Electrochemical Remediation and Stabilization of Contaminated Sediments

A Final Report Submitted to

The NOAA/UNH Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET)

Submitted by

Dr. Kevin Gardner
Civil Engineering Department
University of New Hampshire
Durham, NH 03824

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1. ABSTRACT

A promising contaminated sediment treatment and management technology that uses a low voltage, direct current to degrade organics, remove metals and salts, and dewater sediments was investigated at the University of New Hampshire in conjunction with visiting scholars from the Technical Institute of Denmark and the Institution of Higher Education in Engineering (Nantes, France). One reason this treatment option shows such potential, other than its prospect to address three different treatments, is because it can be applied to sediments in-situ (most likely in confined disposal cells) and ex-situ (such as at a facility that prepares sediment for beneficial uses), and because of it's cost-effectiveness to run the treatment at low electrical current (<50 mA). The three foci of the project investigated at the bench-scale were to determine the effectiveness of electrochemical remediation on the removal of metals and salts, on the degradation or removal of organics (specifically polyaromatic hydrocarbons [PAHs]), and on stabilization of sediments via dewatering. In several 3-4 week laboratory experiments, selected metals plus chloride were mobilized in the electric field and accumulated in the area of the electrolytes, as was theoretically proposed. Initial investigations of the degradation of PAHs proved promising for naphthalene and acenaphthalene, and a more comprehensive month-long bench scale experiments offered more comprehensive results. After 30 days of electrokinetic remediation at a current 20-30 mA, approximately 20% of total PAHs were degraded, and a discrete investigation of the individual PAH compounds concluded that they tend to migrate towards the anode along with the natural organic carbon. Electroosmotic flow was witnessed in the batch experiments visually and in measuring the water content, indicating successful dewatering of the sediments.

KEYWORDS: sediment, electrochemical remediation, polyaromatic hydrocarbons, metals, dewatering

2. INTRODUCTION

Contaminated sediments in rivers, harbors, and estuaries act as continuous sources of contaminants to riverine, estuarine, and coastal ecosystems. Although much of this contamination is diffuse and unrealistic to remediate, in cases where concentrated "hotspots" exist, including some 100 Superfund sites (ie., upper Hudson River, New Bedford Harbor, Housatonic River), remediation of sediments in place may be effective. Further, there is a growing crisis in treating those contaminated sediments removed from navigational dredging activities. Historically, material from navigational dredging was disposed of at open ocean disposal sites, but increasing restrictions to protect benthic biology and ecology have eliminated this option for all but the cleanest sediments. Typically, these sediments contain a wide range of contamination, including heavy metals, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and other persistent organics.

There are two primary methods that are being used to currently try to solve this problem. One is using contaminated sediments at upland sites as inexpensive fill material at Superfund and Brownfields sites to reclaim or redevelop the land (regulated state-to-state). The major consideration in this method is the cost in stabilizing the sediment (dewatering, additives to increase strength) and the cost to decontaminate (including major salts such as chloride). Of note, the technology considered in this research project is effective in both dewatering and chloride removal.

The second material handling method is to place contaminated sediment in Confined Aquatic Disposal (CAD) cells, typically in harbors, estuarine, or near-shore areas. A CAD cell is a pit dug in the sediment which is then refilled with contaminated dredged material and capped, typically with clean sand, although reactive barriers are emerging as well. CAD cells are cost-effective and do achieve some degree of isolation and minimization of exposed contamination. A number of problems with CAD cells exist, however, which may have significant ramifications for the long-term health of our coastal and estuarine systems. Sand caps have a high permeability, which is well understood that due to diffusion, the flux of contaminants can be significant. Release of many contaminants from CAD cells has been measured to reach tons per year (Shine, 2000).

CAD cells do offer a distinct geometrical configuration of contaminated sediments that may be amenable to certain types of in-situ remediation techniques, similar to those used on contaminated terrestrial soils. Confined disposal facilities (CDFs) offer a similarly convenient configuration for treatment of dredged sediments, without the confounding effects of being submerged. There is one type of treatment that is uniquely suited for these types of contaminated sediment storage: electrochemical remediation (Acar, 1992; 1993).

2.1 Electrochemical Remediation Theory

Electrochemical remediation involves the application of a low density direct current to a pair of positive (anode) and negative (cathode) electrodes placed in the soil to mobilize contaminants in the form of charged species. The contaminants within the electric field are transported to the anode or to the cathode where they are removed by one of the following methods: electrodialysis into electrolyte solutions, adsorption onto the electrode, precipitation or co-precipitation at the electrode, pumping next to the electrode, complexing with ion exchange resins, or capturing in permeable reactive barriers.

In the United States and Europe, there is a patent for ElectroChemical Remediation Technologies (ECRTs), which consist of two types. ElectroChemcial GeoOxidation (ECGO) uses a low voltage, low amperage DC/AC current to induce a polarization field within the sediment. The sediment acts as a capacitor, discharging and charging electricity resulting in redox reactions, which cause desorption of the contaminants from the sediments and mineralization of the organics to their inorganic constituents (e.g., carbon dioxide and water). Empirical evidence indicates that reaction rates are inversely proportional to grain size, such that ECRTs remediate faster in finer-grained material typically found at sediment sites. The second method of removal, Induced Complexation (IC), significantly enhances the mobilization of metals and radio nuclides in a sediment matrix through redox reactions that desorb the contaminants from the sediment and create ionic metal complexes (Doering, 2000).

Electrochemical remediation was originally developed for remediation of heavy metal polluted soil (Hansen et al., 1997; Ottosen et al., 1997). The electrokinetic phenomena in porous media are based on the relative motion between a charged surface and the bulk solution at its interface. The formation of an electric double layer at the charged surface of clay particles explains the processes mobilizing the charged particles via three phenomena: electromigration, electroosmosis, and electrophoresis. These processes force the aqueous phase and ions to desorb from the sediment surface and migrate through the electric field either towards the anode or the cathodes, depending on the speciation.

Electromigration is the movement of ions and ionic complexes in a soil solution due to an applied electric field. The ions move towards the electrode of opposite charge: anions towards the anode and cations towards the cathode. Electromigration is the most important transport mechanism aiding electrochemical remediation (Lageman et al., 1989) and is dependent on tortuosity, porosity, and the charge of the ion (Acar, 1993).

Electroosmosis is the movement of water in a porous media in an applied electric field. Soil particles are negatively charged, which creates a diffuse double layer of water and dissolved cations around the soil particles. When an electric field is applied, the cations will migrate in the direction of the cathode along with the water molecules. Whereas values of hydraulic conductivity can vary many orders of magnitude for different soil types, the electroosmotic conductivity lie in a narrow range of $1x10^{-9}$ to $1x10^{-8}$. Thus, an electric field is a much more effective force driving the fluid through fine grained soils of low hydraulic conductivity than a hydraulic gradient (Akram, 1999). Furthermore, electroosmosis is independent of the pore size distribution or the presence of macro-

pores. The effect of the electroosmosis process to the total mass transport varies according to soil type, water content, types of ion species, and pore fluid concentration of ions (Acar, 1993).

The final phenomenon affecting electrochemical remediation is electrophoresis. Electrophoresis is the transport of particles in an applied electric field and includes all charged particles (e.g. colloids, clay particles, organic particles) (Acar, 1993). Figure 1 below shows a visual observation of both electroosmosis and electrophoresis.

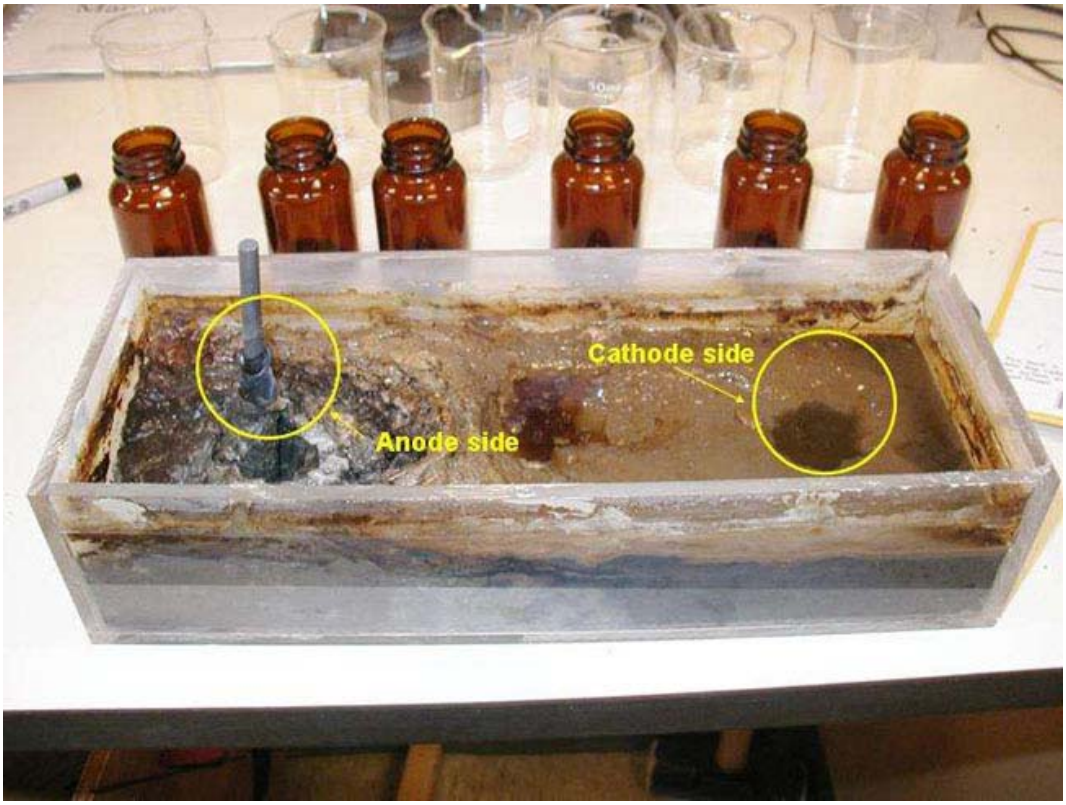


Figure 1: Visual observation of electroosmosis and electrophoresis, the movement of soil and water particles under an applied electric field (anode on left, cathode removed from right).

Since only released ions in the pore water are transported in the electric field during electrochemical remediation, the precipitated and adsorbed metals in the sediment must be converted to mobile ionic forms before they can be removed. Mobilization is enhanced in an electrochemical reactor by pH changes in the sediment during the treatment. Water splitting at the anode occurs via the following reactions (Equations 1 and 2) and results in an acidic front that moves from the anode to the cathode (Ottosen, 2000).

(1) Cathode: $4\ H_2O + 4\ e^- \rightarrow 2\ H_2(g) + 4\ OH^-$

(2) Anode: $2\ H_2O \rightarrow O_2(g) + 4\ H^+ + 4\ e^-$

Theoretically, in an electrochemical reactor, equal amounts of current are carried by anions and cations in solution. Closer to the electrodes, the concentration of anions and cations decreases compared to the bulk concentration. When the concentration reaches zero, the limiting current density has been reached. Operation at current densities higher than the limiting current results in the water splitting phenomenon (formation of H+ and OH-). The limiting current is lower at the anode than at the cathode, thus an acidic front is formed desorbing metals and transporting them with water and soil particles towards the cathode. For metals of concern that are not mobile at low pH (e.g. As or Cr (VI)), surfactants and complexing agents have been used to assist in the migration (Ottensen, 1998). Surfactants have also been used to assist transport of organic contaminants in electrochemical remediation (Elektorowicz, 2001).

2.2 Developments in Electrochemical Remediation

The first electrochemical remediation experiments were performed in soil at the Technical University of Denmark. In their PhD theses, Ottosen (1995) described the development of the experimental cell and first electrodialytic remediation experiments and Hansen (1995) tested the suitability and advantages of different ion exchange membranes for use in the electrodialytic cell (Note that the difference between electrokinetic and electrodialytic experiments are that the former applies current directly to the soil with electrodes in the soil and the latter uses an ion exchange membrane and separate electrolyte solution compartments). From 1995 to 2000, three more PhD studies were completed on electrodialytic soil remediation: Jespersen (1996) built the first pilot and full scale plants and Ribeiro (1998) and Kliem (2000) studied the changes in soil characteristics by different analytical methods during and after electrodialytic remediation.

Together with developing the soil remediation technique, the electrodialytic remediation process was also used to remediate other porous materials, such as fly ash (Pedersen, 2002), impregnated wood waste (Ribeiro, 2000) and waste water sludge (Jakobsen, 2004). Pedersen introduced the stirred electrodialytic treatment cell in her PhD thesis to combat problems of high electrical resistance and hardening of the material. Christensen (2004) used oxalic and phosphoric acid as a desorbing agent to remove Cu, Cr, and As from impregnated wood waste, in the laboratory, bench, and pilot scale. This was the first time large scale experiments were made for other materials other than soil.

There is definite potential for remediating harbor sediments as well by the electrodialytic method (Nyostrom, 2004). Dredged sediment is often too contaminated to be dumped at sea. Sediment consists of many similar components as soil: clay, silt, organic matter, oxides, and carbonates. Therefore, the expectations for the remediation of sediment were based on the past experiences from the electrodialytic remediation of soil. The greatest difference is in the effect of salinity on remediation success, because heavy metals can form uncharged complexes with chloride, thus not being mobile in an electric field.

Grande and Gent (2002) conducted an electrokinetic field scale in-situ experiment in a 2000 m^2 waste lagoon located in a tidal marsh in the United States. The saline sediment was remediated for both heavy metals and chlorinated solvents (PCEs). The field experiment lasted 96 weeks and showed that the heavy metals moved towards the cathode. In 77.5% of the area the chromium level was reduced to under background level (<109 mg/kg) and in 78.8% of the area the cadmium level was reduced to under background level (<3.1 mg/kg). Degradation of up to 99.0% of PCEs was also experienced. The current density had to be lowered during the remediation because of formation of Cl_2 (g) at the anodes. The chloride gas reacted with dissolved organic carbon in the system and formed trihalomethanes, especially chloroform. Air sparging at the anodes and replacement of the electrolytes were used to reduce the production of chloride gas.

Roulier et al. (2000) studied the feasibility of electrokinetic soil remediation in horizontal Lasagna™ cells and described some problems related to the installation and operation of horizontal electrodes. A hydraulic fracturing process (adapted from oil field practice), where a horizontal layer of porous electrode material (e.g. graphite) can be installed, was suggested as a suitable installation method. No major problems were anticipated installing electrodes this way, but in an initial assessment some problems maintaining flow of liquids and electrical current in the electrode layers seemed to occur. Good hydraulic as well as electrical conductivity in the electrode material are critical to the success of the electrochemical process. Evolved gases at the electrodes must be removed continuously to maintain satisfactory electrical conductivity. In a vertical electrode design, the gases can bubble out and do not cause problems, but in horizontal electrodes the gases do not vent readily but may displace water, thereby reducing the contact between the electrodes, leading to decreased electrical conductivity. It was claimed that the use of horizontal Lasagna cells only beneath the water table would reduce the problems with water flow in electrode fractions that exhibit reduced transmissibility due to evolution of H_2 and O_2 from electrolysis of water.

The United States Army Corps of Engineers is mandated by Congress to maintain navigation on the Nation's 40,234 km (25,000 miles) of waterways and 400 ports, and dredging is a significant part of the maintenance activities. As such, the Corps has a keen interest in new contaminated dredged material management tools and techniques. However, even though the Corps' Environmental Laboratory has participated in a pilot program on electrokinetic remediation of terrestrial soils (USACE, 2000), it seems little attention has been given to electrokinetic remediation of sediments. In May 2000, the Corps' Dredging Operations and Environmental Research (DOER) program co-sponsored a workshop on innovative sediment decontamination technology that featured a review of a bench scale and field scale demonstration of electrokinetic remediation in Europe (Francingues, 2000). It stated that processing costs would be \$33/yd^3 for volumes greater than 100,000 yd^3, which compares well with the other technologies reviewed, however, the capital costs were not provided. This remediation method also compared favorably in that it can be performed *in-situ* or *ex-situ*, creates a limited waste stream, and has beneficial use options for creating manufactured soil.

2.3 Advantages and Disadvantages of Electrochemical Remediation

Electrokinetics may be an appropriate remediation technique in sediment remediation because:

- There are currently no other viable *in-situ* methods for treating inorganic and organic compounds in porous media simultaneously.
- Ionic contaminants are absorbed to sediment particles and are often not available for removal by the simple flushing action of water. The pH shift produced by the electrolysis of the water effectively desorbs contaminating ions.
- In clayey sediments, hydraulic flow through pores can be extremely limited. Electrokinetic remediation is an effective method of inducing movement of water, ions, and colloids through fine-grained sediment.
- The process is competitive in cost and remediation effectiveness to other methods currently in use.

However, electrochemical remediation does have associated limitations, such as:

- The electrokinetic process is limited by the solubility of the contaminant and the desorption of contaminants from the soil matrix. Heavy metals in metallic states are difficult to dissolve and separate from soil samples. Organic compounds may be tightly bound to natural organic matter. The process is also not efficient when the target ion concentration is low and non-target ion concentration is high.
- Acidic conditions and corrosion of the anode may create difficulties in *in-situ* efforts.
- Precipitation of species close to the electrode is an impediment to the process. Heavy metals can prematurely precipitate close to the cathode at their hydroxide solubility value.

3. OBJECTIVES

The initial objective of the proposal written to CICEET was not met: to build upon a successful bench-scale demonstration of the low voltage, direct current technology in the PI's laboratory by testing the treatment of sediments at the pilot scale. Rather, the researchers further developed theoretical proof on the bench-scale that electrochemical remediation can be used to reduce the amount of inorganic and organic contamination, as well as dewater sediments in an *in situ* and *ex situ* application.

The initial graduate student chosen to participate on this project as the research assistant left at the end of two semesters due to health constraints. The project sat dormant for several months until a doctoral student from the Technical Institute of Denmark brought her expertise of electrochemical remediation to the University of New Hampshire. In the summer of 2004, a visiting student from Institution of Higher Education in Engineering (Nantes, France) performed several more bench-scale tests. Lastly, a research staff in the Environmental Research Group was requested to complete the project by continuing

work in the laboratory, authoring a journal article, and submitting this final report to CICEET.

- The graduate student determined the electrokinetic setup to be used for the batch experiments at UNH. Testing of Cocheco River sediments showed promise for using the technique to mobilize naphthalene in sediment.
- Gunvor Nystrom from Denmark investigated the leachability of metals from elecrodialytically treated sediments versus those untreated and a control that was batch extracted with distilled water. Her work was recently submitted to Environmental Engineering Science Journal in a paper entitled "Leaching Properties of harbor sediment before and after EDR", which awaits peer review.
- The student from France, Raphael Grand, studied the affect of using an assisting agent, acetic acid, to aid in desorbing metals for better migration during electrokinetic remediation.
- Lastly, the research staff at UNH, Deana Aulisio, performed bench-scale tests on Cocheco River sediments at a short and long time scale to evaluate a comprehensive list of parameters including pH, water content, organic carbon content, chloride, metals, and PAH compounds.

4. METHODS

4.1 Physical and Chemical Laboratory Methods

A baseline description of the untreated sediment properties is necessary in determining the effectiveness of treatment. Characterization falls into two categories, chemical and geotechnical/physical. Chemical analyses included metals, PAHs, salt (Cl^-), and pH. Physical parameters included water content and organic carbon content.

Two methods of metals digestion were applied to experiments to determine total and available metals. Sediment samples were prepared for metals analysis using the Nordtest Dutch Availability Method, Nordtest Envir 003, adapted by research scholars visiting UNH from Netherlands, including Anne Pedersen and Gunvor Nystrom. On-Site Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to analyze metals concentrations in the extracts. Duplicate samples were sent to Eastern Analytical, Inc. (EAI) of Concord, NH for a more rigorous digestion procedure, USEPA Method 3051 Microwave Digestion. ICP-AES was also the means of chemical analysis at the laboratory. Results using Microwave-assisted extraction are considered totals and those from the Nordtest method are considered available metals, which is more pertinent for regulatory considerations and risk determinations.

PAHs in sediments were extracted using ultrasonication and USEPA Method 3550B, which uses methylene chloride and acetone as the extracting solvents, and 2-fluorobiphenyl or o-terphenyl as surrogates to evaluate percent recovery. The concentrations of PAHs in the extracts were measured on a gas chromatograph-mass spectrometer (GCMS) at UNH using SW-846 USEPA Method 8100. Deuterated PAH compounds were used as an internal standard with an internal calibration to calculate analyte concentrations.

Chloride content was measured in samples that were muffled at 360ºC for 2 hours. These samples were added to de-ionized water at a liquid to solid (L/S) ratio of 5 g to 25 mL. After stirring for 24 hours, samples were filtered and the filtrate was measured using a Cl^- selective combination electrode.

pH was measured in a similar manner, however samples were dried at 105ºC instead of using the muffle furnace, the L/S ratio was 5 g to 100 mL, and samples were stirred for only 1 hour before measuring with a pH probe.

Water contents were determined by massing the wet sample and then drying completely at 105ºC. The dry mass was recorded and the percent water content was determined by the following equation:

(3) $WC(\%) = (M_W - M_D)/M_W$;

Where:

WC = water content

M_W = mass wet

M_D = mass dry

The organic carbon content was determined by massing the dried sample and then heating it in a muffle furnace at 360ºC for 2 hours. The difference between the initial mass and the mass after burning off organics is the amount of organic carbon in the sample.

4.2 Experimental Sediments

Sediment obtained from New York Harbor was used for the preliminary testing outlined in the proposal to CICEET. One of the experimental sediments (used by Nystrom), which was contaminated with heavy metals, originated from Haakonsvern Harbor, Bergen, Norway. The harbor sediment was dredged by NCC Norway with a specific dredging device for removing only the finer (< 5 μm), more polluted material. Three more contaminated sediments collected from industrialized rivers in the United States were also subjected to electrochemical remediation in this research: the Gowanus Creek Canal located in north-western Brooklyn, New York; Newtown Creek, the waterway that serves as the border between Brooklyn and Queens; and Cocheco River located in Dover, NH. These river sediments are contaminated with pollution of all kinds, including oils, sewage, PCBs, PAHs, and heavy metals.

4.1 Experimental Design

A schematic of electrodialytic remediation, used primarily by researchers from the Technical Institute of Denmark is shown in Figure 2. In this case, sediment is placed in a central cell and electrolyte solutions are circulated in outer cells. The electrolyte solution and the sediment are separated by permeable ion exchange membranes. pH can be monitored in the electrolyte compartments and adjusted to ideal conditions. The sediment slurry in the center can be stirred to achieve better removals. This experimental

setup is much more controlled than an electrokinetic setup, shown in Figure 3. In the electrokinetic setup, the electrodes are placed directly in the sediment. Contaminants migrate towards the electrodes and will plate out on the electrode or precipitate near the electrode. This setup is more applicable to an *in situ* situation; however pH shifts cannot be controlled.

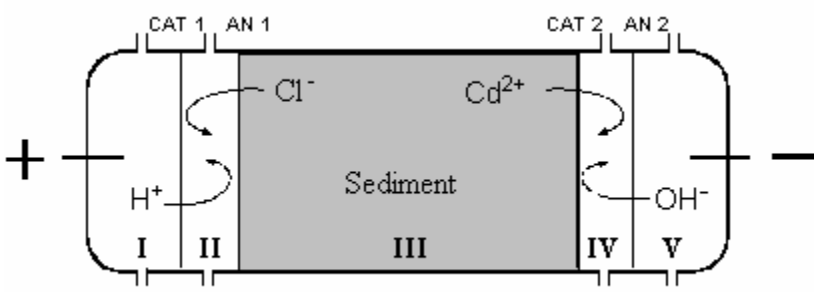


Figure 2: The principle of electrodialytic remediation, where contaminants migrate through the sediment and accumulate in electrolyte solutions. CAT = cation exchange membrane;, AN = anion exchange membrane.

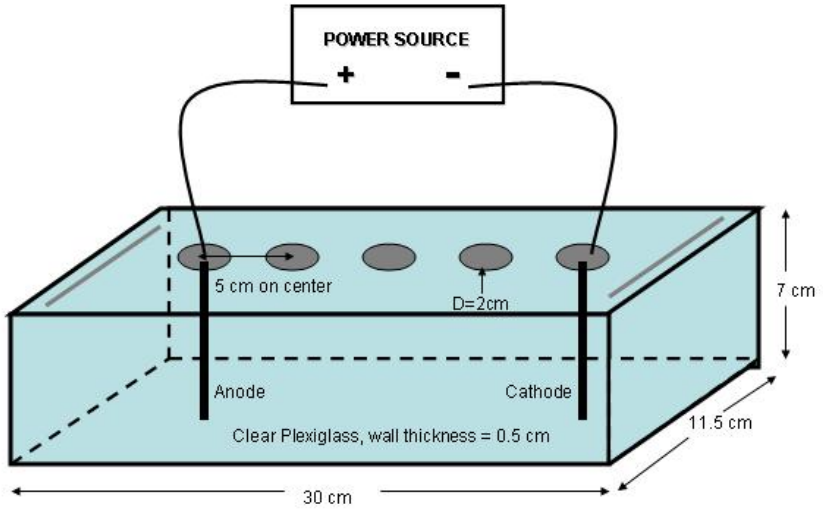


Figure 3: The principle of electrokinetic remediation, where the electrodes are placed directly into the sediment and contaminants migrate to an electrode and form precipitates

The following Table 1 delineates several electrochemical bench-scale tests run by different researchers using the experimental sediments described in Section 4.2. All experiments are referenced and/or described in detail in the Results section of this report.

Table 1: Experimental Parameters for Several Different Sediments and Conditions

Sediment	Experiment Name	Treatment *	Current (mA)	Duration (weeks)	Desorbing agent	L/S or initial WC %	Mass of sediment (g dry)
Haakonsvern	2 HCl-Haak	EDR	30	2	0.6 M HCl	4.0	100
Haakonsvern	2 DW-Haak	EDR	50	2	Distilled water	4.0	100
Haakonsvern	4 DW-Haak	EDR	50	4	Distilled water	4.0	100
Gowanus	Gow	EDR	50	2	Distilled water	5.0	100
Newtown	New	EDR	50	2	Distilled water	3.8	100
Cocheco	Expt 1-Coch	EKR	40	3	Distilled water	72	-
Cocheco	Expt 2-Coch	EKR	40	2	Acetic Acid	74	-
Cocheco	HCST-Coch	EKR	40	2	Distilled water	69	450
Cocheco	HCLT-Coch	EKR	40	4	Distilled water	70	450
Cocheco	R1 – Coch	EKR	10-20	4	Distilled water	74	450
Cocheco	R2 – Coch	EKR	30	5	Distilled water	74	450

* EDR = electrodialytic remediation, EKR = electrokinetic remediation

5.0 RESULTS

5.1 Preliminary Testing

The initial graduate student working on this project performed bench scale experiments to investigate the effects of electrokinetic remediation on chloride removal, dewatering, and PAH migration. Chloride from marine sediments is a significant concern and can limit the beneficial use options for sediment material. Furthermore, its conservative behavior means it is extremely mobile in an electric field, which makes it a good tracer for monitoring the effectiveness of remediation. Figure 4 shows a one-way ANOVA and t-test of chloride content after the electrochemical treatment of the sediment for 24 hours. The results show that the chloride is effectively removed from all three sections of the sediment reactor, and is likely being evolved as chloride gas from the anode by the following reaction:

$$(3) \qquad 2\,Cl^- \rightarrow Cl_2(g) + 2e^-$$

Results from preliminary experiments in which direct current was applied to PAH contaminated sediments from the Cocheco River in Dover, NH are shown in Figure 5. The concentrations of naphthalene before and after remediation clearly show migration of the contaminant towards the anode under an applied electric field.

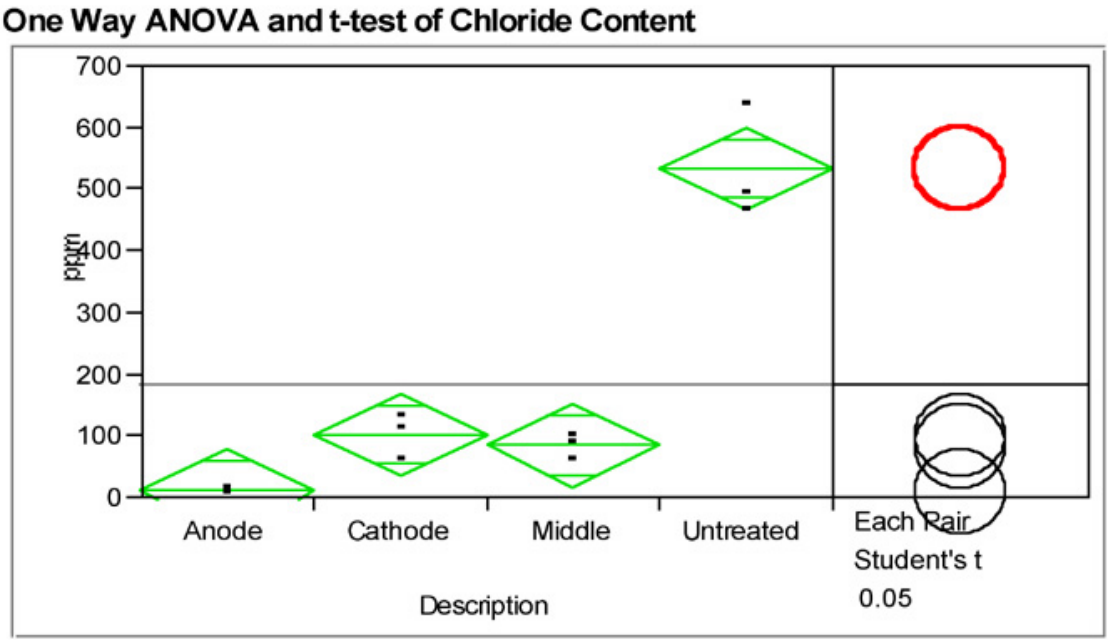


Figure 4: Chloride concentrations and t-test of sediment subjected to electrochemical treatment for 24 hours.

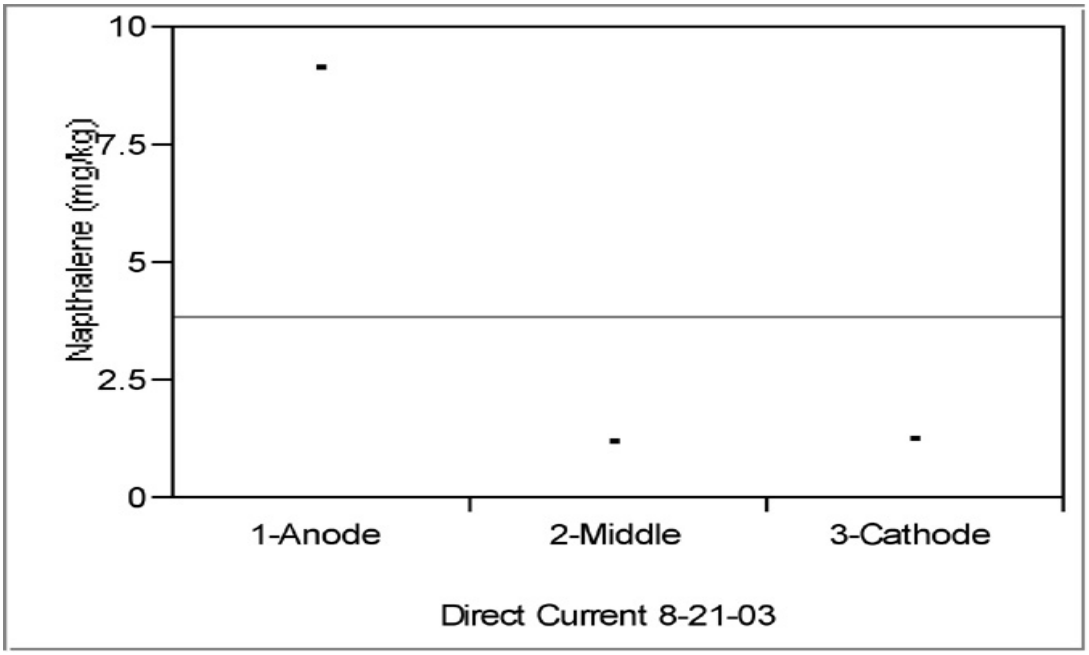
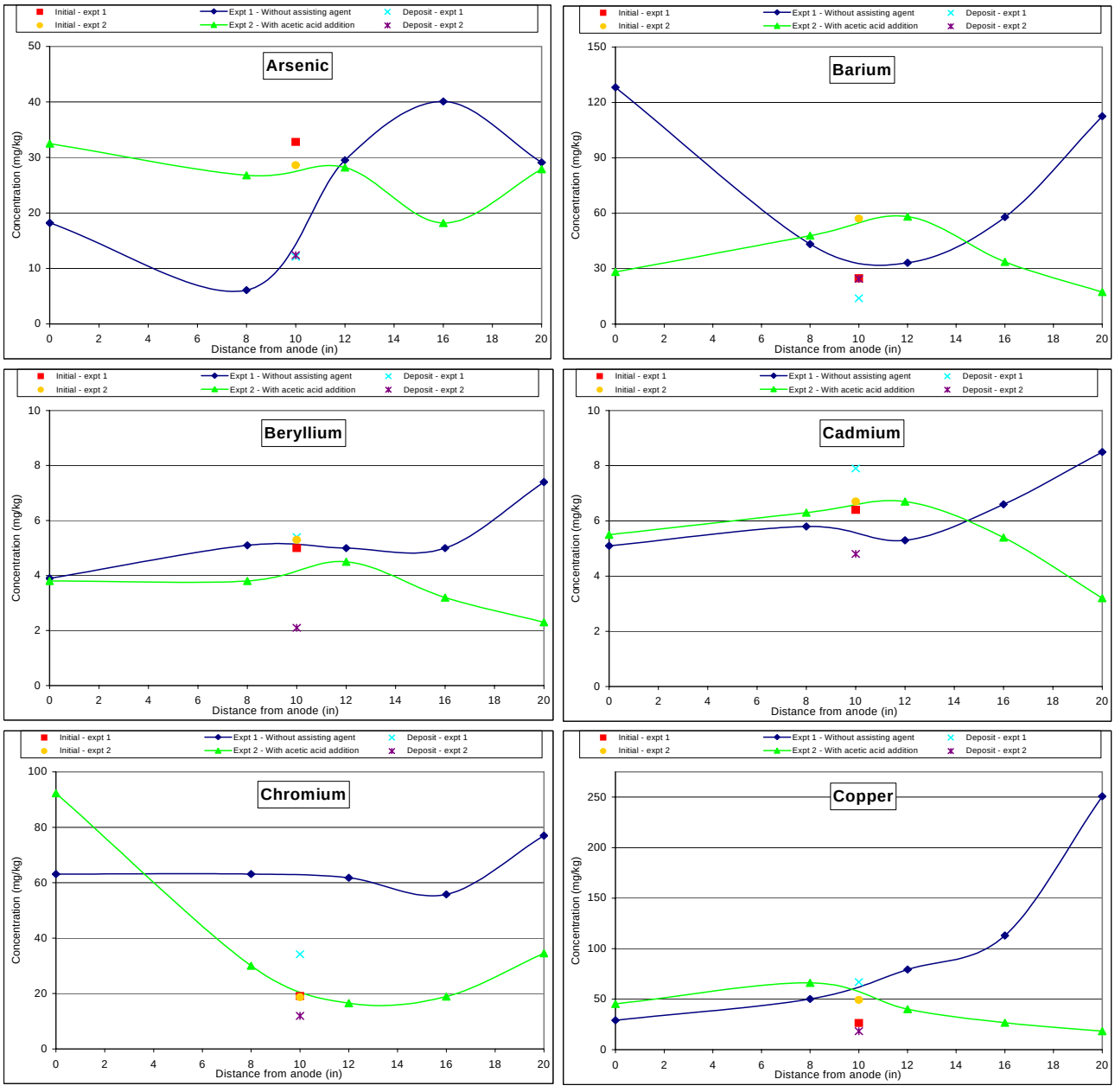


Figure 5: Migration of naphthalene in sediment subjected to electrokinetic remediation for 24 hours.

5.2 Electrokinetic Remediation of Cocheco River Sediments – Bench-scale Testing

At the University of New Hampshire, several electrokinetic experiments were performed with Cocheco River sediments, which are contaminated with PAHs and heavy metals. The work presented here further elucidates the prospect of using electrochemical remediation on sediments, however, was left incomplete by not testing the method at the pilot scale.

The visiting scholar from France witnessed differences in metal migration when acetic acid was used as an assisting agent. The results are presented in Figure 6. There are different results for the two different experiments. The major trends witnessed are reported in Table 2.



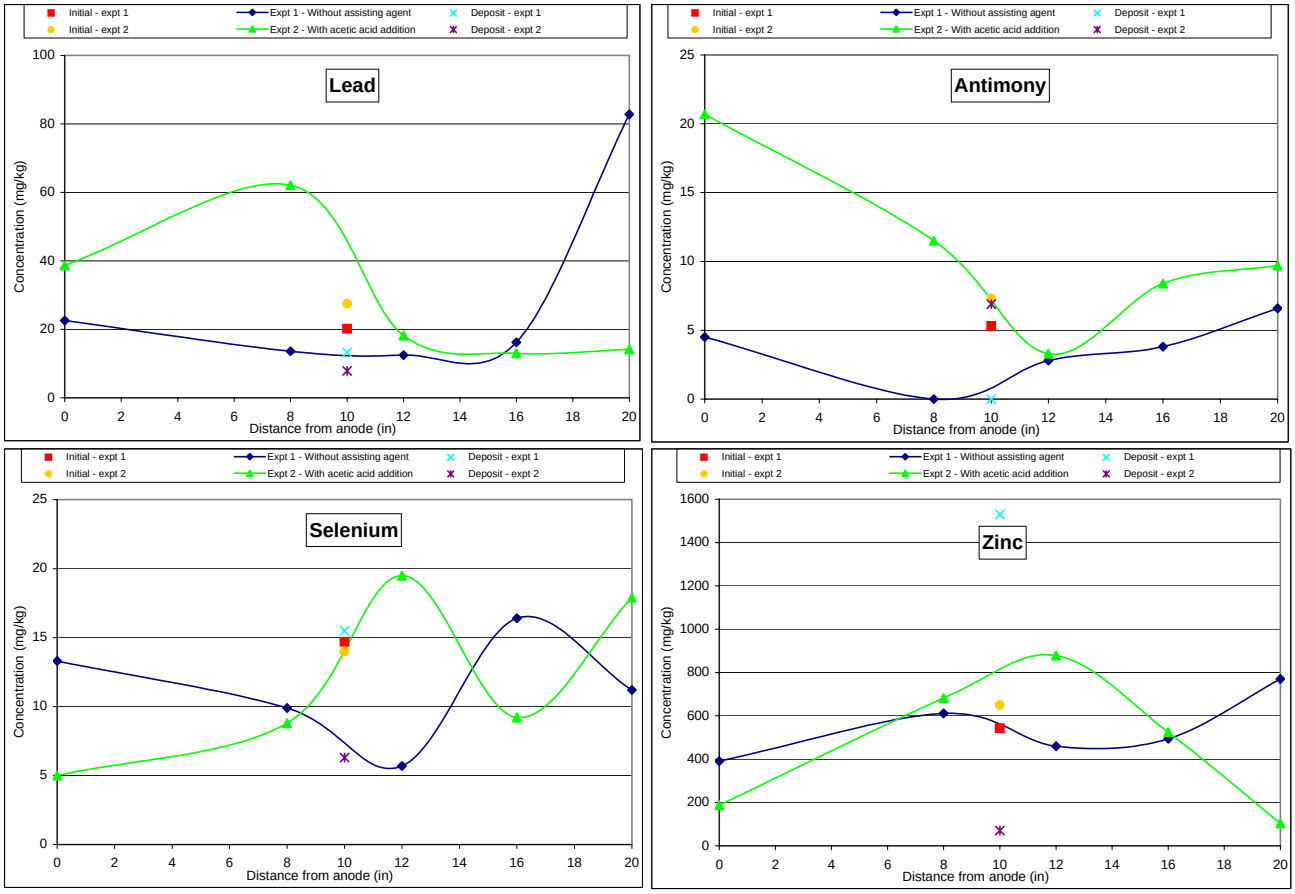


Figure 6: Comparing results of electrochemical experiments using the assisting agent, acetic acid, to mobilize metals.

Table 2: Major trends observed in Figure 6

Expt 1 - Without assisting agent	
Movement to the cathode side:	As, Ba, Be, Cd, Cr, Cu, Pb, Sb, Se, Zn
Movement to the anode side:	Ba (moved in both directions)
Expt 2 - With acetic acid addition	
Movement to the cathode side:	Se
Movement to the anode side:	As, Be, Cd, Cr, Cu, Pb, Sb
Unable to determine:	Ba, Zn

As expected from the first experiment, using only distilled water to solubilize the metals, most constituents migrated towards the cathode and became more available in the acidic side of the reactor. The addition of acetic acid produced opposite results, where metals appeared to have greater availability near the anode side. Since the pH shift was similar for both experiments, it is possible to conclude that complexes were formed with the heavy metals. Essentially, the most appropriate data would include a comparison of the total metals versus the available metals in order to determine the viability of an electrokinetic treatment scheme. This type of data is presented in section 5.2 below.

Two bench-scale experiments (HCST and HCLT) were conducted with Cocheco River sediments under a direct current of 40 mA for 15 and 33 days. Voltage was measured using the Dr. DAQ data collection system employed in previous experiments. Sediment samples were measured pre- and post-remediation for several constituents, including water content, pH, chloride, and organic carbon. Nine metals of concern and the suite of 16 PAH compounds are the contaminants of concern in the sediment; they were investigated to determine removal efficiency of electrochemical remediation.

The two reactors (30x11.5x7.5 cm) were arranged in series, each containing approximately 1500 g of wet sediment and 500 mL of additional overlying tap water. A graphite steel electrode was inserted 5 cm from each end and connected with alligator clips to the outside power source. The clips are also connected, in series, to the Dr. Daq data collector. Figure 7 shows photographs of the laboratory setup.

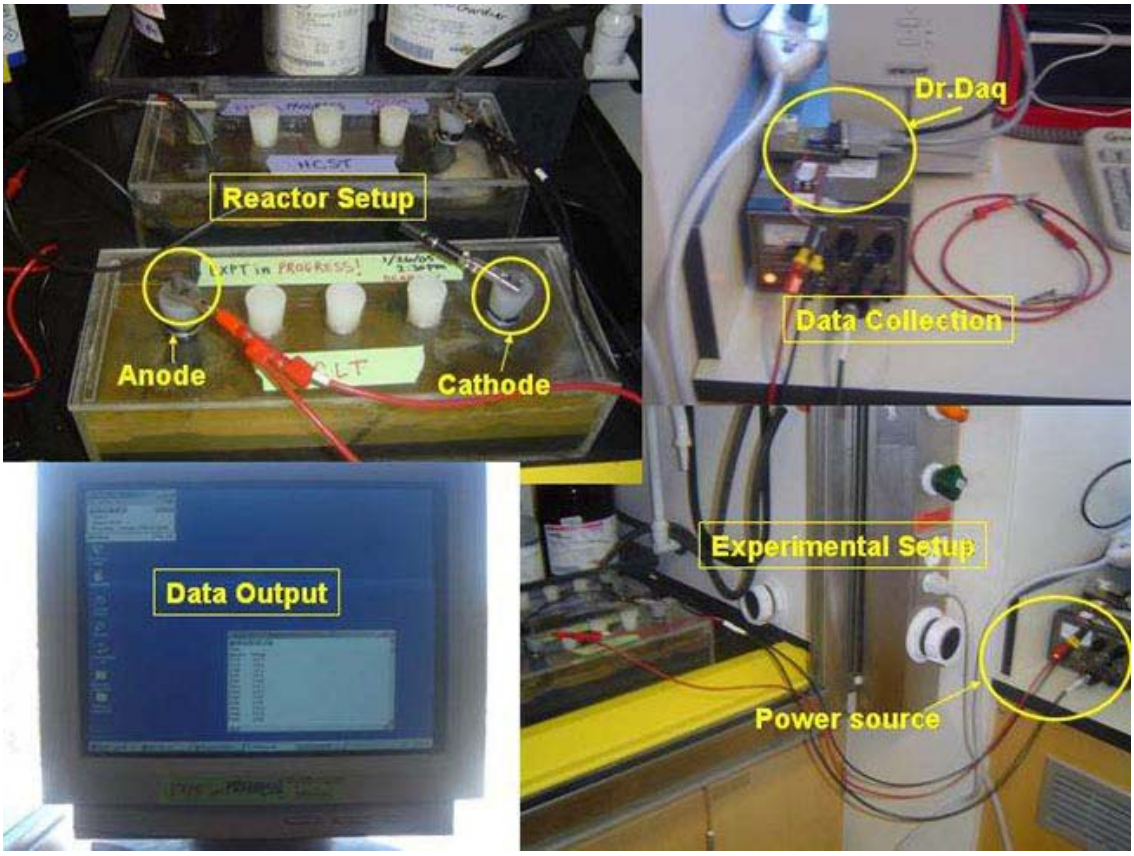


Figure 7: Bench-scale setup of electrokinetic experiments.

During the experiment, adequate water content was maintained to allow migration of the contaminants until the final days when dewatering was permitted to gain shear strength of the sediment. Figure 8 displays the dewatering of sediments during electrokinetic remediation. Significant voltage increase corresponds to a decrease in the electrical conductivity of the medium essentially reflecting a decrease in water content. Additional

water was added to continue solubilizing metals, and the re-wetting and drying phenomenon can be seen on the graph below.

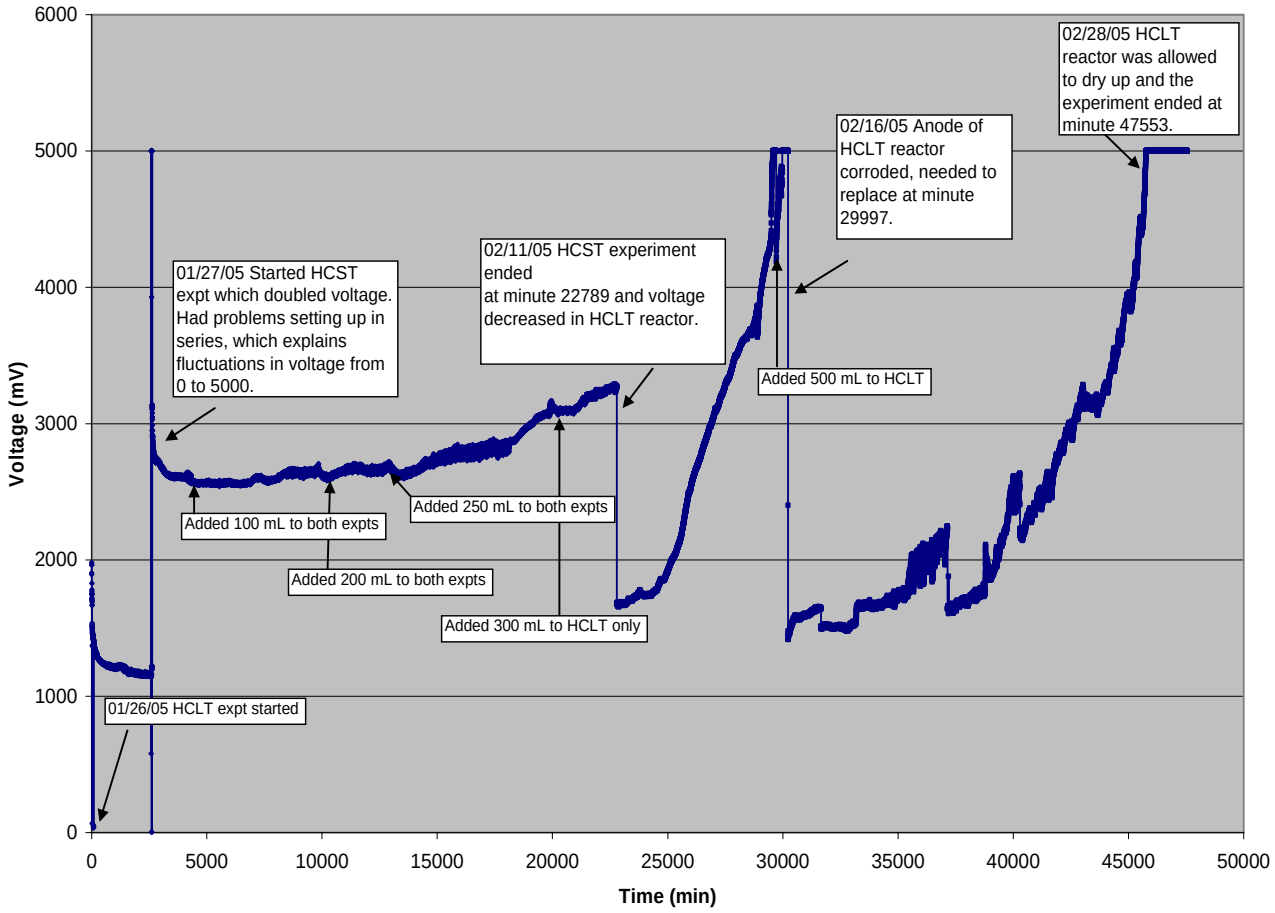


Figure 8: Voltage measurements taken during electrokinetic experimentation over time. Water was added to continue effective remediation of sediments.

Figure 9 shows the solids content of the sediment before remediation, after 15 days (dewatering not allowed at end), and after 33 days (dewatering allowed at end). Note that 5 samples (slices) and one duplicate were collected from each reactor. The theory of electroosmotic flow and electromigration of solutes are responsible for the migration of contaminants from one electrode to another. Electroosmotic flow moves from the anode to the cathode, so that the sediment near the anode is drier.

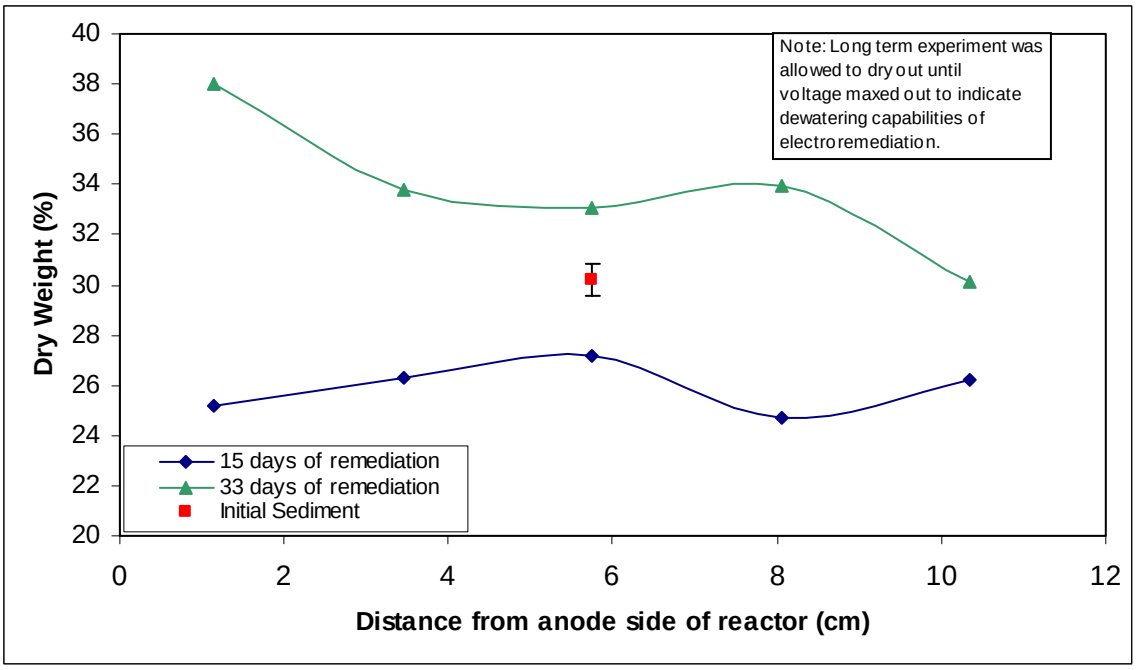


Figure 9: Dry Weight percentage of short and long term experiment.

The pH front within the reactor is also responsible for migration of contaminants. At low pH (near the anode), metals will dissolve and transport with the electroosmotic flow of water. Figure 10 shows the results, which span from a pH of 3 at the anode to above 10 at the cathode.

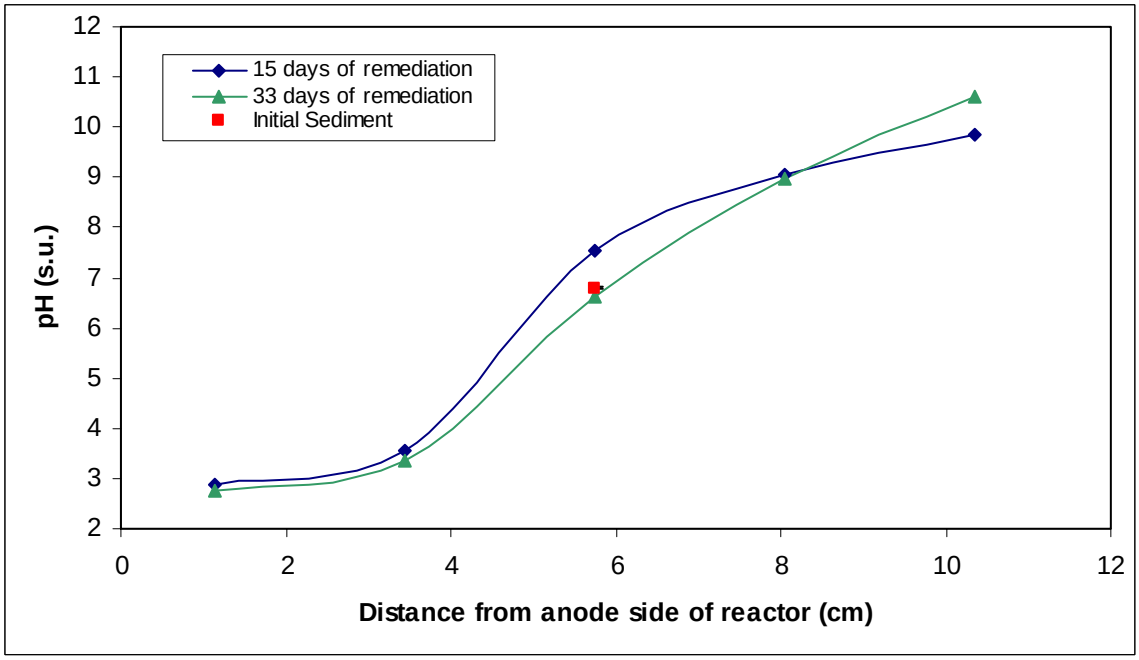


Figure 10: pH gradient in sediment after electrokinetic remediation.

Because organic contaminants tend to sorb to organic carbon found in sediments, organic carbon percentage was an important parameter to measure (Figure 11). Organic carbon tends to increase closer to the anode. PAH concentrations will then theoretically increase at the anode as well.

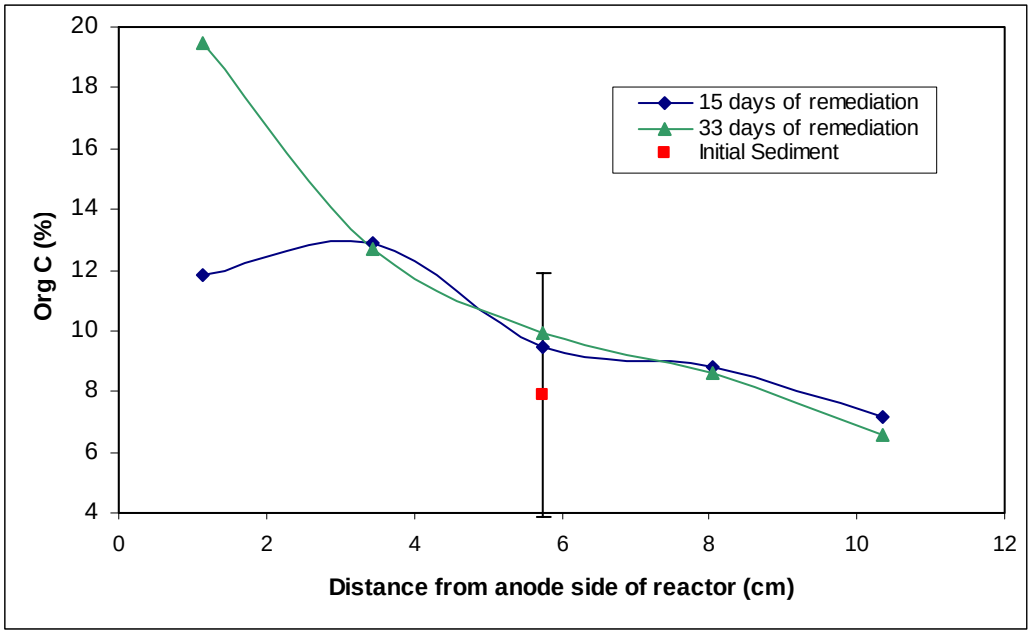


Figure 11: Organic Carbon Content in short and long term experiments.

Each of the five sampled sections was analyzed for total chloride with a chloride probe and mV meter. The results show clearly that chloride is effectively reduced from all sections of the sediment after 33 days except that at the cathode, particularly after dewatering (Figure 12).

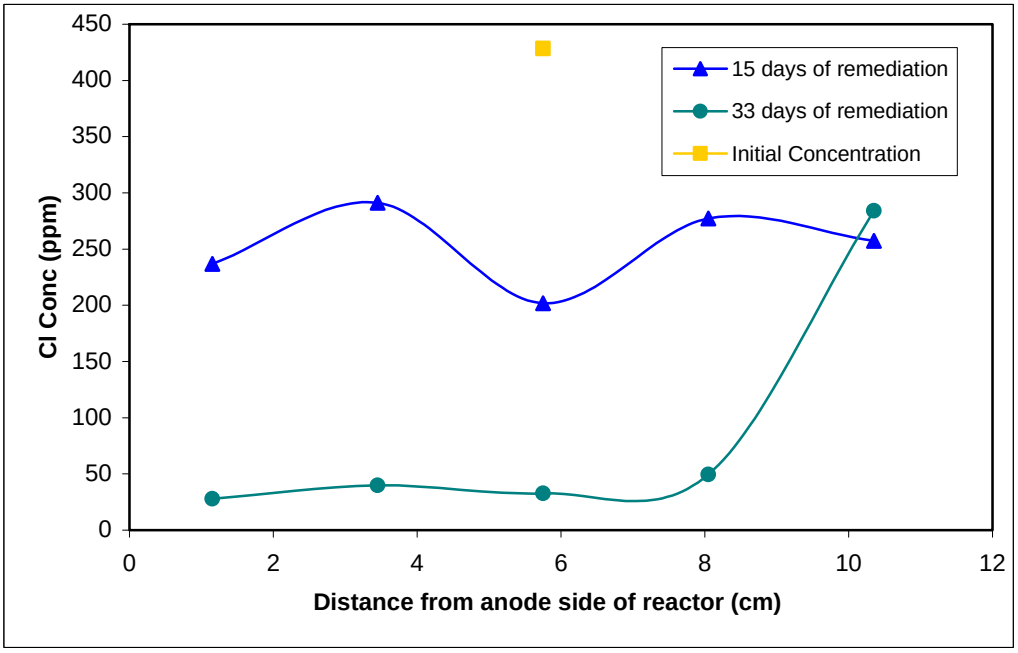
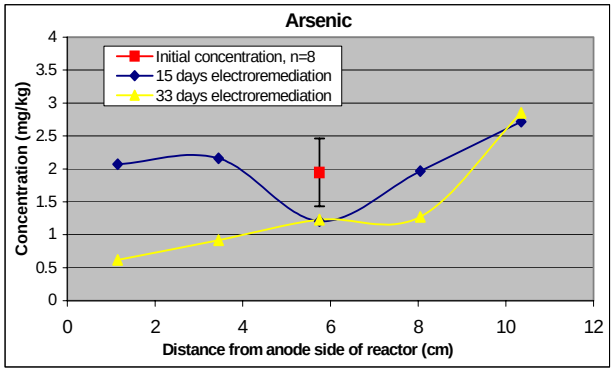
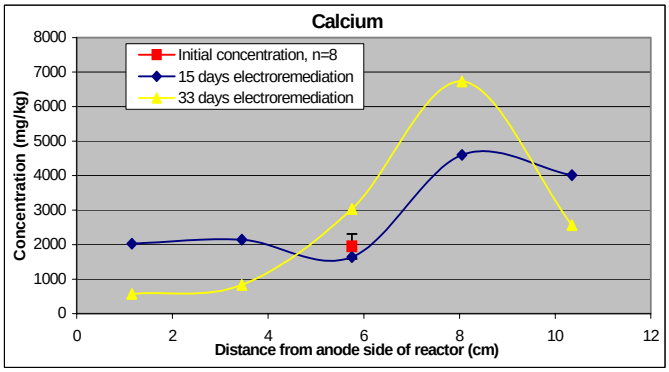


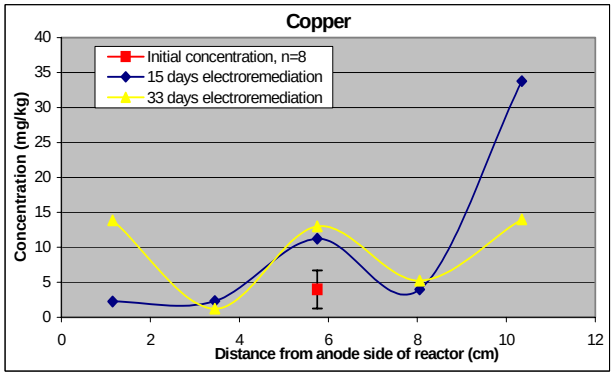
Figure 12: Chloride removal from short and long term experiments.

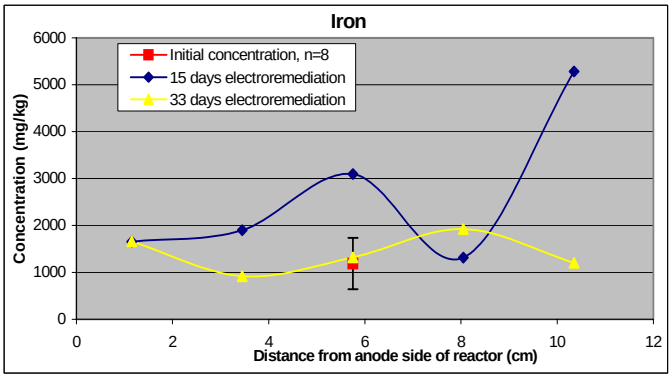
Figure 13 shows the leached results of arsenic, calcium, cadmium, chromium, copper, iron, lead, and zinc after electrokinetic remediation. Available metals concentrations at the cathode were less after 33 days of remediation than after 15 days, except in the case of cadmium and calcium. Another interesting result is that after the 33-day experiment, cadmium, chromium, copper and lead had an increase in concentration at the anode, which seems to be an anomaly in that sample or simply that a percentage of the metals did not migrate towards the cathode in that reactor but became more available after longer treatment time. Where the initial concentrations are lower than the post-remediation concentrations, this indicates that the metal became more available after treatment. Also, metals will become more available in acidic soil, so stabilization of the treated sediment may result in lower availability and should be considered before reuse.

Interpretation of these results is difficult in an electrokinetic experiment because of the physical and chemical gradients that form across the reactor, like pH and organic carbon content. These gradients may have an effect on the availability tests performed to leach the metals, for example, organic carbon content of the sample may affect the amount of metal that leaches at pH 4. In an electrodialytic cell, however, sediments are more homogenous and the gradients are not as explicit. Furthermore, metals migrate outside of the sediment compartment in electrodialytic remediation, but remain in the sediment pore water or as precipitates in an electrokinetic reactor, making calculations of percent removals ambiguous.









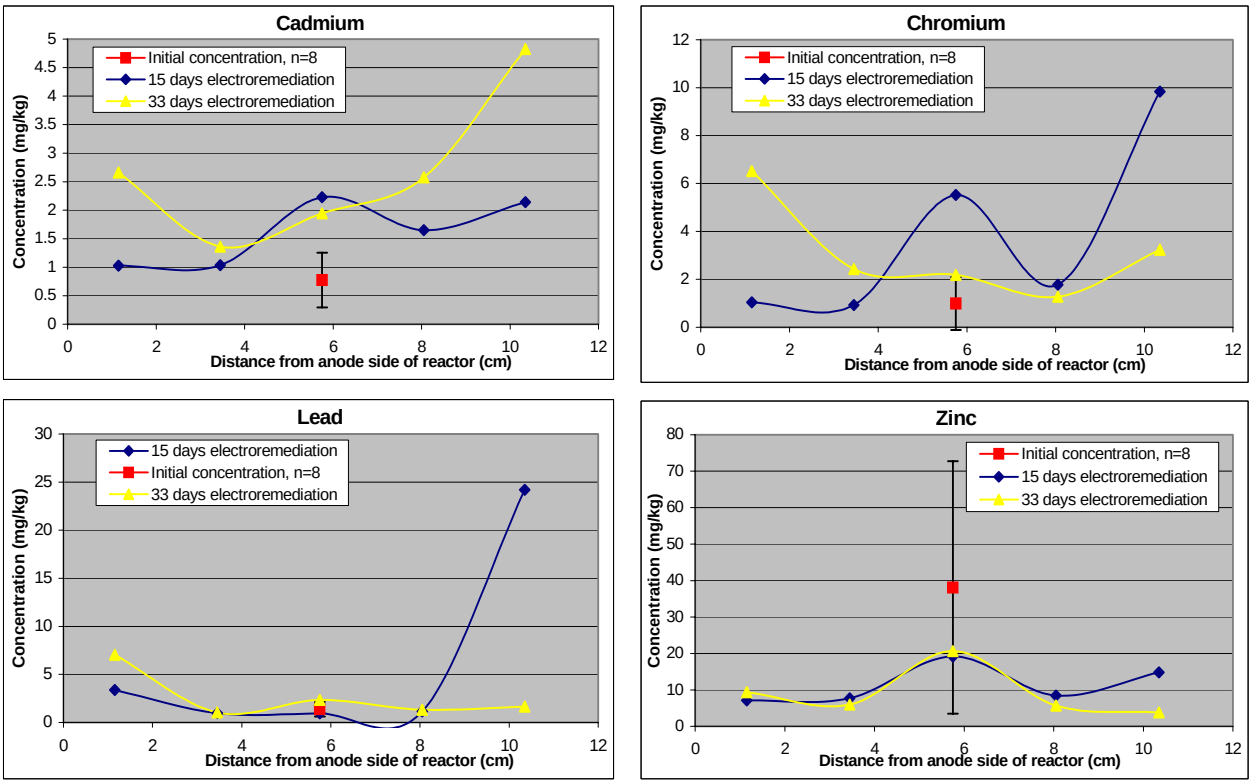


Figure 13: Metals results of slices taken from a reactor of electrochemically remediated sediment. Most metals migrate toward the cathode at 10 cm.

The last set of data is for PAH migration in the sediments. Total PAH migration is shown for experiments R1 and R2 in Figure 14. On average, the electrokinetic experiment only removed approximately 20% and 21%, respectively of total PAHs in the sediment after approximately 30 days. PAHs seemed to move towards both ends of the reactor in the first experiment and primarily to the anode in the second experiment, which is what is predicted due to the migration of organic carbon content observed in experiments HCST and HCLT.

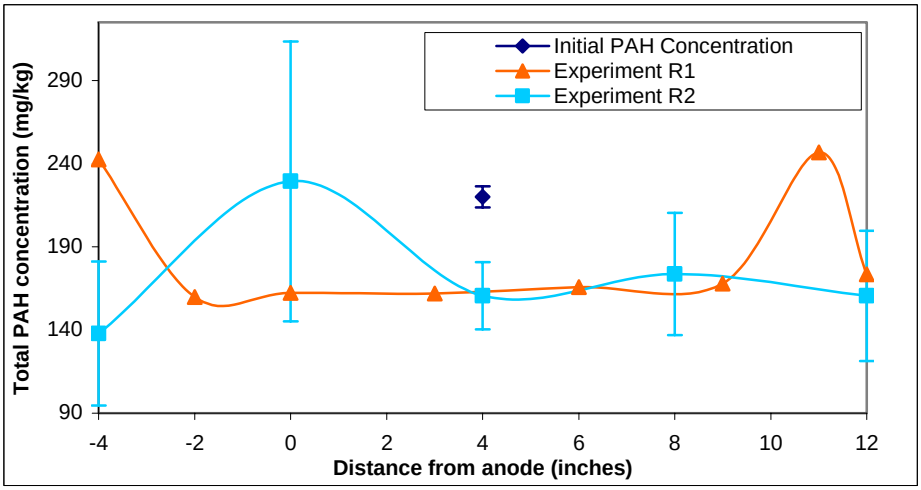


Figure 14: Analysis of PAH concentrations in electrokinetically treated sediments.

An analysis of the migration of individual PAH compounds is even more valuable to investigate, and is shown in Figure 15. In this case, using three duplicate samples, the highest concentration for most of the compounds interestingly occurs precisely at the anode.

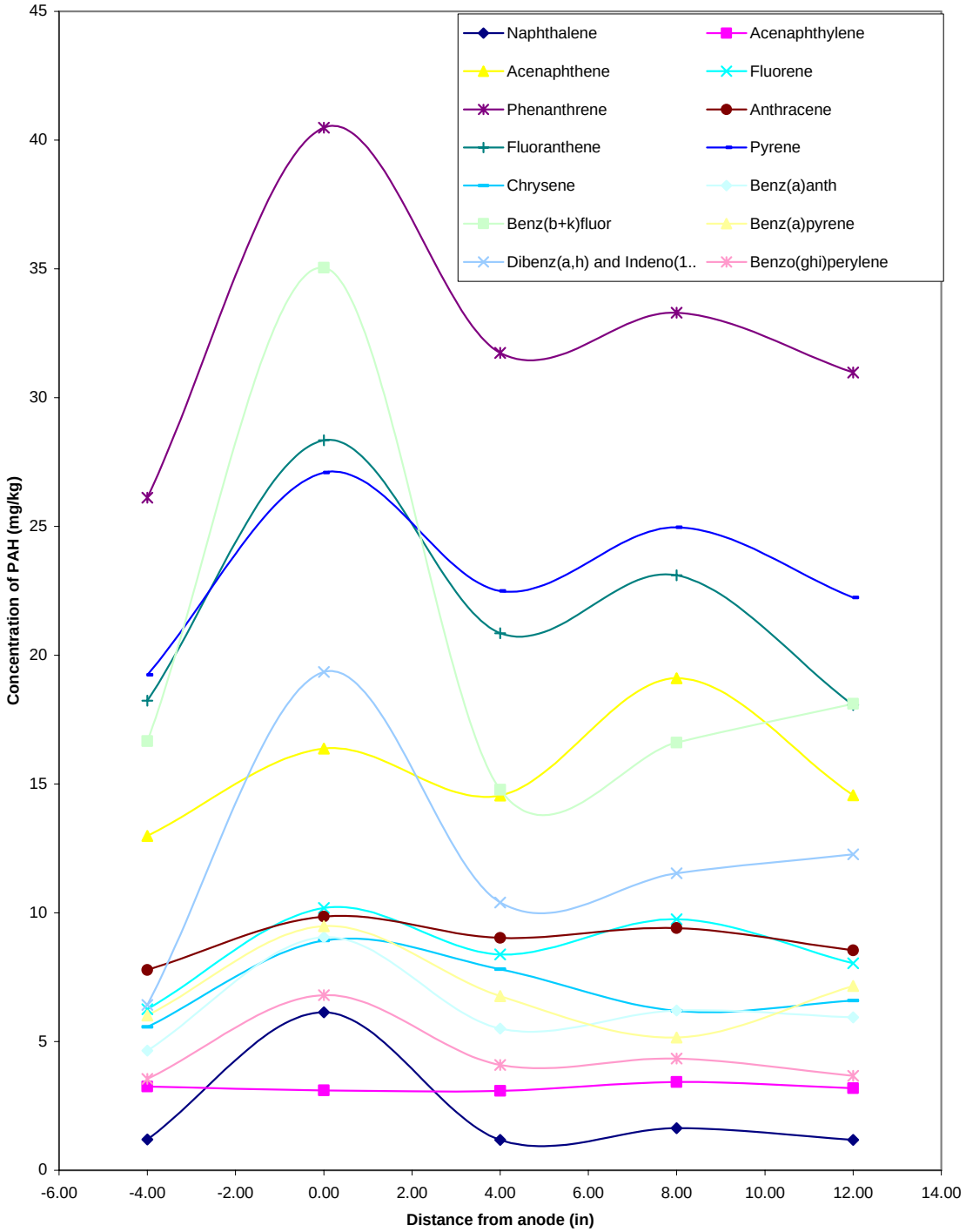


Figure 15: Analysis of individual PAH compounds in electrokinetically-treated sediment.

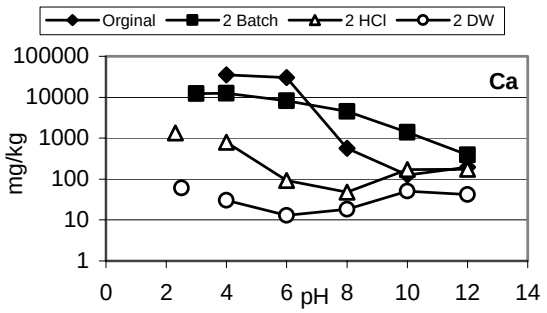
5.2 Continuing work from DTU

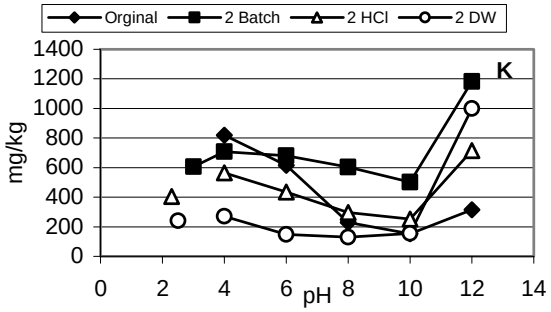
Electrodialytic remediation was used to extract heavy metals from sediment by a visiting scholar obtaining her PhD from the Technical Institute of Denmark. A paper of this work, entitled "Leaching Properties of Estuarine Harbor Sediment Before and After EDR" has been submitted to Environmental Engineering Science Journal and currently awaits peer review. Contaminated harbor sediment from two locations in the U.S. and one in Norway were subjected to electrodialytic remediation, and these were compared to controls that were not electrochemically treated. pH-static leaching, water extractions, and an availability test were used to evaluate changes in leaching properties of the treated and control sediments.

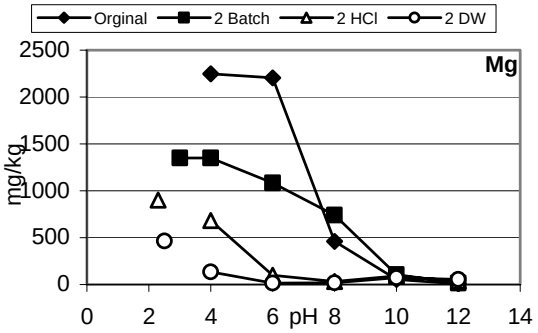
Electrodialytic treatment of contaminated Haakonsvern Harbor sediment effectively removed up to 96% and an average of 57% of the total heavy metals, Cu, Zn, Pb, Cd, Fe, Al, Ni, As, and Ti. A controlled batch experiment run without electrical current and adjusted to a pH of 3.0 with hydrochloric acid removed an average of only 36% of the total heavy metals. Treatment of more highly contaminated sediments from Newtown Creek and Gowanus Canal in the U.S. resulted in average metal removal of 89% (Cu, Zn, Pb, Cd only) and 79% (Cu, Zn, Pb only), respectively.

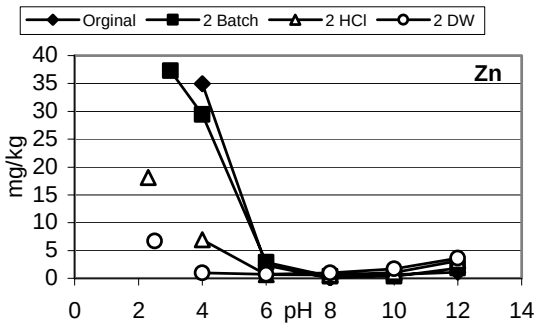
Changes in leaching behavior were witnessed in pH – static leaching experiments when contaminated Haakonsvern Harbor sediment was electrodialytically treated (Figure 16). Treatment of the sediment increased leaching of K, Pb, Cu, Ti, Cd, As, Al, and Fe, even though the total concentrations in the treated sediments were lower than in the untreated sediment for all elements. Thus, the elements were still available in the sediments after treatment, and environmental leaching was not reduced by the treatment. Increased remediation time from 2 to 4 weeks resulted in higher removals of total elements, but with similar leached concentrations of available elements, probably due to continuous changes in speciation and dissolution during electrodialytic remediation. At alkaline pH values, there was an increase in leaching of several heavy metals in the treated sediments compared to the untreated, which could cause problems if the sediment was reused in construction material with natural high pH (e.g., concrete). The water solubility of elements at their natural pH, in the untreated sediments, or achieved pH, in the treated sediments, was solubility and pH controlled. Results from the pH – static leaching showed lowest leaching of elements in the treated sediments at pH 6, and therefore stabilization, by increasing pH after treatment, could be used prior to reuse/disposal.

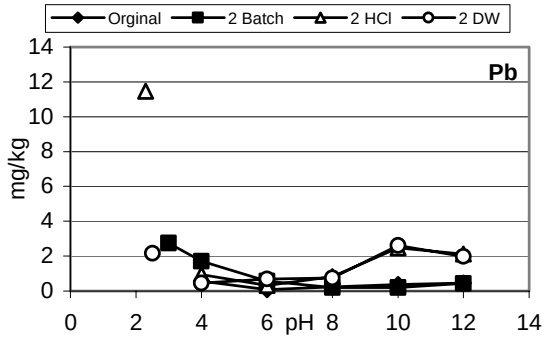
Comparing the availability of the elements before and after treatment (Figure 17), greater concentrations of Cu, Pb, Fe, Al, and Ti were measured in the treated sediment than in the untreated. Increased availability of some elements following EDR treatment is a concern that could be addressed by longer remediation time or adjusting the pH of the sediment prior to reuse. For all other elements of concern, including Zn, Cd, Ni, and As, the availability after treatment went down, demonstrating that electrodialytic remediation of contaminated sediments was effective in decreasing the availability of certain heavy metals.

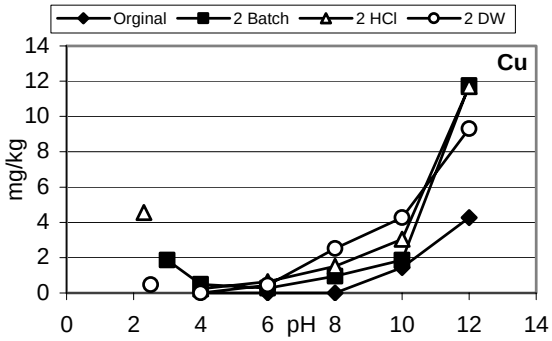

Orginal
2 Batch
2 HCl
2 DW
Ca
mg/kg
100000
10000
1000
100
10
1
0 2 4 6 pH 8 10 12 14

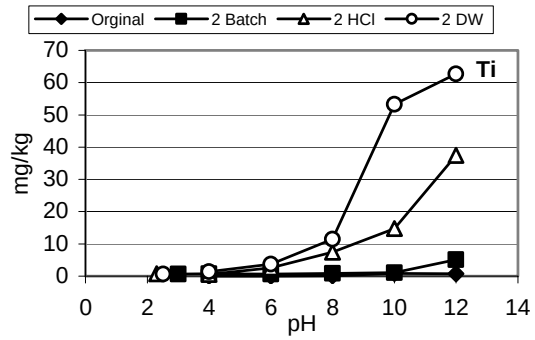

Orginal
2 Batch
2 HCl
2 DW
K
mg/kg
1400
1200
1000
800
600
400
200
0
0 2 4 6 pH 8 10 12 14

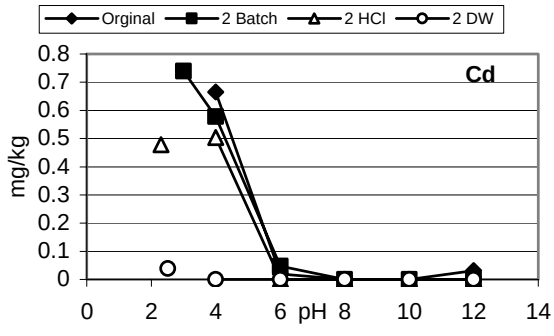

Orginal
2 Batch
2 HCl
2 DW
Mg
mg/kg
2500
2000
1500
1000
500
0
0 2 4 6 pH 8 10 12 14


Orginal
2 Batch
2 HCl
2 DW
Zn
mg/kg
40
35
30
25
20
15
10
5
0
0 2 4 6 pH 8 10 12 14


Orginal
2 Batch
2 HCl
2 DW
Pb
mg/kg
14
12
10
8
6
4
2
0
0 2 4 6 pH 8 10 12 14


Orginal
2 Batch
2 HCl
2 DW
Cu
mg/kg
14
12
10
8
6
4
2
0
0 2 4 6 pH 8 10 12 14


Orginal
2 Batch
2 HCl
2 DW
Ti
mg/kg
70
60
50
40
30
20
10
0
0 2 4 6 pH 8 10 12 14


Orginal
2 Batch
2 HCl
2 DW
Cd
mg/kg
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0 2 4 6 pH 8 10 12 14

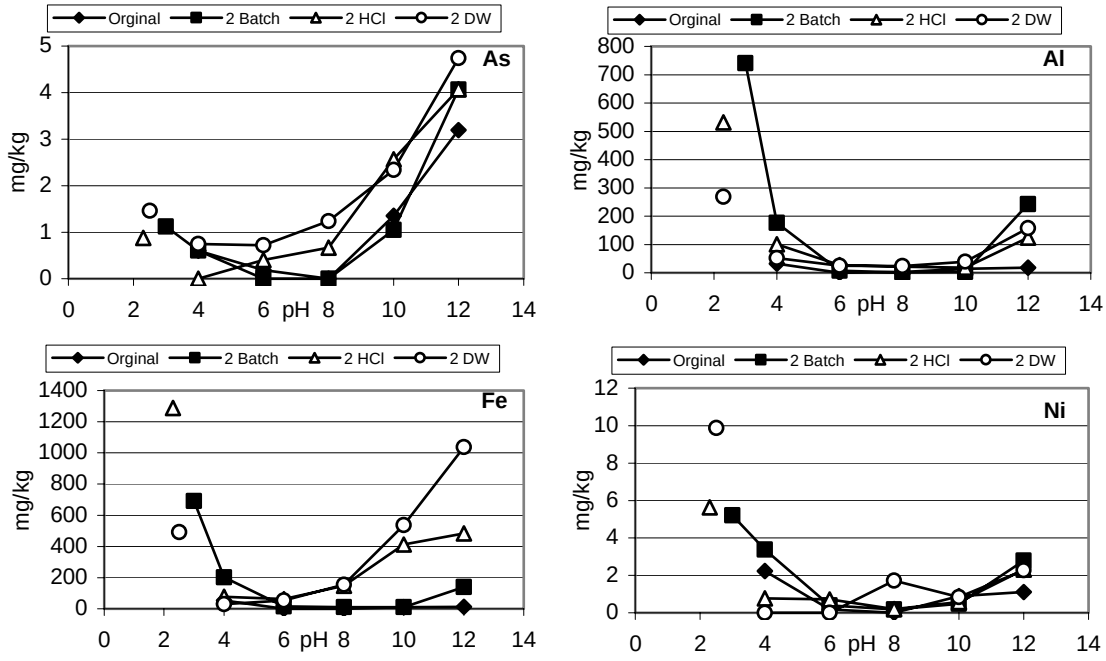


Figure 16: pH – static leaching at several pH for the untreated (original), control (batch) and treated (HCl and DW) Haakonsvern sediments

**Isolated marks represent the leachability in water at the respective, post-treatment pH of each sediment sample.*

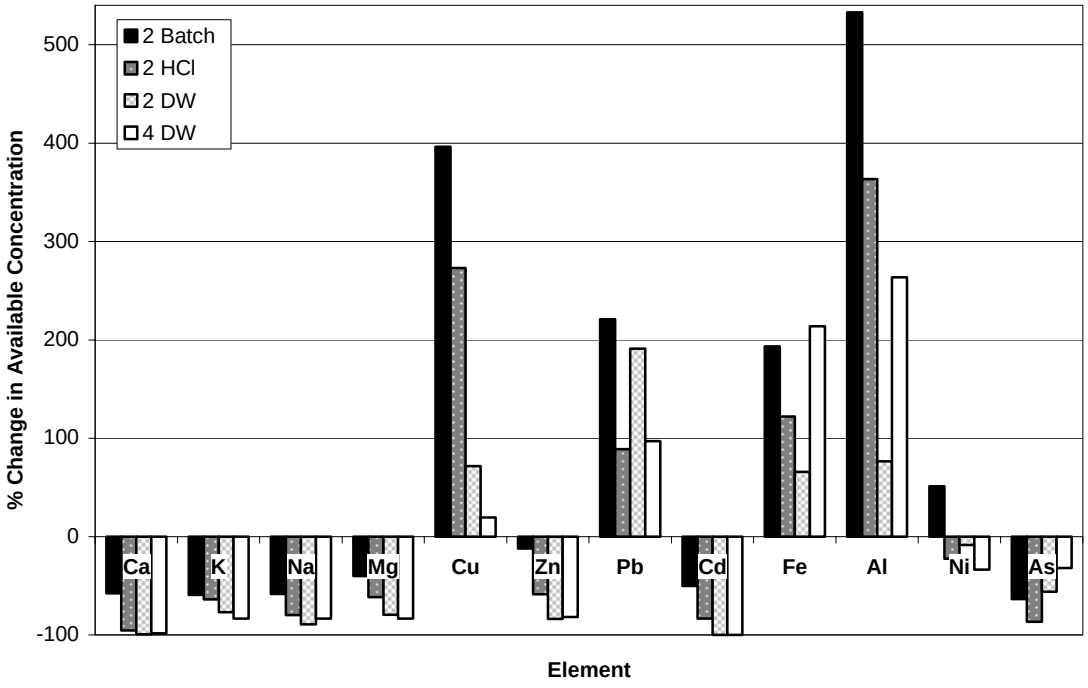


Figure 17: Percent change in availability compared to the untreated Haakonsvern sediment

6. DISCUSSION

Large amounts of sediments are dredged around the world to maintain navigational depths or improve water quality. Ocean dumping or land application are two means to dispose of uncontaminated or slightly contaminated dredged sediments. Sediments can be contaminated with heavy metals, PAHs, PCBs, and other anthropogenic compounds. Disposal of contaminated sediments in confined disposal facilities (CDFs) on land or confined aquatic disposal (CAD) cells at sea are the most common options for handling contaminated dredged sediments. The use of CDFs and CAD cells are simply a means of buying time, because they are not effective solutions to the problem of contaminated sediments.

The alternatives to disposal of contaminated sediments are reuse and treatment. Reuse of sediments depends on the sediment properties, such as strength, oxide content, or contaminant concentrations. Contaminant removal methods, such as those developed for soil, can be applied to sediments, but are still limited by inadequate research at the laboratory scale. Reuse and treatment are not widespread in use, mainly because of increased cost compared to disposal.

Electrochemical remediation is one type of treatment that can be cost-effective because it is performed with a low, direct current between two electrodes. It is a developing technology because it is intended to separate and extract heavy metals and organic contaminants from saturated or unsaturated soils and sediments, as well as stabilizing the media via dewatering. The results obtained from this study indicate that there is potential to use electrochemical remediation to achieve those three treatment goals in sediments in both an *in-situ* or *ex-situ* application.

In this study several chemical and physical parameters were investigated to determine the effectiveness of electrochemical remediation. Several bench-scale studies, and a thorough literature review of past research, indicate success for the mobilization of metals in sediments when subjected to an applied electric field. Comparing past work using electrodialytic experiments (Nystrom, 2004) to the current study using electrokinetic experiments, the electrodialytic setup produced more effective results due to the use of electrolyte solution compartments that attract the metal complexes rather than expecting the metals to plate directly to an electrode to be removed. However, the electrodialytic method can only be applied to *ex-situ* sediments, where the electrokinetic method is accomplished by placing electrodes directly into *in-situ* sediment.

Although there is a great deal of research on using assisting agents in the literature; such as anionic, cationic, and non-ionic surfactants, ethylenediaminetetraacetic acid (EDTA), and ammonium citrate (Kaya, 2005; Giannis; 2005; Pedersen, 2005); results here showed that the use of the assisting agents acetic acid and hydrochloric acid did not produce a significant increase in metal removal percentages. The experiments performed using acetic acid actually reversed the direction of migration for most metallic complexes and ions towards the anode rather than the cathode, which was the case in the distilled water experiments; however, did not increase removal. HCl was evaluated in the EDR

experiment of the Haakonsvern harbor sediments as a desorbing agent to increase removal. HCl dissolves carbonates in the sediment, lowers the pH and releases heavy metals. Chlorocomplexes can be formed to further enhance metal solubility (Nystrom et al., 2004). The potential for chlorocomplexation by HCl did not increase the metal removal compared to using distilled water in these experiments. HCl increases the ionic strength of the solution, which influences the electrical conductivity and current efficiency. H^+ and Cl^- are more mobile in the electric field than divalent ions; and thus, the current efficiency for heavy metal ions is reduced (Acar and Alshawabkeh, 1993). When using HCl, the sediment was acidified immediately, which did not seem to influence the removal efficiency compared to using distilled water, where acidification took place during the course of the experiment. These results suggest low influence of using HCl as a desorbing agent on the solubility of heavy metals, because it did not contribute to greater elemental removals following EDR treatment.

Probably the most significant conclusion to come of this research was that the availability was found to increase for certain metals after treatment of the sediments. In pH dependent leaching tests, element leaching from the sediment was generally pH–dependent, both before and after treatment, and the results also suggested that greater liquid-to-solid ratios (L/S) increase elemental solubility. Acidification of the sediments caused by treatment resulted in higher water dissolution of elements at the sediments achieved pH, compared to the untreated sediment. Significant fractions of total concentrations were removed during treatment (typically 35-95%); however, the total availability of metals in the treated sediment samples increased for Cu, Pb, Fe, and Al (for which total concentrations decreased by up to 56%, 64%, 47%, and 90%, respectively). All other elements of concern were less available after treatment. This research highlights the importance of understanding contaminant speciation and availability, as total metals concentrations, in this particular case, do not relate to estimates of the environmental and ecological availability of metals.

Organic carbon content was measured in the post-treated sediments of an electrokinetic experiment. These results showed that organic carbon content was higher near the anode, demonstrating the electrophoresis phenomena in which negatively charged, natural organic matter will migrate towards the anode. Since organic pollutants, such as PAHs, sorb strongly to natural organic matter, it would be assumed that the PAHs will also travel towards the anode. Several papers suggest that black soot carbon found in sediments is actually the strongest organic sorbent for PAHs and PCBs (Lohmann, 2005; Bucheli, 2003; Gustafsson, 1997). The measurement of the soot carbon fraction of the sediments was measured in the post-treated sediments also; however, did not produce the expected results that indicate migration of soot carbon to the anode. Soot carbon fractions were variable throughout the reactor. Most importantly, however, data collected for PAH migration in electrokinetic experiments showed that most PAH compounds did migrate to the location of the anode and total PAHs were decreased by 20% in one month at a low current of 10-20 mA.

7. TECHNOLOGY TRANSFER AND MANAGEMENT APPLICATION

The lack of cost-effective solutions to the contaminated sediment/dredged material issue has the potential to have significant effects on many coastal environments by putting significant economic and political pressure on the existing legislation; therefore, it is essential that innovative and more cost-effective approaches be developed to treat contaminated sediments. This project investigated a technology that could be extremely cost-effective, particularly if used in conjunction with the beneficial use of sediment post-treatment.

Navigational dredging can be viewed as a means of cleaning up a diffuse, non-point source of contaminants to the coastal environment, however, proper management of the sediment must occur for the dredging to have this fortuitous benefit. Proper management will not be maintainable without cost-effective and sustainable management alternatives.

Future work in order to bring this project to the full scale includes testing at the pilot scale, which was left unfinished in this work, to evaluate removal efficiency and large scale remediation potential. Remediation costs must be estimated and reuse options should be recommended for the remediated sediments.

8. ACHIEVEMENT AND DISSEMINATION

Some very compelling experimental data resulted from research conducted by the visiting scholars from Denmark supported by this project. The following journal articles report the outcomes:

Pedersen A.J., K.H. Gardner. (2003). "Characterization of municipal solid waste incineration fly ash before and after electrodialytic treatment," *Journal De Physique IV* 107: 1029-1032.

Pedersen, A.J., K.H. Gardner (2003). "Electrochemical Remediation of Dredged material for Beneficial Use," *In* Beneficial Use of Recycled Materials in Transportation Applications, T.T.Eighmy Eds., Air and Waste Management Association Press, 389-399.

Nystrom, G.M., K.H. Gardner, and D.A. Aulisio. (under review). Leaching characteristics of estuarine harbor sediments before and after EDR. Environmental Engineering Science.

Anne Pedersen completed her PhD thesis in 2002 at the Technical Institute of Denmark on the Electrodialytic Removal of Heavy Metals from Fly Ashes. Gunvor Marie Nystrom completed her PhD thesis in 2004 at the Technical Institute of Denmark on the Electrodialytic removal of heavy metals from contaminated harbor sediments.

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