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Remediation of Chlorinated Alkanes by Zero Valent Iron with Vitamin B12 and Utilization of a Modified Gradual Release of Responsibility Model in a Large Enrollment Chemistry Course

Nicole Lapeyrouse
University of Central Florida

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REMEDIATION OF CHLORINATED ALKANES BY ZERO VALENT IRON WITH VITAMIN B_{12}
AND
UTILIZATION OF A MODIFIED GRADUAL RELEASE OF RESPONSIBILITY MODEL IN A LARGE ENROLLMENT CHEMISTRY COURSE

NICOLE LAPEYROUSE
Bachelor of Science, Florida International University, 2013
Master of Science, University of Central Florida, 2016

A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Chemistry
in the College of Sciences
at the University of Central Florida
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Major Professor: Cherie L. Yestrebsky

ABSTRACT

The following dissertation looks at addressing environmental contaminants in the environment and the integration of an active learning style in an introductory chemistry course. It begins with addressing the concern for chlorinated propanes and ethane in the environment and the importance of looking into environmental remediation applications. This research looks at incorporating vitamin B_{12} as an environmentally friendly catalyst in the presence of zero valent iron for the reduction of chlorinated propanes and ethane. Chapter 2 presents the analytical methods and conditions in which samples were run. The results from these experiments are discussed in length in Chapter 3. Our results confirmed the hypothesis that vitamin B_{12} could act as an electron mediator to facilitate the reduction of the chlorinated propanes and ethane. Degradation was examined by observing the formation of byproduct peaks and the release of free chloride into solution. In Chapter 4, vitamin B_{12} is integrated into an already established industrial application technique, emulsified zero valent iron, and we observed the degradation of 1,2,3-trichloropropane with the formation of byproducts as the reaction progressed. In Chapter 5, this section of the dissertation focused on chemical education and observing an active learning technique in a fundamental chemistry course. The following study was designed to increase students' positive attitude, engagement, and responsibility in a large enrollment chemistry course by utilizing a modified Gradual Release of Responsibility (GRR) model. GRR progressively transfers responsibility from the instructor to the student, allowing students to be more independent and helping them to address atypical problems. Students were assessed using iClickers to monitor their understanding and engagement, as well as surveys to determine their attitudes regarding this specific style of teaching. The results from this study demonstrated that implementing the GRR teaching style had a positive effect on student academic performance and shows the importance of using an active teaching model in a large enrollment course.

This dissertation is dedicated to all the strong women in my life. I wouldn’t be who I am today if it wasn’t for your guidance and mentorship.

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LIST OF ABBREVIATION

1-CP	1-chloropropane
1,2-DCA	1,2-dichloroethane
1,3-DCP	1,3-dichloropropane
1,2-DCP	1,2-dichloropropane
1,2,3-TCP	1,2,3-trichloropropane
B_{12}	vitamin B_{12}; cyano-cobalamin
B_{12a}	vitamin B_{12}; aquacobalamin
B_{12r}	reduced vitamin B_{12} oxidation state Co(II)
B_{12s}	super-reduced vitamin B_{12} oxidation state Co(I)
Cl-VOC	chlorinated volatile organic compounds
Co	cobalt
DNAPL	dense non-aqueous phase liquid
EZVI	emulsified zero valent iron
GC	gas chromatography
MCL	maximum contaminant level
MS	mass spectrometer
NAPL	non-aqueous phase liquids
NASA	National Aeronautics and Space Administration
NPL	National Priorities List
ppb	parts per billion (µg/L)
ppm	parts per million (mg/L)
PRB	permeable reactive barrier

PVC	polyvinyl chloride
SEE	steam enhanced extraction
TCE	1,2,3-trichloroethene
ZVI	zero valent iron
ZVM	zero valent metal

CHAPTER 1: INTRODUCTION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS

Overview of chlorinated volatile organic compounds

Chlorinated volatile organic compounds (Cl-VOCs) are a class of compounds that pose an environmental concern due to their ubiquitous infiltration and harmful effects. Cl-VOCs were heavily used until the mid-1980s as solvents in industrial applications such as dry cleaning, pharmaceutical synthesis, adhesive manufacture, metal component cleaning, and many others[1-2]. These compounds have been inadvertently released into the environment through spills, leaks, and improper disposal, or intentionally released[3]. Due to the release of these chemicals into the environment they have contaminated many environmental matrices, one particular point of accumulation being groundwater, and there is therefore a need for remediation of these persistent compounds. Chlorinated solvents have been detected at roughly 80% of US Superfund sites and at over 3,000 US Department of Defense sites[4].

Common physical properties of Cl-VOCs include higher densities than water, high volatility, and low water solubility. Due to these characteristics these compounds are able to migrate vertically beneath the water table and persist as dense non-aqueous phase liquids (DNAPLs). After penetrating the saturation zone, DNAPL pools form which can then act as long-term sources of groundwater contamination. **Figure 1** shows how these chemicals are then able to continuously contaminate aquifers[5]. Remediation of Cl-VOCs, such as 1,2,3-trichloropropane (TCP), 1,2-dichloropropane (1,2-DCP), 1,3-dichloropropane (1,3-DCP), 1-chloropropane (1-CP), and 1,2-dichloroethane (1,2-DCA), is of great concern due to their toxicity and their environmental persistence.

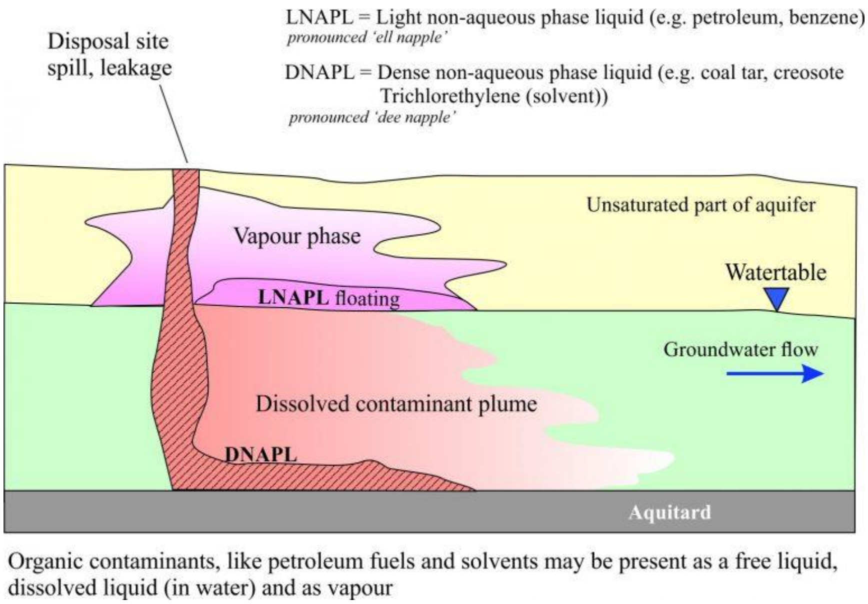
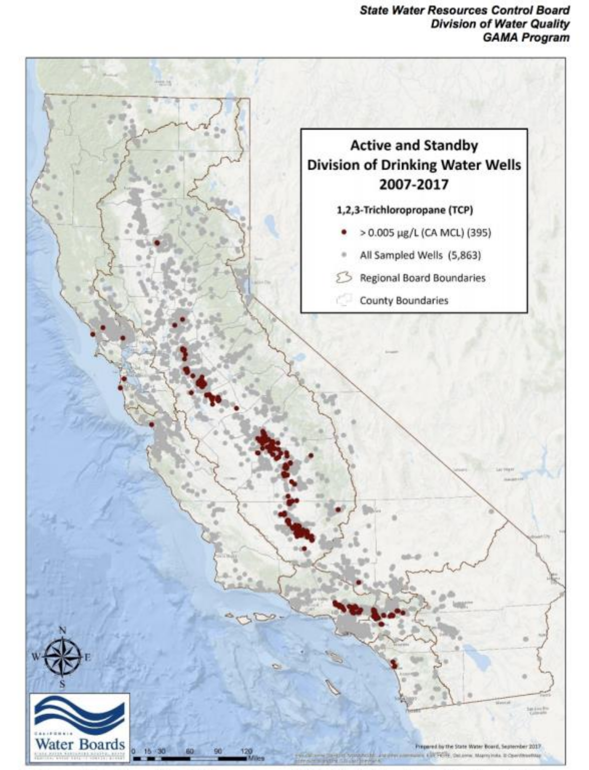


Figure 1: *Diagram of DNAPL and LNAPL (Reproduced from Heron Instruments)*[6]

Chlorinated propanes

Chlorinated propanes were heavily used as soil fumigants, cleaning/degreasing agents, and as precursors in synthesis. 1,2,3-TCP, 1,2-DCP, and 1,3-DCP all pose health risks to humans. Both 1,2,3-TCP and 1,2-DCP are classified as potential human carcinogens. Contamination of environmental matrices with chlorinated propanes, such as 1,2,3-TCP, occurs at industrial and agricultural sites, which can contaminate groundwater.



Active and standby public drinking water wells that had at least one detection of TCP above the MCL, 2007-2017, 395 wells. (Source: Public supply well data in GeoTracker-GAMA.)

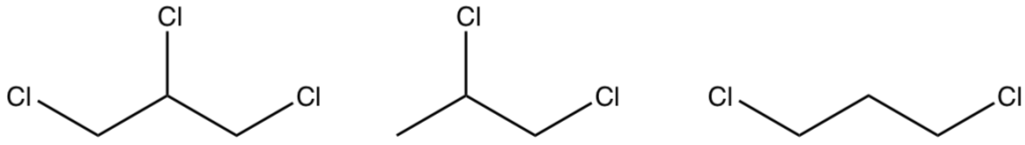
Figure 2*: Well sites contaminated with 1,2,3-TCP in California (Reproduced from California Water Boards)*[7]

Currently, 1,2-DCP is a contaminant of concern at over 100 Superfund sites with a maximum contaminant level (MCL) in drinking water of 0.52 parts per billion (ppb). Despite this low MCL, 1,2-DCP has been found at concentrations exceeding 24 parts per million (ppm) at well sites in Louisiana[8]. Despite the wide usage of 1,2,3-TCP and its likelihood of being a carcinogen, it currently has no defined MCL. 1,2,3-TCP has been detected in more than 300 drinking wells in California above 1,2,3-TCP's notification level. **Figure 2** shows the locations of these contaminated wells. Due to the adverse effects associated with these chlorinated propanes it is vital to find an environmentally friendly way to remediate them.

Chlorinated aliphatics, including chlorinated propanes, have been shown to be recalcitrant to a number of commonly employed remediation techniques, such as in the presence of ZVI[9]. In the case of chlorinated propanes studies have shown little to no degradation under reductive conditions[10-11]. However, in anaerobic conditions, bacterial degradation has been seen for some chlorinated propanes[12-14]. With these compounds showing little degradation in environmental systems, it is important to investigate environmentally friendly methods of remediation.

Chlorinated ethanes

Chlorinated ethanes have been used in a multitude of industries and are still being utilized today. They are often introduced into the environment as a result of industrial production, intentional release, leakages from storage tanks, and spills. The saturated molecule 1,2-DCA has been used as a metal degreaser, household cleaner, chemical intermediate, pesticide, and more. The production of 1,2-DCA is still necessary today to manufacture polyvinyl chloride (PVC) pipes, upholstery, and as a chemical solvent. The yearly global production of 1,2-DCA was over 15 million tonnes in 2002, which is alarming due to it being a reasonably anticipated carcinogen that is known to affect the central nervous system, liver, and renal systems[15-17]. Of the 1,585 National Priorities List (NPL) sites, 1,2-DCA has been detected at least 570[18].



(a) 1,2,3-TCP (b) 1,2-DCP (c) 1,3-DCP

(d) 1-CP (e) 1,2-DCA

Figure 3*: Lewis structures of (a) 1,2,3-TCP, (b) 1,2-DCP, (c) 1,3-DCP, (d) 1-CP, and (e) 1,2-DCA*

Current remediation techniques

Due to the widespread contamination of Cl-VOCs there is an urgent need for remediation. A number of technologies have been employed which strive to contain and remediate these compounds, such as pump and treat, thermal treatment, and zero-valent iron (ZVI) technologies.

Pump and treat

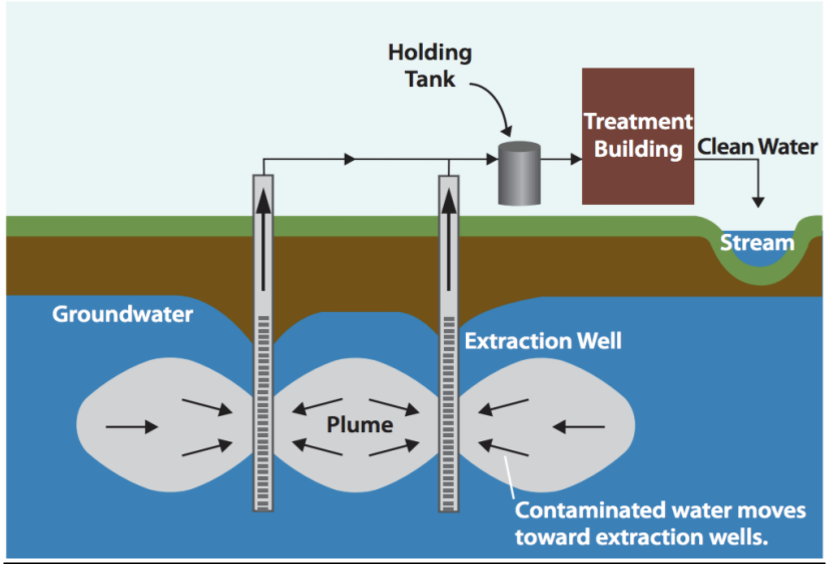


Figure 4: *Diagram of a pump and treat system (Reproduced from USEPA)* [19]

Due to the low solubility of 1,2,3-TCP (1,750 ppm), 1,2-DCP (2,800 ppm), 1,3-DCP (1,750 ppm), and 1,2-DCA (8,600 ppm), these compounds are able to contaminate aquifers for extended periods of time[20-23]. The slow release of DNAPLs into aquifers makes these sources difficult and costly to treat. The pump and treat method for remediating groundwater contamination is a commonly employed treatment option for chlorinated solvents, chemical spills, and fuel oils. In this system, ground water is pumped to the surface where it is then treated. The above ground treatment system may consist of activated carbon, air stripping, and/or other chemical treatment options in order to remove contaminants from the water. However, this treatment can be costly and time-consuming, and the nature and complexity of the contamination may require multiple treatment methods for the same groundwater. Pump and treat systems are primarily used to contain the spreading of contamination rather than to remediate.

Thermal treatment

Thermal treatment has been extensively utilized for the remediation of non-aqueous phase liquids (NAPL). This technique applies heat to contaminant source zones, i.e. soil and in water, in order to increase the removal efficiency of volatile and semi-volatile compounds. Steam enhanced extraction (SEE) is a thermal treatment technique that has been shown to be a robust and effective remediation technique. SEE pumps steam to the contaminant source zone and, once sufficiently heated, volatilization of the organic compounds is induced so those gas phase contaminants may then be removed by multiple extraction wells. This technique has been used to treat chlorinated solvents, fossil fuels, DNAPL, and more. However, this technique has a number of drawbacks to it, including increased cost due to high energy demand and post-treatment excavation of soil to ensure complete remediation of the contaminants.

Zero-valent iron

ZVI has been shown to be effective in the degradation of chlorinated aliphatics, dechlorination of dyes, reduction of metals and more. Iron has gained attention due to it being an abundant, low cost, non-toxic metal, as well as having a useful negative reduction potential (E^0=-0.44V). Due to these characteristics ZVI has been extensively used in a wide range of remediation technologies including both permeable reactive barriers (PRB) and emulsified zero valent iron (EZVI).

PRBs are an *in situ*-remediation technique that employ ZVI and other reactive materials to passively remediate contaminated plumes. A model PRB system is shown in **Figure 5**. These barriers are installed downfield of the source zone and allow polluted ground water to permeate through it, at the same time remediating the contaminants by reaction with the barrier material, the end result being decontaminated groundwater flow. However, a drawback to this remediation system is that it is a passive technique and is dependent on the ground water flow. This technique is time consuming to implement, slow to take effect, and requires long term monitoring of the site.

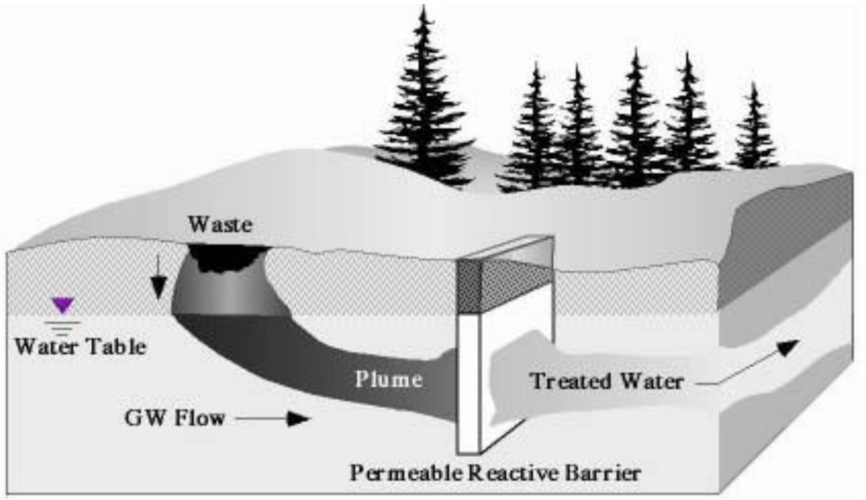


***Figure 5**: Diagram of a PRB layout (Reproduced from the University of Newcastle Australia)*[24]

The above-mentioned remediation technologies have a number of drawbacks, such as prolonged treatment time, high cost of implementation, and limited remediation potential. The National Aeronautics and Space Administration (NASA) funded the development of EZVI in response to chlorinated organic contamination at its Cape Canaveral, Florida facility[25]. EZVI is a biodegradable surfactant-stabilized oil-water emulsion with a water-ZVI core. It has shown success in the remediation of trichloroethene (TCE) both in laboratory bench scale experiments and in field studies to treat source zone contamination[26-28]. The lipophilic nature of DNAPLs encourages their diffusion across the emulsion droplet's enclosing oil membrane into the water-

ZVI core where dehalogenation occurs on the iron surface. In addition, the oil and surfactant promote anaerobic biodegradation of the chlorinated compounds by serving as long-term electron donors.

However, degradation of chlorinated alkanes has been shown to be ineffective in the presence of ZVI. Due to the widespread usage of these compounds, there is a need to focus on remediation technology to address these chemicals.

Vitamin B_{12}

Scientists have always been inspired by nature, such as in the case of understanding naturally occurring catalysts. For instance, in 1948 vitamin B_{12} (cobalamin, or simply B_{12}) was discovered to be a crucial cofactor for a wide range of biological processes. Cobalamin is one of a few naturally occurring organometallic molecules and is a water-soluble vitamin. It is essential in the human body for metabolism and DNA synthesis, is a naturally occurring electron mediator, and plays a vital role in nervous system functions[29]. The structure of B_{12}, as shown in **Figure 6**, contains a cobalt (Co) atom situated in the center of a corrin ring and is a non-toxic cobalt complex. Cobalamin is also known to catalyze enzymatic process including isomerization, methyl transfer, and dehalogenation[30].

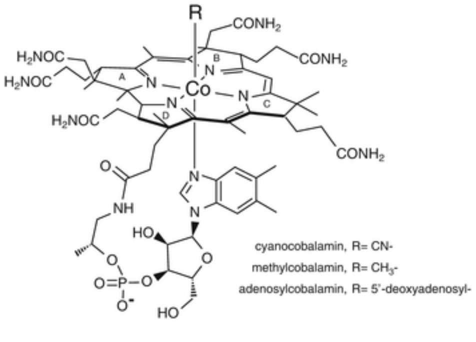


***Figure 6**: Vitamin B_{12} (Reproduced from Yamada, K.)*[31]

The catalytic nature of cobalamin has attracted numerous scientists to study the various organic reactions it catalyzes. Cobalamin derivatives are highly functionalized molecules and can exist in three different oxidation states: Co(III), Co(II), and Co(I). The axial coordination of the cobalt center determines the formal oxidation state of cobalt: if both axial positions are bound, this is Co(III), one axial ligand indicates Co(II) (in the case of cobalamin, this is referred to as reduced B_{12}, or B_{12r}), and Co(I) has no axial ligands bound[32]. The first reduced state, Co(II), is a radical and the further reduced state Co(I) is a super-nucleophile (also referred to as B_{12s}). The mechanism of electron transport depends upon the number of axial ligands bounded to the cobalt center. In the Co(II) state, which has one axial ligand, only a single electron can be transferred. However, in the case of Co(I), which does not have any axial ligands, two electrons can be transferred due to it having two unpaired electrons.

Cobalamin derivatives have been shown to be able to dehalogenate organic compounds in the presence of reducing agents such as titanium citrate. These strong reducing agents act as bulk electron donors to ensure the complete reduction of cobalamin to the super-reduced B_{12s} state. Reduced forms of cobalamins have been shown to successfully reduce chlorinated compounds in the presence of these bulk electron donors[33-35]. However, these reducing agents are not feasible for use in environmental applications.

It is hypothesized that reduced forms of B_{12} will be able to act as an electron transport in order to facilitate the dechlorination of chlorinated alkanes in the presence of ZVI.

Dissertation objectives for Cl-VOCS

Chlorinated alkanes are recalcitrant compounds that have shown minimal degradation in the presence of ZVI. These molecules are contaminants of concern because of the extensive adverse effects associated with them. The following dissertation will explore the reductive dechlorination of the chlorinated alkanes 1,2,3-TCP, 1,2-DCP, 1,3-DCP, 1-CP, and 1,2-DCA in neat samples in the presence of ZVI and B_{12}. In addition, experiments will be performed on 1,2,3-TCP in the presence of a modified EZVI formula containing B_{12}. Based on results from previous studies, a suitable reaction mechanism will be proposed.

CHAPTER 2: MATERIALS AND METHODS FOR CL-VOCS

Standard solutions of 1,2,3-TCP, 1,2-DCP, 1,3-DCP, 1-CP, and 1,2-DCA were purchased from Sigma Aldrich; saturated solutions of each standard were prepared by adding each standard to ultra-purified deionized water until it no longer dissolved. Solutions were thoroughly mixed on a stir plate for 24 hours, then allowed to settle prior to each use. Microscale (µ) ZVI was provided by Provectus Environmental Products.

Emulsions were made with store bought vegetable oil, food grade surfactant (Span 85 or Lonzest® STO-20), µZVI, cyanocobalamin, and ultra-purified deionized water. Surfactant and cyanocobalamin were provided by Provectus Environmental Products.

Experimental Procedures

Neat samples

Ultra-pure deionized water was deoxygenated by purging with argon for 30 minutes prior to spiking it with the chlorinated standard. The final concentration of the solution was calculated based on the solubility of the particular chlorinated compound in water at 25˚C. For the experiments containing B_{12}, solutions were prepared with the appropriate concentration of B_{12} and were then deoxygenated. The neat experiments used 0.50 ± 0.01g of µZVI and were weighed into 20mL glass crimp top vials. Immediately before starting the experiments the iron was washed with 10mL of 1% sulfuric acid solution for 5 minutes then rinsed 3 times with 10mL of ultra-pure deionized water. Vials were then filled to zero-head space with the stock solution and the vials were crimped with an aluminum ring over a butyl rubber septum. Samples were then placed on a Lab Companion Series K-57013 Reciprocating shaker table (50 rpm) until the desired time point, at which point they were removed from the shaker table and placed in a Crest bench top sonicator for 10 minutes. After sonication, samples were removed from the vials via a Hamilton gas-tight syringe into a 40mL VOA vial with septum. The volume removed depended upon the dilution factor of the time point. The internal standard was chlorobenzene.

Emulsions

Emulsions were prepared by using an Oster 6811 blender set to high on the shred setting. For EZVI, the components were combined in the following mass ratios: 39% vegetable oil, 1.5% surfactant, 10.0% µZVI, and 50.5% water. In addition, sulfuric acid was added to the water to a final concentration of 1% in order to clean the oxide layer from the ZVI. The iron and water were blended together for 2 minutes prior to the addition of oil and surfactant. The surfactant was mixed into the oil then slowly added to the water and iron. After this addition, everything was allowed to continue mixing for 3 minutes and was allowed to settle for an hour before using.

B_{12} emulsions were prepared in a similar manner to EZVI, but with a final concentration of 0.5mM B_{12} was added to the water. Emulsion studies were prepared in the same fashion as neat experiments, substituting 0.50 ± 0.01g of emulsion for µZVI.

Analysis

Analysis of samples was performed on a Teledyne Tekmar Atomx Purge and Trap feeding an Agilent 6850 gas chromatograph (GC) coupled to an Agilent 5975c mass spectrometer (MS) with an RTX-VMS column (30m, 0.25mm i.d, 1.40µm d_f). Ultrapure helium acted as the carrier gas and had a constant flow of 1.0 mL/min. The GC/MS had a split flow with a ratio of 20:1 with the injector temperature set to 140˚C and the ion source temperature at 230˚C. All samples were run on the following GCMS method except 1,2-DCP. The oven temperature was initially 32˚C and held for 8 minutes, then ramped to 60˚C at 5.00˚C/min, held at 60˚C for 5.00 minutes, then ramped to 180˚C at 15˚C/min and held at 180˚C for 1 minutes. The method for 1,2-DCP the oven temperature was initially 35˚C then ramped to 60˚C at 5.00˚C/min, held at 60˚C for 5.00 minutes, then ramped to 180˚C at 15˚C/min and held at 180˚C for 3 minutes. The Purge and Trap parameters were as follows: transfer line temperature 140˚C, trap type: #10, purge ready temperature 40˚C, purge time 11 minutes with a flow of 40mL/min, dry purge 0.50 minutes with a flow of 40 mL/min, desorb preheat 245˚C, desorb time 1 minute at 250˚C, bake 2 minutes at 280˚C. Both instruments were equipped with auto-samplers.

Samples were run on an Agilent 8453 UV-visible spectrophotometer and diluted by a factor of 10.

In addition, a Thermo-Fischer Dionex ICS-1100 ion chromatography with suppressed conductivity detection was also used for the analysis of free chloride in solution. The method was a 30-minute isocratic method with a sodium carbonate (4.5mM) and bicarbonate (0.8mM) eluent with a flow of 1mL/min.

Gaussian 09 software package was used to perform all DFT calculations in this research. The geometries and energies of each molecule were optimized and calculated with B3LYP functional and LANL2DZ basis set in order to achieve balanced accuracy and cost. In addition, PCM solvent model was also applied for all calculations. For Vitamin-B12, side chains in the structure were eliminated during calculation.

CHAPTER 3: KINETIC STUDIES ON THE DECHLORINATION OF CHLORINATED ALKANES

1,2,3-TCP

The recalcitrant nature of chlorinated propanes and ethanes is attributed to their chemical and physical properties. The oxidation state of each carbon atom contributes to whether a molecule will be susceptible to reduction or oxidation. Typically, the higher the oxidation number of the carbon atom, the more likely it is to undergo reduction, conversely, lower numbers favor oxidation. Chloropropanes and chloroethanes such as 1,2,3-TCP, 1,2-DCP, 1,3-DCP, 1-CP, and 1,2-DCA all have relatively low average oxidation states compared to chlorinated alkenes, which is why these compounds show little to no degradation under reductive conditions[10-11]. In addition, alkenes are inherently more reactive due to the presence of pi-bonds.

Studies were conducted to determine whether or not the addition of B_{12} would facilitate the reductive dechlorination of chlorinated alkanes. In particular, 1,2,3-TCP, which is only produced by human activities, has been shown to be resistant to degradation due to its high chemical stability[9, 36-39]. Due to its wide spread contamination in the environment it has piqued the interest of scientists seeking potential remediation strategies. However, it has also been shown to not readily degrade in the presence of commonly employed remediation techniques, such as ZVI[37, 40]. Sarathy, *et al.* evaluated the reactivity of 1,2,3-TCP in the presence of zero valent zinc and observed rate constants significantly faster than in the presence of ZVI[37]. While endeavoring to find an alternative method to remediate 1,2,3-TCP, experiments were conducted to determine the rate of dechlorination in the presence of μZVI with and without B_{12}.

The results from these experiments supported the conclusion that, in the presence of just μZVI, no significant degradation was observed, and no by-products were formed throughout the 1-week experiment. **Figure 7** displays the GCMS spectrum of 1,2,3-TCP in the presence of just µZVI. Any observable loss of 1,2,3-TCP concentration can be attributed to sorption onto the iron surface, which is displayed in **Figure 8**.

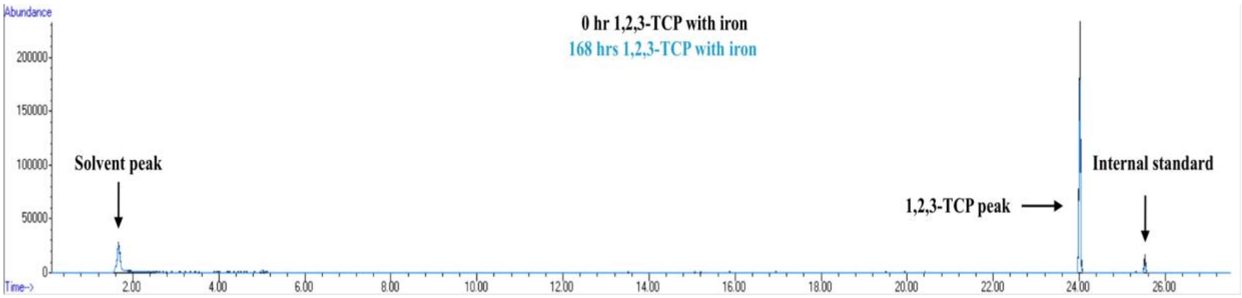


Figure 7*: GCMS spectrum of 1,2,3-TCP at 0hr (black) and 192 hours (blue) in the presence of µZVI*

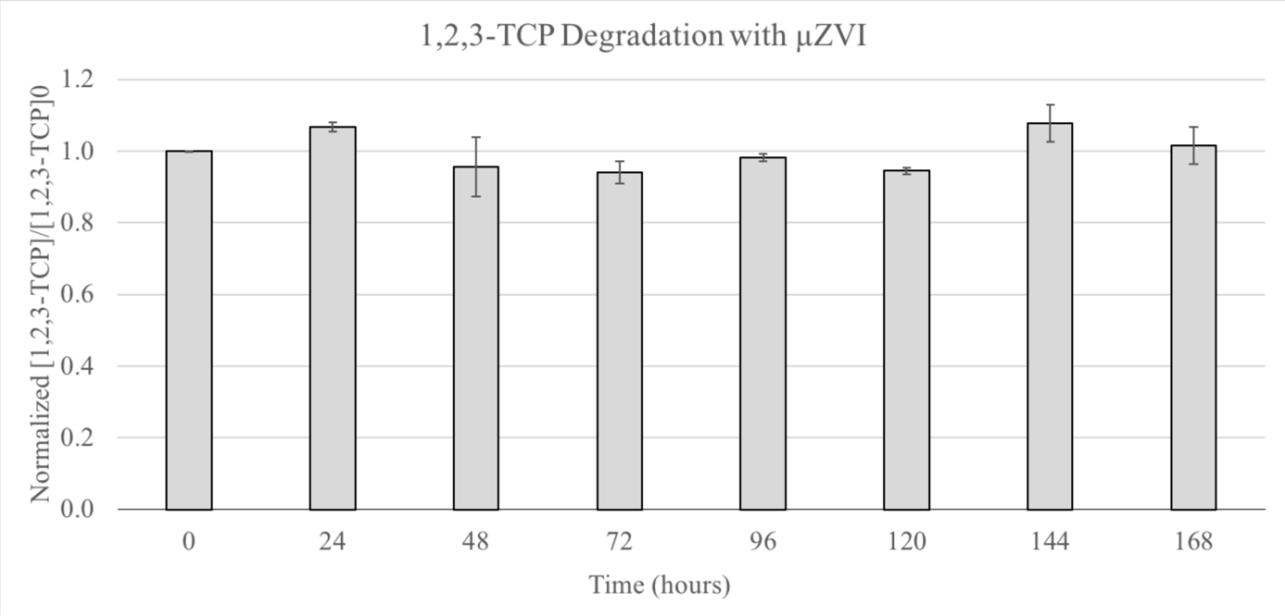


Figure 8*: Degradation of 1,2,3-TCP by µZVI (grey)*

However, in the presence of 1mM B_{12} in addition to µZVI, reduction of 1,2,3-TCP was observed within 24 hours and continued over the course of 192 hours. The loss of 1,2,3-TCP can be observed in **Figure 9**. Throughout the degradation, the formation of propene was observed, which was verified by comparison with a propene standard; propene was the only observable by-product.

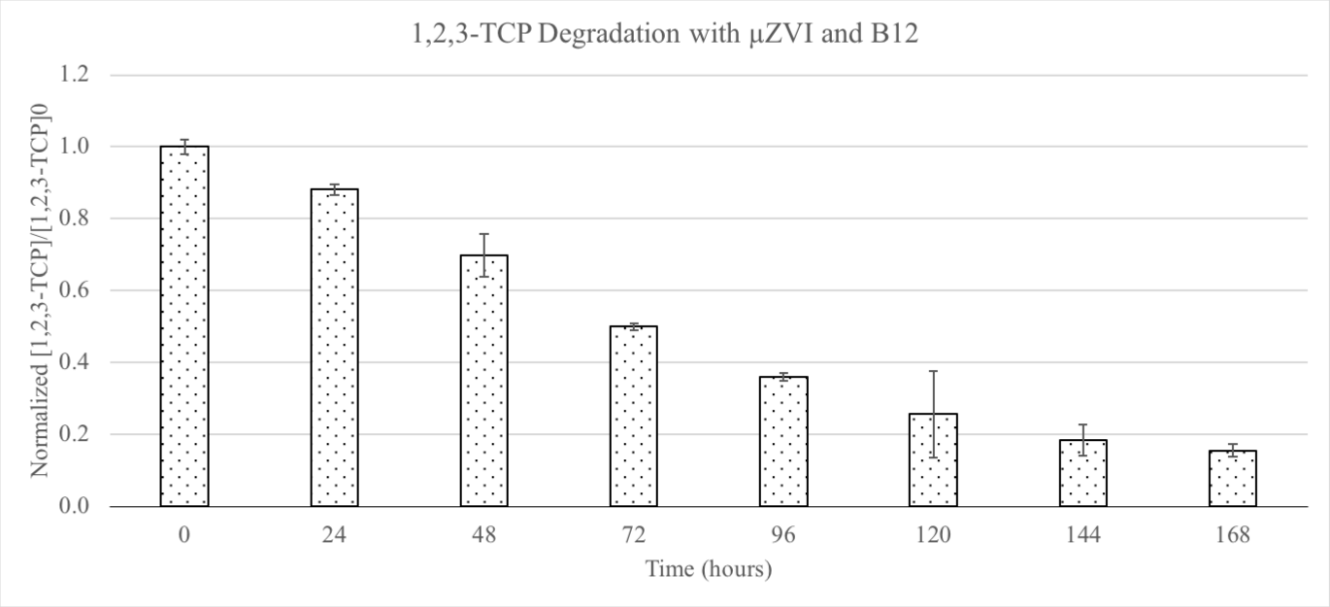


Figure 9: Degradation of 1,2,3-TCP by µZVI with B12 (polka dots)

Propene formation can be observed in **Figure 10**, which of the initial concentrations of propene and 1,2,3-TCP to their concentration after 7 days of exposure to µZVI and B_{12}.

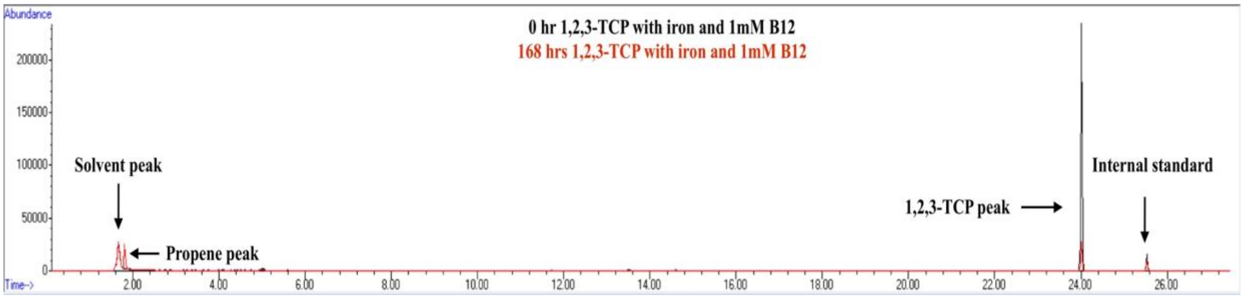


Figure 10: GCMS spectrum showing the formation of propene after 7 days

The reaction follows pseudo-first-order reaction kinetics with respect to 1,2,3-TCP concentration, with an observed rate constant of 0.0121 hr^{-1} and a half-life of 57 hours. The rate equation and half-life are described in **Eq. 1** and **2**, while **Figure 11** displays the pseudo-first-order integrated rate plot. Reactions with zero valent metals (ZVM) and cobalamin with halogenated methanes and ethenes have been similarly reported to follow pseudo-first order reactions [35, 41].

$$Rate = -\frac{\mathrm{d}[1{,}2{,}3-\mathrm{TCP}]}{dt} = k_{obs}[1{,}2{,}3-\mathrm{TCP}] \qquad \textbf{(1)}$$

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k_{obs}} \qquad \textbf{(2)}$$

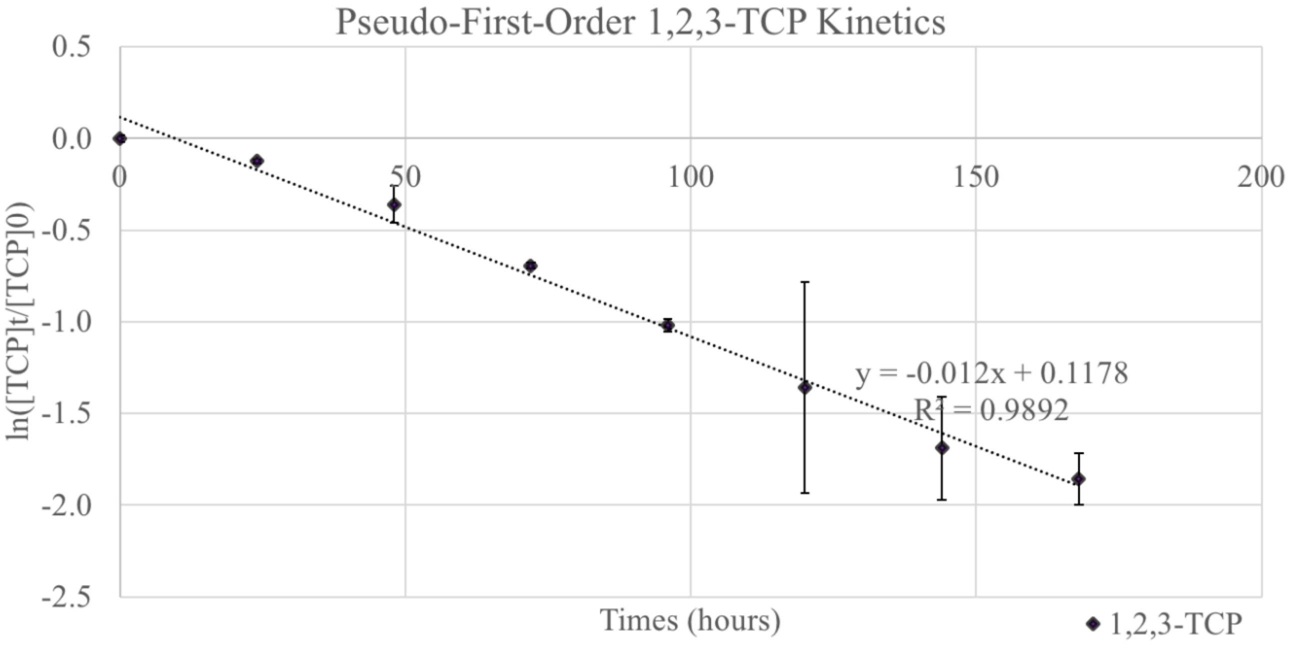


***Figure 11**: Pseudo-first-order reaction kinetics for 1,2,3-TCP with 1mM B_{12} with µZVI*

In order to further verify the reduction of 1,2,3-TCP, samples were run on a Thermo-Fisher Dionex ICS-1100 ion chromatograph with suppressed conductivity detection to verify the increase of chloride in solution to support the degradation. The concentration of chloride in solution was monitored over time in the presence of µZVI and B_{12}. In the presence of just µZVI there was a negligible increase in chloride concentration, as shown in **Figure 12**, due to the release of chloride from the ZVI surface. Samples devoid of chlorinated compounds were analyzed over the course of 4 days to quantify this release.

The results from this experiment agree with the literature in the fact that 1,2,3-TCP is recalcitrant and no degradation is observed in the presence of μZVI alone. However, when μZVI is employed in concert with B_{12}, the concentration of chloride in solution increased significantly throughout the reaction. The formation of propene and increase of chloride in solution support the degradation of 1,2,3-TCP in the presence of μZVI and B_{12}. A mole balance was calculated based on the release of chloride into solution and had a 72.7% ± 2% recovery of chloride. A number of side reactions can occur which can sequester chlorinated intermediates causing a decrease in chloride recovery.

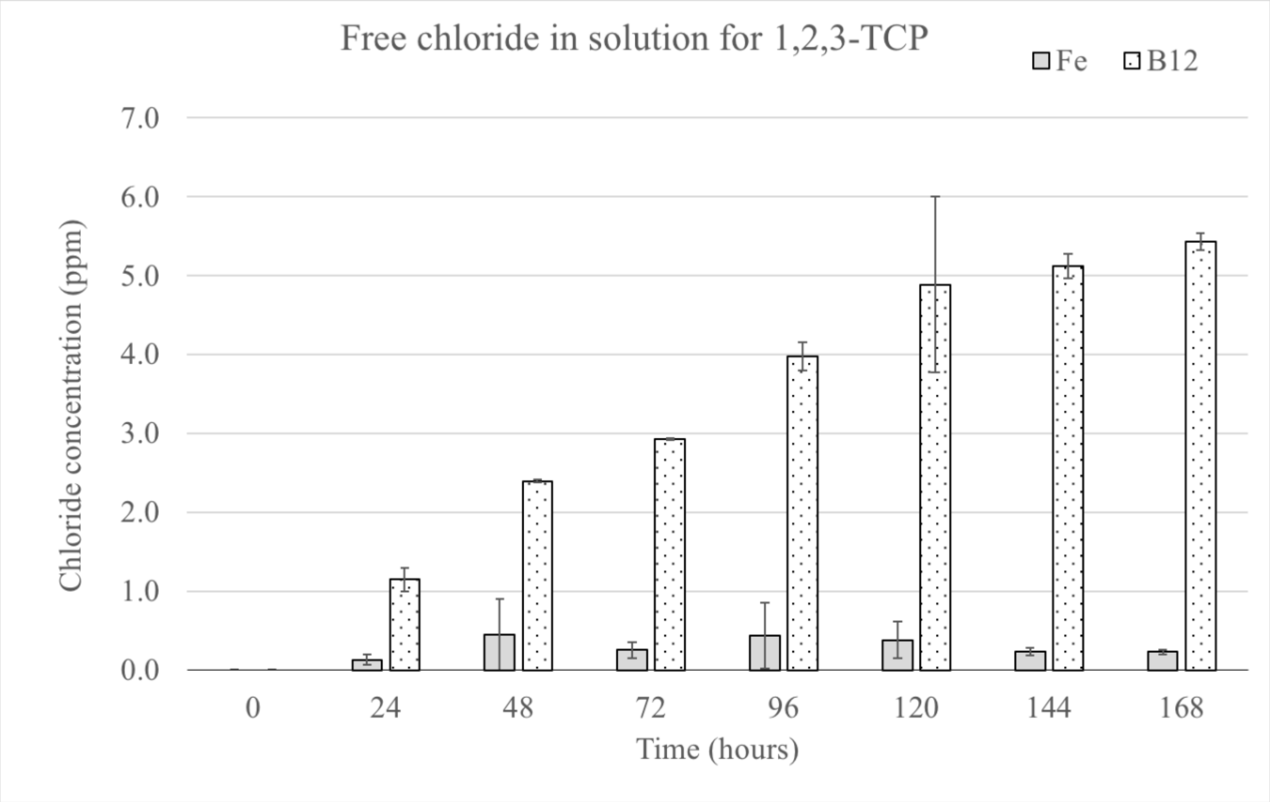


***Figure 12**: Comparison of the increase in concentration of free chloride in solution between µZVI (grey) and µZVI with B12 (polka dots)*

1,2-DCP

1,2-DCP has also been shown to be unaffected by a number of remediation techniques. A study performed by Huang, *et al.* followed the degradation of 59 VOCs with thermally activated persulfate, however, 16 of the targeted compounds, including 1,2-DCP and 1,3-DCP, showed little to no degradation in the presence of persulfate[42]. A study performed by Loffler, *et al.* saw complete reductive dechlorination of 1,2-DCP to propene in the presence of anaerobic bacteria.

Studies were set up to determine whether B_{12} could facilitate the reductive dechlorination of 1,2-DCP. As previously stated, 1,2-DCP has been shown to resist a number of remediation technologies. This was also observed when experiments were conducted in the presence of just µZVI and no significant degradation was observed over a 21-day period. The results of this experiment can be observed in **Figure 13**, which shows the concentration of 1,2-DCP relatively unchanged. **Figure 14** shows that over this period of time no by-products were formed.

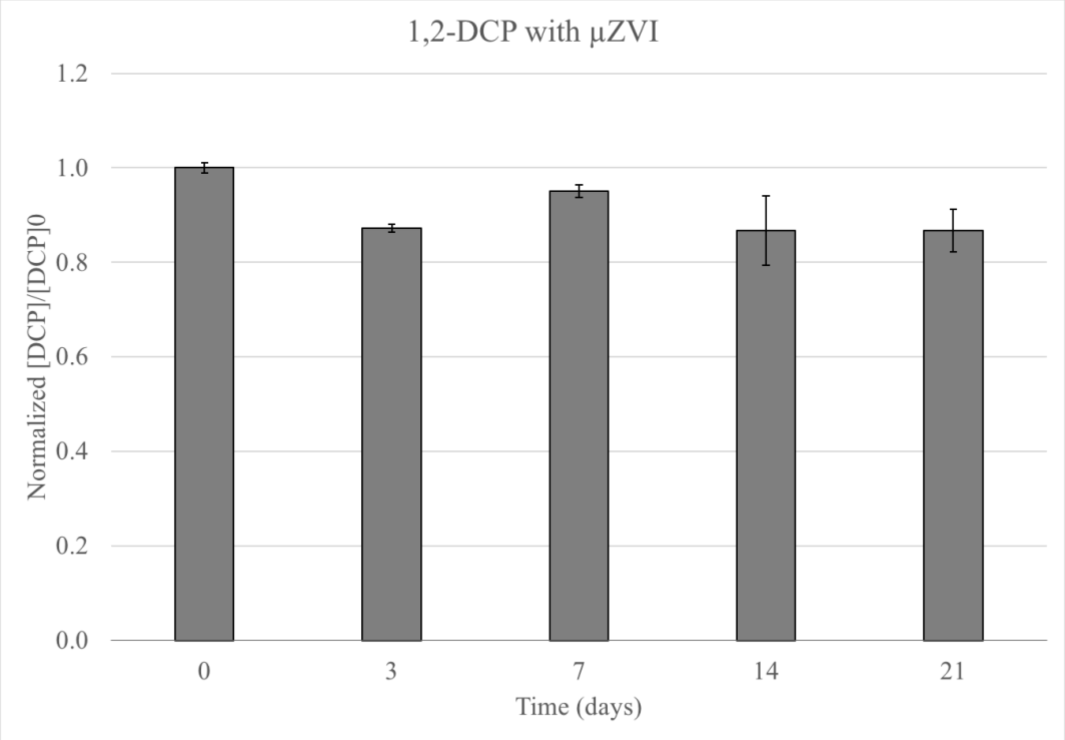


Figure 13: Relative concentration of 1,2-DCP (grey) in the presence of µZVI over a 48-day period

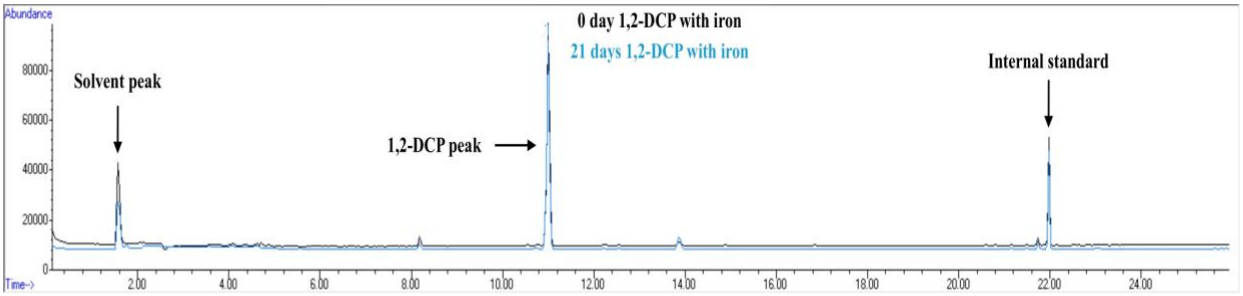


Figure 14: GCMS spectrum of 1,2-DCP at 48days in the presence of µZVI

However, with the addition of B_{12} to the system, degradation of 1,2-DCP was observed with the formation of propene as its only observed by-product. **Figure 15** shows the disappearance of 1,2-DCP from the 0-hour time point to the formation of propene after 21-days of reaction. It is important to note that without the addition of B_{12} no degradation was observed, which indicates that B_{12} is facilitating the reduction, likely through the transfer of an electron.

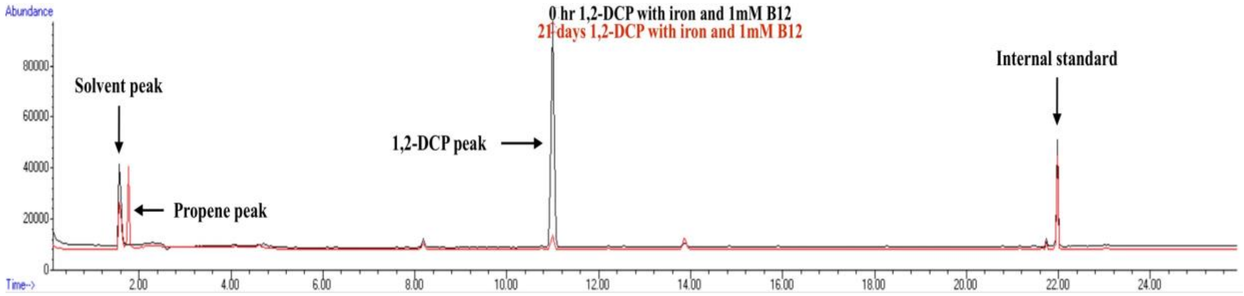


Figure 15 *: GCMS spectrum showing the formation of propene after 48 days*

Experiments were set up to determine the effect of concentration on the degradation of 1,2-DCP in the presence of 0.50g µZVI. The concentrations of B_{12} tested were: 0.0625mM, 0.125mM, and 1mM. Over a 21-day period 1,2-DCP disappeared as time progressed and the formation of propene was observed (**Figure 15**). At varying concentrations of B_{12} the rate constants varied slightly but the actual rate of the reaction remained constant making the reaction zero-order in respect to B_{12} (**Figure 16**), Which is expected with an increase in catalyst concentration. The reaction follows pseudo-first-order reaction kinetics with respect to 1,2- DCP concentration and the observed rate constants and half-lives are displayed in **Table 1**. The rate equation and half-life are described in **Eq. 3-4** and **Figure 17** displays the pseudo-first-order integrated rate plot.

$$Rate = -\frac{\mathrm{d}[1{,}2-DCP]}{dt} = k_{obs}[1{,}2-\mathrm{DCP}] \qquad \mathbf{(3)}$$

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k_{obs}} \tag{4}$$

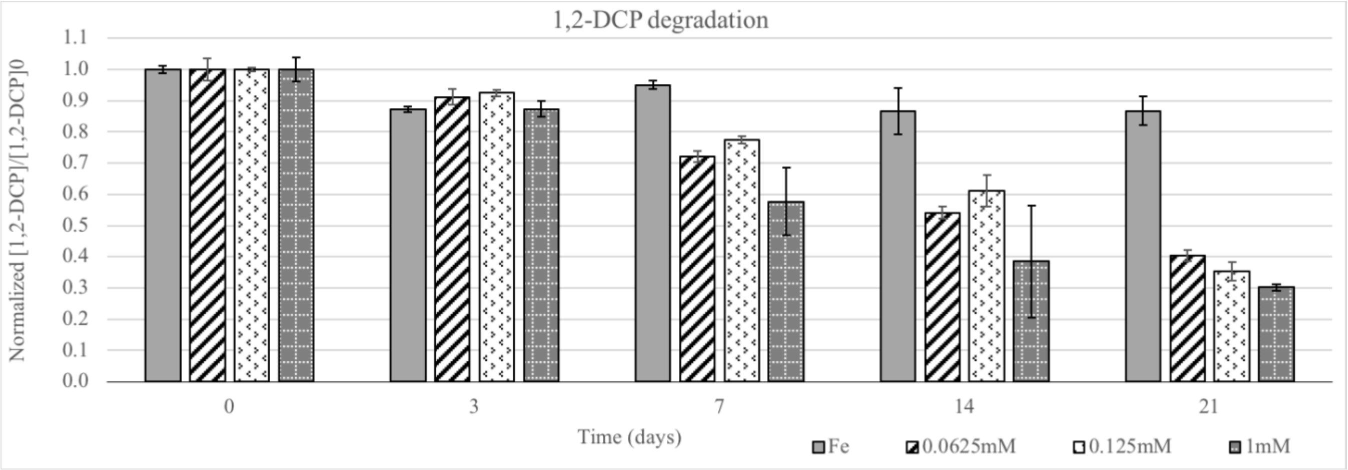


***Figure 16**: Comparison of 1,2-DCP degradation of μZVI versus μZVI with varying concentrations of B_{12} [0.0625mM B_{12} (diagonals), 0.125mM B_{12} (arrows), and 1mM B_{12} (boxes)]*

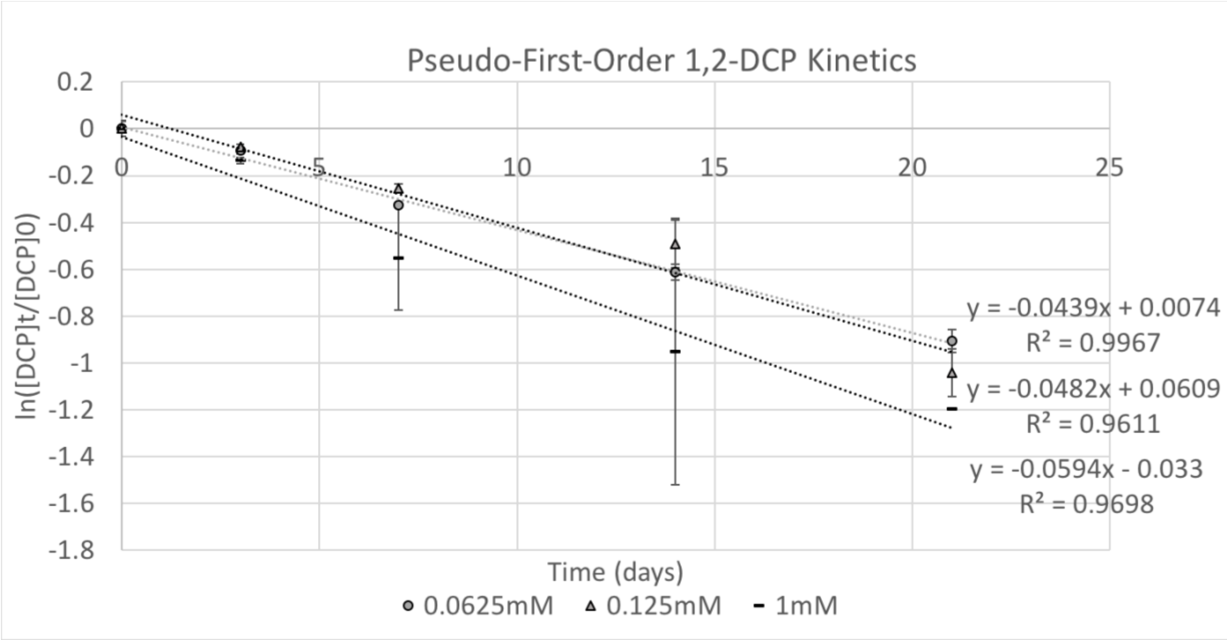


***Figure 17**: Reaction kinetics of 1,2-DCP with varying concentrations of B_{12}*

Table 1: Pseudo -first-order rate constants and half-lives with varying concentrations of B_{12}

Concentration (mM)	Observed Rate Constant (day^{-1})	Half-life (day)
1	0.0594	11.67
0.125	0.0482	14.38
0.0625	0.0439	15.79

Experiments were also conducted to test the effect of µZVI on the reaction in order to determine if increasing the amount of µZVI would increase the rate of reaction. The masses of µZVI that were used were 0.50 ± 0.01g and 2.00 ± 0.05g in the presence of 1mM of B_{12}. At the higher concentration of iron the disappearance 1,2-DCP was increased in comparison to the 0.50g, which can be observed in **Figure 18** but did not affect the rate making it zero-order in respect to iron. The reaction follows a pseudo first-order reaction kinetics in respect to 1,2-DCP and has an observed rate constant of 0.233 $days^{-1}$ and an average half-life of 2.97 days. The rate equation and half-life are described in **Eq. 3** and **4** and **Figure 19** displays the pseudo first order integrated rate plot. However, the iron that was used for the reactions in this dissertation was kept at 0.50g of µZVI unless otherwise stated because the iron primarily served as a reducing agent for the B_{12} and it was above the stoichiometric ratio required to reduce B_{12}.

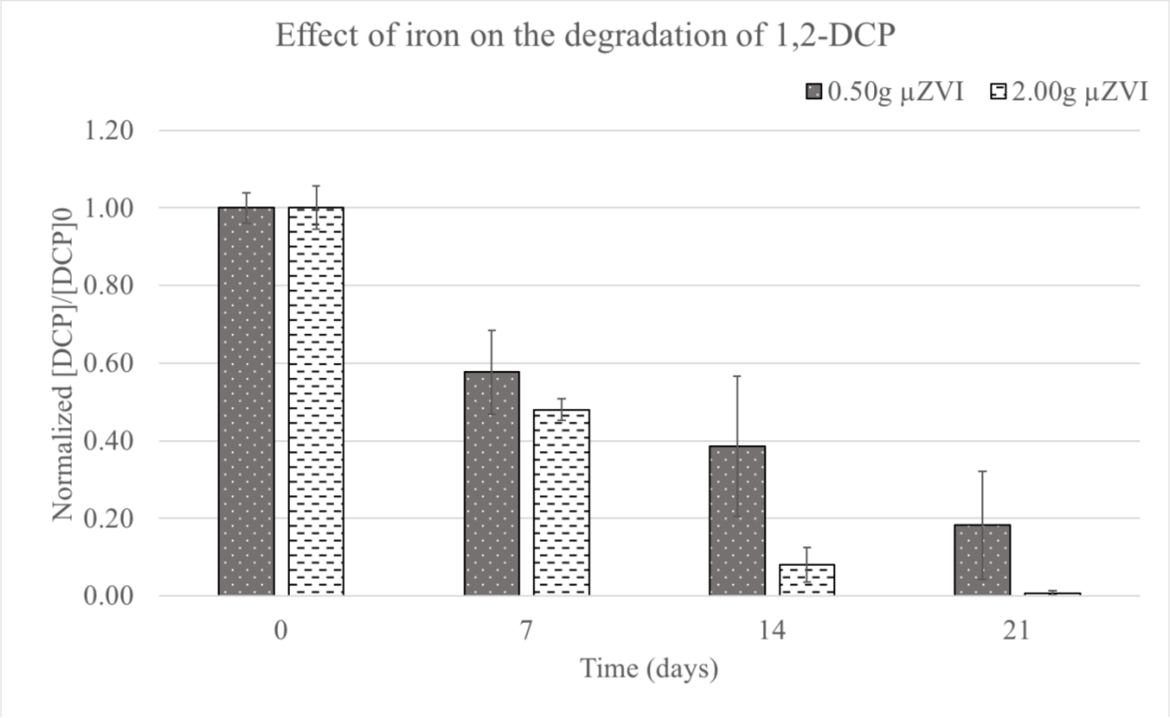


***Figure 18**: Comparison of 0.50g µZVI (polka dots) versus 2.00g µZVI (dashes) on the disappearance of 1,2-DCP with 1mM B_{12}*

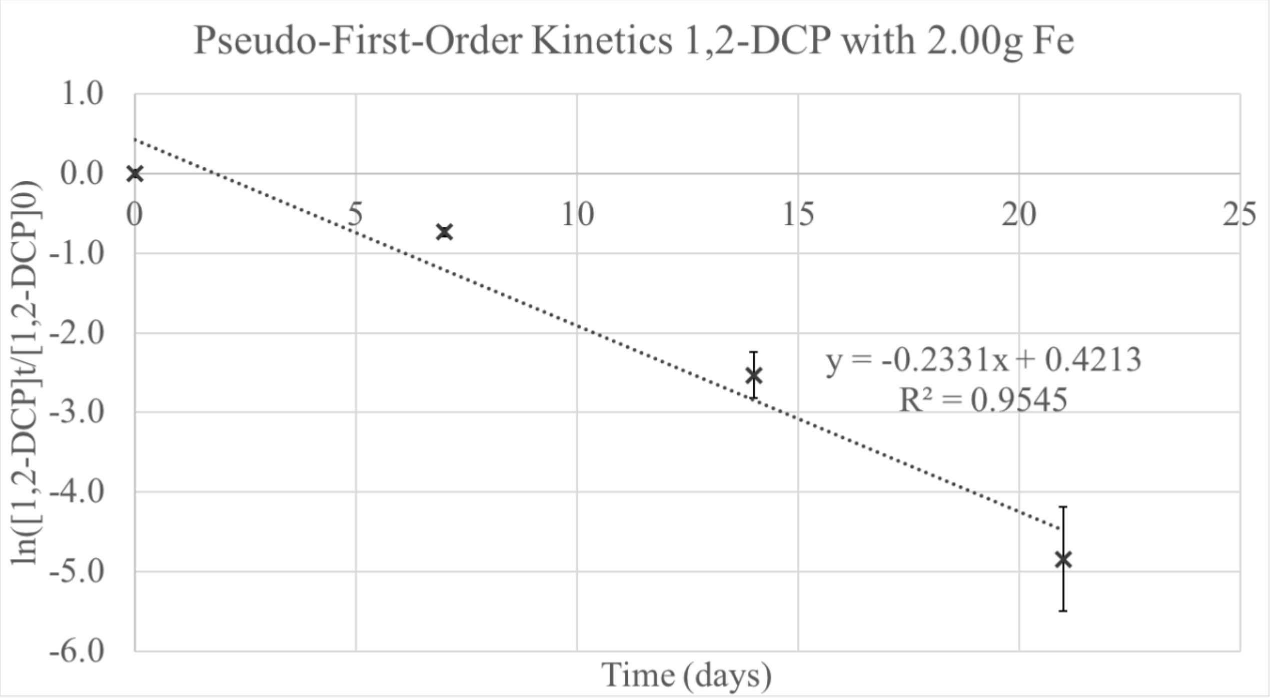


***Figure 19**: Pseudo-first-order reaction for 1,2-DCP with 2.00g µZVI and 1mM B_{12}*

To further support the degradation of 1,2-DCP, ion chromatography was performed to monitor the release of chloride into solution (**Figure 20**). As noted previously, small quantities of chloride present on the iron surface are released into solution over time. In the presence of B_{12} and µZVI the release of chloride increased as the reaction progressed. It is important to note that at the lowest concentration of B_{12} that was monitored (0.0625mM) the reaction still progressed. This is significant in regard to potential industrial scale applications because it reduces the overall cost of supplies, making it more feasible to utilize on site.

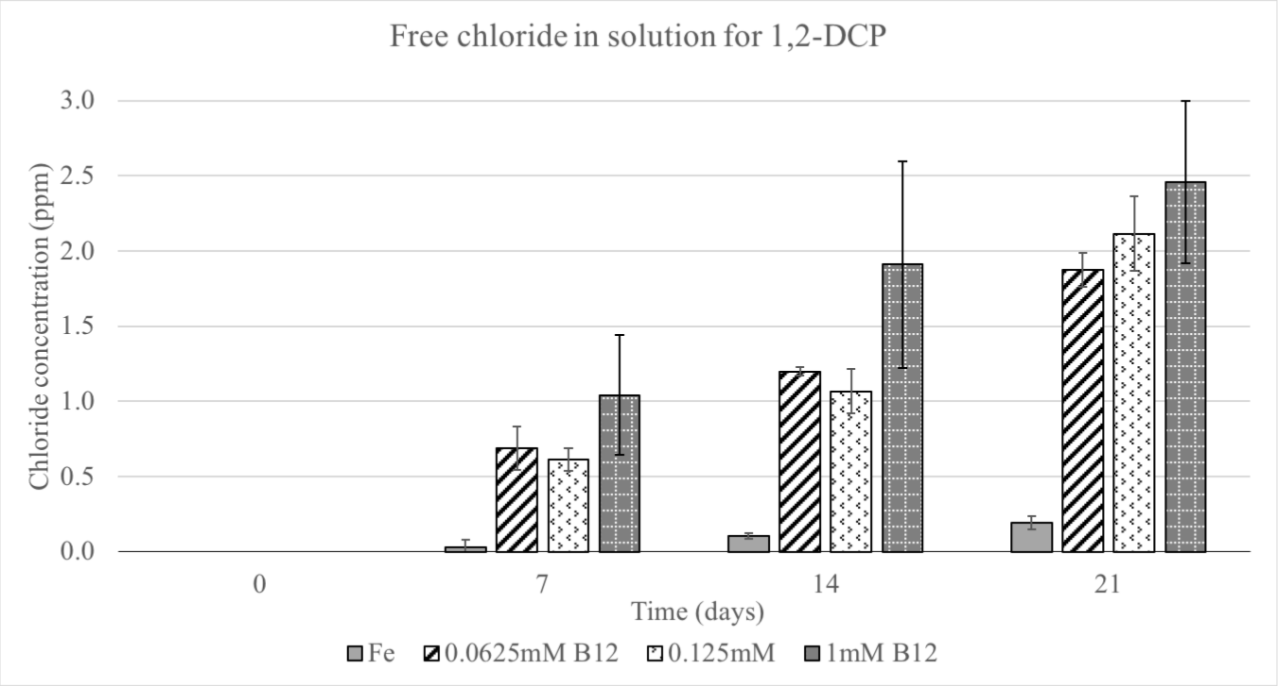


***Figure 20**: Release of chloride into solution for 1,2-DCP in the presence of just µZVI (grey) and varying concentrations of B_{12} [0.0625mM B_{12} (diagonals), 0.125mM B_{12} (arrows), and 1mM B_{12} (boxes)]*

1,3-DCP

Soil fumigants with active ingredients such as 1,3-dichloropropene often include contamination from 1,3-DCP, which is used as a feedstock for the chemical synthesis of other compounds. This dichloropropane is also potentially genotoxic in bacterial systems[43-44]. In 1998, 1,3-DCP was placed on the Contaminant Candidate list and priority was given to conducting further research on haloalkanes, including 1,3-DCP[45]. Studies have shown that 1,3-DCP exhibited kidney and liver toxicity to rats when administered orally[46].

In order to better understand the degradation of chlorinated alkanes, experiments were conducted to determine whether the addition of B_{12} would facilitate the reductive dechlorination of 1,3-DCP. Studies were conducted in the presence of µZVI to determine if iron has a great enough reduction potential to dechlorinate it. The results from the study showed that µZVI was unable to remediate 1,3-DCP over a 28-day period of time, which can be seen in **Figure 21**. In addition, no byproducts were formed, as can be seen in **Figure 22**.

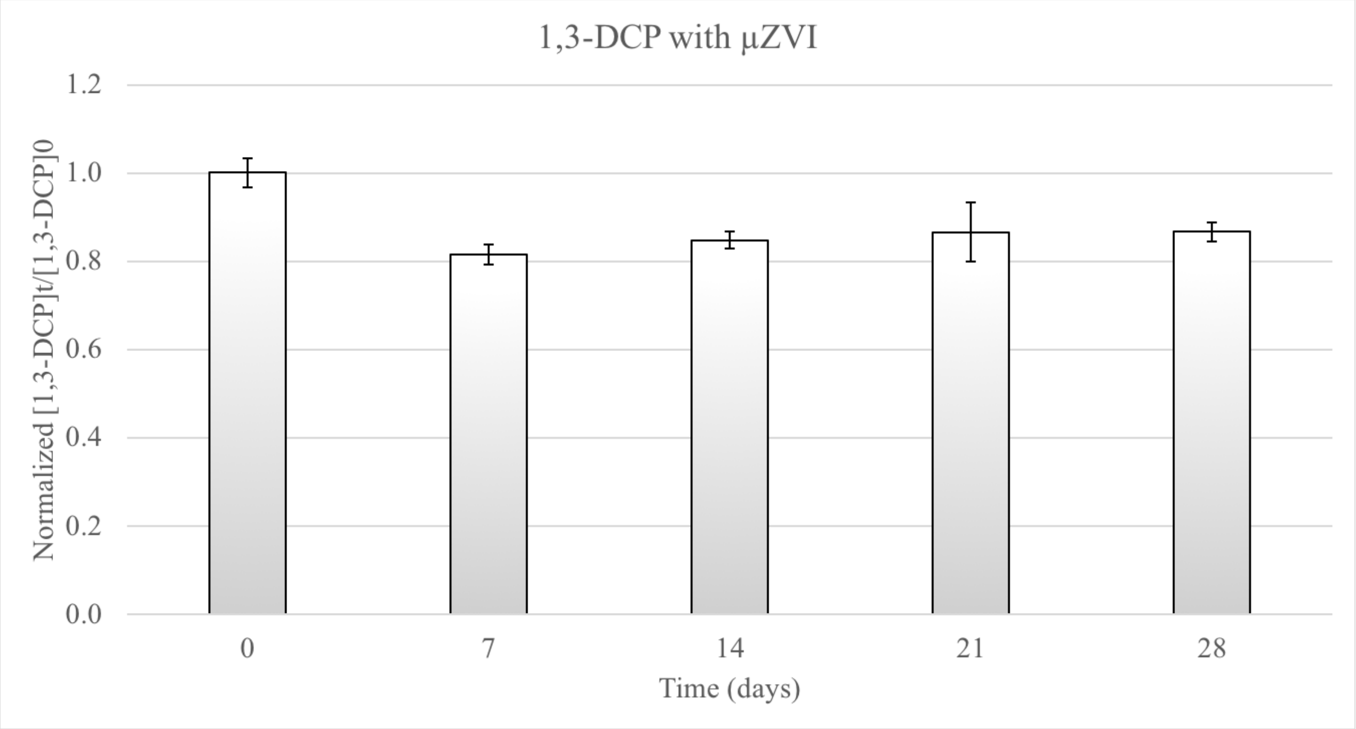


***Figure 21**: Relative concentration of 1,3-DCP in the presence of µZVI (silver)*

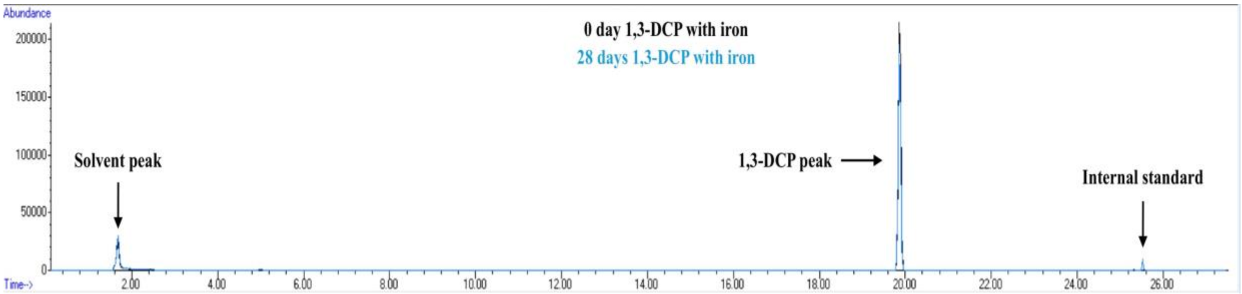


Figure 22: GCMS spectrum of 1,3-DCP with μZVI over 28-days

A further set of experiments were set up incorporating B_{12}, and over a 28-day period of time a significant decrease in 1,3-DCP was observed. However, it is important to note that only one sample retained sufficient 1,3-DCP to be quantified after 28-days of reaction. **Figure 23** shows the degradation of 1,3-DCP. As the reaction progresses 1,3-DCP concentration decreased over time with an increase in cyclopropane, which can be seen in **Figure 24**.

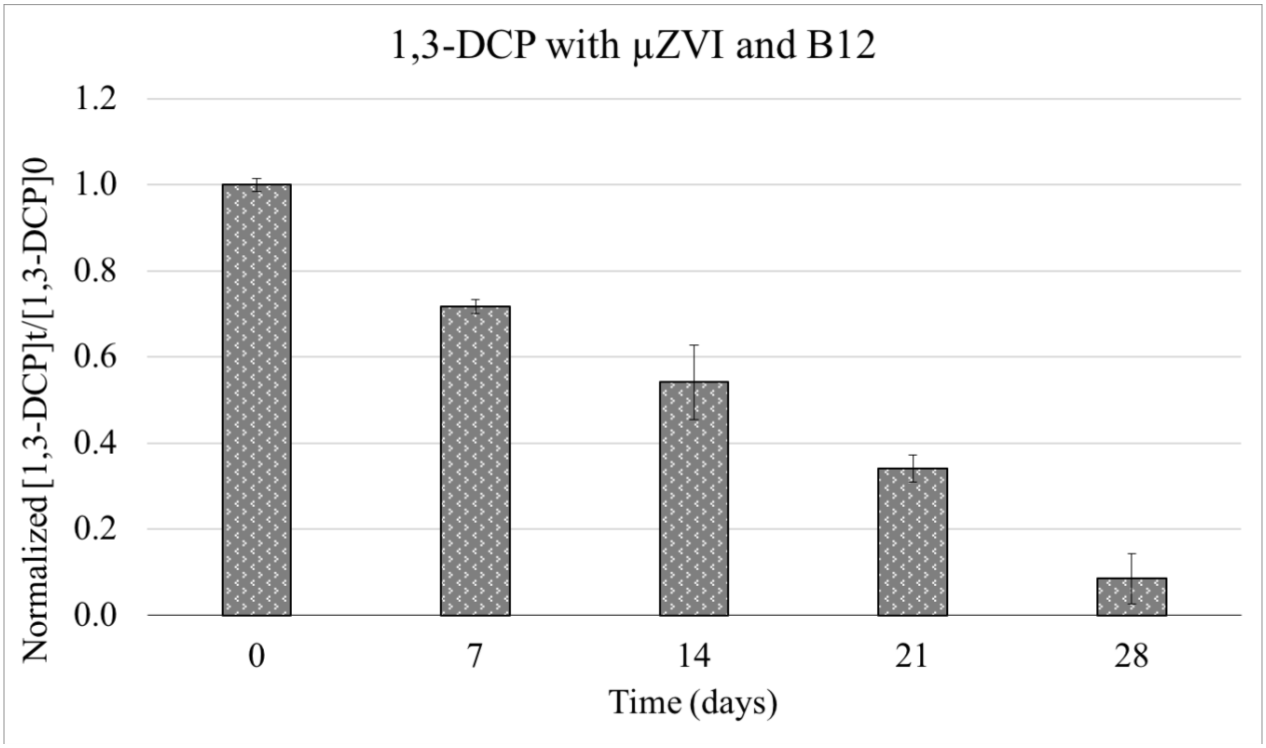


Figure 23: Relative concentration of 1,3-DCP in the presence of μZVI and B_{12} (arrows)

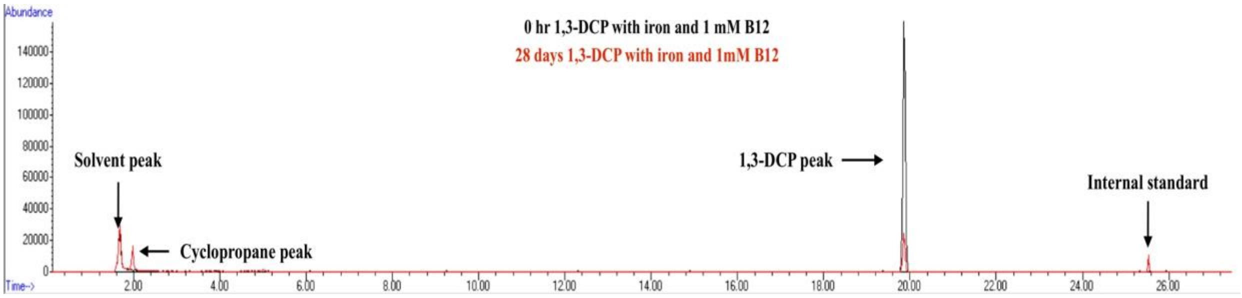


***Figure 24**: GCMS spectrum of 1,3-DCP over 28-days in the presence of µZVI and B_{12}*

The reaction follows pseudo-first-order reaction kinetics with respect to 1,3-DCP concentration, with an observed rate constant of 0.0812 hr^{-1} and an average half-life of 8.54 days. The rate equation and average half-life are described in **Eq. 5** and **6**, while **Figure 25** displays the pseudo-first-order integrated rate plot.

$$Rate = -\frac{\mathrm{d}[1,3-\mathrm{DCP}]}{dt} = k_{obs}[1,3-\mathrm{DCP}] \quad \textbf{(5)}$$

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k_{obs}} \quad \textbf{(6)}$$

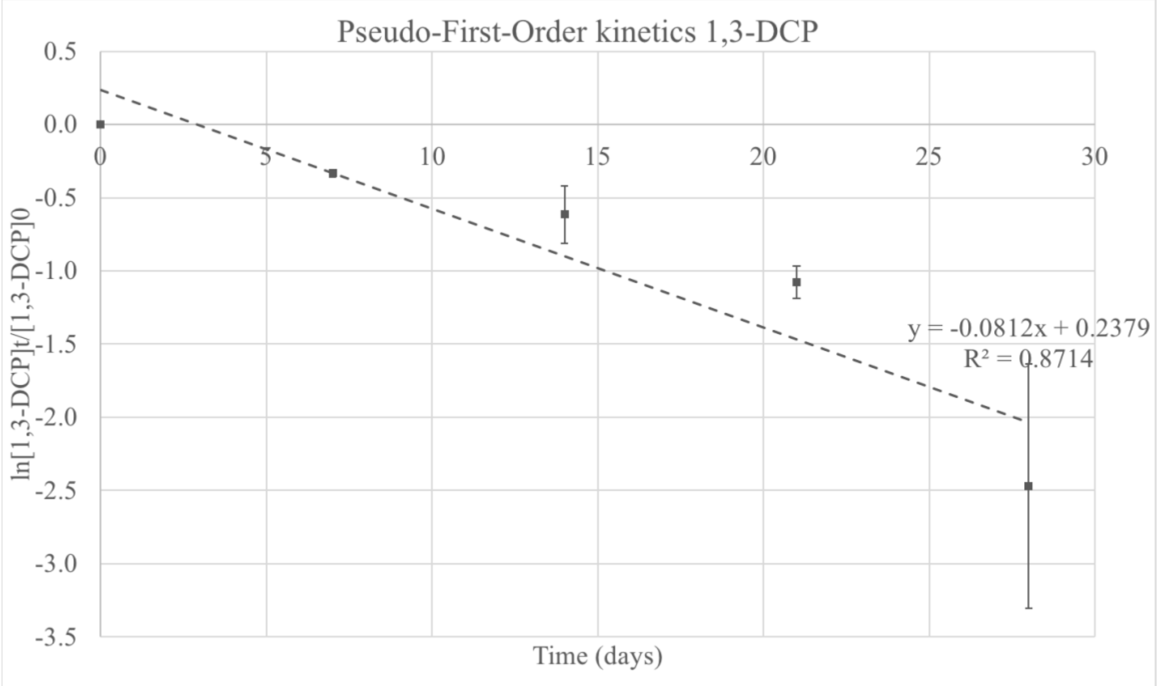


***Figure 25**: Pseudo-first-order kinetics of 1,3-DCP*

Additional studies were conducted to monitor the release of free chloride in solution to further support the degradation of 1,3-DCP. In the case of just µZVI and 1,3-DCP there was not a significant increase of chloride in solution over time and this increase can be attributed to any chloride on the iron surface. However, in comparison to the µZVI with cobalamin there was an increase of chloride in solution over the 28-day experiment, which can be seen in **Figure 26**.

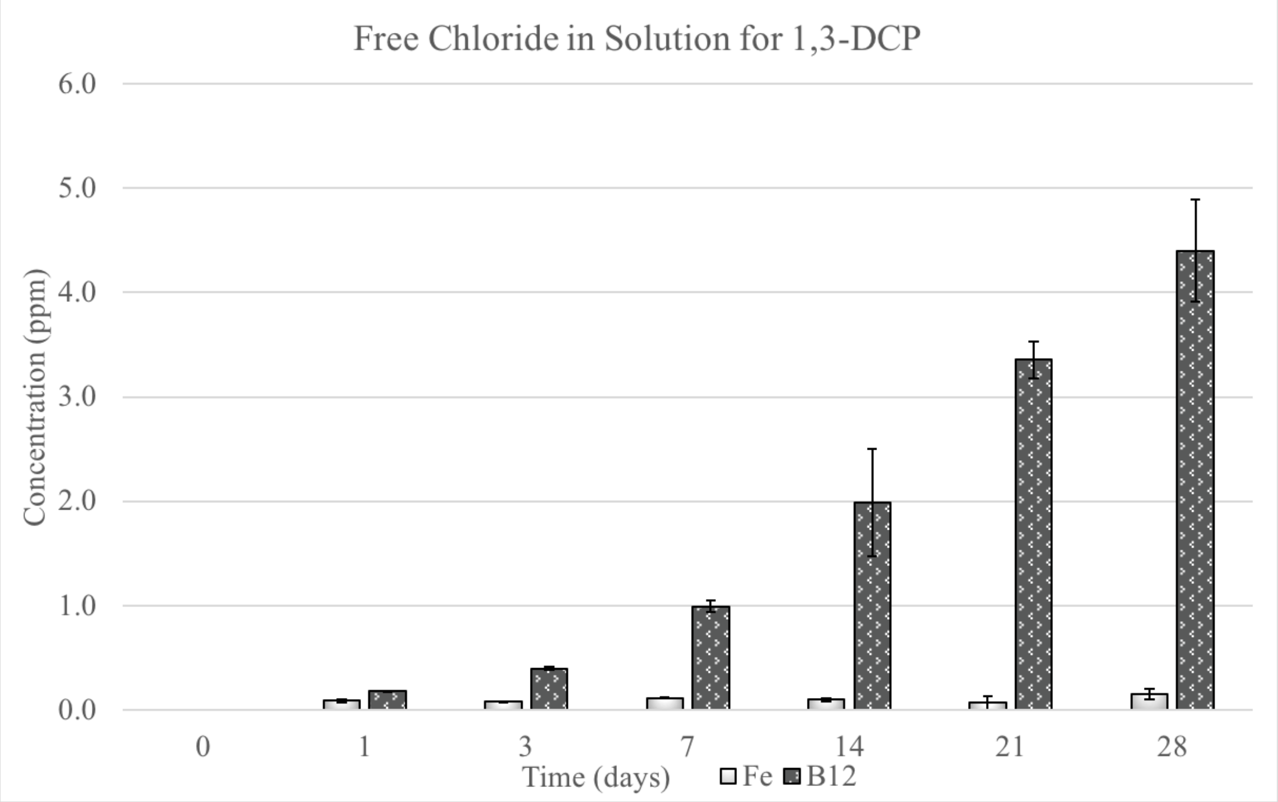


***Figure 26**: Concentration of free chloride in solution for 1,3-DCP in the presence of µZVI (silver) and µZVI with 1mM B_{12} (arrows)*

1-CP

In order to further understand the ability of µZVI and B_{12} to degrade chlorinated propanes, 1-CP was monitored with this same system. The results from the study showed no significant degradation of 1-CP in the presence of µZVI alone and no significant increase in chloride in solution, as can be seen in **Figure 27**, **Figure 28**, and **Figure 31**.

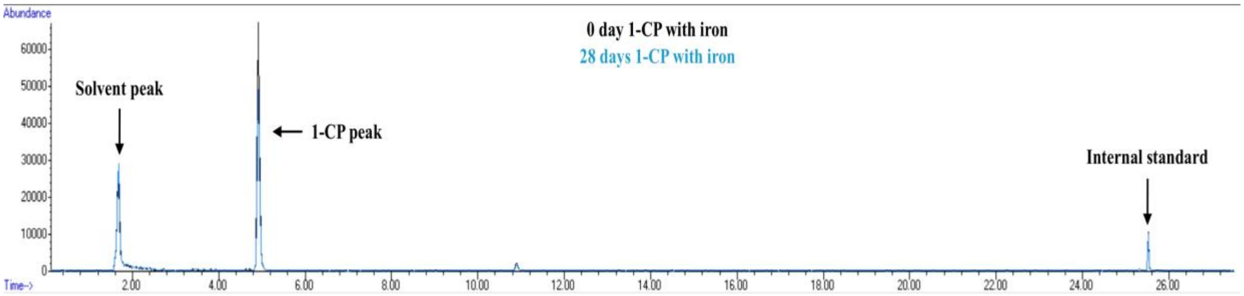


Figure 27*: GCMS spectrum of 1-CP with µZVI over 28-days*

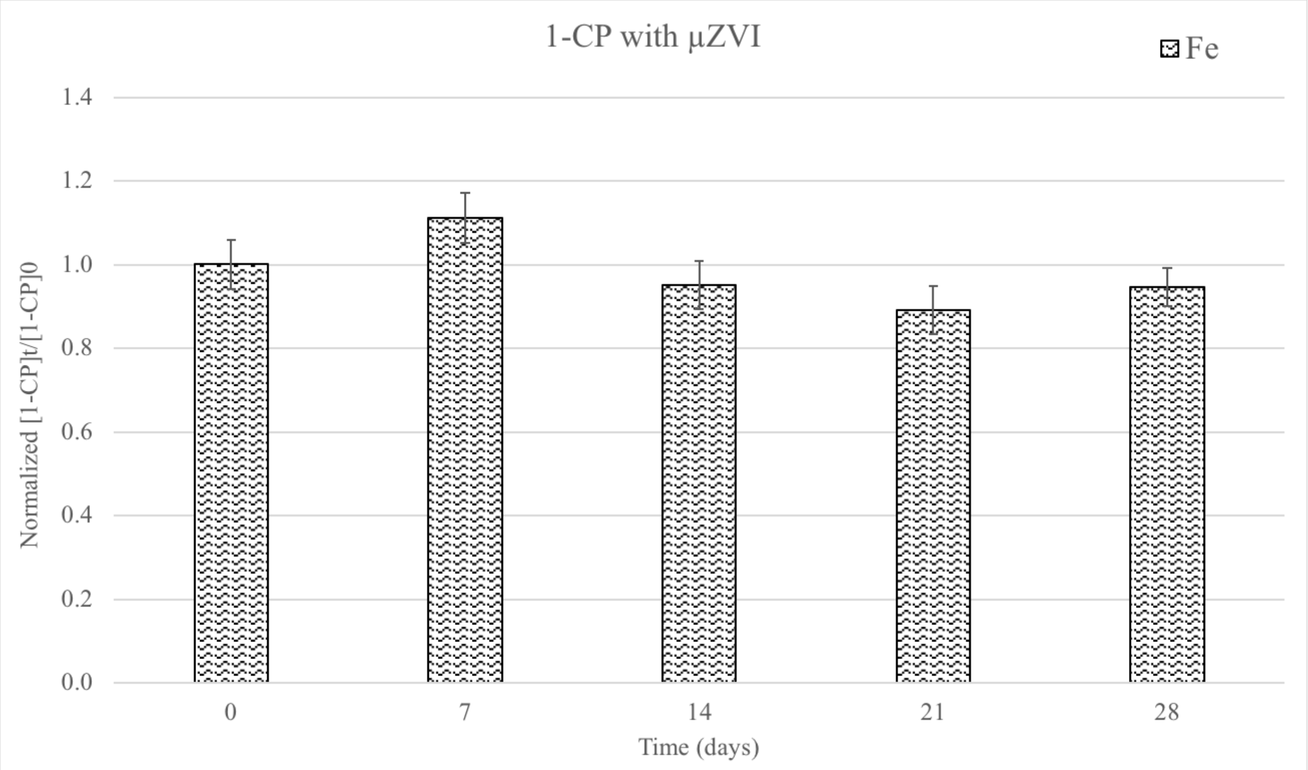


Figure 28*: Relative concentration of 1-CP in the presence of µZVI (tilde)*

However, in the presence of µZVI and B_{12} slight degradation was observed over 32 days. **Figure 29** shows the decrease in concentration of 1-CP over time while **Figure 30** shows the 4-week decrease in the 1-CP peak and small amounts of propane was observed as a byproduct. **Figure 31** shows an increase of free chloride in solution over 32 days.

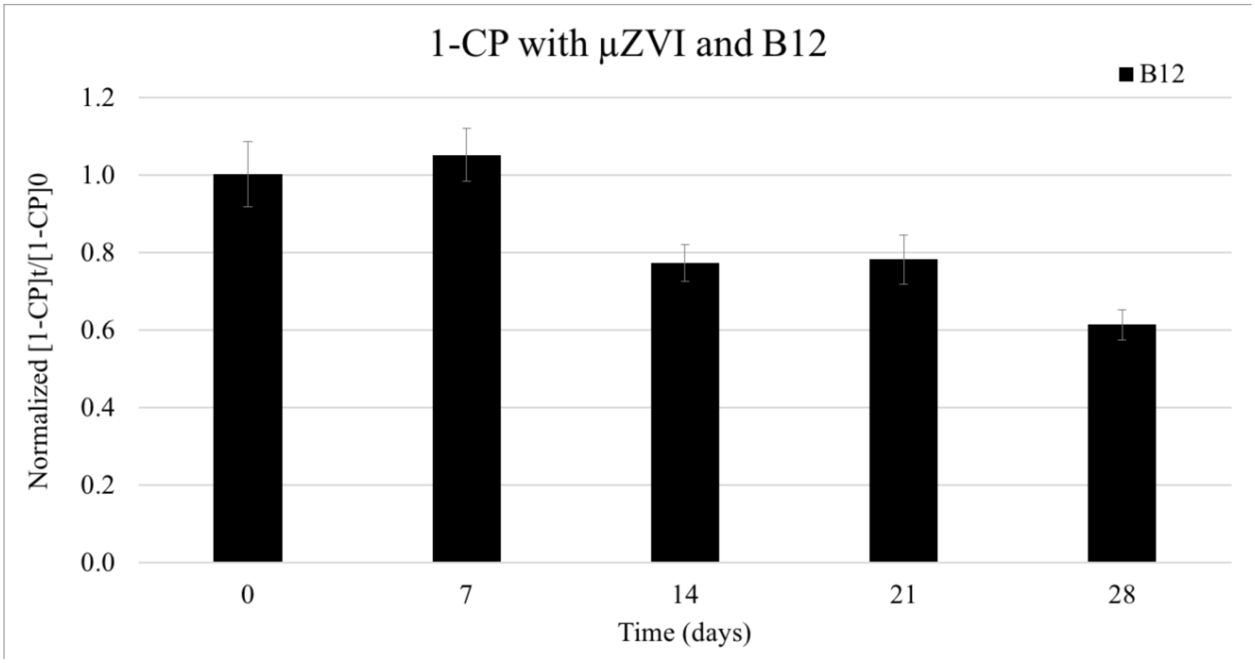


Figure 29: *Relative concentration of 1-CP in the presence of µZVI and* B_{12} *(black)*

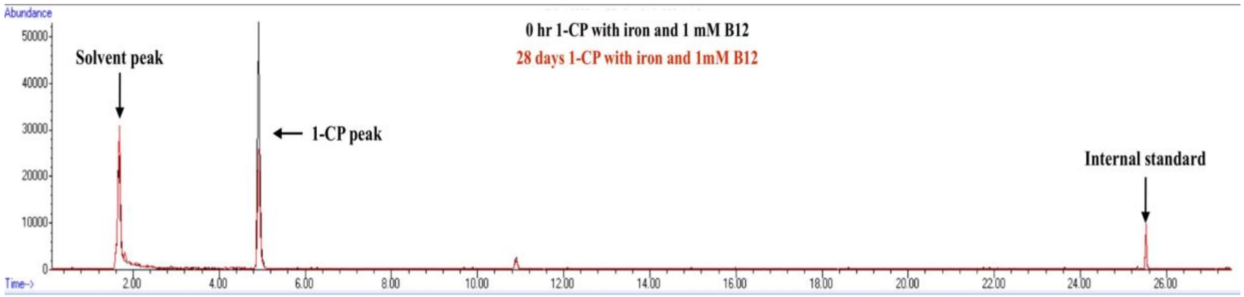


Figure 30: *GCMS spectrum of 1-CP over 28 days in the presence of µZVI and B12*

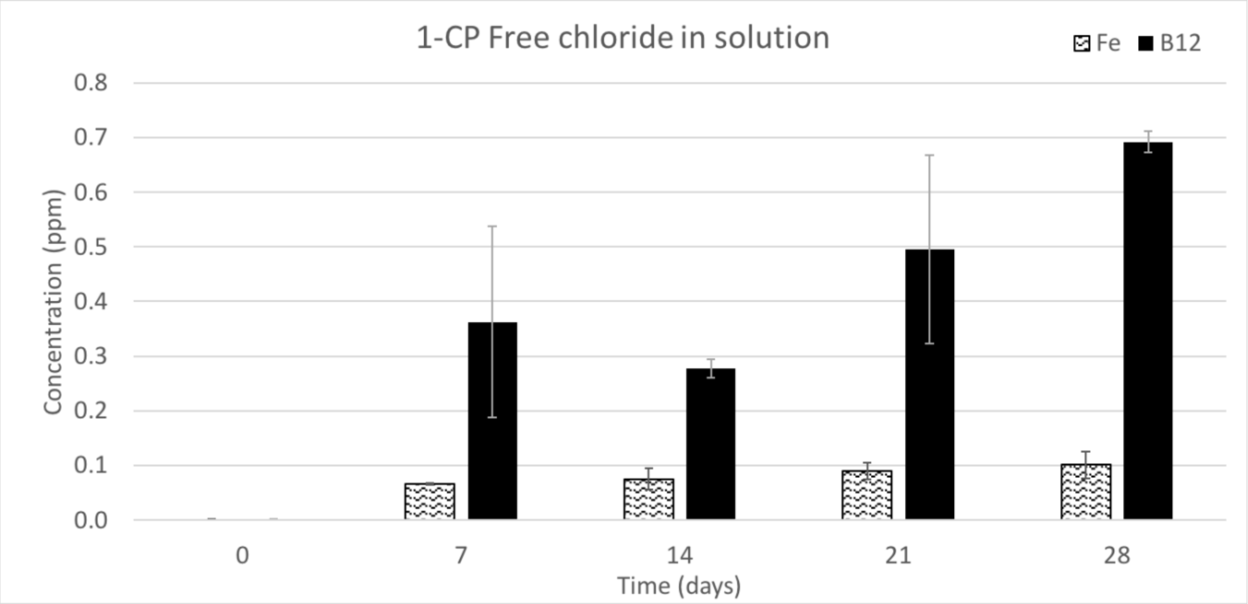


Figure 31*: Concentration of free chloride in solution for 1-CP in the presence of µZVI (tilde) and µZVI with 1mM* B_{12} *(black)*

The reaction follows pseudo-first-order reaction kinetics with respect to 1-CP, with an observed rate constant of 0.0182 day^{-1} and an average half-life of 38.1 days. The rate equation and half-life are described in **Eq. 7** and **8**, while **Figure 32** displays the pseudo-first-order integrated rate plot.

$$Rate = -\frac{\mathrm{d}[1-\mathrm{CP}]}{dt} = k_{obs}[1-\mathrm{CP}] \quad \textbf{(7)}$$

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k_{obs}} \quad \textbf{(8)}$$

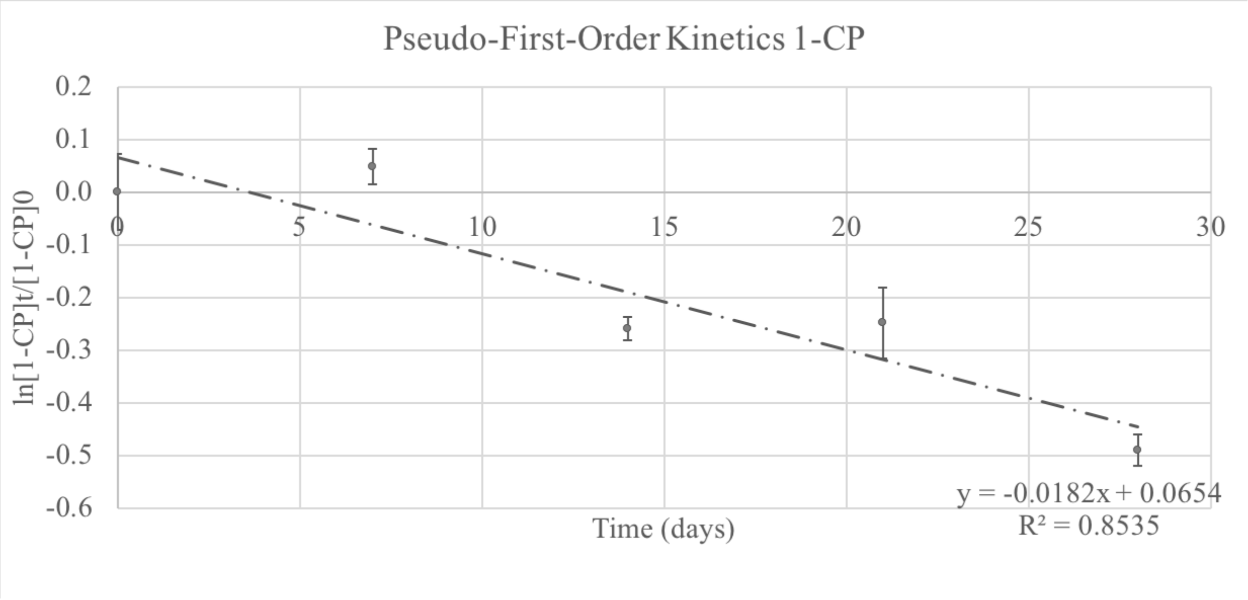


Figure 32*: Pseudo-first-order reaction with respect to 1-CP*

1,2-DCA

Another compound which has garnered increased attention over the years is 1,2-DCA, primarily due to its environmental impact. This species has been studied as a model compound to determine how chlorinated aliphatic compounds are degraded under different biological conditions[15, 47-48]. Over 17.5 million tonnes are produced annually by the United States, Western Europe, and Japan. This contaminant has been detected in a number of environmental matrices, such as rivers, above the observed background level of 0.5µg/L in non-industrialized areas[15, 18, 49]. The biodegradation of 1,2-DCA is known to occur in both aerobic and anaerobic conditions[50-51]. However, 1,2-DCA has been shown to be recalcitrant in the presence of ZVI or other bimetallic systems[52].

Studies were conducted to determine if 1,2-DCA could be degraded in the presence of µZVI and B_{12}. Experiments were also conducted to determine if µZVI alone could remediate 1,2-

DCA. Over a 28-day period no significant degradation of 1,2-DCA was observed in the presence of just µZVI, as shown in **Figure 33**.

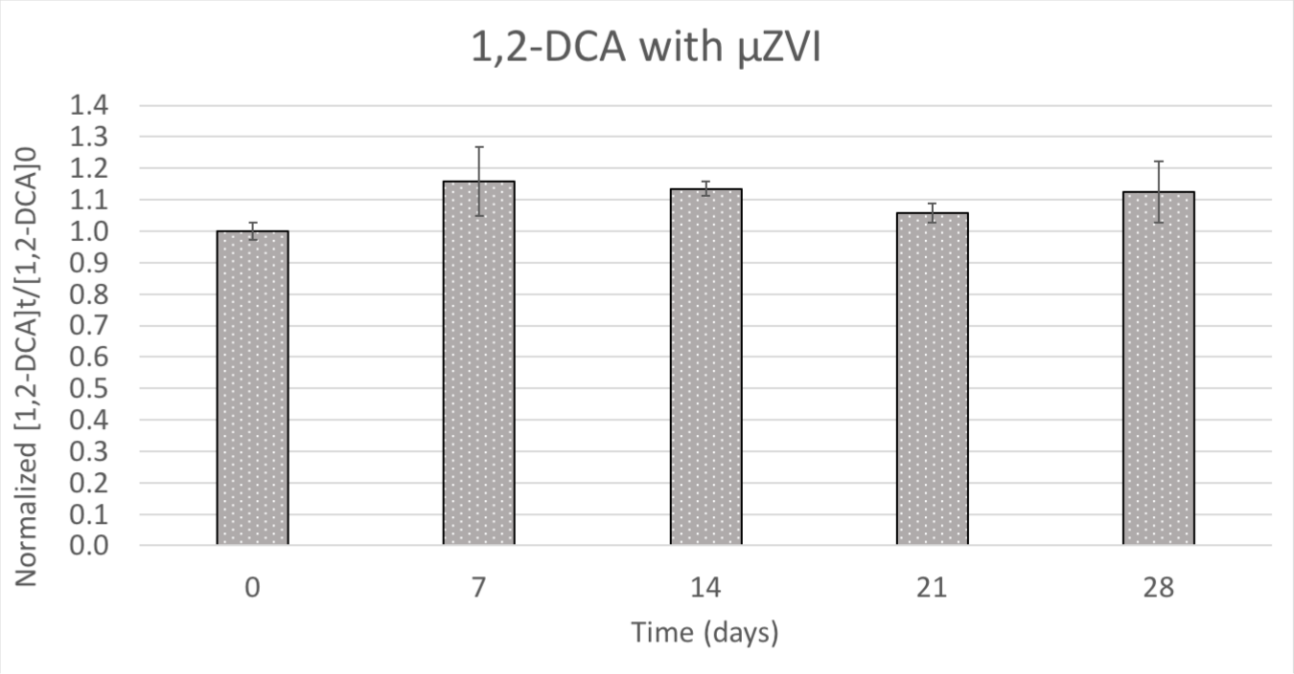


***Figure 33**: Relative concentration of 1,2-DCA in the presence of µZVI (polka dots)*

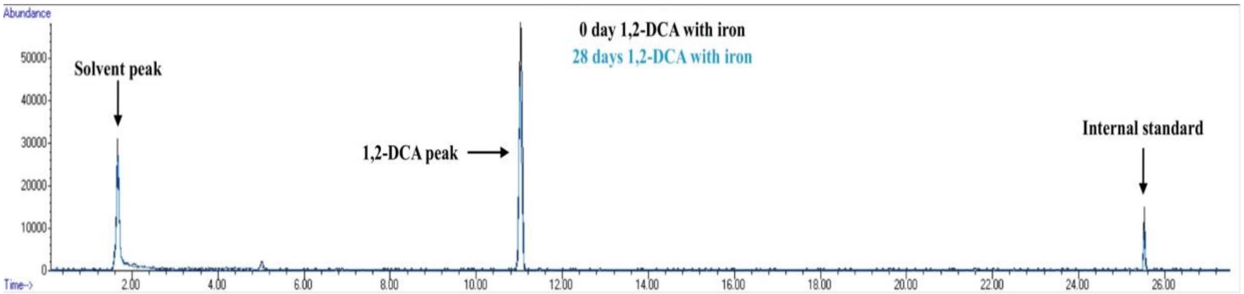


***Figure 34**: GCMS spectrum of 1,2-DCA over 35-days in the presence of µZVI*

Due to 1,2-DCA's persistence in the environment and recalcitrance to remediation, it is important to find an environmentally friendly remediation technique. It was hypothesized that 1,2-DCA could be degraded in the presence of µZVI and cobalamin. Experiments were set up to determine if the reduced state of cobalamin could facilitate the degradation of 1,2-DCA. Over a 3-

week period of time a significant decrease of 1,2-DCA was observed in the presence of µZVI and B_{12}, which can be seen in **Figure 35**.

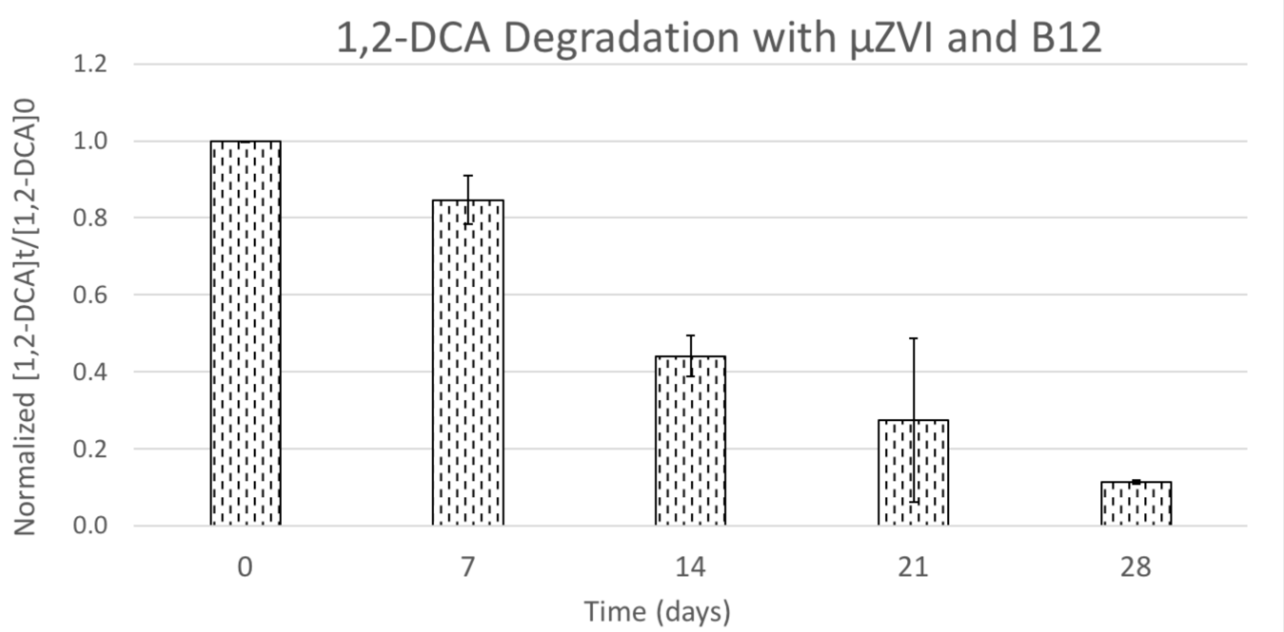


***Figure 35**: Degradation of 1,2-DCA in the presence of µZVI and B_{12} (dashes)*

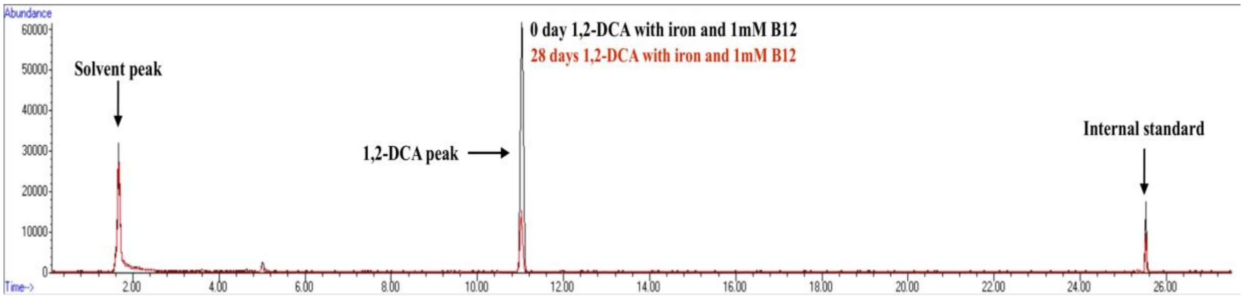


***Figure 36**: GCMS spectrum of 1,2-DCA over 35-days in the presence of µZVI and B12*

The reaction follows pseudo-first-order reaction kinetics with respect to 1,2-DCA, with an observed rate constant of 0.0847 day^{-1} and an average half-life of 8.2 days. The rate equation and half-life are described in **Eq. 9** and **10**, while **Figure 37** displays the pseudo-first-order integrated rate plot.

$$Rate = -\frac{\mathrm{d}[1,2-\mathrm{DCA}]}{dt} = k_{obs}[1,2-\mathrm{DCA}] \qquad \textbf{(9)}$$

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k_{obs}} \tag{10}$$

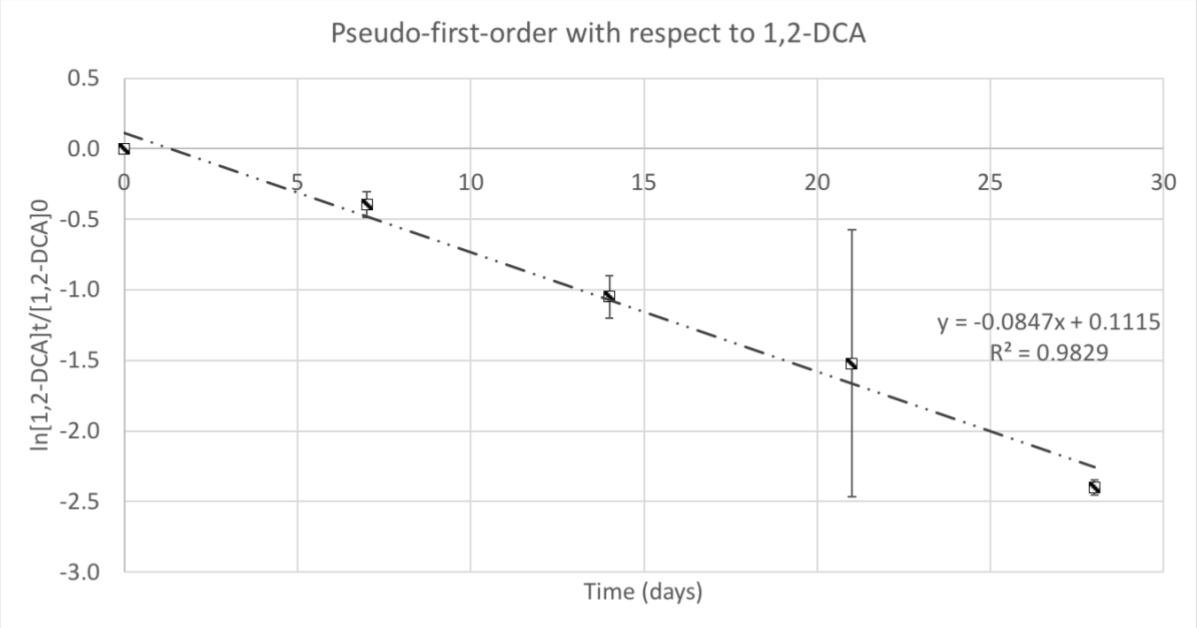


Figure 37*: Pseudo-first-order reaction with respect to 1,2-DCA*

In addition, samples were analyzed by ion chromatography to determine the concentration of free chloride in solution throughout the progression of the reaction. **Figure 38** shows the release of chloride into solution for 1,2-DCA in the presence of just µZVI as compared to the combination of B_{12} and µZVI. The following figure supports that, in the presence of cobalamin and µZVI, degradation of 1,2-DCA is observed. However, without the addition of cobalamin no significant degradation was observed, as supported by ion chromatography.

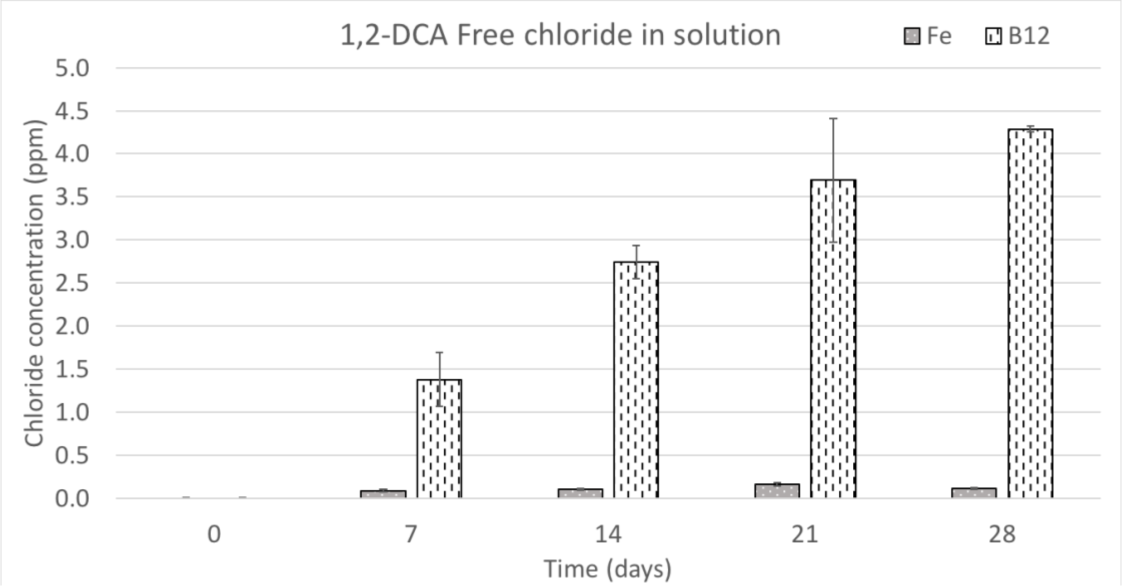


***Figure 38**: Release of chloride into solution for 1,2-DCA in the presence of just µZVI (polka dots) and 1mM B_{12} with µZVI (dashes)*

CHAPTER 4: PROPOSED MECHANISM FOR THE DEGRADATION OF CHLORINATED ALKANES IN THE PRESENCE OF B_{12} AND µZVI

Cobalamins have been shown to enhance the reductive dehalogenation of halogenated alkenes in the presence of strong reducing agents: *e.g.* titanium citrate or bimetallic systems[35, 53-55]. Reduced cobalamin derivatives are known to act as strong nucleophiles, as is the case for the doubly-reduced B_{12s} which is known to be a super-nucleophile. Reduced states of cobalamin are able to facilitate the transfer of electrons to halogenated compounds to promote dehalogenation[56]. B_{12r} is known to act chemically as a free radical and can form stable alkylated intermediates[55, 57-58]. In addition, cyanocobalamin (the predominant commercially available form of cobalamin) can also form aquacobalamin (B_{12a}) by replacement of the cyano group with water[29]. In the following work iron was utilized as a reducing agent in order to reduce cobalamin to B_{12r} in order to facilitate the reduction of 1,2,3-TCP, 1,2-DCP, 1,3-DCP, 1-CP, and 1,2-DCA.

Prior to the start of the initial dechlorination experiments, studies were conducted to determine whether µZVI would be able to reduce cobalamin from Co(III) to Co(II). Vials were set up to monitor the conversion of cobalamin to B_{12r} over a 48hr time period. A review of the literature indicates Co(III) has several characteristic absorbance peaks at the following wavelengths: 361nm and 550nm, whereas Co(II) has characteristic absorbance peaks at 312 nm and 474nm[35]. **Figure 39** shows the UV-vis spectrum of the reduction of cobalamin by µZVI over the course of the experiment.

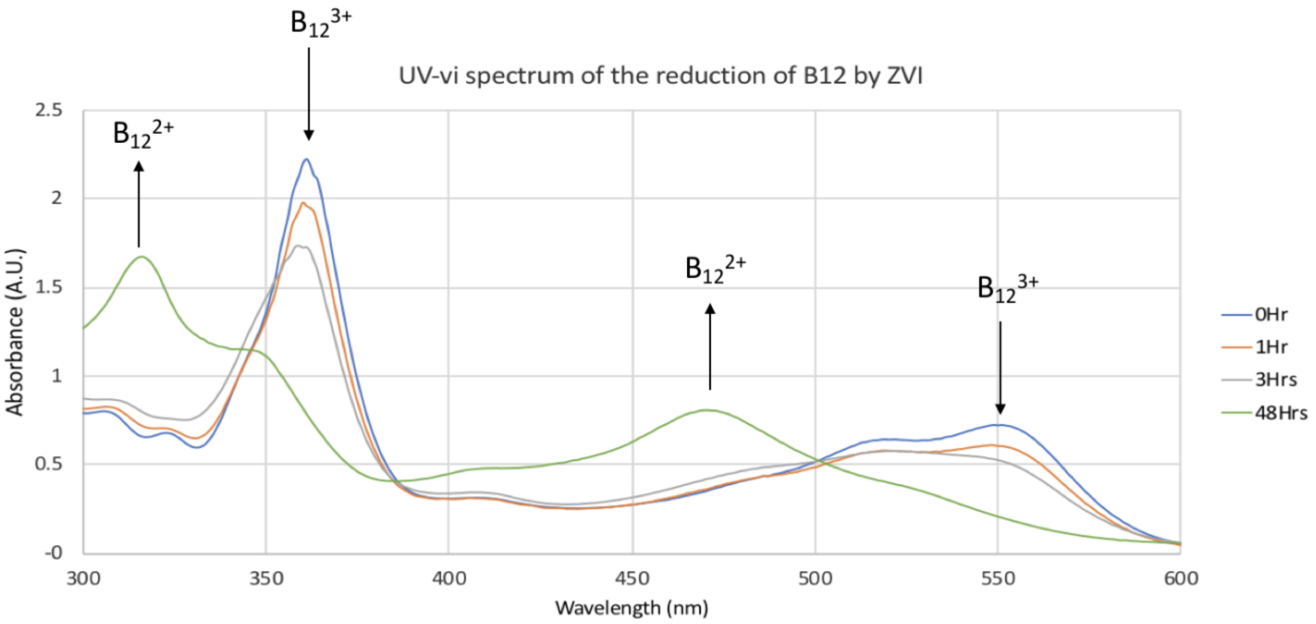


Figure 39: *Cobalamin reduction in the presence of µZVI*

The redox potentials of ZVI and B_{12} explain how this reduction proceeds to the Co(II) oxidation state without reaching the Co(I) state. Coupling the reduction of B_{12} to B_{12r} with iron's redox potential gives a calculated potential of +0.647 V. The reduction of B_{12} occurs in the presence of iron because the redox potential for this reaction is positive, making it a favorable spontaneous reaction. Redox potentials and half reactions are shown in **Eq. 11-13**. Redox potentials also explain why iron is not suitable to completely reduce B_{12} to B_{12s}: the calculated potential for that reduction is -0.163 V, which indicates this is not a spontaneous reaction[35, 59].

$$\mathrm{Fe} \leftrightarrow \mathrm{Fe}^{2+} + 2e^{-} \qquad (\mathrm{E}^{o}=0.447\ \mathrm{V}) \qquad \textbf{(11)}$$

$$\mathrm{Co(III)} + \mathrm{e}^{-} \leftrightarrow \mathrm{Co(II)} \qquad (\mathrm{E}^{o}=0.20\ \mathrm{V}) \qquad \textbf{(12)}$$

$$\mathrm{Co(II)} + \mathrm{e}^{-} \leftrightarrow \mathrm{Co(I)} \qquad (\mathrm{E}^{o}= -0.61\ \mathrm{V}) \qquad \textbf{(13)}$$

It was hypothesized that the reduced form of cobalamin can facilitate the transfer of electrons to chlorinated alkanes in order to induce reductive dechlorination. The experiments that were performed demonstrated reduction of the chlorinated alkanes by a measurable decrease in the compound of interest concurrent with an increase in chloride concentration in solution.

1,2,3-TCP

The proposed mechanism centers on a single electron transfer from the iron surface to cobalamin, reducing the cobalt center from Co(III) to Co(II) as shown in **Figure 40**. Once in the reduced state, cobalamin can then transfer an electron to 1,2,3-TCP. This transfer is accomplished by a net halogen exchange from 1,2,3-TCP to B12r, which may occur via a halogen-bridge transition state yielding an alkyl radical and chlorocobalamin[57-58]. It is also important to note that the Co(III) center of chlorocobalamin can be reduced to Co(II) by a single electron transfer from ZVI or have its chlorine displaced by water to form B_{12a}[58, 60]. This is an important step because it regenerates the catalytic B_{12} to the Co(II) oxidation state for further activity. The alkyl radical can then react either with another B_{12r} to produce a very stable alkyl-cobalamin derivative, or it can accept an electron from ZVI to further be reduced to propene.

The rate-determining step is the formation of the alkyl radical, which can be terminal or secondary, however, the terminal radical is more stable with a greater negative Gibbs free energy of -25.87 kcal/mol. After this radical is formed the reaction proceeds through either pathway 1a or pathway 1b (**Figure 40**). If it proceeds via pathway 1a this intermediate is very stable and is unlikely to undergo further reduction to propene. However, by following pathway 1b the reaction produces allyl chloride via an electron transfer from ZVI, which can then receive another electron from a B_{12r} molecule to produce a radical propene molecule. Radical propene can then follow either pathway 2a or 2b. Pathway 2a shows how the propene radical can react with B_{12r} to form another stable intermediate that is unlikely to be further reduced. Conversely, pathway 2b completes the reduction to propene via an electron transfer from ZVI.

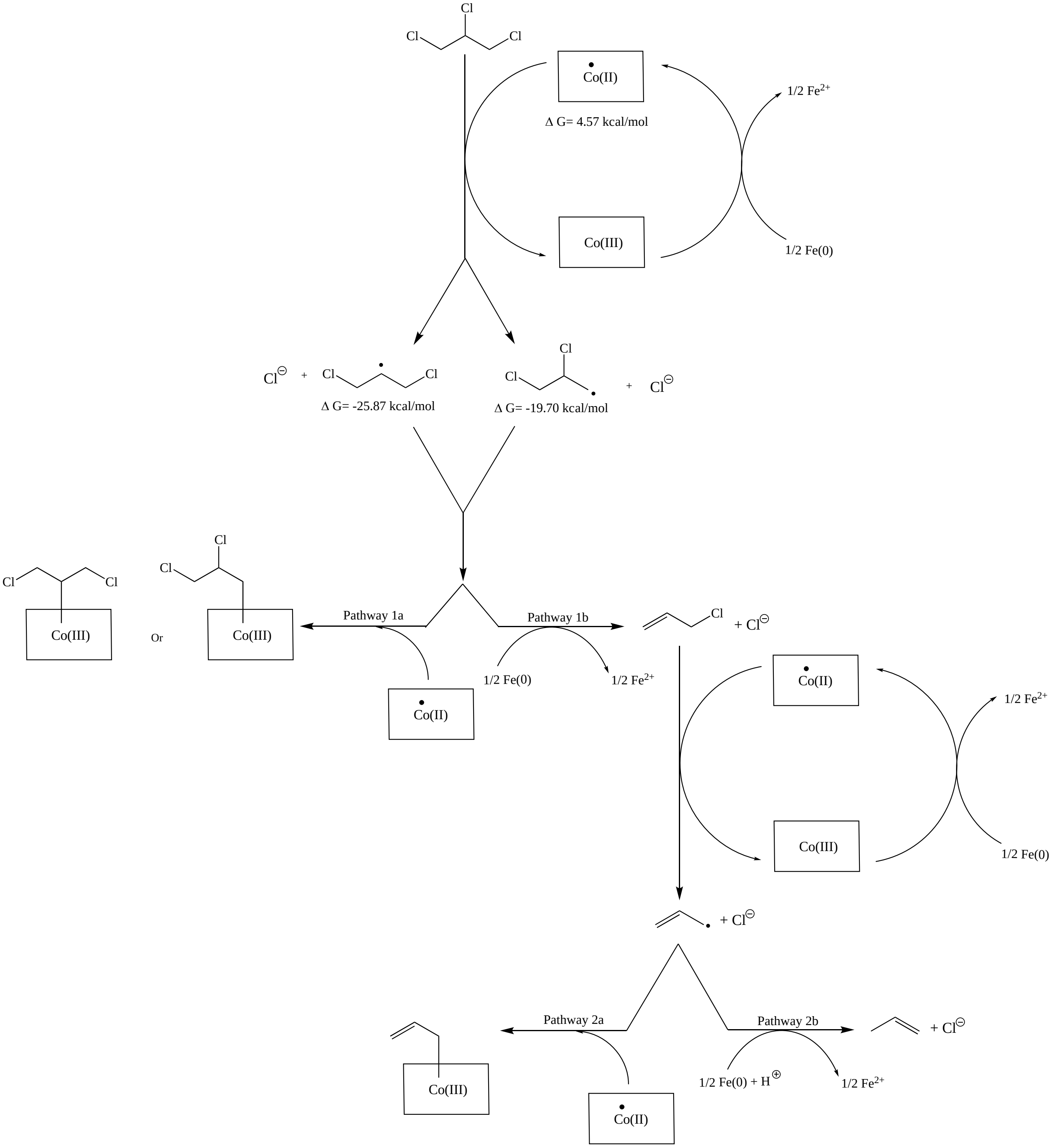


***Figure 40**: Proposed catalytic cycle for 1,2,3-TCP*

Samples were analyzed with a UV-Vis spectrophotometer throughout the reaction of 1,2,3-TCP with ZVI and 1mM B_{12}. As the reaction progressed, reduction of the peaks characteristic of B_{12} decreased (361 nm and 550 nm) and peaks that are unique to B_{12r} (312 nm and 474 nm) and B_{12a} (350 nm and 525 nm) increased (**Figure 41**)[35, 61]. This supports the proposed reaction by providing evidence of the formation of aquacobalamin, which can also be seen for the remaining chlorinated compounds (see supplemental support).

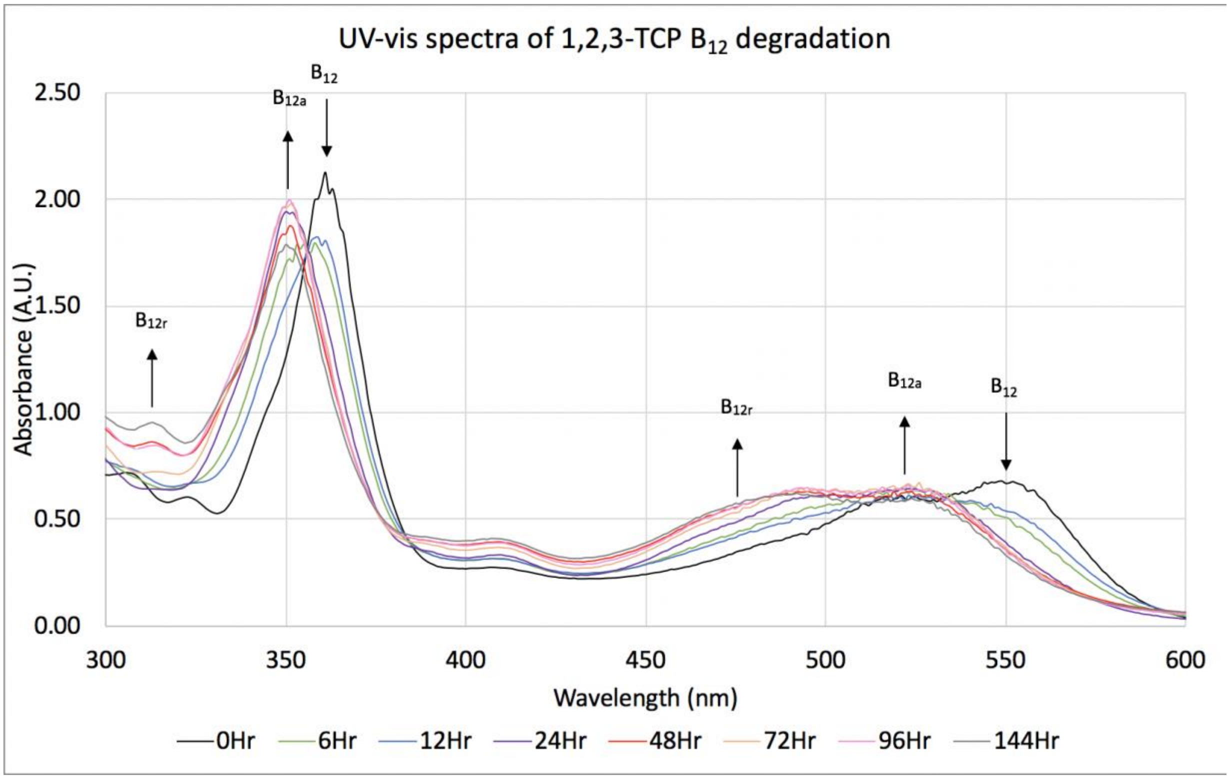


Figure 41: UV-vis spectrum of 1,2,3-TCP over 144hrs

1,2-DCP

The catalytic cycle for 1,2-DCP is displayed in **Figure 42**. The reaction mechanism is initiated when cobalamin is reduced to B_{12r} by a single electron transfer from ZVI. Once reduced, B_{12r} acts as a nucleophile and attacks the partially positive carbon of 1,2-DCP and transfers a single electron, releasing chloride into solution. This reaction is favorable and has a Gibbs free energy of

-22.44 kcal/mol. The radical intermediate can either proceed through pathway 1 or pathway 2. Following pathway 1, a stable chloropropyl cobalamin intermediate is formed, which does not undergo further degradation[55]. Conversely, pathway 2 shows reduction to propene via an electron transfer from ZVI.

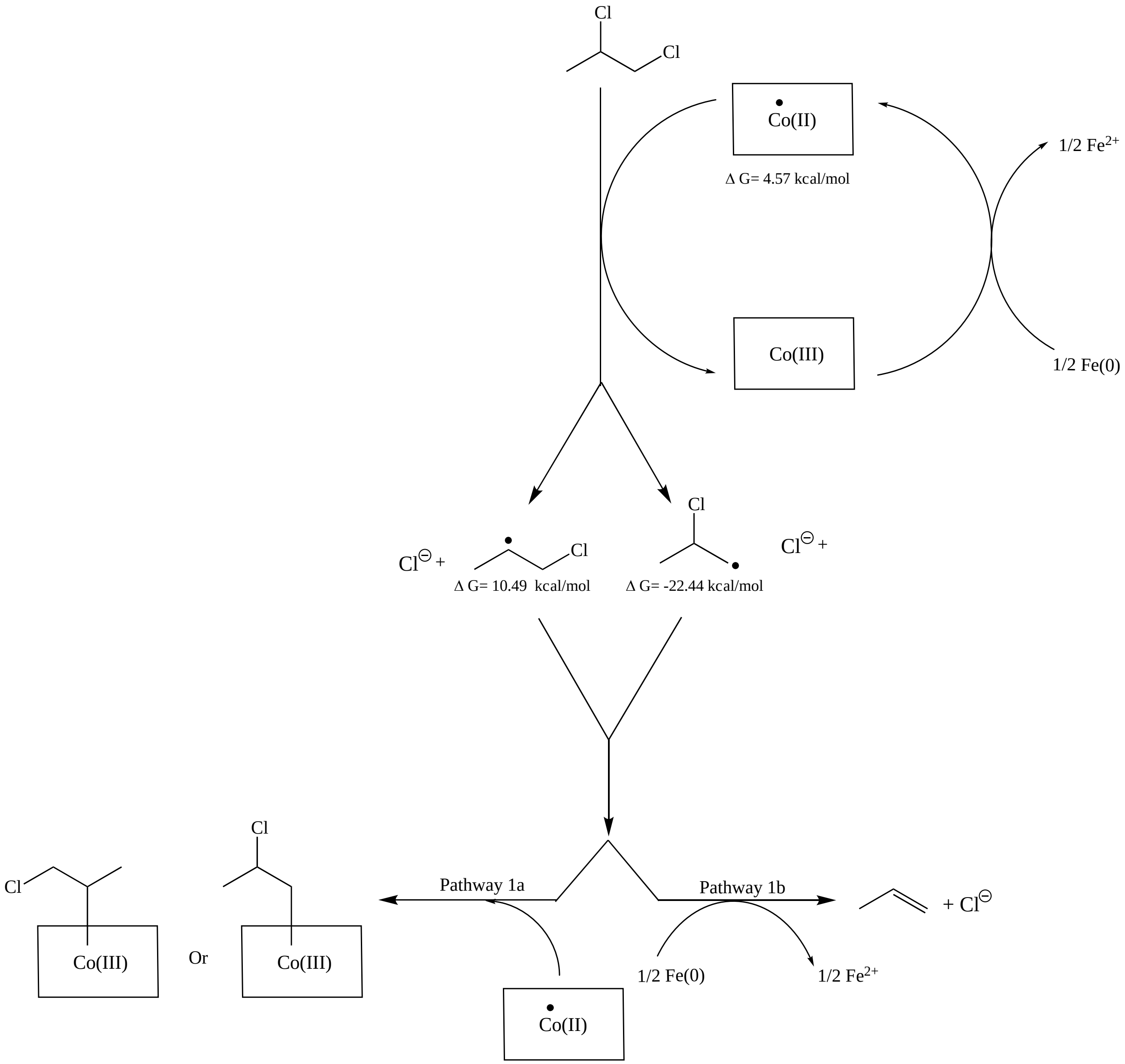


***Figure 42**: Proposed catalytic cycle for 1,2-DCP*

1,3-DCP

The proposed mechanism for 1,3-DCP follows a similar reaction mechanism to that of 1,2-DCP as shown in **Figure 43**. The reaction is initiated by the reduction of cobalamin to B_{12r} by a single electron transfer from ZVI. Once reduced, B_{12r} can then act as a nucleophile and perform a single electron reduction of 1,3-DCP, forming a radical chloropropane compound. The formation of the radical chloropropane molecule can then follow either pathway 1 or pathway 2. Similar to before, if the reaction proceeds via pathway 1 then the reaction is halted because of the formation of a stable intermediate that cannot be further reduced. However, if the reaction follows pathway 2a then it can undergo either reduction to cyclopropane by a single electron transfer from ZVI[29, 62]. Whereas if it follows pathway 2b it can be further reduced to propene, however, this is not nearly as favorable of a reaction in comparison to the formation of cyclopropane (ΔG= 38.81 kcal/mol).

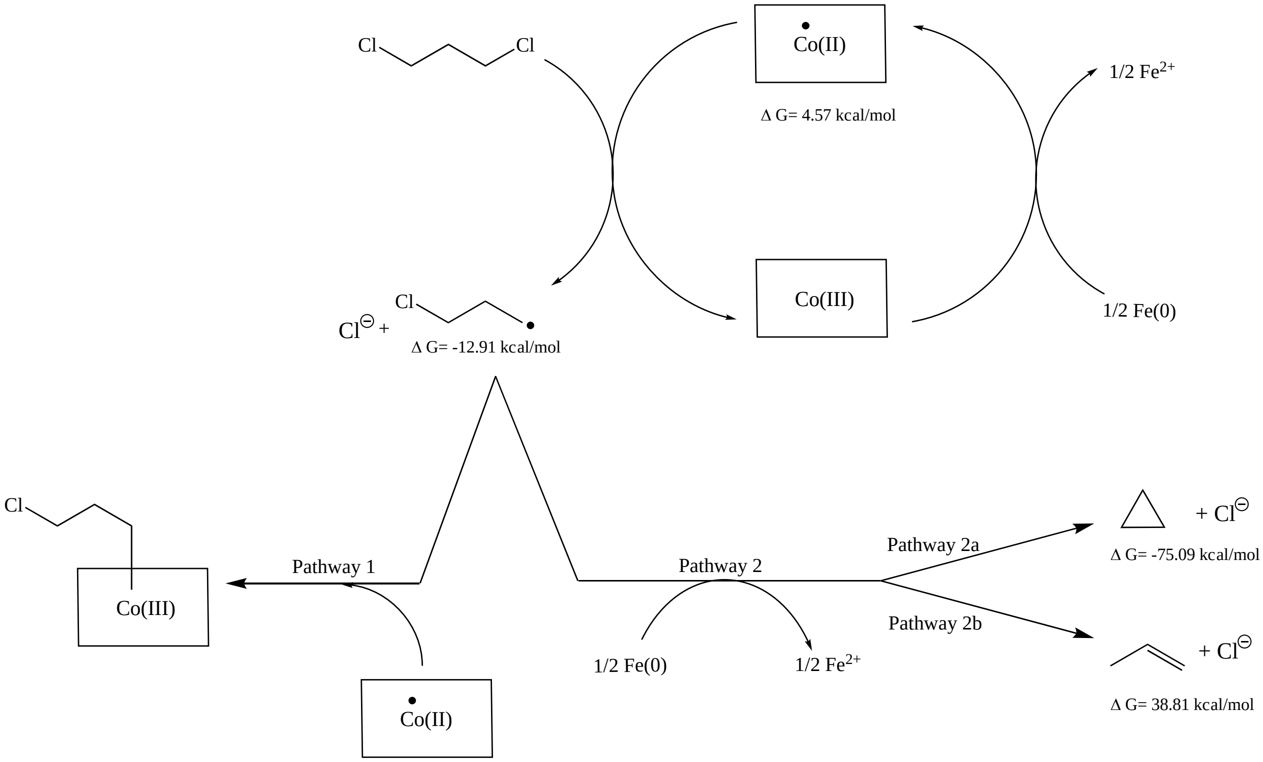


***Figure 43**: Proposed catalytic cycle of 1,3-DCP*

1-CP

The monochlorinated congener, 1-CP, follows a similar reaction pathway to that described for the tri- and di- chlorinated propanes. The reaction is initiated by the reduction of cobalamin to B_{12r}, which then transfers a single electron to 1-CP to form a propane radical, thus releasing chloride into solution. Mechanistic studies indicate the Gibbs free energy is -15.09 kcal/mol for the formation of the radical propane molecule, which supports the proposed catalytic cycle. The reaction may then follow either pathway 1, forming an alkyl cobalamin, or it could undergo further reduction to propane by following pathway 2, as displayed in **Figure 44**.

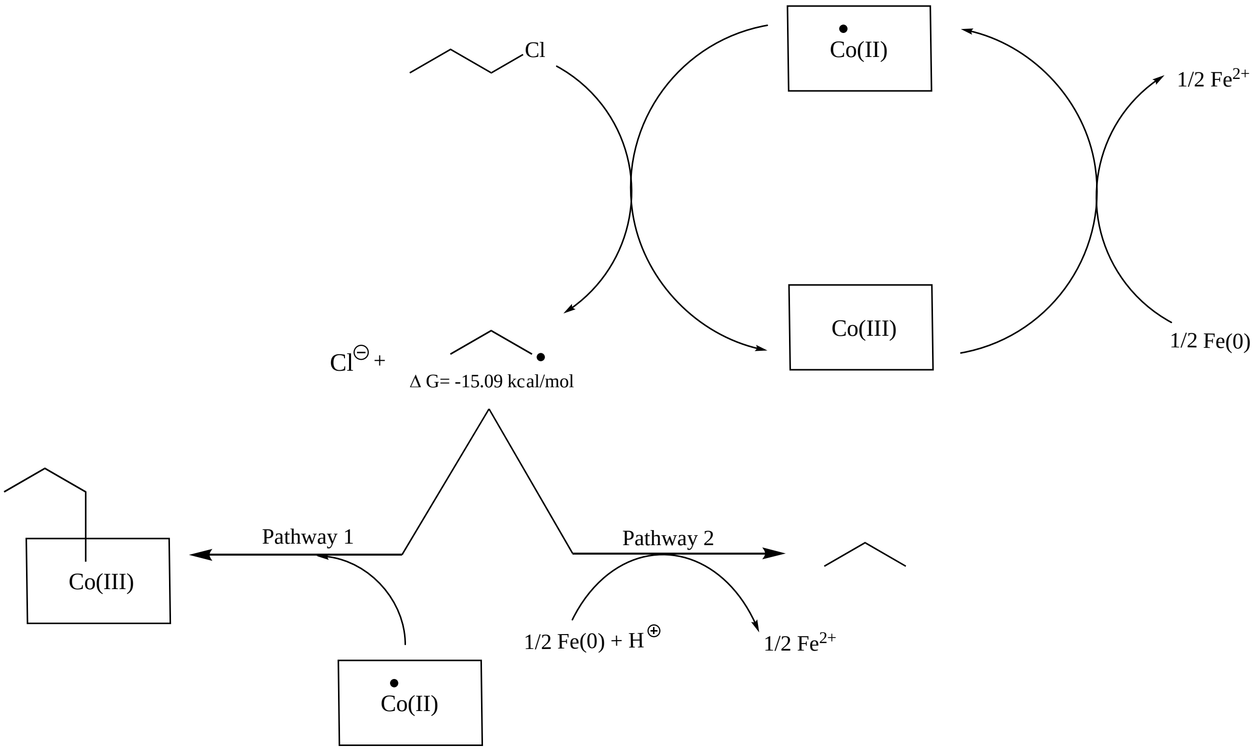


Figure 44: Proposed catalytic cycle 1-CP

1,2-DCA

The mechanism for the reduction of 1,2-DCA followed a similar pathway to the chlorinated propane molecules. Ethene is the major product of this reaction, which is supported by the mechanism shown in **Figure 45**. The formation of the radical intermediate had a Gibbs free energy of -18.61 kcal/mol, demonstrating that this a favorable pathway. No byproducts were observed in the actual experiment, but the measurable increase of chloride in solution and the disappearance of 1,2-DCA support this degradation.

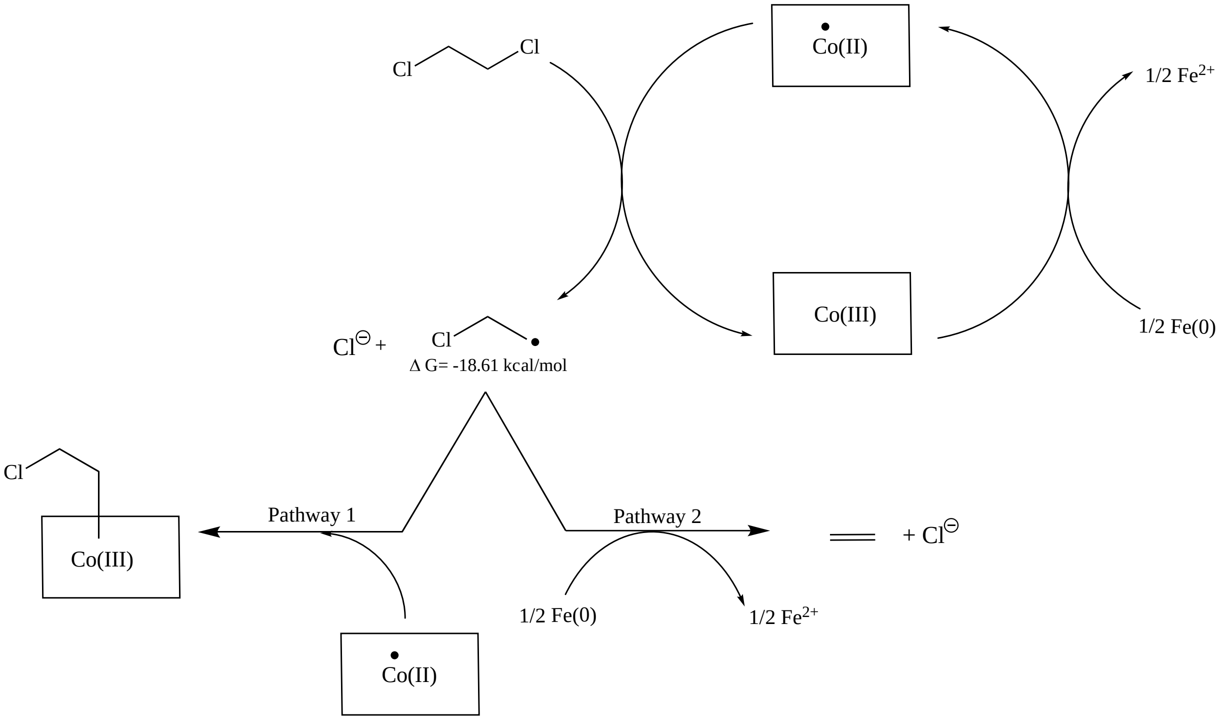


Figure 45: Proposed catalytic cycle for 1,2-DCA

CHAPTER 5: INCORPORATION OF COBALAMIN IN EMULSIFIED ZERO VALENT IRON

In 2003, a US EPA expert panel on DNAPL remediation estimated that there were between 15,000 and 25,000 DNAPL sites in the United States[63]. Remediation of DNAPL-contaminated media has been shown to be challenging, and these contaminated materials can act as long-term sources of groundwater contamination. EZVI is a remediation technology that is capable of treating DNAPL source zones and has been used to effectively treat contaminated media and reduce the flux of chemicals from source zones[25-26]. Due to the lipophilic nature of these chlorinated solvents they are able to pass through the outer oil membrane of EZVI. Once in the interior of the micelle, degradation is initiated by the presence of ZVI particles (**Figure 46**). The following studies examined the ability of EZVI and a modified EZVI formulation including B_{12} to degrade 1,2,3-TCP.

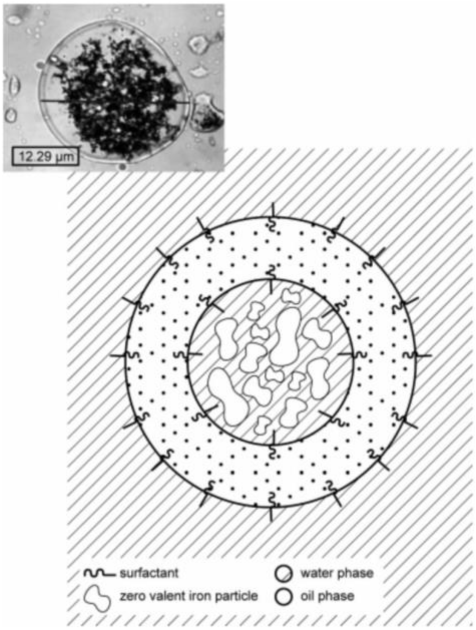


***Figure 46**: EZVI droplet schematic (Reproduced from Quinn, et al.)*[25]

Emulsion studies

These studies were carried out to determine the effectiveness of B_{12} in degrading 1,2,3-TCP using a modified EZVI formula. The results from this study showed that, in the presence of EZVI without B_{12}, no degradation byproducts were observed. However, a decrease in 1,2,3-TCP concentration was observed, which is most likely due to its lipophilic properties encouraging partitioning in the oil membrane of EZVI. Neat (emulsion-free) studies showed that ZVI was not sufficient alone to reduce 1,2,3-TCP**. Figure 47** displays the GCMS spectrum from prior to EZVI introduction and after 24-days exposure.

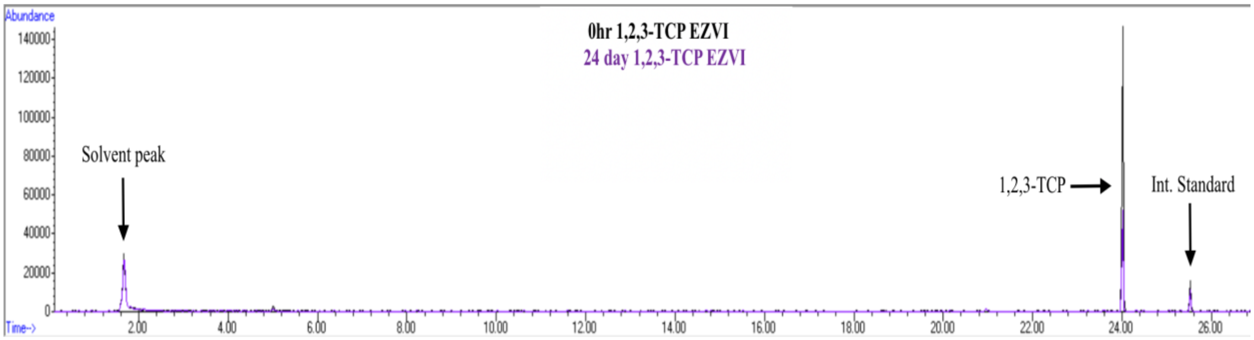


Figure 47*: GCMS spectrum of 1,2,3-TCP in the presence of EZVI*

In the EZVI-B_{12} formulation, 1,2,3-TCP was degraded successfully; byproducts were evident in the formation of propene and 1,3-DCP over 24 days as seen in **Figure 48**. The formation of propene suggests that a similar pathway was followed as described in the mechanistic study. In addition, the formation of 1,3-DCP suggests that the 1,3-dichloropropane accepted a proton from water.

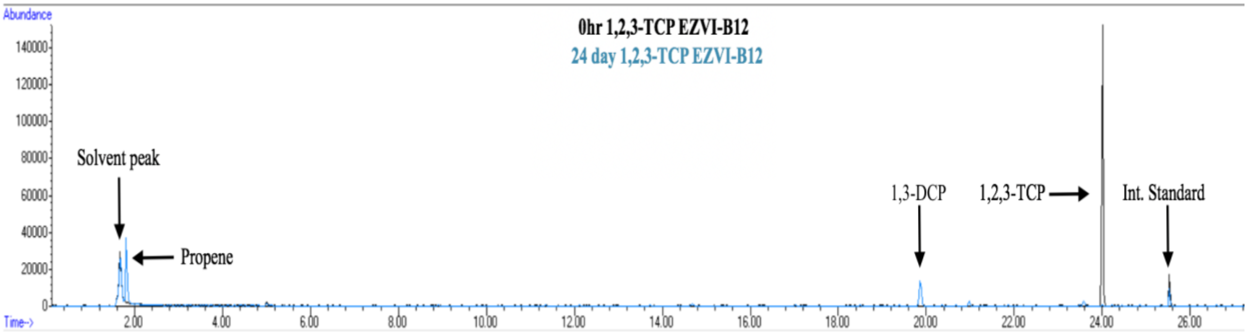


***Figure 48**: GCMS spectrum of 1,2,3-TCP in the presence of EZVI-B_{12}*

CHAPTER 6: INTRODUCTION TO CHEMICAL EDUCATION

Introductory chemistry courses are prerequisites for chemistry, biology, and related fields are typically among the first college science courses incoming students encounter. General chemistry can heavily sway a student's decision to pursue a major in science, technology, engineering, or mathematics (STEM), especially because these introductory courses are typically taken during the most influential period of college. Research indicates that a student's first 2 years of college are critical for development and lay the foundation for the remainder of their studies [64]. The typical American 4-year university loses 25% of new students before the start of their second year, with underrepresented minorities (URM) and low income students more frequently disengaging [65-66]. Women and URM students comprise roughly 70% of college students, which is a population that may have a significant contribution to STEM [67]. In 2012, URMs earned 18.9% of bachelor's degrees, 13.8% of master's degrees, and 6.8% of doctoral degrees in science and engineering (S&E) [68]. While there has been an increase of URMs obtaining baccalaureate and advanced degrees in S&E, there is still a need to increase URM in STEM fields.

The President's Council of Advisors on Science and Technology (PCAST) predicted a deficit of 1 million students graduating with a STEM degree in the next decade, indicating that insufficient people are being educated to fill newly created roles in S&E and those vacated by the previous generation. In order to combat this shortfall, the United States needs to increase the number of STEM graduates by 34% annually, and a large emphasis is placed on retention of women and URM students in STEM [67]. Focusing on these populations and providing opportunities for them can diversify and increase the number of STEM graduates. The PCAST report recommends incorporating evidence-based teaching practices to increase student retention in STEM. Lecture-based courses, although one of the most widely used teaching platforms, have been shown to be among the least effective methods for student comprehension and retention. Research shows that implementing teaching styles which focus on student engagement can reach a larger audience and make STEM classes feel more welcoming to students.

Active learning is a method of teaching that aims to engage students in the learning process by having students participate through activities and/or discussions, and is one of the recommendations from the PCAST report to increase student retention in STEM. A recent meta-analysis of 225 studies that compared student performance under active learning versus traditional lecturing in undergraduate STEM courses showed a significant increase in student learning gains with courses that had active learning interventions. In addition, this study showed that students were 1.5 times more likely to fail in a traditionally taught class than students in courses that incorporated active learning [69].

Active learning has gained considerable attention in academic circles. Academic institutions have begun implementing active learning in the form of immediate electronic student feedback (iClickers), discussions, cooperative learning, guided learning, flipped classrooms, and many more techniques [69-72]. This differs significantly from the traditional lecturing style, which is a passive learning technique where students are not involved in the learning process. This style of teaching does not engage students in higher-order cognitive skills (HOCS) and is primarily a one-way form of communication from lecturer to student. Engaging students in the learning process promotes HOCS and encourages problem solving, decision making, critical thinking, and willingness to ask questions [73].

The Gradual Release of Responsibility (GRR) is a combination of behaviorist and constructivist educational theories and is an active learning teaching model [74-78]. In this model, students begin by learning as a result of observation, imitation and modeling. As the lecture progresses through the framework, it starts to shift to a more constructivist theory where students learn from interacting socially and with their environment. This framework centers around instructional scaffolding paired with collaborative work amongst peers [79]. Increasing student engagement and responsibility by utilizing a GRR model progressively transfers learning responsibility from instructor to student. This transfer of obligation allows students to make more independent choices and helps them approach atypical problems and situations in a way that conventional teaching approaches cannot. This method uses focused learning and instruction, then slowly shifting tasks and responsibilities to the students and allowing them to do guided collaborative work, then finally, independent tasks.

Focused instruction is a time that is used to clearly establish the goals and purpose of the lecture. During this time the objectives are clearly established at the beginning of the lecture and reiterated at the end. Throughout this time new information and concepts are introduced along with application examples and circumstances. Analogies can also be incorporated to make difficult concepts more relatable to students. When working through a problem it is important to thoroughly explain the thought process behind each step, and state common errors to avoid. This is done so students can easily transition to applying new concepts and to alert students to common mistakes. During this time, students are actively listening, writing notes, and asking for clarification.

Guided instruction is a method to guide students to become more complex thinkers through guided questions, prompts, and problems. This a constructivist approach to teaching because students begin constructing knowledge for themselves by interacting with the people around them and their environment. A major component is the construction of a learning framework while working within a student's zone of proximal development, which is what a student can accomplish independently or with help from a more experienced individual [75]. By working within this zone, the instructor is able to bridge the gap between what a student does and does not understand. In a large lecture hall this can be challenging because, instead of working with small groups as described by Fischer and Frey, knowledge is disseminated to the entire class [79]. Guided instruction relies on responses from students to better gauge understating of a particular topic. Prompts are utilized to assist students in a less direct manner by reminding students about background knowledge, procedures, or to reflect on their answers. When prompts are not sufficient, verbal or visual cues are commonly used to be more specific, however, if students are still confused focused instruction can be revisited.

Another important component of this framework is collaborative learning, which is often neglected in large lecture halls. During collaborative learning exercises, students work towards a common goal and collaborate in small groups, which in a large enrollment course typically consists of the students located around them. During this time students work in collaborative groups to work towards a common goal such as in the case of questions, worksheets, or other assignments. This gives students an opportunity to use their critical thinking skills on the material in a peer-oriented environment. Peer-to-peer interactions have been shown to have a positive effect on student learning outcomes and have been implemented in a number of different teaching styles, such as: Peer-Led Team Learning (PLTL), Process Oriented Guided Inquiry Learning (POGIL), and Problem Based Learning (PBL) [80-84]. The positive effects of cooperative learning on students' attitudes and retention are integral to this teaching model.

Independent learning allows students to apply the knowledge that they have gained throughout their academic journey, and students are responsible for their own comprehension. As students progress through the GRR framework, metacognitive skills are developed, such as planning how to solve a task, identifying what strategies to use, correcting any mistakes, and evaluating the work performed.

The motivation behind this research was to help students build a stronger foundation in chemistry by implementing a different teaching style for a large-enrollment chemistry course. These courses are typically taught as a traditional lecture style with very little to no student collaboration. The large number of students and time constraints are often not conducive for collaborative learning. However, studies show that dedicating as little as 10% of class time to active learning can have a significant positive effect on student outcomes [69]. Research also supports the effectiveness of collaborative peer learning among students with different learning capabilities [85-86]. The goal of the following research was to improve students' attitudes towards chemistry, increase understanding of chemistry concepts, monitor the success of minority groups, and observe how DFW (Ds, Fs, withdrawals) rates were affected compared to previously taught courses.

CHAPTER 7: UTILIZATION OF A MODIFIED GRADUAL RELEASE OF RESPONSIBILITY MODEL IN A LARGE ENROLLMENT CHEMISTRY COURSE

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Course description

The following study took place at the University of Central Florida (UCF), a public institution. UCF is the largest university in Florida and one of the largest in the United States. As of the Fall Semester 2017, undergraduate student enrollment made up 86% of the student population, which was over 66,000 students. UCF is a diverse university with 49.2% of its population being White (non-Hispanic), 24.9% Hispanic/Latino, 11.1% Black, 6.2% Asian and Pacific Islander, 3.6% multi-racial, and 4.8% nonresident alien or not specified[87].

Prior to taking chemistry at UCF, students are required to take a chemistry placement exam which assesses students' readiness for general chemistry. The placement exam has been unmodified throughout the course of the data set, including previous semesters. These scores were not available to the researchers. Students scoring less than 76% requires two semesters of Chemistry Fundamentals 1, divided into 1A and 1B. As a result, due to the relatively short time span of the compared data set it can be assumed that student knowledge on entry to this course remained reasonably unchanged. These fundamental courses enroll approximately 300-450 students per section; students on this track typically do not have a strong background in chemistry or strong problem-solving skills. In this course grades equivalent to D+, D, or D- are treated as an NC (no-credit) letter grade, which does not affect a student's overall GPA.

This study focused on a Chemistry Fundamentals 1B course, which covers the following topics: quantum chemistry and atomic structures, periodic properties, chemical bonding, and ideal gases. The GRR model was implanted for two semesters in Fall 2017 and Spring 2018. This course had a predominantly female average student population of 60.2% and a racially diverse student population as shown in Figure 1. The number of course sections offered differs depending on the semester, often one section of Chemistry Fundamentals 1B is taught in Fall while in Spring three sections are offered. Depending on the time slot classes can be 50 to 75 minutes long and are held Monday, Wednesday, Friday or Tuesday, Thursday. The results from this study were compared to Chemistry Fundamentals 1B courses that were taught with a traditional lecture platform at UCF. The following research received approval from UCF's Institutional Review Board (IRB: #SBE-17-13374) and student participation in the study was voluntary. Exams used during this study came from the same test banks as previously taught courses and were of comparable difficulty. Comparison of test difficulty can be found in the supplemental material. The grading rubric for this course is described in **Table 2**.

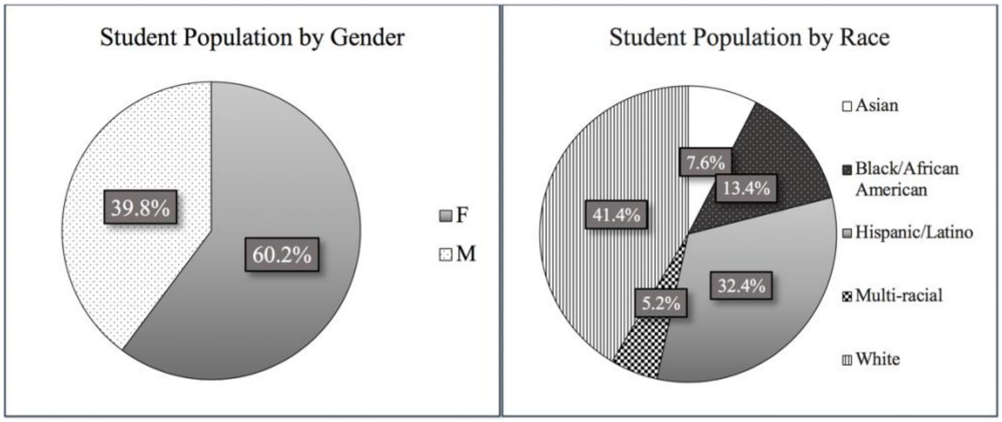

Figure 49*: Student demographic population in the course section employing the GRR teaching model. Gender: Female (grey) and Male (polka dots). Race: Asian (white), Black/African American (polka dots), Hispanic/Latino (grey), Multiracial (checkered), and White (lines)*

Table 2: Grading rubric for course

	Percent value	**Notes**
Exams	40%	Lowest exam grade dropped
ALEKS	20%	Lowest score dropped
iClickers	20%	3 Lowest iClicker scores dropped
Final Exam	20%	

Purposes

1. Help students build a stronger foundation in chemistry through guided instruction, collaboration, and independent work
2. Evaluate how students respond to a modified teaching approach through surveys given at the beginning and end of the semester
3. Observe how DFW rates and overall grades compare to previous semesters and how different student population groups are affected

Methods

Modifications to GRR teaching model

Undergraduate graduate teaching assistants (UTAs) underwent a week-long workshop prior to the start of the semester. This training focused on methods for guiding students' responses and an over view of the teaching model. In addition, weekly meetings were held to review that week's content and activities. A typical lecture had between 4-6 UTAs. The role of UTAs in the classroom was to help facilitate student understanding during group discussions and provided a means to help close the gap between instructor and students.

The course was structured as described by Fischer and Frey with modifications to better suit a large enrolment course. Such modifications included the use of UTAs because it was not feasible for the instructor to interact with all student groups. A major modification to this framework was in guided instructions. Instead of small appointed groups based on student performance, groups were made by the students based on proximity. During this time overall class responses towards questions and prompts were used as a metric to gauge student understanding. Independent learning was assessed through iClickers and ALEKS, an online homework platform and adaptive learning tool that gives students real time feedback.

iClickers were used in both independent and collaborative settings in order to gauge students' responses in real-time. If an iClicker question was originally meant to assess students in an independent manner and less than 70% of students selected the correct answer, then the students were allowed to work on the same question collaboratively.

Figure 50 outlines an example of how a 50-minute GRR course was typically structured. It is important to note that the majority of the lectures were organized in this format, however, if at any point students were not understanding concepts during guided instruction or collaborative learning, then focused instruction was revisited. In addition, some days were solely dedicated to collaboration and students would work on group assignments during that lecture time.

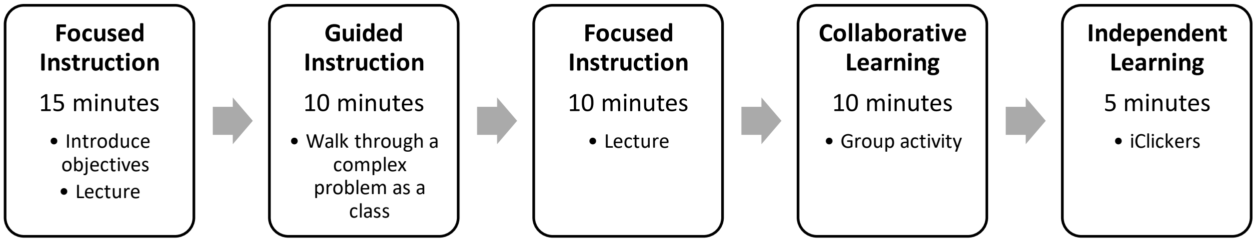

***Figure 50**: Example of how a 50-minute GRR lecture was structured*

Student response survey

A voluntary survey designed for this course was given anonymously online through the learning management platform and students did not receive any credit for completing the survey (UCF Webcourses, a Canvas portal). The survey was created specifically for this study to observe how students' responses towards the GRR teaching model and collaboration changed over the course of the semester. The questions were coded with an inter-rater reliability score of 95% between two raters. Any discrepancies were reconciled for the final categorization. When administered to students the questions were not grouped by code. The results collected spanned two semesters and was taught by the same instructor, Fall 2017 and Spring 2018. Exactly half as many students responded to the end-of-semester survey as the start-of-semester survey, with 427 total respondents across the end of the two semesters and 854 total respondents from the beginning. Since students' responses were anonymous there was no way to discern students' responses from the beginning to the end of the semester and were taken as an aggregate. The survey format used a 5-point Likert scale and gauged students' overall response towards collaboration and key components of the GRR teaching model in terms of their agreement with qualitative statements describing this course in particular and GRR in general. These surveys were used to monitor student attitudes towards these categories over the semester. An average Likert score with a 3 or higher was considered a positive response towards that code.

An example of a statement used to evaluate student response to collaboration was:

I feel that collaborating with my peers helps me more easily apply the material on my own

An example of a statement used to evaluate student response to components of the GRR model was:

I feel that the guided instruction for practice problems helps me better grasp the material

Additional survey questions can be found in **Table *3*.**

Limitations to data set

Limitations to this study included a lack of individual numerical student scores of the unmodified sections, only final letter grades were available. As previously stated, individual placement exam scores were not available to the researcher. In addition, the overall structure of the GRR course in comparison to the Traditional course was largely unmodified with the main difference being instead of weekly quizzes, iclickers were used in its place. There was no instructor overlap between traditional and GRR taught courses. The instructor was kept constant for the two semesters taught as a GRR style.

Results

Student Response Results

The results from the survey are shown in **Table 3** and Error! Reference source not found.. The results from this survey were taken as Likert averages and a score of 3 or larger was considered to be a positive effect. Where **Figure 51** shows a bar graph of the Likert averages and this data shows an increase in respect towards collaboration and a slight decrease in respect to the GRR model. A one-tailed t-test was performed to determine the statistical difference between the Likert averages and there was a significant difference with 95% confidence interval for collaboration and no significant difference in respect to the GRR teaching model. The calculated t-values are displayed in **Table 4**. However, it is important to note that the Likert average was above a 3 both at the beginning and end of the semester, which shows students have a positive outlook on key components of this teaching model. The components of the GRR teaching model that were evaluated were: defined objectives, collaboration, and guided instruction.

Table 3: Survey statements with Likert means and standard deviations for the pre- and post- survey statements

Pre-course survey statements		
GRR questions	Mean	SD
I feel that going over the objectives in lecture creates a more cohesive learning experience	4.12	0.90
Working out problems in lecture helps me better understand the material	4.60	1.58
I am willing to participate in group assignments during lecture	3.18	0.54
I would like to have undergraduate teaching assistants to help answer questions during in class problems	3.80	0.67
I would be comfortable with approaching the undergraduate teaching assistants with questions	3.79	0.65
I am comfortable with approaching my instructor with questions	4.00	0.80
I feel that practicing problems improves my understanding of material	4.63	1.50
I am comfortable with answering other students' questions on the material	2.57	0.34
I am open to new learning styles	4.13	0.89
I am comfortable with approaching my classmates with questions	3.02	0.32
I am able to learn in a large classroom lecture effectively	3.38	0.53
Collaboration questions		
I am comfortable with approaching my classmates with questions	3.12	0.50
I am willing to participate in group assignments during lecture	3.18	0.54
I am comfortable with answering other students' questions on the material	2.86	0.54
I prefer working in small groups	3.03	0.36
Post-course survey statements		
GRR questions	Mean	SD
I would describe my overall attitude towards chemistry with this teaching style	3.60	0.59
I feel that the way this course is structured has helped me better understand chemistry concepts	3.63	0.57
I feel that going over the objectives in lecture created a more cohesive learning experience	3.92	1.15
Working out problems as a class during lecture helped me better understand the material	4.30	1.10
I have enjoyed participating in group assignments during lecture	3.15	0.37
I feel that working with my peers during in class problems has helped me better understand the material	3.36	0.65
I feel that having the undergraduate teaching assistants to help answer questions during in class problems was helpful	3.53	0.80
I feel that collaborating with my peers has helped me more easily apply the material on my own	3.38	0.67
I enjoyed how engaged this course was	3.67	0.59

GRR questions	Mean	SD
I feel that the guided instruction portion of this course helped me tackle chemistry problems	3.71	0.62
I feel that the style of teaching for this course has helped me better grasp chemistry concepts	3.72	0.89
I am comfortable with approaching my classmates with questions	3.30	0.44
Collaboration questions		
I am comfortable with approaching my classmates with questions	3.30	0.44
I have enjoyed participating in group assignments during lecture	3.30	0.63
I feel that working with my peers during in class problems has helped me better understand the material	3.27	0.41
I feel that collaborating with my peers has helped me more easily apply the material on my own	3.66	1.02

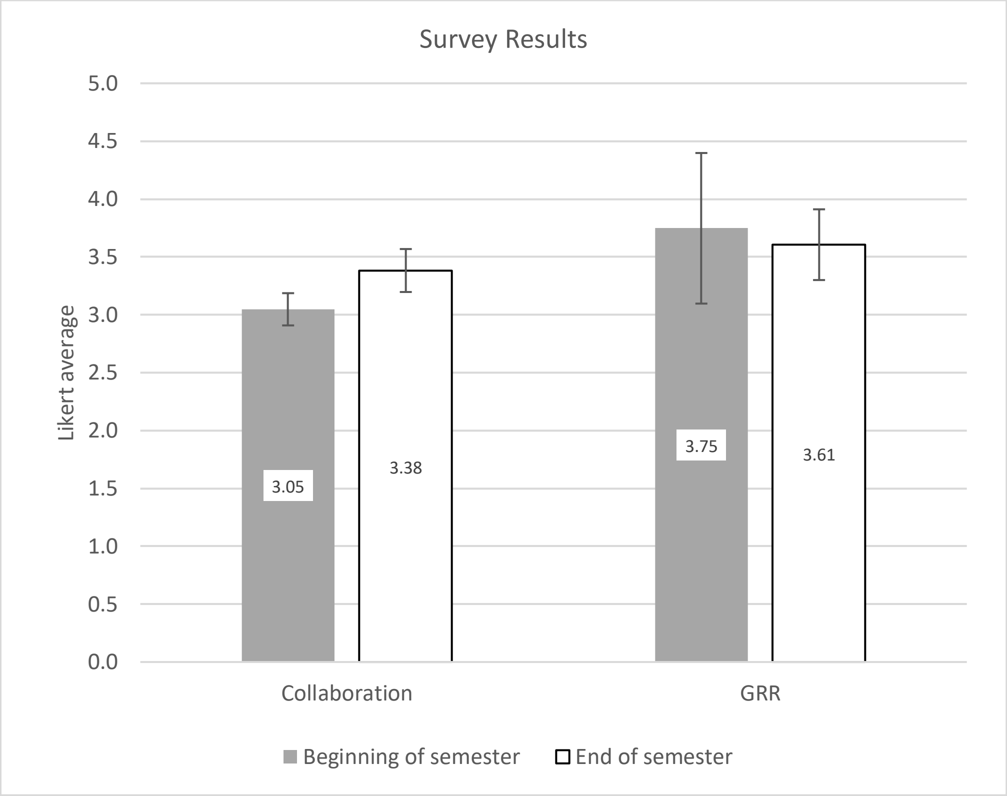

Figure 51*: Comparison of pre- (grey) and post- (white) course survey results*

Table 4: Statistical mean comparison of survey results where the highlighted and bolded value corresponds to a statistical difference higher then p=0.05.

	Collaboration	**GRR**
T-value	**2.89**	0.65
p-value	0.05	0.05

Overall student effect on academic success

In addition, overall grades were compared to six semesters of traditionally taught Chemistry Fundamentals 1B courses, which included courses from Summer 2016 to Spring 2018 taught by multiple faculty members. The population of students from traditionally taught sections was 2,213 and the population in the GRR section was 901 students. The grade distributions of the traditional course (denoted in white) versus the GRR course (denoted in grey) are displayed in **Figure 52**. In comparison, the GRR model had a shift towards students obtaining higher grades and a decrease of DFWs. **Figure 53** shows a divergent graph, which displays the percent difference of students' grades in the GRR course as compared to traditional lectures. A 13.0% increase of students obtaining As and a 10.9% increase of students obtaining Bs was observed with a decrease of students obtaining Cs of 11.0%. Withdrawal rates decreased by 5%, D/NCs decreased by 7.1%, and Fs had a decrease of 1.6%.

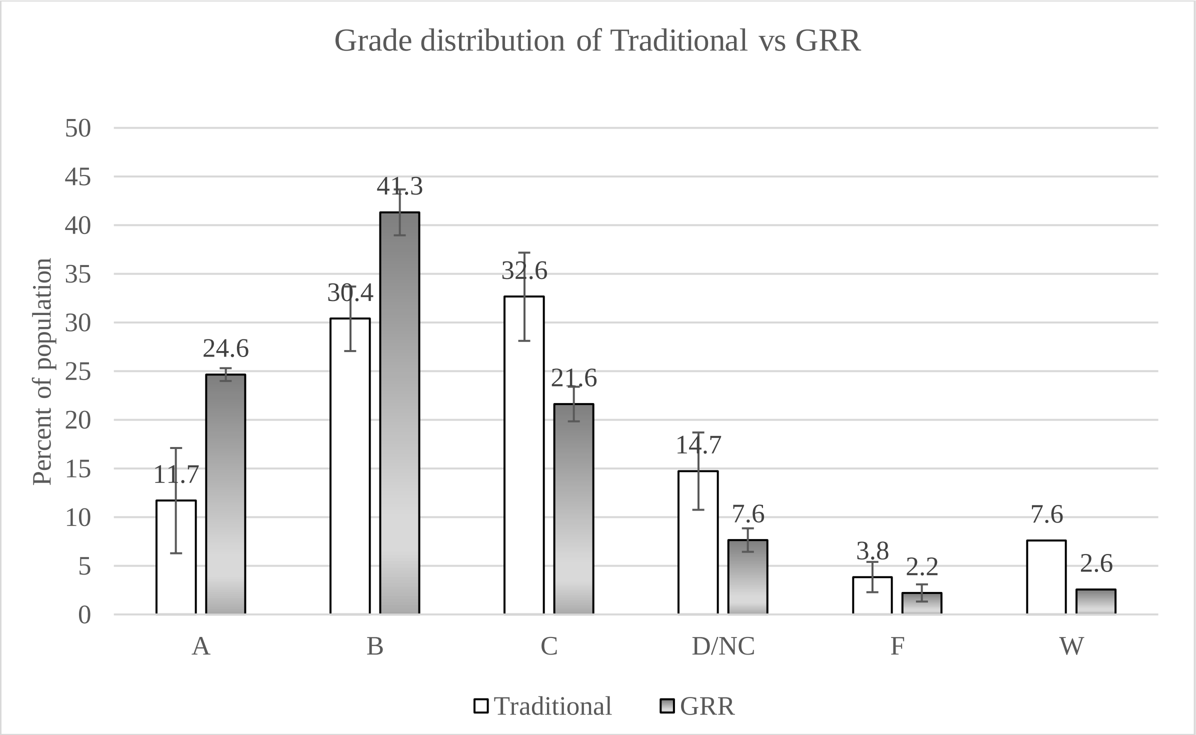

***Figure 52**: Gender grade distribution of Traditional (white) vs GRR (grey) taught course*

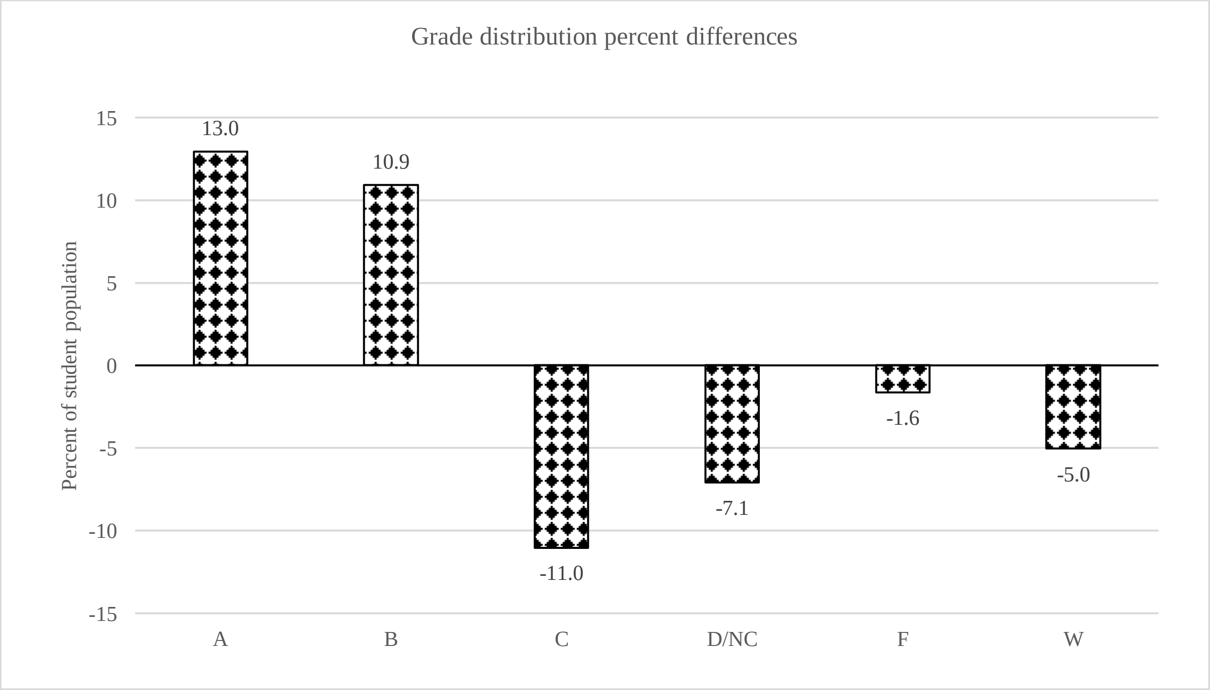

***Figure 53**: Divergent graph of Traditional vs GRR*

Academic success on demographic population

A further objective of this study was to evaluate how different student in differing demographic groups performed throughout this course in comparison to a traditionally taught lecture. The demographic data being compared to the GRR model covers three sections of a traditional-style course, which was taught by different faculty members with a total population of 1,339 students. A divergent graph showing the gender grade distribution difference between GRR and traditional lectures is shown in **Figure 54**. The female student population (polka dots) had an increase in As of 15.9% and 22% in Bs with a decrease in Cs of 3%. In addition, female students receiving D/NCs decreased by 8.3%, Fs by 5.1%, and withdrawals by 4.8%. In comparison to the male population (dashed diagonal lines) which had an increase in As of 14.2% and 10.2% in Bs with a decrease in Cs of 11.6%. Additionally, the number of males receiving D/NCs decreased by 7.0%, Fs by 1.5%, and withdrawals by 2.2%. The results from the gender demographics showed a positive response by both genders to the GRR teaching model, as indicated by a shift to higher grades with respect to traditionally taught courses. In addition, a decrease was also observed in DFW rates amongst both populations.

Student grade distribution by race was also calculated to determine how different demographics responded to a modified teaching model. The percent increase/decrease for each demographic is displayed in **Table 5**. It was observed that all demographics had a positive increase with respect to students obtaining As and Bs. In the case of students obtaining Cs there was a decrease amongst all races except for a small increase of 2.0% for Black/African American students. There was a decrease amongst each demographic with regard to DFW rates. This is important to note because it shows under-represented minorities obtaining higher grades with a decrease in DFWs.

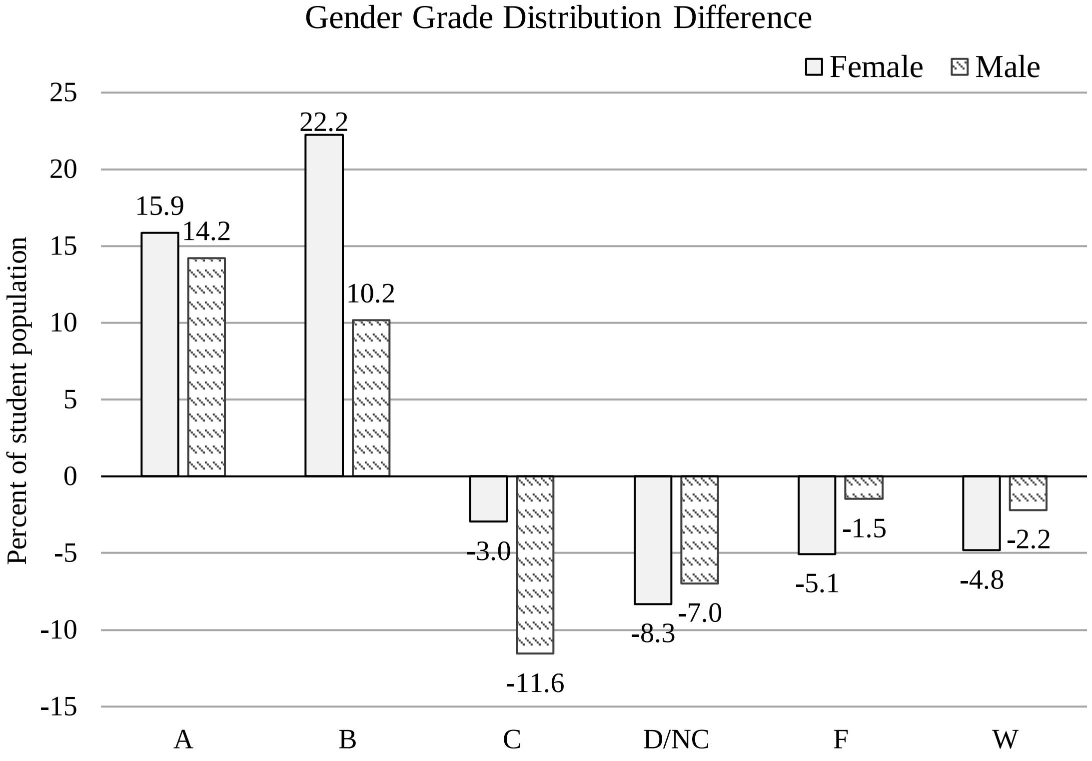

***Figure 54**: Gender grade distribution difference: Female (grey) and male (diagonals*

Table 5: Student demographic grade distribution differences between GRR and Traditional lecture style

Demographic	A (%)	B (%)	C (%)	D/NC (%)	F (%)
Asian	12.0	4.5	-3.2	-10.1	-0.3
Black/African American	0.9	16.8	2.0	-13.4	-5.0
Hispanic/Latino	11.3	14.9	-13.5	-6.6	-4.3
Multiracial	25.6	0.5	-6.7	-8.3	-9.3
White	15.8	11.9	-12.0	-9.8	-4.1

Comparison of overall statistical means

A one tailed t-test analysis was performed to compare statistical means between overall grades between three sections of a Traditional lecture course and two semesters of a GRR taught course. **Figure 55** indicates a statistical difference at 95% confidence interval for As, Bs, and D/NCs and it also displays at a 90% confidence interval a statistical difference for As, Bs, Cs, and D/NCs. Overall this shows that higher grades were statistically affected by the teaching model as well as Cs and D/NCs.

Further statistical comparisons between gender and student demographics were also performed using the same data set and is displayed in **Table 6**. There was a statistical increase in females obtaining As and Bs with a statistical decrease in the numbers of D/NCs observed. In regard to the male population the difference in As, Cs, D/NCs, and Ws were statistically different. Indicating that there was a significant increase in As and Bs with a decrease in D/NCs and Ws. This shows there was a slightly greater effect on male the population in comparison to females.

In regard to student demographic the largest statistical difference in grade distribution was observed for the Hispanic/Latino and White student populations with majority of grades having a statistical difference. These results indicate that the GRR teaching model did have an overall statistical effect on student academic performance.

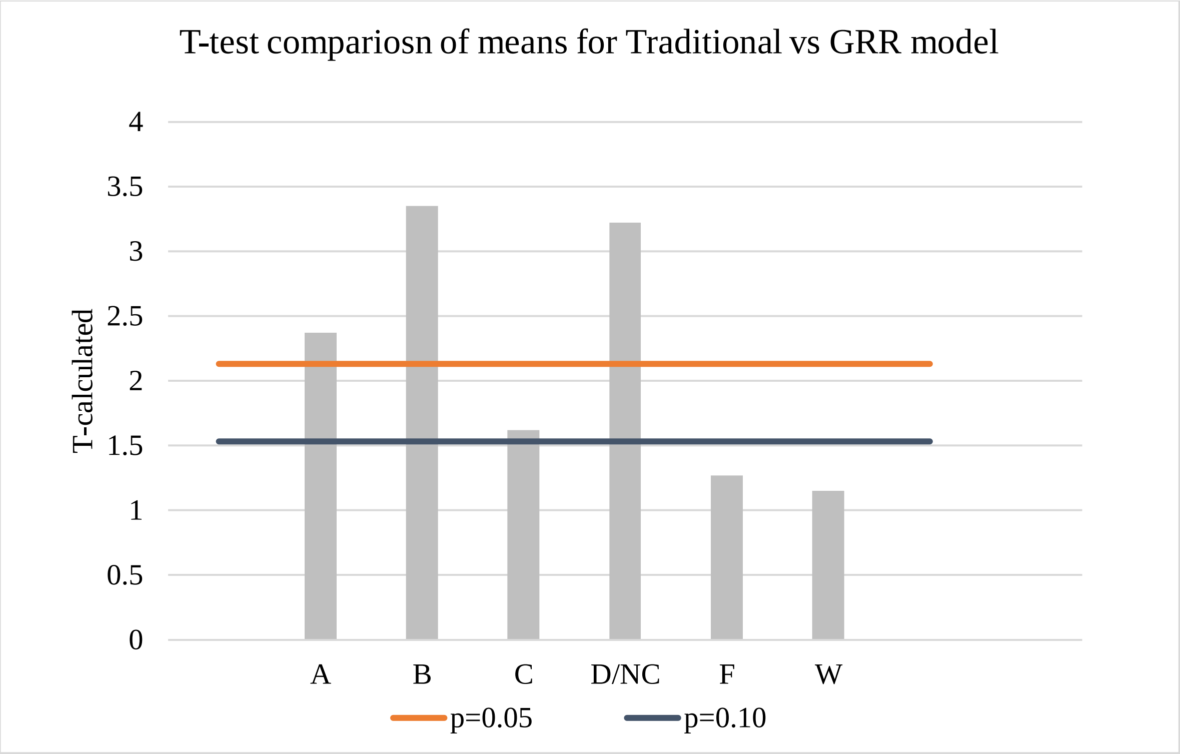

Figure 55*: T-test comparison of means for Traditional lecture to GRR teaching model. The red line indicates a confidence interval of 95% whereas the blue line is a confidence interval of 90%.*

Table 6: T-test comparison of means of Traditional lecture to GRR. Highlighted regions show a statistical difference with p=0.10 or higher. Bolded values correspond to a p≤0.10 or higher where bold and italicized correspond to having p≤0.05.

	A	B	C	D/NC	F	W
Female	***2.327***	***3.120***	0.649	***3.596***	1.373	0.909
Male	***2.156***	0.897	***2.782***	***2.651***	0.781	***2.535***
Asian	1.290	0.102	0.840	***5.367***	0.507	0.293
Black/African American	0.199	0.806	0.337	1.324	0.507	**1.719**
Hispanic/Latino	***2.861***	***6.658***	**1.609**	**1.605**	1.291	**1.715**
Multiracial	***8.050***	0.968	0.000	0.731	0.600	1.074
White	***2.381***	***3.924***	**1.994**	***2.709***	**1.820**	0.948

Comparison of statistical means of individual exam scores

Further statistical analysis was performed by comparing individual average exam scores from a Traditional lecture versus a GRR lecture. The scores used for this data set are from concurrent semesters, Spring 2018. The population from the traditional taught course was 435 students and from the GRR course was 412 students. The exams were of comparable difficulty and can be found in the appendix.

A one tailed t-test was performed on the data set to determine if there was a statistical difference in student performance. **Table 7** displays the average student scores per exam along with the calculate t-value. Three of the four exams were statistically different with a confidence interval of 95%. Exams one and four showed that students in the GRR course were performing statistically higher than the traditional lecture style. However, on exam two students in the traditionally taught course were performing statistically higher than the GRR model. Looking at overall exam averages, students in the GRR model performed statistically higher in comparison to the traditional lecture taught course.

Table 7: Comparison of average exam scores of concurrent semesters with calculate t-values with the highlighted and bold values were larger than $p \leq 0.05$.

Exams	1	2	3	4	Exam Averages
Traditional	62.83	73.92	67.66	70.36	68.63
Std. dev.	20.31	19.62	21.29	22.06	21.22
GRR	78.77	70.01	69.29	75.73	73.39
Std. dev.	13.49	13.71	14.48	16.28	15.05
t-value	**13.367**	**3.352**	1.297	**4.008**	**8.060**

iClicker responses

As previously mentioned, iClickers were used in both independent and collaborative settings in order to gauge students' responses in real-time. An increase in correct student responses was observed after they were allowed to work collaboratively on the iClicker question. This further indicates that collaboration amongst peers has an impact on student performance when working through assignments. An example of an iClicker question is displayed below along with the students' responses in **Figure 56**. The correct answer is indicated in bold script. When students answered this iClicker question in an independent setting, only 25% answered the question correctly. However, after working in small groups, 63% of students obtained the correct result. In addition, after the iClicker polling system was closed, the question was explained by revisiting focused instruction both to ensure students understood the question and to address any misconceptions.

Place the following in order of increasing dipole moment.

A) II < III < I
B) I < II = III
C) II < I < III
D)I<II<III
E) I < III < II

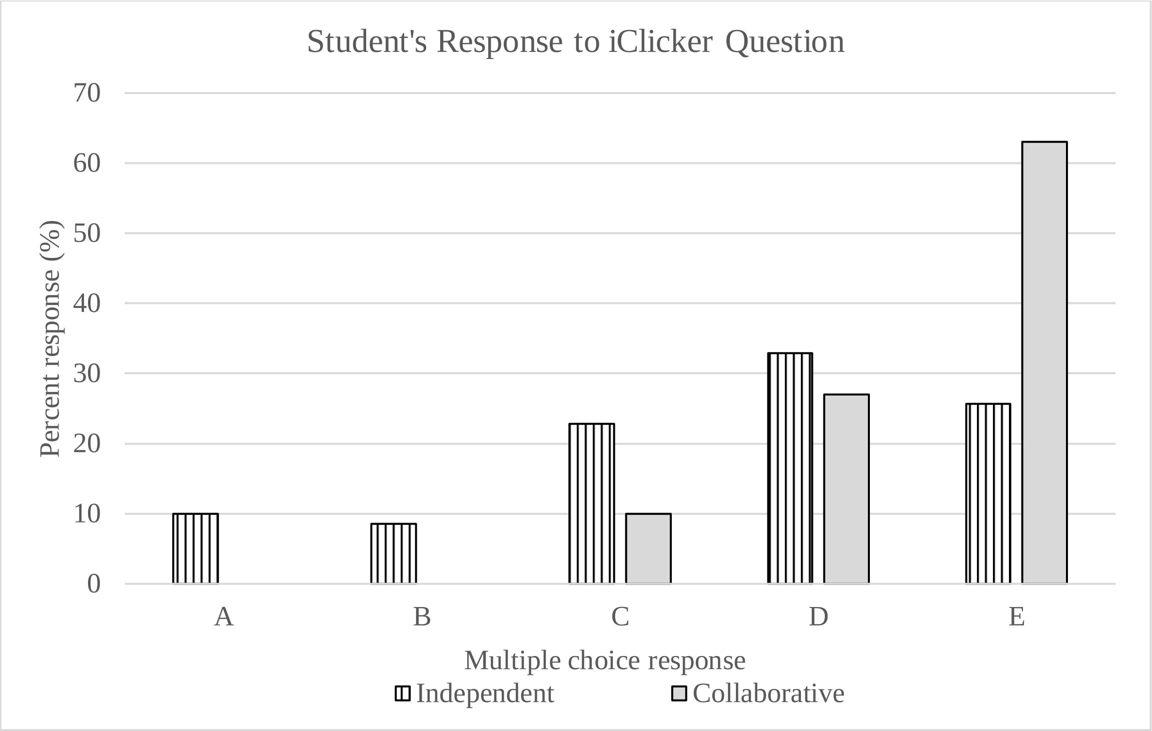

***Figure 56**: iClicker grade comparison before (lines) and after (grey) collaboration; E is the correct response*

APPENDIX A
SUPPLEMENTAL MATERIAL

Table 8: Average concentration of free chloride in solution for DI water and DI water with iron after 4 days

Sample	Average free chloride (ppm)	Std. Dev.
DI water	0.091	0.007
4-day iron	0.15	0.02

Table 9: 1-month degradation [1,2,3-TCP] in the presence of 0.5g Fe

Time point (hours)	Average [1,2,3-TCP] ppm	Normalized concentration	Normalized std.dev.
0	12.21	1.0000	0.0001
24	13.02	1.07	0.01
48	11.67	0.96	0.08
72	11.48	0.94	0.03
96	11.99	0.98	0.01
120	11.54	0.95	0.01
144	13.17	1.08	0.05
168	12.40	1.02	0.05
192	10.73	0.88	0.09

Table 10: 1-month degradation [1,2,3-TCP] in the presence of 0.5g Fe and 1mM B_{12}

Time point (hours)	Average [1,2,3-TCP] ppm	Normalized concentration	Normalized std.dev.
0	12.27	1.00	0.02

24	10.82	0.88	0.02
48	8.57	0.70	0.06
72	6.13	0.50	0.01
96	4.43	0.36	0.01
120	3.15	0.3	0.1
144	2.27	0.18	0.04
168	1.92	0.16	0.02
192	1.32	0.1	0.1

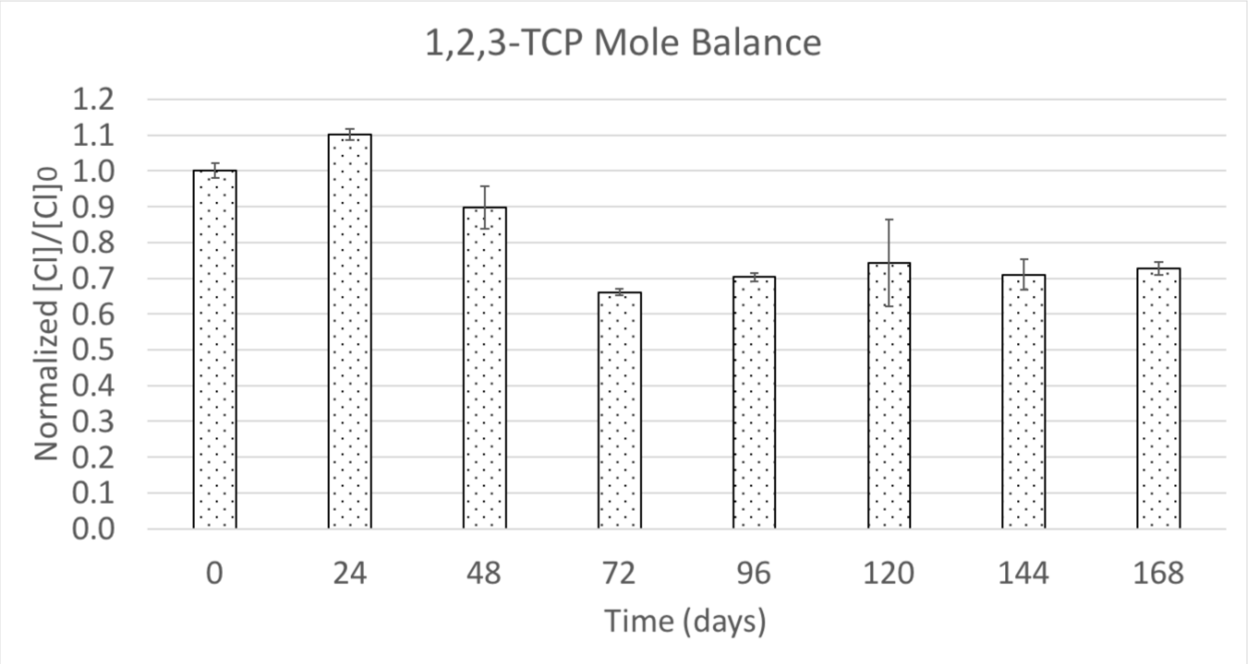

***Figure 57**: Mole balance of 1,2,3-TCP based on release of free chloride into solution for 0.5g μZVI and 1mM B_{12}*

Table 11: 1-month degradation [1,2-DCP] in the presence of 0.5g Fe

Time point (days)	Average [1,2-DCP] ppm	Normalized concentration	Normalized std.dev.
0	9.55	1.00	0.01

7	9.08	0.95	0.01
14	8.27	0.87	0.07
21	8.27	0.87	0.05

Table 12: 1-month degradation [1,2-DCP] in the presence of 0.5g Fe and 0.0625mM B_{12}

Time point (days)	Average [1,2-DCP] ppm	Normalized concentration	Normalized std.dev.
0	9.67	1.00	0.04
7	6.98	0.72	0.02
14	5.23	0.54	0.02
21	3.91	0.40	0.02

Table 13: 1-month degradation [1,2-DCP] in the presence of 0.5g Fe and 0.125mM B_{12}

Time point (days)	Average [1,2-DCP] ppm	Normalized concentration	Normalized std.dev.
0	9.18	1.000	0.007
7	7.12	0.77	0.01
14	5.61	0.61	0.05
21	3.25	0.35	0.03

Table 14: 1-month degradation [1,2-DCP] in the presence of 0.5g Fe and 1mM B_{12}

Time point (days)	Average [1,2-DCP] ppm	Normalized concentration	Normalized std.dev.
0	9.48	1.00	0.04
7	5.5	0.6	0.1

14	3.7	0.4	0.2
21	1.7	0.2	0.1

Table 15: 1-month degradation [1,2-DCP] in the presence of 2g Fe and 1mM B_{12}

Time point (days)	Average [1,2-DCP] ppm	Normalized concentration	Normalized std.dev.
0	11.25	1.00	0.06
7	5.40	0.48	0.03
14	0.90	0.08	0.04
21	0.09	0.01	0.01

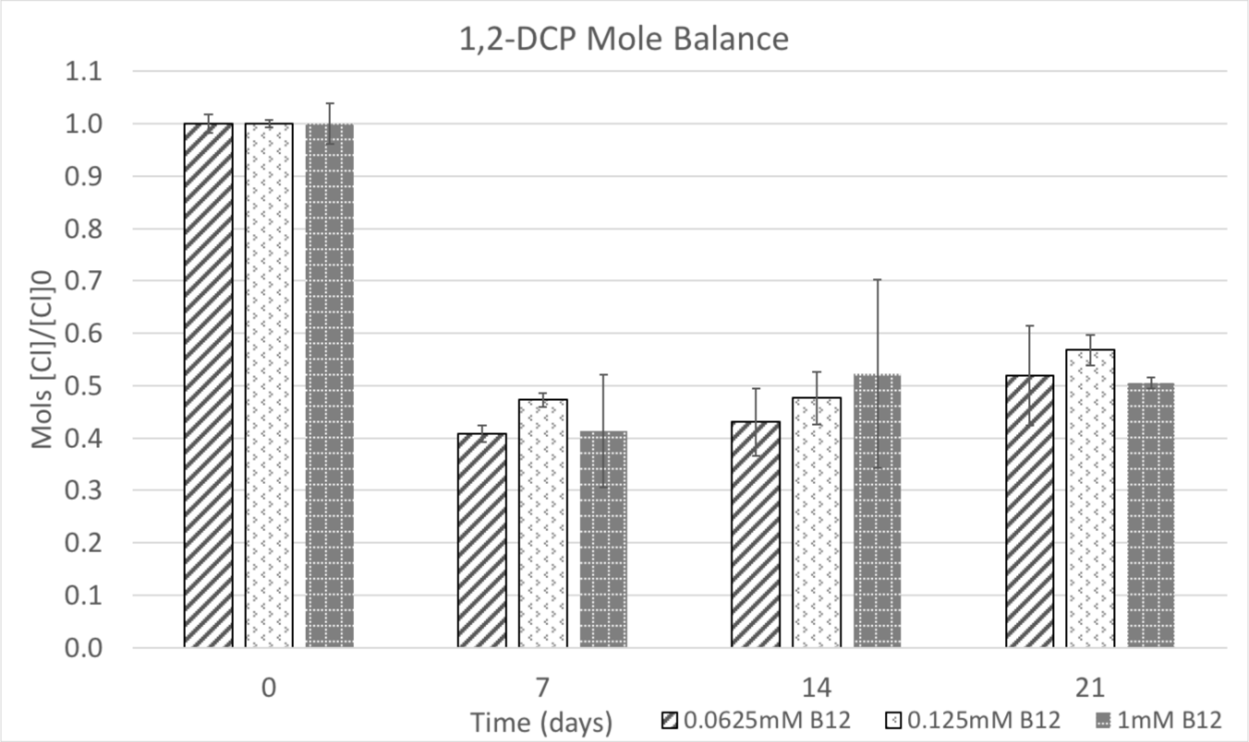

***Figure 58**: Mole balance of 1,2-DCP based on release of free chloride into solution*

Table 16: 1-month degradation [1,3-DCP] in the presence of 0.5g Fe

Time point (days)	Average [1,3-DCP] ppm	Normalized concentration	Normalized std.dev.
0	34.64	1.00	0.03
7	28.20	0.81	0.02
14	29.36	0.85	0.02
21	29.99	0.87	0.07
28	30.00	0.87	0.02

Table 17: 1-month degradation [1,3-DCP] in the presence of 0.5g Fe and 1mM B_{12}

Time point (days)	Average [1,3-DCP] ppm	Normalized concentration	Normalized std.dev.
0	24.79	1.00	0.02
7	17.77	0.72	0.02
14	13.41	0.54	0.09
21	8.43	0.34	0.03
28	2.10	0.08	0.06

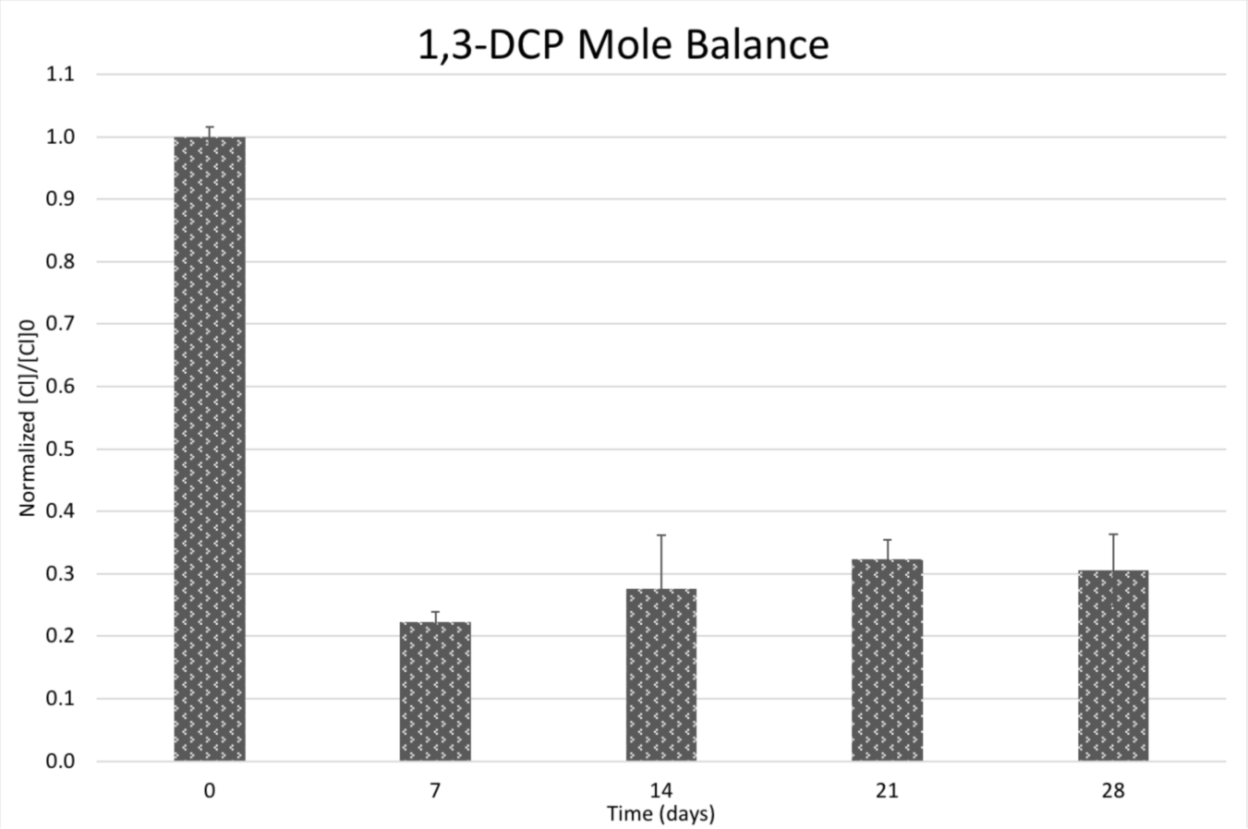

***Figure 59**: Mole balance of 1,3-DCP based on release of free chloride into solution for 0.5g µZVI and 1mM B_{12}*

Table 18: 1-month degradation [1-CP] in the presence of 0.5g Fe

Time point (days)	Average [1-CP] ppm	Normalized concentration	Normalized std.dev.
0	26.49	1.00	0.06
7	29.43	1.11	0.06
14	25.18	0.95	0.06
21	23.60	0.89	0.06
28	25.06	0.95	0.05
32	24.76	0.94	0.04

Table 19: 1-month degradation [1-CP] in the presence of 0.5g Fe and 1mM B_{12}

Time point (days)	Average [1-CP] ppm	Normalized concentration	Normalized std.dev.
0	20.89	1.00	0.08
7	21.91	1.05	0.07
14	16.13	0.77	0.05
21	16.30	0.78	0.06
28	12.79	0.61	0.04
32	10.6	0.5	0.1

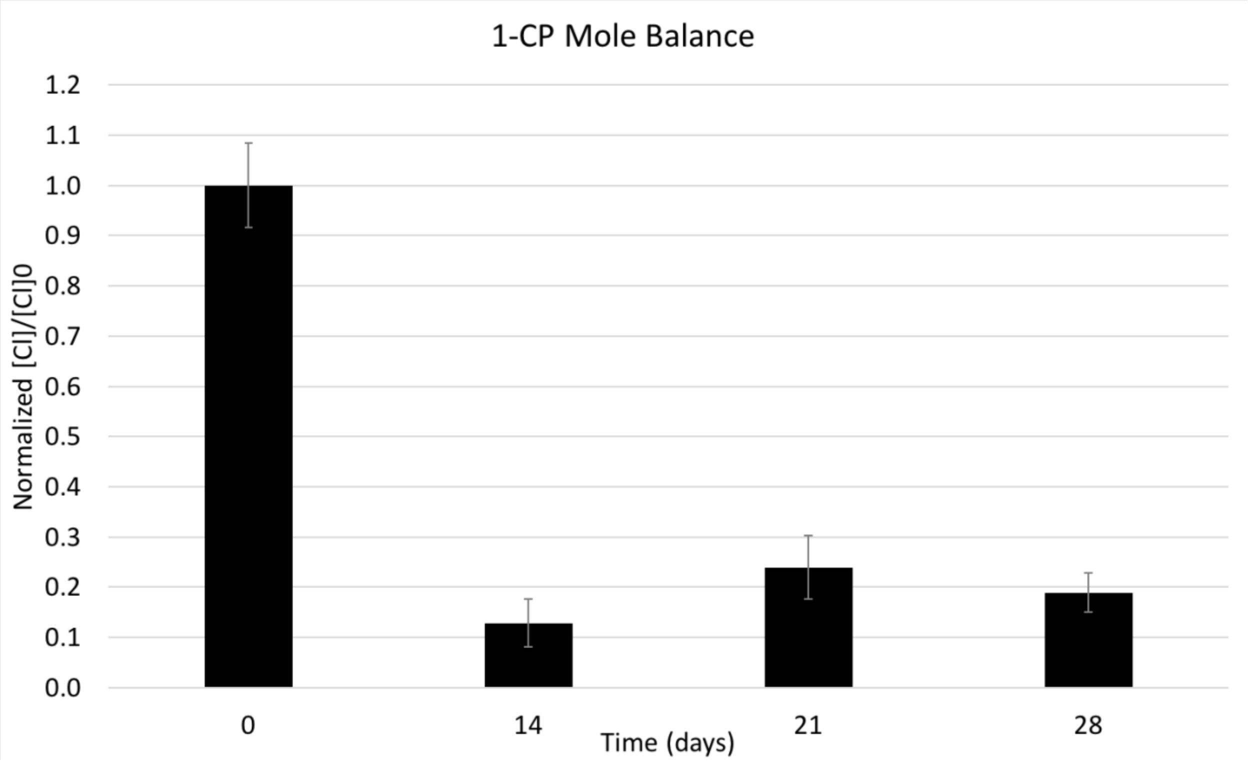

Figure 60: Mole balance of 1-CP based on release of free chloride into solution for 0.5g µZVI and 1mM B_{12}

Table 20: 1-month degradation [1,2-DCA] in the presence of 0.5g Fe

Time point (days)	Average [1,2-DCA] ppm	Normalized concentration	Normalized std.dev.
0	13.66	1.00	0.03
7	12.6	1.2	0.1
14	12.32	1.13	0.02
21	11.48	1.06	0.03
28	12.2	1.1	0.1
35	11.93	1.10	0.06

Table 21: 1-month degradation [1,2-DCA] in the presence of 0.5g Fe and 1mM B_{12}

Time point (days)	Average [1,2-DCA] ppm	Normalized concentration	Normalized std.dev.
0	13.5186	1.0000	0.0001
7	9.09	0.85	0.06
14	4.73	0.44	0.05
21	3.0	0.3	0.2
28	1.225	0.114	0.005
35	0.704	0.066	0.050

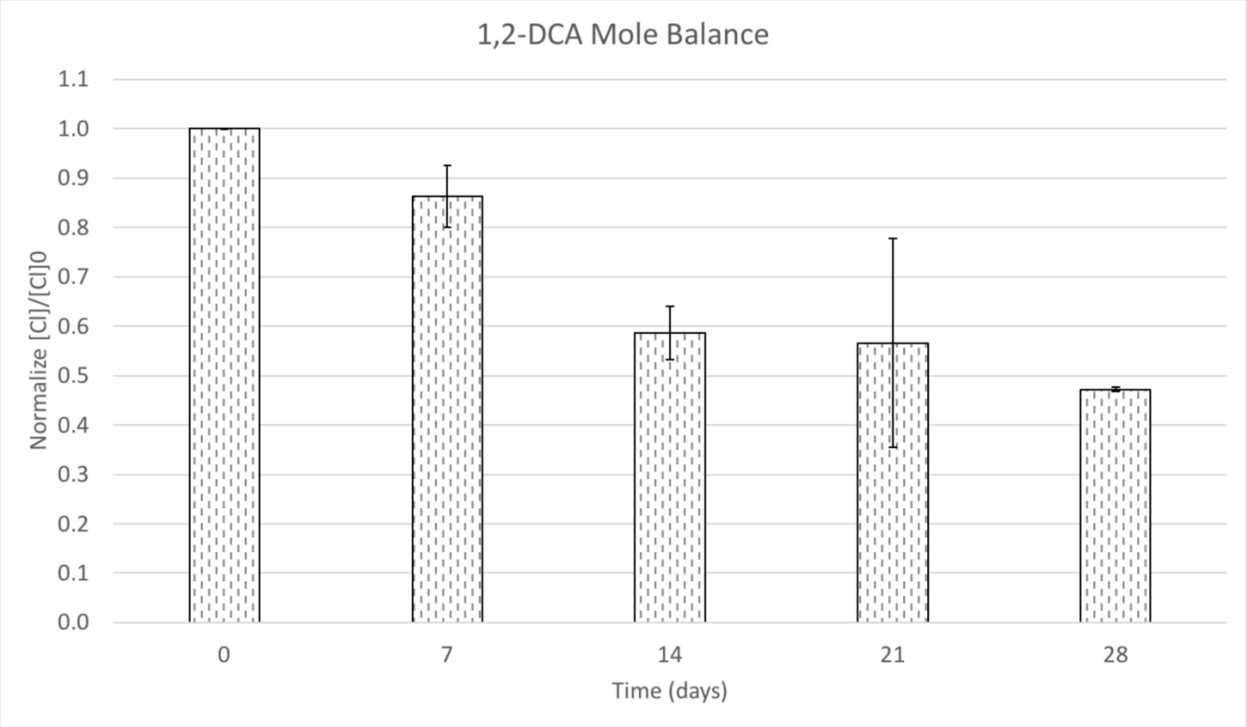

Figure 61*: Mole balance of 1-CP based on release of free chloride into solution for 0.5g μZVI and 1mM B_{12}*

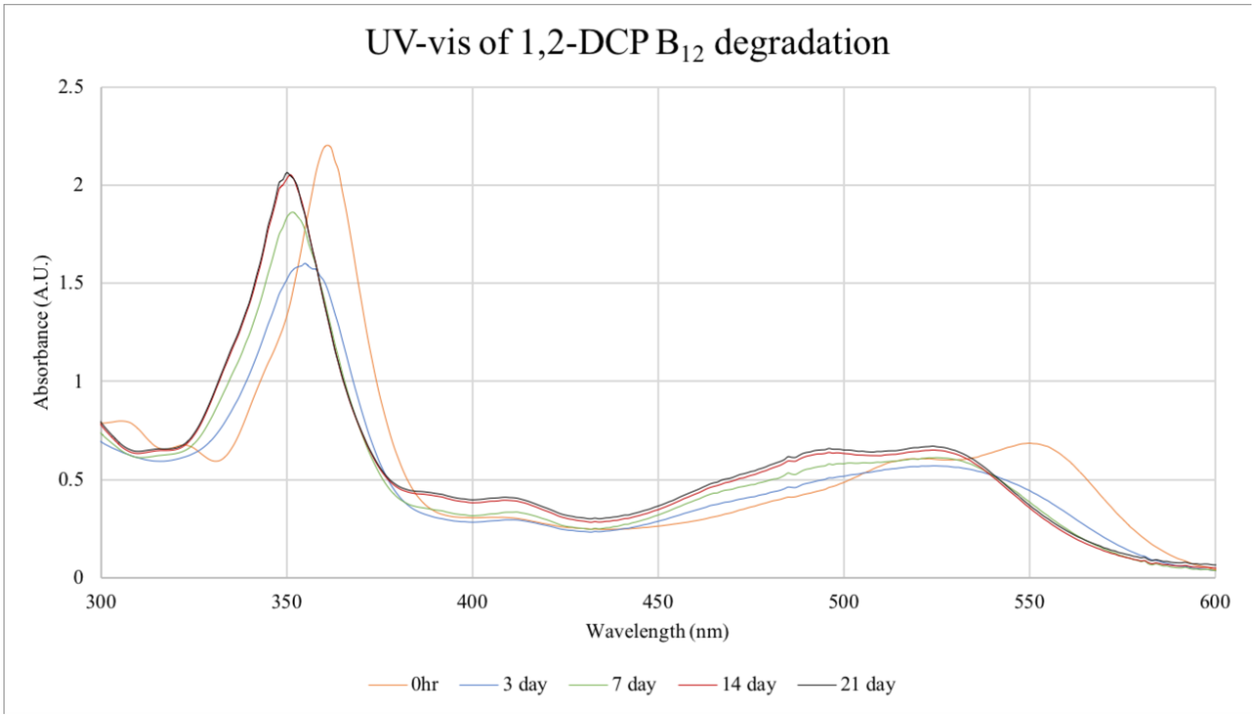

Figure 62: *UV-vis spectrum of 1,2-DCP degradation over 21-days*

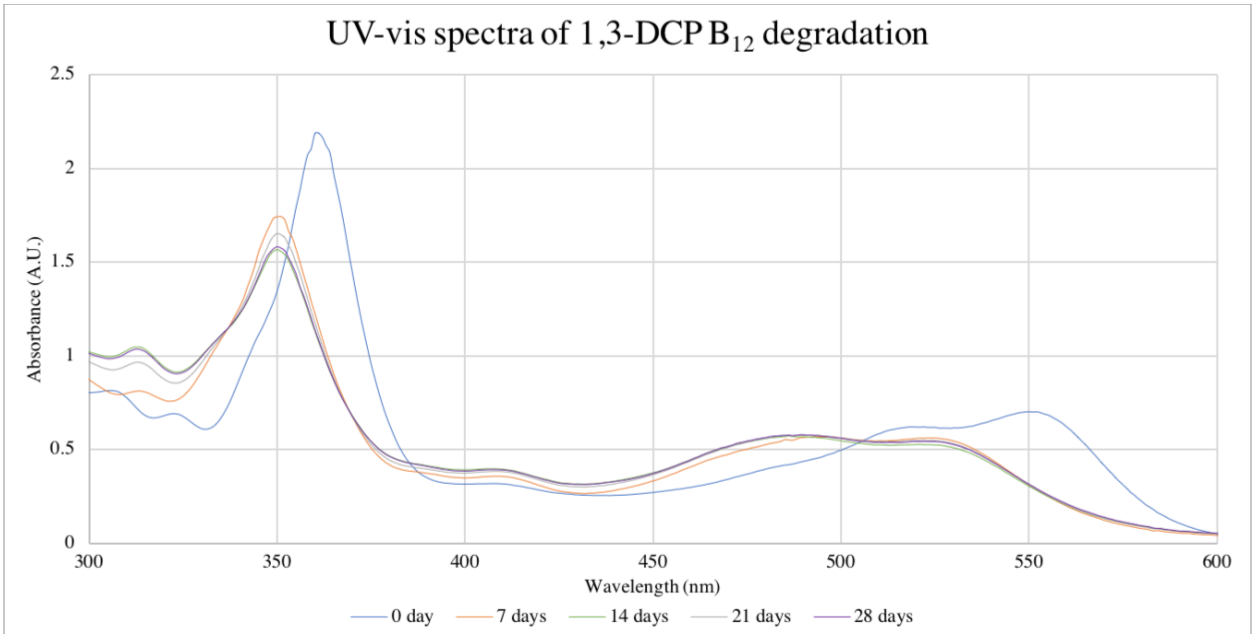

Figure 63: *UV-vis spectrum of 1,3-DCP degradation over 28-days*

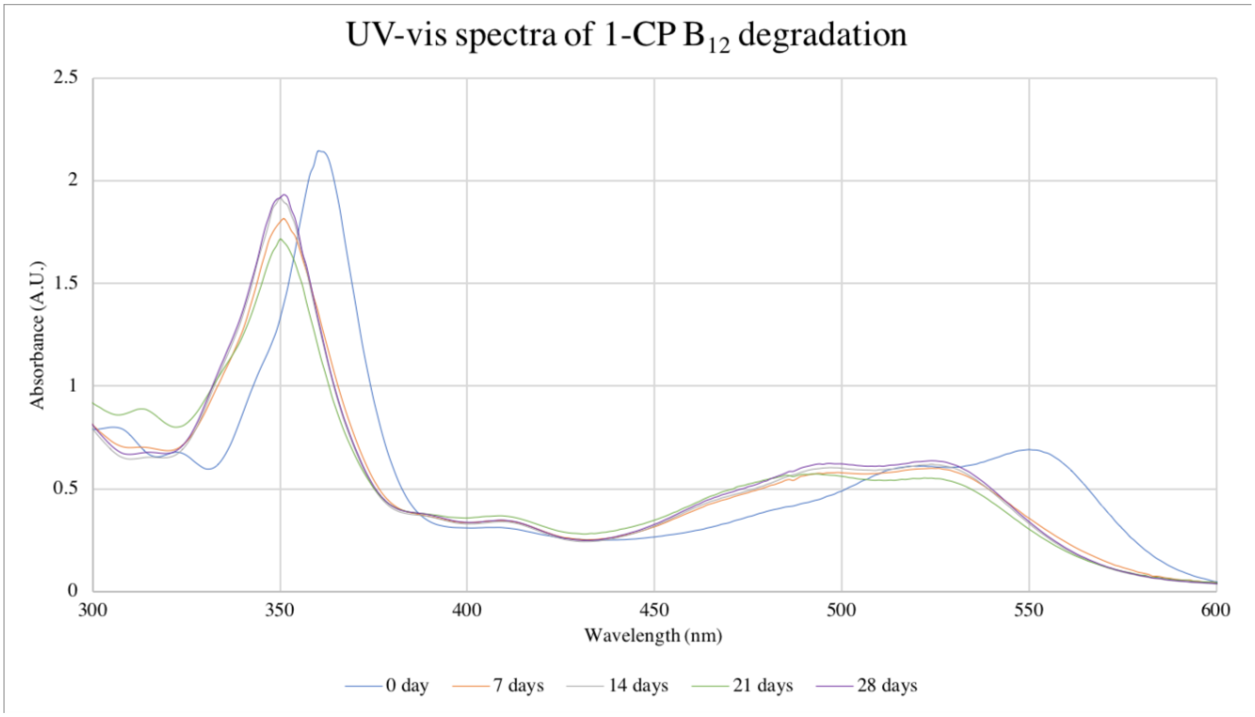

***Figure 64**: UV-vis spectrum of 1-CP degradation over 28-days*

Chapter 7

Table 22 shows a comparison between the average exam difficulty between the GRR course and a Traditional taught course in Spring 2018. The GRR course model was compared to an established professor's assessments. The average exam difficulty was rated on a scale of one to five. These ratings were provided by the publisher for each question.

Table 22: Comparison of test difficulty between GRR vs. Traditional

	GRR		**Traditional**	
EXAM	Average Difficulty	Number of Questions	Average Difficulty	Number of Questions
1	1.92	25	1.90	20
2	1.96	30	2.20	20

3	2.16	25	2.00	20
4	2.16	25	2.70	20
5	1.88	25	--	--
Average	2.02		2.25	

APPENDIX B
IRB APPROVAL LETTER

University of Central Florida Institutional Review Board
Office of Research & Commercialization
12201 Research Parkway, Suite 501
Orlando, Florida 32826-3246
Telephone: 407-823-2901 or 407-882-2276
www.research.ucf.edu/compliance/irb.html

Approval of Exempt Human Research

From: **UCF Institutional Review Board #1**
FWA00000351, IRB00001138

To: **Nicole Lapeyrouse**

Date: **September 25, 2017**

Dear Researcher:

On 09/25/2017, the IRB approved the following activity as human participant research that is exempt from regulation:

Type of Review: Exempt Determination, Category 1and 2
Project Title: Utilization of a Modified Gradual Release of Responsibility Model in a Large Enrollment Chemistry Course
Investigator: Nicole Lapeyrouse
IRB Number: SBE-17-13374
Funding Agency:
Grant Title:
Research ID: N/A

This determination applies only to the activities described in the IRB submission and does not apply should any changes be made. If changes are made and there are questions about whether these changes affect the exempt status of the human research, please contact the IRB. When you have completed your research, please submit a Study Closure request in iRIS so that IRB records will be accurate.

In the conduct of this research, you are responsible to follow the requirements of the Investigator Manual.

On behalf of Sophia Dziegielewski, Ph.D., L.C.S.W., UCF IRB Chair, this letter is signed by:

Renea Carver

Signature applied by Renea C Carver on 09/25/2017 12:48:36 PM EDT

IRB Coordinator

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