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# Analysis and Remediation of Chlorinated Hydrocarbons in Environmental Media

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Analysis and Remediation of Chlorinated Hydrocarbons in Environmental Media

by

Jonathan Ticknor

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Master of Science in Environmental Engineering  
Department of Civil and Environmental Engineering  
College of Engineering  
University of South Florida

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## **Dedication**

I dedicate this thesis to my wife, Emily, who has been there to support me through all of the tough years of study and research. This effort could have never been accomplished without your unyielding love and support, thank you.

I would like to thank my mother, brother, and sister for their support throughout this journey and all of the encouragement they have provided over the years. A special thank you to Dr. Trotz for her help as a mentor, preparing me for research and helping me choose the path of graduate school. Thank you to Claire Osborn for working alongside me during this project and helping me learn the batch system. A final thank you to Dr. Cunningham. You have been an amazing mentor and teacher for the last three years, providing me with the knowledge and mentorship that made this project possible.

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## Abstract

The two objectives of this work were to develop a simplified method for the analysis of chlorinated organics in water samples and to improve an existing soil remediation technology. The contaminants considered for these studies were chlorinated hydrocarbons because of their relative frequency of appearance at contaminated sites. The first half of this study involved the analysis of chlorinated ethenes by gas chromatography with flame ionization detection (GC-FID). I tested the hypothesis that the FID response factor is the same for all chlorinated ethene compounds. The rationale for this investigation is that if the hypothesis is correct, a single calibration curve can be used for GC/FID analysis of all chlorinated ethene compounds, saving time and money during sample analysis. Based on my measurements, a single calibration curve fits PCE, TCE, and cis-DCE ( $R^2=0.998$ ). However, the apparent slope of the calibration curve for vinyl chloride is approximately 45% lower, indicating that a separate calibration curve must be used to quantify vinyl chloride. I believe this difference in vinyl chloride is due to loss of analyte mass due to volatilization.

The second half of the study considered the effect of solvent composition for a soil remediation technology, entitled remedial extraction and catalytic hydrodehalogenation (REACH), developed by Dr. Hun Young Wee and Dr. Jeff Cunningham (Wee and Cunningham, 2008). The objective of this thesis is to convert 1,2,4,5-tetrachlorobenzene (TeCB) to cyclohexane, thus improving on the work of Wee

(2007). Recent work by Osborn (2011) tested successfully the use of palladium and rhodium catalysts for this conversion, though it took twelve hours for full conversion. Osborn (2011) performed her experiments in a 50:50 water-ethanol solvent; previous work by Wee and Cunningham (2008) suggests that using a 67:33 water-ethanol composition may dramatically reduce the reaction time. Therefore, the goal of this research was to use palladium and rhodium catalysts with a 67:33 water-ethanol solvent composition, with an aim of reducing the reaction time required to fully convert benzene to cyclohexane.

The data suggest that the time required for conversion of the analyte to its product was improved dramatically compared to previous experiments. However, powdered palladium catalyst was used in this study instead of pellet form as in previous studies. The powdered palladium allowed for full conversion of the target chemical, TeCB, to benzene in less than 5 minutes. Benzene was fully converted to cyclohexane within 45 minutes in the batch reactor when a rhodium catalyst was used jointly with palladium. This study suggests that the 67:33 water-ethanol solvent composition be utilized in continuous flow tests in the future to improve the efficiency of the REACH system. The results also suggest that powdered palladium catalyst be considered because of its ability to force the reaction to completion in significantly less time than previous experiments.

## **Chapter One:**

### **Introduction and Objectives**

Chlorinated organics are among the most common environmental contaminants found in the United States (NRC, 1994). Two of the most common classes of contaminants contained in the chlorinated organic family are chlorinated ethenes and chlorinated benzenes. For environmental engineers to develop effective technologies to mitigate these contaminants, we must be able to measure them accurately and develop technologies for removing or transforming them.

In this thesis, I explore both the analysis and remediation aspects of the contaminant removal process. The objectives of the study are to develop a simplified method for the analysis of chlorinated organics in water samples and to improve an existing soil remediation technology. The second chapter will present a new, simplified method for quantifying unknown concentrations of chlorinated ethenes in aqueous samples. This method will allow for the reduction in time and money required to analyze such samples.

The third chapter will discuss the improvement of a proposed soil remediation technology. The goal of this work is to improve the efficiency and reaction time required to remove chlorinated benzenes from soil. The analysis builds on existing work done by Wee and Cunningham (2008). This analysis will hopefully move the technology closer to field-scale use.

## **Chapter Two:**

### **Simplified Analysis of Chlorinated Ethenes by GC/FID**

#### **Introduction to Chlorinated Ethene Analysis**

Chlorinated ethenes are a class of compounds found at numerous contaminated sites in the United States (NRC, 1994). This class of compounds includes perchloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE) isomers, and vinyl chloride (VC). Chlorinated ethenes present a risk to human health because they are generally persistent in the environment and are known or suspected carcinogens (Raaschou-Nielsen et al., 2003). Based on their frequent occurrence and health implications, these contaminants are the focus of significant remediation and environmental research.

In order to analyze environmental samples containing these contaminants, analytical methods for detecting the contaminants must be developed. Chlorinated ethenes are volatile or semi-volatile and thus good candidates for analysis by gas chromatography. Gas chromatography with flame ionization detection (GC/FID) is a common method for quantifying the concentration of these chemicals in environmental samples, including water samples (Otson and Williams, 1982). When analyzing environmental samples, calibration curves for target chemicals must be created to quantify concentrations in samples of unknown concentration. Thus, in general, a

scientist or engineer wishing to analyze chlorinated ethenes would need to develop six separate calibration curves, one for each chemical (PCE, TCE, VC, and three DCE isomers).

However, numerous studies have shown that FID response factors for hydrocarbons are linearly proportional to the number of carbon atoms present (Ettre, 1962; Sternberg et al., 1962; Perkins et al., 1962; Leveque, 1967; Tong and Karasek, 1984; Slemr et al., 2004). Other studies have considered the effect of heteroatoms and functional groups on the response factor and have shown that the “effective carbon number” for these substituted compounds may be different than the unsubstituted hydrocarbon (Perkins et al., 1962, 1963; Mockel, 1976; Kallai et al., 2001). In other words, a hydrocarbon containing heteroatoms or functional groups may exhibit a different FID response factor than the unsubstituted hydrocarbon.

Some researchers have attempted to predict FID response factors for substituted compounds by predicting the effective carbon number or by converting general FID response factors to FID carbon response factors (Jorgensen et al., 1990; Yieru et al., 1990). However, for compounds with simple heteroatom substitution, such as chlorinated hydrocarbons, these rigorous calculations may not be necessary. It has been observed that the presence of a single halogen atom has limited impact on FID response (Sternberg et al., 1962). This leads me to hypothesize that the FID response factor will be the same for all chlorinated ethenes because all chlorinated ethenes have the same number of carbon atoms, and the different number of chlorine atoms will have a negligible effect on the overall response.

This hypothesis is significant because, if validated, it may allow me to simplify the analysis of chlorinated ethenes (and/or other chlorinated hydrocarbons) in water samples. If the FID response factor for all chlorinated ethenes is the same, then one calibration curve could be used for all target analytes during analysis of samples with unknown concentration. Instead of creating six separate calibration curves, only one would be required, resulting in a savings of time and money during sample analysis. To the best of my knowledge, no previous researchers have tested if all chlorinated ethenes exhibit the same FID response factor.

Therefore, the objective of this work was to test the hypothesis that all chlorinated ethenes have the same FID response factor. The implication of this hypothesis is that a single calibration curve could be used for GC/FID analysis of all chlorinated ethenes. The rationale for this study is that, if verified, a calibration curve could be generated for a single chemical and then used for all chemicals in the family, thereby reducing the need for separate calibration curves, and reducing time and cost of analysis.

## **Materials and Methods**

### ***Chemicals and Reagents***

The chlorinated ethenes utilized in this research are listed in Table 2.1. Both vinyl chloride (1000  $\mu\text{g}/\text{mL}$ , from SPEX CertiPrep) and cis-1,2-dichloroethene (2000  $\mu\text{g}/\text{mL}$ , from Restek) were obtained as analytical standards in methanol. Trichloroethene (99.5%, Fisher Scientific), tetrachloroethene (99%, Acros Organics), and methanol (99.9%, Fisher Scientific) were obtained as pure-phase liquids. A stock solution was prepared by adding 1.2 mL of VC in methanol, 1.2 mL of cis-1,2-DCE in methanol, 5  $\mu\text{L}$  of neat-phase TCE,

5  $\mu\text{L}$  of neat-phase PCE, and 1 mL of methanol to a 5-mL glass screw-top vial. The vial containing the stock solution was closed and kept in a freezer to minimize volatilization.

Table 2.1. Properties of Chlorinated Ethenes Used in Analysis

IUPAC Name	Common Name	Abbreviation	Molecular Weight (g/mole)	Henry's Constant* at 21.7 °C
Tetrachloroethene	Perchloroethylene	PCE	165.83	0.580
Trichloroethene	Trichloroethylene	TCE	131.39	0.338
cis-1,2-dichloroethene	cis-Dichloroethylene	cis-DCE	96.94	0.150
Chloroethene	Vinyl Chloride	VC	62.50	0.936

\* Henry's constants are in dimensionless form and were estimated at 21.7°C using equation (3) and Table 2 of Staudinger and Roberts (2001)

In this study I utilized only one of three DCE isomers to ensure that all target analytes could be separated on the GC; inclusion of multiple DCE isomers can result in co-elution or in overlap of the chromatographic peaks. I selected cis-DCE because it is the dominant isomer produced during reductive dechlorination of PCE and TCE (McCarty, 1997).

Aqueous samples were generated using deionized water from a Barnstead water purification system.

### ***Preparation of Stock Solutions***

Sequential dilutions of the original stock solution were performed to obtain solutions of target contaminants in methanol at known concentrations. A solution was

prepared by adding 0.5 mL of solution to a glass screw-top vial and then adding 1 mL of methanol. The new solution was shaken for ten minutes and allowed to sit undisturbed for another ten minutes to ensure complete mixing in the vial. This procedure was repeated to create a total of five solutions of known concentration, where each daughter solution was one-third the concentration of the parent solution.

The methanol solutions were used to create aqueous standards of known concentrations. These aqueous standards mimic environmentally relevant samples such as what might be collected from a contaminated groundwater site. Aqueous standards were made by adding 2 mL of de-ionized water to a 5-mL (nominal size) glass screw-top vial, then adding 20  $\mu$ L of methanol solution containing the chlorinated ethenes. Vials were sealed with an open-hole cap with PTFE septum, and then shaken on a shaker table for 30 minutes.

By using the five different methanol solutions, I produced aqueous standards of five different concentrations. All aqueous standards were created in duplicate; thus I had a total of ten aqueous standards, i.e., two samples each of five different concentrations. Concentrations of the different aqueous standards are shown in Table 2.2. The concentrations of chlorinated ethenes ranged from 43  $\mu$ g/L in the least concentrated to 24 mg/L in the most concentrated standard; this represents a realistic range of concentrations such as what might be found at a contaminated groundwater site.

### ***Analysis of Aqueous Standards***

Headspace analysis was performed on each of the aqueous standards (cf. Otson and Williams, 1982). The aqueous standards in the 5-mL screw-top vials were allowed to

equilibrate with the headspace in the vial for 12 hours at room temperature (21.7 °C). After equilibration between the aqueous phase and the headspace, 1 mL of headspace gas was withdrawn by piercing the septum with a gas-tight syringe. Headspace was analyzed by gas chromatography with flame ionization detection. The chromatography was performed on a Perkin-Elmer Clarus 500 GC. The chromatographic column used was an RTX-1301 (Restek), 30 m length, 0.53 mm inner diameter, 3 µm film thickness. The oven temperature in the GC was held at 35°C for 8 minutes, then increased to 200 °C at 20 °C/min, then was held at 200 °C for 1 minute. The temperature of the FID was 240 °C throughout the experiment. The flow rate of helium carrier gas was 3 mL/min. The temperature of the injector was 180 °C and the injector split ratio was 15:1.

Table 2.2. Concentrations of Chlorinated Ethenes in Aqueous Standards

Aqueous Sample #	PCE Conc. (mg/L)	TCE Conc. (mg/L)	cis-DCE Conc. (mg/L)	VC Conc. (mg/L)
1	24	21	7.0	3.5
2	7.9	7.1	2.3	1.2
3	2.6	2.4	0.77	0.39
4	0.87	0.79	0.26	0.13
5	0.29	0.26	0.086	0.043

Because aqueous standards were created by adding 20 µL of methanol solution to 2 mL of deionized water, the final samples are approximately 0.99% methanol (by volume, neglecting volume change upon mixing). I assume that the presence of this small amount of methanol does not affect the partitioning of the chlorinated ethenes between the aqueous phase and the headspace in the vial.

## Results and Analysis

### *Use of GC/FID Peak Area versus Aqueous Concentration*

Results of the GC/FID analyses of the aqueous standards are shown in Fig. 2.1. The measured GC/FID peak area is plotted versus aqueous concentration for each of the four target contaminants. In other words, Fig. 2.1 presents the GC/FID calibration curves for each of the chlorinated ethenes in aqueous solution. The data in Fig. 2.1 are plotted with logarithmic axes to allow observation of the data points across the entire measured concentration range. The concentration range of the aqueous standards spans two orders of magnitude (as seen in Table 2.2), and thus low-concentration data would not be visible if Fig. 2.1 were plotted with a linear concentration scale.

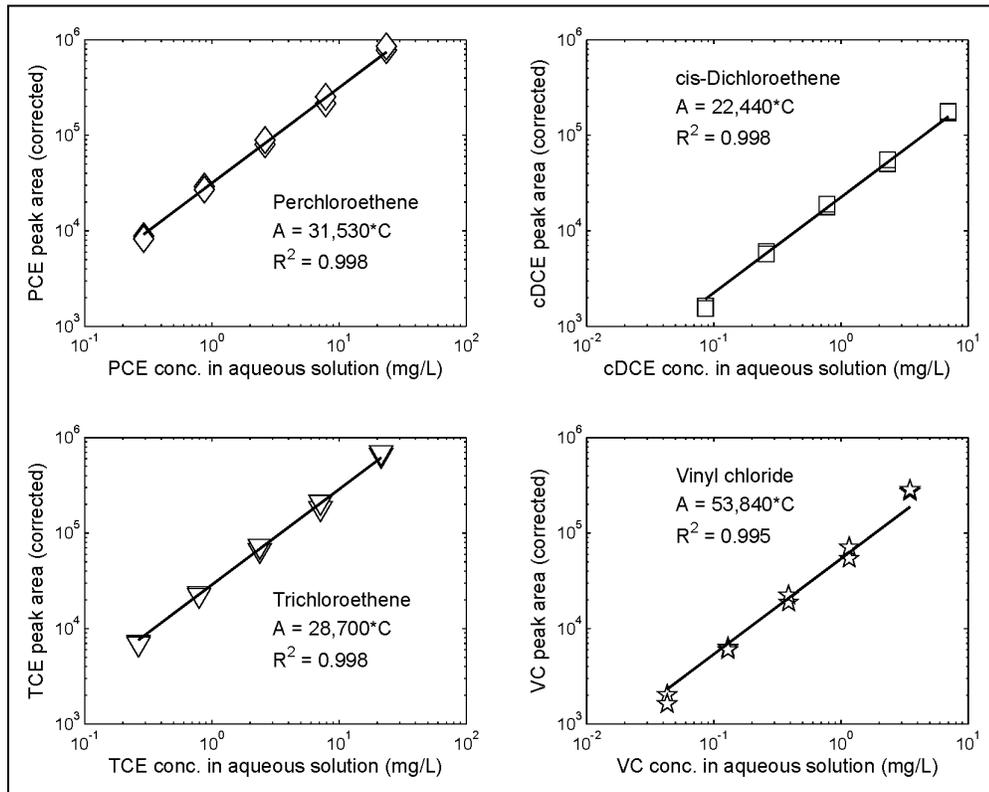


Figure 2.1. Calibration Plot of Peak Area versus Aqueous Concentration

Measured peak areas are corrected using methanol as an internal standard, because all aqueous samples contain the same methanol concentration (0.99% by volume, neglecting change of volume upon mixing). Correction of the peak areas is performed according to the following formula:

$$A_{analyte}^{corrected} = A_{analyte}^{measured} \times \frac{A_{methanol}^{average}}{A_{methanol}^{measured}} \quad (1)$$

where  $A_{analyte}^{corrected}$  is the corrected peak area for the target analyte in a given sample,

$A_{analyte}^{measured}$  is the measured (uncorrected) peak area for that target analyte in that sample,

$A_{methanol}^{measured}$  is the measured peak area for methanol in that sample, and  $A_{methanol}^{average}$  is the average methanol peak area measured for all 10 standards.

It can be seen from Fig. 2.1 that, as expected, the FID peak area is linear with respect to the aqueous concentration of the target analyte. This was observed for all four chlorinated ethenes tested. However, it is important to note that when peak area is plotted versus aqueous concentration, the slopes are different for each of the four calibration curves. In other words, when calibration curves are presented as peak area versus aqueous concentration, a separate calibration curve is required for each target analyte.

### ***Use of GC/FID Peak Area versus Moles of Analyte in Headspace***

The hypothesis of this study is that all chlorinated ethenes have the same FID response factor. To test this hypothesis, I compute the number of moles of each target analyte in the headspace of each sample vial after the aqueous solution and the headspace have reached equilibrium. This computation is performed as follows:

$$M_i^{air} = f_i^{air} M_i^{total} \quad (2)$$

where  $M_i^{air}$  is the number of moles of compound  $i$  in the headspace,  $M_i^{total}$  is the total number of moles of compound  $i$  in the vial, and  $f_i^{air}$  is the fraction of the mass in the headspace. The total number of moles in the vial is easily computed from the initial aqueous concentration:

$$M_i^{total} = \frac{C_i^{aq} V^{water}}{MW_i} \quad (3)$$

where  $C_i^{aq}$  is the initial aqueous concentration of compound  $i$  (as given in Table 2.2),  $V^{water}$  is the volume of aqueous solution in the sample vial (2.02 mL), and  $MW_i$  is the molecular weight of the target analyte (given in Table 2.1). The fraction of mass in the headspace is given by

$$f_i^{air} = \frac{V^{air} H_i}{V^{air} H_i + V^{water}} \quad (4)$$

where  $V^{air}$  is the volume of air in the vial (4.38 mL) and  $H_i$  is the dimensionless Henry's constant for compound  $i$  at the equilibration temperature of 21.7 °C (given in Table 2.1). Equation (4) assumes that the air and water reach full equilibrium within the 12-hr equilibration time. Equation (3) assumes that there are no mass losses (e.g., biodegradation or volatilization) of any of the contaminants once they are introduced into the vials. Note that, although the vials have a 5-mL nominal size, the actual volume of the vial is 6.40 mL, of which 2.02 mL is aqueous solution and 4.38 mL is headspace.

Equations (2)-(4) are used to calculate  $M_i^{air}$ , the mass of contaminant in the headspace, for each chemical in each vial. Figure 2.2 graphs the measured GC/FID peak area versus  $M_i^{air}$  for each of the four target contaminants. Figure 2.2, like Figure 2.1, can be considered a GC/FID calibration curve for chlorinated ethenes in aqueous solution. Also

like Figure 2.1, the data in Figure 2.2 are plotted with logarithmic axes to allow observation of the data points across the entire measured concentration range.

It can be seen clearly from Figure 2.2 that PCE, TCE, and cis-DCE share the same calibration line when the GC/FID peak area is graphed versus the moles of compound in the vial headspace. A single calibration line was determined from the combined PCE, TCE, and cis-DCE data and was found to fit the measured data with  $R^2 = 0.998$ . This indicates that, as hypothesized, these three chlorinated ethenes exhibit the same response factor on the FID: one micromole of PCE results in the same peak area as one micromole of TCE or one micromole of cis-DCE. However, the measured peak areas for VC do not lie on the same line. The slope of the VC calibration curve is about 45% lower than the slope of the PCE/TCE/cis-DCE curve, indicating that the apparent VC response factor is about 45% lower than the response factor for the other three analytes.

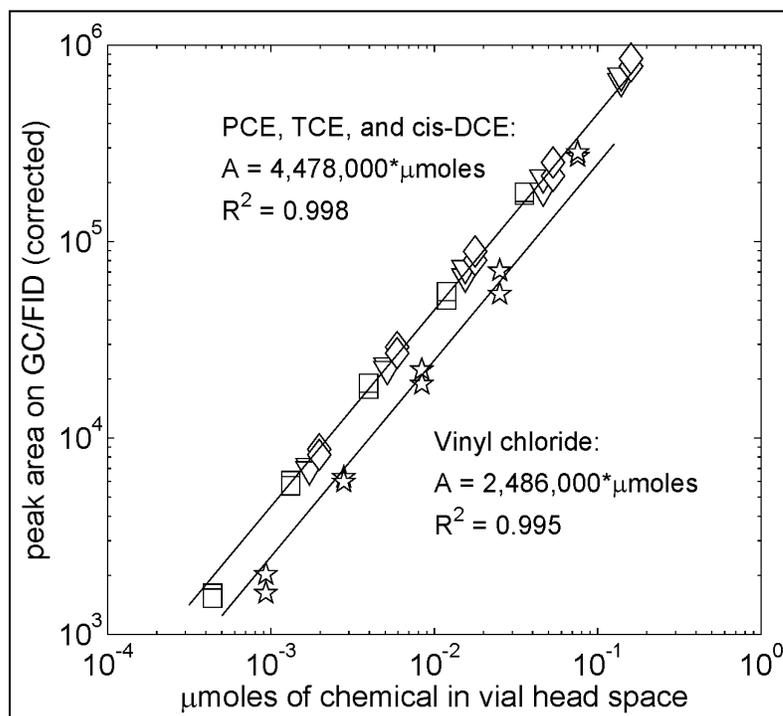


Figure 2.2. Calibration Plot for Headspace Analysis

## Discussion

The finding that PCE, TCE, and cis-DCE all share the same GC/FID response factor is significant. This implies that separate calibration curves do not need to be generated for all three compounds. Any one of these three compounds could be used to generate the calibration curve shown in Fig. 2.2, and the other two compounds would share the same calibration curve. The calibration curves in Fig. 2.1, which are presented as GC/FID peak area versus aqueous concentration, could be computed by starting with the best-fit calibration line from Fig. 2.2 and using equations (2)–(4). This finding will allow scientists and engineers to save time and money in the future by obviating the need to generate separate calibration curves for each individual chlorinated ethene.

However, the observation that the apparent VC response factor is about 45% lower than the PCE/TCE/cis-DCE response factor is surprising. There are three possible reasons for this surprising observation:

1. the central hypothesis of this work is incorrect, and chlorinated ethenes do not all exhibit the same response factor when analyzed by FID;
2. the VC-in-methanol standard from which I constructed my aqueous standards had a concentration which was lower than the promised concentration of 1000  $\mu\text{g/mL}$ , so that I have over-estimated the VC concentration and mass in all samples; or
3. about 45% of the VC was lost out of the vials by volatilization during the 12-hr equilibration period.

Of these three, the third hypothesis seems the most likely. VC is the most volatile of the four chlorinated ethenes considered, as evidenced by its higher Henry's constant (Table 2.1), and thus is the most likely to be lost by volatilization. I am unable to conceive of a

plausible physical mechanism by which a flame ionization detector would respond differently to VC than it does to cis-DCE, TCE, or PCE (cf. Sternberg et al., 1962).

It would be possible to test this hypothesis by, for instance, directly injecting gas standards of VC into the GC/FID, rather than testing the headspace of aqueous standards. However, my focus is on methods of analyzing chlorinated ethenes in aqueous environmental samples, such as what might be collected from a contaminated groundwater site. Therefore, I believe that the headspace analysis conducted here is appropriate. The results of this study suggest that, even if VC does have the same FID response factor as all other chlorinated ethenes, it is still necessary to develop a separate calibration curve for VC; losses due to volatilization may be significant during sample analysis, and must be taken into account by the corresponding calibration curve.

## **Conclusions**

In this chapter, I tested the hypothesis that chlorinated ethenes all exhibit the same FID response factor. The hypothesis was tested by conducting headspace GC/FID analysis of aqueous standards of known concentration. I observed that PCE, TCE, and cis-DCE do exhibit the same FID response factor, as hypothesized. When GC/FID peak area is graphed versus moles of contaminant in vial headspace, a single calibration line is able to fit the PCE, TCE, and cis-DCE data with  $R^2 = 0.998$ . However, the apparent VC response factor is approximately 45% lower than that of the other three chemicals, perhaps due to losses of VC by volatilization during a 12-hr equilibration period. These results imply that it is not necessary to develop separate calibration curves for PCE, TCE, and cis-DCE; this finding may save time and money during analysis of environmental

samples containing chlorinated ethenes. However, it is necessary to develop a separate calibration curve for VC so that any losses from volatilization will be taken into account during sample analysis.

## **Chapter Three:**

### **Remediation of Chlorinated Hydrocarbons in Soil**

#### **Introduction to REACH System**

##### *Motivation for Development of Treatment System*

Chlorinated organics are common soil contaminants found in the United States (NRC, 1994). For this study, a class of compounds known as halogenated hydrophobic organic compounds (HHOCs) was considered. Common subgroups found in this class of compounds include chlorinated benzenes, chlorinated phenols, and polychlorinated biphenyls (PCBs). These contaminants are typically found in soil rather than water because of their low aqueous solubility and fairly low vapor pressure. For this thesis, I chose to consider 1,2,4,5-tetrachlorobenzene (TeCB), as it was used in previous studies for the development of the REACH system (Wee and Cunningham, 2008, 2011).

In the United States, a common method for treating soils contaminated with these compounds is solvent extraction with activated carbon sorption (US EPA, 2001). A major drawback of utilizing this technology for remediation projects is the generation of a secondary waste stream. Instead of destroying the contaminant, the HHOC is transferred to another phase, in this case activated carbon, and then disposed of at a landfill or cleaned by a secondary process (US EPA, 2001). This creates added risk of human exposure at a later time and spreads the original contamination to a new location. Thus, it

is desirable to develop a treatment technology that effectively destroys the contaminant while eliminating the secondary waste stream. Wee and Cunningham (2008, 2011) proposed the remedial extraction and catalytic hydrodehalogenation, or REACH, process to extract HHOCs from contaminated soil and destroy them catalytically without generating a secondary waste.

### ***Previous Research for REACH System***

The original REACH system utilized a palladium (Pd) catalyst for hydrodehalogenation of TeCB to benzene and was tested in batch and semi-continuous configurations to test the viability of the proposed technology (Wee and Cunningham, 2008, 2011). Dr. Wee was successful in dehalogenating the target contaminant (TeCB), but the REACH system was only capable of converting the target contaminant to another toxic compound, benzene. To make the technology commercially viable, the end product of the system must be benign.

### ***Developing an Improved REACH System***

Based on the deficiencies of the previous research, i.e. conversion of the target compound to another harmful contaminant, further research needs to be performed to improve the viability of the REACH system. The fundamental purpose of this study is to fully convert TeCB to cyclohexane through the use of a catalytic process. To achieve this objective, another catalyst must be introduced to hydrogenate benzene, as shown in Figure 3.1. Rhodium (Rh) has been shown to be effective when used in conjunction with Pd for conversion of chlorinated benzenes (Coq et al., 1986). Recent studies by Osborn

(2011) have quantified the removal efficiency and kinetics of the proposed catalyst set up in batch reactor experiments. These studies were run at a 50:50 water-ethanol solvent composition because Wee and Cunningham (2008, 2011) identified that as a likely solvent for full-scale application.

The objective of this research was to convert benzene to cyclohexane, improving on the work of Wee (2007), while reducing the required reaction time seen in the work of Osborn (2011). In recent studies, Osborn (2011) showed that palladium and rhodium is effective at converting benzene to cyclohexane, though the reaction took 12 hours to reach completion. Based on data concerning solvent composition reported by Wee and Cunningham (2008), I hypothesized that increasing the concentration of water in the solvent would improve the effectiveness of the reaction. Therefore, the purpose of this work was to significantly reduce the reaction time by altering solvent composition for the conversion of benzene to cyclohexane.

This study will consider the use of a 67:33 water-ethanol solvent composition as this ratio was shown to be more effective in previous studies (Wee and Cunningham, 2008). Though this reduction in ethanol will negatively affect the solvent extraction of contaminant from soil, the benefits of significantly reducing the reaction time could improve the system overall. The experiments will be run in the same batch system as earlier tests run by Osborn (2011) and Wee (2007) to ensure experimental consistency.

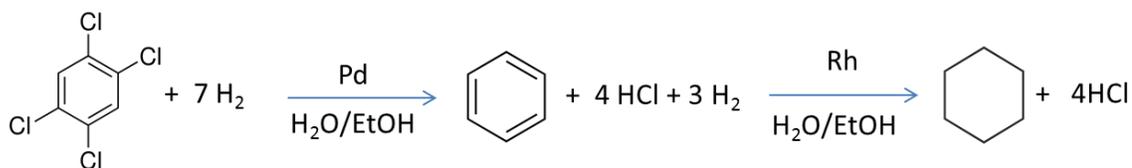


Figure 3.1. Reaction Schematic for REACH System

## **Development of TeCB Calibration Plot**

### ***Chemicals and Reagents***

For this study, ethanol (99.5%, ACS, Aldrich), 1,2,4,5-tetrachlorobenzene (98 %, Sigma Aldrich), trichloroethene (TCE) (ACS, Fischer Scientific), deionized water, and n-pentane (Fischer Scientific) were used to develop a TeCB calibration plot. A stock solvent of 67:33 (vol:vol, before mixing) water-ethanol was prepared by adding the deionized water and 99.5% ethanol together, in appropriate amounts.

### ***Preparation of Standard Solutions***

The stock solution for this study was made by adding 50 mg of TeCB to 20 mL of ethanol in a 20 mL glass vial, producing a stock concentration of 2500 mg/L. This stock was then diluted in a mixture of water-ethanol to form standard solutions of known concentration that could then be analyzed to form a calibration plot. The concentrations of the standard solutions ranged from 10 mg/L to 1.25 mg/L.

### ***Analysis of TeCB Standards***

For each of the TeCB standards, 2 mL were added to 2 mL of n-pentane solution in a 5 mL glass vial. The n-pentane solution was spiked with a known concentration (10 mg/L) of TCE to serve as an internal standard. A screw cap was used to secure the vials and prevent possible volatilization or loss of contaminant from other means. The vials were then shaken on a shaker table for one hour in order to allow the TeCB to transfer into the organic n-pentane phase.

After one hour of mixing, the vials were left to sit for one hour in order to allow equilibration of the solution. Then, 1 mL of n-pentane was drawn off by syringe and put into an auto-sampler vial for analysis by a Perkin Elmer Clarus 500 Gas Chromatograph (GC) with Electron Capture Detection (ECD). An autosampler was used to inject standards into the column, and software was utilized to analyze the results. The autosampler injects 0.5  $\mu\text{L}$  of the pentane to be analyzed by the GC. The column used for this analysis was a DB-5ms capillary column (30 m length, 0.53 mm ID, 1.5  $\mu\text{m}$  film thickness) from J&W Scientific. Peak areas for TCE and TeCB are reported by the software.

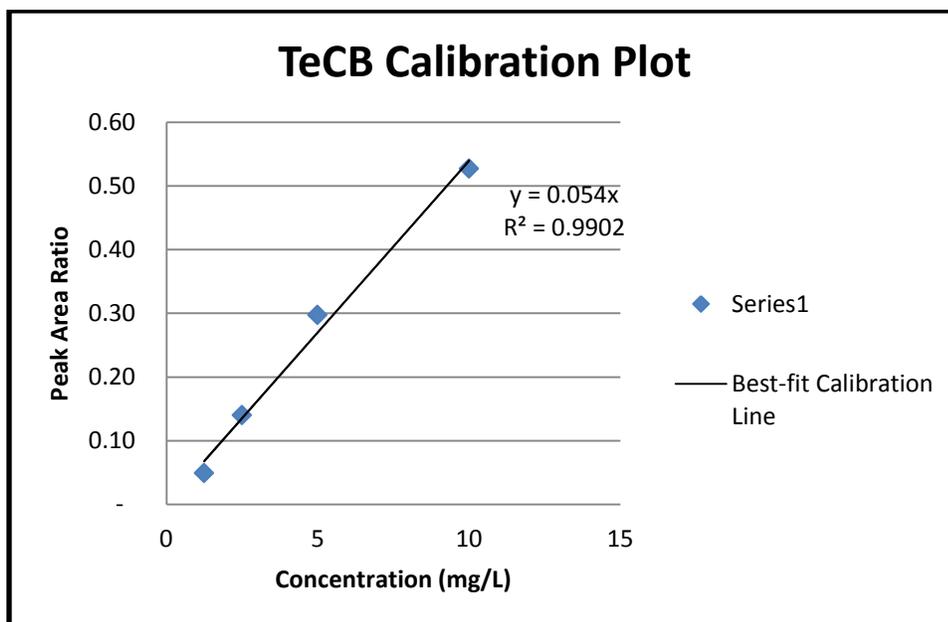


Figure 3.2. TeCB Calibration Plot

### *TeCB Calibration Plot*

The calibration plot developed from this analysis is shown in Figure 3.2. To reduce the error associated with sampling differences, the ratio of the peak areas

(TeCB:TCE) was plotted versus the known concentration of TeCB in the water-ethanol solution.

## **Development of Benzene and Cyclohexane Calibration Plots**

### ***Chemicals and Reagents***

For this portion of the study, ethanol (99.5%, ACS, Aldrich), benzene (99%, Aldrich), cyclohexane (99%, Aldrich), and deionized water were used to make analytical standards for the development of a calibration plot. A 67:33 water-ethanol solvent (vol:vol, before mixing) was prepared by adding appropriate volumes of ethanol and deionized water in a glass beaker.

### ***Preparation of Standard Solutions***

The stock solutions for this study were made by adding 10  $\mu\text{L}$  of both benzene and cyclohexane to 20 mL of the 67:33 water-ethanol solvent in a 20 mL glass vial. Based on liquid densities of 0.876 g/mL for benzene and 0.779 g/mL for cyclohexane, this produced a stock solution of concentration 438 mg/L for benzene and 389.5 mg/L for cyclohexane. This stock was then diluted into 67:33 water-ethanol to form standard solutions of known concentration that could then be analyzed to form a calibration plot. The concentrations of the standard solutions ranged from approximately 4 mg/L to 0.5 mg/L.

### ***Analysis of Standards***

For each of the standard solutions, 2 mL were added to a 5 mL glass vial. A screw cap with PTFE septum was used to secure the vials and prevent possible volatilization or loss of contaminant from other means. The septum is used to allow for headspace analysis through use of a gas tight syringe. The vials were then shaken on a shaker table for one hour in order to ensure proper mixing and equilibration.

After one hour of mixing, the vials were left to sit for twenty-four hours in order to allow equilibration of the solution. Then, a 1 mL headspace sample was extracted from the vial via gas-tight syringe. The 1 mL sample was then manually injected into the Perkin Elmer Clarus 500 GC and analyzed via flame ionization detection. The column used for this analysis was an RTX-1301 capillary column (30 m length, 0.53 mm ID, 3  $\mu\text{m}$  film thickness) from Restek.

### ***Benzene and Cyclohexane Calibration Plots***

The calibration plots for cyclohexane and benzene were prepared by plotting peak area ratio versus concentration in the 67:33 water-ethanol solution. The calibration plots can be seen in Figures 3.3 and 3.4. Since these samples were tested using headspace analysis, ethanol was utilized as an internal standard to account for error associated with differences in sample collection in injection. To utilize this internal standard, the peak area of the target contaminant was divided by the peak area of ethanol to obtain a peak ratio. This ratio was then plotted versus the concentration to obtain the calibration plots shown.

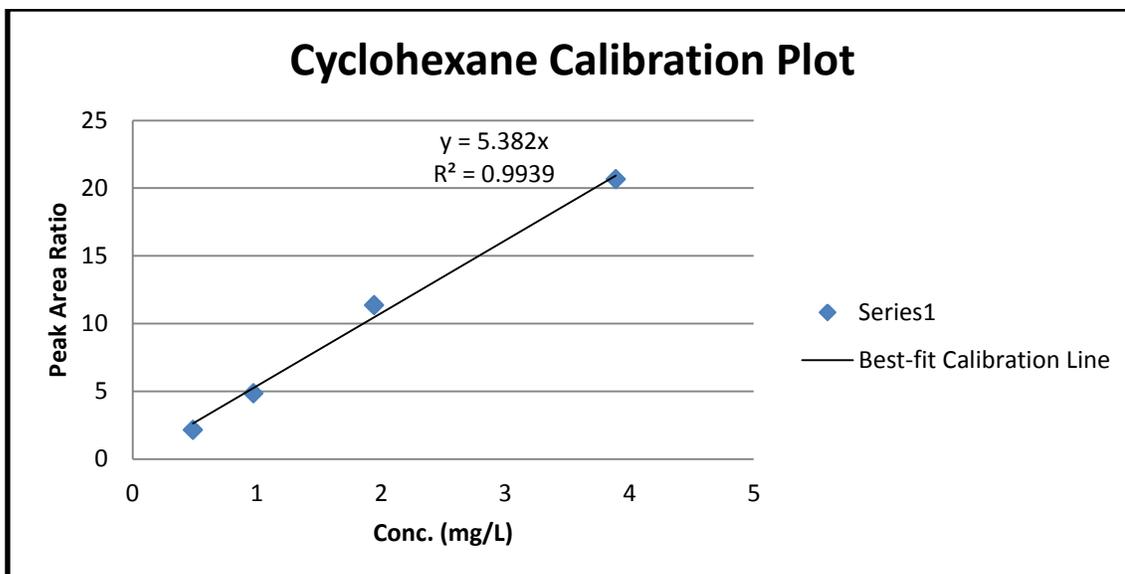


Figure 3.3. Cyclohexane Calibration Plot

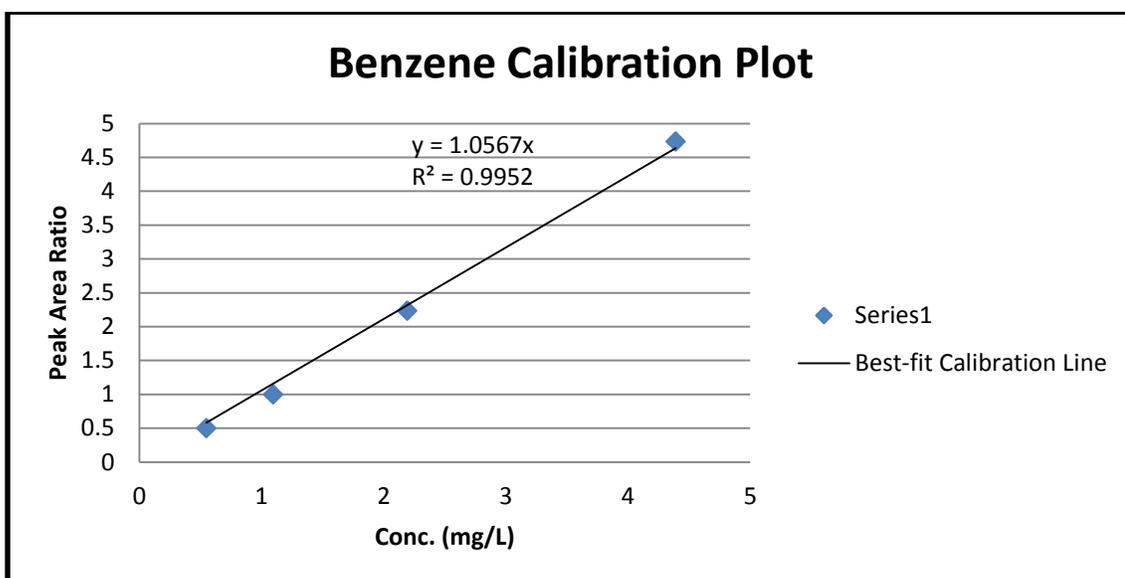


Figure 3.4. Benzene Calibration Plot

## Batch Reactor Analysis of Pd and Rh Catalyst

### *Chemicals and Catalysts*

The chemicals used for this portion of the study include ethanol, deionized water, and 1,2,4,5-tetrachlorobenzene, as described previously. The Rh catalyst (Aldrich)

employed is 0.5 % (wt.) on a  $\text{Al}_2\text{O}_3$  support, while the Pd catalyst (Aldrich) is 5 % (wt.) powder catalyst on  $\text{Al}_2\text{O}_3$  support. For ease of study, it is assumed that the weight percent specified by the manufacturer is correct. The stock solution that is utilized to spike the batch reactor was created by adding 50 mg of TeCB to 20 mL of ethanol in a 20 mL glass vial to form a 2500 mg/L solution. The stock solution was kept in a freezer to prevent volatilization and promote consistency across studies.

### ***Previous Research Utilizing Pd and Rh Catalysts***

As mentioned previously, experiments have been run by Osborn (2011) to test the effectiveness of utilizing Pd and Rh catalysts together to improve the REACH system. These experiments utilized a 50:50 water-ethanol concentration and the same Rh catalyst described above. However, for those studies a pellet form of the Pd catalyst was used, where a powder catalyst is used in this analysis. Osborn (2011) showed that full conversion of TeCB to cyclohexane could be obtained within 12 hours. Her study not only provided proof of concept, but also set a base from which future optimization of the REACH system could be compared. The goal of this study was to improve the reaction time and efficiency of the system by altering the solvent composition within the reactor.

### ***Reaction Study Set Up***

For this study, all batch reactor experiments were performed utilizing a Parr 3911 hydrogenation apparatus (Parr Instrument Company). This system was used to maintain consistency with tests run by Wee (2007) and Osborn (2011), where this same system was used to perform batch reactor experiments.

For these experiments, a 300 mL solution of 67:33 water-ethanol was formed by adding 200 mL of water and 100 mL of ethanol to a 500 mL glass reaction bottle. The solution was then spiked by adding 1.2 mL of the 2500 mg/L TeCB stock solution to the reaction bottle. This should result in an initial TeCB concentration of 10 mg/L in the reactor. Two initial samples were taken to confirm the initial concentration of TeCB in the reactor before starting the system. To prepare the reactor for the experiment, 1 g of Rh catalyst and 0.2 g of Pd catalyst were added to the bottle. The bottle was then placed in the reactor and sealed with a stopper that contains a hose for hydrogen gas. Air contained in the headspace of the bottle was removed by filling the bottle with 45 psi of hydrogen gas and venting to ensure all air was removed prior to experimentation.

The headspace of the reactor was then filled with 50 psi of hydrogen gas, at which time shaking began. The reactor bottle was shaken at 200 rpm to ensure complete mixing, and the reaction was run at room temperature. After shaking for the required reaction time, the reactor was removed. Four samples were taken, two of which were analyzed for TeCB and two for benzene and cyclohexane. After sampling, the contents of the reactor were disposed of and the reactor was cleaned. I selected reaction times of 5 min, 15 min, 30 min, and 45 min. All experiments were performed in duplicate.

### ***Sampling and Analysis***

At the end of each batch reactor experiment the reaction bottle was removed from the apparatus and four separate samples were taken for analysis. To ensure that no catalyst material was present in the samples, the samples were filtered. This procedure ensures that no powder Pd catalyst is introduced in the sample which could then be

injected in the gas chromatograph and possibly destroy the column. Of the four samples, two were taken to be analyzed by GC/FID to quantify cyclohexane and benzene concentrations while the other two were taken to be analyzed by GC/ECD to quantify TeCB concentrations. The remaining solution containing the catalyst was then disposed in a proper waste container.

Separate samples were taken at the beginning and end of each run for the desired reaction times. To ensure accurate measurements, one experiment was performed for each desired reaction time instead of removing samples at each of the target times for one total reaction. This method allows me to check the mass balance of the system and eases the calculations necessary to derive the final contaminant concentrations.

## **Results and Discussion**

The results of these experiments are shown in Figure 3.5, which shows the disappearance of TeCB in the hydrodehalogenation reaction followed by the conversion of benzene to cyclohexane through a hydrogenation reaction. The initial TeCB that is spiked into the system is fully converted within 5 minutes, which is significantly faster than earlier experiments have shown (Wee, 2007; Osborn, 2011). Figure 3.5 also shows that hydrogenation is complete within 45 minutes of total reaction time, which is a significant reduction in required reaction time from previous studies (Osborn, 2011). The hydrogenation reaction appears to move rapidly after 15 minutes, and benzene concentration in solution is reduced to less than 50% of its maximum value by 30 minutes of reaction time.

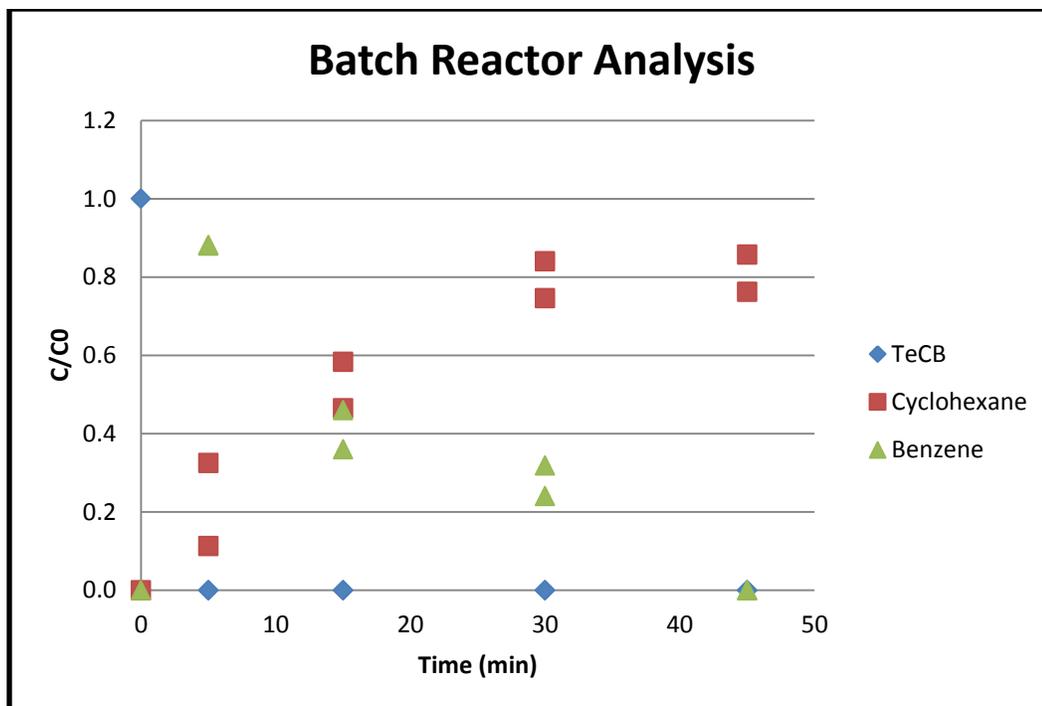


Figure 3.5. Reaction Data for Pd and Rh Catalyst Experiments

Table 3.1 shows the data for reaction times and the associated mass fractions of each of the contaminants. It can be seen that all experiments had mass balance errors of less than 25%, and most had mass balance errors of less than 10%. The data in Table 3.1 show clearly that the use of a 67:33 water-ethanol solvent composition allows for full conversion of TeCB to cyclohexane in less than one hour. When comparing the results of these experiments to previous studies with Pd and Rh for the REACH system, this solvent composition produces significantly shorter reaction time. Experiments performed by Osborn (2011) with a 50:50 water-ethanol solvent ratio showed complete conversion of TeCB within 12 hours. This is significantly longer than the 45 minutes required after altering the solvent composition.

Table 3.1. Batch Reactor Experiment Mass Fraction Data

Time (min)	TeCB (C/C <sub>0</sub> )	Benzene (C/C <sub>0</sub> )	Cyclohexane (C/C <sub>0</sub> )	Total (C/C <sub>0</sub> )
0	1	0	0	1
5	0	0.88	0.32	1.21
5	0	0.88	0.11	0.99
15	0	0.36	0.58	0.94
15	0	0.46	0.46	0.92
30	0	0.24	0.84	1.08
30	0	0.32	0.75	1.07
45	0	0	0.86	0.86
45	0	0	0.76	0.76

There are a few possible explanations for the significantly shorter reaction time observed in these experiments. Two separate experiment parameters were changed from the experiments run by Osborn (2011) for the experiments described in this study. The parameter of interest to this researcher is the solvent composition and its effect on reaction time. However, due to availability from vendors, a powder form of the Pd catalyst was utilized in these experiments compared to pellet sized catalyst used in previous experiments (Osborn, 2011). The increased surface-to-volume ratio provided by the powder catalyst could be part of the reason for increased reaction rate seen in the hydrodehalogenation reaction. The data show that this reaction is complete with 5 minutes, where in previous experiments TeCB was completely converted within 6 hours (Osborn, 2011).

However, the data also indicate that the hydrogenation reaction occurred much faster in the experiments performed here, with full conversion of benzene to cyclohexane within 45 minutes of reaction time. The previous study with 50:50 solvent composition showed complete hydrogenation in approximately 4 hours, which is significantly longer than observed in this study (Osborn, 2011). Generally we would not expect the rate of the hydrogenation reaction to be affected by the Pd catalyst, only by the Rh catalyst; see Figure 3.1. The Rh catalyst utilized in this study was identical to that used in previous experiments. It is possible that the Pd catalyst is contributing to the hydrogenation reaction, but Wee (2007) did not observe hydrogenation of benzene when Pd was used without Rh.

A single experiment was performed to test the hypothesis that the decreased dehalogenation time was due to the solvent composition solely. I used the same initial experiments as those done by Osborn (2011), i.e. 50:50 solvent composition, with the powder catalyst. I observed that that the reaction time is almost identical to my experiments with 67:33 solvent composition, significantly faster than earlier experiments performed by Osborn (2011). This leads me to believe that the increased surface area-to-volume ratio of the powder catalyst is having a dramatic impact on the reaction rate. Future experiments will need to test the solvent composition effect on just the hydrogenation step to see if the solvent is in fact affecting the hydrogenation rate. Also, future experiments should consider the use of powder catalyst in the system as it dramatically reduces reaction time.

## Conclusions

These experiments have shown that the proposed change in solvent composition to 67:33 water-ethanol solution was successful at a hydrogen pressure of 50 psi. Both the hydrodehalogenation and hydrogenation reactions occurred in a shorter period of time than observed previously, reducing the required reaction time from 12 hours (Osborn, 2011) to approximately 45 minutes. However, the decreased reaction time may not be wholly due to the change in solvent composition. Another possible reason for this dramatic increase in hydrodehalogenation rate could be the use of powdered Pd catalyst as opposed to the pellet form used in previous experiments. Future tests would need to be run at a solvent composition of 50:50 water-ethanol to see if the reduction in reaction is due to the new catalyst, altered solvent composition, or a combination of both.

This experiment does suggest that utilizing powder Pd catalyst in the REACH system would be an effective solution to improving the existing technology. Though powder Pd would be more difficult to filter and would require larger liquid pressure to push contaminated solvent through the packed reactor, the reduction in reaction time could offset this issue. However, to fully consider this option, the contribution of the powder catalyst in the reaction must be quantified. The decreased reaction time for hydrogenation would seem to indicate that the change in solvent composition is the most likely reason for decreased reaction time, because we would not expect hydrogenation rate to be affected by the Pd catalyst.

This research indicates that changing the solvent composition to a higher water percentage is beneficial for improving the catalytic step of the technology. Another possible scenario for improving the technology would be to increase the reaction

hydrogen pressure, which could improve the efficiency. Reactions using the scenario considered in this thesis will need to be run in a continuous flow system to assess their viability for field-scale technology implementation.

## **Chapter Four:**

### **Summary and Future Work**

#### **Summary**

The research contained in this thesis explored the analysis and remediation of chlorinated organic contaminants in different environmental media. A simplified method for analyzing aqueous samples containing unknown concentrations of chlorinated ethenes was developed. I have shown that the FID response factor for all chlorinated ethenes, except vinyl chloride (VC), is the same. This means that calibration plots for one or two chemicals can be developed and then utilized for all of the other target contaminants. This discovery will save time and money for researchers or practitioners who need to analyze water samples for chlorinated ethenes.

Calibration plots for each of the chemicals were developed over a broad range of realistic environmental concentrations. The data suggest that the VC response factor is approximately 45% less than the other chlorinated ethenes. I believe this apparently low response factor is actually due to volatilization of the compound (see Table 2.1 for Henry's constant) and does not refute the hypothesis that all chlorinated ethenes have the same FID response factor. This simplified method may lead to the reduction in time and money spent for analysis, despite the fact that a separate plot for VC will likely need to be developed.

The second half of the thesis focused on the optimization of the REACH system developed previously by Wee and Cunningham (2008, 2011), and recently expanded by Osborn (2011). The REACH system was developed as a novel technology for the treatment of halogenated hydrophobic organic contaminants to reduce the production of secondary waste and harmful reaction byproducts. An improved REACH system that utilized Pd and Rh catalysts, for hydrodehalogenation and hydrogenation respectively, was tested by Osborn (2011) at a hydrogen pressure of 50 psi and 50:50 water-ethanol solvent composition. In this thesis, I explored changing the solvent composition to 67:33 water-ethanol to improve the reaction rate and efficiency of reaction.

The data contained in Chapter 3 indicate that increasing the solvent composition to 67:33 improved the required reaction time considerably. The hydrodehalogenation and hydrogenation reactions went to completion within 45 minutes, significantly faster than the previous 12 hours (Osborn, 2011). Though some of this improvement may be attributable to the powder Pd catalyst used, the data suggest that the hydrogenation reaction was also improved dramatically. Improvement to the hydrogenation reaction is likely the result of the change in solvent composition, not the result of a change in Pd catalyst, because the hydrogenation reaction is expected to be catalyzed by Rh, not by Pd. A significant contribution of this work is showing that the solvent composition plays a key role in the REACH system, and that the proposed solvent composition for the original system, utilizing Pd only, was not optimal for the new system. This research is a key step in improving the REACH system and moving the technology towards field-scale use.

## **Future Work**

To confirm the hypothesis presented with the simplified method for analyzing chlorinated ethenes with GC/FID, tests will need to be run on the other DCE isomers to prove beyond a reasonable doubt that all of the contaminants have the same FID response factor. Another important study will be to analyze what exactly is happening to the 45% of VC that is being lost throughout the experimentation. This can be performed by injecting known amounts of gaseous VC directly into the GC to confirm that volatilization was in fact the mechanism present here and that the behavior of VC does not violate the hypothesis of a single response factor for all chlorinated ethenes.

The REACH system will require significantly more work to move to field-scale usage, despite the major steps of the research performed by Osborn (2011) and me. Optimization of the hydrogen pressure, reaction temperature, and catalyst employed are among the possible considerations. The first step in improving the REACH system will be the testing of the conditions presented in this thesis in a continuous flow system. This is vital as the final technology seeks to create a closed loop continuous system (Wee and Cunningham, 2011).

Improving the efficiency of the system is vital to the cost and effectiveness of this technology in the broad market of soil remediation technologies. The high cost of using precious metal catalysts is a significant consideration, but reduction in reaction time and catalyst usage obtained by optimizing parameters, as in this thesis, will improve the viability of the technology. I hope the data collected in this thesis will ultimately help improve the technology and move it toward use in field-scale applications.

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