Degradation of Chlorinated Butenes and Butadienes by Granular Iron

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Sites where 2-chlorobutadiene-1,3 (chloroprene) and 2,3-dichlorobutadiene-1,3 (DCBD) are synthesized for use in chlorobutyl rubber have the potential to release a mixture of at least five chlorinated butenes and butadienes including trans-1,4-dichlorobutene-2 (1,4-DCB-2), 3,4-dichlorobutene-1 (3,4-DCB-1), 2,3,4-trichlorobutene-1 (2,3,4-TCB-1), chloroprene and DCBD into the groundwater environment. Granular iron has been shown to be effective in the remediation of groundwater contaminated with chlorinated organic compounds by reductive dechlorination. To evaluate the possibility of using granular iron in the remediation of the above contaminants a series of batch and column experiments were conducted at the laboratory scale. Chlorine mass balance calculations showed that each compound, with the exception of DCBD, could be fully dechlorinated by the use of granular iron. Kinetic data and proposed reaction pathways, however, suggest that DCBD can also be fully dechlorinated by granular iron. Normalization of observed pseudo-first-order reaction half-lives indicated that compounds were degrading much slower in batch experiments than in column experiments. This, along with the observation that temperature did not affect degradation in batch experiments, led to the conclusion that mass transport to the iron surfaces was limiting degradation rates in batch experiments. Results showed that the three chlorinated butenes degraded much faster (normalized column half-lives ranged from 1.6 to 5.2 min) than the two chlorinated butadienes (normalized column half-lives ranged from 115 to 197 min). Chlorinated and non-chlorinated intermediates were identified. It was determined that all contaminants degrade to 1,3-butadiene as a reaction intermediate which then degraded to a mixture of non-harmful end products consisting of 1-butene, *cis*-2-butene, *trans*-2-butene and n-butane. The reaction pathway from 1,4-DCB-2 to 1,3-butadiene was proposed to be a reductive elimination similar to reductive β-elimination. 3,4-DCB-1 and 2,3,4-TCB-1 were proposed to undergo reductive β-elimination reactions resulting in 1,3-butadiene and chloroprene intermediates, respectively. Degradation of chloroprene and DCBD occurred via hydrogenolysis pathways while 1,3-butadiene underwent catalytic hydrogenation resulting in the observed end products. The results suggest that granular iron may be an effective treatment for groundwater contaminated with these compounds.

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Dedication

I dedicate this thesis to my parents, Tim and Karen Hughes, for their support throughout my academic career and their understanding of my desire for knowledge and quality.

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1. Introduction

A mixture of five chlorinated aliphatics, 1,4-dichlorobutene-2 (1,4-DCB-2), 3,4-dichlorobutene-1 (3,4-DCB-1), 2,3,4-trichlorobutene-1 (2,3,4-TCB-1), 2-chlorobutadiene (chloroprene) and 2,3-dichlorobutadiene (DCBD) arising from the synthesis of the chloroprene and DCBD monomers are used in the manufacture of polychloroprene polymer (PCP), latex and neoprene rubber. These compounds frequently occur in waste streams and have the potential to be released to the subsurface. The use of granular iron has been shown to be an effective treatment in the remediation of other chlorinated aliphatics by reductively dechlorinating contaminants as they come in contact with iron surfaces (Gillham and O'Hannesin, 1994, Johnson *et al.*, 1996, Arnold and Roberts, 2000). It is therefore postulated that groundwater contaminated with chlorinated butenes and butadienes can also be effectively treated using granular iron. The potential use of granular iron for remediation must first be investigated at the laboratory scale by such means as batch and column experiments. For granular iron to be an effective treatment it must fully dechlorinate each compound and the products of degradation must not be harmful to human or environmental health. The kinetics of degradation must also be determined to aid in the design and implementation of potential remediation strategies. Furthermore, the identification of degradation intermediates and reaction pathways can help to fully understand the behaviour of the interaction of chlorinated compounds with granular iron.

1.1 Chlorinated aliphatics from the synthesis of chloroprene

1.1.1 Chloroprene production

2-chlorobutadiene-1,3, also known as chloroprene, is the monomer used in the production of polychloroprene polymer (PCP). The polymer is commonly marketed as latex, or it can be isolated and dried to produce a solid product. If a copolymer such as 2,3-dichlorobutadiene-1,3 (DCBD) is used, chloroprene rubber (neoprene) can be produced. The production of chloroprene and DCBD can be responsible for the release of several environmental contaminants including 1,4-dichlorobutene-2 (1,4-DCB-2), 3,4-dichlorobutene-1 (3,4-DCB-1), 2,3,4-trichlorobutene-1 (2,3,4-TCB-1), as well as chloroprene and DCBD themselves. Recent figures on the global production of chloroprene are unavailable; however, in 1989 the annual production was estimated at 373 000 tonnes (OECD SIDS, 1998).

There are two reaction processes used in the commercial production of chloroprene; one uses 1,3-butadiene as the starting material and the other uses acetylene. Table 1-1 shows which production processes are used in different locations worldwide. Lynch (2001) and Tassara et al. (1997) summarize the most common method of chloroprene production, which converts 1,3-butadiene to chloroprene through the two-step process shown in Figure 1-1a. In this process 1,3-butadiene is reacted with chlorine (Cl_2) to produce a mixture of 3,4-DCB-1 and 1,4-DCB-2. The isomers are separated and the 1,4-DCB-2 is converted to 3,4-DCB-1 using dicopper chloride (Cu_2Cl_2). This material is then reacted with aqueous sodium hydroxide (NaOH) which dehydrohalogenates the 3,4-DCB-2 to chloroprene. The second, less common method of producing the chloroprene monomer is shown in Figure 1-1b. This method involves the dimerization of

acetylene using dicopper chloride followed by the chlorination of monovinylacetylene with dicopper chloride and hydrochloric acid (HCl). The copolymer DCBD is produced by the hydrochlorination of chloroprene to produce 2,3,4-TCB-1 then reacting the 2,3,4-TCB-1 with an excess of liquid ammonia in the presence of a polymerization inhibitor such as diethylhydroxylamine (Karapetian *et al.,* 1977). The synthesis of DCBD is shown in Figure 1-1c.

The reaction processes outlined above take place in "closed" systems which are designed to avoid exposure to humans and the environment. However, some leaks and accidental spills inevitably occur (Lynch, 2001) and thus the chemicals 1,4-DCB-2, 3,4-DCB-1, 2,3,4-TCB-1, chloroprene and DCBD have the potential to be released into the environment. Also, water is used in the production of these chemicals and thus the release of process and rinse water further contributes to environmental exposure.

1.1.2 Environmental behaviour and toxicology

Due to the large volume of these compounds produced each year (OECD SIDS, 1998) and the history of groundwater problems created by the release of chlorinated organic contaminants (Makay and Cherry, 1989) it is important to know how these five compounds will act in the event of their release to the subsurface. It is also useful to know to what degree these compounds can be toxic to humans as well as their ecological effects. Table 1-2 shows some physical and chemical properties for 1,4-DCB-2, 3,4-DCB-1, 2,3,4-TCB-1, chloroprene and DCBD. All compounds except chloroprene can be classified as dense non-aqueous phase liquids (DNAPLs) in that the compounds have a higher density than water in their pure phase, and have relatively low water solubilities. Other chemicals such as tetrachloroethene (PCE) and trichloroethene (TCE), also

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classified as DNAPLs, have been found to, once introduced into the environment, enter the subsurface and penetrate deep below the water table (Makay and Cherry, 1989). The solubilities of PCE and TCE are 237 mg/L and 1385 mg/L respectively (Pankow and Cherry, 1996). These numbers are in the same range as the contaminants in this study (Table 1-2). It is therefore likely that the release of these contaminants into the subsurface would result in similar dissolution behaviour as PCE and TCE which, once below the water table, slowly dissolve into the aqueous phase at the water-DNAPL interface and consequently contaminate groundwater that passes the DNAPL source. This can result in the generation of large-scale long-term plumes that are difficult to remediate by conventional methods such as pump-and-treat remediation (Makay and Cherry, 1989).

Chloroprene has a density that is very close but slightly lower than that of water (Table 1-2) and thus is classified as a light non-aqueous phase liquid (LNAPL). Petroleum products are the most common examples of this class of contaminants which tend to accumulate on the top of the water table and can dissolve at the water-LNAPL interface. LNAPLs tend to be less problematic in terms of remediation than DNAPLs (Makay and Cherry, 1989) however in the case of chloroprene it may be accompanied by other contaminants such as the DNAPL compounds mentioned above and the mixture of these compounds would therefore likely exist as a DNAPL.

There are no maximum contamination limits (MCLs) for the five chlorinated aliphatics of Table 1-2, however they are toxic and in most cases carcinogenic (see below). Thus their release into the environment could have detrimental effects on human and ecological health and their presence in the subsurface may justify remediation efforts. Below is a summary of the environmental behaviour and toxicity of each compound.

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Trans-1,4-dichlorobutene-2 (1,4-DCB-2)

The aqueous solubility of 1,4-DCB-2 is the highest (7190 mg/L, Blaha *et al.,* 1998) of the five compounds of interest. The contaminant is expected to partition from the aqueous phase to the gas phase based on a calculated Henry's Law constant of 18.8 atm L/mol at 25°C (Table 1-2). This compound is not expected to sorb strongly to organic matter as indicated by its K_{OC} of 4.8 cm^3/g (NDEQ, 2006). Milano *et al.* (1988) found a hydrolysis half-life for 1,4-DCB-2 of 2 days at 25°C, suggesting that this compound may be degraded naturally in a groundwater environment. Unpublished studies conducted by Gui and Noble (pers. comm., 2006) found a similar degradation half-life of 2.5 days at 25°C, however it was found that at 10°C, the hydrolysis half-life increased significantly to 48 days. Thus hydrolysis alone may not be effective in degrading this contaminant in places where groundwater temperatures are low. No literature was found to suggest that 1,4-DCB-2 undergoes biodegradation in the natural environment.

In addition to 1,4-DCB-2 being the most soluble of the five compounds of interest it is perhaps also the most toxic. Clary (1977) states a 50% lethal dose (LD_{50}) of 89 mg/kg by oral ingestion in rats and also describes 1,4-DCB-2 as a very severe eye and skin irritant which can cause burns and irreversible eye damage. Blaha *et al.* (1998) found a 50% effective concentration (EC_{50}) for a five minute exposure of 8.81 mg/L in aqueous solution via the Microtox test in which the inhibition of bioluminescence of a marine bacterium (*Photobacterium phosphoreum*) is measured. Bartsch *et al.*(1979) found that 1,4-DCB-2 was mutagenic by a plate incorporation assay. This contaminant is also considered carcinogenic. Two studies by Mullin *et al.* (2000, 2002) found 1,4-TCB-2 to be carcinogenic to the upper respiratory system (nasal tumours) in rats by inhalation,

while Purdy (1996) predictes 1,4-DCB-2 to be carcinogenic based on its electronic structure.

3,4-dichlorobutene-1 (3,4-DCB-1)

The solubility of 3,4-DCB-1 is approximately 1600 mg/L at 20°C (OECD SIDS, 2004). Aqueous phase 3,4-DCB-1 is expected to partition from water to air, with a Henry's Law constant of 15.9 atm L/mol, and from the aqueous phase to the organic phase with a log Kow of 2.37 at 25°C (OECD SIDS, 2004). Sorption to organic material is considered to be significant with a Koc of 160 cm^3/g (NDEQ, 2006). This compound is not readily biodegradable however abiotic degradation may occur by hydrolysis with a half-life of 33.3 days at pH 7 and 25°C (OECD SIDS, 2004). Hydrolysis half-lives at lower temperatures have not been studied.

The toxicity of 3,4-DCB-1 is considered to be significantly lower than 1,4-DCB-2 (Gizhlaryan *et al.,* 1981). Toxicological tests using rats found an oral LD_{50} of 940 mg/kg (OECD SIDS, 2004). Bartsch *et al.* (1979) tested 11 unsaturated chlorinated aliphatics for mutagenicity by plate incorporation assay and found 3,4-DCB-1 to be the most mutagenic of all compounds tested. Although its carcinogenicity has not been reported, the OECD SIDS (2004) report states that 3,4-DCB-1 "could be considered a potential carcinogen".

2,3,4-trichlorobutene-1 (2,3,4-TCB-1)

This compound has a moderate solubility of 600 mg/L at 20°C and a relatively low vapour pressure of 0.23 kPa at 20°C. Based on the calculated Henry's Law constant of 11.5 atm L/mol at 25°C (Table 1-2), 2,3,4-TCB-1 would have a tendency to partition from water to air. This compound is also said to have a low tendency to partition from

water to soil (OECD SIDS, 1993). A calculated log Kow of 2.4 (OECD SIDS, 1993) suggests that the compound will partition from the aqueous phase to the organic phase. No literature was found to suggest that this compound will undergo hydrolysis. The OECD SIDS (1993) report states that it is not biodegradable and that it has a photo-oxidative half life of 1.4 days.

Acute toxicological tests using rats found 2,3,4-TCB-1 to have a high acute inhalation toxicity and an oral toxicity with a LD_{50} of 351 mg/kg (OECD SIDS, 1993). 2,3,4-TCB-1 has been found to be carcinogenic to the upper respiratory tract in rats (Feron *et al.,* 1990) and has been predicted to be carcinogenic based on its electronic structure (Purdy, 1996).

2-chlorobutadiene-1,3 (chloroprene)

Chloroprene has a moderate solubility of 256-480 mg/L at 20°C and a relatively high vapour pressure of 25 kPa at 20°C (OECD SIDS, 1998). The Henry's Law constant of 78.7 atm L/mol at 20°C suggests that it will partition from water to air while its Log Kow of 2.2 and Koc of 68 cm^3/g suggest that it will partition from the aqueous phase to the organic phase (OECD SIDS, 1998). No literature was found to suggest that this compound will undergo degradation by hydrolysis in the natural environment. The OECD SIDS (1998) report states that biodegradation was responsible for a 10% disappearance after 28 days (following the OECD 301D protocol). Fishbein (1979) describes pure phase chloroprene as extremely reactive and can polymerize spontaneously at room temperature. Polymerization is catalyzed by light, peroxides and other free radical initiators.

Acute toxicity tests conducted on rats showed an oral LD_{50} ranging from 251 to 450 mg/kg (OECD SIDS, 1998). Bartsh *et al.* (1979) found chloroprene to be mutagenic by plate incorporation assay. Chloroprene is considered carcinogenic by inhalation in rats and mice (OECD SIDS, 1998) and Purdy (1996) predicts chloroprene to be carcinogenic based on its electronic structure.

2,3-dichlorobutadiene-1,3 (DCBD)

Little literature was found regarding the environmental fate and behaviour of DCBD. DCBD is said to be insoluble in water (EC ECB, 2000), however in this study an aqueous concentration of 5.5 mg/L was observed during laboratory experiments. Actual solubility is expected to be greater than that observed during the laboratory experiments as there was no attempt to achieve maximum solubility. A calculated Henry's Law constant of 40.3 atm L/mol at 25°C (Table 1-2) suggests that DCBD will partition from water to air. DCBD is said to have a photodegradation half-life of 5.9 days and aerobic biodegradation is slow with a disappearance of only 1% in a 28 day study (EC ECB, 2000). There was no literature found to suggest that DCBD will degrade by hydrolysis.

Acute oral toxicity tests conducted on rats have shown a LC_{50} as low as 222 mg/kg (EC ECB, 2000). No literature was found regarding the mutagenic or carcinogenic potential of DCBD.

1.2 Granular Iron

1.2.1 Compounds shown to degrade by granular iron

Granular iron has been shown to provide effective treatment for groundwater contaminated with common halogenated organic contaminants by both laboratory (Gillham and O'Hannesin, 1994) and field studies (O'Hannesin and Gillham, 1998).

Gillham and O'Hannesin (1994) showed iron to be effective in the degradation of fourteen halogenated methanes, ethanes and ethenes. Since then, other authors have confirmed the effectiveness of iron in degrading compounds that were studied in the original Gillham and O'Hannesin (1994) study including, among others, carbon tetrachloride (CT) (Johnson *et al.,* 1996, 1998), 1,1,1-trichloroethane (1,1,1-TCA) (Johnson *et al.,* 1996, Lookman *et al.*, 2004), tetrachloroethene (PCE) (Arnold and Roberts, 2000, Johnson *et al.,* 1996), trichloroethene (Arnold and Roberts, 2000, Chen *et al.,* 2001, Johnson *et al.,* 1996, Kohn and Roberts, 2006), *cis-* and *trans*-dichloroethene (*cis-* and *trans*-DCE) (Arnold and Roberts, 2000, Johnson *et al.,* 1996, Kohn and Roberts, 2006) and vinyl chloride (VC) (Johnson *et al.,* 1996). Other reducible compounds have also been shown to be removed from solution by iron including uranium (Fiedor *et al.,* 1998), chromium (Powell *et al.,* 1995), dichloro-diphenyl-trichloroethane (DDT) (Sayles *et al.,* 1998), nitrobenzene and trinitrotoluene (TNT) (Agrawal and Tratnyek, 1996), atrazine (Singh *et al.,* 1998), 4-aminoazobenzene (Weber, 1996), nitrate (Ritter, 2000) and N-nitrosodimethylamine (NDMA) (Gui *et al.,* 2000).

1.2.2 Granular iron permeable reactive barriers and long term performance

Granular iron is used to construct permeable reactive barriers (PRBs) in the subsurface (Figure 1-2). PRBs are designed to allow contaminated water originating from a source such as a DNAPL below the water table to flow passively through the reactive porous medium by having a higher hydraulic conductivity than the surrounding subsurface material. Granular iron PRBs typically consist of granular iron mixed with a non-reactive granular material such as sand. In the first field demonstration of the technology (O'Hannesin and Gillham, 1998) a mixture of 22% granular iron and 78% sand (by

weight) was used. The reactivity of the PRB can be controlled by the percentage of iron

used (a higher percentage provides a higher reactivity) or by the type of iron used. O

(2006) showed the difference in reactivity of 4 types of iron: Connelly, Gotthart-Maier,

Ispat and Peerless irons.

The long-term performance of granular iron PRBs is an active area of research.

Jeen *et al.* (2006) showed that long-term PRB performance can be affected by mineral

precipitation at the iron surface. In the study, precipitation on the iron surfaces was found

to significantly inhibit degradation rates of TCE in columns receiving high concentrations

of calcium carbonate (100 to 500 mg/L) as well as columns receiving deionized water. In

a later study (Jeen *et al.,* 2007) the major precipitates at the surface were found to be iron

hydroxy carbonate (green rust) and aragonite for columns receiving high calcium

carbonate solution and magnetite-maghemite for columns receiving deionized water.

Ritter *et al.* (2002) also found that iron corrosion leads to the formation of magnetite and

green rust at the iron surfaces. The porosity of the reactive porous media may be reduced

by precipitate formation (Kluasen *et al.,* 2003, Yabusaki *et al.,* 2001) but Jeen *et al.*

(2007) state that this is not likely to occur to the extent that a substantial loss in hydraulic

conductivity is observed.

1.2.3 Reaction processes with granular iron

Reductive dechlorination by iron occurs as a redox reaction at the iron surface where iron

acts as an electron donor. In this reaction zero-valent iron (Fe^0) is oxidized (corroded) to

Fe^{2+} while two electrons are donated. In the presence of clean water, the electron acceptor

is water itself and hydrogen from the water molecule is reduced to form hydrogen gas

(Figure 1-3a) (Gillham and O'Hannesin, 1994). In the presence of a chlorinated organic

compound, the contaminant can be reductively dechlorinated. Arnold and Roberts (2000) and Weber (1996) suggest that this is a surface mediated process.

The pathway by which dechlorination occurs depends on the molecular structure of the compound. Some reductive pathways of dechlorination are: hydrogenolysis (Matheson and Tratnyek, 1994, Roberts *et al.,* 1996, Arnold and Roberts, 2000) in which one chlorine atom is removed and replaced by a hydrogen atom (see Figure 1-3b), reductive β-elimination (Roberts *et al.,* 1996, Arnold and Roberts, 2000), also referred to as reductive dihalo-elimination (Vogel *et al.*, 1987), in which two chlorine atoms on adjacent carbons (α, β pair) are removed resulting in the creation of a double bond or a triple bond where a double bond previously existed (i.e. a unit increase in bond order, Figure 1-3c), and reductive α-elimination (Roberts *et al.,* 1996, Arnold and Roberts, 2000) in which two chlorine atoms are removed from the same carbon resulting in the creation of a metal-stabilized carbenoid intermediate which can further react to effectively replace both chlorine atoms with hydrogen atoms (Figure 1-3d). Once the molecule has been completely dechlorinated, any existing unsaturated bonds can be further reduced until the molecule becomes saturated. This happens through a process known as catalytic hydrogenation (Matheson and Tratnyek, 1994, Arnold and Roberts, 2000) in which iron acts as a catalyst in the addition of hydrogen gas to a double or triple bond (Figure 1-3e).

The corrosion of iron is accompanied by an increase in pH (generation of hydroxide ions, Figure 1-3a) and a decrease in Eh (Gillham and O'Hannesin, 1994). The increase in pH is important since it has been shown that dechlorination rates decrease as pH increases (Chen *et al.,* 2001).

1.3 Hypothesis and Objectives

The hypothesis of this thesis is that granular iron can be used to effectively remediate groundwater contaminated with the five chlorinated organic compounds arising from the synthesis of chloroprene and DCBD. These compounds are 1,4-dichlorobutene-2 (1,4-DCB-2), 3,4-dichlorobutene-1 (3,4-DCB-1), 2,3,4-trichlorobutene-1 (2,3,4-TCB-1), 2-chlorobutadiene-1,3 (chloroprene) and 2,3-dichlorobutadiene-1,3 (DCBD).

The particular objectives are: 1) to determine if each of the contaminants can be fully dechlorinated using granular iron, 2) to determine if each contaminant can be degraded into compounds that are relatively non-harmful to the environment or human health, 3) to propose major reaction pathways and hence identify all reaction intermediates in the degradation of each compound and 4) to estimate the pseudo-first-order degradation half-lives of all contaminants and intermediates. This will be accomplished by performing a series of batch and column experiments on each contaminant. The next section explains the methods used for these experiments.

2. Materials and Methods

2.1 Chemicals and Materials

Granular iron was obtained from Connelly-GMP Inc. The iron batch identification number was UW 297, Connelly CC-1004, 18-Apr-2006, Pail #1. The granular iron was used as received and all batch and column experiments used iron from the same batch. Surface area analysis was performed previously using the N_2 BET method with a Micromeritics Gemini III 2372 surface area analyzer. Two samples were analyzed giving specific surface areas of 1.37 m^2/g and 1.29 m^2/g (average 1.33 m^2/g). Figure 2-1 shows the grain size distributions for Connelly iron measured previously. For some column experiments, Ottawa silica sand was mixed with the iron material. The grain-size distribution for the sand is included in Figure 2-1 and was determined using U.S. standard sieves and hand shaking for five min. Before use, the sand was acid washed twice with 5% Nitric acid then rinsed with MilliQ water until the rinse water reached a pH of 6.5.

The chemical reagents used in all experiments are listed in Table 2-1. Stock solutions were prepared in methanol for the five chlorinated organic contaminants and concentrations are included in Table 2-1. It is important to note that DCBD was received as a 1:1 (wt/wt) mixture with tetrachloroethene (PCE) and thus all batch and column experiments with DCBD also contained PCE.

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2.2 Experimental Procedures

2.2.1 Batch Experiments

Batch experiments were conducted as a preliminary investigation into the behaviour of each compound (in an aqueous solution) when interacting with granular iron. Each contaminant was investigated separately. Batch experiments for 1,4-DCB-2, 3,4-DCB-1 and 2,3,4-TCB-1 were performed in glass vials with an average volume of 37.24 ± 0.42 ml while batch experiments for chloroprene and DCBD were performed in glass vials with an average volume of 14.01 ± 0.30 ml. Figure 2-2 shows the experimental set up for the batch experiments. Each experiment consisted of 8 to 12 sets of 4 vials. Each set was sampled and analyzed at different times during the experiment. Each set of vials consisted of a contaminant control vial (contaminant solution only), a chloride control vial (iron with uncontaminated water), and duplicate reaction vials (iron with contaminant solution). Reaction and chloride control vials for experiments on 1,4-DCB-2, 3,4-DCB-1 and 2,3,4-TCB-1 contained 10.01 ± 0.01 g of iron while the same vials for the chloroprene and DCBD experiments contained 3.51 ± 0.02 g of iron.

Some contaminant solutions were prepared with deionized (DI) water while others were prepared with 40 mg/L calcium carbonate ($CaCO_3$) in DI water, referred to as simulated groundwater or GW. Before spiking the starting solutions with the contaminant, the pH was adjusted to between 6 and 7. pH adjustments were performed by sparging solutions with carbon dioxide gas to lower the pH or nitrogen gas to increase the pH. For the 1,4-DCB-2, 3,4-DCB-1 and 2,3,4-TCB-1 experiments the starting solutions were spiked with the stock solution of contaminant, stirred for 15 min then the contaminant control and reaction vials were filled leaving no headspace. The chloride

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controls were filled with similar but unspiked water. The vials were then capped with crimp-top lids and Teflon® lined septa. For the chloroprene and DCBD experiments, the vials were filled with uncontaminated water and capped in the same manner as above. The contaminant control and reaction vials were then spiked individually with stock solution of contaminant. The specific surface area-to-solution volume ratio was 0.357 ± 0.004 m^2/ml for the 1,4-DCB-2, 3,4-DCB-1 and 2,3,4-TCB-1 experiments and 0.340 ± 0.008 m^2/ml for the chloroprene and DCBD experiments. Experiments were also performed at two temperatures (10°C and 25°C) with the exception of 1,4-DCB-2. All batch experiments were mixed by gently inverting each vial three times by hand. Mixing occurred at least twice per day as well as prior to all sampling events. Constant rotary mixing was not used because many experiments were conducted in the refrigerator where that option was unavailable. Experiments conducted outside the refrigerator were mixed in the same fashion for consistency. Table 3-1 presented in the Results and Discussion section outlines which experiments were conducted in DI water versus 40 mg/L $CaCO_3$ (GW) as well as the temperature and starting concentration of each experiment.

All vials were sampled and analysed for initial contaminant concentration, free chloride ion, pH and Eh. During analysis for initial contaminant concentration, any unknown compounds and intermediates appearing in the batch experiments were monitored. Monitoring for initial contaminant concentration allowed for the development of degradation profiles (normalized concentration versus time) used to estimate pseudo-first-order degradation half-lives of each contaminant. Free chloride ion concentration allowed for the use of a chlorine mass balance to ensure all chlorine atoms were being removed from the initial compound. The chloride control vials were necessary because

some chloride was found to be leaching from fresh iron surfaces. These vials indicated the amount of chloride leaching from the iron into solution. This concentration was subtracted from the concentration of chloride observed in the reaction vials giving an estimate of chloride concentrations originating from the chlorinated organic contaminant. The pH was monitored to verify that the interaction of water with iron was causing an increase in pH. Eh was monitored to ensure that corrosion of iron was promoting reducing conditions.

2.2.2 Column Experiments

Column experiments were conducted to investigate the behaviour of each compound (in an aqueous solution) while flowing through reactive granular iron porous media. Column procedures also allow the degradation profiles for each contaminant to reach steady state thus avoiding the effects of sorption and changes at the iron surface on the shapes of the profiles.

Column configuration

The setup for the column experiments is shown in Figure 2-3. All columns used were made of clear Plexiglas® tubing. The ends of the columns were sealed with clear Plexiglas® end caps with rubber o-rings. Each column was 30.0 cm in length by 2.50 cm I.D., giving an internal volume of 147 cm^3. The sampling ports along the column were evenly spaced at 1 cm intervals giving a total of 29 ports along the column. Each sampling port consisted of a Swagelok® fitting (0.16 cm O.D. tube x 0.16 cm NTP male connectors) that tapped into the side of the column wall. Each fitting held a 16 ½ gauge, 3.8 cm long PrecisionGlide® needle with a Luer-Lock® fitting packed with glass wool. The needles penetrated the porous media so the tips were aligned at the centre of the

column while the outer Luer-Lock® fitting remained outside of the column. Needle plugs, made by sealing the cut ends of plastic 3ml syringes, were used to block the sampling ports from flowing during column operation.

Columns were weighed prior to and after being packed with the porous media. Two porous media compositions were used: 1) 100% granular iron and 2) 30% granular iron, 70% Ottawa Silica sand (by wt.). The 30% iron columns were used because some contaminants degraded too fast to obtain a degradation profile in the 100% iron columns. Reducing the amount of iron effectively reduced the reactivity of the bulk porous medium enough to achieve a measurable degradation profile. The columns containing the porous materials were flushed for 30 min with carbon dioxide gas. This was done to replace the air in the column, which is relatively insoluble in water, with CO_2 which is much more water soluble. The columns were then wet up with DI water. The amount of DI water that was allowed to run through each column before the contaminant was introduced is summarized in Table 2-2. The columns were then reweighed while totally saturated with water. The measured pore volume, porosity, bulk density of porous media, iron to solution ratio (wt/wt) and iron surface area-to-volume of solution ratio were then calculated. Table 2-2 summarizes these characteristics for each column.

Source Solutions

The source solutions were contained in collapsible Teflon® bags to avoid volatile loss through headspace. The solutions were pumped using a peristaltic pump (Ismatec®) through Teflon® tubing and delivered to the bottom of the columns. Solution flowed vertically from bottom to top through the columns then exited via Teflon® tubing into a pre-weighed waste container. Source solutions were prepared by filling the Teflon bags

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with DI water, pH adjusted between 6 and 7, then spiking with the stock contaminant solution. All column experiments were conducted in DI water. Starting concentrations varied and are summarized in Table 2-3.

Column Operation and Sampling

All column experiments were performed at 25°C except for 1,4-DCB-2 which was conducted at 10°C. Flow rate measurements were taken prior to each sampling event and were measured by collecting effluent in a graduated cylinder over a measured amount of time. Table 2-3 shows the average flow rates measured for each column experiment. Also measured prior to each sampling event was the number of pore volumes that had passed through the column since the contaminant solution was introduced. This was done by measuring the amount of water collected in the waste containers.

Samples were obtained from selected sampling ports by removing the plugs and attaching a glass syringe to the needle while the effluent end of the column was clamped. The solution was allowed to flow freely into the syringe as to not change the residence time of the sample being collected. Samples were also taken from the influent and effluent ends of the columns. The time required for each sample depended on the flow rate of the column and the volume of sample needed. Columns were sampled regularly for contaminant and free chloride ion concentration. During analysis for contaminant concentration, any unknown compounds and intermediates were also monitored. pH and Eh in the columns was monitored but less frequently than contaminant and chloride concentrations and during separate sampling events. The number of sampling events (contaminant and chloride) taken for each column experiment are listed in Table 2-3 along with the total number of pore volumes that had passed through the column by the

last sampling event. The experiments were terminated when steady state degradation profiles were reached. The exception to this is the column experiment for DCBD in which the experiment was terminated because the starting solution had run out and no more was available at the time. The profiles taken, however, suggest that steady state had almost, if not already, been achieved.

An important note is that chloroprene was observed as an intermediate of 2,3,4-TCB-1 degradation. This intermediate was observed to degrade much slower than the parent compound and therefore a second column (100% iron) was run using 2,3,4-TCB-1 as the starting material to investigate its degradation. Once steady state (with respect to the degradation profile of the observed intermediate) was reached the influent was changed to chloroprene as the starting material and the column was further monitored.

An attempt was made to monitor and identify end products of the reactions. Compounds that were monitored include 1,3-butadiene, 1-butene, *cis*-2-butene, *trans*-2-butene and n-butane. End product samples were taken as the last sampling events and thus were taken just prior to the termination of each column experiment.

2.2.3 Analytical Methods

Analyses of 1,4-DCB-2, 3,4-DCB-1, 2,3,4-TCB-1, chloroprene and DCBD

Samples were diluted by adding 1 ml of sample (2 ml for chloroprene and DCBD) to 3 ml of Milli-Q water (2 ml for chloroprene and DCBD) in a 10 ml crimp-top GC vial. The vials were then capped creating a 6 ml headspace. The samples were placed on a rotary shaker for 15 min to allow the aqueous and gas phases to equilibrate. Samples were then placed on a Hewlett Packard 7694 Headspace autosampler. Headspace samples, 1 ml in volume, were injected into a Hewlett Packard 5890 series II gas chromatograph (GC)

with a Ni[63] electron capture detector (ECD) and a J&W DB-624 capillary column (30 m x 0.533mm). The oven temperature program started with an initial temperature of 40°C, held for 2.0 min. Temperature was then ramped up at a rate of 10°C/min until the final temperature of 100°C was reached. The final temperature was held for 10.0 min for analysis of 2,3,4-TCB-1 and 5.0 min for all other compounds. The detector temperature was held at 300°C and the injector temperature was held at 200°C. The carrier gas was helium and had a constant flow rate of 7.0 ml/min. The make up gas was 5% methane and 95% argon. At the time of each analysis, an 8-point calibration curve was constructed (concentration versus peak area). The calibration ranges for each compound were such that the highest concentration on the calibration curve was higher than the highest concentration in the diluted samples. For most cases the response of the ECD detector was non-linear at higher concentrations and did not fit any other types of curves. In these cases a point-to-point calibration curve was used in which concentrations between one standard and the next higher standard were assumed to increase linearly. This introduced some error when calculating absolute concentrations for these compounds. However, because an 8-point calibration curve was used it is believed that calibration points were sufficiently close to provide adequate concentration values.

Analyses of DCBD and PCE

Because the DCBD compound was received as a 1:1 (wt/wt) mixture with PCE, it was desirable to analyse by a second method as to accurately track the behaviour of PCE in the batch and column experiments. Samples, 1.0 ml in volume, were added to 1.0 ml of pentane containing 500 µg/L 1,2-dibromoethane (EDB) as an internal standard in 5.0 ml vials with Teflon® lined septa and screw caps. These vials were placed on a rotary shaker

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for 15 min to allow the contaminant in the aqueous phase to partition into the organic phase. The vials were then opened and the pentane phase was transferred via disposable glass pipette to 2 ml glass crimp-top GC vials. The GC vials were placed on a Hewlett Packard 7673 GC/SFC autosampler. Liquid samples, 1µl in volume, were injected into a Hewlett Packard 5890 series II gas chromatograph (GC) with a Ni^{63} electron capture detector (ECD) and a J&W DB-624 capillary column (30 m x 0.533mm). The oven temperature program started with an initial temperature of 50°C and immediately ramped up at a rate of 15°C/min until a final temperature of 150°C was reached and held for 2.5 min. The detector temperature was held at 300°C and the injector temperature was held at 200°C. The carrier gas was helium and had a constant flow rate of 25 ml/min. The make up gas was 5% methane and 95% argon. Once again 8-point calibration curves were constructed using the stock solution of DCBD and PCE (concentration versus peak area). The calibration ranges were such that the highest concentrations on the calibration curves were higher than the highest concentrations in the samples. For some cases, non-linear calibration curves were observed at higher concentrations. For these cases a point-to-point calibration curve was used.

Analyses of anions

The main anion of interest was free chloride ion (Cl^-), however nitrate (NO_3^-) and sulphate (SO_4^{2-}) were also monitored. Samples, 0.75 ml in volume, were transferred to Dionex IC vials with filter caps then placed on a Dionex AS-40 autosampler. The samples were injected into a Dionex ICS-2000 ion chromatograph (IC) equipped with an ion-eluent generator (IEG) and a conductivity detector, with an injection volume of 25 µl. The column was an IonPac AS18 column (4 x 250 mm) and the guard column was an

IonPac AG18 column (4 x 50 mm). The mobile phase was a 30 mM solution of potassium hydroxide (KOH) and was operated at a flow rate of 1.2 ml/min. Calibration curves for anions were run regularly and were observed to be linear.

Analyses of non-chlorinated intermediates and end products

Samples, 2.5 ml in volume, were put into 5.0 ml vials with Teflon® septa and screw caps leaving 2.5 ml of headspace. The vials were placed on a rotary shaker for 15 min to allow the aqueous and gas phases to equilibrate. Headspace samples, 250 μl in volume, were then injected manually into a Hewlett Packard 5790 GC with a flame ionization detector (FID) and a GS-Q plot capillary column (30m x 0.53mm). The oven temperature program started with an initial temperature of 90°C held for 5.0 min. Temperature was then ramped up at a rate of 15°C/min until a final temperature of 120°C was reached. The final temperature was held for 5.0 min for analysis of the end products of chloroprene and DCBD and 1.0 min for analysis of the end products of all other compounds. Calibration curves were constructed using various standards. DCBD standard was received as a solution in methanol, therefore aqueous standards were used and prepared in the same fashion as the samples. A gaseous mixture of methane, ethane, ethyne, ethane, propane, propene, iso-butane, 1-butene and n-butane was used as a standard for the construction of calibration curves for 1-butene and n-butane. Another gaseous mixture of 1,3-butadiene, n-butane, 1-butene, *cis*-2-butene, *trans*-2-butene, ethyl acetylene, isobutene and isobutylene was used for the construction of calibration curves for *cis*-2-butene and *trans*-2-butene. This gas standard was received at concentrations below what was needed for the calibration curves; therefore data points for higher concentrations were achieved by injecting higher sample volumes. The concentrations of the gaseous mixtures were

converted to aqueous concentrations using Henry's Law constants, calculated using the procedure outlined in Schwarzenbach *et al.* (2003, p. 206-207), and assuming a 1:1 headspace-to-aqueous solution ratio. See appendix A for Henry's Law constants and a sample calculation of the conversion of gaseous standards to aqueous standards. The calibration ranges were such that the highest concentration on the calibration curve was higher than the highest concentration in the samples. Calibration curves in all cases were observed to be linear.

Identification of chloroprene as an intermediate of 2,3,4-TCB-1 degradation

Chloroprene was positively identified as the intermediate of 2,3,4-TCB-1 degradation by three different gas chromatographs: the Hewlett Packard 5890 series II GC with Hewlett Packard 7694 headspace autosampler and ECD detector, the Hewlett Packard 5890 series II GC with Hewlett Packard 7673 GC/SFC liquid autosampler and ECD detector, as well as the Hewlett Packard 5790 GC with FID detector. Chromatograms of the intermediate of 2,3,4-TCB-1 degradation were compared with those of the chloroprene standard. Retention times and expected peak areas matched for all three methods. Chloroprene gave a characteristic broad peak with FID detection; this was also seen in the FID analysis of 2,3,4-TCB-1 degradation. Furthermore, after the degradation profile for the 2,3,4-TCB-1 intermediate in column 731 had reached steady state (with respect to the degradation profile of the intermediate), the source solution was changed to chloroprene as the starting material. Degradation profiles for the 2,3,4-TCB-1 intermediate and chloroprene as a starting material were virtually identical (see Figure 3-17 in Results and Discussion section). This solidified the conclusion that chloroprene was in fact the intermediate of 2,3,4-TCB-1 degradation.

3. Results and Discussion

3.1 Degradation of chlorinated aliphatics

3.1.1 Batch Experiments

In the batch experiments, the concentrations of the five compounds of interest generally showed an exponential decline in concentration over time. Thus degradation of the compounds was interpreted following the pseudo-first-order kinetic model:

$$\frac{d\mathrm{C}}{d\mathrm{t}} = -k_{obs} \, \mathrm{C}_0 \qquad\qquad (3\text{-}1)$$

Where k_{obs} is the observed rate constant which can be estimated as the slope of the plot of the natural logarithm of normalized concentration (Ln C/C_0) versus time, C_0 is the concentration of the contaminant at time zero and C is the concentration of the contaminant at time t during the batch experiment. Integration of (3-1) at $\mathrm{C} = \mathrm{C}_0/2$ yields the expression for the pseudo-first-order degradation half-life, $t_{1/2}$:

$$t_{1/2} = \frac{\ln 2}{k_{obs}} \qquad\qquad (3\text{-}2)$$

A summary of initial batch conditions (water composition, temperature, duration of experiments and starting concentrations) and batch results (pseudo-first-order degradation half-lives, correlation coefficients (R^2, fit to pseudo-first-order kinetic model), percent disappearances, final chlorine mass balances and observed intermediates) is shown in Table 3-1. A significant amount of error is expected to be associated with the chlorine mass balances for batch experiments since the amount of chloride determined to

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be originating from the contaminant was estimated by subtracting the amount of chloride observed in the chloride control vials from the chloride observed in the reaction vials.

Batch experiment results for each compound are discussed below. Profiles for degradation, controls and chlorine mass balances are provided. Profiles showing the generation of observed chlorinated intermediates are provided where necessary. For the most part pH and Eh profiles were very similar for each experiment regardless of initial conditions. Figure 3-1 shows Eh and pH profiles for the 2,3,4-TCB-1 experiments and is representative of what was seen for all batch experiments. The pH of contaminant control vials stayed relatively constant throughout the experiments while the pH in reaction vials quickly increased (within 3 hours) to values above 8.6 then increased slowly to values ranging from 9.3 to 10.4 by the end of the experiments. Eh profiles taken for earlier experiments tended to show higher values than those taken for later experiments. This has been attributed to premature readings of the Eh meter for earlier experiments as generally lower values of Eh, such as those shown in Figure 3-1, were observed in later experiments where the Eh meter was allowed to stabilize for a longer period of time.

Trans-1,4-dichlorobutene-2 (1,4-DCB-2)

Previous results by Gui and Noble (pers. comm., 2006) are shown in Table 3-2. These results show that 1,4-DCB-2 will undergo hydrolysis with a half-life of 59.8 h at 25°C. However when temperature is dropped to 10°C the hydrolysis half-life increases significantly to 1155 h. Therefore, to minimize the amount of contaminant loss due to hydrolysis, batch experiments for 1,4-DCB-2 were done at 10°C. Two batch experiments were performed, one using DI water and the other using a 40 mg/L $CaCO_3$ simulated groundwater solution (noted as GW from here on). The degradation profiles for 1,4-

DCB-2 are shown in Figure 3-2. The fit to the pseudo-first-order kinetic model was good in both cases ($R^2 = 0.98$) and no appreciable difference in degradation rate was observed due to the presence of $CaCO_3$. Degradation half-lives for batch experiments using DI and GW were found to be 21.7 h and 20.5 h respectfully and less than 0.7% of the original contaminant mass was present at the end of the experiments. These results showed good replication of the previous results of Gui and Noble (pers. comm., 2006) which had degradation half-lives of 18.5 h and 21.3 h for DI and GW respectively. Chlorine mass balances ranged from 80% to 106% throughout the experiments demonstrating the large amount of error associated with calculating chlorine mass balances for batch tests. However these results also suggest that 1,4-DCB-2 was at least close to being fully dechlorinated by granular iron. No chlorinated intermediates were observed by headspace GC-ECD analysis.

Controls for the batch experiments showed little degradation with 16% and 18% mass removed at the end of the experiments for reaction in DI and GW respectively, suggesting that hydrolysis alone may not be sufficient for contaminant removal at this temperature.

3,4-dichlorobutene-1 (3,4-DCB-1)

Batch experiments for 3,4-DCB-1 were performed at 10°C in both DI water and GW and at 25°C in DI water. Profiles for degradation, controls and chlorine mass balances for 3,4-DCB-1 are shown in Figure 3-3. The degradation showed a good fit to the pseudo-first-order kinetic model in all three cases ($R^2 > 0.98$). There were no appreciable differences in half-lives between the three cases (average $t_{1/2} = 14$ h $\pm$ 3 h) indicating that neither the presence of calcium carbonate nor temperature affected degradation rates. The

observation that temperature did not affect degradation is surprising since O'Hannesin *et al.* (2004) found that degradation rates for TCE decreased exponentially with decreasing temperature and decreased by a factor of 4 between 25°C and 9°C. This observation seems to suggest that mass transport to the iron surfaces was the limiting factor for degradation rates in these batch tests since only periodic mixing was used (see Materials and Methods section under Batch Experiments).

At the end of the experiments less than 0.2% of the original contaminant mass was present in all cases. Chlorine mass balances ranged from 81% to 130% throughout the batch experiments suggesting that 3,4-DCB-1 was fully dechlorinated by granular iron. There were no chlorinated intermediates observed by headspace GC-ECD. Controls did not appear to degrade to a significant degree (less than 13% disappearance in all cases) during the experiments suggesting that hydrolysis is not a significant factor in contaminant removal at either 10°C or 25°C.

2,3,4-trichlorobutene-1 (2,3,4-TCB-1)

Batch experiments for 2,3,4-TCB-1 were performed at 10°C in DI and GW and at 25°C in GW. The degradation profiles, behaviour of controls and chlorine mass balances are shown in Figure 3-4. Similar to the other two chlorinated butenes the degradation profiles for the three batch experiments demonstrated a good fit to pseudo-first-order degradation kinetics ($R^2 > 0.92$) with no appreciable difference in degradation half-lives (average $t_{1/2}$ = 16.4 h ± 0.1 h) again indicating that neither $CaCO_3$ nor temperature affected degradation. By the end of the experiments less than 0.3% of the contaminant was present in the reaction vials.

The chlorine mass balance ranged from 59% to 118% and averaged 89% throughout the experiments indicating that perhaps some chlorine was not being accounted for. One chlorinated intermediate was observed for reaction of 2,3,4-TCB-1 with iron and was identified as chloroprene. Figure 3-5 shows the degradation of 2,3,4-TCB-1 and the generation of the chloroprene intermediate in the batch experiment at 10°C in DI water (only one set of results shown for simplicity). In this batch experiment it does not appear that chloroprene is degrading. Furthermore, the carbon mass balance (70% at end of experiment based on compounds analysed by GC-ECD) suggests that not all of the original contaminant had been converted to chloroprene. This as well as the slightly low chlorine mass balance can perhaps be explained by the observation of an unidentified hydrolysis product present in both the controls and reaction vials.

Figure 3-6 shows the generation of the hydrolysis product for the batch experiment at 10°C in GW which was believed to be chlorinated due to its detection by headspace GC-ECD analysis. One can see that this hydrolysis product was present at the beginning of the experiment. In the reaction vials the signal intensity (observed by headspace GC-ECD) increased by 800% in 6.3 h then appeared to degrade (pseudo-first order $t_{1/2}$ = 105 h) by reaction with granular iron. The transformation of 2,3,4-TCB-1 by hydrolysis early in the reaction vials could explain why a less than complete carbon mass balance was observed in the transformation of 2,3,4-TCB-1 to chloroprene. In the control vials the signal intensity increased by 144% in 148 h only reaching 24% of the maximum signal intensity observed in the reaction vials. The slower production rate of the hydrolysis product can perhaps be explained by the significant difference in pH between the control and reaction vials (see Figure 3-1). At a pH of 8 or higher the rate at which

hydrolysis occurs can increase dramatically; referred to as base-catalyzed hydrolysis in which the hydroxide ion (OH⁻) acts as a nucleophile (Klausen *et al.,* 1997, Schwarzenbach *et al.,* 2003). For example Beltran *et al.* (2000) found the degradation of isoxaflutole (an herbicide) by hydrolysis to be 100 times faster at pH 9.3 than at pH 3.8. Another possibility is that surface-catalyzed hydrolysis occurred at the iron/solution interface. Torrents and Stone (1991) found that the hydrolysis rate of phenyl picolinate (PHP) increased significantly in the presence of goethite (FeOOH), a mineral commonly found on iron surfaces (Phillips *et al.,* 2003).

Despite the observation of the hydrolysis product, controls did not appear to degrade to a significant degree with a maximum of 14% mass removed at 10°C in DI water and no observable mass removed at 10°C in GW.

2-chlorobutadiene-1,3 (chloroprene)

Batch experiments for chloroprene were conducted at 10°C in DI water and 25°C in GW. Profiles for degradation, controls and chlorine mass balances are shown in Figure 3-7. As one can see, chloroprene did not degrade to completion in either of the batch tests with 44% remaining at 10°C in DI water and 52% remaining at 25°C in GW at the end of the experiments. The degradation curves did not fit well with the pseudo-first-order kinetic model, having R^2 values of 0.66 (10°C in DI) and 0.67 (25°C in GW). The chlorine mass balance for reaction at 25°C in GW appears to show complete dechlorination except perhaps the data point at 155 h which shows a low chlorine mass balance of 66%. Reaction at 10°C in DI, however, shows a low chlorine mass balance at 52% at the end of the experiment. The poor fit to the pseudo-first-order kinetic model and a low chlorine mass balance seem to suggest that disappearance of chloroprene was at least partially due

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to sorption at the iron surface. The degradation half-lives estimated at 377 h (10°C in DI) and 233 h (25°C in GW) are therefore thought to be inaccurate. In the case where sorption is thought to be responsible for an initial sharp decrease in concentration, one may consider only using later data points to determine degradation kinetics. In this case, however, the fit to the pseudo-first-order kinetic model did not improve when only considering later data.

Controls did not appear to significantly degrade with only 12% mass removal observed at 10°C in DI water and less than 2% mass removal observed at 25°C in GW.

2,3-dichlorobutadiene-1,3 (DCBD)

Results for the DCBD batch experiments performed at 10°C in DI and 25°C in GW are shown in Figure 3-8. The behaviour was similar to that of chloroprene, in which the compound did not fully degrade by the end of the experiment with 19% (10°C in DI) and 13% (25°C in GW) of the contaminant mass present at the end of the experiments. The degradation profiles for DCBD appear to fit the pseudo-first-order kinetic model better than chloroprene with R^2 values of 0.822 (10°C in DI) and 0.881 (25°C in GW) but were still considered to be a poor fit. By only using data points taken after 24 hours, a good fit to the kinetic model was achieved in both cases ($R^2 = 0.94$) and half-lives of 187 h (10°C in DI) and 114 h (25°C in GW) were obtained. The rapid decrease in contaminant mass at early time is thought to be a consequence of sorption at the iron surface, similar to that observed in the chloroprene experiments. Chlorine mass balances for the DCBD batch tests were low at the end of the experiments (16% at 10°C in DI and 19% at 25°C in GW).

Controls did not degrade significantly as only 6% and 5% contaminant mass was removed for reactions at 25°C in GW and 10°C in DI respectively. DCBD batch experiments were performed with PCE as a co-contaminant (1:1 wt/wt mixture with DCBD). Figure 3-9 shows degradation profiles for PCE from the DCBD batch experiments as well as an independent batch experiment at 25°C in GW where PCE was the only initial contaminant. The degradation half-lives were 86.1 h (10°C in DI with DCBD), 99.6 h (25°C in GW with DCBD) and 87.7 h (alone at 25°C in GW). These results suggest that DCBD did not significantly affect the degradation of PCE however it is not known if PCE affects the degradation of DCBD since there has been no batch test done using only DCBD as the initial contaminant. Trichloroethene (TCE), a known intermediate of PCE degradation by iron (Roberts *et al.,* 1996, Arnold and Roberts, 2000), was not observed at an appreciable concentration in the batch experiments. However other known chlorinated intermediates of PCE degradation such as the 1,1-, *cis-* and *trans-* isomers of dichloroethene (DCE) and vinyl chloride (VC) (Roberts *et al.,* 1996, Arnold and Roberts, 2000) were not monitored. The presence of these breakdown products of PCE along with sorption may have been responsible for the low chlorine mass balance.

3.1.2 Column Experiments

Pseudo-first-order degradation half-lives were estimated in the same way as for the batch experiments, but using column residence time as equivalent to reaction time. Columns were sampled until steady state with respect to the degradation profile was believed to have been reached. The exception is DCBD where the experiment was terminated because the starting solution had run out and additional DCBD was unavailable. The

DCBD degradation profile, however, was believed to be close to if not already at steady state. All column experiments were conducted at 25°C with DI water except 1,4-DCB-2 which was done at 10°C with DI water. Experiments for 1,4-DCB-2, 3,4-DCB-1 and 2,3,4-TCB-1 were done using 30% iron columns while experiments for chloroprene and DCBD were done using 100% iron columns.

Table 3-3 shows a summary of column experiment results. Below the results for each compound are discussed including the steady state degradation profiles (normalized concentration versus residence time) and chlorine mass balances. Chlorine mass balances were calculated differently than for the batch experiments. It was found that flushing of the columns with DI water prior to the experiment effectively removed excess chloride from the iron surfaces, eliminating the need to use a chloride control. Also provided are Eh and pH profiles for each column experiment.

Trans-1,4-dichlorobutene-2 (1,4-DCB-2)

The steady state degradation profile and chlorine mass balance for the 1,4-DCB-2 column experiment at 429 pore volumes are shown in Figure 3-10. The concentration of 1,4-DCB-2 had decreased from 10.1 mg/L to below the detection limit after 21 min of column residence time. The fit to the pseudo-first-order kinetic model was good ($R^2 =$ 0.95) giving a degradation half-life of 2.0 min in a 30% iron column at 10°C. The chlorine mass balance ranged from 90% to 114% with a value of 99% at the last sampling port indicating that iron was successful in dechlorinating 1,4-DCB-2. Similar to the batch experiments, no chlorinated intermediates were observed for 1,4-DCB-2. The pH and Eh profiles are shown in Figure 3-11. One can see that the pH stayed relatively constant throughout the column (pH ranged from 6.1 to 6.6) which differs from the batch

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experiments where pH quickly increased. This can be attributed to decreased contact time of solution with granular iron as a result of relatively fast pore velocity (7.18 x 10^{-3} cm/s) and a column residence time (70 min) which was much less than the reaction time in the batch experiments. Fluctuations in Eh measurements were observed throughout the column. This is thought to be due to small sample volumes representing microenvironments present in the column. The observed decrease in Eh indicated that iron corrosion was occurring promoting reducing conditions.

3,4-dichlorobutene-1 (3,4-DCB-1)

The steady state degradation profile and chlorine mass balance for the 3,4-DCB-1 column experiment at 317 pore volumes are shown in Figure 3-12. Contaminant concentration had decreased to below the detection limit by 9.6 min residence time. A good fit to the pseudo-first-order kinetic model was found ($R^2 = 0.95$) and a rapid degradation half-life of 0.74 min in a 30% iron column was observed. The chlorine mass balance (ranging from 100% to 101%) indicated that 3,4-DCB-1 was fully dechlorinated by granular iron and no chlorinated intermediates were observed. The pH and Eh profiles are shown in Figure 3-13. Again a fast pore velocity (7.61 x 10^{-3} cm/s) and short residence time (72 min) resulted in the relatively constant pH (ranged from 6.2 to 6.6) observed throughout the column.

2,3,4-trichlorobutene-1 (2,3,4-TCB-1)

The steady state degradation profile and chlorine mass balance for the 2,3,4-TCB-1 column experiment at 260 pore volumes are shown in Figure 3-14. Results show that 2,3,4-TCB-1 concentrations decreased rapidly to below the detection limit by 19 min of column residence time. A good fit to the pseudo-first-order kinetic model was observed

($R^2 = 0.98$) and a half-life of 2.3 min was obtained in a 30% iron column. The chlorine

mass balance ranged from 92% to 107% throughout the column and chloroprene was

observed as an intermediate as it was in the batch experiments. Figure 3-15 shows the

generation of the chloroprene intermediate along with the degradation of 2,3,4-TCB-1

and the carbon mass balance. The carbon mass balance, which was based on 2,3,4-TCB-1

and chloroprene only, ranged from 88% to 109% indicating that nearly all if not all of the

2,3,4-TCB-1 was transformed to chloroprene. In the column, hydrolysis was not observed

to occur to a great degree. This differs from the batch experiments where a significant

increase in signal intensity of the hydrolysis product was observed at early time. This can

be explained by a much lower pH in the column (Figure 3-16, pH ranged from 6.5 to 7.4)

than was present in the reaction vials (Figure 3-1) of the batch experiments and also

suggests that base-catalyzed hydrolysis rather than surface-catalyzed hydrolysis was

responsible for the increase in signal intensity of the hydrolysis product in the batch

experiments. The hydrolysis product was observed in the starting solution but degraded

to less than 1% of its original signal intensity by the first sampling port (or residence time

of 2.1 min) of the column. The lower pH is consistent with the other two 30% iron

columns where pore velocities were fast (in this case 7.81×10^{-3} cm/s) and residence

times were short (in this case 65 min).

2-chlorobutadiene-1,3 (chloroprene)

The chloroprene column experiment was done in two parts. The first part used 2,3,4-

TCB-1 as the starting material in a 100% iron column with a significantly reduced pore

velocity (6.71×10^{-4} cm/s). All of the 2,3,4-TCB-1 was observed to be converted to

chloroprene by the first sampling port (or residence time of 26.3 min). Once the

degradation profile of the chloroprene intermediate had reached steady state, the influent solution was changed so that chloroprene itself was the initial contaminant and the column was run for an additional 14 pore volumes. This was done to conserve the chloroprene starting material as well as to examine any differences in degradation between the chloroprene intermediate of 2,3,4-TCB-1 and chloroprene itself. Figure 3-17 shows the steady state degradation profiles for both chloroprene as an intermediate and as the initial contaminant. In this figure the residence time at the first sampling port for chloroprene as an intermediate has been shifted from 26.3 min to zero so that profiles can be compared. From this plot it appears that the degradation profiles for chloroprene (both as an intermediate and as the initial contaminant) are virtually identical. Both profiles had a good fit to the pseudo-first-order kinetic model ($R^2 > 0.99$) and degradation half-lives of 15.4 min (as intermediate) and 12.3 min (as initial contaminant) were obtained in a 100% iron column. Chlorine mass balances for 2,3,4-TCB-1 (ranged from 94% to 102%, 102% at last sampling port) and chloroprene (ranged from 80% to 104%, 103% at last sampling port) suggest that granular iron was successful in the dechlorination of both contaminants. The pH and Eh profiles for this column experiment are shown in Figure 3-18 and the pH profile differs from those observed for the 30% iron columns. The decrease in pore velocity (6.89 x 10^{-4} cm/s, average of the two sampling events), increase in residence time (788 min, average of the two sampling events) as well as an increase in iron surface area-to-solution ratio (8.30 m^2/ml for the 100% iron column compared to an average of 2.20 m^2/ml in the 30% iron columns) can explain the pH increase across the column (pH ranged from 9.1 to 9.8 after 53 min residence time) as the pore water had more contact time with iron and was therefore more affected by iron corrosion and the

release of hydroxide ions. This pH data is consistent with what is commonly observed in studies using pure iron columns (Jeen *et al.,* 2006, O, 2006).

2,3-dichlorobutadiene-1,3 (DCBD)

As mentioned above all DCBD experiments were conducted with PCE as a co-contaminant (1:1 wt/wt mixture). The degradation profiles for DCBD and PCE and the chlorine mass balance are shown in Figure 3-19. DCBD concentrations decreased to levels below the detection limit by 264 min residence time in the column. A good fit to the pseudo-first-order kinetic model was found ($R^2 = 0.98$) with respect to DCBD degradation and a half-life of 23.7 min was observed in a 100% iron column. The chlorine mass balance shows less than complete dechlorination (70% by last sampling port) however this was calculated while taking into account the presence of PCE in the column. The degradation profile for PCE shows that concentrations decreased below the detection limit by 264 min. Similar to the batch experiments for DCBD, the 1,1-, *cis*- and *trans*- isomers of DCE and VC, which are the breakdown products of PCE, were not monitored. Degradation half-lives for the DCE isomers and VC have been found to be considerably higher (more than an order of magnitude in the case of *cis*-DCE and VC) than PCE (Gillham and O'Hannisen, 1994) and therefore were likely present in the column experiment and not detected which could explain the low chlorine mass balance. Trace amounts (maximum of 1.0×10^{-8} M) of chloroprene were detected in the first and second sampling ports (26 min and 53 min residence time respectively). This result would be expected if chloroprene was an intermediate since the half-life for DCBD was found to be higher than that for chloroprene (i.e chloroprene would not have accumulated in the column as it was degrading faster than it was being produced). It is therefore

believed that chloroprene is an intermediate of DCBD degradation and that DCBD was fully dechlorinated by granular iron. It is however recommended that an experiment be conducted using only DCBD as the initial contaminant to confirm complete dechlorination by chlorine mass balance. The pH and Eh profiles for the DCBD column experiment are shown in Figure 3-20. Again, the slower pore velocity (6.24×10^{-4} cm/s), increased residence time (793 min) and increased iron surface area-to-solution ratio (8.30 m^2/ml) resulted in a higher pH throughout the column (pH ranged from 9.3 to 10.0 after 26 min residence time) than was observed in the 30% iron columns.

3.1.3 Comparing Batch and Column Results

The pseudo-first-order degradation half-lives reported for the batch and column experiments can not be directly compared nor can the results from the 30% iron columns and the 100% iron columns. To compare results the measured half-lives need to be normalized to the iron surface area-to-solution ratio. Johnson *et al.* (1996) found that previously reported first-order rate constants from both batch and column experiments varied widely without meaningful correlation. They found that normalization to iron surface area concentration (the same as iron surface area-to-solution ratio) yielded specific rate constants that varied by less than an order of magnitude and were therefore more meaningful when comparing previous data. For this study the pseudo-first-order half-lives were normalized rather than the rate constants, however since rate constants are inversely proportional to half-lives the results of normalization should be the same. Table 3-4 shows each reported pseudo-first-order half-life which has been normalized to an iron surface area-to-solution ratio of 1 m^2/ml. Average half-lives for batch experiments have been reported here since no appreciable differences were found due to differences in

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temperature (10°C vs. 25°C) and solution compositions (DI vs. GW). One can see from

Table 3-4 that normalized degradation half-lives from batch experiments are in most

cases two orders of magnitude higher than those for column experiments. The one

exception is DCBD where half-lives differ by one order of magnitude however the

average half-life from batch experiments is still over thirty times greater than that from

the column experiment. One possible reason for these differences is the difference in pH

observed in the 30% iron columns (used for the 1,4-DCB-2, 3,4-DCB-1 and 2,3,4-TCB-1

column experiments) and the batch tests. As mentioned in the introduction lower pH has

been found responsible for higher degradation rates (Chen *et al.*, 2001). However this is

not thought to be the sole cause of the differences in normalized half-lives between batch

and column experiments since pH values were similar in the batch and column

experiments for chloroprene and DCBD and large differences in normalized half-lives

were observed. As mentioned above, temperature did not seem to have an appreciable

affect on degradation half-lives in batch experiments. This was seen as an unusual result

and led to the belief that mass transport effects were limiting the reaction rates in the

batch experiments. If this is true it could also explain the large differences in normalized

degradation half-lives observed for batch and column experiments since transport to iron

surfaces is believed to be much more efficient in column experiments where water is

constantly flowing past the porous medium compared to batch experiments where the

solutions were hand mixed only twice per day plus before sampling events.

When comparing the normalized degradation half-lives of the different

compounds, one can see that the three chlorinated butenes (1,4-DCB-2, 3,4-DCB-1 and

2,3,4-TCB-1) showed much faster degradation than the two chlorinated butadienes

(chloroprene and DCBD). This observation is consistent with the observation by Johnson *et al*. (1996) that dechlorination is more rapid at saturated carbon centers than it is at unsaturated carbon centers (i.e. since all of the chlorinated butenes have chlorine atoms at saturated carbon centers and the chlorinated butadienes only have chlorine atoms at unsaturated carbon centres).

Column experiments seemed to be more effective in investigating the degradation of these compounds by granular iron. Sorption, which seemed to play a role in contaminant disappearance in batch experiments for chloroprene and DCBD, did not affect the shapes of the degradation profiles in column experiments since steady state with respect to degradation profiles was allowed to be reached (or at least close to steady state in the case of DCBD). Furthermore, flushing the columns with DI water at the beginning of the column experiments washed away chloride and sulphate that had initially adsorbed to the iron surface and were observed to accumulate in the batch experiments. This allowed for a more accurate estimation of chlorine mass balance and ensured that accumulating ions from unwashed iron did not interfere with degradation of the contaminants.

3.2 End Products

Samples from column experiments for each contaminant were analysed for non-chlorinated intermediates and end products. Observed end products included 1,3-butadiene, 1-butene, *cis*-2-butene, *trans*-2-butene and n-butane. Of these, the only compound that presents a serious concern to environmental or human health is 1,3-butadiene which has an estimated 96-hour LC_{50} of 44.8 mg/L for freshwater fish (fathead minnow) and has been found to be carcinogenic in mice and rats (EC JRC, 2002). A 96-

hour LC$_{50}$ of 58 mg/L for freshwater fish (fathead minnow) has been estimated (OECS SIDS, 1993b) for *cis*- and *trans*-2-butene however OECS SIDS (1993b) also states that both will undergo hydrolysis (concentrations decreased from 700mg/L to <1mg/L in a 3 hour experiment at ambient temperature) when released into the environment. No studies indicating 1-butene or n-butane as a threat to environmental health have been found.

Table 3-5 shows the non-chlorinated intermediates and end products observed in the column experiments. In some cases non-chlorinated compounds were observed to be degrading in which case observed and normalized pseudo-first-order degradation half-lives have also been included. Below is a brief discussion of the observed end products and their behaviour for each column experiment.

Trans-1,4-dichlorobutene-2 (1,4-DCB-2)

The end product profiles for 1,4-DCB-2 degradation are shown in Figure 3-21. For this experiment it appears that 1,4-DCB-2 was converted initially to 1,3-butadiene which then appeared to degrade by interaction with granular iron with a pseudo-first-order half-life of 136 min ($R^2 = 0.96$). As 1,3-butadiene degraded a mixture of 1-butene, *cis*-2-butene and *trans*-2-butene was generated. This is reasonably consistent with previous work by Consorti *et al.* (2003) where butadiene underwent hydrogenation catalyzed by transition metal complexes resulting in a mixture of 1-butene, *cis*-2-butene, *trans*-2-butene and n-butane. No n-butane was detected in this column, however results from other column experiments (those for 2,3,4-TCB-1/chloroprene and DCBD, discussed below) with higher residence times have led to the belief that n-butane would have eventually been detected had residence times been sufficient. The carbon mass balance was fairly close to

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complete at 93% by the last sampling port (79 min residence time) suggesting that 1,4-DCB-2 was close to, if not fully, degraded to the observed end products.

3,4-dichlorobutene-1 (3,4-DCB-1)

The end product profiles for the 3,4-DCB-1 column experiment are shown in Figure 3-22. Results are similar to those of 1,4-DCB-2 as 3,4-DCB-1 appeared to be converted to 1,3-butadiene which was then converted to a mixture of 1-butene, *cis*-2-butene and *trans*-2-butene. In this case however 1,3-butadiene was observed to degrade faster with a half-life of 41.3 min ($R^2 = 0.89$). This is thought to be due to the difference in temperature between the two columns (25°C in this case opposed to 10°C for 1,4-DCB-2 degradation). Again n-butane was not detected in the column however would be expected to appear if residence times were longer. The carbon mass balance was low (71% at the last sampling port). Some losses were expected to occur during sampling and transfer of solutions as 1,3-butadiene, 1-butene, *cis*-2-butene, *trans*-2-butene and n-butane all exist as gases at room temperature and are expected to partition into the gas phase from water (see appendix A for Henry's Law constants). OECS SIDS (1993b) also states that both *cis*- and *trans*-2-butene undergo hydrolysis which may explain some loss of mass for these compounds since analysis for alcohols was not performed. Such large losses were not observed for the 1,4-DCB-2 experiment however the lower temperature (10°C vs. 25°C in this case) would have likely reduced losses during sampling as well as reduced hydrolysis reaction rates for *cis*- and *trans*-2-butene.

2,3,4-trichlorobutene-1 (2,3,4-TCB-1) and 2-chlorobutadiene-1,3 (chloroprene)

Since 2,3,4-TCB-1 was observed to be completely converted to chloroprene during column experiments it is assumed that these two compounds will have the same end

products. Therefore only the 100% iron column using 2,3,4-TCB-1 as the initial

contaminant was sampled for end product analysis. The end product profiles are shown in

Figure 3-23. By the first sampling port (28.3 min residence time) all of the 2,3,4-TCB-1

had been converted to chloroprene. 1,3-butadiene was present at the first sampling port

along with 1-butene, *cis*-2-butene and *trans*-2-butene. 1,3-butadiene was then observed to

degrade ($t_{1/2}$ = 24.2 min, R^2 = 0.89) as 1-butene, *cis*-2-butene and *trans*-2-butene

concentrations continuously increased. After 160 min 1-butene was observed to degrade

($t_{1/2}$ = 174 min, R^2 = 0.82) as n-butane was detected and concentrations began to increase,

indicating that 1-butene was being converted to n-butane. Again the carbon mass balance

was low (53% at last sampling port) but is believed to be due to losses during transfer and

hydrolysis reactions occurring for *cis*- and *trans*-2-butene.

2,3-dichlorobutadiene-1,3 (DCBD)

The end product profiles for DCBD are shown in Figure 3-24. Here no 1,3-butadiene was

detected however this does not necessarily mean that it was not present (discussed below

in section 3.3). The same mixture of 1-butene, cis-2-butene and trans-2-butene was

observed with concentrations increasing at early time then 1-butene beginning to degrade

($t_{1/2}$ = 270 min, R^2 >0.99) after 85 min of residence time as n-butane concentrations

began to increase. Carbon mass balance was again low at 58% at the last sampling port.

3.3 Reaction Pathways

The above observations have led to the proposed reaction pathways as presented in

Figure 3-25. It is proposed that each contaminant is converted to 1,3-butadiene which

further reacts by interaction with granular iron. Below is a brief discussion of the

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proposed reaction pathways for the conversion of each contaminant to 1,3-butadiene as well as the proposed reaction pathways of 1,3-butadiene degradation.

Trans-1,4-dichlorobutene-2 (1,4-DCB-2)

Figure 3-25a proposes that 1,4-DCB-1 is converted to butadiene via a reductive elimination pathway. This pathway is similar to the reductive β-elimination and dihalo-elimination reactions described in Roberts *et al.* (1996), Arnold and Roberts (2000) and Vogel *et al.* (1987) in that two electrons donated by iron corrosion result in the release of two chloride ions and a unit increase in bond order of the organic compound. It does however differ in the fact that chlorine atoms are not on adjacent (α, β) carbons; they are instead on unsaturated carbons adjacent to the olefinic carbons of the existing double bond. The result is an additional double bond (along with a rearrangement in position) on the organic compound instead of a triple bond where the original double bond previously existed.

3,4-dichlorobutene-1 (3,4-DCB-1)

Figure 3-25b shows that 3,4-DCB-1 is converted to 1,3-butadiene via a reductive β-elimination pathway similar to that described by Roberts *et al.* (1996), Arnold and Roberts (2000) and Vogel *et al.* (1987).

2,3,4-trichlorobutene-1 (2,3,4-TCB-1) and 2-chlorobutadiene-1,3 (chloroprene)

Figure 3-25c shows that 2,3,4-TCB-1 is converted to chloroprene via a reductive β-elimination pathway similar to that described by Roberts *et al.* (1996), Arnold and Roberts (2000) and Vogel *et al.* (1987). Chloroprene, as an intermediate of 2,3,4-TCB-1 degradation or as the initial contaminant, is converted to 1,3-butadiene via a

hydrogenolysis reaction pathway similar to that described in Matheson and Tratnyek (1994), Roberts *et al.* (1996) and Arnold and Roberts (2000).

2,3-dichlorobutadiene (DCBD)

Figure 3-25d shows that DCBD is converted to chloroprene then to 1,3-butadiene via a hydrogenolysis reaction pathway similar to that described in Matheson and Tratnyek (1994), Roberts *et al.* (1996) and Arnold and Roberts (2000). It is important to note that this is hypothesized only since trace amounts of chloroprene were detected in the column experiment and 1,3-butadiene was not detected. Conversion of DCBD to chloroprene via hydrogenolysis can be supported by the fact that the degradation half-life of DCBD is slightly higher yet on the same order of magnitude as that observed for chloroprene which also undergoes hydrogenolysis. Arnold and Roberts (2000) observed that, in general, higher chlorinated substrates will degrade at a slightly slower rate than less chlorinated substrates when being degraded by the same reaction pathway. They found degradation half-lives of PCE and TCE by hydrogenolysis to differ by less than an order of magnitude. However comparing TCE degradation by hydrogenolysis versus β-elimination yields a difference of two orders of magnitude in observed half-lives with hydrogenolysis being the slower pathway. This suggests that a different degradation pathway of DCBD, i.e. a reductive elimination pathway in which both chlorine atoms are removed simultaneously, would yield a much faster half-life for DCBD similar to those observed for the degradation of 1,4-DCB-2, 3,4-DCB-1 and 2,3,4-TCB-1. The conversion from chloroprene to 1,3-butadiene by hydrogenolysis is likely as this was observed in the 2,3,4-TCB-1/chloroprene column experiment. The fact that no 1,3-butadiene was detected is not surprising since it would not be expected to accumulate in the column as

its observed half-life ($t_{1/2}$ = 24.2 min) is similar to the observed half-life of DCBD ($t_{1/2}$ = 23.7 min) which were both evaluated in the same column (col. 731).

1,3-Butadiene

Figure 3-25e shows the reaction pathways for 1,3-butadiene degradation by granular iron. Consistent with Consorti *et al.* (2003) 1,3-butadiene degrades into a mixture of 1-butene, *cis*-2-butene, *trans*-2-butene and n-butane via a catalytic hydrogenation reaction pathway which is also described in Matheson and Tratnyek (1994) and Arnold and Roberts (2000). It was observed however that 1-butene, *cis*-2-butene and *trans*-2-butene were produced initially and n-butane was then produced via catalytic hydrogenation of 1-butene. *Cis*-2-butene and *trans*-2-butene were not observed to degrade in any of the column experiments and it is not known if these compounds would undergo catalytic hydrogenation under these conditions had residence times been greater.

4. Conclusions

Through a variety of laboratory scale batch and column experiments granular iron has been shown to be a potentially effective material to treat groundwater contaminated with 1,4-DCB-2, 3,4-DCB-1, 2,3,4-TCB-1, chloroprene and DCBD, which arise due to the synthesis of the chloroprene and DCBD monomers used in the manufacture of polychloroprene polymer (PCP), latex and neoprene rubber. All compounds except DCBD have been confirmed to be fully dechlorinated by granular iron by using a chlorine mass balance. DCBD dechlorination has not been confirmed by chlorine mass balance however is believed to be fully dechlorinated due to the proposed reaction pathways and the likely presence of chlorinated co-contaminants affecting the chlorine mass balance calculations. A chlorinated intermediate was observed for the degradation of 2,3,4-TCB-1 by granular iron and was identified as chloroprene. Chloroprene is also believed to be an intermediate of DCBD degradation as trace levels were observed in the column experiment and kinetic data suggested a hydrogenolysis reaction pathway which would result in chloroprene being an intermediate. Results suggest that all compounds degrade to 1,3-butadiene which is then degraded to a mixture of 1-butene, *cis*-2-butene and *trans*-2-butene. 1-butene was then found to degrade to n-butane. The end products of all compounds were therefore found to be non-harmful to human or environmental health.

Reaction pathways for contaminants were proposed. The reductive elimination reaction pathway from 1,4-DCB-2 to 1,3-butadiene is thought to be similar to reductive β-elimination however differs with respect to the position of chlorine atoms in the starting material and the rearrangement of unsaturated bonds in the product. 3,4-DCB-1

and 2,3,4-TCB-1 underwent similar reductive β-elimination reactions resulting in 1,3-butadiene and chloroprene intermediates respectively. Degradation of chloroprene and DCBD occurred via hydrogenolysis pathways while 1,3-butadiene underwent catalytic hydrogenation resulting in the observed end products.

Pseudo-first-order degradation half-lives were determined for all contaminants and intermediates. Normalization of half-lives to iron surface area-to-solution ratio demonstrated that batch experiments showed much slower degradation than column experiments. This trend is believed to be due to the limiting nature of mass transport to the iron surfaces taking place in the batch experiments. This conclusion was further supported by the observation that temperature did not affect degradation rates in batch experiments. In general, degradation of the chlorinated butenes (normalized column half-lives ranged from 1.6 to 5.2 min), which degraded by reductive elimination pathways, was much faster than for the chlorinated butadienes (normalized column half-lives ranged from 115 to 197 min) which degraded by hydrogenolysis pathways. The degradation half-lives observed for 1,3-butadiene (average normalized column half-life of 195 min) were comparable to those observed for chloroprene and DCBD.

5. Recommendations

It is recommended that DCBD be evaluated by batch and column experiments in which it is the only initial contaminant. This should be done so that a chlorine mass balance can be used to verify that it can in fact be completely dechlorinated by granular iron. Such an experiment would also eliminate any potential effects on degradation due to the presence of PCE. It is also recommended that batch and column experiments be performed using mixtures of the five contaminants to evaluate any competitive behaviour on degradation rates. Temperature was not seen to affect the degradation of contaminants in batch experiments however this was thought to be due to insufficient mixing. It is therefore recommended that column experiments be done at different temperatures to evaluate the extent of the effects of temperature on degradation kinetics, and that better mixing practices be used if contaminant degradation is to be evaluated using batch experiments. Since chloride was observed to be desorbing from fresh iron surfaces in the batch experiments it is recommended that iron be washed with DI water prior to use in batch experiments. This may eliminate the need for a chloride control and increase accuracy in chlorine mass balance calculations. Finally, it is recommended that field scale research be done at a site contaminated with some or all of these compounds. This work could be done by transporting contaminated water from the field to the lab, by using an in-situ iron column or by implementing a pilot scale PRB.

6. Appendices

6.1 Appendix A

Conversion of Gaseous Concentrations to Aqueous Concentrations

Compound	Henry's Law Constant (atm L/mol)*	Gaseous Concentration (ppm)	Aqueous Concentration (mg/L)
1,3-butadiene	72.2	15.4	0.0521
1-butene	128.5	15.3	0.0485
		5000	15.9
cis-2-butene	151.6	15.4	0.0478
trans-2-butene	151.6	15.4	0.0478
n-butane	930.2	15.4	0.0446
		4960	14.4

* Calculated using the procedure outlined in Schwarzenbach et al. (2003, p. 206-207), calculated at 25°C

Sample calculation for 1-butene (15.3 ppm):

Assume gaseous concentration is headspace concentration above aqueous phase at equilibrium and headspace-to-solution ratio is 1:1 (vol/vol). The aqueous concentration before equilibrium is desired.

Headspace concentration = 15.3 ppm

Therefore partial pressure, $p = 1.53 \times 10^{-5}$ atm (at STP)

$K_H = p/C_w$

128.5 atm L/mol = $(1.53 \times 10^{-5} \text{ atm})/C_w$

$C_w = 1.191 \times 10^{-7}$ M (this is the aqueous concentration at equilibrium)

Now find gaseous concentration at equilibrium in M:

For ideal gas, PV = nRT

At STP: P = 1 atm, T = 25°C = 298.15 K, R = 0.08206 L atm/mol K,

assume V = 1L

$$n = \frac{(1 \text{ atm x } 1 \text{ L})}{(0.08206 \text{ L atm/mol K})(298.15 \text{ K})}$$

= 0.04873 mol

Therefore molar concentration of 1-butene in gas phase at equilibrium is:

$(0.04873 \text{ M})(1.53 \text{ x } 10^{-5}) = 7.456 \text{ x } 10^{-7} \text{ M}$

Aqueous concentration before equilibrium is sum of aqueous concentration and gaseous concentration at equilibrium:

$1.191 \text{ x } 10^{-7} \text{ M} + 7.456 \text{ x } 10^{-7} \text{ M} = 8.647 \text{ x } 10^{-7} \text{ M}$

In mg/L:

$(8.647 \text{ x } 10^{-7} \text{ M})(56.1072 \text{ g/mol})(1000 \text{ mg/g})$

= 0.0485 mg/L

Therefore conversion to aqueous concentration yields 0.0485 mg/L.

7. Tables

Table 1-1. Chloroprene manufacturers worldwide. Adapted from Lynch (2001).

Company	Facility	Method
Bayer	Dormagen, Germany	1,3-butadiene
DuPont Dow Elastomers	Louisville, Kentucky, USA	1,3-butadiene
DuPont Dow Elastomers	LaPlace, Louisiana, USA	1,3-butadiene
Denki Kagaku Kogyo	Niigata Prefacture, Japan	Acetylene
Showa DDE Manufacturing	Kanagawa, Japan	1,3-butadiene
Tosoh Corporation	Yamaguchi Prefecture, Japan	1,3-butadiene
Nairit	Yerevan, Armenia	Acetylene and 1,3-butadiene
Enichem	Usine de Champagnier, France	1,3-butadiene
Ministry of Chemical Industry	Changshou, China	Acetylene
Ministry of Chemical Industry	Datong, China	Acetylene

Table 1-2. Physical properties and constants of contaminants.

Compound	Solubility in water	Density	Vapour Pressure	Henry's Law constant (K_H)	Log K_{OW}	Koc	Source(s)
1,4-DCB-2	7190 mg/L[a]	1.183 g/cm^3 @ 25°C [a]	N/A	18.8 atm L/mol @ 25°C [b] *	N/A	4.8 cm^3/g [c]	[a]Blaha *et al.*, 1998 [b]Schwarzenbach *et al.*, 2003 [c]NDEQ, 2006
3,4-DCB-1	1600 mg/L @ 20°C [d]	1.117 g/cm^3 @ 20°C [d]	2.91 kPa @ 25°C [d]	15.9 atm L/mol [d]	2.37 [d]	160 cm^3/g [d]	[d]OECD SIDS, 2004
2,3,4-DCB-1	600 mg/L @ 20°C [e]	1.34 g/cm^3 @ 20°C [e]	0.23 kPa @ 20°C [e]	11.5 atm L/mol @ 25°C [b] *	2.4 [e]	N/A	[e]OECD SIDS, 1993 [b]Schwarzenbach *et al.*, 2003
Chloroprene	256-480 mg/L @ 20°C [f]	0.9598 g/cm^3 @ 20°C [f]	25 kPa @ 20°C [f]	78.7 atm L/mol @ 20°C [f]	2.2 [f]	68 cm^3/g [f]	[f]OECD SIDS, 1998
2,3-DCB-1,3	> 5.5 mg/L**	1.1829 g/cm^3 @ 20°C [g]	2.85 kPa @ 10°C [g]	40.3 atm L/mol @ 25°C [b] *	2.5 [g]	N/A	[g]EC ECB, 2000 [b]Schwarzenbach *et al.*, 2003

*Calculated values for Henry's law constants using method outlined in Schwarzenbach et al., 2003, p. 206-207.
** Solubility data not available from literature, this is the aqueous concentration observed during laboratory experiments from this study. Actual solubility in water is expected to be higher than this value.

Table 2-1. List of chemicals used in laboratory experiments

Chemical	Provider	Stock Solution Conc. (in MeOH)	Additional notes
Trans-1,4-dichlorobutene-2 (1,4-DCB-2)	DuPont/Sirem	127197 mg/L 518.0 mg/L	Delivered as pure compound
3,4-dichlorobutene-1 (3,4-DCB-1)	Sigma Aldrich	346279.6 mg/L 515.8 mg/L	Delivered as pure compound
2,3,4-trichlorobutene-1 (2,3,4-TCB-1)	Dupont/Sirem	113864.5 mg/L 499.8 mg/L	Delivered as pure compound
2-chlorobutadiene-1,3 (Chloroprene)	Supelco	2000 mg/L 500 mg/L	Delivered as 2000 mg/L standard
1:1 (w/w) mixture of 2,3-dichlorobutadiene-1,3 (DCBD) and tetrachloroethene (PCE)	DuPont/Sirem	898.36 mg/L	Concentrations (mg/L) are same for ACR and PCE
1,3-butadiene (BD)	AccuStandard	2000 mg/L 500 mg/L	Delivered as 2000 mg/L standard
Mixture of gases including: Methane, ethane, ethyne, ethane, propane, iso-butane, n-butane, 1-butene	Praxair	n-butane: 14.4 mg/L* 1-butene: 15.9 mg/L*	Gas sample used as standards for n-butane and 1-butene
Mixture of gases including: 1,3-butadiene, n-butane, 1-butene, *cis*-2-butene, *trans*-2-butene, ethyl acetylene, isobutene, isobutylene	Scott Specialty Gases	*cis*- and *trans*-2-butene: 0.0478 mg/L*	Gas sample used as standards for *cis*-2-butene and *trans*-2-butene.
Calcium Carbonate (CaCO$_3$) powder	Sigma Aldrich	N/A	

Gaseous standard, the concentration noted is the theoretical aqueous concentration, see appendix A for details.

Table 2-2. Characteristics of columns used.

Column #	Composition (wt % iron)	Volume DI flushed (ml)	Measured Pore Volume (ml)	Bulk Density of Porous Media (g/cm^3)	Iron : Solution Ratio (wt/wt)	Iron Surface Area : Solution Volume Ratio (m^2/ml)
731	100%	2750	77.0	3.27	6.25	8.30
732	30%	1983	54.5	2.09	1.69	2.24
733	30%	807.1	57.2	2.10	1.62	2.16

Table 2-3. Column experiment details including number of sampling events, average starting concentrations, flow rates and total pore volumes. Note that the data presented here differs from that presented in Table 3-3 in the Results and Discussion section as this table summarizes average starting concentrations and flow rates from all sampling events where as Table 3-3 presents data from a specified pore volume.

Contaminant (starting material)	Column #	Number of Sampling Events	Average Starting Concentration (mg/L)	Average Flow Rate (ml/min)	Total Number of Pore Volumes
1,4-DCB-2	733	9	11 ± 1	0.82 ± 0.03	587
3,4-DCB-1	733	8	9.6 ± 0.9	0.87 ± 0.04	317
2,3,4-TCB-1*	732, 731	7, 8	13 ± 1, 10.9 ± 0.8	0.85 ± 0.03 , 0.103 ± 0.006	260, 95
Chloroprene	731	2	3.0 ± 0.2	0.109 ± 0.001	14
DCBD	731	4	1.66 ± 0.07	0.096 ± 0.004	68

*2,3,4-TCB-1 was conducted using a 30% iron column (732) to monitor the disappearance of the parent compound and the generation of 2-chloro-1,3-butadiene (chloroprene), an observed intermediate. The 100% iron column (731) was used to monitor the disappearance of the intermediate.

Table 3-1. Summary of batch experiment initial conditions and results.

Contaminant	DI or GW	Temp. (°C)	Starting Conc. (mg/L)	Duration of Experiment (h)	Pseudo-first-order $t_{1/2}$ (h)	Correlation coefficient (R^2)	% disappearance at end of exp.	Final Cl mass bal. (%)	Observed chlorinated int.'s
1,4-DCB-2*	DI	10	11.5	157	21.7	0.98	99.3	93	None
	GW	10	13.9	169	20.5	0.98	99.8	79	None
3,4-DCB-1	DI	10	9.6	198	11.3	1.00	99.8	84	None
	GW	10	9.3	155	14.8	0.99	>99.9	101	None
	DI	25	8.3	149	17.1	0.98	99.9	124	None
2,3,4-TCB-1	DI	10	9.2	193	16.5	0.92	99.9	79	Chloroprene
	GW	10	8.8	193	16.5	0.99	>99.9	87	Chloroprene
	GW	25	8.7	216	16.3	0.98	99.7	59	Chloroprene
Chloroprene	DI	10	11.2	297	377	0.66	47.5	52	None
	GW	25	8.5	218	233	0.67	56.0	102	None
DCBD	DI	10	5.5	251	187**	0.94**	80.9	16	None
	GW	25	2.8	242	114**	0.94**	87	19	None

Additional results for 1,4-DCB-2 from Gui and Noble are shown in Table 3-2.

**Used data points after 24h only*

Table 3-2. Previous results from L. Gui and W. Noble (2006)

		$t_{1/2}$ hours	$t_{1/2}$ days
Hydrolysis	10 C	1155	48.1
	25 C on bench top	59.8	2.5
	25 C in dark	59.2	2.5
Reduction, DI	with Connelly, 10 C	18.15	0.76
Reduction, simulated GW	with Connelly, 10 C	21.3	0.9

Table 3-3. Summary of column experiment conditions and results at the specified number of pore volumes.

Contaminant	Column % iron	Pore vel. (cm/s)	Total residence time (min)	# of Pore Volumes	Starting Conc. (mg/L)	Pseudo-first-order $t_{1/2}$ (min)	Correlation coefficient (R^2)	Final Cl mass bal. (%)	Observed chlorinated int.'s
1,4-DCB-2	30	7.18×10^{-3}	70	429	10.1	2.0	0.95	99	None
3,4-DCB-1	30	7.61×10^{-3}	72	317	9.6	0.74	0.95	102	None
2,3,4-TCB-1	30	7.81×10^{-3}	65	260	14.2	2.3	0.98	101	Chloroprene
Chloroprene*	100	6.71×10^{-4}	788	95	6.0**	15.4	1.00	102	None
		7.07×10^{-4}	706	109	2.9	12.3	0.99	103	None
DCBD	100	6.24×10^{-4}	793	52	1.7	23.7	0.98	70	None

Chloroprene column experiment was done initially as intermediate of 2,3,4-TCB-1 (95 pore volumes) then as initial contaminant (additional 14 pore volumes)

*** Calculated concentration assuming complete conversion of 2,3,4-TCB-1 to chloroprene*

Table 3-4. Observed and normalized pseudo-first-order degradation half lives from batch and column experiments.

Contaminant	Batch Experiments			Column Experiments		
	Iron surface area-to-solution ratio (m^2/ml)	Average Observed $t_{1/2}$ (min)	Average Normalized $t_{1/2}$ (min)*	Iron surface area-to-solution ratio (m^2/ml)	Observed $t_{1/2}$ (min)	Normalized $t_{1/2}$ (min)*
1,4-DCB-2	0.357	1270	452	2.16	2.0	4.3
3,4-DCB-1	0.357	864	308	2.16	0.74	1.6
2,3,4-TCB-1	0.357	986	352	2.24	2.3	5.2
Chloroprene	0.340	36600	12400	8.30	13.9	115
DCBD	0.340	18100	6140	8.30	23.7	197

* *Half-lives are normalized to a common iron surface area-to-solution ratio of 1 m^2/ml*

Table 3-5. Observed non-chlorinated intermediates and end products, final carbon mass balances and relevant observed and normalized pseudo-first-order degradation half-lives of contaminant degradation.

Contaminant	Observed non-chlorinated intermediates and end products	Final carbon mass bal. (%)	1,3-butadiene Observed $t_{1/2}$ (min)	1,3-butadiene Normalized $t_{1/2}$ (min)*	1-butene Observed $t_{1/2}$ (min)	1-butene Normalized $t_{1/2}$ (min)*
1,4-DCB-2	1,3-butadiene, 1-butene, *cis*-2-butene, *trans*-2-butene	93	136	294	-	-
3,4-DCB-1	1,3-butadiene, 1-butene, *cis*-2-butene, *trans*-2-butene	71	41.3	89.2	-	-
2,3,4-TCB-1/ Chloroprene	1,3-butadiene, 1-butene, *cis*-2-butene, *trans*-2-butene, n-butane	53	24.2	201	174	1442
DCBD	1-butene, *cis*-2-butene, *trans*-2-butene, n-butane	58	-	-	270	2241

Half-lives are normalized to a common iron surface area-to-solution ratio of 1 m^2/ml

8. Figures

a)

Dichlorobutene synthesis

1,3-butadiene   Chlorine   3,4-dichlorobutene-1   trans-1,4-dichlorobutene-2
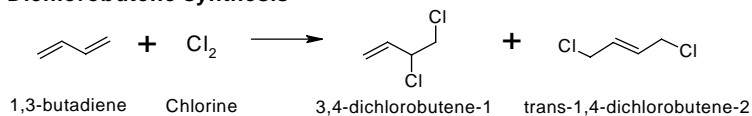
Dichlorobutene isomerization
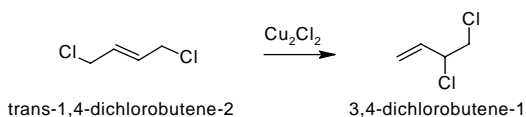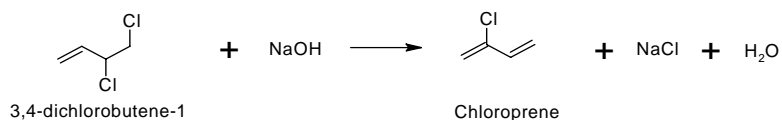
trans-1,4-dichlorobutene-2   3,4-dichlorobutene-1

Chloroprene synthesis

3,4-dichlorobutene-1   Chloroprene

b)

Dimerization of acetylene

Acetylene   Monovinylacetylene

Chloroprene synthesis

Monovinylacetylene   Chloroprene

c)

Hydrochlorination of chloroprene

Chloroprene   1,3-dichlorobutene-2   2,3,4-trichlorobutene-1
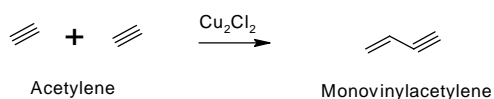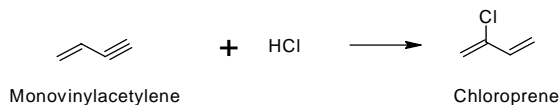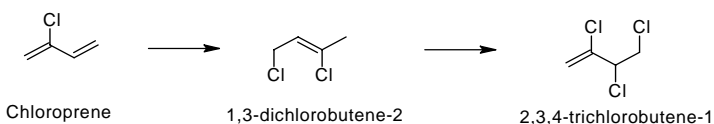
2,3-dichloro-1,3-butadiene Synthesis

2,3,4-trichlorobutene-1   2,3-dichlorobutadiene-1,3   Ammonium chloride
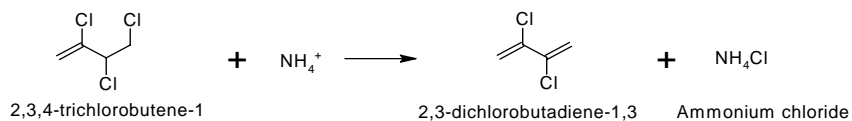
Figure 1-1. *a) Synthesis of chloroprene from 1,3-butadiene starting material. b) Synthesis of chloroprene from acetylene starting material. c) Synthesis of 2,3-dichlorobutadiene-1,3 comonomer.*
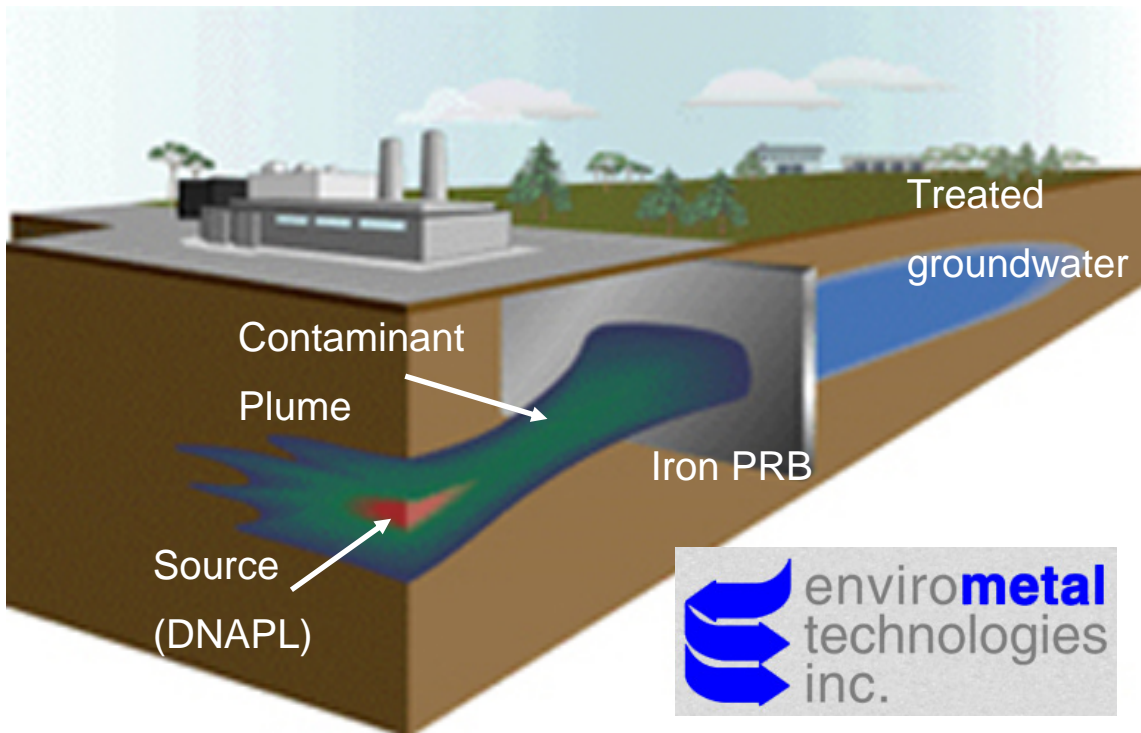
Figure 1-2. *Design of a granular iron permeable reactive barrier (PRB). Adapted from www.eti.ca*

a) Corrosion of iron and production of hydrogen
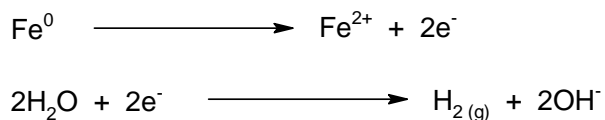
$$Fe^0 \longrightarrow Fe^{2+} + 2e^-$$

$$2H_2O + 2e^- \longrightarrow H_{2\,(g)} + 2OH^-$$

b) Hydrogenolysis

$$R_3C-Cl + H^+ + 2e^- \longrightarrow R_3C-H + Cl^-$$

c) β-elimination

$$R_2\overset{\overset{\textstyle Cl}{|}}{C}-\overset{\overset{\textstyle Cl}{|}}{C}R_2 + 2e^- \longrightarrow R_2C=CR_2 + 2Cl^-$$

OR

$$R\,\overset{\overset{\textstyle Cl}{|}}{C}=\overset{\overset{\textstyle Cl}{|}}{C}R + 2e^- \longrightarrow RC\equiv CR + 2Cl^-$$

d) α-elimination

1)
$$R_2-\overset{\overset{\textstyle Cl}{|}}{C}-Cl + 2e^- \longrightarrow R_2-C\text{:} + 2Cl^-$$
carbenoid
intermediate

2)
$$R_2-C\text{:} + 2e^- + 2H^+ \longrightarrow R_2-CH_2$$

e) Cataytic hydrogenation

$$RC\equiv CR + H_2 \xrightarrow{\text{Fe}} R\,\overset{\overset{\textstyle H}{|}}{C}=\overset{\overset{\textstyle H}{|}}{C}R$$

OR

$$R_2C=CR_2 + H_2 \xrightarrow{\text{Fe}} R_2\overset{\overset{\textstyle H}{|}}{C}-\overset{\overset{\textstyle H}{|}}{C}R_2$$
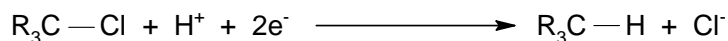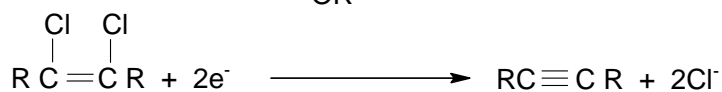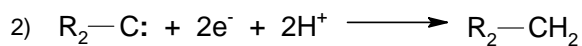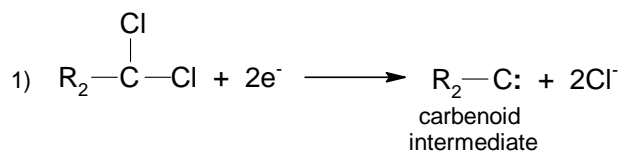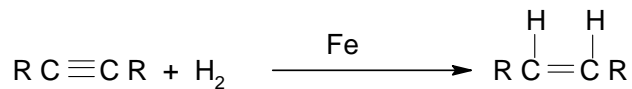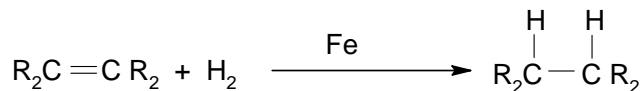
Figure 1-3. *a)Reaction of iron with water, b) pathways of reductive dechlorination via hydrogenolysis, c) reductive β-elimination, d)reductive α-elimination, and e) examples of catalytic hydrogenation.*
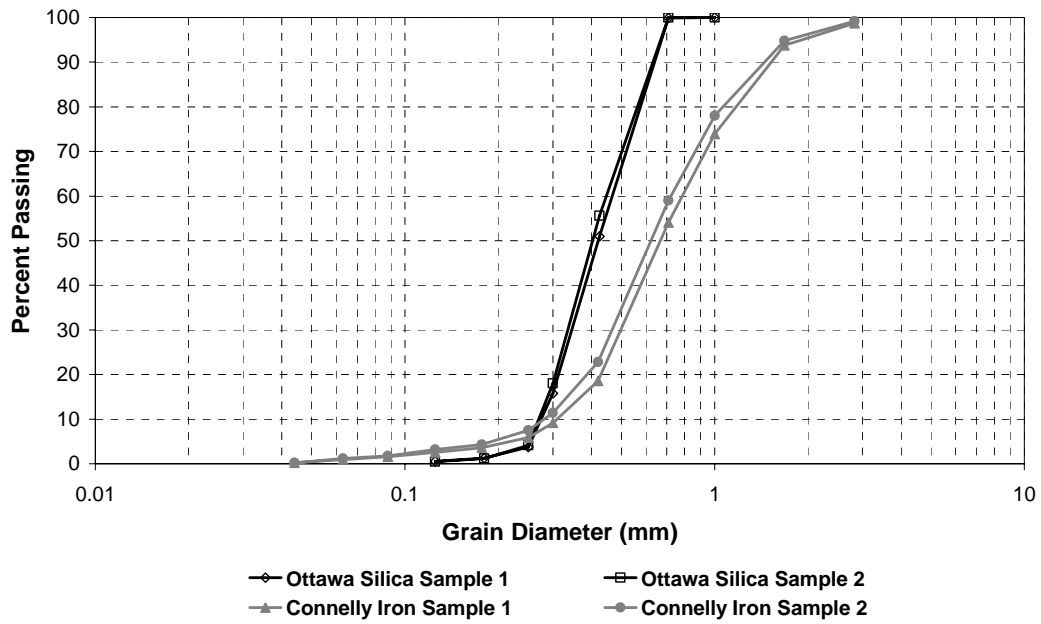
Figure 2-1. *Grain Size Distribution Curves for Ottawa Silica Sand and Connelly Iron CC-1004 (UW# 297)*
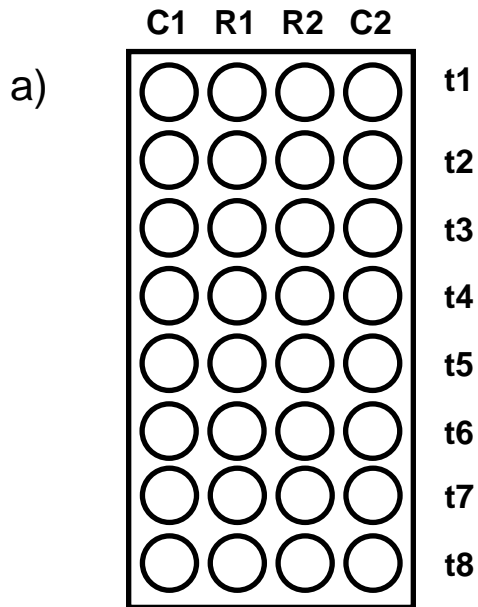
Figure 2-2. *Experimental set up for batch tests. a) The numbers t1, t2, etc. represent different sets of vials. Each set was analyzed at a different time during the experiment. The numbers C1 and C2 represent the contaminant control vials (contaminant solution only) and the chloride control vials (iron with uncontaminated solution) respectfully. The numbers R1 and R2 represent the reaction vials (iron with contaminant solution, done in duplicates). b) Shows a photograph of one set of vials from a batch test for chloroprene.*
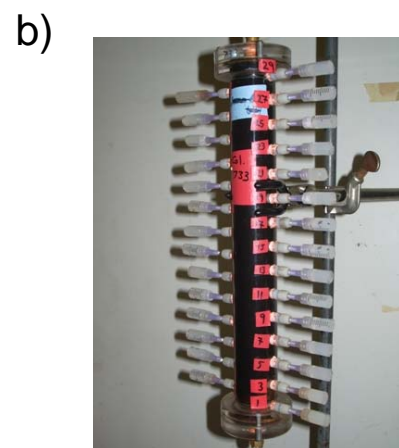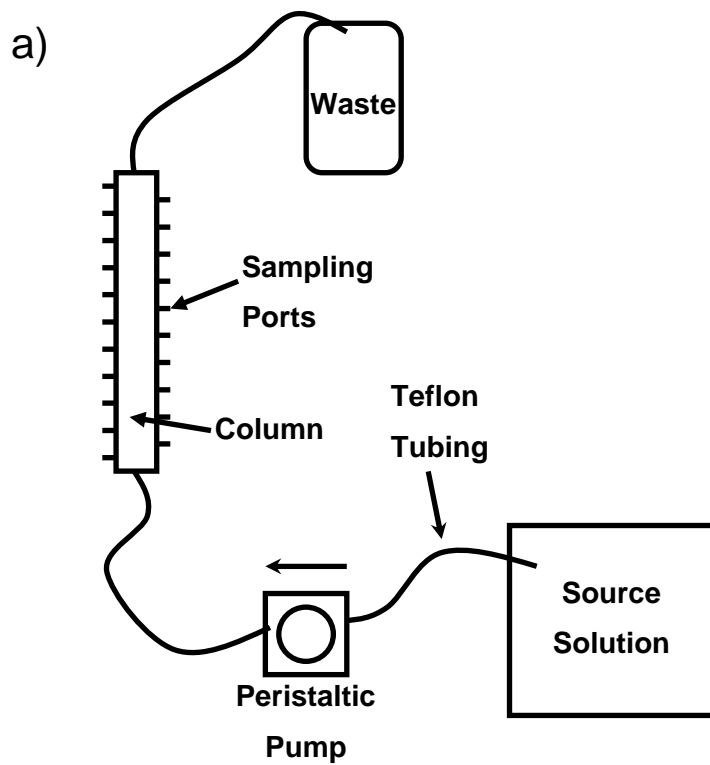
Figure 2-3. *a) Experimental set up for column experiments. b) Photograph showing operational column.*
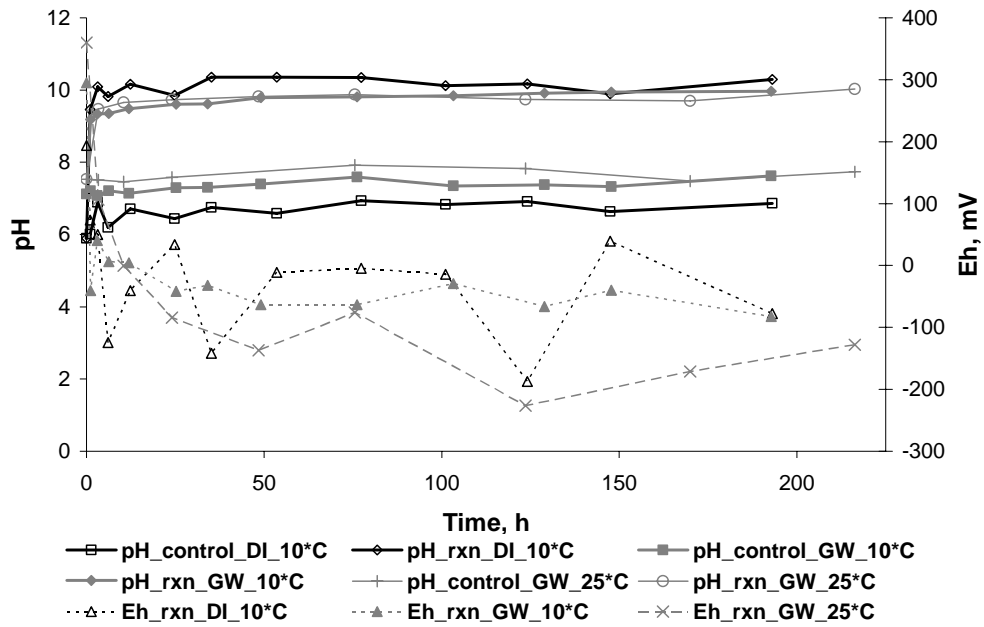
Figure 3-1. *pH and Eh profiles for 2,3,4-TCB-1 batch experiments. These profiles are representative to what was observed for all batch experiments.*
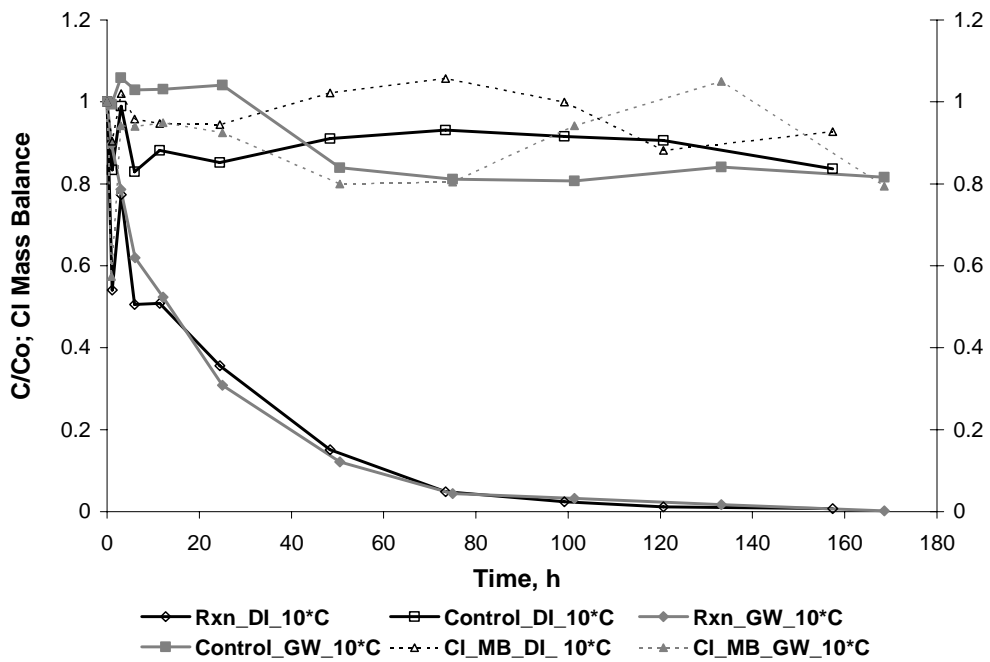

Figure 3-2. *Degradation profiles (Rxn), controls and Cl mass balances for 1,4-DCB-2 batch experiments at 10°C in DI water and 40 mg/L CaCO₃ (GW).*
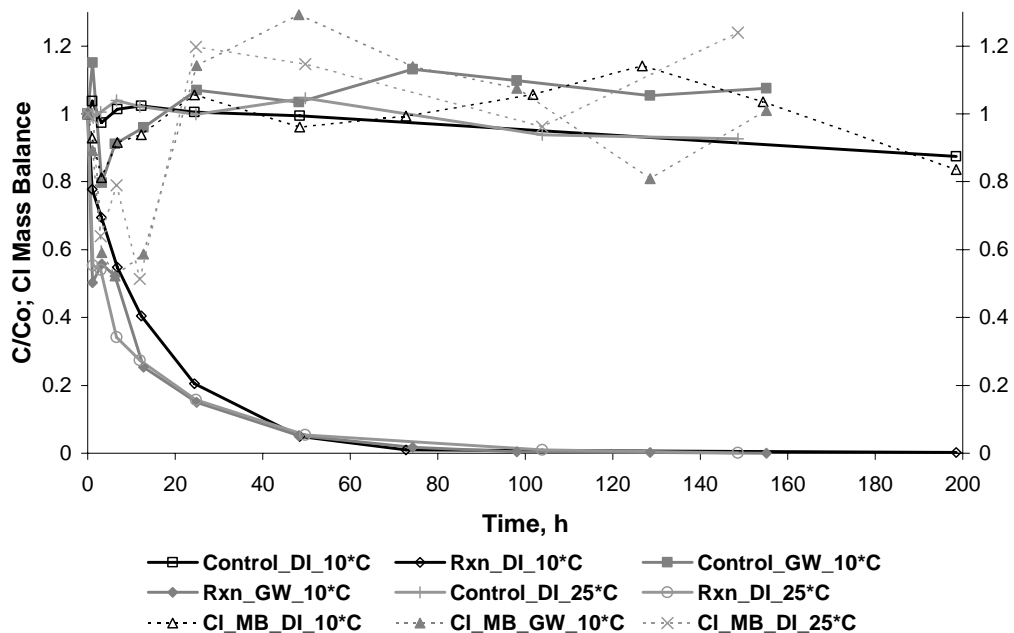
Figure 3-3. *Degradation profiles (rxn), controls and Cl mass balances for 3,4-DCB-1 batch experiments at 10°C in DI water and 40 mg/L CaCO₃ (GW), and at 25°C in DI water.*
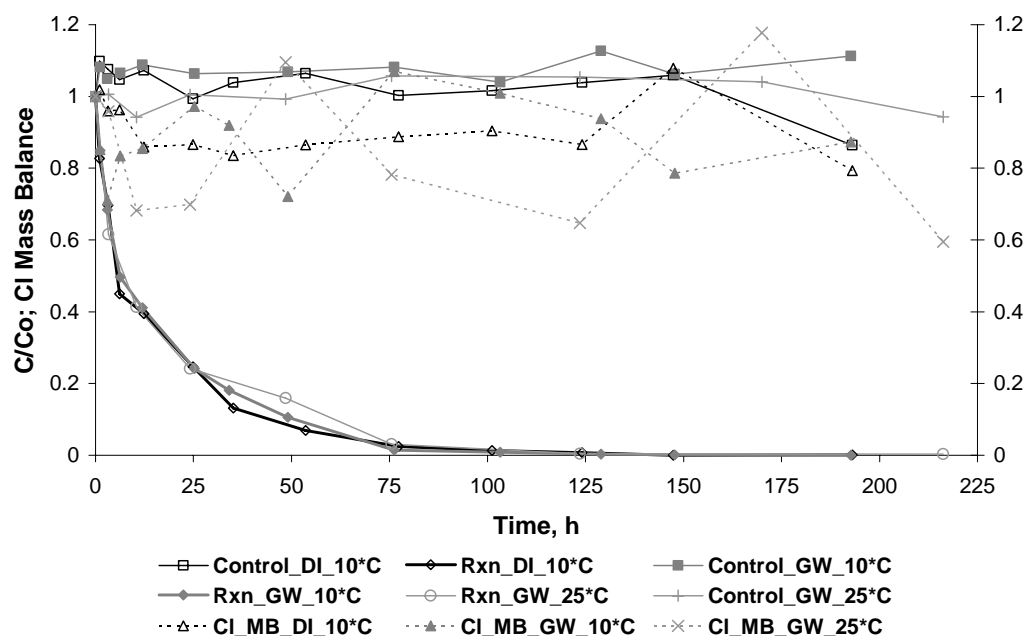

Figure 3-4. *Degradation profiles (rxn), controls and Cl mass balances for 2,3,4-TCB-1 batch experiments at 10°C in DI and 40 mg/L CaCO₃ (GW), and at 25°C in 40 mg/L CaCO₃ (GW).*
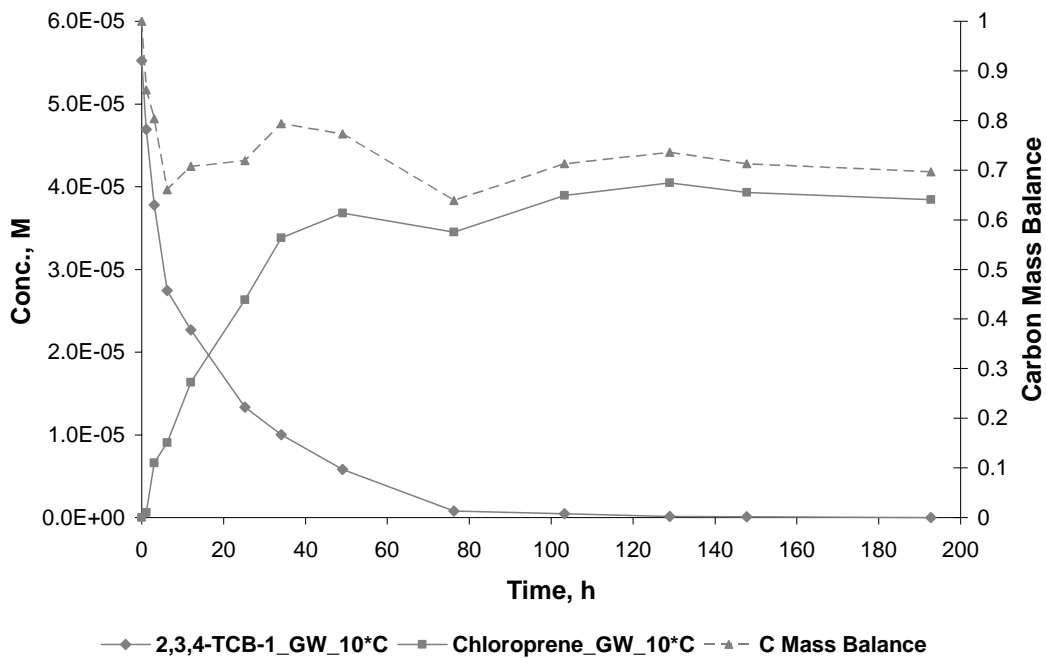
Figure 3-5. *Degradation of 2,3,4-TCB-1, generation of chloroprene intermediate and carbon mass balance for batch experiment at 10°C in GW.*
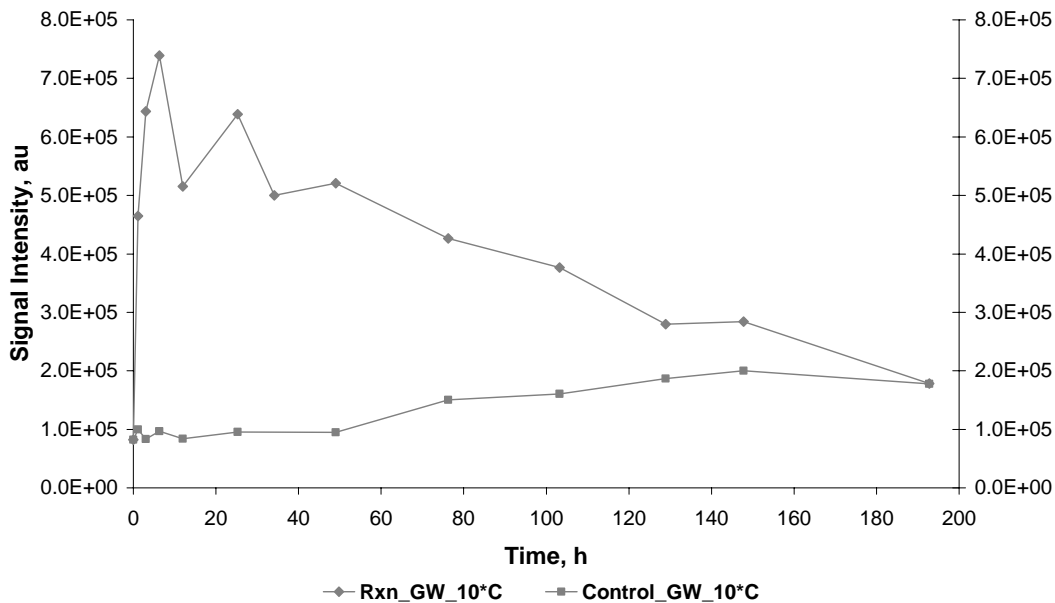
Figure 3-6. *Generation of an unidentified hydrolysis product of 2,3,4-TCB-1 present in reaction (rxn) and control vials for batch experiment at 10°C in GW.*
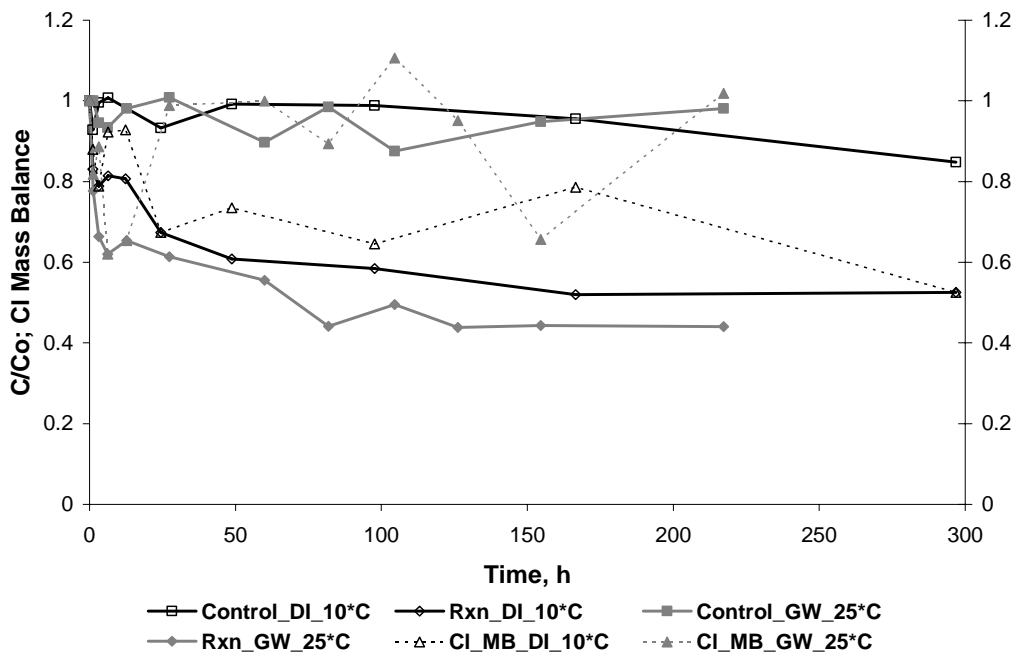
Figure 3-7. *Degradation profiles (rxn), controls and Cl mass balances for chloroprene batch experiments at 10°C in DI water and at 25°C in 40 mg/L CaCO₃ (GW).*
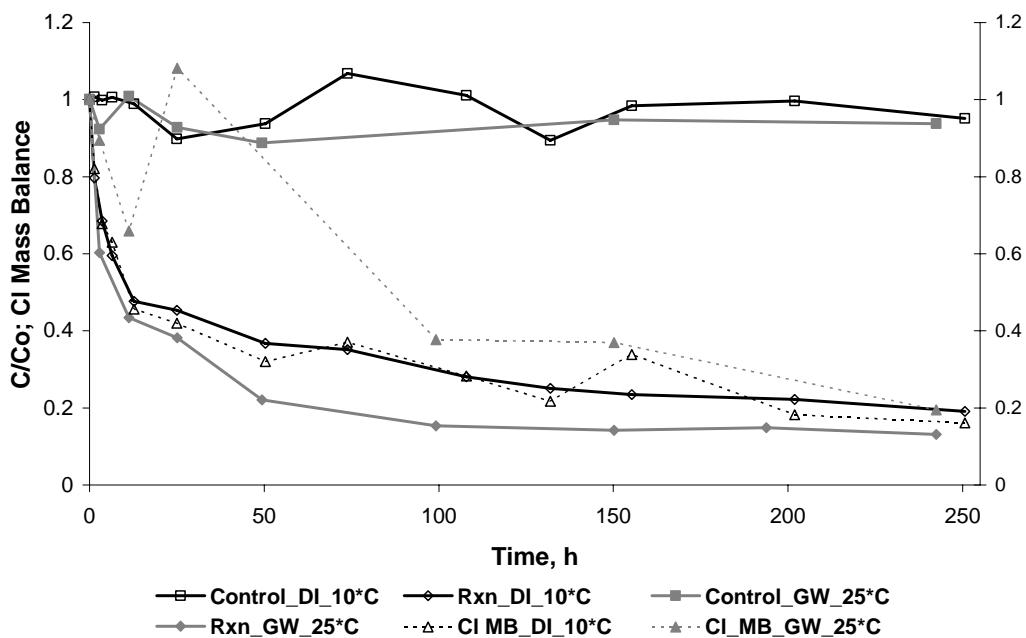
Figure 3-8. *Degradation profiles (rxn), controls and Cl mass balances for DCBD batch experiments at 10°C in DI water and at 25°C in 40 mg/L CaCO₃ (GW).*
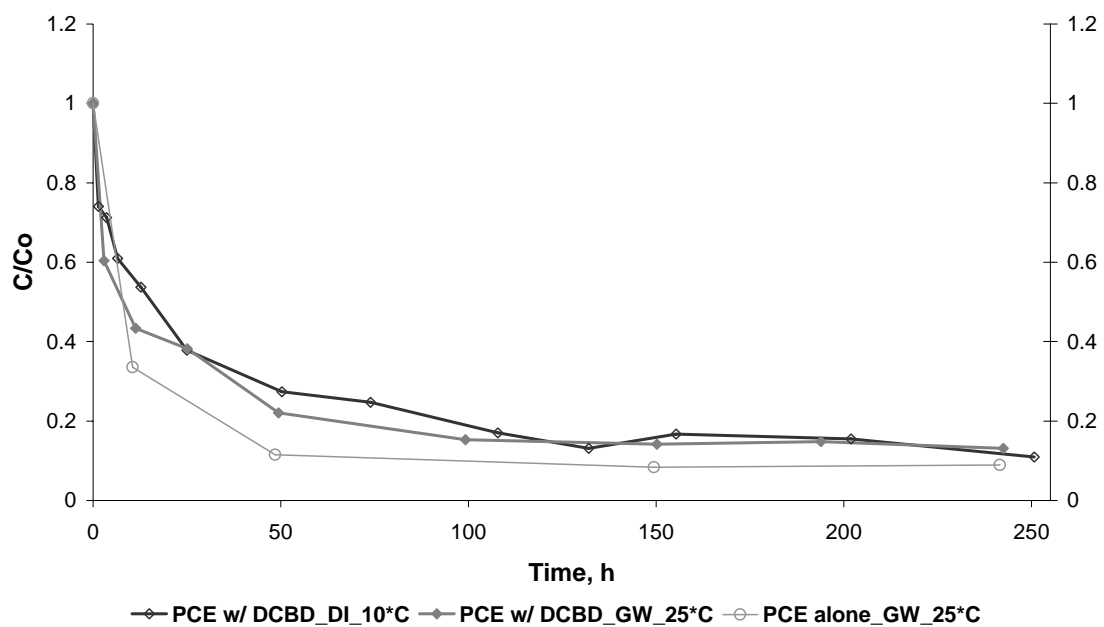
Figure 3-9. *Degradation of PCE in batch tests (10°C in DI and 25°C in GW) with DCBD and alone in a separate batch test (25°C in GW).*
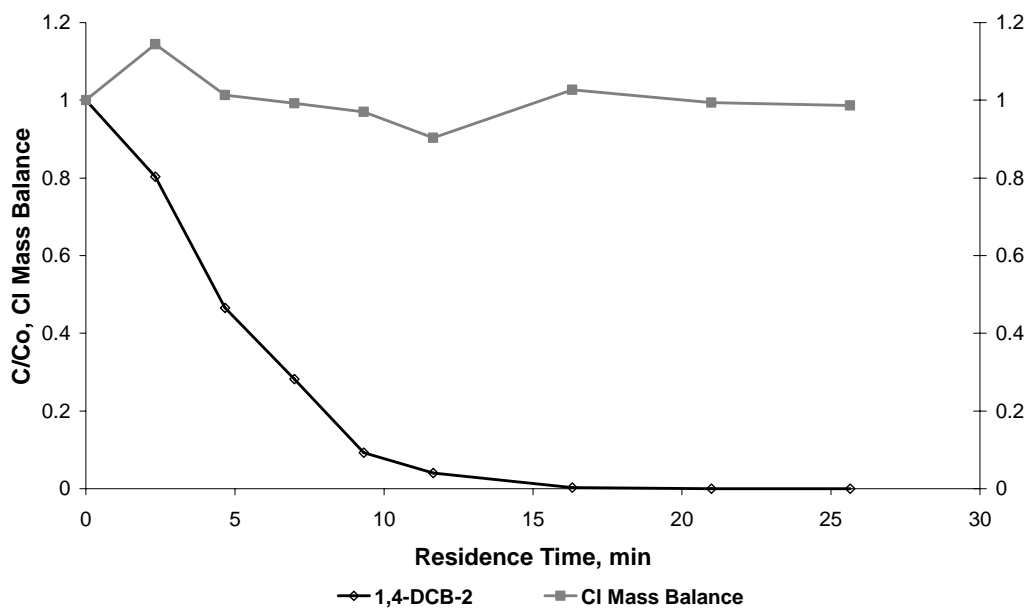
Figure 3-10. *Steady-state degradation profile and Cl mass balance for 1,4-DCB-2 column experiment at 429 pore volumes.*
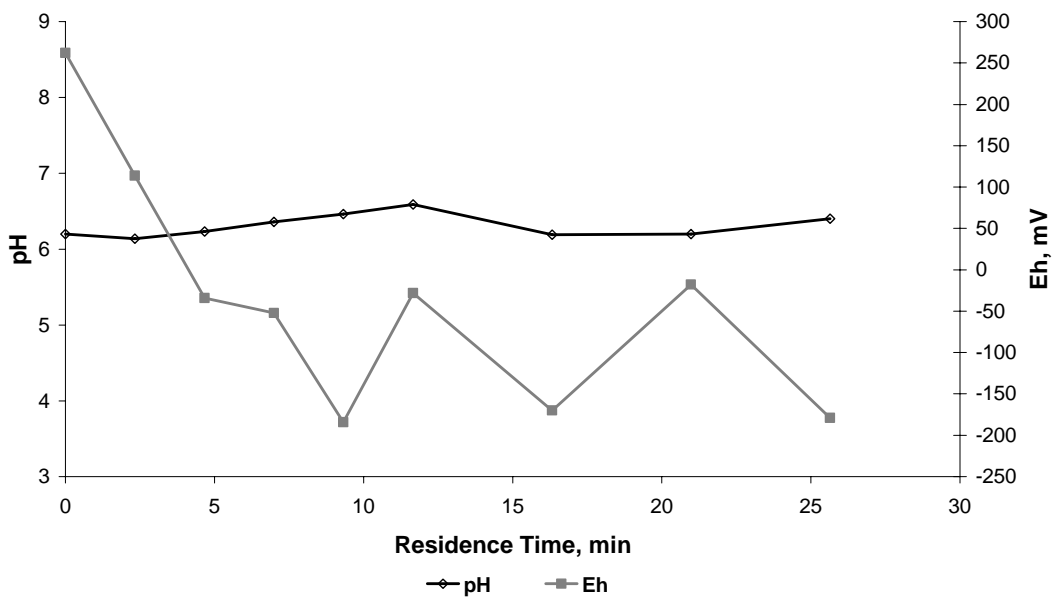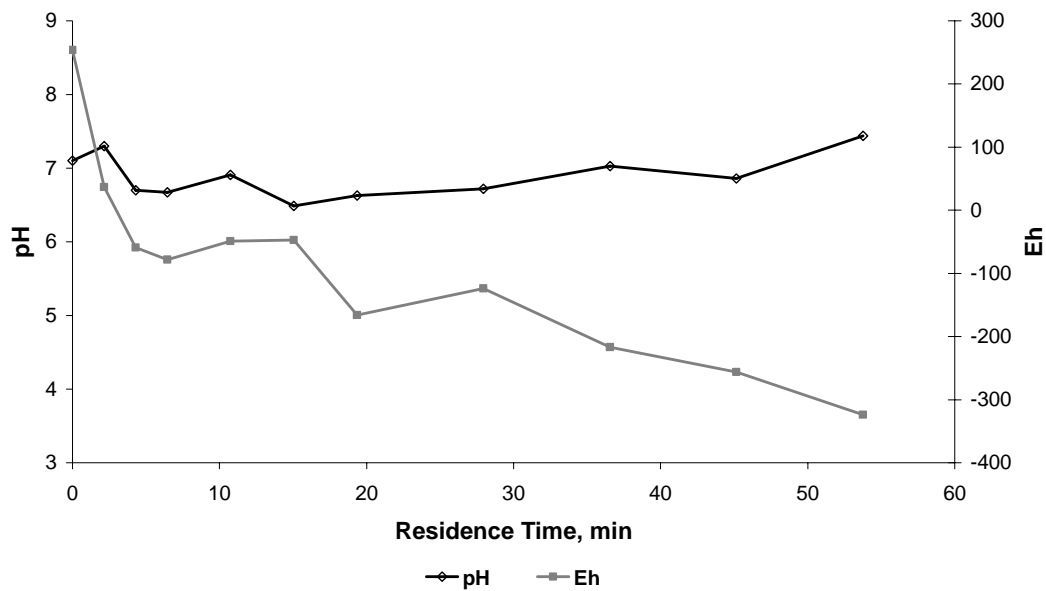

Figure 3-11. *pH and Eh profiles for 1,4-DCB-2 column experiment at 366 pore volumes.*
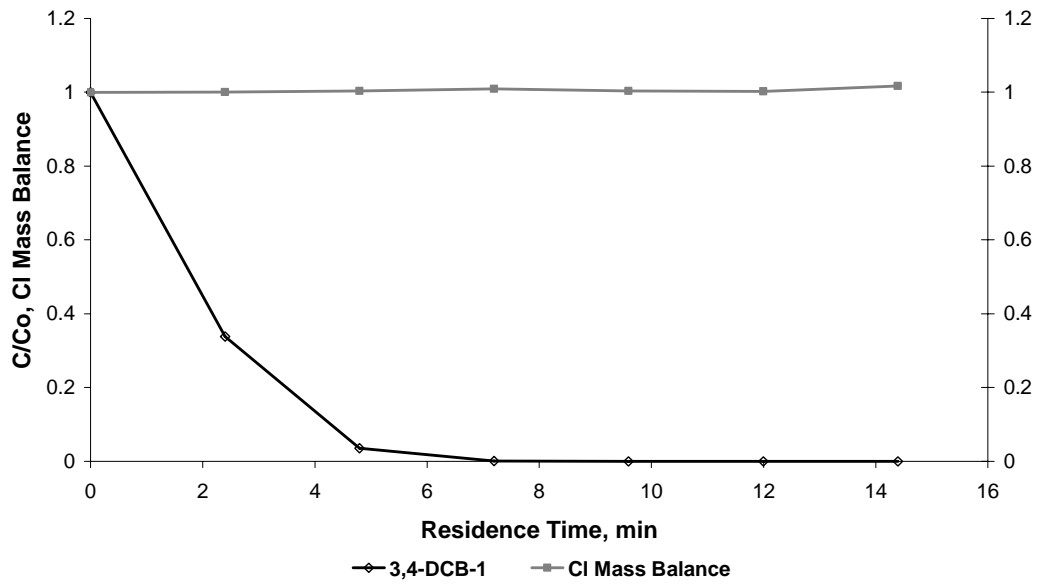
Figure 3-12. *Steady-state degradation profile and chlorine mass balance for 3,4-DCB-1 column experiment at 317 pore volumes.*
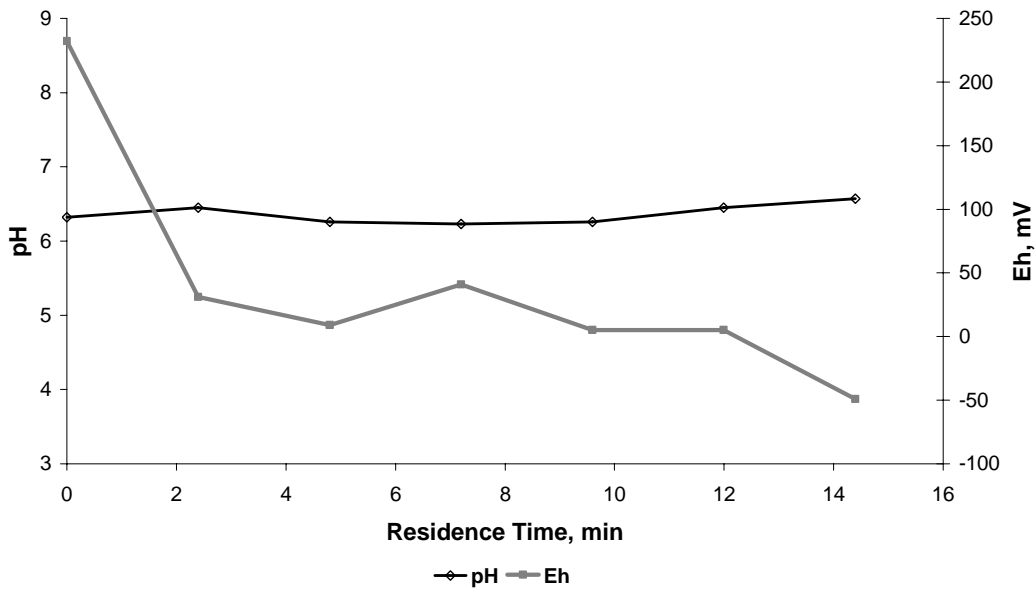
Figure 3-13. *pH and Eh profiles for 3,4-DCB-1 column experiment at 321 pore volumes.*
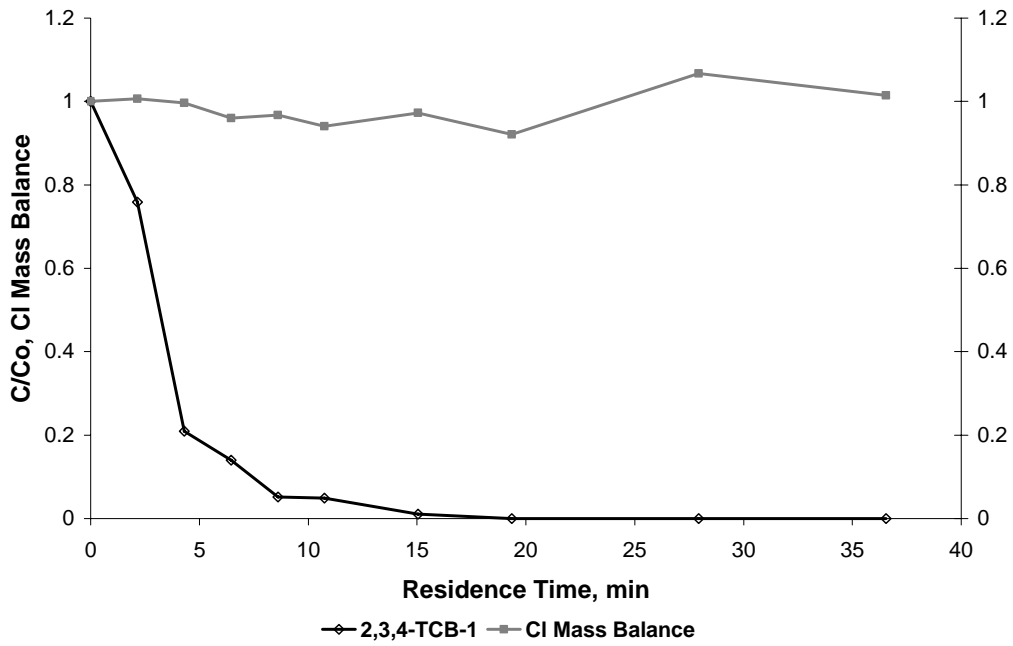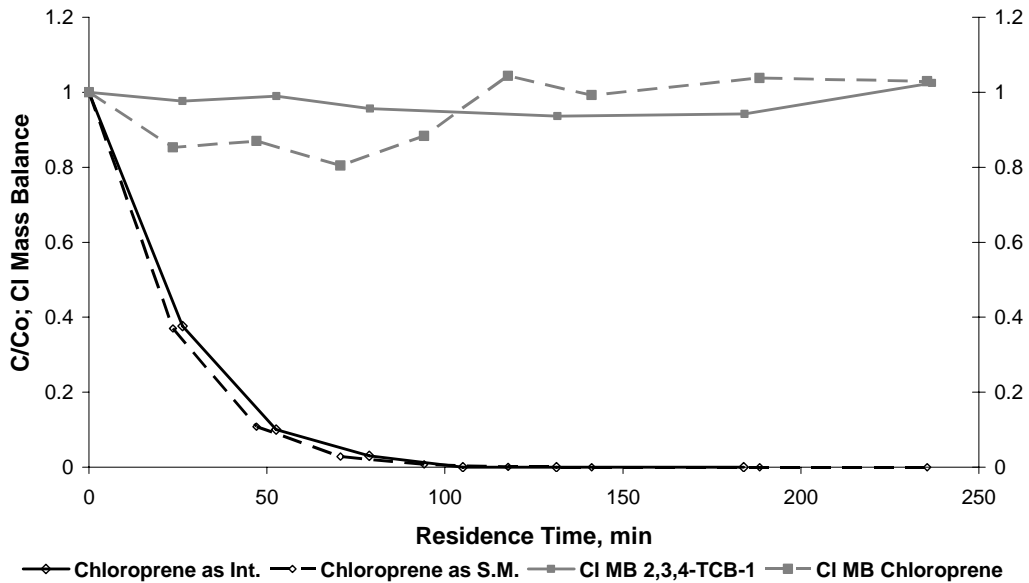
Figure 3-14. *Steady-state degradation profile and chlorine mass balance for 2,3,4-TCB-1 column experiment at 260 pore volumes.*
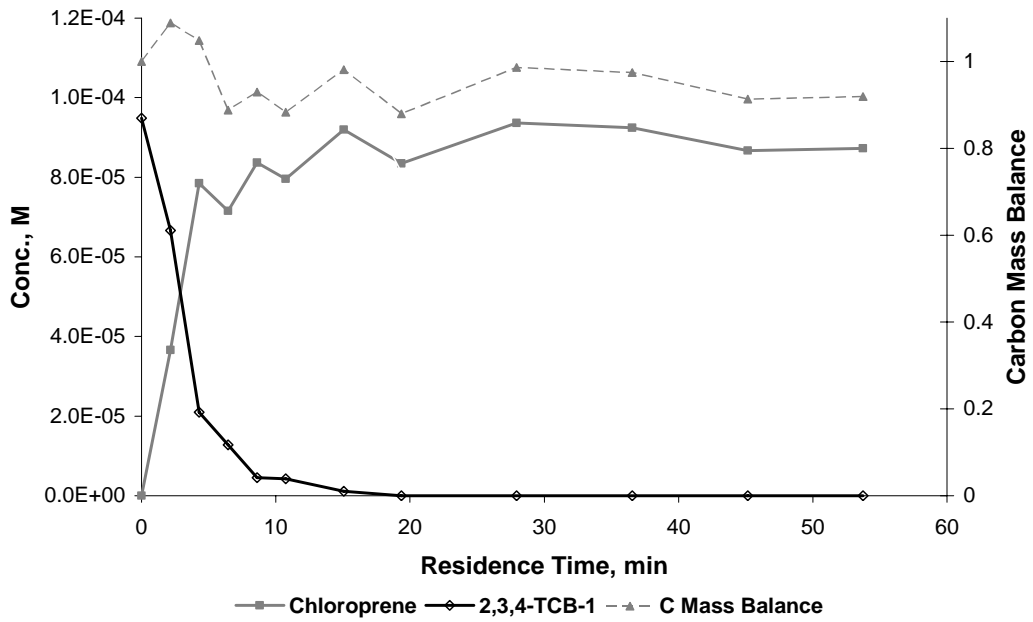

Figure 3-15. *Steady-state degradation of 2,3,4-TCB-1, generation of chloroprene intermediate and carbon mass balance at 260 pore volumes.*
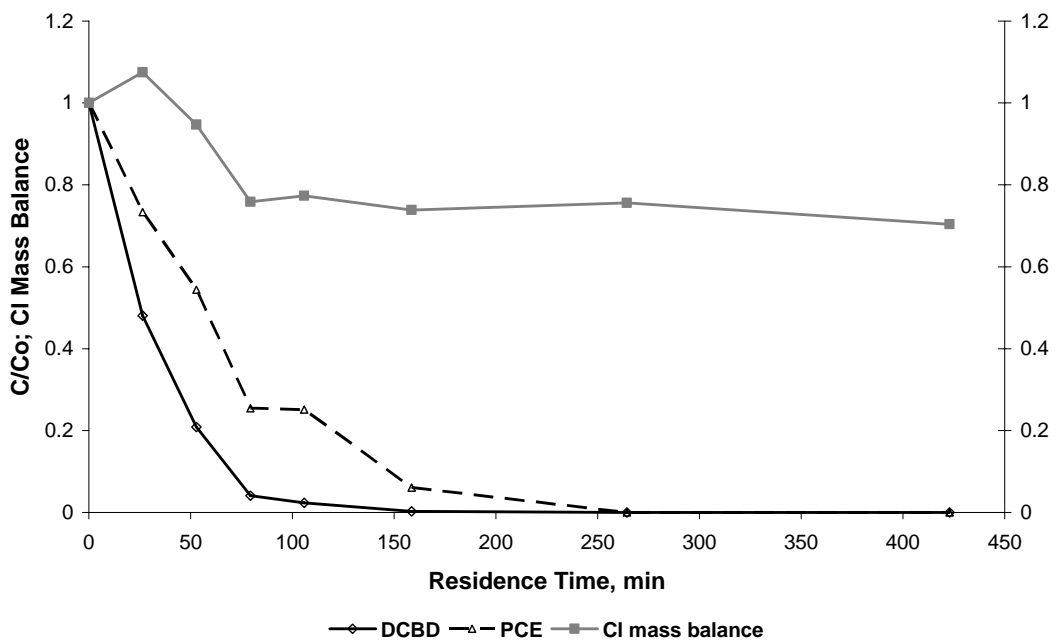
74

Figure 3-16. *pH and Eh profiles for 2,3,4-TCB-1 column experiment at 281 pore volumes.*


Figure 3-17. *Steady-state degradation profile and chlorine mass balance for chloroprene as an intermediate of 2,3,4-TCB-1 at 95 pore volumes and as the initial contaminant at 109 pore volumes.*
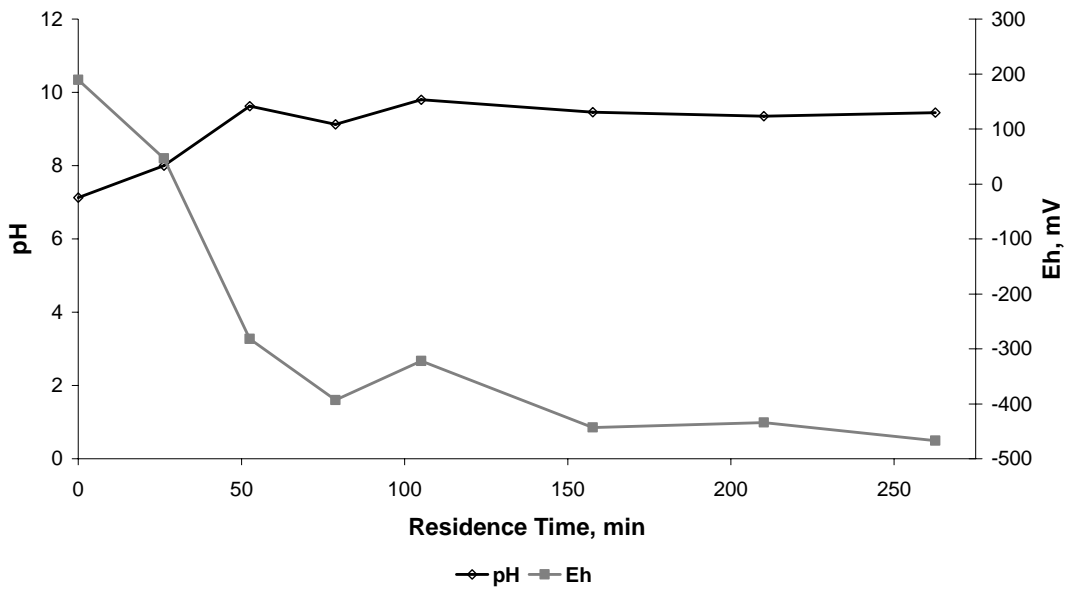
Figure 3-18. *pH and Eh profiles for the 2,3,4-TCB-1/chloroprene column experiment at 100 pore volumes.*

Figure 3-19. *Degradation profiles for DCBD and PCE and chlorine mass balance for the DCBD column experiment at 52 pore volumes.*
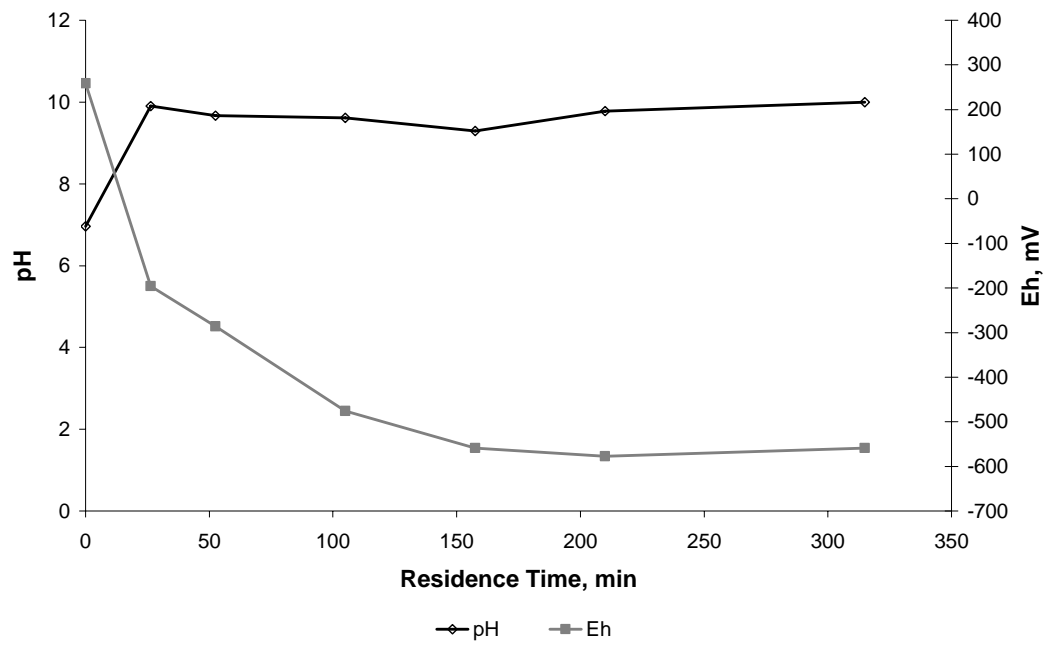
Figure 3-20. *pH and Eh profiles for the DCBD column experiment at 31 pore volumes.*
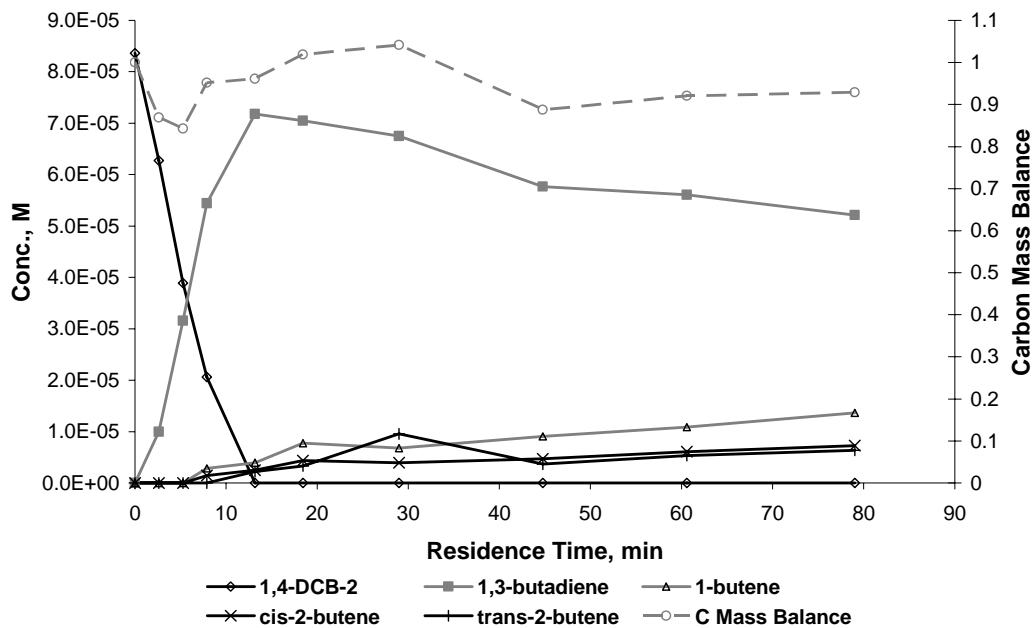
Figure 3-21. *End product profiles for the 1,4-DCB-2 column experiment.*
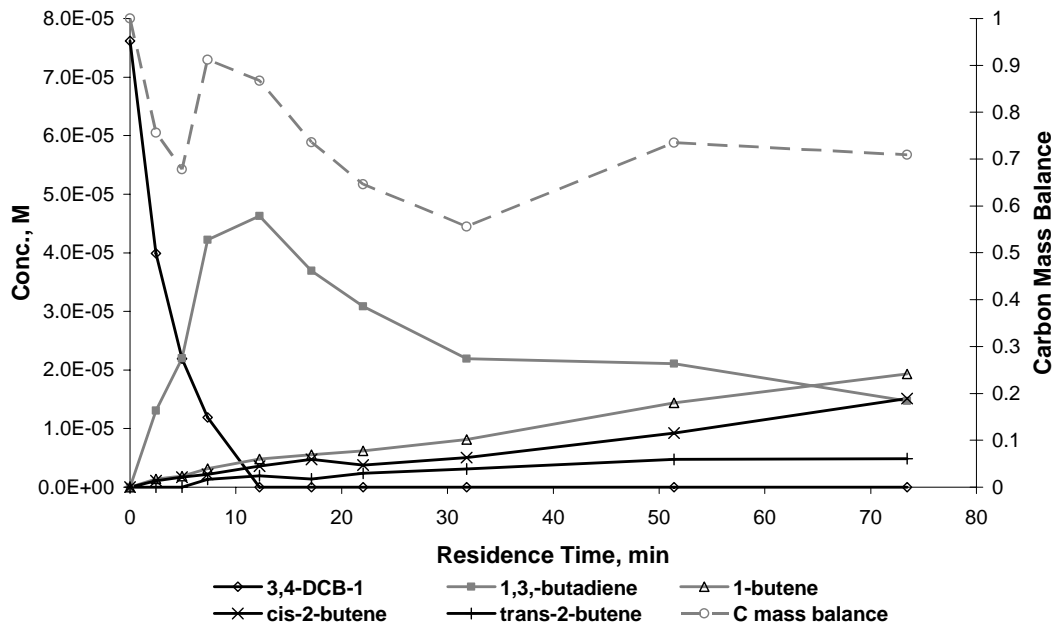

Figure 3-22. *End product profiles for the 3,4-DCB-1 column experiment.*
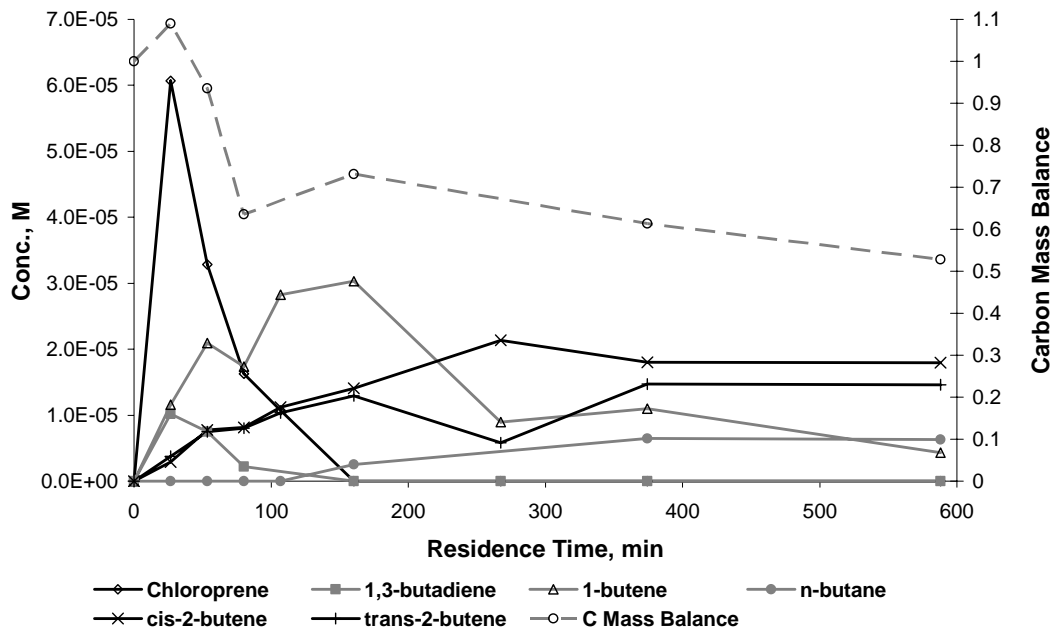
Figure 3-23. *End product profiles for the 2,3,4-TCB-1/chloroprene column experiment.*
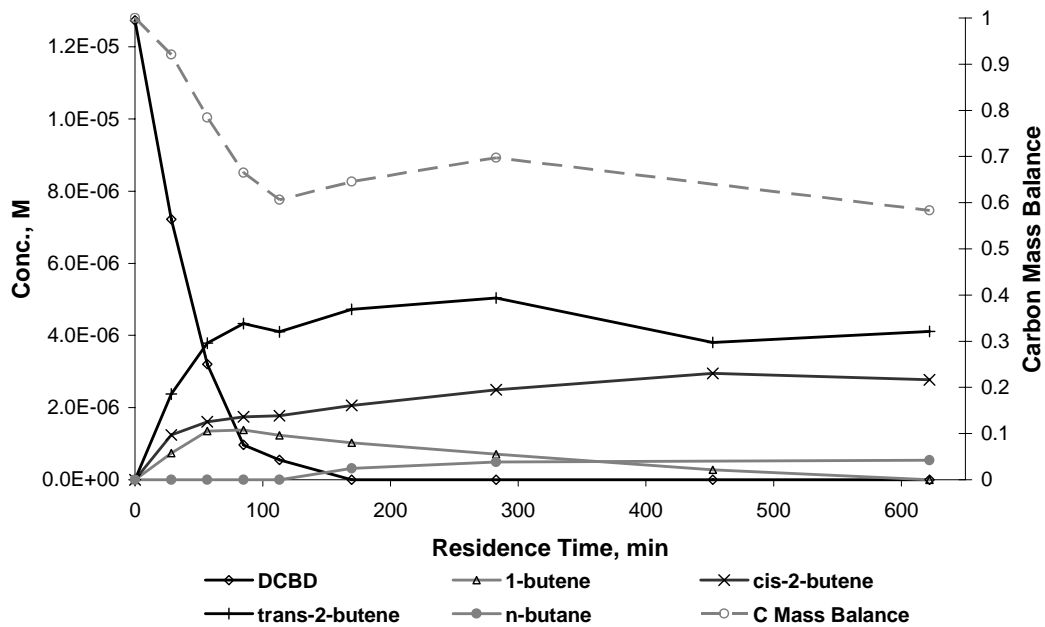

Figure 3-24. *End product profiles for DCBD column experiment.*
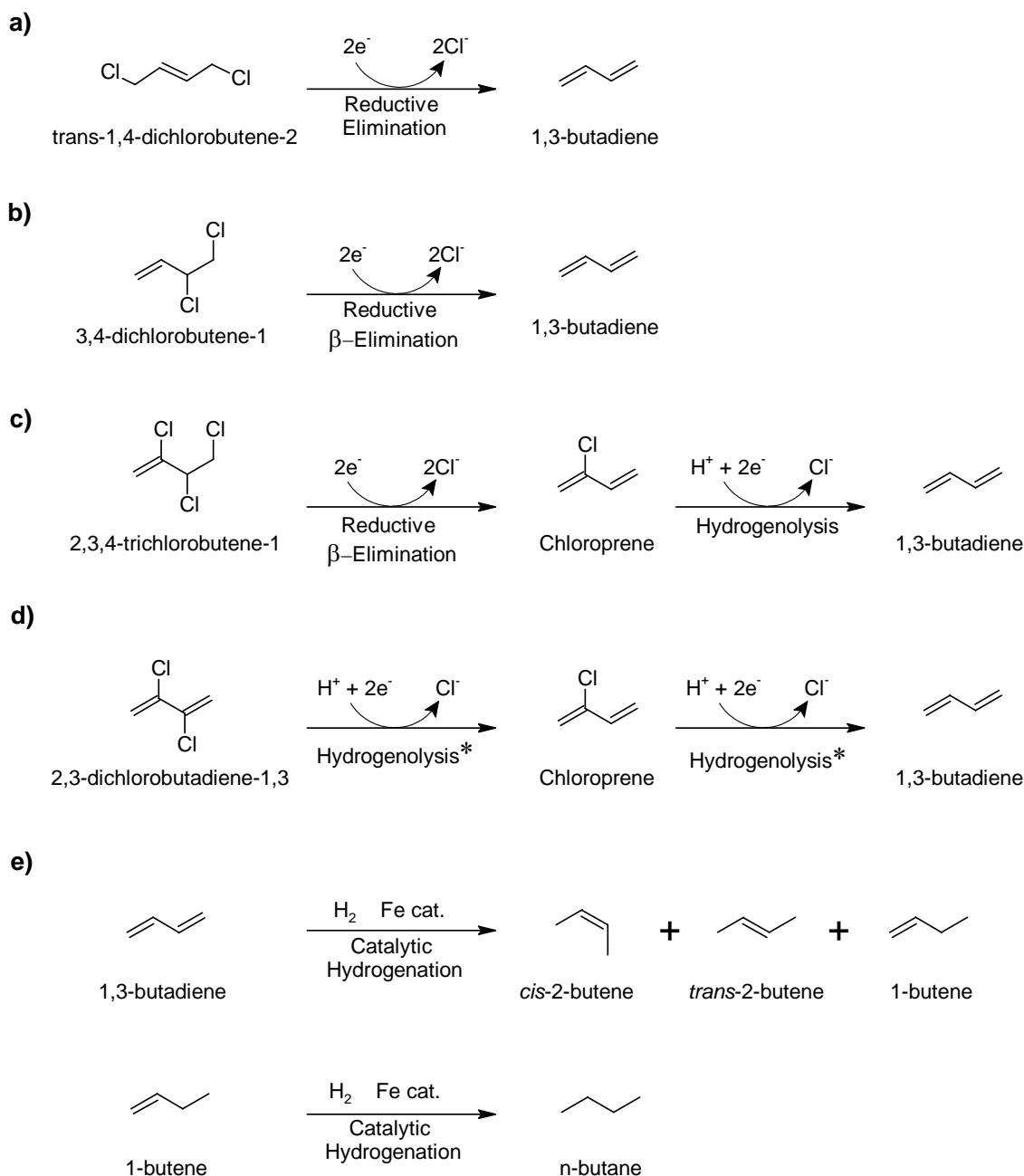
Figure 3-25. Proposed reaction pathways for the degradation of chlorinated aliphatics by granular iron. Each chlorinated compound reacts via reductive elimination (a), reductive β-elimination (b, c) and/or hydrogenolysis (c, d) to form 1,3-butadiene which reacts via catalytic hydrogenation (e) to form a mixture of *cis*-2-butene, *trans*-2-butene, 1-butene and n-butane.
* *These hydrogenolysis pathways are hypothesized since only trace chloroprene was observed and 1,3-butadiene was not observed in the column experiment.*

9. References

Agrawal, A., Tratnyek, P.G., 1996. Reduction of nitro-aromatic compounds by zero-valent iron metal. Environmental Science and Technology, 30: 153-160.

Arnold, W.A., Roberts, A.L., 2000. Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reactions with Fe(0) particles. Environmental Science and Technology, 34: 1794-1805.

ATSDR, 2006. Medicinal Management Guidelines for 1,3-butadiene. Agency for Toxic Substances and Disease Registry.

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