A Sustainable Remediation Approach for Complete Destruction of Chloroethanes in Groundwater

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A SUSTAINABLE REMEDIATION APPROACH FOR COMPLETE DESTRUCTION OF CHLOROETHANES IN GROUNDWATER

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University
Agriculture and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science in Civil Engineering

in

The Department of Civil and Environmental Engineering

by

Michael Cheatham
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ABSTRACT

An up-flow column study was operated in a greenhouse composed of a sand/peat mixed media to investigate the effectiveness of an aerobic zone on the disappearances of chloroethane. The oxygen was supplied by mean of porous Silastic tubing under pressure with a breathing air gas cylinder. Chloroethane was generated via reductive dechlorination of 1,1,1-trichloroethane (TCA) and 1,1-dichloroethane (DCA) in anaerobic bioreactors (ABRs). The columns study was conducted with two duplicate reactors (operated in parallel) that underwent separate perturbations of breathing air introduction. Aqueous samples were collected in 160 mL microcosm bottles and analyzed on a GC equipped with a Flame Ionization Detector. A statistical analysis of the data was conducted using a 2-tailed Student’s T-test. Results showed that decreases in aqueous chloroethane were greater during periods of aeration in both reactors, with approximately 41% changes in chloroethane concentration from the influent to the final port (Port 3), during periods of aeration.

An analysis of changes that ensued from implementation of a full-scale anaerobic bioreactor system (ABR) to replace a physical/chemical treatment scheme was conducted using site specific data. Carbon dioxide emissions and energy requirements associated with operation of the site with each treatment scheme were compared. Specifically, source of energy to run the site, transportation of generated sludge, and utilization of chemicals (sodium hydroxide and sulfuric acid) were studied. Production of grid-based energy for site operation was eradicated through implementation of a solar-system. Generated sludge production decreased, resulting in a 92% decrease in implied inputs to the Petroleum Refineries sector. Carbon dioxide emissions and energy inputs to commercial production of sodium hydroxide and sulfuric acid also decreased by 92%.
Chapter 1: Introduction, site background, and purpose of study

1.1 A brief history of Chlorinated Volatile Organic Compounds of interest

Anthropogenic production of synthetic chemicals has offered solutions to problems in industrial processes throughout history. Namely, the production and commercialization of chlorinated volatile organic compounds (cVOCs), following the industrial revolution, has been of interest in environmental research and toxicology due to the frequency of spills and subsequent exposure of these chemicals to wildlife and humans. cVOCs were popular throughout the latter half of the 20th century in various industries such as aerospace, military, dry-cleaning, automotive, and electronics (Doherty et al., 2005). These solvents were of particular interest for their ability to degrease complex molecules such as fats, oils, waxes and resins (USGS, 2014). However, their production, utilization, and disposal have created concerns throughout the United States especially due to their presence as Dense Non-Aqueous Phase Liquids (DNAPLs) that can deeply penetrate groundwater aquifers and bedrock, making approaches to their remediation quite complex. For example, roughly 15% of projects governed by Brownfields and Environmental Restoration Programs, in the Department of Toxic Substances Control in California, include the presence of cVOCs (Department of Toxic Substances Control; California Environmental, 2010).

Two cVOCs studied in environmental sciences are 1,1,2-trichloroethene (TCE) and 1,1,1-trichloroethane (TCA). TCE commercialization began in 1921 in many of the aforementioned fields and production peaked in the U.S. at 272 thousand pounds/year in 1970 (Doherty, 2005). It was also in the 1970’s that adverse health effects were discovered from TCE exposure, and demand decreased drastically following. TCA production peaked shortly after the downfall of TCE in the 1980’s, with 121,000 metric tons being produced throughout the entire decade. Dow
Chemical was the first and only major producer of TCA. Having similar characteristics to TCE, TCA quickly became a popular cVOC for cleaning and degreasing. Shortly after however, section 604 of the 1990 Clean Air Act Amendments proposed that all production and utilization of TCA was to cease as of January 1st, 2002 (EPA; Section A. Clean Air Act Requirements, 2013).

Toxicological studies have found that both TCE and TCA impact the neurological system in humans, and TCE is considered a Group 2b, or “probable”, human carcinogen (ATSDR, 1997). The United States Environmental Protection Agency (USEPA) reports the Maximum Contaminant Levels (MCLs) for both TCE and TCA to be 0.005 mg/L in drinking water sources (USEPA, 2014). 1,1-Dichloroethane (DCA) and cis-1,2-dichloroethene (cDCE) are daughter products resulting from the degradation of 1,1,1-TCA and TCE respectively via anaerobic processes. Anaerobic and abiotic degradation pathways of 1,1,1-TCA, TCE, and subsequent daughter products are understood (Figure 1.1) (RE-SOLVE Inc. Superfund Site Environmental Restoration Program, 2009). As seen in the anaerobic degradation of TCE, production of 1,1-DCE and trans-1,2-DCE are possible; however, cDCE is the dominant anaerobic daughter product of TCE. cDCE is a hepatotoxic and renal-toxin and considered a human carcinogen. The EPA reports an MCL of 0.07 mg/L for cDCE in drinking water sources (USEPA, 2014). Acute exposure to DCA inhalation has resulted in central nervous system depression and cardiac arrhythmias in human subjects (USEPA, 2013). Although there is currently no federal MCL assigned to DCA in drinking water, the California Department of Public Health (CDPH) does enforce an MCL of 0.005 mg/L in their drinking water sources for DCA, citing evidence of cancer causing effects being associated with consumption of this organic compound (CDPH, 2014). Vinyl chloride and chloroethane are daughter products that result in the anaerobic,
microbial degradation of cDCE and DCA, respectively (Figure 1.1). Vinyl chloride is a known human carcinogen in addition to being a cardiovascular toxicant, and a deterrent to proper development of most organ systems (USEPA, 2007). Accordingly, the EPA has issued an MCL of 0.002 mg/L in drinking water sources for vinyl chloride (USEPA, 2014). Chloroethane is also a cardiovascular and developmental toxicant that has been listed as a priority pollutant by the Clean Water Act but currently has no federal EPA MCL regulation in drinking water, and is classified as a Group 3 carcinogen (not classifiable as a human carcinogen) according to the Wisconsin Department of Natural Resources (WDNR, 2011). Although Figure 1.1 indicates that chloroethane may proceed to ethane under anaerobic conditions, as discussed later in the thesis, chloroethane has been found to accumulate under some anaerobic conditions. In summary, the presence of these organic compounds in the environment poses various negative health effects to humans, as well as wildlife, and their removal from groundwater is important for remediation approaches at individual sites.

1.2 Natural attenuation and anaerobic bioreactor systems

In the past, site remediation technologies for chlorinated organic compounds were based on high-energy input systems that diminished in effectiveness over time, in what is known as pump and treat methods (The Interstate Technology and Regulatory Council, 2008). While these conventional methods are sometimes effective at treating contaminated water, the operation and maintenance demands of these systems are usually high. The treatment methods sometimes do not result in reaching regulatory levels of contaminants in a timely manner because of the mass transfer limitations for cVOCs present in DNAPL or sorbed onto aquifer solids.

Natural attenuation is the process by which pollutants in groundwater and soil are passively attenuated via natural processes, such as microbial metabolism (U.S. EPA, 2014). If
natural attenuation is completely effective, this approach often eliminates high chemical and energy demands of

Figure 1.1: Anaerobic and abiotic degradation pathways of 1,1,1-TCA and TCE (RE-SOLVE Inc. Superfund Site Environmental Restoration Program, 2009).

conventional pump and treat systems. Various in-situ processes may contribute to the minimization of contaminants’ concentrations and toxicities including mass losses through biodegradation, dilution, adsorption, volatilization, and abiotic degradation processes. Fortunately, biodegradation of many cVOCs, such as TCE and TCA to daughter compounds will occur under favorable conditions, which makes natural attenuation a popular remediation technique (USGS, 2014). At many sites, however, processes are not rapid enough to be
protective of the surrounding environment and active remediation processes must be employed. Typically, active remediation systems require pumping of large amounts of groundwater to contain a contaminated plume. After the water arrives at the surface through pumping, conventional physical/chemical processes are used for remediation of contaminants. Recently, alternate low energy, sustainable treatment schemes have been proposed to replace the high-energy systems. These include engineered wetland systems (Kassenga et al, 2004) which treat cVOCs by retarding their movement through a system through sorption, coupled with anaerobic metabolism of cVOCs by microbial populations that can use cVOCs as electron acceptors in their metabolism. When these systems are built without vegetation, they can be termed anaerobic bioreactors (ABRs). In this context, ABRs encourage reductive microbial processes, often associated with natural attenuation, to take place thereby eliminating chemical dependency and the energy necessary to drive physical processes in conventional pump and treat systems.

1.3 The project site: RE-SOLVE Inc.

RE-SOLVE Inc. is a former waste reclamation facility located in North Dartmouth, Massachusetts (EPA, 2014; Figure 1.2). The site was in operation for 24 years, from 1956 to 1980, and handled wastes produced by industrial processes for the purpose of recycling the solvents for further use by its clients. After its closure, the site was put on the Environmental Protection Agency’s National Priority List (NPL) in 1983 to conduct remediation of the soils and groundwater on the site (roughly 6 acres, in total). Situated on the site were 4 un-lined lagoons where wastes were often disposed of or stored. A large area designated for land farming of polychlorinated biphenyls was also present. Oil waste from distillation towers was often spread across the site to control dust. Polychlorinated biphenyls (PCBs) and various cVOCs, including
vinyl chloride, 1,1-dichloroethene, TCE, cDCE, chloroethane, and 1,1,1-TCA can be found in the soils, sediments, ground waters, and surface waters surrounding the site (EPA, 2014).

Figure 1.2: Aerial view of RE-SOLVE Superfund site in North Dartmouth, MA (RE-SOLVE Inc. Superfund Site Environmental Restoration Program, 2009)

The RE-SOLVE Superfund site is located roughly 500 feet from the Copicut River that flows from the northern Copicut Reservoir down into the Cornell Pond (Figure 1.3) (RE-SOLVE Inc. Superfund Site Environmental Restoration Program, 2009). Many locals use residential wells as sources for groundwater. Over the years the treatment process for the RE-SOLVE site has been modified, implementing new and eliminating old steps that will help make the process more eco-friendly, cost efficient, and sustainable.
1.3.1 Physical/chemical management of migration system

Initially, site clean-up consisted of the removal of cVOC and PCB-contaminated media through off-site disposal and on-site thermal desorption. Still, the groundwater below RE-SOLVE was found to be contaminated with cVOCs, BTEX, and PCBs so the groundwater was proposed to be pumped and treated to an acceptable level within 11 years. Later, DNAPL detection was realized and the approach had to be altered. Construction of a new pump and treat, multi-step management of migration treatment process was completed in 1998, followed by startup on April 27th, the same year. This system was in operation until 2013, when sustainability enhancements to the system were implemented, which are a subject of this thesis.

Originally, system specifics included a 48 gallon per minute flow rate, equalization and phase separation steps, metal removal by precipitation followed by multimedia filtration, to
remove the remaining solids, followed by air stripping to remove VOCs and carbon sorption for polishing (Figure 1.4). Following extraction, phase separation resulted in a large amount of metal sludge production that was disposed of off-site, accordingly, throughout the year. Various chemicals were used to treat contaminants along with filtration and air stripping. Carbon adsorption, which required regeneration, was used to polish the treated water just before discharge.

![Figure 1.4: Physical/chemical treatment process flow diagram (RE-SOLVE Inc. Superfund Site Environmental Restoration Program, 2009)]

1.3.2 Anaerobic bioreactor implementation

A pilot study for site optimization utilizing activated carbon and anaerobic bioreactors (ABR) was initiated at the RE-SOLVE site in 2001. The ABR systems were installed within the ground on-site and composed of a sand/peat mixture meant to host bacterial colonies that are known to actively degrade chlorinated compounds. The genera present in the beds included *Dehalococcoides* and *Dehalobacter* (known to degrade chlorinated ethenes and chlorinated ethanes, respectively) (Boudreau, 2013). Subsequently, at the completion of an extensive pilot scale program, the ABR system was constructed at full-scale in 2012. Two ABR beds, capable of operating in series or in parallel were constructed to treat the primary cVOCs in groundwater. The primary cVOCs of concern at the sites are chlorinated ethenes (cDCE and vinyl chloride) at around 1 mg/L, chlorinated ethanes (1,1,1-TCA and 1,1-DCA) at around 0.2 mg/L and small quantities of BTEX compounds. A schematic of the ABRs’ dimensions and additional details can
be seen in Figure 1.5 (RESOLVE Inc. Superfund Site Environmental Restoration Program, 2009).

Figure 1.5: Schematic of Anaerobic Bioreactor design (RE-SOLVE Inc. Superfund Site Environmental Restoration Program, 2009)

The flow entering the ABR beds is pretreated with activated carbon, and then polished upon exit with activated carbon, specifically to aid in removal of PCBs that are present in regulatory significant quantities in the groundwater. Fortunately, this approach eliminates the use of most chemicals that were used prior to ABR implementation in the physical/chemical treatment system. The temperature of the groundwater treated at the RE-SOLVE site stays at approximately 12° C around the year (verbal communication with John Pardue). Figure 1.6 shows the process flow for the modified ABR system (RE-SOLVE Inc. Superfund Site Environmental Restoration Program, 2009).
1.4 The practice of sustainability engineering

Sustainability is a broad science that involves methods that do not completely use up or destroy natural resources (Merriam Webster Dictionary, 2014). Sustainability engineering manages the amounts, as well as generation and disposal, of inputs and outputs by observing processes and altering them to have a more desirable impact. Sustainability studies of interest consider energy consumption, CO₂ production, waste disposal techniques, efficiency analyses, and climate impacts. An example of sustainability’s application in the United States is the implementation of the Superfund Green Remediation Strategy; a program designed by the EPA to reduce greenhouse gas emissions and other negative effects that result from site evaluation and remediation (USEPA, 2010).

1.5 Purpose of the study

As previously mentioned, cVOC contamination in groundwater and sediment presents an ongoing hazard to human health and the environment. While various treatment processes exist that aid in the removal of cVOCs, their presence as DNAPLs in groundwater aquifers often make pump and treat methods, that are heavily energy intensive and chemical dependent, the primary remediation pathway for their clean-up. By understanding complex biotic and abiotic mechanisms that may remediate cVOCs in a more passive way, engineers and scientists may
develop systems that have a smaller energy, chemical, and CO\textsubscript{2} footprint than traditional pump and treat methods. With these thoughts in mind, two research goals were proposed for development in this thesis project.

1) Enhanced cVOC degradation processes: While RE-SOLVE’s ABR and activated carbon techniques have successfully shown decreases in contaminant concentrations, improvements to any treatment process are always a possibility and goal of modern science and engineering. Alternative approaches to contaminant removal, namely introduction of oxygen in the treatment zone for removal of chloroethane, was explored. Mineralization, and other non-anaerobic removal processes, of certain cVOCs has already been documented and will be presented later in the Literature Review. Aerobic processes could effectively decrease chloroethane levels exiting the RE-SOLVE site treatment process and being discharged, which would be one more step towards a better treatment process for this site.

2) Sustainability analysis of chemical/physical vs. ABR biodegradation at RE-SOLVE Inc.: Implementation of a bioremediation system that degrades chlorinated compounds reduced the amount of chemicals needed for the clean-up process at RE-SOLVE. In addition, 2 less steps were needed for treatment which led to a reduction in overall energy consumption. Installation of a solar system now allows the site to operate independently of Massachusetts’ energy grid. These alterations have resulted in various changes in carbon dioxide (CO\textsubscript{2}) emissions resulting directly from energy consumption, and sludge disposal as well as indirectly from a cease in contribution to the commercial production
of certain chemicals. Specifics concerning the numerical changes of inputs and outputs that were analyzed for CO₂ differences are summarized in Table 1.1 for comparison of each system, side by side. It should be noted that due to a limited amount of available data from studies for analysis, some of the changes resulting from the bioremediation system implementation are not described in this report, such as: a 300 gallon/yr decrease in propane, an approximate 140 lb./yr reduction in VOC discharge, a 2,200 lb./yr potassium permanganate reduction, and a 270 lb./yr coagulant-polymer reduction. The greenhouse gas emissions and energy requirements necessary for the production, installation, and maintenance of the photovoltaic system are not included in this study; only their operation. Furthermore, the ABR systems’ operation encompasses treatment processes for all contaminants at the site including chloroethane, 1,1-dichloroethane, vinyl chloride, cis-1,2-dichloroethene, 1,1,1-Trichloroethene, and Polychlorinated Biphenyls- which are treated before entering the bed by activated carbon.

Table 1.1: Conventional vs. sustainable system comparison

<table>
<thead>
<tr>
<th>Impact Parameter</th>
<th>Annual Basis (excluding Electricity)</th>
<th>Conventional Treatment System</th>
<th>ABR System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td></td>
<td>Electrical demand: 27 KW</td>
<td>Electrical demand: 19 KW</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electricity Use: 19,700 KWH/Month</td>
<td>Electricity Use: 13,600 KWH/Month</td>
</tr>
<tr>
<td>Transportation and Disposal of Sludge Off-Site</td>
<td></td>
<td>56,000 lbs.</td>
<td>&lt;5000 lbs.</td>
</tr>
<tr>
<td>25% Sodium Hydroxide</td>
<td></td>
<td>38,000 lbs.</td>
<td>7,600 lbs.</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td></td>
<td>5,400 lbs.</td>
<td>0 lbs.</td>
</tr>
</tbody>
</table>
1.6 Literature Review

1.6.1 Chlorinated solvent biodegradation

The establishment of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA) in the 1980s was followed by the realization that chlorinated solvents were present in thousands of sites across the nation as a result of their widespread utilization and improper disposal (Stroo and Ward, 2010). Cost estimates for the economic impact of cleaning up over 300,000 sites (not including around 440,000 leaking underground storage tanks that introduced hydrocarbons or 19,000 landfills) in the U.S. exceeds $500 billion dollars (Alvarez and Illman, 2005). As such, a major factor contributing to the popularity of bioremediation for clean-up techniques is that of decreased remediation costs. Above-ground bioremediation’s average costs can be about 10% that of incineration, 40% that of soil washing, and 76% that of thermal desorption (Alvarez and Illman, 2005).

It was not until the 1970’s that bioremediation was successfully reported for the cleanup of hydrocarbon-contaminated aquifers. In 1974, Richard Raymond was granted the first ever patent for “Reclamation of hydrocarbon contaminated ground waters” (Alvarez and Illman, 2005). The discovery that chlorinated solvents were disappearing passively in low oxygen, groundwater aquifers was realized, shortly after, and studies confirming anaerobic biodegradation followed in the 1980’s. In 1985, for instance, mineralization of 24% of tetrachloroethylene (PCE) to CO$_2$ was confirmed in a column study along with anaerobic, reductive dechlorination of PCE to TCE, cDCE, and VC (McCarty and Vogel, 1985). Reductive dechlorination techniques have been utilized ever since to degrade various cVOCs. Before McCarty’s findings, it was largely believed that only aerobic processes could degrade
chlorinated solvents, such as those processes driven by air sparging. However, further research support the prevalence of anaerobic reductive dechlorination processes. For instance, methanogenic cultures placed in a microcosm with radioactive labeled TCE showed sequential degradation to cDCE, VC, and approximately 50% CO₂ (Fogel et al., 1986).

The development of bioremediation as an active remedial technology has continued to benefit from the discovery of reductive dechlorination and the associated mechanisms, pathways, and processes. In some instances, dechlorination is achieved through a cometabolic process in which the chlorinated compound is being degraded as a result of some other intended process (Maymó-Gatell et al., 1997). However in some cases, organisms benefit from dehalogenation of organic compounds by using them as an electron acceptor for growth and energy benefits. These organisms are often referred to as dehalorespiring. Various strains of bacteria in the Dehalococcoides family have successfully been shown to dechlorinate and grow from the reduction of common groundwater pollutants, such as chlorinated ethenes and ethanes (Löffler et al., 2013). Sequential dechlorination of compounds, such as PCE, requires organisms that can successfully utilize each intermediate daughter product of the process—thereby reducing PCE all the way to harmless ethene (Figure 1.7) (Hinchee et al., 1995).

Figure 1.7: Sequential anaerobic reductive dechlorination of PCE to daughter products: TCE, DCEs (cis or trans), VC, and ethene; associated electron donor hydrogen and loss of chlorine in the form of HCl also shown (Hinchee et al., 1995)

Incomplete reduction can lead to the production of harmful, even carcinogenic, intermediates such as vinyl chloride (Figure 1.7). While some strains of Dehalococcoides have
been shown to reduce PCE completely to ethene, not all strains are able to utilize each intermediate for energy gain (He et al., 2003). For instance, vinyl chloride can be reduced to ethene via a cometabolic process that does not contribute to the net energy gain of the organism by *Dehalococcoides ethenogens* strain 195. Furthermore, research has been conducted that has identified an organism capable of utilizing vinyl chloride as an electron acceptor and linking it to growth (designated BAV1) (He et al., 2003).

*Dehalobacter* and *Dehalococcoides* are two genera of bacteria proven to utilize chlorinated ethanes and ethenes as electron acceptors respectively, thereby gaining energy from their degradation (Grostern and Edwards, 2006). In one study, both of these bacterial groups were shown to grow during dechlorination of 1,2-DCA, but only *Dehalobacter* grew during the dichloroelimination to vinyl chloride from 1,1,2-TCA (Grostern and Edwards, 2006). Furthermore, only *Dehalococcoides* thrived during degradation of vinyl chloride to ethene. As such, we find that the utilization of microorganisms for bioremediation is a delicate process to which environmental conditions can be manipulated to promote or hinder growth, and subsequently affect chlorinated solvent degradation performance of ABRs.

Three mechanisms by which sites may be remediated are through natural attenuation, biostimulation, and bioaugmentation. The EPA defines the phenomena of natural attenuation as a “naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media” (Wiedemeier, 1999). *In-situ* processes associated with natural attenuation are becoming more and more accepted as a remedial technique for chlorinated organics and may include adsorption, volatilization, biodegradation, phytodegradation, dispersion, dilution, and chemical or biological stabilization of contaminants (Wiedemeier et al., 1996). Evidence from
field studies has been provided supporting that natural attenuation of 1,2-DCA to VC, as well as.ethene, has occurred in various natural, anaerobic, reducing conditions- such as a shallow, sand.aquifers (Nobre and Nobre, 2004) proving that natural attenuation conditions are present without.human intervention.

Biostimulation is the addition of any additive that promotes respiration/growth of.microorganisms in a system (Swannel et al, 1996; Venosa et al, 1996). At a U.S. Department of.Energy site contaminated with TCE, sodium lactate additions to the deep, fractured basalt.resulted in the complete dechlorination of TCE to ethene by enriching indigenous communities.already present at the site (Macbeth et al, 2004). *Dehalococcoides* was identified via genus-.specific primers to be present at this site, indicating the occurrence of anaerobic, reductive.dechlorination. In addition, other studies have compared stimulated and non-stimulated field.studies side by side concerning biotransformation of TCE, cDCE, and trans-dichloroethylene.(trans-DCE) (Semprini et al, 2005). The system, a saturated, semiconfined aquifer, was amended.with oxygen and methane to promote cometabolic degradation of the chlorinated aliphatic.compounds. The non-stimulated system had observed levels around 95% of injection.concentrations at the effluent showing negligible biotransformation whereas the methane and.oxygen amended study showed transformations ranging from 20-30%, 45-55%, 80-90%, and 90-95% of initial TCE, cis-DCE, trans-DCE, and VC respectively, within the first two meters of.flow. Typically oxygen and methane are not present together in high concentrations in the.natural world- suggesting that biostimulation of a system aids in the biological degradation of.compounds. This study proved that biotransformation rates were improved through.biostimulation for observed halogenated organics.
While biostimulation through addition of carbon sources and electron acceptors has been proven to promote growth in communities that are present in a system, in some cases the desired communities are not present which will result in the growth of communities with undesirable degradation capabilities (Battelle and USEPA, 2004). For instance, not all species of *Dehalococcoides* are able to dechlorinate TCE beyond VC, which will intensify contamination issues by transforming TCE into a more harmful compound (VC). KB-1™ is a mixture of organisms that are naturally occurring and known to transform TCE to ethene. This consortium was implemented at a DNAPL site at which TCE was present to evaluate the technical and cost performance of biostimulation and bioaugmentation by the EPA (Battelle and USEPA, 2004). The study found that the total mass of TCE was reduced after stimulation and augmentation with ethanol and KB-1™ (respectively) by 98.5%. Another study indicates that bioaugmentation of a shallow, ground water aquifer, with an enriched inoculum from the aquifer containing *Dehalococcoides*, resulted in a near stoichiometric transformation of PCE to ethene within six weeks of augmentation (Lendvay *et al*, 2003).

### 1.6.2 Development of ABRs for chlorinated solvent treatment

Studies have documented order-of-magnitude decreases in contaminant concentrations as contaminated groundwater discharges relatively short distances (several feet) upward through the base of highly organic wetlands heavily vegetated with *Phragmites* (Lorah *et al*, 1999a, 1999b; Pardue *et al*, 2000). The rapid attenuation observed in the natural wetland systems suggested that a constructed treatment wetland approach based on the presence of reductive dechlorinating and methanotrophic microbial populations known to degrade chlorinated solvents may be possible. The treatment concept is that cVOCs could be reductively dechlorinated to lower chlorinated daughter products as the compounds pass through the highly organic soil of the wetland. The
organic matter retards the movement of contaminants relative to groundwater flow, resulting in a longer detention time of the contaminants in the wetland sediments. Plant uptake and metabolism of the compounds in the rhizosphere would provide further treatment. Since the major fate mechanisms occur at some depth in the wetland bed, the potential risk to wetland biota is not of concern when standard risk assessment methodology is applied. Design criteria have been developed (Pardue et al, 2000) and greenhouse-based systems have been constructed and tested (Kassenga et al, 2004). In the absence of vegetation, this approach is more accurately described as an anaerobic bioreactor or ABR.

A potential advantage of ABRs built from highly organic soils is that fermentive organisms can convert complex organics into simple organic compounds (lactate and ethanol, for example). These simple organic compounds can be further converted to compounds such as acetate and hydrogen which can be utilized by dehalorespirers. Hydrogen can be used by dehalorespiring bacteria as an electron donor in the reductive dechlorination of chlorinated organic compounds, as shown in Equation 1.1 below with R representing an ambiguous, chlorinated functional group (Holliger et al, 1998).

\[ R \text{--} Cl + 2[H] \rightarrow R \text{--} H + H^+ + Cl^- \]  \hspace{1cm} \textit{Equation 1.1}

Dehalorespiring bacteria work in syntrophy with fermenters to reduce overall hydrogen concentrations in a system (DeLaune and Reddy, 2008). The rate-limiting step for reductive dechlorination can be the availability of hydrogen. With that in mind, ABRs designed for the treatment of chlorinated organic compounds may be constructed to contain a high amount of organic matter allowing fermenting bacteria to transform it into a steady supply of hydrogen over the long-term.
When approaching the design phase for an ABR, treatment goals and a thorough understanding of relevant removal processes within the system are required (Pardue et al., 2000; Gwenaël et al., 2008). These factors can change relative to the contaminants present, retention time desired for removal of pollutants, and various environmental parameters such as soil composition and biological communities present.

1.6.3 Enhancements of ABR approach

Successful implementation of an ABR process may be benefited by understanding the interactions of microbes with contaminants. For example, joint dechlorination of cis-1,2-DCE and 1,2-DCA was studied at a serum bottle scale in ABR media (Kassenga et al., 2004). This study showed that cis-1,2-DCE degraded prior to 1,2-DCA. High H₂ concentrations resulted in methanogenesis, and the subsequent degradation of 1,2-DCA, but that cis-1,2-DCE degradation occurred at H₂ concentrations that did not allow for methanogenesis. The authors suggest that 1,2-DCA dechlorination was co-metabolic with the process of methanogenesis and that dechlorination of cis-1,2-DCE was mediated by dehalorespiring bacteria.

In other studies, 1,1,1-TCA and 1,1-DCA reductive dechlorination by Dehalobacter via dehalogenase enzymes was shown to be inhibited in the presence of chlorinated ethenes (Grostern and Edwards, 2009). Results of this study indicated that chlorinated ethenes most likely affect the reductive dehalogenase enzymes associated with the dechlorination of 1,1,1-TCA. However, results also indicated that cDCE and VC presence inhibited the ability of Dehalobacter to carry out reductive dechlorination, rather than that of the dehalogenase enzyme(s) associated with the degradation of DCA to chloroethane. This study did not report any anaerobic transformation of chloroethane, however. Preferential cDCE degradation preceding that of 1,1-DCA has been demonstrated in a down-flow column study inoculated with
Dehalobacter and Dehalococcoides from the Superfund site as to which this study pertains (Boudreau, 2013). The aforementioned findings suggest that anaerobic 1,1-DCA degradation to chloroethane only occurs after the cis-1,2-DCE (present at the same concentration as 1,1-DCA in the system) was degraded to vinyl chloride. This study, again, does not suggest any degradation of chlorinated ethanes beyond chloroethane. Such findings allow ABR designers and engineers to plan where contaminants may be degraded in a system based on reducing conditions, other contaminants present, enzyme activity, and activity of microbial communities.

Incomplete degradation of chlorinated aliphatic compounds under anaerobic conditions introduces daughter compounds that may be more, less, or equally as hazardous as the original contaminant. An example discussed earlier would be the anaerobic dehalogenation of higher chlorinated ethenes to vinyl chloride, a compound that is more carcinogenic than its parent compounds. While chloroethane is a daughter product resulting in the anaerobic reductive dechlorination of higher chlorinated ethanes, TCA and DCA, this compound is not always further transformed under anaerobic conditions (Boudreau, 2013). On the other hand, while no aerobic biodegradation has been documented of higher chlorinated organics such as TCA and TCE (other than co-metabolism), lower chlorinated compounds may be used as growth substrates for aerobic bacteria (Kocamemi et al, 2009). Mineralization is a process by which compounds are transformed from organic compounds to mineral, or inorganic, products (McCarty and Rittman, 2001). Various studies support the addition of plants to promote aerobic zones in EWSs via subsurface roots and rhizomes. However, artificial aeration (through use of perforated tubing) has been shown to improve removal efficiency in horizontal subsurface flow EWSs, for fish farm effluents regarding nutrients (Chazarenc et al, 2006). In addition, BTEX removal rates were shown to reach discharge limits and be higher in both an aerated (through use
of aeration tubing) pilot-scale and full-scale, subsurface wetland as opposed to a non-aerated subsurface wetland (Wallace et al, 2005). These studies suggest that aeration may aid in further mineralization of chloroethane to CO$_2$. 
Chapter 2. Enhanced cVOC degradation of chloroethane using aerobic processes

2.1 Introduction

While degradation through reductive dechlorination of many higher chlorinated ethanes has been observed in various studies, there are a few compounds that have been documented to remain stable and persistent under anaerobic conditions, such as chloroethane (Boudreau, 2013; Sun et al., 2002). The concentration of this contaminant does not proceed to decrease via reductive dechlorination as its parent compounds (1,1,1-TCA, and 1,1-DCA). An aforementioned column study analyzed the degradation pathways of 1,1-DCA to CA by Dehalococcoides and Dehalobacter but did not report further dehalogenation of CA (Boudreau, 2013). An alternative approach must be considered for the degradation of CA if the aliphatic compound is to be completely dechlorinated.

Aerobic mineralization has been documented as a pathway leading to decreases in various organic chemical concentrations by means of the compound serving as a carbon source rather than an electron acceptor, as is the case under anaerobic conditions (Kocamemi et al., 2009). By observing carbon dioxide concentrations, microcosm studies of radioactively labeled VC and 1,2-cDCE have proven that significant microbial mineralization of said compounds has occurred in aerobic, iron (III) reducing, sulfate reducing, and methanogenic conditions; although mineralization rates were shown to decrease with increasing reducing levels of the system (Bradley et al., 2002). As such, investigation of the possibility of CA mineralization, a similar chlorinated organic compound, should be explored.

Gathering knowledge on the degradation processes of contaminants, as utilized by microbial colonies, allows researchers to understand complex metabolic pathways and practices of bacteria that may be exploited by engineers and scientists for environmental remediation. In-
**situ** research can often be inconclusive and difficult to analyze due to a vast array of complexity in natural systems (Abbott, 1966). By controlling environmental parameters under which microbes are grown and function, researchers may subject species to a plethora of perturbations that enhance or reduce a microbial consortium’s ability to decrease levels of various contaminants, and record their findings in a concise manner for the scientific community (Banchuen *et al*., 2002). With current technology, researchers are able to influence many different factors at a remediation site that affect microbial activity, such as temperature, pH, carbon content, nutrient availability, mineral content, carbon sources, electron acceptors, and the presence or absence of certain species of microbes, making knowledge of how these parameters affect the fate of a contaminant invaluable (Boopathy, 2000). Two ways to gather such information are through laboratory set-ups of column and microcosm studies. The following analyses focus on decreases of chloroethane by means of oxygen addition through breathing air in a column study and pure gas in a microcosm study.

### 2.2 Materials and methods

**2.2.1 Enhanced cVOC degradation of chloroethane; set-up of column study**

Two replicate reactors (A and B) were assembled to study aerobic decreases in aqueous chloroethane concentrations. The reactors’ dimensions were 44.5 cm x 44.5 cm x 66 cm, equating to a volume of 0.13 m³. The reactors were operated in upflow mode to treat contaminated water resulting from anaerobic dechlorination of 1,1,1-trichloroethane (1,1,1-TCA) in a peat-sand anaerobic bioreactor in the greenhouse. The temperature in the greenhouse was observed to exceed 20° C. The bottom of reactors A and B, where the influent stream enters, was composed of a 5.6 cm-deep sand layer (Quikrete Companies Inc.; Atlanta, GA). Above this layer was a 60/40%, compost (Hope Agri Products Inc.; Hope, AZ)/sand (respectively) mixture that
was 26.4 cm deep. Immediately following this layer was another layer of pure sand at 2.4 cm deep. Above the middle sand layer was a final 60/40% compost/sand (respectively) mixed media at 30 cm deep. The remaining 1.6 cm was composed of top-soil (Scott’s Miracle-Gro Company; Marysville, OH). Each respective layer was separated by a filter fabric called GeoFabric (Ace Hardware; Oak Brook, IL). 3 sampling ports were located 19 cm apart, vertically (Figure 2.1).

Within the middle, 4-cm deep sand layer of reactor A and B, 24 feet of Silastic Laboratory Tubing (Dow Corning Cat. No. 508-010) was placed, that bled breathing air from 4, 6-foot-long pieces (Figure 2.2) connected in parallel. On one end, the bleeding-tubing was plugged with a 1/8” barbed plug (Cole Parmer Cat No. 31220-13; Vernon Hills, IL). Opposite of the plugged end, the 4 pieces were connected at the sand layer to airline tubing (1/8” I.D.) that did not bleed air (PetCo; San Diego, CA) by 1/8”, barbed, nylon connectors (Cole-Parmer Cat. No. 30622-54; Vernon Hills, IL). This was done to limit air bleeding to the middle sand layer exclusively. Each of the 4 non-bleeding pieces were connected to a combining 4-way gang valve (PetCo; San Diego, CA) on the side of the reactors, to which one non-bleeding air tube supplied all of the breathing air (can also be seen in Figure 2.1 at the top left). The one, non-bleeding air tube coming from each 4-way gang valve (one for A and one for B) was first connected to a brass airline T-valve (PetCo; San Diego, CA), then to a breathing air gas cylinder (American Air Liquide, Houston, TX) via an HC-61190 Breathing Air Regulator (Victor Technologies; St. Louis, MO). The external connections and configuration of the tubing can be seen in Figure 2.3.
Figure 2.1: Reactor B of duplicate with sample ports (influent on the left bottom, effluent on the top right)

Figure 2.2: View of buried bleeding-air tubing connected to non-bleeding tubing that leaves the reactor
Both reactors A and B were subjected to various perturbations regarding oxygen introduction, which will be described in more detail in the results and discussion sections. Initially, both reactors received oxygen via the aforementioned tubing configuration at 45 psi. Later, oxygen to Reactor A and Reactor B was stopped. Reactor A was allowed to become anaerobic with no gas introduction. Reactor B immediately started to receive Nitrogen gas at 45 psi through the tubing that was previously introducing oxygen, to account for volatilization losses.

The influent of Reactors A and B was generated by the Anaerobic Bioreactor (ABR) System described by Boudreau, 2013 (Appendix; Section 1, Figure A.6) with minor changes.
Since chloroethane is a gas at room temperature, it was more practical and cost effective to generate chloroethane in a liquid phase rather than use a gas standard to dose Reactors A and B. Therefore, the ABR system’s initial dosing was done with 300 mL of saturated 1,1,1-TCA solution with the intention of reductively dechlorinating the TCA to liquid phase chloroethane in the ABR system.

### 2.2.2 Column study sample procurement

To obtain samples from the chloroethane-aerated reactors (A and B) 160 mL, glass, microcosm bottles were sealed with a Teflon-coated, silicon septa (Sigma-Aldrich; St. Louis, MO) then capped with an aluminum crimp cap (Sigma-Aldrich; St. Louis, MO). Two 60 mL syringes of air were then withdrawn from each bottle to create a vacuum within the sealed bottle. Water samples were collected from biopsy needles (Becton Dickinson % Co.; Franklin Lakes, NJ) using 60 mL syringes. Samples of water (100 mL) were withdrawn from each sampling port, and injected into the crimped and capped bottle under vacuum conditions (resulting in 100 mL liquid total), to prevent any volatile losses of sample. Upon completion of sample injection into the bottle, the syringe was unscrewed from the injection needle (while the needle was still piercing the septa) to allow equilibrium with the atmosphere to take place within the microcosm bottle. Water samples were analyzed using GC-FID as described below (Section 2.2.4).

### 2.2.3 Serum bottle study set-up

A chloroethane biodegradation serum bottle study was constructed to observe biodegradation under more controlled conditions without the complication of transport processes. Nine bottles were prepared for the chloroethane microcosm study, with three groups composed of three bottles each, for replication. The 5 grams of soil slurry placed in each bottle was a mixed core sample of the top portion of Reactor B that was previously described. The core
was taken after approximately 3 months of breathing air introduction to Reactor B to allow aerobic microbial communities to establish themselves within the sediment. The anaerobic water consisting of chloroethane was generated from the column study described by Boudreau, 2013. Glass microcosm bottles (160 mL) were used with silicon septa and aluminum crimp caps. All bottles were marked with a 100 mL liquid volume mark at the beginning. All bottles were prepared and sealed in an anaerobic glove box. The first group of bottles were Killed Controls A, B, and C. These three bottles had 5 grams of soil slurry placed in them before they, their septa, and their caps were autoclaved. After autoclaving, the pieces were moved to the glove box where 3 mL of a formaldehyde/methanol solution was added, followed by addition of 1 mL of a resazurin stock solution. The final concentration of formaldehyde and resazurin were 1% by volume and 1 mg/L, respectively. Finally, the bottles were filled to the 100 mL volume mark with anaerobic, chloroethane-containing water before they were sealed and crimped in the anaerobic glove box. The second triplicates were labeled as Anaerobic A, B, and C microcosms. These microcosms were filled with 5 grams of soil slurry, resazurin at a concentration of 1 mg/L, and anaerobic, chloroethane-containing water to a total volume of 100 mL before they were sealed and crimped in the anaerobic glove box. The final triplicate study was called Oxygen Amended A, B, and C. These bottles were prepared in the exact same way as the Anaerobic triplicates, initially. These three bottles were then amended with 0.2 mL of pure oxygen gas via a gas tight syringe for final concentrations of approximately 1.5 mg O₂/L (as calculated from the Henry’s constant of 0.13E-2 M/atm from National Institute of Standards and Technology, 2011 and transformed to dimensionless using www.henrys-law.org) in the liquid phase after diffusion in the bottle. The first oxygen amendment was done immediately after the initial sampling for time zero concentrations of chloroethane. Subsequent additions of 0.2 mL oxygen gas were
added immediately following weekly sampling of the microcosms. All bottles were inverted and static throughout the entirety of the study, with no shaking performed. Bottles were stored at ambient indoor air temperatures.

### 2.2.4 Sample analysis methodology

Samples for the column study were allowed to sit inverted for at least 3 (but never more than 24) hours before analysis with a gas chromatograph equipped with a flame ionization detector (Agilent Technologies, Model no. 6850) that contained a 2.4 m x 2.1 mm ID column packed 1% SP by Supelco. For both the column study and the microcosm study, 1.5 mL gas headspace samples were extracted from each individual microcosm bottle via a gas-tight syringe, and injected into the flame ionization detector. The temperature profile was programmed to sustain 60°C for the first minute of analysis, then increased to 130 °C at 10 °C/min, then held at 130 °C for 3 minutes. Helium was used as the carrier gas at a flow rate of 40 mL/min in combination with air and hydrogen at 100 and 35 mL/min respectively to the flame. Calibration of vinyl chloride, chloroethane, 1,1-DCA, *cis*-1,2-DCE, and 1,1,1-TCA was performed with aqueous external standards prepared from neat or methanolic stock solutions (Sigma- Aldrich, St. Louis, MO) in 160 mL microcosm bottles containing 100 mL of liquid and subsequent concentrations of each compound individually to form calibration curves for each compound (standard curves found in Appendix Section 1). Gas concentrations were back calculated using resultant peak areas and the ‘slope of the line’ for the appropriate calibration curve plotted on a concentration vs. peak area plot. The gas concentration and Henry’s Law of each compound were used to calculate aqueous phase concentration, and the total mass of the bottle was reported in all studies’ figures and tables. A duplicate analysis for sample procurement was performed to ensure that techniques were adequate (Table 2.1). All statistical analyses in this paper were
performed using a Two-tailed Student T-test with a 95% confidence interval. A two- tail test was done to account for the possibilities of both increases and decreases of chloroethane within the systems.

Table 2.1: Percent difference between sample replicates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Area of primary analysis</th>
<th>Peak area of secondary duplicate</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent A (Chloroethane)</td>
<td>741.12</td>
<td>692.04</td>
<td>6.85%</td>
</tr>
<tr>
<td>Influent B (1,1-DCA)</td>
<td>1102.3</td>
<td>1166.5</td>
<td>5.66%</td>
</tr>
<tr>
<td>Influent ABR1 (TCA)</td>
<td>5773.2</td>
<td>5613.0</td>
<td>2.80%</td>
</tr>
</tbody>
</table>

Statistical analyses were performed to determine if decreases in chloroethane concentrations between ports were affected by breathing air introduction. For each sampling event (Day 0, 7, 21, 28, etc.) the difference in CA concentration between consecutive ports was determined (Influent vs Port 1, Port 1 vs Port 2, and Port 2 vs Port 3). The average differences during the aerated and anaerobic incubation periods were compared using a 2-tail, Student’s t-test. Percent difference calculations between ports were calculated via following Equation 2.1.

\[
\left| \frac{C_p - C_{p+1}}{C_p} \right| \times 100\% = \% \text{ difference}
\]

*Equation 2.1*

Where: \( C_p = \text{CA concentration at a port [µmol/L]} \) and
\( C_{p+1} = \text{CA concentration at the next consecutive port [µmol/L]} \)
2.2.5 Oxygen data for column study; BOD$_5$, COD, OCR, and O$_2$ introduction to column study methodology

**BOD, COD, and OCR**

Various tests were done to account for oxygen output and demand levels within the chloroethane column study. Biological Oxygen Demand (BOD$_5$) tests were performed in accordance with the 5-Day BOD Test described in *Standard Methods for the Examination of Water and Wastewater*, 20$^{th}$ Edition method 5210 B. The studies were performed in triplicate and diluted to a ratio of 1/10$^{th}$ pure volume with deionized reagent water. All reagents for phosphate buffer, magnesium sulfate, calcium chloride, and ferric chloride solutions were obtained from HACH or Sigma Aldrich chemical vendors and prepared in the laboratory. The samples were not seeded. The BOD bottles were stored at 20° C during a 5-day incubation.

Chemical Oxygen Demand (COD) tests were performed in accordance with Method 8000, Colorimetric high range, described in *Standard Methods for the Examination of Water and Wastewater*, 20$^{th}$ Edition. The standard range for calibration was from 20-500 mg O$_2$/L and a HACH DR2000 Direct Reading spectrophotometer was used for analysis. All tests for COD were performed in triplicate. Some tests contained only water while others were analyzed with sediment. Samples containing sediment were diluted by a ratio of 1/100$^{th}$ with deionized reagent water. Strictly-liquid samples were not diluted. All reagents for COD tests were obtained from HACH.

A test of oxygen-consumption rate, based on Method 2710 B, described in *Standard Methods: For the Examination of Water and Wastewater* was performed to quantify oxygen consumption by solids within Reactor A and Reactor B. However, core sediment was used instead of activated sludge so the method had to be modified. A core was taken of the oxygen amended zone in Reactor B. Solid material was obtained from the core for each of three tests (for
triplicate replication) through centrifugation of the core slurry at 25°C and 9,092 RPM for 10 minutes. The process was repeated three times for 30 minutes of centrifugation, total. Excess water was decanted after each centrifuge, and 40 grams wet core-solids was placed with a mixing bar into each of three 300 mL BOD bottles. The BOD bottles were then filled with water generated from the scrubber for the original column study influent; however, since the water was anaerobic, it was aerated for 12 hours to saturate it with oxygen prior to addition to the BOD bottle. Measurements were taken at 25 °C while stirring with a magnetic stirrer using a DO probe (YSI 5100) in increments in accordance to those described in Standard Methods: once every 0.25 minutes for the first two-minutes, then once every minute for a total of 15 minutes or until dissolved oxygen became limiting in the sample. Oxygen consumption rate was determined from the average slope of the DO vs. time curves for each three tests and was expressed in units of 1/min. Two controls were assessed that did not contain any solid material, one with reagent water and one with aerated scrubber water.

\[
O_2 \text{ introduction through Silastic tubing into column study}
\]

Tests focused on the oxygen-output of the Silastic tubing in the column study were done using a UNISENSE Oxygen Microsensor and SensorTrace Basic microprofiling software. Anaerobic water (generated in the same way Reactor A and B influents were, via an organic-laden scrubber) was placed in a 15 gallon fish tank with the same length (24 ft.) of Silastic tubing that was placed in Reactor A and Reactor B’s aerated zones, with the same connection configuration to a breathing air tank that was described earlier (Section 3.2.1; \textit{set-up column study}) under the same pressure as that described in the column study (45 psi). This ensured that the same potential for mass introduction of oxygen was present between the test apparatus and the column study. Construction sand was used to hold the tubing at the bottom of the tank. A
The flow-through system was set up using a 500 mL piece of glassware equipped with a barbed connector on either side. The Microsensor probe was placed through the top of the glassware and surrounded with plastic to mitigate oxygen exchange with the atmosphere. Anaerobic water that was pumped out of the tank (where it was exposed to oxygen-bleeding tubing) and through the glassware (containing the probe for oxygen measurement) was continuously replaced with more anaerobic water at the same pump speed so that the level of water in the tank remained constant. The pump speed was identical to that of Reactors A and B (2.5 gallons per day). Water exiting the flow through system where oxygen was measured was caught in a 5 gallon bucket. The oxygen content of the water in the flow-through system was recorded in 5-minute increments over a 13-hour period.

### 2.3 Results and Discussion

#### 2.3.1 Chloroethane degradation; column study

Figure 2.4 displays the concentration of chloroethane in water vs. time in various sampling points in the 2 reactors. 1,1-dichloroethane concentrations are also shown for the sake of completion. The vertical line at 63 days represents the point at which O2 to Reactor A was discontinued. From time 0 to 63, Reactor A possessed a breathing air supply beginning just before Port 2, as previously described. The vertical line at day 76 represents the point at which breathing air was replaced with nitrogen gas in Reactor B. Reactor B possessed a breathing air supply from day 0 to 76. An upward trend can be seen in the chloroethane concentrations in the influent to Reactor A and in the influent of Reactor B attributed to the improved performance for 1,1-DCA degradation in ABR reactors feeding Reactor A and B since contaminant dosing remained constant throughout the study. While Figure 2.4 is shown to start at day 0, the time frame is meant to refer to time of sampling- not time of aeration; day 0 was the day that the first
set of chloroethane samples were gathered from the study. Actual aeration of the system began 18 days before the first sampling event occurred to allow Reactor A and Reactor B to acclimate to breathing air introduction; this is why chloroethane decreases may be observed at day 0.

In some instances, especially during early stages of breathing air introduction, Port A1 and B1 can be observed to have higher concentrations of chloroethane than that of the Influent. This can be explained by the positioning of the aeration tubing in the middle of the reactors. Since Reactors A and B are up-flow, Port 1 (located before reaching the aeration tubing) is located in an anaerobic zone, where degradation greater than 90±4.89% of influent 1,1-DCA occurred, thereby increasing levels of chloroethane. Average chloroethane concentration at the Influent and Port 1 are not statistically different during or after aeration (Section 1 of Appendix; Table A.1), demonstrating that aeration further in the bed did not impact the influent and Port 1 samples.

All sampling events for Reactor A and Reactor B reflect a decrease in chloroethane concentration from Port 1 to Port 2, after passing through the aeration zone (Figure 2.4) while O₂ was being applied. During aeration (Reactor A: 0-63 days; Reactor B: 0-76 days), chloroethane percent differences between Port 1 and Port 2 averaged 44.33±2.84% in Reactor A and 36.63±2.80% in Reactor B. After aeration (Reactor A: 64-146 days; Reactor B: 78-146 days), chloroethane percent differences between Port 1 and Port 2 averaged 20.29±3.31% for Reactor A and 17.58±2.65% for Reactor B. The statistically significant decreases in the percent difference of Port 1 and Port 2 chloroethane concentrations (pₐ=0.000110, pₐ=0.000190) during and after aeration indicate that rates of disappearance of chloroethane are decreasing without a breathing air supply.
By examining the averages of the differences between Port 1 and Port 2 concentrations for each day that a sample was taken (Table 2.2), it is evident that there is a difference in chloroethane decreases during and after aeration in both reactors. During breathing air introduction, Reactor A showed an average decrease of 5.90±0.40 µmol/L and Reactor B showed an average decrease in 5.45±0.46 µmol/L chloroethane between Port 1 and Port 2. After breathing air was turned off, Reactor A showed an average decrease in 3.20±0.77 µmol/L and Reactor B showed an average decrease in 2.68±0.60 µmol/L chloroethane. Comparing average decreases during and after breathing air introduction between Port 1 and Port 2 indicates that decreases in aqueous chloroethane concentrations were significantly lower after breathing air was turned off in both Reactor A and Reactor B (Reactor A: p=0.00898, Reactor B: p=0.00268).

The average differences between Port 2 and Port 3 do not differ significantly during and after aeration, in Reactors A or B (Table 2.2; p_A=0.074, p_B=0.35). However, while oxygen introduction to the system is calculated to be below that of the overall demand of the system (presented later in section 2.3.3), average chloroethane concentrations between Port 2 and Port 3 do differ significantly in Reactor A and Reactor B during and after aeration, indicating significant chloroethane degradation between Port 2 and Port 3 (Section 1 of Appendix; Table A.1; During aeration: p_A=0.015, p_B=0.0038; After aeration: p_A=0.00021, p_B=0.00011).

Table 2.2: Statistical analysis of consecutive port differences in chloroethane concentration during and after aeration

<table>
<thead>
<tr>
<th>Treatment Zones</th>
<th>Avg. CA loss Reactor A (µmol/L)</th>
<th>Reactor A p value</th>
<th>Ave. CA loss Reactor B (µmol/L)</th>
<th>Reactor B p value</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>During Aeration</td>
<td>After Aeration</td>
<td>During Aeration</td>
<td>After Aeration</td>
<td></td>
</tr>
<tr>
<td>Influent to Port 1</td>
<td>0.6±1.10</td>
<td>1±0.82</td>
<td>0.67</td>
<td>0.6±1.00</td>
<td>2±0.54</td>
</tr>
<tr>
<td>Port 1 to Port 2</td>
<td>6±0.40</td>
<td>3±0.61</td>
<td>0.0039</td>
<td>5±0.46</td>
<td>3±0.44</td>
</tr>
<tr>
<td>Port 2 to Port 3</td>
<td>3±0.58</td>
<td>5±0.76</td>
<td>0.074</td>
<td>4±0.51</td>
<td>5±0.90</td>
</tr>
</tbody>
</table>
Figure 2.4: Chloroethane (bottom) and 1,1-Dichloroethane (top) concentrations of Reactor A and Reactor B in column ports vs. time
Decreases in aqueous chloroethane concentrations could be due to multiple processes including mineralization by microbial activities to CO₂, volatilization to the overlying headspace in the reactors, or diffusion into the tubing supplying the breathing air. For volatilization, the only air:water interface in the saturated reactors is within bubbles which form within the reactors, presumably from production of methane. These were not observed leaving the surface of the reactor, however, and the volume of bubbles was much lower than the volume of water. Data from Table 2.2 can help elucidate the importance of the various processes. The aeration zone is between Port 1 to 2 and average decreases across this zone were 5-6 umol/L in Reactors A and B while receiving breathing air. Once the breathing air supply was terminated, average decreases in both reactors declined to ~3 umol/L. This suggests some baseline diffusive loss into the tubing on the order of a few umol/L.

As stated in the methods section, initial dosing of the ABR system was done with 300 mL of saturated 1,1,1-trichloroethane solution. This method introduces perturbations to the influent of Reactors A and B because it is based on the performance of the ABR reactor’s reductive dechlorination of 1,1,1-TCA. Figure 2.5 shows the performance of the ABR reactors in generating chloroethane over time. Loading of these reactors was approximately 0.36 g/m²/day for 1,1,1-TCA. Again, day 0 refers to the time that sampling of Reactor A and Reactor B began; not initial start-up of the system- which has been in operation since 2013 (Boudreau, 2013).
2.3.2 Chloroethane degradation; microcosm study

Serum-bottle studies were used to examine the biodegradation process more closely by including killed controls. Chloroethane concentrations in Oxygen Amended bottles show a significant decrease while oxygen is steadily added to the bottles week to week, between day 0 and 30 \((p=0.0288)\). 1,1-DCA concentration decreases are also significant \((p=0.0226)\) during the time that oxygen was consistently added to the bottles. After analysis on day 30, oxygen was not added to the bottles for one week and concentrations of chloroethane can be seen in Figure 2.6 to increase with decreases in 1,1-DCA concentrations. Quantification of the mass of 1,1-DCA loss vs. the mass of chloroethane loss in the Oxygen Amended bottles shows that (from day 0 to 30) \(0.13\pm0.003\ \mu\text{mol}\) of DCA were lost and \(0.74\pm0.15\ \mu\text{mol}\) of chloroethane were lost. Anaerobic bottles showed a significant increase in chloroethane from day 0-30 \((p=0.083)\). During this time, the decrease in 1,1-DCA was \(0.09\pm0.003\ \mu\text{moles}\) and the increase in chloroethane was \(0.09\pm0.02\).
µmoles suggesting that 100% of 1,1-DCA lost can be accounted for as chloroethane gain from reductive dechlorination. Killed controls did not show a significant change in chloroethane from day 0-30 (p=0.28).

Oxygen Amended bottles, throughout the entirety of the study (day 0 to 63), show an overall loss in 0.84±0.16 µmols of CA and an overall loss of 0.64±0.03 µmols of DCA. Anaerobic triplicates show an overall increase in CA of 0.36±0.07 µmols and a decrease in DCA of 0.62±0.01 µmols throughout the entire course of the study. The kill controls show an insignificant change in CA (p=0.28) and an insignificant change in DCA (p=0.11) throughout the entirety of the study. After day 30, both the Oxygen Amended and Anaerobic bottles can be seen to show increased rates of DCA reduction and CA production with similar rates and trends between the two studies until DCA approaches 0 µmols at day 49 (Figure 2.6). Although bottles were not shaken throughout the study, the Oxygen Amended triplicates show significant decreases in the amount of chloroethane present (p=0.0251), the anaerobic triplicates report significant increases to chloroethane concentrations (p=0.001), and kill controls do not reflect a significant change in chloroethane concentration (p=0.283). Findings from this microcosm study, therefore, support the theory that the presence of oxygen influences microbial processes in a way that decreases aqueous chloroethane concentrations.
Figure 2.6: Kill Control, Anaerobic, and Oxygen Amended serum studies of chloroethane and 1,1-dichloroethane vs. time
2.3.3 Oxygen dynamics in treatment system

The results of BOD$_5$ measurements in water for the influent to Reactor B and water removed from Port 2 of Reactor B (Table 2.3 sample taken during the time when O$_2$ was being supplied). Average values were 29.5±0.19 mg/L for the influent and 21.97±0.46 mg/L for the effluent. From the Influent to Port 2, a decrease in 7.6±0.27 mg O$_2$/L can be seen between the means of the tests indicating that a level of organic consumption is occurring between these two points in Reactor B. Statistically, the mean BOD$_5$ differs significantly between the Influent and Port 2 water samples ($p_{value}$=.000248). By converting this value to its respective electron equivalence (0.95 meq/L) and comparing that to the electron equivalence associated with the average reduction of chloroethane (0.054 meq/L) and 1,1-DCA (0.006 meq/L) we can see that chloroethane and 1,1-DCA reduction account for 6.25% of the BOD$_5$ consumed between the Influent and Port 2 of Reactor B.

The COD tests for Reactor B. COD of the water increases significantly as it moves through the reactor (Table 2.4; $p_{value}$=.0000799), increasing from 101.3±1.67E-03 to 168±1.15E-03 mg/L. The overall increase in COD from influent to effluent can be attributed to release of dissolved organic carbon from the peat media to the water. This process did not increase the BOD$_5$, which suggests that it may consist of humic and fulvic substances that did not substantially metabolize during the 5 days of the BOD test.

Figure 2.7 shows data for the oxygen consumption rate (OCR) of Reactor B media. By averaging the slopes of the triplicate tests fitted to a first order equation, a value of $k= -88.52$/day (-0.061/min) can be seen for oxygen consumption. Alternatively, a 100% sand mixture and DI control (Section 1 of Appendix; Figure A.7 and A.8)
Table 2.3: BOD$_5$ triplicate study for Reactor B Influent and Port 2

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<thead>
<tr>
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<td>Influent</td>
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<td>BOD$_5$</td>
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<td>29.57±0.19</td>
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<td>Port 2</td>
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<td>A</td>
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<tr>
<td>C</td>
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<td>BOD$_5$</td>
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<td>21.97±0.46</td>
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Table 2.4: COD tests of Reactor B water and core samples

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<th>Sample</th>
<th>Average COD [mg O$_2$/L]</th>
<th>Notes:</th>
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<tr>
<td>Influent</td>
<td>101.3±1.67E-03</td>
<td>Water only</td>
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<tr>
<td>Effluent</td>
<td>168.0±1.15E-03</td>
<td>Water only</td>
</tr>
<tr>
<td>Top of Core (Port 3)</td>
<td>13,200.0±3.06E-03</td>
<td>Water and sediment</td>
</tr>
<tr>
<td>Bottom of Core (Port 2)</td>
<td>8,933.3±8.67E-03</td>
<td>Water and sediment</td>
</tr>
</tbody>
</table>
resulted in well below 2 mg D.O./L-min (the minimum according to Method 2710 B). For illustrative purposes, the first-order reaction rate constant for the slurry oxygen consumption rate was multiplied by a concentration of 1 mg/L (Table 2.5) to calculate the mass uptake of oxygen per time by reactor solids. Porewater monitoring of O\textsubscript{2} always revealed D.O. levels <1 mg/L (Appendix Section 1; Table A.3).

After approximately 2 hours, the dissolved oxygen level exiting the aquarium, where tubing is venting oxygen, is relatively constant (Figure 2.8). This suggests that the system was reaching its maximum dissolved oxygen concentration given the retention time and mass flux of oxygen within the aquarium. The change in concentration from the influent (3.84 mg/L) to the maximum (5.58 mg/L) within the aquarium was 1.74 mg/L. This value combined with the flow rate (2.5 gallons per day) results in a mass input from the tubing of 16.5 mg/day (Table 2.5).

A control volume comparison of oxygen inputs and outputs can help elucidate the performance of the reactor. If we establish a 10 cm deep volume of the reactor containing the aeration tubing to perform the analysis, the residence time of water within the control volume (10 cm x 44.5 cm x 44.5 cm) is 2.09 days. Assuming that the water entering the bottom of the control volume is completely anaerobic (Winkler tests suggest anaerobic; Section 1 of Appendix; Table A.3), the only input of oxygen to the water is from the tubing at 16 mg/day. Consumption of oxygen within the control volume consists of oxygen consumption in the water flowing through the volume and oxygen consumption associated with the solid media itself. The BOD\textsubscript{5} of the applied water is approximately 25 mg/L; over the control volume, with porosity of 0.5, demand will be 49 mg/day (Table 6).
Figure 2.7: A triplicate analysis of oxygen-consumption rate in Reactor B media

- A: $y = 5.582e^{-0.0894x}$, $R^2 = 0.977$
- B: $y = 5.726e^{-0.0591x}$, $R^2 = 0.953$
- C: $y = 6.164e^{-0.0359x}$, $R^2 = 0.901$
Figure 2.8 Oxygen addition to water via Silastic tubing in a flow through system over a 13-hour period from the pore water. When combined with the aforementioned demand from the soil (Table 6), it is evident that the oxygen demand of the system far outweighs that supplied from the aeration zone. However, it should be noted that the OCR test was performed under complete mixing conditions that allowed optimal uptake rates to be measured—which is not the case in the actual column study. The aeration zone used in this experiment may be comparable to the performance of aeration within a rhizosphere by plant roots. The tubing does not output enough oxygen to aerate water as it crosses the tubing interface, but still results in an average chloroethane reduction of approximately 41% from the Influent of Reactors A and B to Port 3 of Reactors A and B at an average
concentrations of 13.65±0.37 µmol/L in the Influent to 5.58±0.41 µmol/L in Port 3, during periods of aeration.

2.3.4 Future work and recommendations

The results of this study indicate that decreases of chloroethane can be promoted by addition of oxygen, through breathing air, to up-flow peat-sand substrate reactors. This will allow for complete removal of higher chlorinated ethanes. A beneficial continuation of this study that would aid in further proving these findings would be to perform a mass balance of radioactively labeled chloroethane and track CO\textsubscript{2} emissions resulting from the reactors. Additionally, a more consistent method to producing influent chloroethane concentrations could limit the variability in observed mass changes throughout the Reactors over time. While breathing air-gas was used in this study, pure oxygen gas may positively influence mass removal. Equivalently, a longer retention time may also increase the degradation of chloroethane, possibly resulting in complete removal of all organic contaminants. Finally, other commercially available oxygen sources may decrease maintenance (such as gas cylinder replacement and possible future replacement of tubing) that the Silastic tubing required during this study.

Microcosm bottles that were amended with oxygen should have a higher mass of oxygen added to them on a more regular basis, as opposed to once a week. In addition, oxygen amended bottles should be shaken or stirred at all times to encourage thorough mixing of oxygen, eliminating the possibility of anaerobic sections in the media. Again, radioactively labeled chloroethane and CO\textsubscript{2} tracking would also benefit the microcosm study. Finally, a method to generate aqueous CA without the presence of DCA would also eliminate interference with CA tracking.
Table 2.5: Control volume analysis of inputs and outputs of oxygen within the column stu

<table>
<thead>
<tr>
<th>Oxygen Process</th>
<th>Estimation approach</th>
<th>Equation/value</th>
<th>Term</th>
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<td>Inputs</td>
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<td></td>
<td></td>
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<tr>
<td>$O_2$ from Silastic tubing @35 psi</td>
<td>Lab CSTR with equivalent length of tubing</td>
<td>$\frac{dM}{dt} = Q(S_0 - S) + I$</td>
<td>$I_1 = 16 \text{ mg/day}$</td>
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<td>Influent water</td>
<td>Measurements</td>
<td>&lt;.3 mg/L in influent water (Winkler method)</td>
<td>&lt;3 mg/day</td>
<td>Oxygen not detected in influent water</td>
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<tr>
<td>Outputs</td>
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<td>Consumption of oxygen in porewater</td>
<td>Measurement of BOD$_5$ in porewater</td>
<td>25 mg/L over 5 days; ~5 mg/L-day. Pore volume of section is 9.9L</td>
<td>$O_1 = 49 \text{ mg/day}$</td>
<td></td>
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<tr>
<td>Consumption of oxygen by soils</td>
<td>Measurement of oxygen consumption rate with 40 g of well-mixed laboratory slurry</td>
<td>$\frac{dC}{dt} = -kC$ where $k = 88.52 \text{ day}^{-1}$; if $C = 1 \text{ mg/L } O_2$ and total soil mass = 9,901 cm$^3$ * 1.6 g/cm$^3$ = 15,842 g</td>
<td>$O_2 = &lt;34,214 \text{ mg/day}$</td>
<td>Potential soil uptake well exceeds inputs</td>
</tr>
</tbody>
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3.1 Introduction

A sustainability analysis focusing on CO₂ emissions associated with the physical/chemical treatment scheme at the RE-SOLVE site and the emission’s subsequent reduction after implementation of the bioremediation system for treatment will be analyzed based on various impact parameters: Electricity consumption, transportation and disposal of sludge off-site, and sodium hydroxide/sulfuric acid usage reduction.

3.1.1 Direct electricity impact analysis

According to the Institute for Energy Research, Massachusetts is 4ᵗʰ highest in the United States for energy cost per kWh, at 15.53¢, with 52.9% of their energy originating from natural gas and 24.6% from coal (Institute for Energy Research, 2010). Additionally, the United States Energy Information Administration reports that 24% and 74% of CO₂ emissions (involved in electricity production) are associated with natural gas and coal, respectively, with less than 1% contributed from alternative energy sources (U.S. Energy Information Administration, 2013).

3.1.2 Sludge disposal- transportation: CO₂-eq and electricity impacts

Following behind electricity, the EPA reports that transportation accounts for the 2ⁿᵈ largest portion of CO₂ emissions within the United States, contributing 32% of total annual CO₂ production (EPA, 2012). The original treatment system used at the RE-SOLVE Superfund site (Table 1.1; Section 1.5) had an annual production of 56,000 lbs. of waste, requiring trucks to drive from Massachusetts to Ohio for disposal. Following
the sustainable alteration of the system, an annual decrease of around 91% can be observed (Table 1.1; Section 1.5), with less than 5,000 lbs. of waste in need of off-site disposal annually. The distance traveled for waste-transport from North Dartmouth, MA to a hazardous waste landfill in Columbus, OH, according to Google Maps, is a distance of roughly 746 miles (one way).

3.1.3 Chemical impacts on CO$_2$ and energy emissions

The transition of the system to the more sustainable ABR treatment approach reduced the utilization of many chemicals that are common in water treatment processes. Chemicals can be used for various steps of water treatment such as precipitation of dissolved constituents (such as metals or other solids), pH alterations, disinfection, smell reduction, dissolved oxygen alteration, and alkalinity. Use of these chemicals often adds additional costs to the operation of the system. Also, upstream manufacturing of these chemicals requires energy input and associated CO$_2$ emissions. This portion of the study will analyze the changes in the systems’ energy and carbon dioxide footprints associated with differences in chemical consumption between the traditional treatment system and the sustainable ABR system. These changes reflect the indirect CO$_2$ and energy impacts associated with the consumption, and implied production, of these chemicals. It should be noted that CO$_2$ production and energy demands will vary between different processes used for the following chemicals’ manufacturing. The following calculations are solely based on data available, since the origin and manufacturing processes used for the systems’ chemicals are unknown.
3.2 Materials and methods

3.2.1 Methodology for direct electricity impact calculations

Electricity impact mitigation from the transition from grid-based electricity to a solar system was determined using emission calculations using the current mix of electricity in Massachusetts. Currently, natural gas (52.9%) and coal production (24.6%) make up 77.5% of the energy production in the state of Massachusetts with 5 smaller methodologies (nuclear, biomass, hydroelectric, petroleum, and other) accounting for the remaining 22.5% (Institute of Energy Research, 2010). Since the majority of electricity production is either natural gas or coal, only potential impacts resulting from these two electricity sources were analyzed. Average emissions ratings are 1,135 lbs. /MWh of carbon dioxide for natural-gas fired production and 2,249 lbs. /MWh of carbon dioxide for coal utilization (EPA, 2013). Furthermore, the EPA states that a lack of fuel combustion associated with solar cells results in a negligible amount of emissions from operation (EPA, 2013). Although there are CO$_2$ emissions and energy requirements associated with other aspects of a photovoltaic solar panel’s life cycle, such as the production and installation of the panels, those calculations were not factored into this study. The only aspect considered was a lack of CO$_2$ production resulting from their operation.

By combining the electricity requirements of the system before solar system implementation and the weighted CO$_2$ production rates explained above, we can calculate the electricity-based emission impacts that the system produced while the process was run on grid-based energy and compare them to the reported zero emissions based on the solar energy. Annual CO$_2$ emissions can be calculated with equation 3.1. 19,700
kWh/month of electricity were needed to run the conventional system (Table 1.1; Section 1.5). This value was multiplied by 12 (months) to account for a year of operation and converted from kWh to MWh before being multiplied by the EPA’s CO₂ production rates.

\[
CO₂_{-A} = E_{req} \times t \times CO₂\text{-impact} 
\]

Equation 3.1

Where: \( CO₂_{-A} \) = Annual CO₂ emissions resulting from operation of the RE-SOLVE system [lbs.]

\( E_{req} \) = the amount of energy per year required to operate the RE-SOLVE system [MWh/yr]

\( t \) = timeframe for desired calculation [yr]

\( CO₂\text{-impact} \) = the corresponding reported rate of CO₂ production from the EPA from either coal or natural gas sources for electricity production [lbs. /MWh] (interchangeable for appropriate source)

3.2.2 Methodology for transportation impact calculations

The transition to the bioremediation system reduces monthly wastes in need of transport and disposal from 4,667 lbs. /month to less than 417 lbs. /month (found by dividing annual production by 12 months). This waste stream is sludge produced from metal precipitation required prior to air stripping of VOCs. This analysis assumed that the same, gasoline-based vehicle was used to transport the waste from both the conventional and ABR-based systems. Furthermore, it was assumed that in order to accommodate the original system’s waste production, 1 trip per month (12 a year) was made from North Dartmouth, MA to Columbus, OH. Alternatively with the ABR system, one trip was made every 12 months to transport the waste the same distance. The average fuel economy of a heavy-duty pickup truck with a typical payload capacity of 5,250 lbs. (sufficient for transporting the 4,667 lbs. of sludge per month) was found to be 10.5 miles per gallon for a gasoline-based truck (National Academies, 2010). By dividing the distance traveled (746 miles) by the average MPG, the average consumption of gasoline
consumed in a one-way trip from North Dartmouth, MA to Columbus, OH was calculated with Equation 3.2. This number was used in combination with the frequency of trips to find the annual gasoline consumption associated with each system.

\[
G_c = \frac{x}{MPG}
\]  
*Equation 3.2*

Where: \(G_c\) = annual consumption of gasoline [gallons]  
\(x\) = annual distance traveled [miles]  
\(MPG\) = fuel economy of vehicle used for transport [miles per gallon]

The U.S. Energy Information Association provides weekly evaluations of gasoline prices across the United States for different areas of the country. First, the annual average of 2012 was taken for Boston, MA and Cleveland, OH (raw data in Table 3.1; data from [www.eia.gov](http://www.eia.gov), accessed October, 2013). Second, these prices were averaged to account for the possibility of the truck driver getting fuel in either Massachusetts or Ohio. This price value with the annual gallons of gasoline was used to compute total annual economic contribution to the fuel sector by both the conventional and the ABR system via Equation 3.3:

\[
C_g = G_c \times P_{avg}
\]  
*Equation 3.3*

Where: \(C_g\) = annual cost of gasoline for sludge transportation [dollars]  
\(G_c\) = annual consumption of gasoline [gallons]  
\(P_{avg}\) = average price of gasoline in area of travel [dollars/gallon]
Table 3.1: Raw data for gasoline prices provided by Energy Information Association

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The reported CO₂-equivalent emissions and energy impacts for gasoline consumption were calculated using an Economic Input-Output Life Cycle Assessment (EIO LCA) model that can be found at www.EIOLCA.net. The model used was the US 2002 Benchmark and the economic activity was set to one million dollars to mitigate rounding errors that can occur during calculations. The results from the one million dollar model were then scaled using the calculated annual fuel expenditures in combination with the appropriate Consumer Price Index (CPI) values for 2002 and 2012 to account for the difference in economic impact within the sector between the two years (since the model is based on the year 2002, and the expenditures are from 2012- scaling was needed with the ratio) using Equation 3.4. The ratio values that most accurately described CO₂-eq and energy from the Petroleum and Power Generation/Supply Industries from the Bureau of Labor Statistics can be seen in Table 3.2 (www.BLS.gov, accessed October, 2013). In short, this equation transforms the dollars spent on Gasoline and Power Generation and Supply from 2012 to equivalent dollars of 2002 accounting for

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<td>Dec 31, 2012</td>
<td>3.48</td>
<td>3.364</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>3.71</td>
<td>3.632</td>
<td></td>
</tr>
<tr>
<td>Overall Average</td>
<td>3.671</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
economic changes between the two years, so that they may be applied to the model that was constructed in 2002.

\[ C_{2002} = C_g \times R_{CPI} \]

*Equation 3.4*

Where: 
- \( C_g \) = annual cost of gasoline for sludge transportation from 2012 [dollars]
- \( R_{CPI} \) = appropriate category’s CPI ratio between years of interest (2002 and 2012)
- \( C_{2002} \) = annual cost of gasoline for sludge transportation adjusted to 2002

<table>
<thead>
<tr>
<th>Category</th>
<th>December 2002 CPI</th>
<th>December 2012 CPI</th>
<th>Ratio of 2002 to 2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline (all types)</td>
<td>119.1</td>
<td>304.04</td>
<td>0.39</td>
</tr>
<tr>
<td>Power Generation and Supply</td>
<td>134.1</td>
<td>191.87</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Table 3.2: CPI data from the Bureau of Labor Statistics

The sector used in the Producer Price model from EIO LCA to evaluate gasoline impacts was *Petroleum refineries*. This sector encompasses all activities involved in upstream exploring and processing of petroleum. Downstream activities, such as transportation to retailers and dispensing, are considered negligible in comparison. The scaled costs (from dollars of 2012 to 2002) were divided by $1 million to equate a fraction of impacts that scales the CO₂-eq and TJ of energy calculated by the model (run at $1 million input) to the actual values contributed from running the systems. The fraction of impacts values were then multiplied by the CO₂-eq and TJ of energy given from running the model resulting in the actual CO₂-eq and TJ of energy associated with
running the systems in 2012. The aforementioned process can be described in Equation 3.5.

\[
I_{\text{actual}} = \frac{C_{2002}}{\$1,000,000} \times S_{\text{total}} \quad \text{Equation 3.5}
\]

Where: 
- \(I_{\text{actual}}\) = actual annual impact resulting from system operation [tons CO\(_2\)-eq or GJ energy]
- \(C_{2002}\) = annual cost of gasoline for sludge transportation adjusted to 2002
- \(S_{\text{total}}\) = Sector total from $1,000,000 economic input model [tons CO\(_2\)-eq or TJ energy]

The results of the model express greenhouse gas emissions in terms of CO\(_2\)-eq which encompasses carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, and perfluorocarbons. CO\(_2\)-eq is a unit that expresses the impacts of contaminants in terms of the amount of CO\(_2\) that is required to have the same impact as the contaminant being described. Emissions are reported in terms of CO\(_2\)-eq because the EPA considers carbon dioxide to be the most important of anthropogenic greenhouse gas, claiming that carbon dioxide accounted for 82% of all greenhouse gas emissions emitted through human activities in 2012 (EPA, 2014).

### 3.2.3 Methodology for chemical manufacturing impact calculations

**Sodium Hydroxide**

Sodium Hydroxide (NaOH), also known as caustic soda or lye, is used in the conventional remediation system to adjust pH. Sodium hydroxide is produced commercially by the chloralkali process via the electrolysis of NaCl solution with the anode and cathode separated by a membrane (National Council for Air and Stream Improvement, 2009). Previously published data shows that a range of 1.37-2.8 kWh/kg of NaOH is required for sodium hydroxide production from various processes (NCASI). An average of 2.085 kWh/kg NaOH (0.946 kWh/lb. NaOH) was used for estimating energy
demands of each system revolving around NaOH consumption. Emissions of CO$_2$ from production of NaOH in 2007 was estimated as 3.975 tons of CO$_2$/ton of NaOH in China’s chemical industry (Bing Zhu)$^1$. This value was used in combination with appropriate NaOH quantities necessary for both system’s operation to quantify CO$_2$ emissions associated with NaOH production.

*Sulfuric acid*

According to the Inorganic Chemical Industry (ICI), there are two processes that can be used to manufacture sulfuric acid used to lower pH in the remedial system under study (ICI, 2014). U.S. facilities all use the contact process over the lead chamber process because it is more economical (ICI, 2014). Electricity consumption for sulfuric acid production has been reported as 35.0 kWh/ton acid (0.0175 kWh/pound) (Inorganic Chemical Industry, 2014). This value, in combination with the mass of sulfuric acid utilized in each system, was used to calculate annual kWh of electricity needed to produce the necessary amount of sulfuric acid for each system. Additionally, CO$_2$ emission rates of 8.10 lb. CO$_2$/ton of acid produced are also reported (Inorganic Chemical Industry, 2014). This value, along with mass per system, was used to calculate CO$_2$ emissions associated with the production of necessary sulfuric acid for each system.

3.3 Results and Discussion

The conventional treatment system utilized for the remediation of the RE-SOLVE Superfund site required chemicals and grid-energy to remove contaminants from groundwater. The ABR system utilizes bacterial degradation of contaminants and solar power in an effort to provide the same level of treatment while improving the energy and

---

$^1$ Value reported average emissions from diaphragm process and ion membrane process production of NaOH

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CO₂ emission profile of the system. The sustainable enhancements to the RE-SOLVE remediation process has resulted in a reduction in energy and CO₂ impacts related directly and indirectly to the systems as described below.

3.3.1 Direct electricity impacts

By assuming that the electricity from the grid was produced by means of natural-gas firing, a production of 119.82 tons CO₂/yr can be found. Alternatively, by assuming that the electricity from the grid originated from coal sources, a production of 237.32 tons CO₂/year can be calculated. As previously mentioned, solar power is reported to have zero CO₂ emissions resulting from energy production. As such, the current ABR system can be assumed to produce no CO₂ from direct energy consumption at the site. Implementation of a solar-powered system to power the ABR process has resulted in a significant decrease in CO₂ from energy consumption (decreases of between 134-266 tons of CO₂ per year when compared to the conventional physical/chemical system that relied on grid-based electricity.

3.3.2 Sludge disposal- transportation: CO₂eq and energy impacts

The calculated gallons of gasoline for each system per year for round trips between the waste pick-up location in Massachusetts and the waste disposal location in Ohio (Table 3.3; calculated from equation 3.2). An average retail price for all gasoline based fuel types of $3.67/gal calculated and used for 2012 by using the information from the EIA for average fuel prices between Boston, MA and Cleveland, OH. The associated costs for said gasoline consumption are also displayed in Table 3.3 (calculated via Equation 3.3). The calculated 2012 expenditures were combined with Equation 3.4 to adjust them to 2002 dollars, so that they may be used in the EIOLCA model (shown in Table 3.4 as CPI Adjustment- $’s of 2002). The conventional system contributed an
economic value of $6,257.87 for gasoline expenses annually in 2012, whereas the ABR system only contributed a value of $521.49 annually for sludge disposal. Additionally, when combined with the CPI ratios (Table 3.2; .3917 for Gasoline and .6989 for Power Generation and Supply between the two years) the Traditional system had an economic input of $2,451.21 for Gasoline in 2002 and $4,373.63 for Power Generation and Supply. The Bioremediation system, on the other hand, only contributed an equivalent 2002 value of $204.27 for Gasoline and $364.47 for Power Generation and Supply.

Table 3.3: Gasoline consumption and expenditures per year for each system based on assumed number of trips, average fuel economy, and trip distance

<table>
<thead>
<tr>
<th>System type</th>
<th>Disposal trips/year</th>
<th>Miles driven (round-trip)/year</th>
<th>Gasoline consumption (gal/year)</th>
<th>Annual fuel expenditures for waste disposal (2012)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Treatment System</td>
<td>12</td>
<td>17,904</td>
<td>1,705</td>
<td>$6,257.87</td>
</tr>
<tr>
<td>ABR System</td>
<td>1</td>
<td>1,492</td>
<td>142</td>
<td>$521.49</td>
</tr>
</tbody>
</table>

Table 3.4: CPI adjustment for expenditures between 2002 and 2012 corresponding CO₂-eq values

<table>
<thead>
<tr>
<th>Category</th>
<th>Ratio</th>
<th>$1 million activity</th>
<th>Annual Expense ($'s of 2012)</th>
<th>CPI Adjustment ($'s of 2002)</th>
<th>Fraction of Impacts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline (all types)</td>
<td>0.39</td>
<td>2790 tons of CO₂-eq</td>
<td>$6,257.87</td>
<td>$2,451.21</td>
<td>.0025</td>
</tr>
<tr>
<td>Power Generation</td>
<td>0.69</td>
<td>31.7 TJ energy</td>
<td>$6,257.87</td>
<td>$4,373.63</td>
<td>.0044</td>
</tr>
</tbody>
</table>
Tables 3.5 and 3.6 show the output from the EIO-LCA model associated with $1,000,000 dollars contribution to the Petroleum Refineries sector for greenhouse gas emissions and energy consumption, respectively. The total values CO2 (as tons CO$_2$-eq) and energy (as TJ) for a $1,000,000 expenditure (Table 3.4) are 2790 and 31.7 respectively. The top ten sectors associated with these CO$_2$-eq emissions and total energy consumption are shown in each Figure.

The total-$1,000,000 values of tons CO$_2$-eq and TJ energy were combined with the Fractions of Impacts (shown in Table 3.7 for each system in each sector) to calculate the tons CO$_2$-eq and TJ energy associated with the Traditional and Bioremediation system (Table 13).

**Table 3.5: Greenhouse gas production with 1 million dollar economic input into Petroleum refineries sector**
Table 3.6: Energy consumption with 1 million dollar economic input into Petroleum refineries sector

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total for all sectors</td>
<td>31.7</td>
<td>2.59</td>
<td>12.9</td>
<td>13.0</td>
<td>1.15</td>
<td>2.09</td>
</tr>
<tr>
<td>Petroleum refineries</td>
<td>17.4</td>
<td>0.006</td>
<td>4.65</td>
<td>11.3</td>
<td>0.856</td>
<td>0.620</td>
</tr>
<tr>
<td>Oil and gas extraction</td>
<td>7.28</td>
<td>0</td>
<td>5.95</td>
<td>0.620</td>
<td>0</td>
<td>0.714</td>
</tr>
<tr>
<td>Power generation and supply</td>
<td>3.16</td>
<td>2.30</td>
<td>0.674</td>
<td>0.112</td>
<td>0</td>
<td>0.074</td>
</tr>
<tr>
<td>Pipeline transportation</td>
<td>1.12</td>
<td>0</td>
<td>0.852</td>
<td>0</td>
<td>0</td>
<td>0.269</td>
</tr>
<tr>
<td>Other basic organic</td>
<td>0.336</td>
<td>0.042</td>
<td>0.128</td>
<td>0.046</td>
<td>0.101</td>
<td>0.018</td>
</tr>
<tr>
<td>chemical manufacturing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonresidential maintenance</td>
<td>0.225</td>
<td>0</td>
<td>0.019</td>
<td>0.199</td>
<td>0</td>
<td>0.007</td>
</tr>
<tr>
<td>and repair</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Petrochemical manufacturing</td>
<td>0.209</td>
<td>0.003</td>
<td>0.082</td>
<td>0.080</td>
<td>0.035</td>
<td>0.009</td>
</tr>
<tr>
<td>Iron and steel mills</td>
<td>0.181</td>
<td>0.107</td>
<td>0.049</td>
<td>0.002</td>
<td>0</td>
<td>0.022</td>
</tr>
<tr>
<td>Truck transportation</td>
<td>0.154</td>
<td>0</td>
<td>0.153</td>
<td>0</td>
<td>0</td>
<td>0.001</td>
</tr>
<tr>
<td>Plastics material and resin</td>
<td>0.113</td>
<td>0.005</td>
<td>0.059</td>
<td>0.025</td>
<td>0.012</td>
<td>0.013</td>
</tr>
<tr>
<td>manufacturing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.7: CO$_2$-eq and Energy impacts related to Conventional Treatment and Anaerobic Bioreactor systems

<table>
<thead>
<tr>
<th>Sector</th>
<th>CO$_2$-eq Impacts (tCO$_2$-eq/yr)</th>
<th>Energy Impacts (GJ energy/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional Treatment System ABR System</td>
<td>Conventional Treatment System ABR System</td>
</tr>
<tr>
<td>Petroleum refineries</td>
<td>6.84 .57</td>
<td>138.64 11.55</td>
</tr>
</tbody>
</table>

It can therefore be determined that switching from the conventional system’s metal removal process to the ABR system’s approach (that produces less sludge) reduced tons CO$_2$-eq produced per year from sludge transportation by around 92% (from 6.84 to 0.57 tCO$_2$-eq/yr) in the Petroleum Refineries sector, as shown in Table 3.8. Furthermore,
the system change also resulted in a reduction of energy contributed to the Petroleum Refineries sector by around 92%, reducing GJ energy/year from 138.64 to 11.55. These results conclude that the sustainable, ABR system change has helped cut the environmental impacts associated with sludge transportation at the RE-SOLVE Superfund site.

3.3.3 Impacts for sodium hydroxide/sulfuric acid production for usage

The aforementioned values for chemical dependency between each system were combined with reported production impact rates to give CO$_2$ and energy rates per year for each chemical in the different systems, as shown in Table 3.8. The conventional treatment scheme reported 19 tons of NaOH used annually—implying values of 75.525 tons of CO$_2$ and 35,938.2 kWh/yr needed for production of this mass of NaOH. Since the bioremediation system only consumed 3.8 tons of NaOH, the implied values for tons of CO$_2$ and kWh/yr of energy associated with sufficient production of NaOH dropped to 15.105 and 7,187.6 respectively; roughly 80% decreases in both regards. Furthermore, the elimination of the 5,400 lbs./year of sulfuric acid with the bioremediation system implementation resulted in the total elimination of the .011 tons CO$_2$/yr and 94.5 kWh/yr associated with sulfuric acid production.

These implications, although mostly based on justified assumptions and available data, indicate that the practice of sustainability has positively impacted the environmental footprint associated with the clean-up of the RE-SOLVE Superfund site in Massachusetts. This impact is a small step in the goal of helping the state reduce its carbon dioxide emissions by 50% by the year 2050. Continued study of process
efficiency and alternatives will be a key factor in helping the state reach this goal in the
time frame allotted, but with sustainable solutions, the goal can be reached.

Table 3.8: Implied Energy and CO\textsubscript{2} differences from production of chemicals
needed in conventional and ABR systems

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Implied CO\textsubscript{2} from production (tons/year)</th>
<th>Implied energy impact from production (kWh/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional Treatment System</td>
<td>ABR System</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>75.525</td>
<td>15.105</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>.011</td>
<td>0</td>
</tr>
</tbody>
</table>

3.3.4 Future work and recommendations

Besides sodium hydroxide and sulfuric acid, there are many other chemicals that
were eliminated, reduced, or increased with the sustainable change of the remediation
system at RE-SOLVE. In the future, values should be found for the CO\textsubscript{2} and energy
impacts associated with the production of said chemicals, and comparisons should be
made between the two processes, as done with NaOH and sulfuric acid. Additionally,
such data is not available for all of the chemicals involved. Research should be done to
analyze their production processes and data should be recorded concerning their
footprints.
Chapter 4: Conclusions

Results from chapter 2, overall, supported the hypothesis that addition of oxygen (weather from pure gas or breathing air gas introduction) will decrease aqueous levels of chloroethane in a mixed media system. The column study, that was built and operated in a greenhouse, resulted in approximately 41% reductions of aqueous chloroethane concentration during periods of breathing air introduction; from about 14 µmol/L to 6 µmol/L from the influent to port 3. Oxygen Amended bottles in the microcosm study also resulted in decreases of chloroethane at 0.84±0.16 µmols throughout the course of the study.

Implementation of the ABR system to replace the conventional physical/chemical portion of the pump and treat remediation implemented at RE-SOLVE Inc. Superfund site resulted in positive sustainability impacts regarding the aspects studied. Operation of the solar photovoltaic system requires no emission of carbon dioxide, thereby eradicating the emissions resulting from energy to run the system (119.82 tons CO₂/yr if natural gas were the original source of energy production and 237.32 tons CO₂/year if coal were the original source). Additionally, a decrease in sludge transportation resulted in reduced contribution to the Petroleum Refineries sector. This decreased stimulus resulted in an implied 92% reduction of CO₂-eq emissions and energy required to refine and manufacture petroleum in the Petroleum Refineries sector. Finally, by minimizing the need of chemicals to treat contaminants at the site, implied CO₂ emissions and energy requirements, contributed to the commercial production of sodium hydroxide and sulfuric acid, were both reduced by 80%.
References


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Appendix

Standard curves for FID analysis of chlorinated organics of interest in column and microcosm study

Figure A.1: Chloroethane standard curve

Chloroethane

\[ y = 2800.2x \]

\[ R^2 = 0.99 \]

Figure A.2: 1,1-Dichloroethane standard curve

1,1-DCA

\[ y = 1086.3x \]

\[ R^2 = 0.99 \]
Figure A.3: 1,1,1-Trichloroethane standard curve

Figure A.4: Vinyl chloride standard curve
Figure A.5: cis-1,2-Dichloroethene standard curve

![cis-1,2-DCE graph](image)

Figure A.6: Anaerobic bioreactor set up for chloroethane generation (Boudreau, 2013)

![Anaerobic bioreactor diagram](image)
Table A.1: T-test for significant difference in chloroethane concentration between consecutive ports; analyzed during and after aeration

<table>
<thead>
<tr>
<th>Period</th>
<th>Ports</th>
<th>Ave. CA, Reactor A (µmol/L)</th>
<th>Reactor A p value</th>
<th>Ave. CA Reactor B (µmol/L)</th>
<th>Reactor B p value</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>During Aeration</td>
<td>Influent vs Port 1</td>
<td>14±0.73 vs 14±0.92</td>
<td>0.61</td>
<td>14±0.91 vs 15±0.76</td>
<td>0.62</td>
<td>No significant difference</td>
</tr>
<tr>
<td></td>
<td>Port 1 vs Port 2</td>
<td>14±0.92 vs 8±0.70</td>
<td>0.00023</td>
<td>15±0.76 vs 10±0.68</td>
<td>0.000033</td>
<td>Significant difference</td>
</tr>
<tr>
<td></td>
<td>Port 2 vs Port 3</td>
<td>8±0.70 vs 5±0.67</td>
<td>0.015</td>
<td>10±0.68 vs 6±0.84</td>
<td>0.0038</td>
<td>Significant difference</td>
</tr>
<tr>
<td>After Aeration</td>
<td>Influent vs Port 1</td>
<td>17±0.86 vs 16±0.53</td>
<td>0.25</td>
<td>17±0.78 vs 16±0.67</td>
<td>0.102</td>
<td>No significant difference</td>
</tr>
<tr>
<td></td>
<td>Port 1 vs Port 2</td>
<td>16±0.53 vs 13±0.67</td>
<td>0.0014</td>
<td>16±0.67 vs 13±0.53</td>
<td>0.0057</td>
<td>Significant difference</td>
</tr>
<tr>
<td></td>
<td>Port 2 vs Port 3</td>
<td>13±0.67 vs 8±0.77</td>
<td>0.00021</td>
<td>13±0.53 vs 8±0.69</td>
<td>0.00011</td>
<td>Significant difference</td>
</tr>
</tbody>
</table>

Table A.2: Statistical analysis of the similarity in chloroethane concentrations between Reactor A and Reactor B while Reactor A has no gas introduced and Reactor B has nitrogen being introduced

<table>
<thead>
<tr>
<th>CA average concentration (µmol/L)</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor A</td>
<td>Reactor B</td>
</tr>
<tr>
<td>Influent</td>
<td>17.48±0.86</td>
</tr>
<tr>
<td>Port 1</td>
<td>16.28±0.53</td>
</tr>
<tr>
<td>Port 2</td>
<td>13.03±0.67</td>
</tr>
<tr>
<td>Port 3</td>
<td>8.28±0.77</td>
</tr>
</tbody>
</table>
Table A.3: Winkler method results of dissolved oxygen levels within Reactor B

<table>
<thead>
<tr>
<th>Port</th>
<th>D.O. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>0.35±0.16</td>
</tr>
<tr>
<td>A1</td>
<td>0.46±0.02</td>
</tr>
<tr>
<td>A2</td>
<td>0.24±0.04</td>
</tr>
<tr>
<td>A3</td>
<td>0.23±0.01</td>
</tr>
<tr>
<td>B1</td>
<td>0.26±0.01</td>
</tr>
<tr>
<td>B2</td>
<td>0.24±0.07</td>
</tr>
<tr>
<td>B3</td>
<td>0.24±0.12</td>
</tr>
</tbody>
</table>

*OCR results for water controls with no solids*

**OCR for Scrubber Water**

\[ y = -0.0092x + 8.3937 \]

\[ R^2 = 0.60 \]

Figure A.7: Oxygen Consumption Rate of Scrubber Water

**OCR for DI Water**

\[ y = -0.0037x + 8.631 \]

\[ R^2 = 0.59 \]

Figure A.8: Oxygen Consumption Rate of DI Water
Vita

Michael Cheatham is from Livingston Parish, Louisiana and the only son of Joseph and Arlene Cheatham. Following high school, Michael proceeded to complete a B.S. in Environmental Engineering at Louisiana State University while beginning work on his graduate thesis the last semester of his senior year due to his interest in bioremediation of hazardous wastes. One year following completion of his B.S., Michael completed his M.S. in Civil and Environmental Engineering under the instruction of Dr. John Pardue in December of 2014. He plans to begin work at Geosyntec Consultants following graduation.