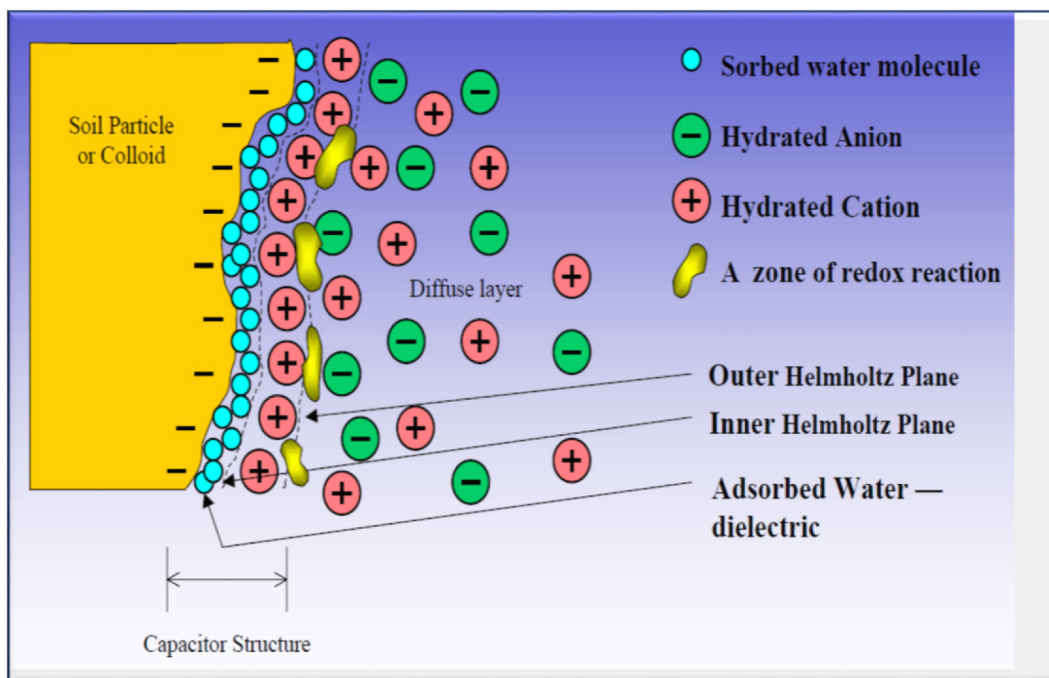


Fig. 2. Conceptualized schematic of a clay particle with DDL structure that mimics the electric interface of an electrode with a “zone of redox reaction”.

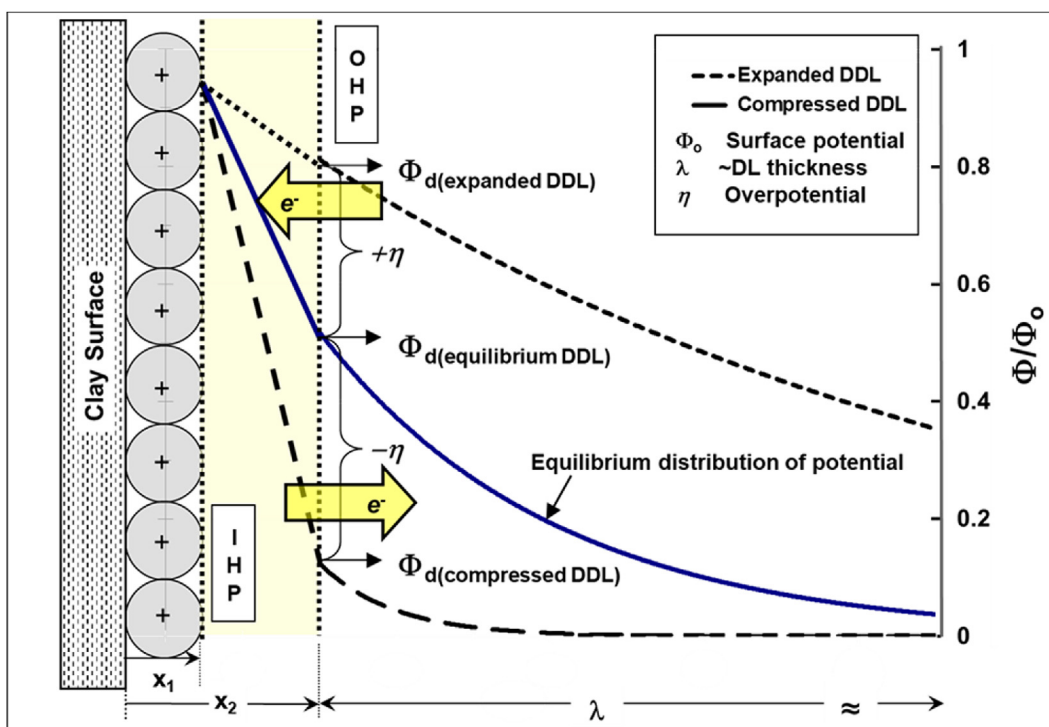


Fig. 3. The concept of Faradic current development in GCSG model of clay DDL (Pamukcu et al., 2008).

capacitance term, C_{ddl} , or vice versa. The change in capacitance can be expressed by the measure of degree of polarization, or the overpotential, η as follows:

$$\Delta\Phi = q_i/C_{ddl} + (\Phi_d \pm \eta) \quad [5]$$

where, Φ_d is the new adjusted OHP potential, determined by the degree of polarization under the dielectric. Hence, as the

overpotential (i.e. overvoltage) drives the charges across OHP, the equilibrium potential $\Phi_{d(eq)}$ is restored, as shown in Fig. 3 and described in Equation [5].

2.2. ECGO: induced polarization driven technology

Overpotential in soils is established whenever current is caused to flow across a DDL interface by ionic conduction [93]. Overpotentials are due to an accumulation of ions on the electrolyte side of the interface waiting to be discharged, as explained in the section above. These voltage gradients will have the same external appearance as polarization effects due to separation of charges, hence “induced polarization” or IP. Wet soil layers in the subsurface can become electrically polarized, forming a battery when energized with an electric current. Upon turning off the polarizing current, the soil gradually discharges and returns to equilibrium. The decaying potential difference as a function of time is one way of measuring IP in the time domain. Another technique involves measuring the changing resistivity under applied alternating currents of varying frequency, which is called IP in the frequency domain.

The propriety technology for the electrochemical remediation of organic and metal-organic pollutants in soils referred to as the Electro Chemical Geo-Oxidation (ECGO) is developed based on in-part the use of Induced Polarization (IP) in subsurface [94,95]. ECGO depends on the electric conduction in wet contaminated soil, which comes in two parts: 1. the electric conduction in the electrolyte in the soil pores and, 2. the electronic conduction in the DDL comprising of the IHL and OHL lining the capillaries. Current passage in the soil pores happen via ionic conduction. There are two pathways by which current may pass through the DDL interface between the solid particle and the electrolyte: Faradaic and non-Faradaic pathways. Current passage in the Faradaic path is the result of electrochemical reactions (i.e., redox reactions) and comprises also of the diffusion of charge towards or away from the DDL interface (“Warburg Impedance”). In the non-Faradaic case, charged particles do not cross the interface. Instead the current is carried by charging and discharging of the double layer, as the electrons move between adjacent DDLs, behaving as a capacitor. Empirical evidence indicates that both types exist simultaneously [96].

Under undisturbed field conditions, soils in general have a capacitance in the range of 5–15 μF (μF). In ECGO treatment, the soil capacitance can increase significantly. For example, in an ECGO test project in the New York State the capacitance of a soil cell of 1 cubic meter increased from 13 μF to 1020 μF at a voltage of 100 V DC and 5 A within 90 days [23]. The groundwater, which carries a portion of the electrical current, often possess relatively high electrical resistance ($>20 \Omega$; Ω). The DDL is comprised of high concentrations of ions, which permit a resistance between 0 and 10 Ω at low voltages (regularly $< 75\text{V DC}$). The current is mostly carried at the DDL interface at low applied voltages. When increasing the voltage by a rheostat, the transition from the DDL conductivity to the ionic conductivity in the pore fluid can be detected by an oscilloscope, as the discharge signals caused by the capacitance variations at DDL disappear beyond a critical magnitude of voltage.

The main electrical requirement for ECGO process is direct electric current application via in-situ electrodes creating an electric field in the soil. The electrodes are often placed at separation distances of 5–30 m in the field, but may be as large as 300 m. This means that the electric field strength may range from 0.0025 to 0.25 V/cm for up to 100 V applied across electrodes. At lower strengths of the electrical field, the soil DDL lining the pore space

become polarized and electrons begin to migrate from the working anode to the cathode primarily within the diffuse layer of each individual soil particle. The continuity of this process necessitates that the DDLs are connected and continuous. The electrons, migrate across the boundaries of the diffuse layers between adjacent particles, and if the rate and quantity of electron donation and acceptance are constant throughout a continuous thread of double layers, then no other effect but an electroosmotic flux and some ionic conduction should be observed. At high applied electric fields, i.e., beyond a critical potential, contraction of the diffuse layer lowers the electrokinetic (zeta) potential at OHP to such values that electronic conduction no longer can compete with ionic conduction, hence the ionic transport takes over the process. In most field situations the idealization of continuous and connected DDLs lining the pore walls do not hold. Therefore, at low electric fields (i.e., 0.0025–0.25 V/cm) as electrons are induced to leave and enter the adjacent diffuse layers, physical discontinuities do not allow their easy “hopping” from one DDL to another, resulting in permanent chemical transformations in the form of red-ox reactions in the DDL. This means that each soil particle serves as a “micro-electrode” accepting electrons for reduction of the species within, or donating electrons for oxidation of species in the adjacent layer or near interface. This micro-electrode role of the DDL is explained in detail in the section above. Furthermore, ECGO generates itself in-situ the agents for reduction (i.e., H as ion or its radical) and oxidation (O elemental, OH ion and its radicals, HO_2 and its radicals) at the electrode sites as well as within the pores.

The second important electrical requirement for ECGO is the alternating current. Under the conditions of polarization, DDL acts as capacitor which charges and discharges electricity at the frequency of the alternating current. Looking more closely into this electric behavior, we find that the soil particle may fulfill the requirements of an “RCL” element which describes a simple electronic amplifier, as shown in Fig. 4. In this model R stands for resistance (soil resistance, Warburg Impedance), C for capacitance, and L for induction, similar to the conceptual model shown in Fig. 4. The RCL element works as an electronic amplifier, amplifying the electric discharges of the double layer by a factor up to 10,000. This phenomenon of amplification, is responsible for ECGO working at low voltages and amperages supplying the required energies (including activation energy) to the redox reactions [23].

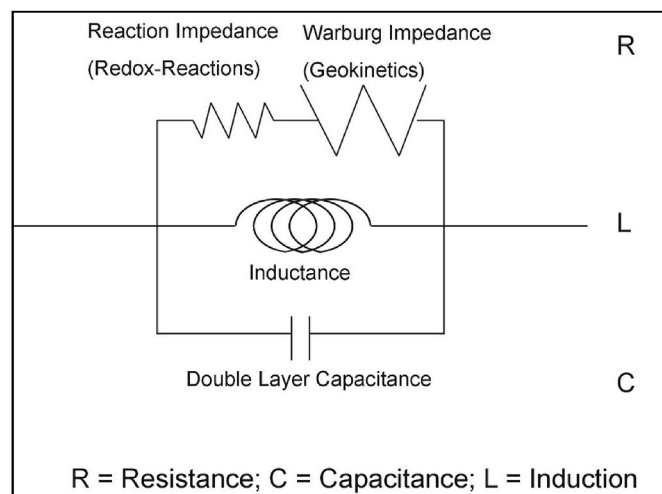


Fig. 4. ECGO equivalent electrical circuit model (Wittle et al., 2009.).

3. ECGO: PCB treatment case

3.1. Coleraine test facility

In late 2002, a long-term field test case was commenced at Coleraine sediments test facility at University of Minnesota, Duluth, Natural Resources Research Institute (NRRI) and its Coleraine Minerals Research Laboratory (CMRL), in Coleraine, MN. The establishment of the CMRL facility was based, in part, on findings from a 2002–2003 field study overseen by the U.S. Army Corps of Engineers. In that study [23], sediments from a Duluth, MN, harbor location, contaminated with polycyclic aromatic hydrocarbons (PAH), was treated with ECGO in a simulated in-situ setting. In addition to PAHs, traces of PCBs were found, and preliminary data indicated PCB concentrations were also reduced using the ECGO treatment process. The new field project objective was to evaluate the effectiveness of ECGO for reducing PCB levels in saturated and submerged sediments. Originally conceived as a two-year (24-month) study (November of 2003 through October of 2005), the project was extended by six months, with additional treatment, sampling, and analyses continuing into 2006. Following the 2006 sampling, the system was kept running through July 2008. A final sampling event occurred on March 8, 2010, with analyses performed on un-aerated and aerated ECGO treatment cell sediments prior to their disposal.

The Coleraine facility was designed to conduct ECGO treatment studies on multiple one cubic yard samples of contaminated sediments from a variety of sources over long periods of time in a controlled and monitored environment. The cubic yard polyethylene treatment (test) cells were contained within a larger (24' x 32') lined test area filled with saturated sand. The treatment cells that contained the sediments were fitted with steel electrode plates (anodes and cathodes) placed vertically on opposite sides of each cell along their full depths and widths. The lined test area was also fitted with steel plate anodes and cathodes. This configuration of the electrode plates allowed for each test cell be subjected to ECGO individually or collectively.

The active system was designed to model actual field conditions for voltage and current input. The treatment (test) cells were also instrumented with voltage, pH, E_h (oxidation-reduction potential (ORP)), and temperature sensors connected to a PC-based data acquisition system. The system allowed for remote access and web-based monitoring in real time. Fig. 5 presents the web-page representation of the test area and the associated data readings from each active cell. The inset photo in Fig. 5 shows the individual treatment cells. Figs. 6 and 7 show the photographs of the cubic yard treatment cells emplaced within the larger test area in saturated sand. In these pictures, note that the rust-colored sand which reflects iron staining due to the dissolved iron in the water used for maintaining a wet conductive state in the sand bed, and also by slow oxidation of the steel anodes over time.

3.2. Sediment acquisition and placement

PCB-contaminated sediment from New Bedford Harbor (NBH), Massachusetts, was selected as the candidate sediment for the ECGO treatability study because of its high levels of PCB content. The PCB-containing materials are regulated according to the concentration of PCBs present.¹ For a material to be considered non-PCB containing, it must contain less than 5 ppm (mg/kg) [or 5000 ppb ($\mu\text{g/kg}$) PCBs]. The New Bedford Harbor (NBH) sediments were considered PCB-contaminated as its' PCB content fell between

the 5–500 ppm (mg/kg) [or 5000 to 500,000 ppb ($\mu\text{g/kg}$) PCBs] range. The NBH sediments were dark gray to black in color and exhibited a sheen during sample homogenization. In general, the contaminated NBH sediment was darker, looser, and more organic than the underlying sediment, which comprised primarily of silt and clay-sized materials, within which mollusk shells and fragments and minor amounts of sand and gravel were interspersed. The physico-chemical characteristics of the contaminated NBH sediments have been documented in previous studies [97–99].

Following EPA approval several 55-gallon drums of NBH sediment was delivered to CMRL in the fall of 2003. Two one-cubic yard polyethylene containers were placed within the lined and confined treatment area. The first treatment (Un-aerated Test) cell was partially filled with NBH sediment and water at about a 2:1 ratio in November of 2003. Because the harbor sediment environments are typically reducing (anaerobic), a second cell (Aerated Test) was filled and air was introduced to change its environment from anaerobic to aerobic and increase the sediment oxidation-reduction potential (ORP). The aeration was started approximately one year after the power-up in 2003, in October 2004 and continued until power-off in July of 2008. This aeration step was taken to assess how changing sediment redox conditions potentially impacted the ECGO treatment process in comparison to the reducing conditions of the un-aerated test cell. One 55-gallon drum was retained as untreated sediment source for control samples (Control Test).

3.3. System start-up and parameters

Following collection of the initial set of Test and Control samples on November 21, 2003, the ECGO system was energized and ran nearly continuously through the final sampling of May 30, 2006, as did the data acquisition system described previously. In the event that future test cell sampling was of interest, power was supplied to the ECGO treatment which continued through the end of 2008. Throughout the treatment period between 2003 and 2008, the daily average voltage and current measured in the un-aerated cell was about 2V DC and 0.5A, respectively. The voltage and amperage in the aerated cell were slightly higher at 2.6V DC and 0.6A, respectively. The ORP for the un-aerated cell remained mostly negative with an average of about -400 mV, while it was a positive average for the aerated cell at $+190$ mV during the aeration period. The pH values were fairly consistent for the un-aerated cell at about 10, while it decreased over time for the aerated cell with a time average value of 8.7. Detailed depictions of the ORP and pH evolution for the two test cells are provided later in section 3.6.

3.4. Sampling and sample preparation

Sampling was performed from a catwalk/bridge set above the treatment area (see Figs. 6 and 7). Clean sections of 6 feet long and 2-inch diameter PVC pipes were used to collect "cores" from the test cells and the control sediment drum. Each cubic yard cell contained about two feet of sediment covered by about 1 foot of water. To retrieve a core sample, the pipe was hand-driven into the sediment, its upper end sealed to create a vacuum, and then withdrawn. Before the sediment was released from the pipe, the pipe was tipped to allow excess water to decant back into the cell. The sample pipe was then positioned vertically above a large stainless-steel mixing bowl and gently shaken until the core slid from the pipe into the bowl. This process was repeated until four to five cores were retrieved from each of the treatment cells at a time. A minimum of three cores from the smaller (55-gallon) sediment control drum was similarly retrieved and prepared.

Samples were mixed and homogenized in the stainless-steel

¹ <http://www.ehso.com/PCBregs.htm>.

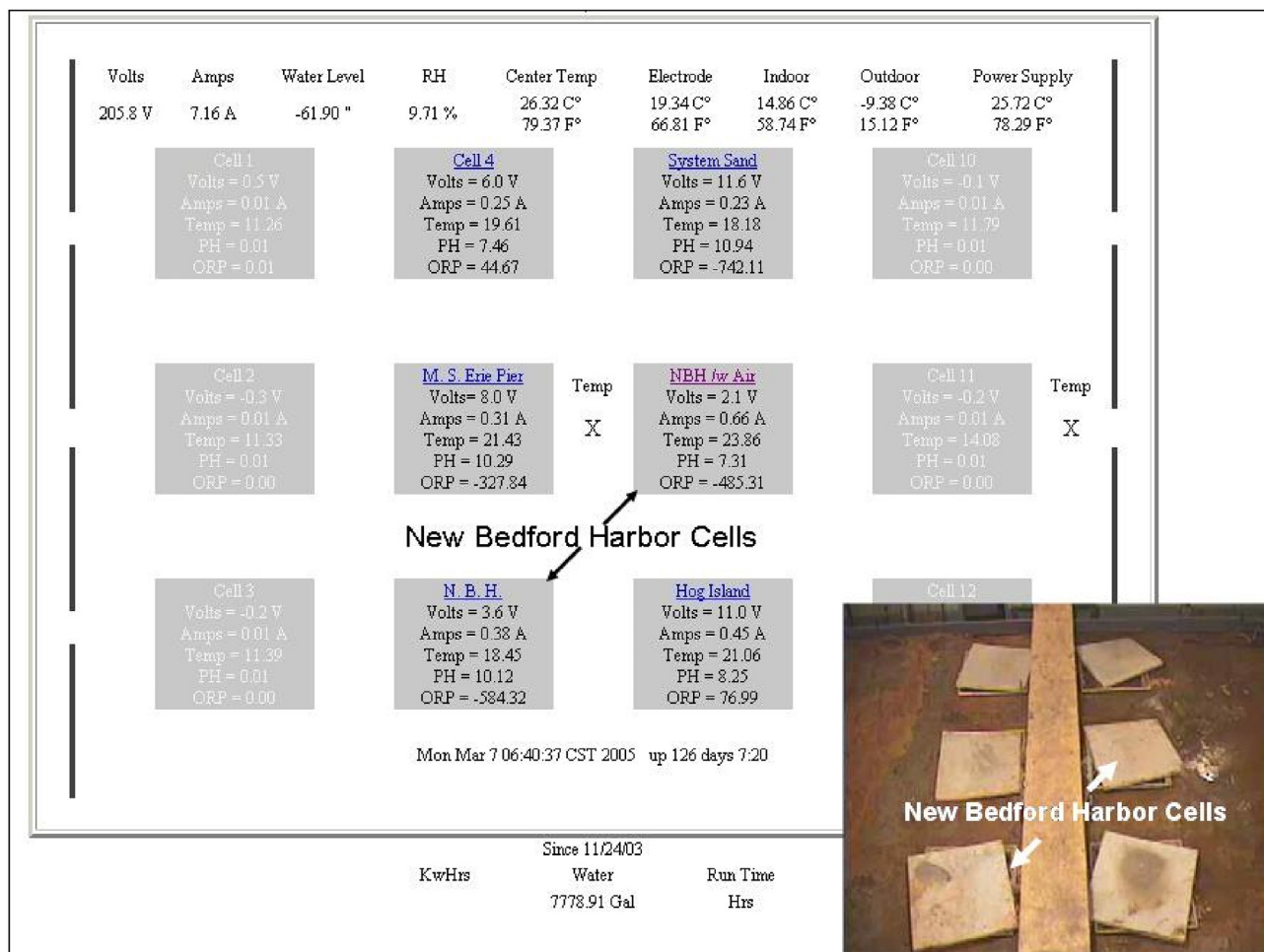


Fig. 5. Schematic of Coleraine Sediments Treatment Facility, and inset photo showing New Bedford Harbor cells.



Fig. 6. Photograph of sediment treatment area cells and catwalk (3' x 3' cell lids for scale).

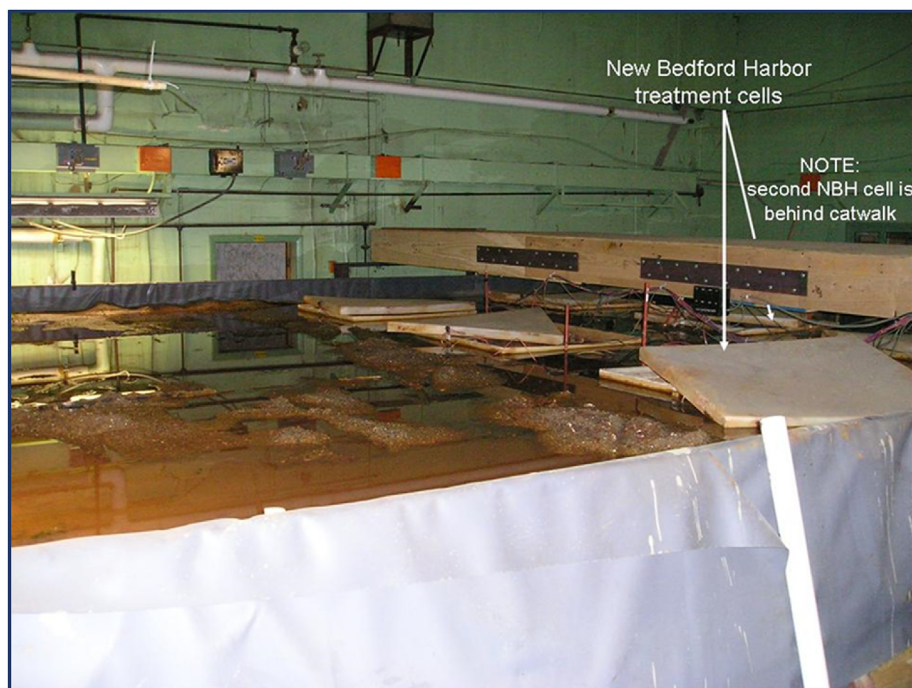


Fig. 7. Photograph showing view of sediment treatment area and cells.

bowl using a stainless-steel spoon. The non-sediment debris or objects such as rocks or clam shells were removed and returned to the treatment cell or control drum. Following a thorough mixing and homogenization, the sediment samples had the appearance and consistency similar to that of thick black mud. Samples were partitioned into quarters in the bowl, and two sterile amber glass sample jars were filled with alternating scoops of sediment taken from opposite quarters in the mixing bowl. One sample was sent out to an accredited external laboratory for analysis, and the other was retained as a back-up. Leftover sample material was returned to the cell and drum. Samples intended for analysis were placed on ice in a cooler, and retained samples were stored in a laboratory refrigerator. The chilled samples were packed with ice, wrapped in insulating packing material, and shipped same day for next-day arrival for analysis, along with a letter and chain-of-custody form.

3.5. Analytical methods

During the 2003–2006 study period, Severn Trent Laboratories (STL), a professional analytic and diagnostic services laboratory for water, land, and waste monitoring, performed the full (209 PCB congener analysis; EPA 22 1668A) and the partial (53 PCB congener analysis; EPA Method 8082) scans, as well as supplemental PAH, metals, percent solids, and total organic carbon analyses. STL also performed most of the detailed PCB analyses. It should be noted that STL is currently known as Test America Laboratories, Inc.². Additionally, partial PCB analyses (24 congeners) on one un-aerated test and one control sample collected in July of 2004 was conducted at the Chemistry Department Laboratory of Western Michigan University (WMU), Kalamazoo. All PCB concentrations were reported and presented as mg/kg (ppm) and $\mu\text{g/kg}$ (ppb).

Since the aerated test cell was not placed into service with aeration until October, 2004, it was sampled three times as opposed to the seven samplings of the un-aerated test cell. The aerated test samples were subjected to partial PCB scan (EPA Method 8082) as opposed to the full 209 congener scans performed on the un-

aerated test samples.

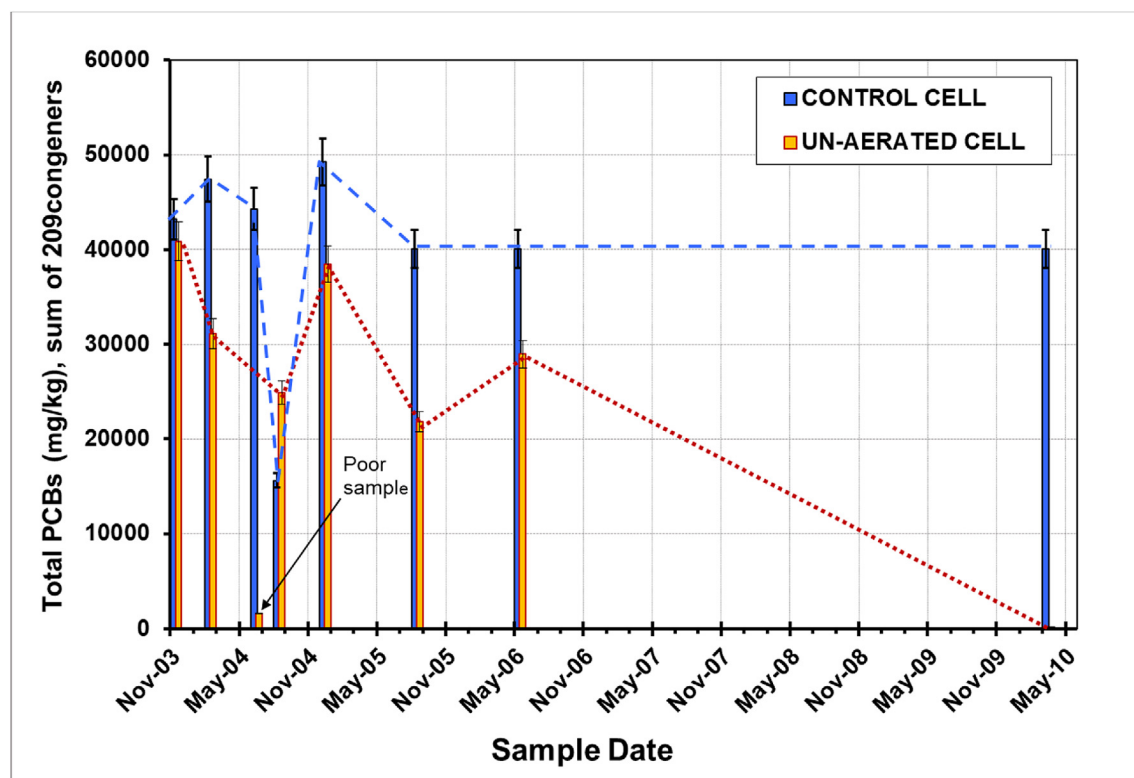
3.5.1. Treatment results through May 30, 2006 EPA 22 1668A method

The PCBs in the un-aerated test and control containers were the focus of the study. Seven sampling events took place between November 23, 2003 and May 30, 2006. Total PCBs obtained from these sampling events, that is the sum of all 209 PCB congeners excluding the redundant co-eluted values, are summarized in Table 1 and illustrated graphically in Fig. 8. It should be noted that the redundant co-eluted values are the reproducible results whereby two or more PCB congeners elute from a chromatographic column at the same time, making it difficult to separate and identify. The results show that over the initial 30-month (2003–2006) treatment period ECGO affected to reduce total PCB levels by about 30% in the un-aerated New Bedford Harbor sediment. There were two questionable analytical results, one for the 6/2/2004 un-aerated cell and the other for 8/4/2004 control sample. Both are lower than prior and subsequent sample analyses, with the 6/2/2004 un-aerated test result being the most extreme. This inconsistent result was likely due to the very watery composition of this particular sample, measurements of which yielded percent solids up to only 11% by volume. This value was deemed significantly lower than those of other samples which yielded average percent solids of 60%. The 8/4/2004 control result of 15,624 $\mu\text{g/kg}$ remained challenging to explain, and was deemed anomalous, as the other control sample totals typically fell within $\pm 10\%$ of their 43,599 $\mu\text{g/kg}$ average, as shown in Fig. 8. Regardless, when this low value was included, total PCBs average for control remained at 40,102 $\mu\text{g/kg}$. This conservative value of control PCB content was adopted for comparison purposes. EPA Method 8082.

The analytics performed on the aerated test cell were limited, as a total of three samplings were conducted through 5/30/2006, and they were analyzed using partial scan EPA Method 8082. The results shown in Table 2 indicate that aeration had little or no effect on reducing PCB levels. In fact, the PCB total on 5/30/2006 was

Table 1Total final PCB results for **EPA 22 1668A** for **un-aerated** and **control** samples through March 8, 2010 sampling (sum of all 209 PCB congeners).

SAMPLING DATE	CONTROL Total PCBs (ppb)	UN-AERATED CELL Total PCBs (ppb)	Comments
11/21/2003	43,195	40,856	PRE-TEST SAMPLES
2/11/2004	47,426	31,118	
6/2/2004	44,257	1611	
8/4/2004	15,624	24,881	POOR TEST SAMPLE ANAMOLOUS CONTROL VALUE
12/14/2004	49,256	38,418	
8/24/2005	-	21,812	RE-CONFIRMED TEST RESULTS
5/30/2006	-	28,945	
3/8/2010	-	202	
RAW CONTROL AVERAGE	40,102 ^a	Average of 5 control values: includes the anomalous control and the pre-test value	
SELECT CONTROL AVERAGE	43,566	Average of 4 control values: does not include the anomalous control value	Control average taken 40,102 ppb
PRE-TEST AVERAGE	42,025	Average of two pre-test values	
5/30/2006	Reduction in total PCBs relative to control average (%)	28	
3/8/2010		99	Control average taken 40,102 ppb

^a This conservative value was used as CONTROL AVERAGE in all comparative computations.**Fig. 8.** Histogram comparison of un-aerated and control cell total PCBs, through final sampling of March, 2010.**Table 2**Total PCB results for **EPA Method 8082** for **un-aerated**, **aerated** and **control** samples through March 8, 2008 (sum of partial PCB congeners).

SAMPLING DATE	CONTROL Total PCBs (ppb)	UN-AERATED CELL Total PCBs (ppb)	AERATED CELL Total PCBs (ppb)
8/4/2004	16,590	12,037	-
12/14/2004	-	-	13,764
8/24/2005	13,732	9877	9588
5/30/2006	20,322	16,524	17,798
3/8/2010	-	64	13,088
CONTROL AVERAGE	16,881		
Reduction in total PCBs relative to control average (%)	-	99.6	22.5

actually higher than the cumulative control average. Interestingly, at this stage the EPA Method 8082 also showed little difference between the cumulative control average PCB total and the un-aerated test cell results for 5/30/2006.

3.6. Western Michigan University analysis

Partial PCB analyses (24 congeners) performed at Western Michigan University on samples collected in July of 2004 showed the un-aerated test cell's total PCB level (18,672 $\mu\text{g/kg}$) to be 46.2% lower than the Control's (34,702 $\mu\text{g/kg}$). While these results represent only a single set of analyses, they reinforced the generally consistent PCB reductions indicated by the full PCB congener (EPA 22 1668A Method) analytics.

3.6.1. Treatment results by March 8, 2010

Prior to the packaging, sealing, and disposition of the NBH sediments, a final set of samples was collected from the test cells for PCB analysis, given that the ECGO power was kept on well beyond the May 30, 2006 sampling, through July 2008, for an additional 25 months. The system then remained unpowered and undisturbed for about 20 more months through March 8, 2010. The final samples were collected from both the un-aerated and aerated ECGO treatment cells by NRRI on March 8, 2010, and submitted to Test America Laboratories, Inc. (formerly Severn Trent Laboratories) for analysis. As before, full (209) PCB congener analyses (EPA 22 1668A, Table 1), and partial [27] PCB congener analyses (EPA Method 8082, Table 2) were run, as well as percent solids and total organic carbon (TOC, Table 3) analyses. A final analysis of the control would have been desirable, but the control sediments had already been inadvertently removed and disposed of by the University's Department of Environmental Health and Safety Office before a final sample could be collected. However, since the previous control analyses indicated little change (i.e., within $\pm 10\%$) in total PCBs from 2003 to 2006 in 4 out of 5 samples, it was plausible that a new analysis would have produced a similar result. Therefore, the total PCBs for the control was averaged at the conservative value of 40,102 $\mu\text{g/kg}$. Likewise, the analyses performed on the aerated-ECGO cell samples showed that the aerated-ECGO cell exhibited a similar lack of discernible change in PCBs over time relative to the control. Fig. 9 shows the PCB content by chlorinated group for the control average (2003–2006), and for the aerated cell sampled in 2010. Indeed, little change is observed between the results of the control average and the aerated cell of 2010. This observation supports the assumption that the conservative average of 40,102 $\mu\text{g/kg}$ for control cell was plausibly valid by 2010.

The final analysis of PCB levels (all 209 congeners) in the un-aerated ECGO test cell sample of March, 2010 totaled to only about 200 $\mu\text{g/kg}$ (ppb). This represented a greater than 99%

reduction in total PCBs relative to both the starting un-aerated treatment cell levels and the project's control cell average as depicted in Figs. 8 and 10, and summarized in Table 1. In contrast, the final aerated cell sample of March 2010 did not show much reduction in total PCB levels compared to that of control average, consistent with the previous (2004–2006) aerated cell analyses given in Table 2 and depicted in Fig. 9.

Both the un-aerated and aerated test samples were collected and prepared identically, and both contained similar percent solids at 64.7% and 63.9%, respectively. Importantly, the 209-congener EPA 22 1668A method was performed twice (on different dates) for quality assurance by Test America, Inc. on all samples. Unique sub-samples (aliquots) were collected from each sample jar for the analytical re-check, and the re-check results confirmed the results reported for the first set of analyses. The re-check step was, in effect, analogous to having duplicate analyses run on each sample. Significantly, the supplemental EPA Method 8082 analyses also returned results, i.e., a 99.6% reduction in un-aerated cell, comparable to the 209-congener EPA 22 1668A method as shown in Tables 1 and 2. Still, confirmation of the analytical results was immediately requested by the investigators given the startlingly low PCB levels in the un-aerated treatment cell sample, in part to rule out any potential errors. In response to this request, Test America Laboratories, Inc. reviewed and re-evaluated the data, and confirmed the veracity of the originally-reported analytical results.

3.7. Discussion of results

The overall data set, as presented in Fig. 10, shows that a reduction in total PCBs took place within the first year of the treatment, followed by a rebound in December of 2004, a decline in August of 2005, and another smaller rebound in May 2006, before declining to the very low total PCB levels reported in the March 8, 2010 sample. While it could be argued that these oscillating results are merely reflecting typical analytical variability and are a numeric/statistical artifact, similar oscillating patterns in analytical data from ECGO remediation projects in Europe have been reported in field projects earlier [100]. The pattern can be attributed to preferential and/or sequential decomposition/de-chlorination, as well as ongoing desorption and "release" of previously unavailable PCBs from soil surfaces as the ECGO proceeds over time. Fig. 11 shows the time evolution of the change in PCBs content from control average by chlorinated group for the un-aerated cell samples. Superimposed on the graph is the March, 2010 distribution of the change in PCBs by chlorinated group for the aerated cell for comparison. Possible preferential and/or sequential de-chlorination with possible desorption may be inferred from the cyclic distribution of the PCBs, where the magnitudes of the alternating peaks and troughs decrease over time displaying a more uniform distribution.

Due to the number of congeners involved and the immense number of potential pathways of degradation, interpretation of the analytical results for this discussion has been limited to total PCB levels, i.e., the sum of all 209 congeners and their distribution by chlorinated groups. From Fig. 9, it is observed that the tri- and tetra-chlorinated groups of the March, 2010 un-aerated cell sample make up a smaller percentage of total PCBs, whereas the penta- and hexa-chlorinated groups make up a higher percentage of the total. The data presented in Fig. 9 illustrates also the shift in the percentage of total PCBs contributed by each chlorinated group for the 2006 and 2010 un-aerated cells. The data shows that the most significant changes are contributed by the tri-, tetra-, penta-, and hexa-chlorinated groups between 2006 and 2010. Fig. 12 expands on this shift by illustrating the percent difference in total PCBs contributed by the tri-, tetra-, penta-, and hexa-chlorinated groups

Table 3
Total Organic Carbon (TOC) and percent solids results.

SAMPLING DATE	CONTROL		UN-AERATED CELL		AERATED CELL	
	TOC ppm	Solids %	TOC ppm	Solids %	TOC ppm	Solids %
11/21/2003	54,400	52.6	43,000	58.2	N/A	N/A
2/11/2004	54,500	44.7	54,800	63.4	N/A	N/A
6/2/2004	86,400	24.8	228,700 ^a	7.4 ^a	N/A	N/A
8/4/2004	46,100	40.6	38,700	59.0	N/A	N/A
12/14/2004	38,400	60.9	39,400	66.4	39,300	56.7
8/24/2005	41,500	63.1	42,600	59.0	51,500	50.9
5/30/2006	53,200	54.4	39,600	62.5	40,400	55.3
3/8/2010	N/A	N/A	33,400	64.7	48,500	63.9

^a Poor sample: Watery with very low solids content.

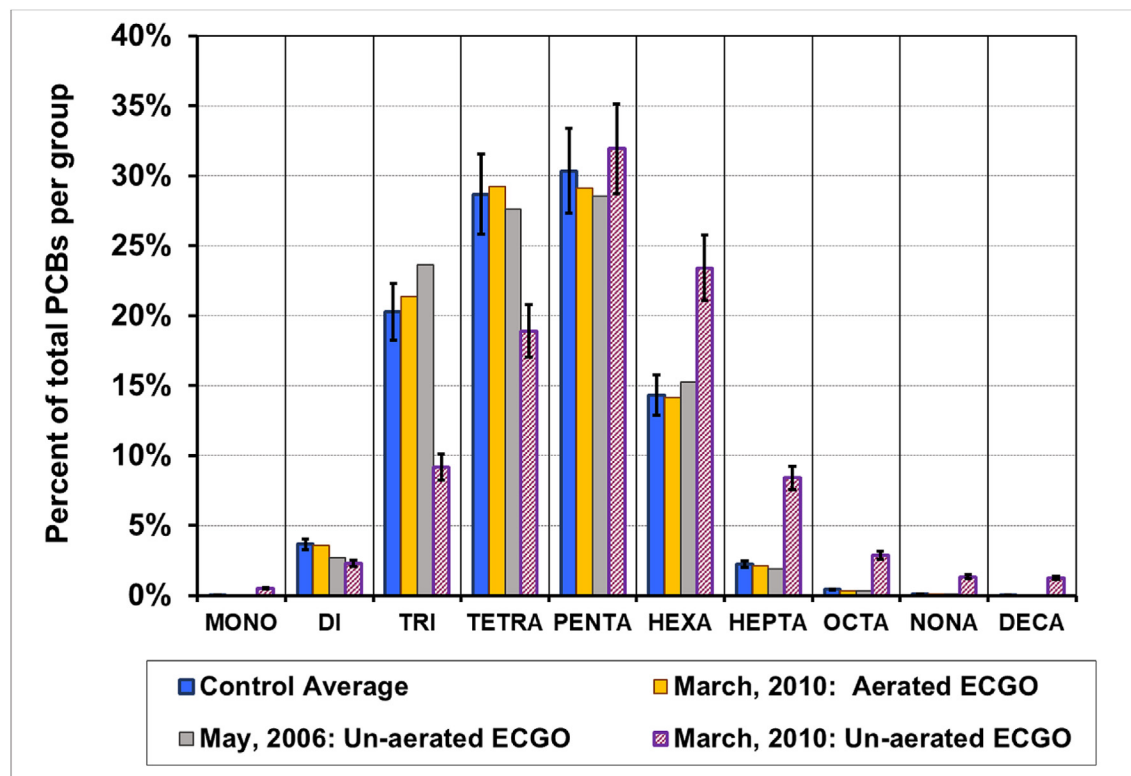


Fig. 9. Percentage of total PCBs by chlorinated groups for the control average, aerated (2010) and un-aerated (2006 and 2010) cells.

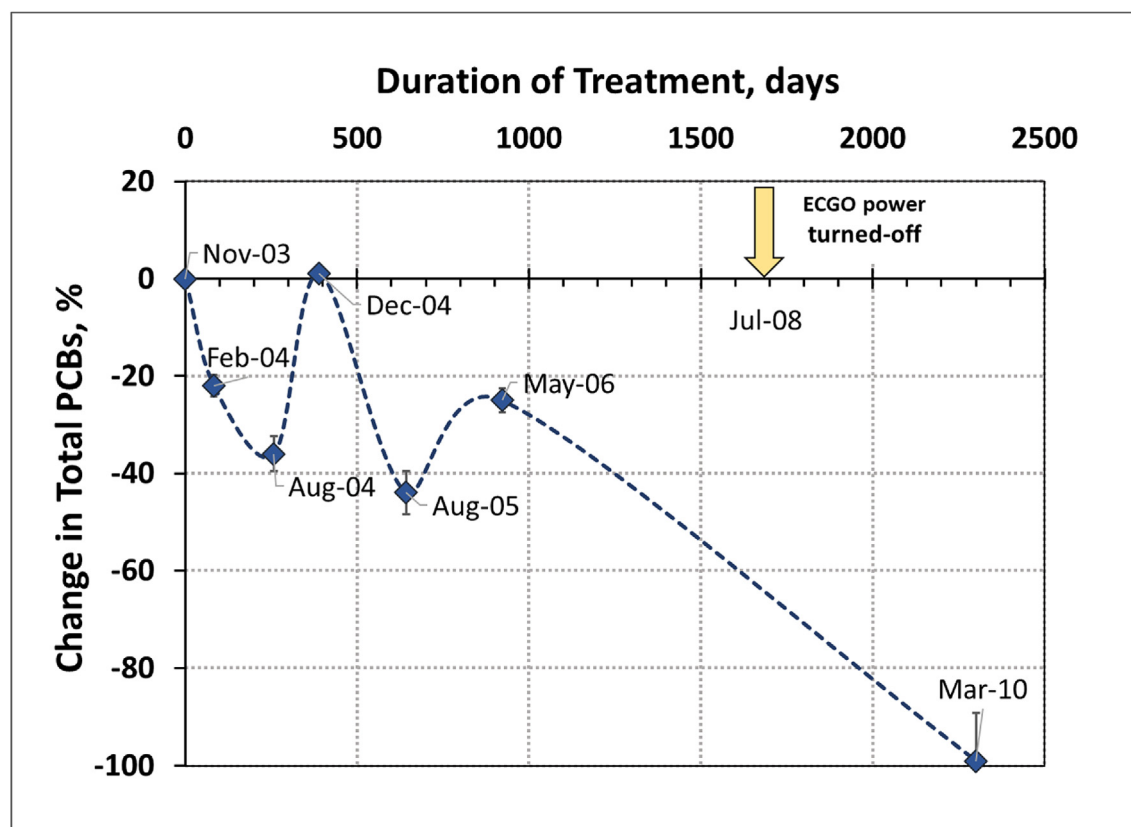


Fig. 10. Percent change in total PCBs level in un-aerated treatment cell over time relative to control average.

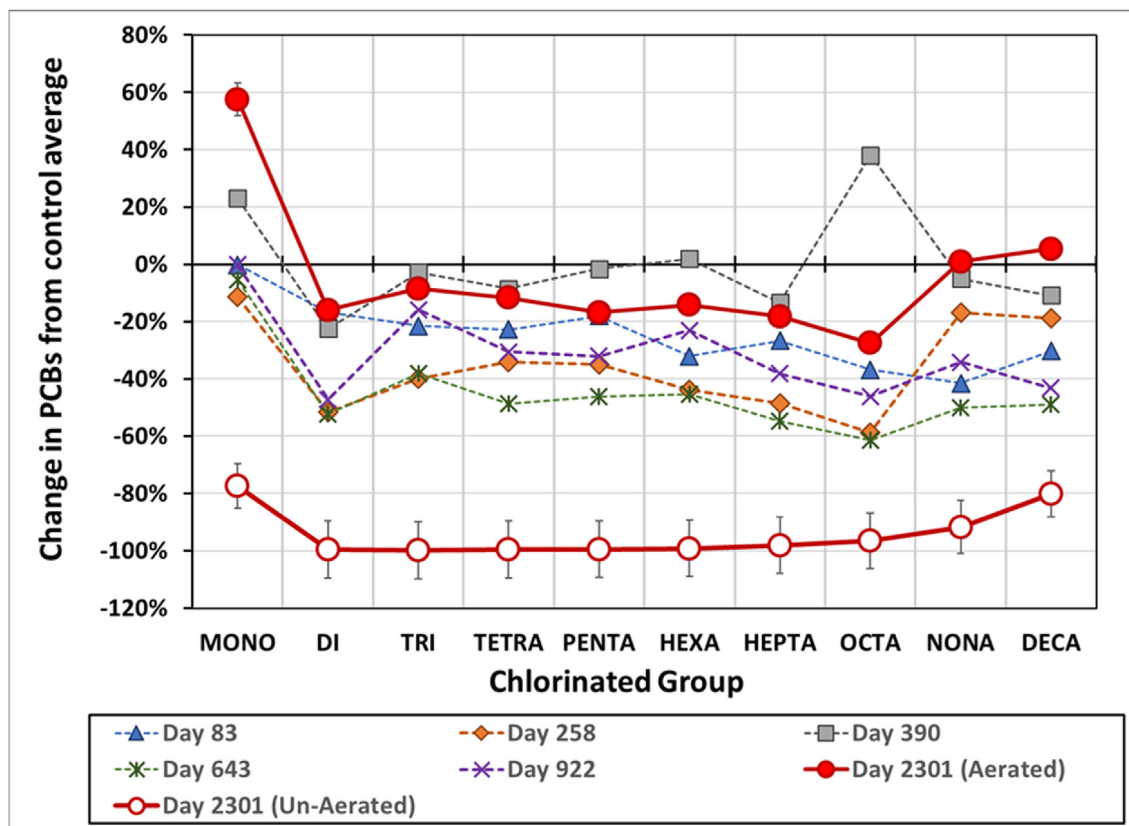


Fig. 11. Percent change in PCBs by chlorinated group in un-aerated treatment cell over time relative to control average (final aerated cell data also included).

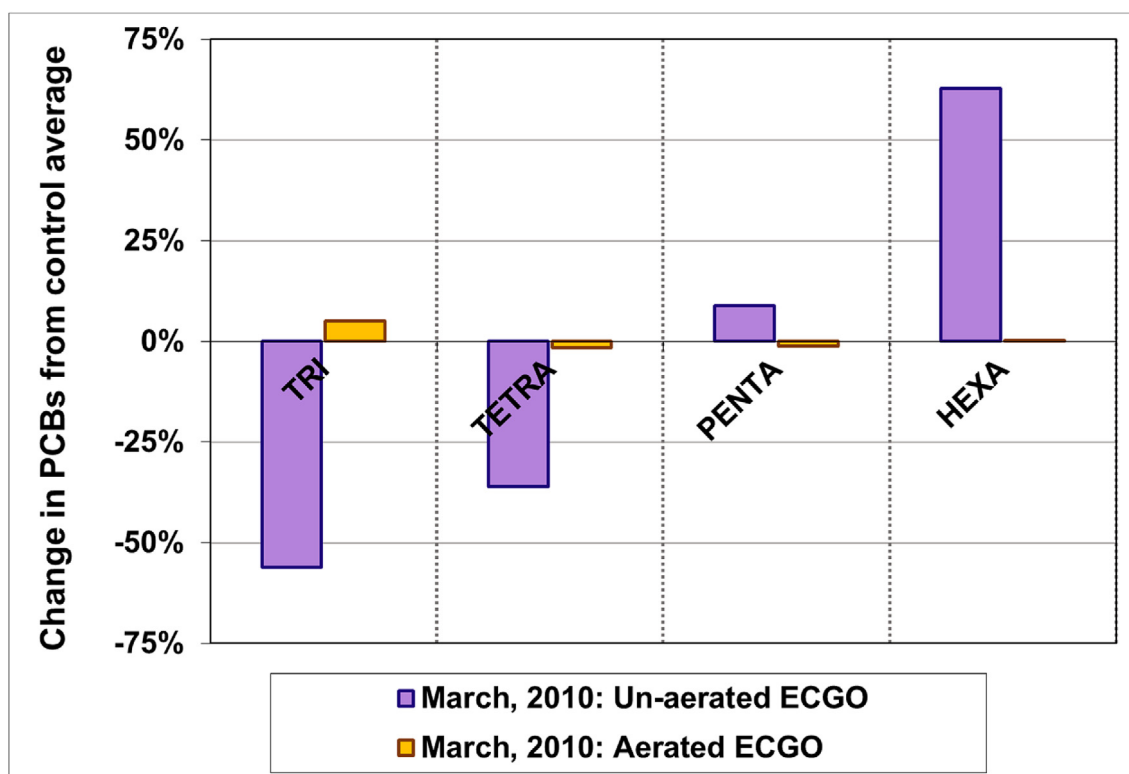


Fig. 12. Percent change in total PCBs contributed by the tri-, tetra-, penta-, and hexa-chlorinated groups in the March 2010 un-aerated and aerated cells, relative to the control averages for the four separate groups.

by 2010 in the un-aerated and aerated cells, relative to the cumulative control averages for these four groups. The control averages are, in effect, representative of the study's starting PCB levels, because when combined, these four groups comprise over 93% of the total PCBs in the NBH sediment received originally. The di- and hepta-chlorinated groups provide another 5%, with minor amounts of the mono-, octa-, nona-, and deca-chlorinated groups rounding out the total.

The results presented in Figs. 9 and 12 indicate ECGO's eventual preferential de-chlorination of the less-chlorinated PCB congeners within the tri- and tetra- as these groups decrease in percentage of total. This is inconsistent with microbial reductive (anaerobic) de-chlorination pathways described by others in previous studies [60,61,64]. PCBs have been shown to degrade by aerobic oxidative or anaerobic reductive processes, or a combination of both [101,102]. Abramowitz [60] found that under aerobic conditions lightly chlorinated PCBs could be degraded and oxidized to chlorobenzoic acids but higher chlorinated PCB were more resistant to oxidation. Anaerobic bacteria attack more highly chlorinated PCB congeners through reductive de-chlorination by preferential removal of meta- and para- chlorines, resulting in depletion of highly chlorinated PCBs with corresponding increases in lower chlorinated, ortho-substituted, mono- through tetra-chlorobiphenyls [60]. Widely ignored in looking at the impact of treatment of PCBs is the wide range of solubilities of each of the congeners in water and their adsorption/desorption trends in the sediment matrix. Solubilities of PCB congeners in water are well documented in the literature and vary by orders of magnitude [103]. The importance of desorption is illustrated by a study by Rybnikova et al., [102], where they showed that the overall PCB degradation did not exceed 30%, suggesting that only a small part of

PCBs in soil was available for reaction with catalyst and/or oxidant. In this study, the rapid decrease in tri-tetra chlorinated congeners and an increase in hexa-hepta congeners is attributed to the lower solubility of the hexa-hepta PCBs in water relative to the tri-tetra substituted PCBs. As reported by Erickson [103], the hexa-chlorobiphenyls can be up to 1000 times less soluble in water than the lower chlorinated biphenyls. Their availability in the water probably had an impact on their reactivity and depletion as percent of total PCBs available.

In planning the series of tests, it was anticipated that successive de-chlorination reactions would take place in the PCB found in the NBH sediments under anerobic conditions and less degradation under aerobic conditions. In the simplest terms a tetra-chlorinated PCB should degrade to a tri-chlorinate, followed by a di-substituted and then mono-substituted PCB, and then ultimately to biphenyl [101,103]. Since it was decided to run chemical analysis for all 209 congeners for the PCBs during the test period, consideration of all chemical reactions possible for the entire 209 congeners became infeasible, hence were left out of the scope of this paper.

Total Organic Carbon (TOC) values for the un-aerated and aerated 2010 samples were 33,400 ppm (3.34%) and 48,500 ppm (4.85%), respectively, as presented in Table 3. The TOC for the un-aerated treatment cell was the lowest level measured, perhaps a supporting condition for the high PCB reduction levels observed in the cell. Similar observations were reported by others [102] where the PCB degradation efficiency increased with decreasing soil organic content.

Figs. 13 and 14 show the evolution of the un-aerated and aerated cell ORP and pH during the treatment/sampling period. The predominantly negative ORP for the un-aerated cell, as shown in Fig. 13, supports our findings that a low ORP created under anerobic

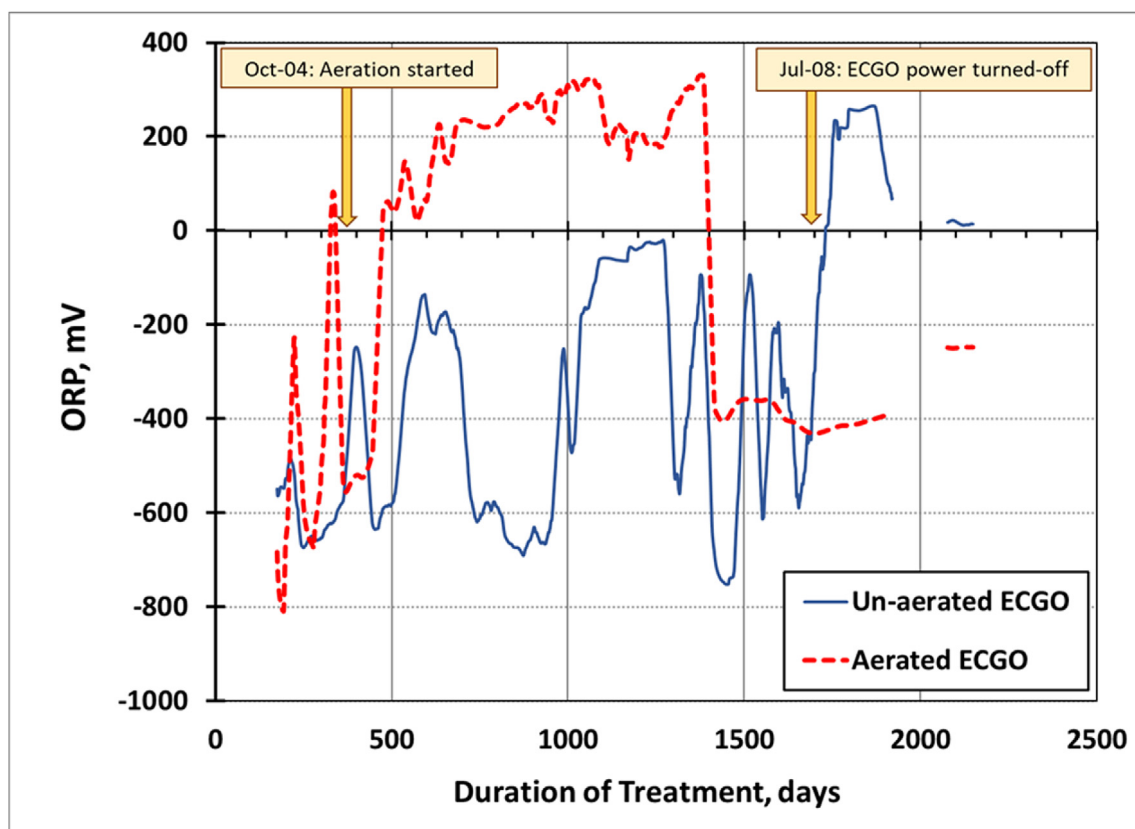


Fig. 13. Evolution of the daily average ORP of the un-aerated and aerated cells for the duration of treatment and sampling.

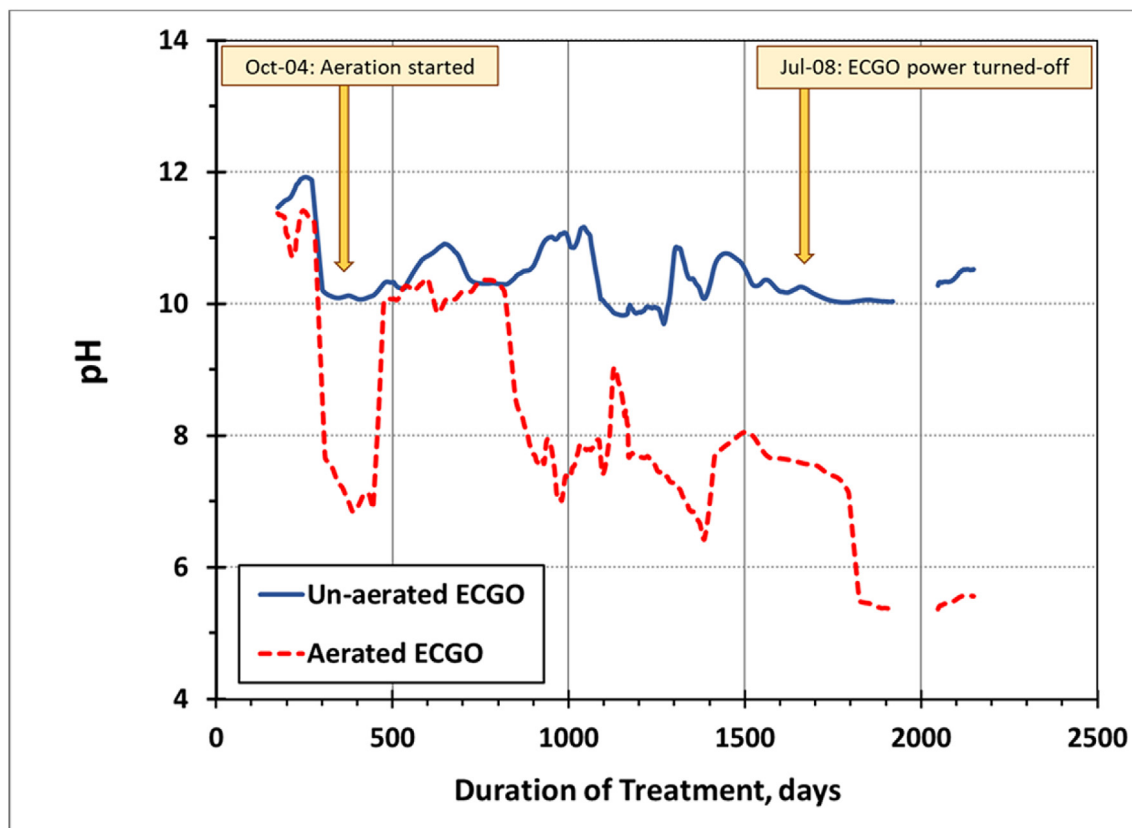


Fig. 14. Evolution of the daily average pH of the un-aerated and aerated cells for the duration of treatment and sampling.

conditions and driven by the induced polarization effect of ECGO could potentially be responsible for the reduction of PCBs in the sediment. It is observed that the ORP in the un-aerated cell returns to a positive value after the power was turned off on day 1695 (Jul-08). This indicates ECGO to be the driving process that maintain negative ORP in the cell. The aerated cell displayed negative ORP before the start of aeration in Oct-04. The sharp drop in the ORP from +300 to −400 by day 1410 for the aerated cell is due to a failure in the aeration system. The pH was found to be fairly constant at around 10 for the un-aerated cell, while it fluctuated for the aerated cell, potentially due to the aeration scheme.

After 1695 days of treatment, the power was cut off to both cells, and they were left undisturbed until the final sampling. The ORP and pH recordings were continued after the power-off. At the time of final sampling on March, 2010, the ORP of the un-aerated cell measured a low positive value close to zero and its pH did not change much from previous. The ORP and pH recordings of the aerated sample after the aeration failure on day 1410 were deemed not reliable, although aeration were continued until the power-off on day 1695.

In ECGO treatment, upon turning off the polarizing current the soil gradually discharges and returns to equilibrium, as discussed in the section 2.2 previously. Therefore, it is conceivable that some of the reactions continued until the NBH sediments discharged completely after the power-off in July 2008. Indeed, the ORP-pH behavior of the un-aerated cell after the power-off may be indicative of gradual returning to equilibrium. However, it is still difficult to conclude with any certainty if electrical discharge (or microbial) driven reactions had continued within either of the cells beyond the power-off time based on the extended ORP-pH data. Regardless, since both cells were left undisturbed under the same conditions until sampling time, it is reasonable to assume little change, if any,

had occurred in the PCB contents that was reached at the time of power termination. Hence, the reasonable conclusion is that the final PCB content obtained from March, 2010 samples reflect the values reached by the end of 1695 days of ECGO treatment of the NBH sediments. The final analysis of sediment collected from the un-aerated test cell recorded about 200 ppb total PCBs, which indicated that the ECGO treatment achieved the clean-up goal by moving the NBH material out of the PCB-contaminated category.

4. Conclusions

The analytical results indicate that ECGO, an induced polarization-based treatment of contaminated soil, appears to be effective at reducing PCBs in an anaerobic environment, but the technology may need to operate for a much longer period of time than originally envisioned to achieve significant reduction. The total treatment time was 1965 days and 209 congeners were analyzed from un-aerated and aerated test cells over time. ECGO reduced total PCB levels in the un-aerated cells of contaminated sediments by about 30% over the initial 30-month treatment period. An extended period of treatment under the un-aerated conditions for another 25-month period caused over 99% deterioration of total PCBs. The study demonstrated higher rate of destruction for the PCB congeners by the ECGO treatment under un-aerated condition over aerated one. As a result, since most natural sediment environments are anoxic, ECGO treatment could be a viable in-situ alternative for the remediation of such PCB-contaminated sediments.

Credit author statement

Conceptualization, Formal analysis, Investigation, and

methodology tasks of the original project were equally shared by the authors as well as the writing, reviewing and editing of this manuscript. Lawrence M. Zanko, J.Kenneth Wittle, Sibel Pamukcu.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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