ABSTRACT

Long, Cameron Michael. ENHANCED REDUCTIVE DECHLORINATION IN EDIBLE OIL BARRIERS – EXPERIMENTAL AND MODELING RESULTS. (Under the direction of Dr. Robert C. Borden.)

Recent laboratory and field studies have shown that injection of edible, food-grade oils can provide an effective, low-cost approach for stimulating reductive dechlorination in the subsurface. A biologically active Permeable Reactive Barrier (PRB) can be installed by injecting emulsified edible oils through a line of conventional wells or direct push points. Over time, the oils are slowly hydrolyzed by naturally occurring bacteria providing a slow-steady release of long-chain fatty acids to enhance the anaerobic biodegradation of contaminants migrating through the barrier. The concerns of this study are the lifetime of the emulsified oil injected, the average hydraulic retention time (HRT) needed for complete dechlorination, permeability loss, and if the process can be modeled. All materials used in the process are Generally Recognized As Safe (GRAS), food-grade materials to aid in gaining regulatory approval. O&M costs are expected to be low since the oils are expected to last up to five years between injections.

In this project, we evaluated the performance of edible oil barriers for stimulating reductive dechlorination by monitoring the performance of four laboratory columns (10 cm dia. by 100 cm long) that were continuously fed simulated groundwater with dissolved perchloroethene (PCE). Column 1 was treated with emulsified soybean oil and received an influent feed containing dilute HCl to inhibit biological activity. Column 2 was treated with emulsified oil only. Column 3 was treated with emulsified oil and anaerobic digester sludge to evaluate the effect of excess methane production on barrier performance. Column 4 received an influent solution containing lactate and yeast extract

to evaluate the effect of soluble substrate addition on PCE degradation. All live columns were effective in stimulating reductive dechlorination of PCE. Complete conversion to ethene was enhanced by bioaugmenting the live columns with an enrichment culture of complete dechlorinators. Experimental results were then compared with numerical simulation results generated using the sequential first order decay module within the computer program RT3D to show if modeling the reductive dechlorination process was possible.

ENHANCED REDUCTIVE DECHLORINATION IN EDIBLE OIL BARRIERS – EXPERIMENTAL AND MODELING RESULTS

by

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BIOGRAPHY

My name is Cameron Long and I grew up in Durham, NC. I graduated high school from Southern Durham High School in 1998. I then decided to attend North Carolina State University to pursue a B.S. degree in Civil Engineering. I concentrated in Water Resources and upon graduation (May 2002) I decided to stay at NCSU to attain my Masters of Science degree form the Civil, Environmental, and Construction Management Engineering Department. My course requirements will be completed by May 21st to get my degree in Water Resources. Being from Durham I have always liked the area and that is why I have decided to take a job with Dewberry and Davis in their Raleigh office and stay in the area for a while longer. I'll start my new career as a Water Resources Specialist on June 1st 2004.

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1.0 INTRODUCTION

A variety of anaerobic bioremediation processes are being developed for the in-situ treatment of hazardous constituents including chlorinated solvents (tetrachloroethene [PCE] and trichloroethene [TCE]), perchlorate (ClO_3^-), chromate (CrO_4^{-2}) and oxidized radionuclides (TcO_4^-, UO_2^{+2}). Essentially all of these processes require that the contaminant be brought in contact with a biodegradable organic substrate. This substrate serves as a carbon source for cell growth and as an electron donor for energy generation.

1.1 Anaerobic Biodegradation of Chlorinated Solvent

Chlorinated ethenes such as tetrachloroethene (PCE) and trichloroethene (TCE) are some of the most abundant contaminants in groundwater (McCarty and EPA, 1993). These contaminants may be present as dense non-aqueous phase liquids (DNAPL) that cannot be effectively remediated using conventional technologies such as pump and treat systems. However, dissolved plumes and source zones can be anaerobically bioremediated (Bradley and Chapelle 1999). During this process, a carbon source is provided to generate an anaerobic environment conducive for reductive dechlorination. Under anaerobic conditions, the carbon source may then be fermented releasing hydrogen that can be used as an electron donor with chlorinated ethenes used as the electron acceptor. PCE is degraded first to TCE then to dichloroethene (DCE) followed by vinyl chloride (VC) and finally to ethene. Other degradation pathways may also exist for DCE and VC degradation including anaerobic oxidation and mineralization. Recently, Bradley and Chapelle (1999) have shown that ethene may be further degraded to methane. During reductive dechlorination of PCE, TCE, DCE, and VC the chlorine atoms are replaced by hydrogen. Typically, as chlorine is replaced with hydrogen, the compound provides less and less

energy to the microbes responsible for reduction. As a result, each daughter product becomes more difficult to degrade because less and less energy is produced from the process.

1.2 Anaerobic Bioremediation using Soluble Substrates

The Remedial Technologies Development Forum (RTDF) has completed a large-scale pilot study of anaerobic TCE bioremediation at a contaminated site on Dover Air Force Base (DAFB). In this project, lactate and a dechlorinating enrichment culture were flushed through the contaminated zone, resulting in complete conversion of TCE to ethene. This process is now being implemented at full scale to treat a highly contaminated source area at DAFB. While the RTDF demonstration was successful, there are a number of very important limitations to this approach.

- When an easily biodegradable, dissolved substrate is injected into a formation containing residual phase chlorinated solvents, contaminants immediately surrounding the injection well will be removed by both flushing and enhanced biodegradation. Over time, this will result in a 'clean' zone surrounding the injection well. To be effective, the dissolved substrate will have to pass through this clean zone to reach the contaminants. If the substrate is fermented to methane in the clean zone, it will be wasted and will not enhance the degradation of the chlorinated solvents. A similar problem has been observed when hydrogen peroxide (H_2O_2) is injected to treat petroleum-contaminated aquifers – most of the H_2O_2 decomposes in the first few feet after injection and never reaches the contaminated material.

- In many aquifers, the rate of cleanup is controlled by the rate of contaminant dissolution and transport by the mobile groundwater. Chlorinated solvents are often present as Dense Non-

aqueous phase liquids (DNAPLs) with very slow dissolution rates. If the substrate is supplied more rapidly than the NAPL dissolves, it will be wasted and will not increase the cleanup rate.

- Continuously feeding a soluble, easily biodegradable substrate can be expensive. There is a significant initial capital cost associated with installation of the required tanks, pumps, mixers, injection and pumping wells, and related process controls. In addition, operation and maintenance costs are high because of problems associated clogging of pumps, piping, and mixers and the labor for extensive monitoring and process control.

1.3 Anaerobic Bioremediation using Low Solubility Substrates

To overcome some of the problems described above, investigators have examined the use a variety of low solubility or insoluble organic substrates. These substrates range from bark mulch, compost, peat, a commercially available polymerized lactate ester (Hydrogen Release Compound or HRC®) and a variety of food-grade edible oils. In the project, we focus on the use of edible oil emulsions to provide an easy to inject slow release carbon source. Emulsified oils can be injected using wells. When properly spaced, these wells can create a permeable reactive barrier (PRB) providing carbon, and creating an anaerobic environment to promote reductive dechlorination. As contaminated groundwater flows through the PRB, microbes will use the organic carbon to enhance the degradation of chlorinated ethenes. If successful, this approach should have major operational and cost advantages over other remediation processes.

A number of important questions need to be resolved prior to wide spread application of the emulsified oil bioremediation process including the following.

1. Will biomass growth and/or gas production result in excessive permeability loss?

2. How much organic carbon is needed for "clean up" at a site and how frequently must additional substrate be added to maintain efficient biodegradation?

3. Is bioaugmentation needed to achieve complete dechlorination of PCE to non-toxic end-products such as ethene?

4. What hydraulic residence time (HRT) is required to achieve the desired level of treatment?

5. Can the reductive dechlorination process in edible oil barriers be adequately simulated using currently available models?

1.4 Project Objectives

In this project, we are evaluating the use of emulsified edible oil for enhancing the anaerobic biodegradation of PCE in flow through columns. The oils are intended to slowly biodegrade over time, enhancing the biodegradation / immobilization of groundwater contaminants.

Objective 1 Evaluate the efficacy of emulsified edible oils for enhancing the anaerobic biodegradation of PCE in continuous flow column experiments.

Objective 2 Identify issues that may enhance or limit the successful degradation of chlorinated solvents using the emulsified oil process.

Objective 3 Estimate the time period that a single injection of edible oil emulsions will support contaminant biodegradation.

Objective 4 Monitor permeability changes in laboratory columns with time to determine if permeability loss due to biological activity can be expected to limit field scale performance.

Objective 5 Evaluate the use of the sequential 1st order decay module in RT3D for simulating reductive dechlorination in edible oil barriers.

2.0 EXPERIMENTAL DESIGN

To accomplish the project objectives, continuous up-flow columns were packed with fine clayey sand, treated with emulsified soybean oil, and operated with a continuous feed of dissolved PCE for 435 days. Measurements were also taken to track carbon usage, permeability changes over time, and tetrachloroethene (PCE) biodegradation.

The continuous flow laboratory column experiments were established in August 2002. The columns were 10.475 cm in diameter by 100 cm long and were packed with fine clay sand from a local quarry. Figure 1 shows a photograph of the columns. All of the columns were operated in a continuous flow mode at an average flow rate of 100 - 150 mL/d which is equivalent to a groundwater velocity of ~3-4 cm/d. The influent to each column was amended with 15-20 mg/L PCE. Four columns were operated in parallel for 435 days.

(1) Column 1 was operated as a biologically inhibited control. The influent to this column was a 100 mg/L $CaCl_2$ solution amended with HCl to reduce the pH to less than 3 inhibiting biological activity.

(2) Column 2 was designed to represent in situ conditions in a typical aquifer. During packing, the field sand was amended with 250 mL of bioaugmentation culture enriched from a site in Lumberton, NC. The influent to this column was a 100 mg/L $CaCl_2$ solution.

(3) Column 3 was designed to represent in situ conditions in an aquifer with an active methanogenic population. During packing, the sediment was amended with 250 mL of the Lumberton bioaugmentation culture and 300 mL of anaerobic digester sludge. The influent to this column was a 100 mg/L $CaCl_2$ solution.

(4) Column 4 was operated to represent a soluble substrate bioremediation process. During packing, the sediment was amended with 250 mL of the Lumberton bioaugmentation culture and 300 mL of anaerobic digester sludge. The influent to this column was a 100 mg/L $CaCl_2$ solution amended with 2000 mg/L sodium lactate and 1000 mg/L yeast extract.

Figure 1: Photograph of 10 cm by 100 cm long continuous flow columns.

3.0 METHODS

3.1 Column Construction and Operation

Columns were packed with two inches of washed concrete sand at the bottom, followed by clayey field sand, and finally topped off with another two inches of concrete sand. The column packing took place under saturated conditions. Two to three inches of 100 mg/L deaired $CaCl_2$ solution was maintained above the sediment surface during column packing to reduce

entrapment of air bubbles in the column and reduce oxygen exposure. Anaerobic digester sludge was also added to columns 3 and 4 to evaluate the effects of a large methanogenic population on reductive dechlorination.

Following packing, the columns were mounted in a constant temperature room maintained at 21^{o} C. The influent feed to each column was a 100 mg/L $CaCl_2$ solution containing 2 – 4 mg/L of dissolved oxygen. This influent was designed to represent aerobic groundwater flowing into an edible oil barrier in the field. A 1-100 RPM Masterflex pump along with L/S 13 Masterflex tubing was used to inject the influent. Gasbags were set up on the influent reservoirs and effluent collection to reduce oxygen exposure and collect any volatile organic chemicals (VOCs) released during the process.

Column operation started on September 16, 2002 (Day 0). Shortly after start up, all of the columns were switched over to an influent solution containing 2000 mg/L lactate and 1000 mg/L yeast extract for 18 days to establish anaerobic conditions. On day 17, 250 mL of Lumberton bioaugmentation culture was injected through the column inlet to enhance anaerobic biodegradation. On day 18, the attached pumps were then used to inject 500 mL of oil-water emulsion. The 10% oil-water emulsion was prepared using a dairy homogenizer and included the addition of polysorbate 80 and GMO. At the time of the emulsion injection 1000 mg/L yeast extract was also added to the emulsion and the continuous lactate / yeast extract feed was discontinued. The emulsion injection took place over a 5 hr time period and then the columns were shut down to allow the oil to sorb to the sediment inside the column. Column operation resumed on October 7, 2002 (Day 21) after a 3 day shut down period with the influent reservoirs for each column now amended with a mixture of pure PCE and hexadecane designed to maintain

an influent concentration of 15 - 20 mg/L PCE. The influent for column 1 was also amended with HCl to inhibit biological activity by lowering the pH. Column 4 influent was amended with sodium lactate (2000 mg/L) and yeast extract (1000 mg/L). Columns 2, 3, and 4 received a second bioaugmentation on day 123 by pumping 250 mL of Lumberton bioaugmentation into the column inlet. The first and second bioaugmentation consisted of 250 mL of Lumberton culture. Between day 252 and 268, a third bioaugmentation treatment consisting of feeding 400 mg/L yeast extract for 16 days followed by addition of 375 mL of Lumberton bioaugmentation culture for columns 2 and 3 by injecting through the inlet.

The influent and effluent from each column were regularly monitored for tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE) isomers, and vinyl chloride (VC), oxygen, methane, ethene, ethane, pH, organic carbon, total carbon, chloride, nitrate, acetate, bromide, and sulfate. Sampling frequency was weekly for the first 112 days and then every other week for the remainder of the experiment. During sampling, the pumps were turned up to increase the flow rate so that a 10 mL sample could be taken in 5 – 10 minutes. Syringes (10 mL) were attached to inlet, outlet, and side sampling ports. The side sampling ports were sampled monthly after day 224. When only the outlet and inlet were sampled, a total of 40 mL per column (2 syringes from each sample port) were collected. When all ports were sampled a total of 100 mL were collected. Samples for VOC analysis were collected by injecting 2 mL of sample below the water surface of a partially filled 40 mL vial and then topping the vial off with D.I. water. The 40 mL vial was then analyzed for chlorinated solvents (PCE, TCE, and DCE isomers) by standard method 6200C (Purge and Trap Capillary Column Gas Chromatography). Another 5 mL was injected into a 10 mL vial and then the sample head space was analyzed by gas chromatography for VC, methane, ethene, and ethane. An additional 2 mL was injected in a

TOC vial capped and stored in a refrigerator until analyzed for total organic carbon and inorganic carbon. An Orion pH meter was used to measure the pH in a 5 mL sample from the second syringe. Finally, dissolved oxygen was monitored using Chemetrics 0-1 mg/L D.O. test kits. Samples (5 mL) were collected monthly, mixed with sodium bicarbonate eluent, allowed to sit over night to precipitate iron, filtered, and analyzed by ion chromatography following Standard Method 4110B for chloride, nitrate, acetate, bromide, and sulfate (Standard Methods 19th Edition, 1995).

3.2 Bromide Tracer Test

A bromide tracer test was performed to monitor breakthrough of a non-reactive tracer and estimate the hydraulic retention time of each column. A syringe pump was spliced into the influent of each column just before the inlet, allowing us to amend the influent solution with a 4000 mg/L bromide solution. Carefully recorded dates and volumes pumped, from both the syringe pump and influent reservoir, allowed the influent concentration of bromide to be calculated over the length of the test. During the bromide test, 5 mL samples were taken weekly and analyzed for bromide by ion chromatography.

3.3 Gas Production

The composition of gas released from columns 2, 3, and 4 were determined by attaching a 1 mL airtight glass syringe to gas sample ports located at the top of the columns. After collection, a 0.4 mL gas sample was injected into a GOW MAC gas chromatograph equipped with a thermal conductive detector and analyzed for carbon dioxide, methane, oxygen, and nitrogen. Gas

composition was monitored on two separate occasions and similar results were found. Total gas production was tracked by attaching a 5 mL syringe to the sample port and measuring the volume of gas trapped since the previous sampling event.

3.4 Sediment Analysis

At the end of the project, the columns were shutdown and drained for 4 days. The sediment in each column was then sampled for total carbon, PCE, TCE, DCE isomers, and VC by driving two 1 inch diameter steel tubes through the length of the column. The tubes were then extracted, the ends plugged with rubber stoppers, and stored in a cold room for 5 days. The tubes were then cut into 10 cm segments, and each 10 cm sub-sample was analyzed for total carbon, PCE, TCE, and DCE isomers.

3.5 Carbon Mass Balance Analysis

The amount of contaminant degraded can be determined from the effluent monitoring results and the sediment samples collected at the end of the experiment. The theoretical carbon usage was estimated based on the electron acceptor load entering each column. The amount of carbon required for degradation of PCE and its daughter products was then assessed. The carbon required for dechlorination of PCE to each daughter product was estimated from the equations listed below. Total carbon usage was calculated by accounting for carbon used in oxygen reduction and methanogenic fermentation. Other electron acceptors such as iron (III) were not analyzed and were not included in the carbon balance. Sulfate, nitrate, and phosphate were not present in significant amounts in the column influents or effluents. The following chemical equations show what compounds were considered in the carbon use calculation.

Electron Accepting Half Reactions

PCE → TCE	$C_2Cl_4 + H^+ + 2\ e^- \rightarrow C_2Cl_3H + Cl^-$
PCE → DCE	$C_2Cl_4 + 2\ H^+ + 4\ e^- \rightarrow C_2Cl_2H_2 + 2\ Cl^-$
PCE → VC	$C_2Cl_4 + 3\ H^+ + 6\ e^- \rightarrow C_2ClH_3 + 3\ Cl^-$
PCE → Ethene	$C_2Cl_4 + 4\ H^+ + 8\ e^- \rightarrow H_4 + 4\ Cl^-$
O_2	$½\ O_2 + e^- + H^+ \rightarrow ½\ H_2O$
CO_2 → CH_4	$CO_2 + 8\ H^+ + 8\ e^- \rightarrow CH_4 + 2\ H_2O$

Electron Donating Half Reactions

Soy Bean Oil	$C_{56}H_{100}O_6 + 106\ H_2O \rightarrow 56\ CO_2 + 312\ H^+ + 312\ e^-$
Lactate	$C_3H_6O_3 + 3\ H_2O \rightarrow 3\ CO_2 + 12\ H^+ + 12\ e^-$
Yeast Extract	$C_5H_7O_2N + 8\ H_2O \rightarrow ½\ N_2 + 5\ CO_2 + 23\ H^+ + 23\ e^-$

The fraction of added carbon used for reductive dechlorination can then be calculated based on the inorganic carbon that was collected in the effluent.

3.6 Permeability Measurements

Permeability measurements were taken at the beginning of the project and after 3, 6, 10, and 13 months of operation to evaluate the effects of each treatment on permeability loss. Flexible tubing was connected to the inlet, outlet, and 3 sample ports. The flowrates in the columns were then adjusted to generate a measurable head loss over the length of the column and the column effluent was collected in a 25 mL graduated cylinder. At the end of the test, total flow, time, and heads were recorded. This information along with the column dimensions allowed calculation of permeability by the following equation

$$K = Q/(AI)$$

where K is the permeability, Q is the flow rate, A is the cross sectional area, and (I) is the hydraulic gradient.

4.0 EXPERIMENTAL RESULTS

4.1 Bromide Tracer Tests

Bromide tracer tests were conducted after 10 to 11 months of operation to estimate the effective porosity and average hydraulic retention time (HRT) of each column. Figure 2 shows the breakthrough curves for each test. Table 1 shows the average influent bromide concentration for each column during the tracer tests. Once the effluent bromide concentration reaches 50% of the average influent concentration, then the volume pumped through the column at that point is considered to be one pore volume. Columns 1 and 4 had a five-week tracer test performed where columns 2 and 3 had a seven-week tracer test performed. Although columns 1 and 4 tracer test lasted for a shorter duration, they were still ran long enough for the effluent concentration to reach 50% of the average influent concentration and estimate a pore volume that allows the HRT to be calculated.

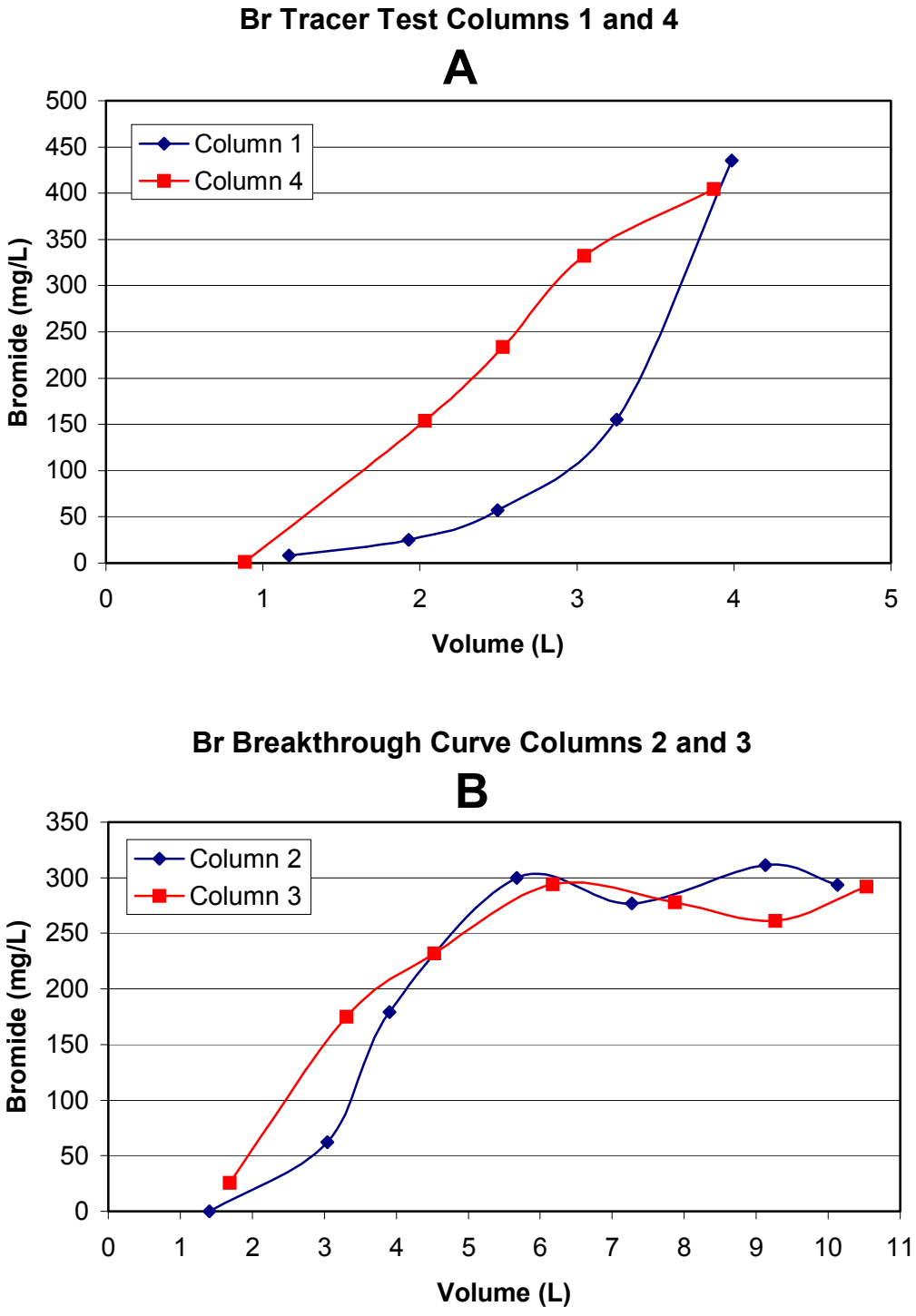


Figure 2: Bromide tracer test results: (A) Columns 1 and 4, (B) Columns 2 and 3

Table 1: Pore volume and hydraulic retention times (HRT) estimated from bromide tracer tests.

	Column 1	**Column 2**	**Column 3**	**Column 4**
Average Influent Concentration (mg/L)	828	424	365	733
Pore Volume (L)	3.8	3.6	3.0	3.3
Average HRT (Days)	38	33	20	30
Effective Porosity	0.44	0.42	0.35	0.38

The average hydraulic retention time (HRT) for each column was calculated based on the pore volume and the average flow rate over the course of the project, not the duration of the tracer test. Column 3 had the lowest effective porosity and shortest HRT of the four columns. Since the same procedure was used to pack all of columns, the observed differences in effective porosity between the columns are believed to be due to column operating conditions. Processes that could lead to a lower effective porosity include biomass growth and accumulation of gas bubbles. Column 3 which produced the most gas over the course of the project had the lowest estimated porosity (0.35) and column 1 which had the lowest gas production had the highest effective porosity (0.44). With increasing porosity, a general trend of increased average HRT was observed. The longer the HRT the more contact time the contaminated water has with the carbon source, which may result in more efficient degradation.

4.2 Column 1 – Low pH

In Column 1 (Low pH), the effluent pH was initially around 4 and then dropped to below 3 as the acid front migrated through the column (Figure 3). Around 200 days, the effluent dissolved oxygen increased to 3-4 (similar to influent concentrations) indicating aerobic biological activity

had been effectively suppressed. TOC concentrations averaged around 100 mg/L from shortly after emulsion injection until around 150 days when concentrations declined to ~ 20 mg/L. At around 100 days, significant levels of TCE began to appear in the column effluent, presumably due to incomplete inhibition of biological activity by the low pH. However by 200 days, TCE concentrations declined and PCE was, by far, the dominant ethene in the column effluent. PCE concentrations in the column effluent have gradually increased with time, eventually reaching half the average influent concentration of ~60 μmol /L. This indicates that the effective travel time for PCE through Column 1 is approximately 400 days or approximately 10.5 times the travel time for a non-reactive tracer (38 days). The longer travel time is attributed to PCE sorption to residual oil in column one.

Chlorinated ethene partitioning between soybean oil and water can be approximated using the octanol-water partition coefficient (K_{ow}). Assuming instantaneous partitioning, retardation factors for the different chlorinated ethenes were calculated using the equation

$$R = 1 + \rho_B f_o K_{ow} / n$$

and are presented in Table 2. The values presented in Table 2 are preliminary estimates. Best estimate partition coefficients developed by calibrating the transport model to the observed breakthrough will be presented in the modeling section. Porosity (n) was estimated from the bromide tracer test. Sediment bulk density was estimated from the porosity and specific gravity of quartz sand. The fraction oil (f_o) in the sediment is based on the amount of sediment in column 1 and the amount of soybean oil emulsion injected and is similar to oil retention values observed in prior work (0.001 to 0.01 g/g) by Coulibaly and Borden (in press). K_{ow} values were taken from various literature sources (Bedient et al., 1997).

Using the published range of K_{ow} values, the effective retardation factor for PCE is expected to vary between 7 and 38 while the observed retardation factor was 14 -19. The close match between calculated and observed retardation factors for PCE in Column 1 suggests that chlorinated ethene retardation in edible oil barriers can be reasonably approximated using a linear partitioning approach.

Sorption of PCE to the entrapped oil will delay breakthrough in field scale edible oil barriers. Table 1 also lists the estimated time for chlorinated ethene breakthrough in a typical field scale barrier (3 m thick) with a groundwater flow velocity of 0.1 m/d (non-reactive travel time of 0.08 yr or 1 month). This breakthrough time is relevant because the HRT of the columns was approximately one month. As can be seen in Table 2, PCE has the highest retardation factor and could be retained in an edible oil barrier for up to 3 years. However, K_{ow} values for the other ethenes are lower and the maximum retention times for TCE, cis-DCE and VC are estimated to be 0.4, 0.2 and 0.1 yr. This suggests that a significant amount of PCE may initially partition into the soybean oil. However once an acclimated microbial community develops, PCE will be converted to more soluble daughter products and these daughter products will rapidly migrate through the column or barrier. The rapid breakthrough of TCE in Column 1 supports this interpretation. High concentrations of TCE appeared in the Column 1 effluent approximately 112 days after the start of PCE injection. This is equivalent to a retardation factor of 3 for TCE, similar to the estimated retardation factor shown in Table 2 of 3.5.

Table 2: Estimated retardation factors for different chlorinated ethenes in Low pH - Column 1.

Parameter	**PCE**	**TCE**	**cis-DCE**	**VC**
Sediment Bulk Density, ρ_B (g/cm^3)	1.49	1.49	1.49	1.49
Oil fraction, f_o (g/g)	0.0028	0.0028	0.0028	0.0028
Porosity, n	0.44	0.44	0.44	0.44
Low estimate of K_{ow}	400	263	72	4
Low estimate of R	4.8	3.5	1.7	1
Low estimate of travel time through a field scale barrier	0.6 yr	0.4 yr	0.2 yr	0.1
High estimate of K_{ow}	3500	263	72	24
High estimate of R	34	3.5	1.7	1.2
High estimate of travel time through a 3m wide field scale barrier	3.1 yr	0.4 yr	0.2 yr	0.1 yr

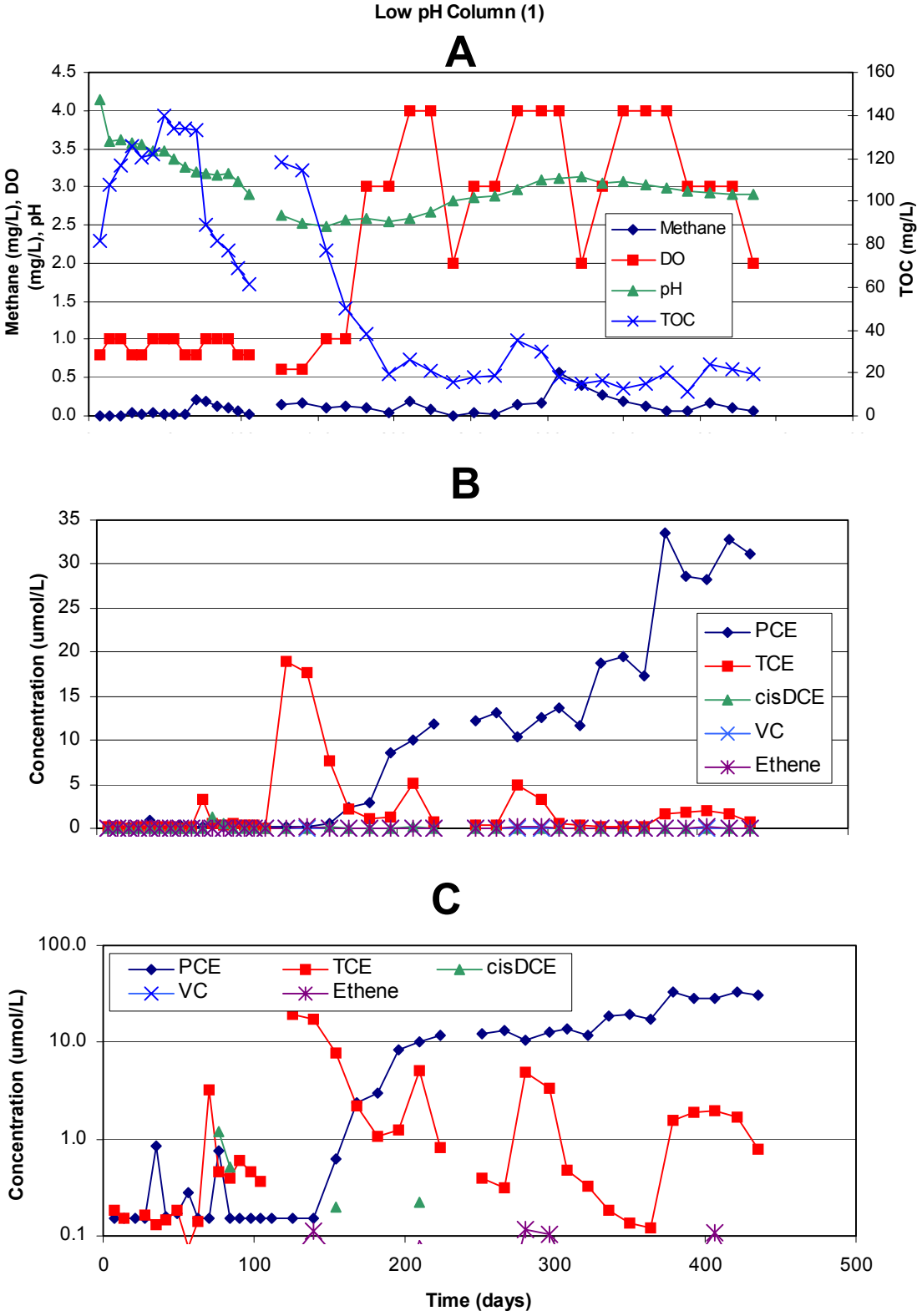
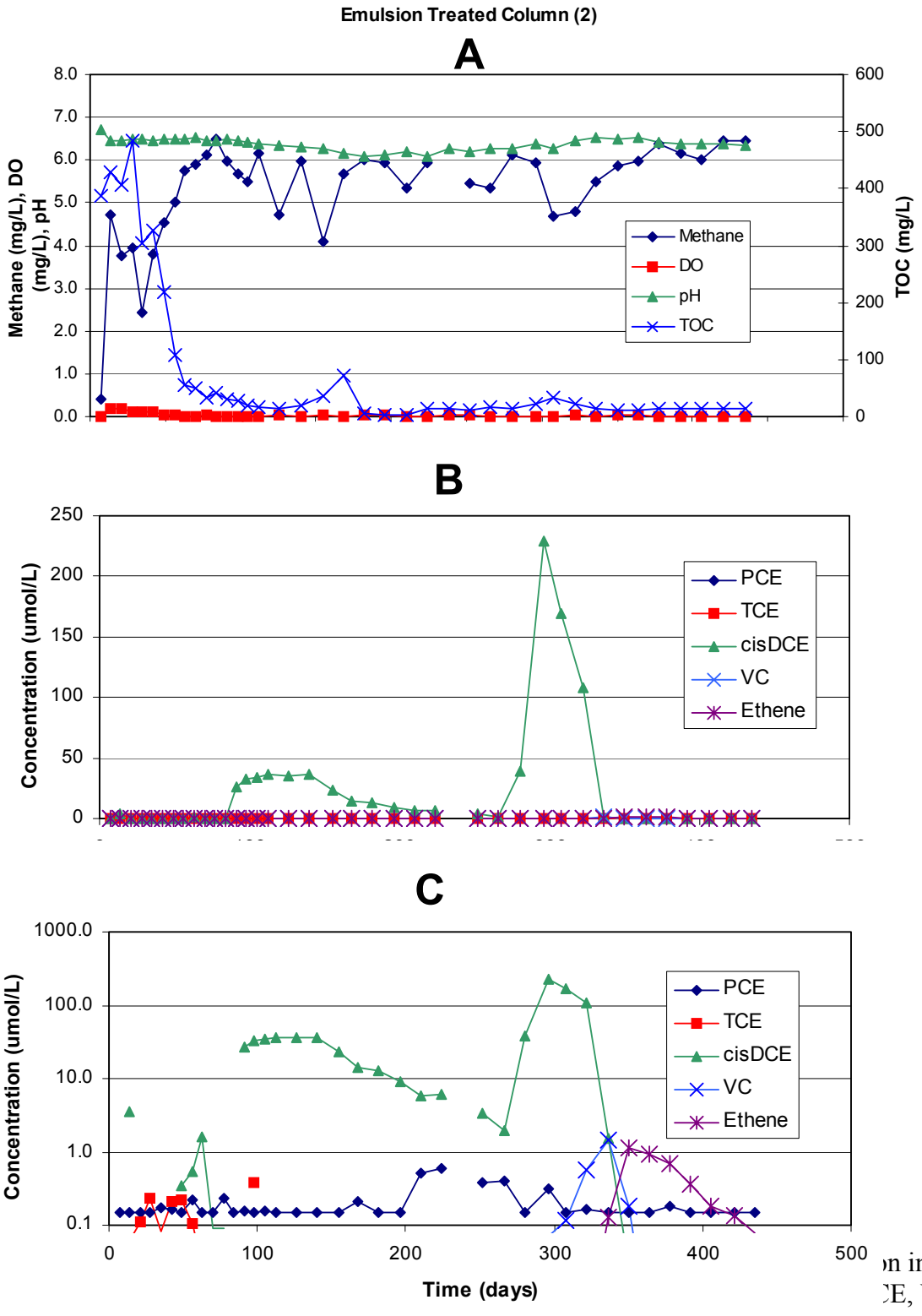


Figure 3: Column 1 results: (A) ethene, methane, DO, pH and TOC (B) Variation in effluent PCE, TCE, DCE, VC (C) Variation in effluent PCE, TCE, DCE, VC (log scale).



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CE, VC (log
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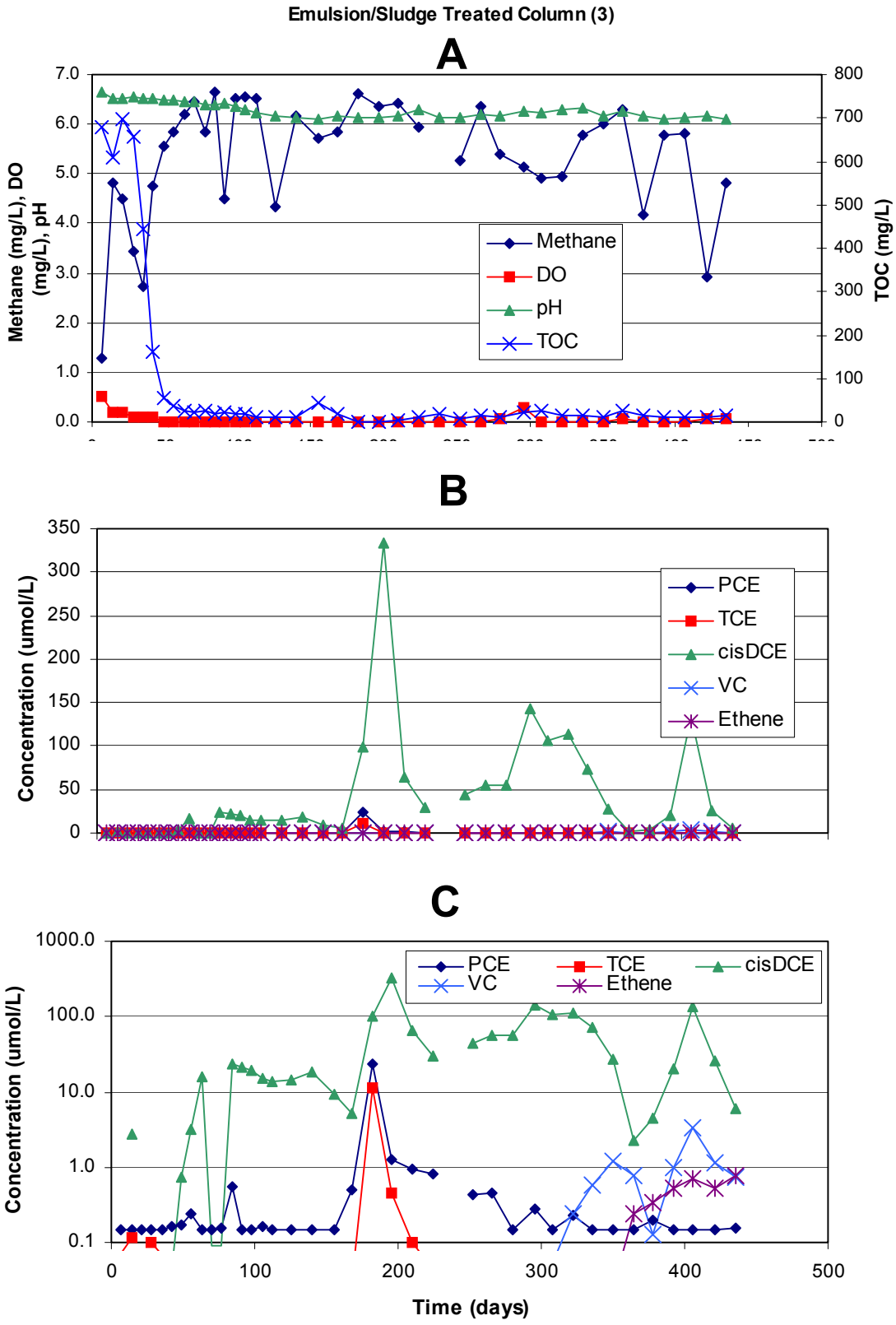

Figure 5: Column 3 results: (A) ethene, methane, DO, pH and TOC (B) Variation in effluent PCE, TCE, DCE, VC (C) Variation in effluent PCE, TCE, DCE, VC (log scale).

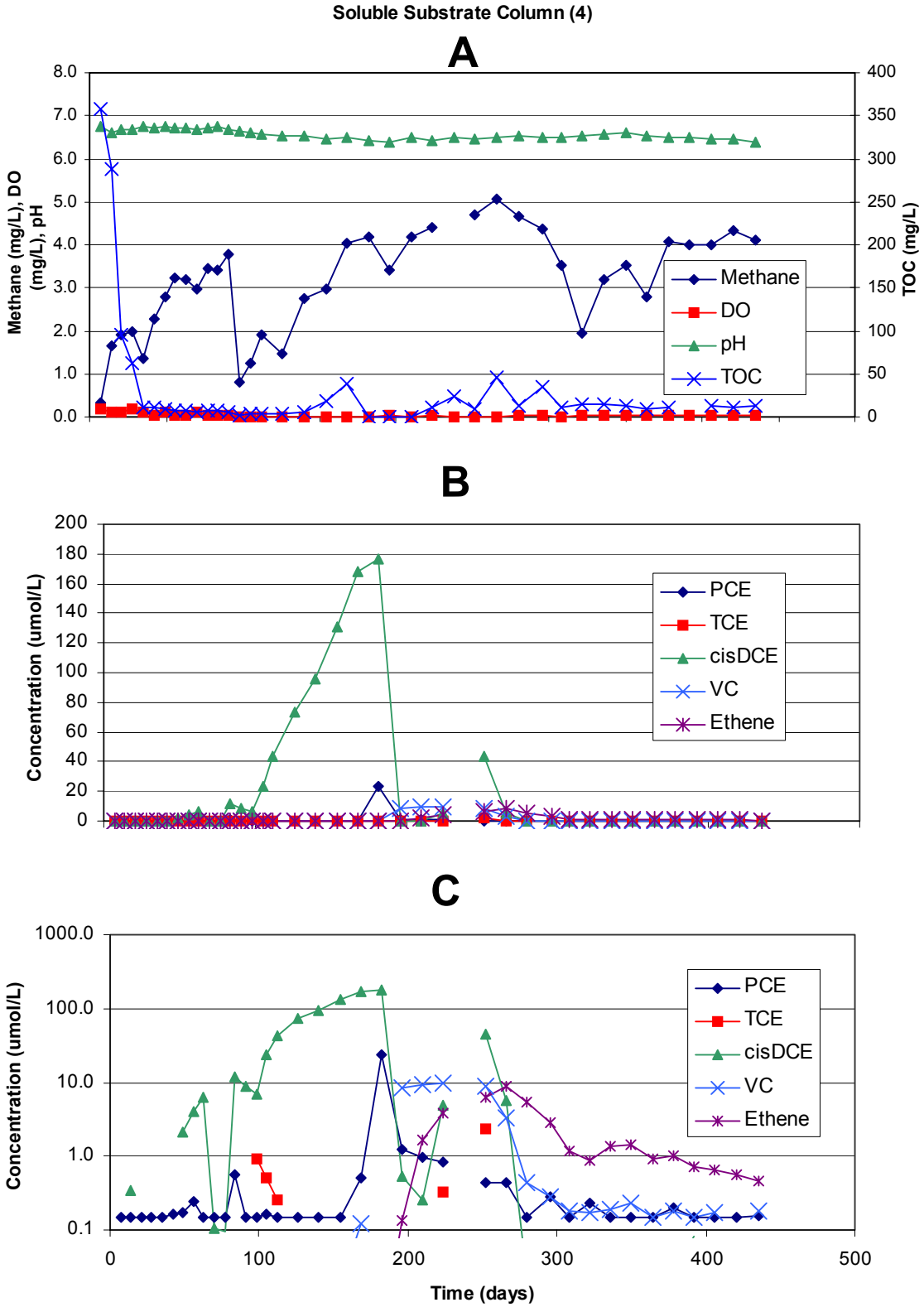

Figure 6: Column 4 results: (A) ethene, methane, DO, pH and TOC (B) Variation in effluent PCE, TCE, DCE, VC (C) Variation in effluent PCE, TCE, DCE, VC (log scale).

4.3 Column 2 – Emulsion Treated

In Column 2 (emulsion treated column), the pH varied between 6 and 7 and DO remained below 0.1 mg/L indicating emulsion injection had generated condition appropriate for reductive dechlorination (Figure 4). High concentrations of TOC broke though in the Column 2 effluent shortly after emulsion injection. However TOC concentration then declined to 20-50 mg/L concurrent with an increase in effluent methane concentrations. After day 100, methane concentrations remained relatively constant varying between 4 and 6 mg/L. In addition, Column 2 released roughly 2 mL of gas bubbles each week. This gas is about 44% methane indicating aqueous methane concentrations in the column effluent are slightly below equilibrium with the gas released (0.44 * 24 mg/L, aqueous solubility of methane = 10 mg/L).

DCE broke through in Column 2 effluent at around 90 days and then remained constant at concentrations comparable to the amount of PCE in the influent indicating relatively efficient conversion of PCE to TCE to cis-DCE. However VC concentrations remained low (< .03 μmol/L) and there was no evidence of appreciable ethene production. Similar results were obtained for Columns 3 and 4. In an attempt to stimulate complete reductive dechlorination of cis-DCE to ethene, Columns 2, 3 and 4 each received an additional 250 mL of bioaugmentation culture on day 123. This treatment was effective in stimulating complete reductive dechlorination in Column 4 (lactate/yeast extract feed) but did not result in complete reductive dechlorination in Column 2 (cis-DCE remained high; VC remained < .08 μmol/L, no significant ethene production). On day 252, we began feeding a 400 mg/L solution of yeast extract to Columns 2 and 3, followed by 375 mL of bioaugmentation culture on day 268. Immediately following bioaugmentation, the yeast extract feed to Columns 2 and 3 was discontinued.

The final treatment of yeast extract and bioaugmentation culture was successful in stimulating complete dechlorination in Column 2. Around day 300, there was a dramatic increase in cis-DCE in the Column 2 effluent followed by a rapid decline in cis-DCE, temporary production of VC and finally production of ethene. By day 400, TCE, cis-DCE and VC were below detection with significant amounts of ethene present in the column effluent. However throughout this period, low levels of PCE (up to 0.18 μmol/L) have been periodically detected in the effluent of all the live columns (2, 3 and 4). However, up to 0.15 μmol/L (25 μg/L) PCE were occasionally detected in laboratory blank samples, suggesting that the PCE detected in the column effluent was likely due to carry over from the high concentration influent samples (60-120 μmol/L).

The high DCE concentration observed in the Column 2 effluent around day 300 was well in excess of the influent PCE concentration (on a molar basis). The large pulse of cis-DCE released is likely due to the biotransformation of PCE and/or TCE that had sorbed to the residual soybean oil. The dramatic increase in microbial activity may be due to injection of yeast extract solution from day 252 to 268 or due to bioaugmentation on day 268.

After 435 days of operation, Column 2 continued to reduce TCE, cis-DCE and VC to below detection and remove over 99% of the influent PCE. Significant amounts of ethene were detected in the column effluent. Columns 2, 3, and 4 had gas ethene production measured on November 10, 2003 and the concentrations were 186 ppm, 759 ppm, and 332 ppm, respectively. However these concentrations are orders of magnitude below the levels expected based on the influent PCE loading. At this time, it is not clear what is happening to the ethene. Ethane concentrations remain very low (< 0.04 μmol/L). Ethene has been detected in gas bubbles released from the column. However we are not able to efficiently capture the gas bubbles so we

cannot accurately estimate the mass of ethene released in the bubbles. Bradley (2003) proposed several alternatives for the lack of ethene production during reductive dechlorination including: (1) anaerobic oxidation of VC and DCE to yield CO_2 or CO_2 and CH_4 (Bradley and Chapelle, 1996); (2) net oxidation with chloroethanol as intermediate (Vogel and McCarty, 1985); (3) syntrophic oxidation with acetate as intermediate (Bradley and Chapelle, 1999, 2000); and (4) syntrophic oxidation with ethene as intermediate (Bradley and Chapelle, 2002).

4.4 Column 3 – Emulsion and Digester Sludge Treated

In Column 3 (column treated with emulsion and anaerobic digester sludge), results were generally similar to Column 2, which received emulsion only. In Column 3, the pH was also between 6 and 7, with low DO (Figure 5). TOC concentrations where high immediately after emulsion injection and then stabilized at around 10 mg/L once methane production increased. Gas bubble production appears to have been slightly greater in this column, possibly due to inoculation with anaerobic digester sludge. However aqueous methane concentrations are similar and the gas produced is 30 – 45% methane at a rate of ~2.2 mL/wk.

DCE broke through in the Column 3 effluent at around 90 days and then reached a quasi-steady-state. As in the emulsion only column, bioaugmentation of Column 3 at 123 days appears to have stimulated conversion of some PCE or TCE trapped in the column but did not result in significant VC or ethene production. However, injection of yeast extract and bioaugmentation culture on day 268 appears to have stimulated some conversion of DCE to VC and ethene. Around day 320, we observed significant levels of VC in the Column 3 effluent followed by significant ethene production at day 400. While VC and ethene production have increased in Column 3, cis-DCE concentrations remained high indicating that this column was not effective

in fully degrading PCE. The less complete conversion of DCE in this column may be due to the greater number of methanogens that could consume the bioavailable carbon before it can be effectively used for reductive dechlorination. The shorter HRT for Column 3 (~ 20 days) compared to Column 2 (~ 33 days) may also have contributed to the less efficient DCE degradation.

4.5 Column 4 – Soluble Substrate

In Column 4 (fed lactate and yeast extract in column influent), results were generally similar to Column 2 which received emulsion only. In Column 4, the pH was also between 6 and 7, with low DO (Figure 6). TOC concentrations were high immediately after the start of soluble substrate addition and then dropped to around 10 mg/L in the column effluent after day 35. The soluble substrate column also released significant levels of dissolved methane (2- 5 mg/L). However the gas bubble production was slightly lower, at ~1.4 mL/wk, than in Column 2 with a somewhat lower methane fraction (20-25%).

DCE concentrations exceeded 10 µmol/L on day 84 and then steadily increased to over 606 µmol/L on day 184. The rapid increase in DCE after day 100, may be due to a second bioaugmentation of Column 4 on day 123. Immediately following the decrease in DCE on day 184, we observed a temporary increase in VC followed by an increase in ethene. Column 4 provided very effective treatment up to day 450 with TCE, DCE and VC degraded to below the analytical detection limit. As with the other columns, up to 0.18 µmol/L of PCE was occasionally detected in the Column 4 effluent samples. These detections are believed to be due to analytical carry over from the high levels of PCE in the column influent. Overall, the soluble substrate column consistently achieves a PCE removal efficiency of over 99%. Column 4 had an

average HRT of 30 days, which could account for its more effective degradation when compared to column 3.

4.6 Variations in Chloroethene Concentrations with Distance

Beginning on day 224, the side sampling ports were sampled monthly to measure the distribution of each contaminant and associated indicator parameters. Sample ports A, B, and C are at distances 0.25 m, 0.5 m, and 0.75 m respectively from the inlet of each column. In column 1, only the movement of PCE through the column can be observed. However, each of the other columns (2, 3, and 4) showed biodegradation of PCE to its daughter products (TCE, DCE, VC, and ethene). By studying the migration of these daughter products through the columns, we can gain a better understanding of the biotransformation processes occurring. The concentration profiles for columns 2, 3, and 4 at various times are shown in Figures 7 - 9.

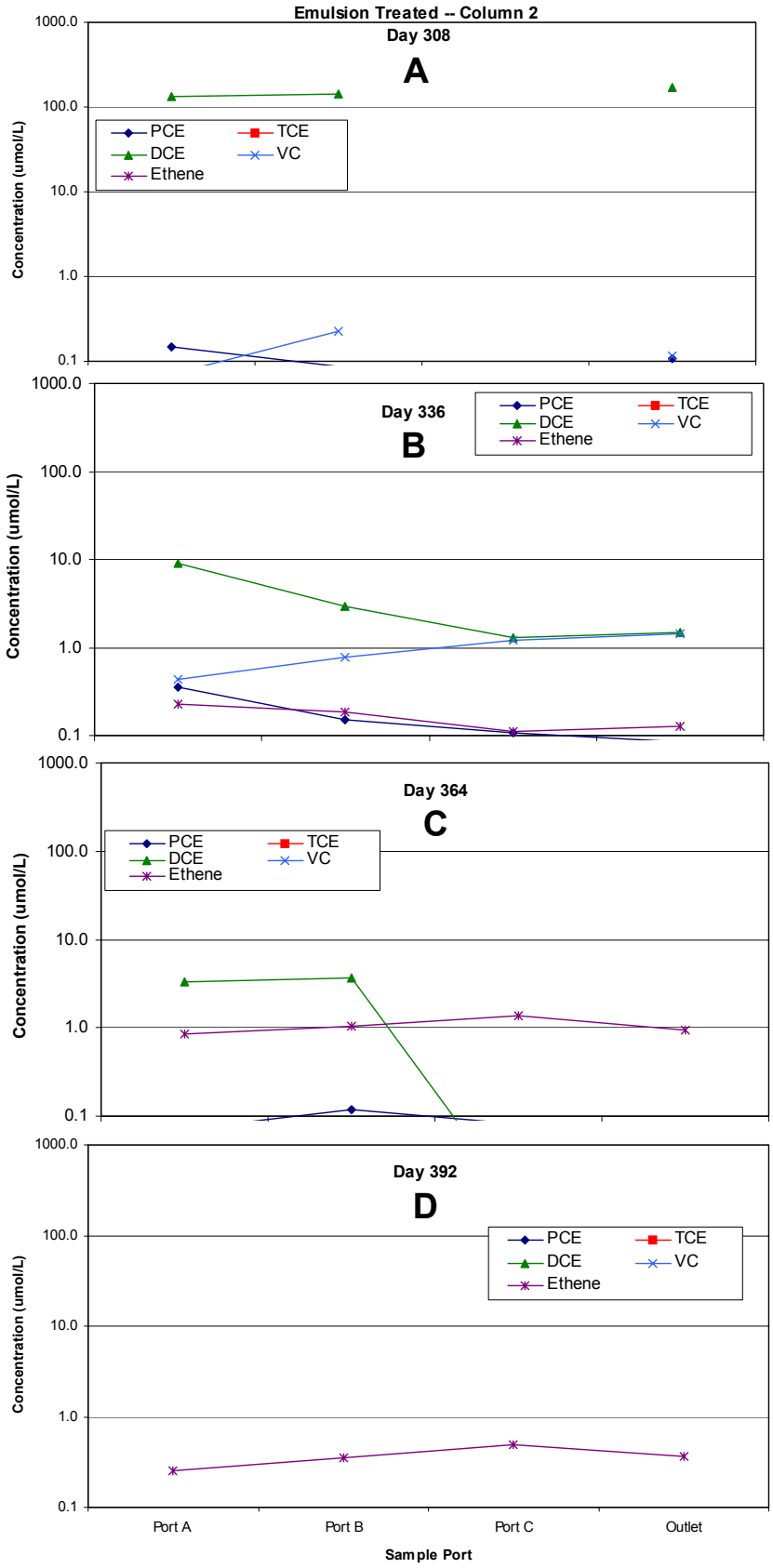

Figure 7: Chloroethene concentration profile over time in Emulsion Treated – Column 2: (A) Day 308 (B) Day 336 (C) Day 364 (D) Day 392.

4.6.1 *Emulsion Treated – Column 2*

Figure 7 shows the spatial variation in the different ethenes in Column 2 following the third and final bioaugmentation of the column on day 268. By day 308 the most prevalent compound in all sample ports was DCE. This was expected since the average HRT is estimated at 33 days for column 2. This means the bioaugmentation or yeast extract feed solution before bioaugmentation was successful at stimulating reductive dechlorination to the point of DCE. By day 336 DCE concentrations had declined by a factor of 10 in Port A and by a factor of 100 in Port C. At this time, VC concentrations were increasing with distance along the length of the column indicating gradual conversion of DCE to VC. On day 364, DCE was below detection in the second half of the column, VC was below detection throughout the column, and ethene was the dominant compound observed. All compounds other than ethene were non-detect by day 392. There was PCE in the effluent, but not in concentrations greater than the detection limit. The general trend is for an initial production of DCE, followed by conversion of VC and ethene once a large population of DCE degraders has developed. This suggests that for each daughter product to be produced, a small acclimation period is needed for the microbes to adjust to the changing contaminant environment. Once adaptation to the environment occurs, biodegradation is very rapid and goes to completion by the first sampling point (Port A).

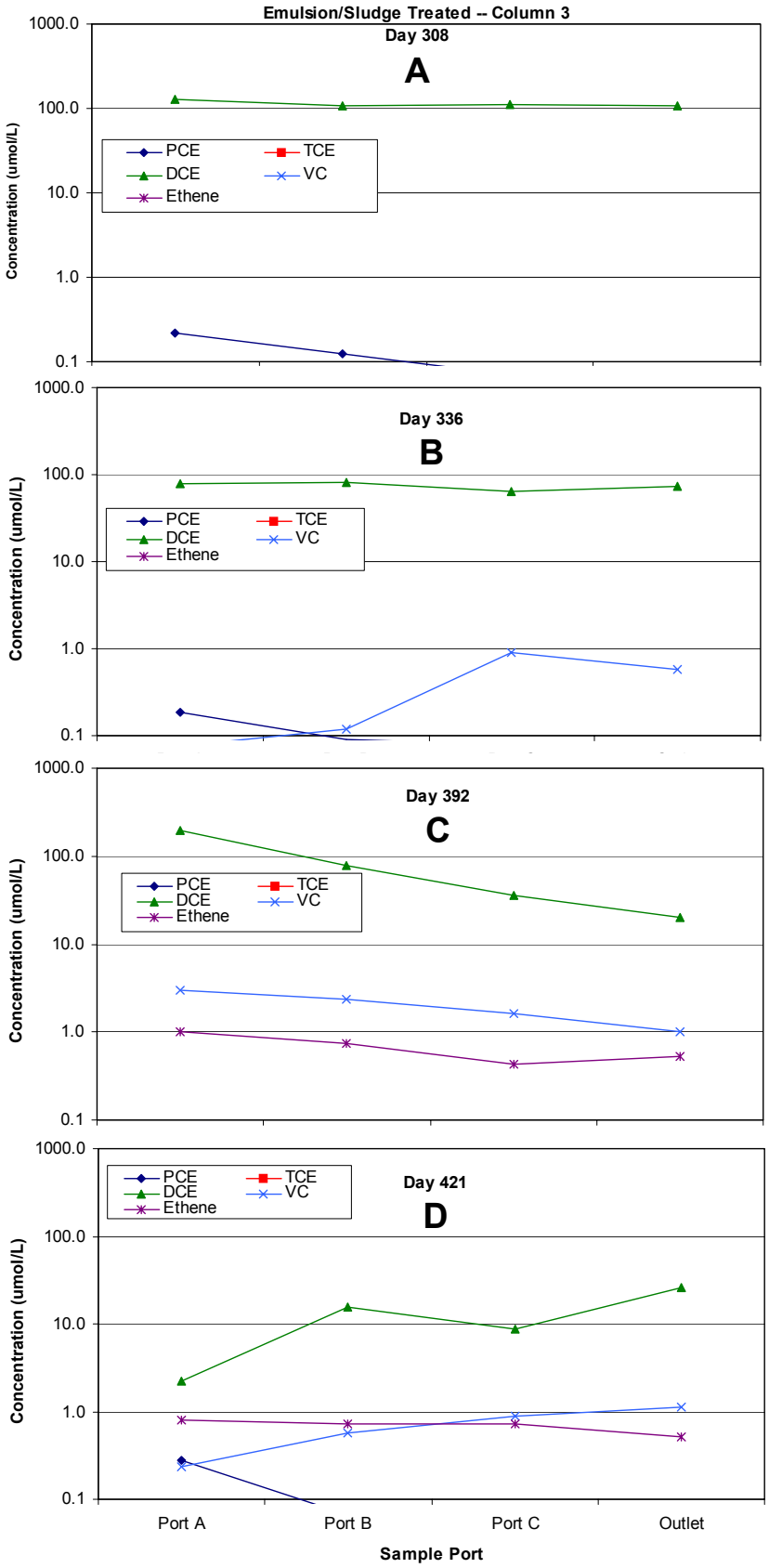

Figure 8: Chloroethene concentration profile over time in Emulsion/Sludge Treated – Column 3: (A) Day 308 (B) Day 336 (C) Day 392 (D) Day 421.

4.6.2 *Emulsion/Sludge Treated – Column 3*

Figure 8 shows the spatial variation in the different ethenes in Column 3 following the third and final bioaugmentation of the column on day 268. Similarly to column 2, addition of the bioaugmentation culture and/or yeast extract solution was successful in stimulating DCE production by day 308. By day 336, VC concentrations were beginning to increase with distance from the inlet. By day 392, there was a significant decline in DCE concentrations over the length of the column and production of significant amounts of VC. Significant levels of ethene were also observed for the first time on day 392. By day 421, DCE concentrations were at the columns lowest levels observed and VC concentrations were now increasing over the length of the column. Ethene production on day 421 was sustained at a similar level to that on day 392 over the length of the column. The same trends observed in column 2 were also observed in column 3, but at a somewhat slower rate. There was a period of DCE accumulation, followed by VC production, then finally ethene production. However in column 2, DCE was degraded to below detection by day 392 while significant levels of DCE were detected in column 3 past day 4251. The less effective conversion of DCE may be due to competition for available substrates by methanogens introduced into column 3 and/or the lower average HRT of column 3.

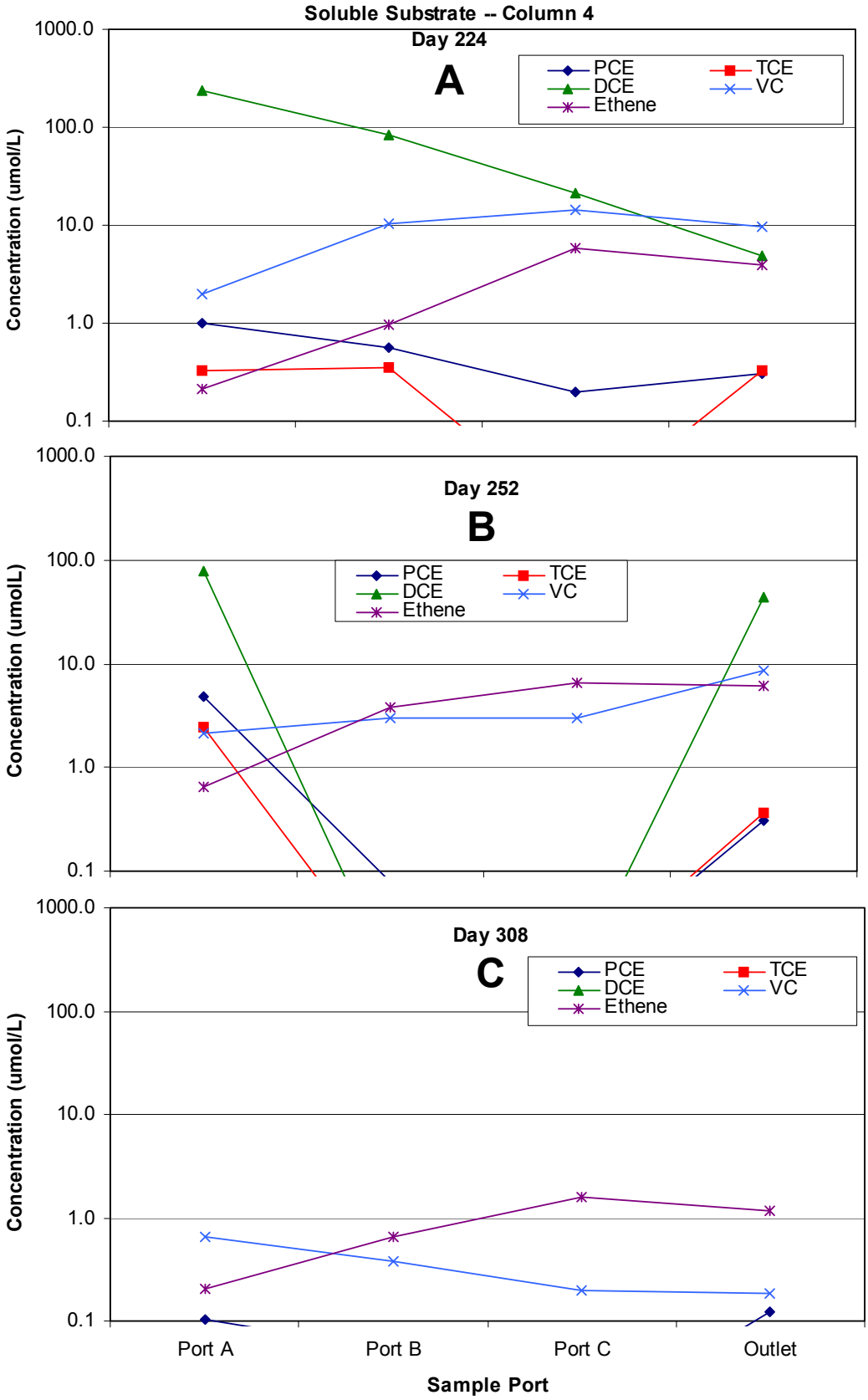

Figure 9: Chloroethene concentration profile over time in Soluble Substrate – Column 4: (A) Day 224 (B) Day 252 (C) Day 308.

4.6.3 *Soluble Substrate – Column 4*

Figure 9 shows the spatial variation in the different ethenes in Column 4 following the second bioaugmentation of this column on day 123. By day 224, DCE concentrations were already declining with distance in column 4 with concurrent production of VC and ethene. By day 252, DCE concentrations had declined further, with a slight decrease in VC and a slight increase in ethene over the length of the column. On day 308, DCE was below detection in all sampling ports, VC was low and ethene was the predominant compound in the column outlet. TCE, DCE and VC were not observed in significant concentrations in any of the side sampling port in column 4 on or after day 308. Degradation of PCE was more rapid and complete in column 4 than the other two live columns. The more efficient conversion of PCE in this column could be due to: (a) the increased bioavailability of the soluble substrate (lactate) in the column feed, (2) the presence of important nutrients in the yeast extract in the column feed, and/or (3) the longer HRT of this column (30 days).

4.6.4 *Summary of Results*

By the completion of the project, all of the live columns (2, 3, and 4) were successful in reducing PCE by over 99%. All columns also exhibited significant production of DCE before VC was observed, and significant production of VC before production of ethene. By day 392, column 2 was only producing VC and ethene with ethene being the primary degradation product observed. Column 3 took until day 392 to produce significant levels of ethene and by day 421 was still producing substantial amounts of DCE. The lack of complete dechlorination in column 3 when compared to column 2 may be due to methanogenic competition or the lower average HRT of column 3. By day 308, ethene was the predominant degradation product in the column 4 effluent

with lower levels of VC. The shorter acclimation period for complete dechlorination in Column 4 may be due to the greater bioavailability of the soluble substrate and/or trace nutrients in the yeast extract feed.

Comparison of the side port monitoring results from columns 2 and 3 suggest that the observed differences in contaminant degradation in these columns is not due to the shorter HRT of column 3. Most of the degradation occurred in the first 0.25 m of every column. Significant levels of PCE and TCE were never observed in any of the side sampling ports. This suggests that substrate availability may have limited contaminant biodegradation. Substrate could be limited due to: (a) competition by high levels of methanogens; and/or (b) retention of most of the organic substrate in the first 0.25 m of the column. In the carbon analysis section, results are presented demonstrating that higher levels of organic substrate are present near the column inlet with much lower levels present throughout the remainder of the column.

4.7 Final Chloroethene and Organic Carbon Distribution in Sediment

Sediment samples were collected after the completion of the PCE injection phase to determine the final distribution of chloroethenes (PCE, TCE, and DCE) and carbon in the column sediment. Two steel tubes were driven through the sediment. One tube was sectioned and analyzed for chloroethenes while the second was analyzed for total carbon. In many cases, sediment samples were not recovered from the full length of the column. As a consequence, the number and location of samples analyzed for chloroethenes and carbon vary. For chloroethene analysis, samples were recovered in 10 cm increments from 10 cm to 90 cm from the inlet in column 1,

from 50 cm to 100 cm in column 2, from 80 to 100 cm in column 3, and from 30 to 100 cm in column 4. For carbon analysis, samples were recovered in 10 cm increments from 20 to 90 cm in column 1, and from 40 to 100 cm in columns 2, 3 and 4.

PCE, TCE and DCE concentrations versus distance from the inlet of each column are presented in Figure 10. PCE and DCE concentrations in sediment are highest in the low pH column 1 with much lower levels observed in the three live columns. The total mass of chloroethenes in each column was estimated as the product of the arithmetic mean chloroethene concentration and the mass of sediment in the column. In all cases, chloroethene concentrations were highest immediately adjoining the column inlet. Where only a few sediment samples were analyzed, a single high measurement could result in a biased estimate of the mass of chloroethenes recovered in the sediment.

Total carbon concentrations versus distance from the inlet of each column are presented in Figure 11. Significant amounts of organic carbon were distributed through out the length of the three emulsion treated columns. However, there was also considerable variation between adjacent samples indicating the emulsion was not uniformly distributed. With the exception of one sample from the column 3 inlet, carbon concentrations were often significantly higher in low pH column 1 than the two live emulsion columns (2 and 3) or soluble substrate column 4. The higher levels of carbon remaining in column 1 is presumably due to the inhibition of biological activity. The high carbon concentration in the column 3 inlet sample may have been due to straining of a few large oil droplets.

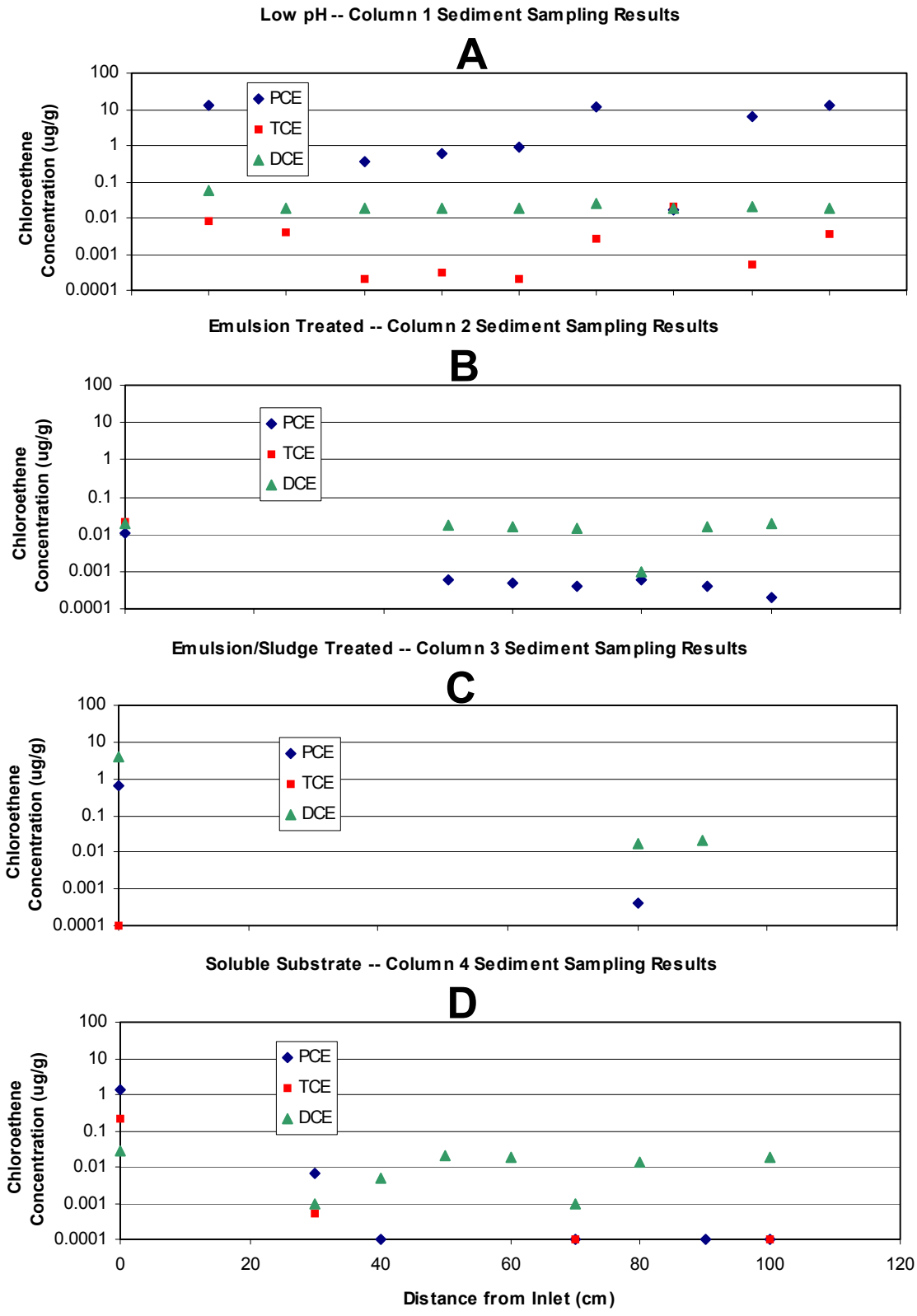

Figure 10: Chloroethene sampling over the length of each column: (A) Column 1 (B) Column 2 (C) Column 3 (D) Column 4.

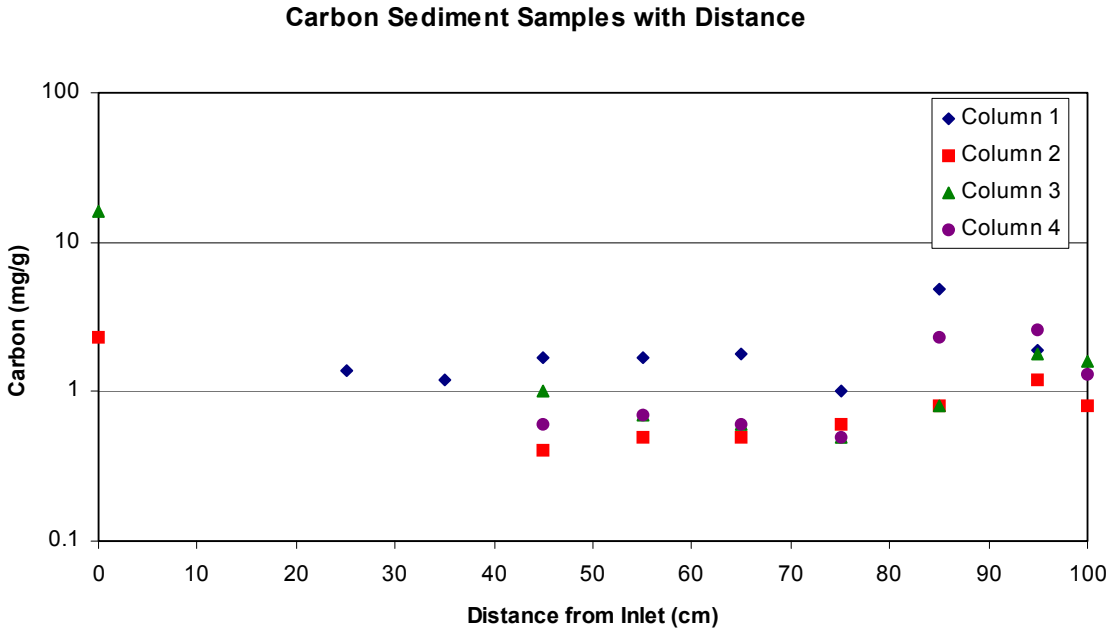

Figure 11: Final carbon content versus distance for columns 1-4.

4.8 Chloroethene Mass Balance

An overall chloroethene mass balance was developed for each column by comparing the mass injected with the cumulative mass in the effluent and mass sorbed to the sediment at the end of the project. The cumulative mass of chloroethenes in the influent and effluent of each column are shown in Figure 11. Cumulative mass was calculated as the sum of measured concentration times the volume of water injected since the previous chemical analysis. During the experimental period, there were four times when extremely high PCE concentrations were detected in the column 1 influent samples. These very high concentrations are thought to have occurred due to pumping non-aqueous phase PCE into the sample lines when the flow rates were increased for sample collection. These very high concentrations are not believed to be representative of what actually entered the column and were not included in the calculation of cumulative mass entering the column. The observed concentrations may be high due to the sampling method that requires the flow rate to be increased during the sample period. Overall

mass balance results for each column are presented in Table 3 including the amount of chloroethenes recovered in the sediment.

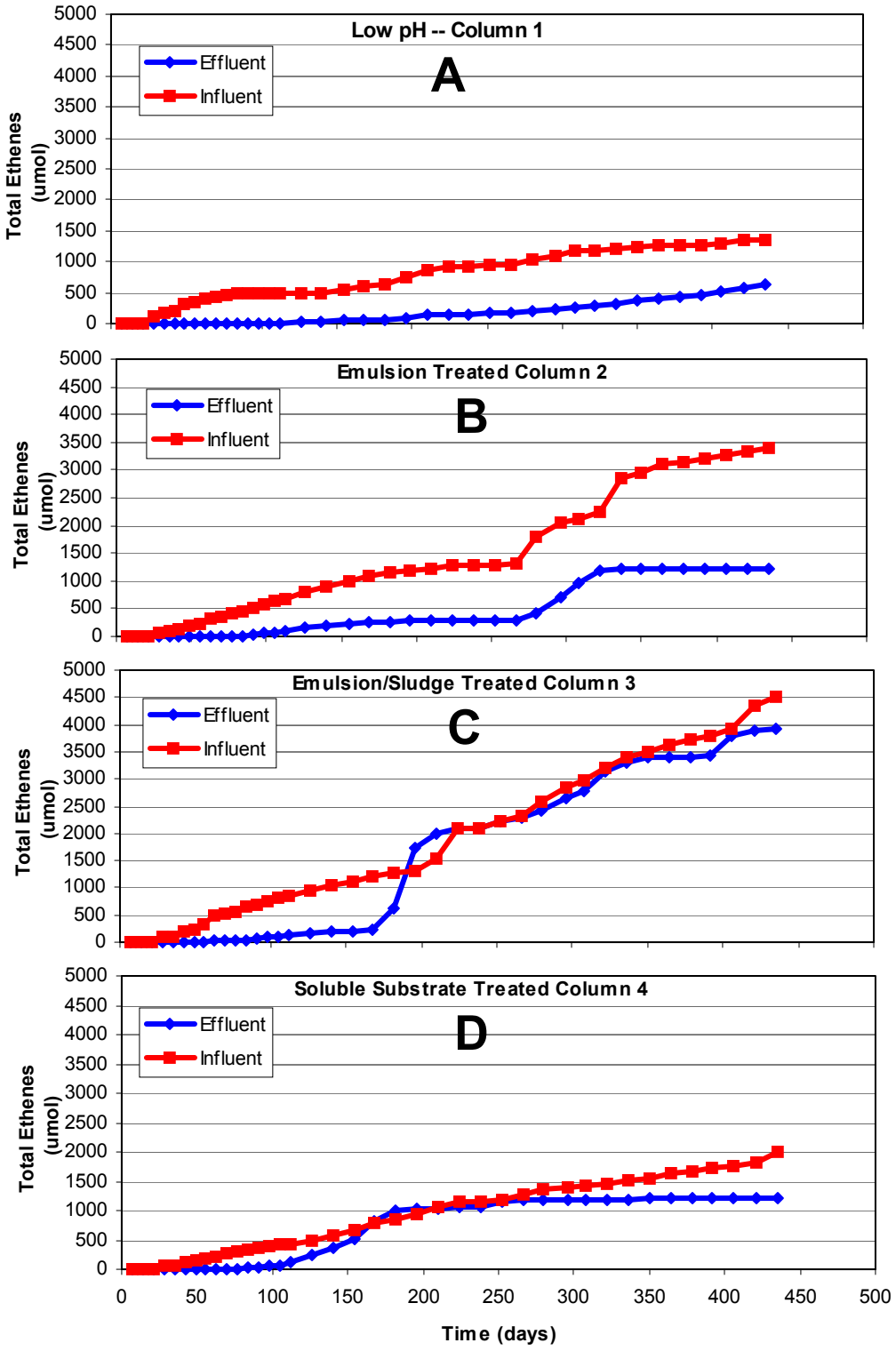

Figure 12: Cumulative mass of ethenes in the influent and effluent: (A) Column 1 (B) Column 2 (C) Column 3 (D) Column 4.

4.8.1 *Column 1 – Low pH*

As illustrated in Figure 12, substantially less chloroethene was discharged in the column 1 effluent than was introduced in the influent. However, most of this material was recovered as PCE in sediment resulting in a final mass balance error of 18.6% ± 26%. The small residual error may have been due to two leaks that occurred January 6 and May 12, 2003.

4.8.2 *Column 2 – Emulsion Treated*

In column 2, influent chloroethene mass was much greater than that of the effluent over the first 270 days. This difference indicates chloroethenes were being stored in the column and is consistent with sorption of the more chlorinated species (PCE and TCE) to the entrapped soybean oil. Around day 270, we see a rapid increase in effluent chloroethene mass due to high concentration of DCE being released. However after day 350, total ethene levels in the effluent remained low and influent mass remained greater than that in the effluent. By the end of the experiment, the cumulative chloroethene mass in the influent was significantly greater than in the effluent (Table 3). The total amount of chloroethenes recovered in the sediment at the end of the experiment was less than 0.1% of the influent mass indicating that sorption to the sediment was negligible.

In column 2, 36% of the influent mass was recovered in the column effluent with 64% unaccounted for. The large mass balance error could be due to three factors: (1) errors in estimation of the influent mass; (2) poor recovery of ethene in gas bubbles released from the column; and (3) conversion of ethene to methane. As described above for column 1, excessively high PCE concentrations were observed in the column 2 influent on several occasions. These

high concentrations may have been due to the sample collection procedure and may not have been representative of what was actually introduced into the column. However for column 2, these high concentrations were retained in data set using for calculating influent mass. A portion of the mass balance error could also be due to release of VC and ethene in gas bubbles. During column operation, it was obvious that the gas collection procedure was not 100% effective and some gas was being discharged in column effluent. However, based on the measured ethene concentrations in the captured gas, this term is expected to make up only a small fraction of the missing mass. Finally, ethene could potentially be oxidized to carbon dioxide or reduced to methane as described by Bradley (2003).

4.8.3 *Column 3 – Emulsion/Sludge Treated*

Trends in cumulative influent and effluent chloroethenes in column 3 followed the same general trends as in column 2. For the first 200 days, the influent mass of chloroethenes is much larger than that of the effluent, which is consistent with sorption of PCE and TCE to the entrapped soybean oil. Around day 200, there is a rapid increase in effluent chloroethene due to high concentrations of DCE being released so by day 225, cumulative ethenes in the effluent are approximately equal to those in the influent. From that point on column 3 continues to produce chloroethene in the amount that are injected until significant VC and ethene production occur around day 392. By the end of the experiment influent masses were greater than effluent concentrations by 464 μmol (Table 3). Again, the difference is not due to sorption, but could be due to limitations in of ability to monitor gaseous ethenes such as VC and ethene.

4.8.4 *Column 4 – Soluble Substrate*

As shown in Figure 10, chloroethene mass recovery in the column 4 influent exceeded the effluent until day 112. This indicates that significant sorption occurred in column 4, but not to the extent in columns 2 and 3 which were treated with oil-water emulsions. Around day 112, the effluent chloroethene mass recovery increased rapidly due to high concentrations of DCE being released. By day 168, the total ethenes in the effluent are approximately equaled to that of the influent. As occurred for columns 2 and 3, once significant levels of VC and ethene are produced at around day 210, cumulative influent begins to exceed cumulative effluent.

Table 3: Summary of ethene mass balance results*.

	In (µmol)	**Out (µmol)**	**Sediment (µmol)**	**Error (µmol)**	**Error (%)**
Low pH - Column 1	1350	620	474 ± 345	256 ± 345	19 ± 26
Emulsion Treated - Column 2	3380	1220	2.4	2158	64
Emulsion/Sludge Treated - Column 3	4510	3910	136	464	10
Soluble Substrate - Column 4	2010	1210	16	784	39

* For column 1, 95% confidence limits are presented.

4.8.5 *Summary of Chloroethene Mass Balance Results*

In low pH column 1, sorption of PCE to the residual oil was significant. Sorption of PCE and/or TCE was also important in the live emulsion treated columns. However once the columns were effectively bioaugmented, the more highly chlorinated ethenes were converted to cis-DCE which was rapidly discharged in the column effluent. These results are consistent with retardation factors for PCE, TCE and cis-DCE estimated using a simple linear partition relationship and published values of the octanol water partition coefficient.

In both columns 2 and 4, a significant fraction of the total ethenes introduced in the column influent cannot be accounted for. These two columns were also very efficient in completely dechlorinating PCE to gaseous endproducts. The poor mass balance observed in these two columns may be due to poor recovery of ethene in gas bubbles released from each column or further conversion of ethene to carbon dioxide or methane. While some portion of the ethene mass was very likely released in the gas bubbles, it is unlikely that this can account for the entire mass balance error.

4.9 Carbon Distribution in Column Effluent – Substrate Life

Figure 13 shows the cumulative mass of methane, organic, and inorganic carbon in aqueous samples from the effluent of each column over the life of the project. Table 4 shows cumulative carbon as methane, total organic carbon (TOC), and inorganic carbon (IC) as a mass and as a percent of the organic carbon injected into each column as soybean oil emulsion or soluble substrate.

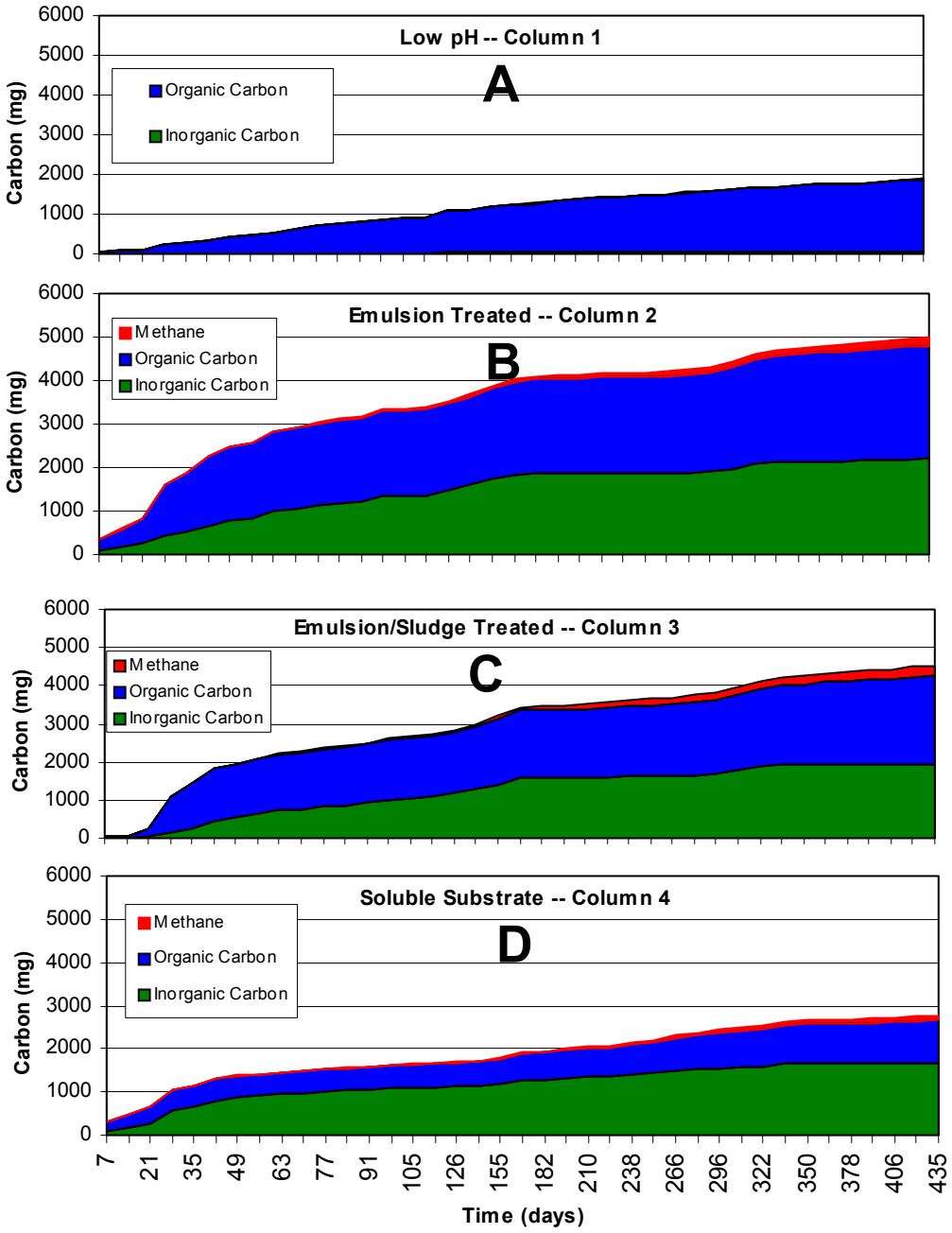

Figure 13: Effluent carbon distribution as methane, organic carbon, and inorganic carbon (A) Column 1 (B) Column 2 (C) Column 3 (D) Column 4.

Table 4: Carbon Released from columns 1 - 4 over the 435 day treatment period.

Column	Carbon (mg)			Percent Carbon Used		
	CH_4	TOC	IC	CH_4	TOC	IC
Low pH – Column 1	4	1850	27	0.01	4.79	0.07
Emulsion Treated – Column 2	192	2590	2200	1.12	6.69	5.68
Emulsion/Sludge Treated – Column 3	271	2310	1940	0.70	5.97	5.00
Soluble Substrate – Column 4	109	986	1670	1.06	9.61	16.3

4.9.1 *Carbon Distribution*

As shown in Figure 13, over 98% of the carbon released from column 1 was in the form of organic carbon indicating that biological activity was effectively suppressed. In columns 2 and 3, there is a rapid release of dissolved organic carbon shortly after emulsion injection. This did not occur in column 1, suggesting that this rapid release is associated with microbial conversion of the readily biodegradable material in the emulsion (probably the surfactants). With the absence of biological activity, column 1 retained more organic carbon (only discharged 1850 mg) compared to columns 2 and 3 (discharged 2590 mg and 2310 mg respectively). Methane production also accounted for a larger portion of the injected organic carbon in columns 2 and3, presumably because of an elevated methanogen population. Columns 2 and 3 did allow approximately the same amount of un-utilized organic carbon to flow through them. The soluble substrate column released a greater percent of its carbon as inorganic carbon, but that is because the soluble substrate is a great deal more readily utilized.

Table 5 presents estimates of the amount of inorganic carbon expected to be produced based on the amount of oxygen consumed, and TCE, DCE, VC, ethene and methane produced. These estimates are based on the reaction stoichiometry presented in the methods section. The last row in Table 5 show the percent of inorganic carbon (IC) produced that cannot be accounted for based on the consumption of oxygen or production of methane and more reduced ethenes (TCE, DCE, VC and ethene). IC is presented as total mass produced and as a percentage of IC observed in the column effluent over the duration of the project.

In column 1, most of the IC produced can be attributed to oxygen consumption and the reduction of PCE to TCE, with a small amount associated with methane production. In column 2 the majority of the inorganic carbon produced came from the fermentation of soybean oil (6.55%) with only a very small fraction (0.48%) of IC produced was associated with reductive dechlorination. This result is consistent with prior studies showing that most carbon is not directly used in the reductive dechlorination process. Column 3 shows similar results to column 2. Only 1.69% of the inorganic carbon that was produced is associated with reductive dechlorination. Again, the majority of the inorganic carbon came from the fermentation of soybean oil (10.5%). In either case there is a significant amount of inorganic carbon that cannot be accounted for. The unaccounted IC may come from the reduction of solid phase iron. If the sediment inside the column was only 1% iron, it could account for more than the amount of IC produced during the monitoring period. However, without iron concentrations from the columns, it is impossible to say for sure. Column 4 received only soluble substrate. As a result, most of the inorganic carbon produced in column 4 should have been from the fermentation of the soluble substrate to methane and carbon dioxide (4.9%). As with the soybean oil columns (2

and 3) only a small fraction of inorganic carbon produced (0.83%) resulted from reductive dechlorination

4.9.2 *Overall Carbon Mass Balance*

The overall carbon mass balance for each column is presented in Table 6 including the amount of methane, inorganic carbon (IC), and total organic carbon (TOC) observed in the effluent, carbon in sediment after project completion, and unaccounted carbon. The organic carbon mass was estimated as the average organic carbon concentration (g/g) times the mass of sediment in each column.

For column 1, 55 % (± 33) of the injected carbon was recovered in the sediment at the end of the project with 40% (± 33) unaccounted for. The mass balance error (67% ± 17) was much higher in column 2 with only 19.6% of the injected carbon recovered in the sediment. The low carbon recovery may be due to the poor sample recovery during sediment coring or an overall poor carbon sampling method. The mass balance was much better in column 3 (~2% error) with 86% (± 150) of the injected carbon still present in the sediment. Column 4 showed a carbon recovery range of 45% to 222% of its injected carbon. The high uncertainty is due to the large variation in sediment carbon and the smaller amount of organic carbon injected.

These sampling results indicate that the carbon distribution was not uniform, mass greatly reducing the reliability of the mass balance results.

Table 5: Theoretical carbon usage for reductive processes and the fraction of inorganic carbon each process uses based on the total amount of inorganic carbon produced.

	Column 1			**Column 2**			**Column 3**			**Column 4**		
	µmol	**mg**	**% IC Produced**	**µmol**	**mg**	**% IC Produced**	**µmol**	**mg**	**% IC Produced**	**µmol**	**mg**	**% IC Produced**
PCE->TCE	89	11.9	43.3	n/a	n/a	n/a	37	0.2	0.0	5	0.0	0.0
PCE->DCE	2	0.0	0.1	1193	10.3	0.5	3731	32.2	1.7	1051	9.1	0.7
PCE->VC	0	0.0	0.0	6	0.1	0.0	24	0.3	0.0	63	0.8	0.1
PCE->Ethene	2	0.0	0.1	8	0.1	0.0	7	0.1	0.0	55	0.9	0.1
O_2->CO_2	1571	13.5	49.2	5092	43.9	2.0	7182	61.9	3.2	4587	39.5	2.4
soy->CO_2+CH_4	302	3.6	13.2	12022	144.3	6.6	16950	203.4	10.5	6794	81.5	4.9
Total Inorganic Carbon Produced	n/a	27.5	100	n/a	2202.4	100	n/a	1936.9	100	n/a	1668.5	100
Unaccounted for Inorganic Carbon	n/a	-1.5	-5.8	n/a	2003.7	91.0	n/a	1638.8	84.6	n/a	1536.7	91.9

Table 6: Carbon Mass Balance Result for Columns Summary Table as Percent Carbon Injected.

	Column 1		**Column 2**		**Column 3**		**Column 4**	
	g	**%**	**g**	**%**	**g**	**%**	**g**	**%**
Injected	38.7	100	38.7	100	38.7	100	10.3	100
Effluent – Methane	0.005	0	0.19	0.5	0.27	0.7	0.11	1.1
Effluent - Organic Carbon	1.853	4.8	2.59	6.7	2.31	6	0.99	16
Effluent - Inorganic Carbon	0.027	0.1	2.20	5.7	1.94	5	1.67	9.6
Sediment Organic Carbon	21.0 ± 13	54.7 ± 33	7.55 ± 6.7	19.6 ± 17	33.3 ± 57.6	86.4 ± 150	10.9 ± 9.1	106.5 ± 88
Sum Effluent + Sediment	22.9 ± 13	59.6 ± 33	12.54 ± 6.7	32.6 ± 17	37.8 ± 57.6	98.1 ± 150	13.7 ± 9.1	133.4 ± 88
Unaccounted for Carbon	15.6 ± 13	40.4 ± 33	26.0 ± 6.7	67.4 ± 17	0.7 ± 57.6	1.9 ± 150	-3.4 ± 9.1	-33.4 ± 88

4.9.3 *Carbon/Substrate Lifetime Based on Carbon Recovered in the Sediment*

The carbon usage rate was estimated as the initial organic carbon injected minus the final sediment carbon divided by the 435 day operation period. The substrate lifetime was then estimated from the carbon injected divided by the average usage rate. Column 4 was not included in the calculation because it received a soluble substrate solution.

Table 7: Carbon substrate life/usage rate in columns 1 - 3.

	Column 1	**Column 2**	**Column 3**
Injected Carbon (g)	38.7	38.7	38.7
Sediment Organic Carbon (g)	21.0 ± 13	7.6 ± 6.7	33.3 ± 58
Usage Rate (g/d)	0.01 ± 0.03	0.07 ±0.02	0.013 ±0.13
Substrate Lifetime (yrs)	1.5 - 9.6	1.2 - 1.9	0.73 - 8.5

Table 7 shows the total amount of carbon used in all columns as well as a usage rate per day based on the total amount of carbon recovered at the end of the project lifetime. Column 2 had a predicted lifetime of 1.2 to 1.9 yrs depending on how much carbon is actually left in the column. If the carbon numbers are accurate, we would expect the efficiency of reductive dechlorination to have declined towards the end of the 1.2 year (435 day) monitoring period. However, there was no evidence of declining efficiency sufficient organic carbon was still present in column 2 to support very efficient reductive dechlorination. The large uncertainty in the final organic carbon content in column 3 resulted in a proportionately high uncertainty in the substrate lifetime ranging from less than the experimental period to lasting another 8.5 years.

4.10 Summary of Mass Balance Results

Sediment samples collected from the columns at the end of the project were used to develop mass balances for total carbon and for chloroethenes. Because of poor sample recovery, there are significant uncertainties in the total mass of carbon remaining in the sediment. However, the carbon mass balance did demonstrate that: (a) a uniform carbon distribution may not be a valid assumption; and (b) most of the inorganic carbon produced was not directly associated with

reductive dechlorination. The chloroethene mass balance results indicate that significant amounts of chloroethenes were not sorbed to the sediment in any of the live columns but were sorbed in the low pH – column 1. These results demonstrate that reductive dechlorination of PCE to less hydrophobic compounds substantially reduced the impact of sorption on contaminant transport.

4.11 Permeability Loss in Columns

4.11.1 *Permeability Loss from Inlet to Outlet*

One of the major concerns raised about the potential use of edible oil emulsions for aquifer bioremediation has been the potential impact on aquifer permeability. To evaluate the potential for aquifer clogging due to biomass growth and/or gas production, the effective permeability of the columns were periodically determined by measuring the head loss between the column influent and effluent while maintaining a constant flow rate. Figure 14 shows the variation in the measured hydraulic conductivity (K) divided by the initial hydraulic conductivity (Ko) over the course of the experimental period. The value plotted at 0 months is the K/Ko immediately following emulsion injection. Measured values of K are shown as m/d in Table 8.

Table 8: Permeability variation with time from column inlet to outlet.

	Average Permeability from Inlet to Outlet (m/d)			
Time Period	**Low pH - 1**	**Emulsion Treated - 2**	**Emulsion/Sludge Treated - 3**	**Soluble Substrate - 4**
Beginning	3.92	2.25	3.23	1.82
After Injection	5.45	1.11	1.29	n/a
3 – Months	5.76	0.32	0.40	1.08
6 – Months	3.57	0.75	0.70	0.63
10 – Months	2.04	0.25	0.25	0.08
13 – Months	2.25	1.64	0.38	0.06

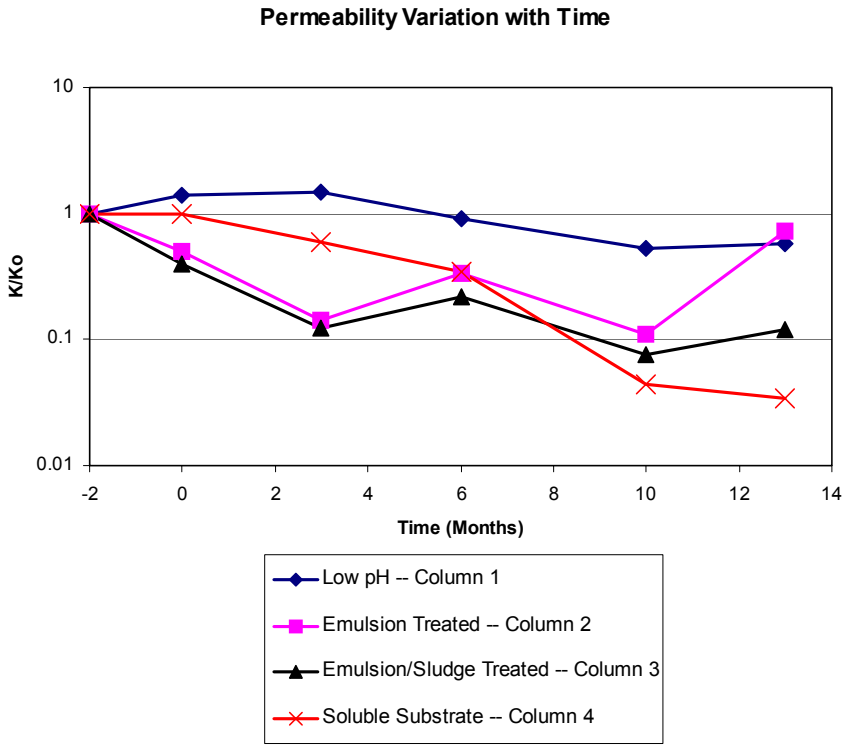

Figure 14: Change in relative permeability (K/Ko) from inlet to outlet during column operation.

The effective hydraulic conductivity of the biologically inhibited column (low pH) increased slightly following emulsion injection and then declined to approximately 50% of the pre-injection value. The cause of this small decline is unknown but may be related to gradual compaction of the sediment in the column or could reflect the limited precision of the measurement technique. In Column 2 (emulsion treated), the effective hydraulic conductivity declined following emulsion injection and then recovered to near the preinjection value at the 13 month measurement. In Column 3 (emulsion and sludge), permeability loss was somewhat greater and did not recover during the last measurement. The somewhat greater permeability loss could be due to the greater biological activity in this column associated with addition of the anaerobic digester sludge. Finally, permeability loss was greatest in the soluble substrate fed column, presumably due to the large amount of readily biodegradable substrate available to the microorganisms.

4.11.2 *Variation in Permeability over the Length of the Column*

Figure 15 shows the variation in permeability between the different sampling ports before emulsion injection, immediately after emulsion injection, and 3, 6, 10, and 13 months after injections. Permeability values are present from the columns inlet to port A (I-A), from ports A to B (A-B), from port B to C (B-C), and from port C to the column outlet (C-O).

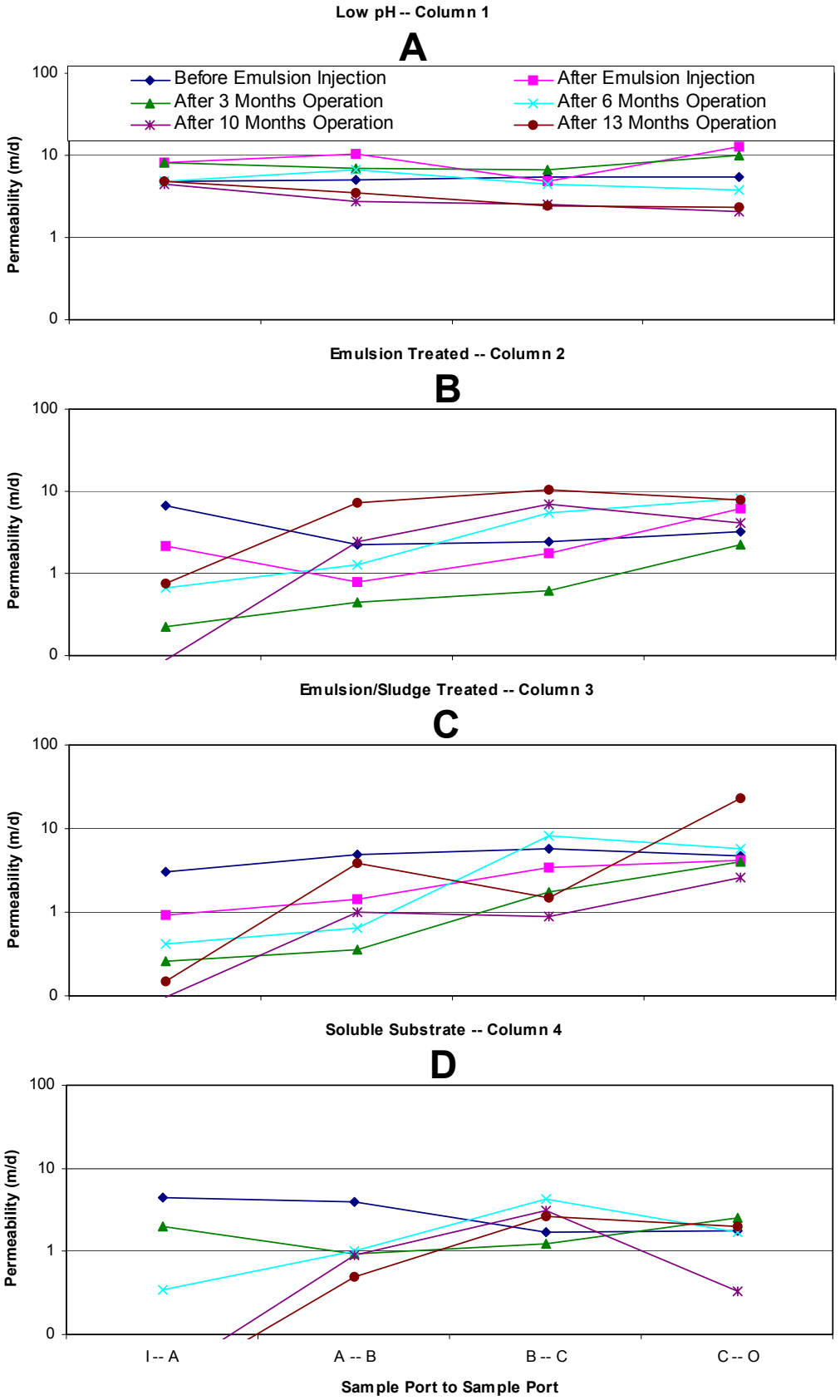

Figure 15: Permeability variation from sample ports over length of the column: (A) Column 1 (B) Column 2 (C) Column 3 (D) Column 4.

In column 1, there was a small decline in permeability over the course of the project, but there was no strong trend in variation in permeability with distance along the column. However, in columns 2, 3, and 4, the lowest permeability was found between the inlet and port A with increasing permeability observed between the other sampling points. As previously discussed, biological activity was most extensive near the column inlet and coincides with the region of greatest permeability loss. However, the lower permeability could also be due to sediment compaction. Given that fine sand was used for column packing, significant compaction of the sediment seems unlikely.

5.0 MATHEMATICAL MODELING OF CHLORINATED SOLVENT TRANSPORT AND BIOTRANSFORMATION

5.1 Methods of Modeling Literature Review

A variety of modeling approaches have been employed to simulate reductive dechlorination ranging from simple first-order decay equations to complex numerical models that incorporate the effect of electron donor availability and presence of competing electron acceptors on decay rates (SEAM3D, Widdowson, 2002). In this work, we chose to use the sequential 1st order decay model incorporated as module in RT3D within GMS 4.0. As discussed by Corapcioglu et al. (2004), 1st order decay models may be appropriate for simulating Michaelis-Menton type reactions when the contaminant concentrations are less than the half-saturation constant. When using GMS a program called MODFLOW can simulate the water flow in 1, 2, or 3 dimensions. After the appropriate head distribution is simulated RT3D can be used to simulate the reductive dechlorination process. RT3D is a modified version of MT3DMS and is contained in the MT3D menu. RT3D utilizes alternate chemical reaction packages and has one available for simulating

reductive dechlorination. In RT3D, sequential 1st order decay of chlorinated solvents can be represented by the following equations.

$$R_A \frac{\partial [A]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij} \frac{\partial [A]}{\partial x_j} \right) - \frac{\partial (v_i [A])}{\partial x_i} + \frac{q_s}{\phi}[A]_s - K_A [A]$$

$$R_B \frac{\partial [B]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij} \frac{\partial [B]}{\partial x_j} \right) - \frac{\partial (v_i [B])}{\partial x_i} + \frac{q_s}{\phi}[B]_s - K_B [B] + Y_{B/A} K_A [A]$$

$$R_C \frac{\partial [C]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij} \frac{\partial [C]}{\partial x_j} \right) - \frac{\partial (v_i [C])}{\partial x_i} + \frac{q_s}{\phi}[C]_s - K_C [C] + Y_{C/B} K_B [B]$$

$$R_D \frac{\partial [D]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij} \frac{\partial [D]}{\partial x_j} \right) - \frac{\partial (v_i [D])}{\partial x_i} + \frac{q_s}{\phi}[D]_s - K_D [D] + Y_{D/C} K_C [C]$$

where,

K_x = 1st order degradation rate for compound x

[ ] = Concentration

$Y_{x/y}$ = Stoichiometric yield coefficient for conversion of compound y to x

R_x = Retardation factor for compound x

In this approach, A = PCE, B = TCE, C= DCE and D = VC. The stoichiometric yield coefficient, Y, represent the mass of degradation product produced per mass parent compound degraded. Note that all decay reactions in this model are assumed to occur only in the aqueous phase, which is a conservative assumption.

Retardation is found from the below equation:

$$R = 1 + (K_p * P_B)/n_e$$

where,

R = Retardation factor

K_p = Partition Coefficient

P_B = Bulk Density

n_e = Effective Porosity

These parameters can be found in Tables 8 and 9.

5.2 Modeling Objectives

The objective of this portion of the project was to evaluate the ability of the sequential 1st order decay module in RT3D to simulate reductive dechlorination in an edible oil barrier, and if this was successful, to estimate decay rates that could be used in the design of full-scale barriers. When designing a barrier, the barrier dimensions required to achieve a certain HRT and associated pollutant removal efficiency must be determined. Ideally, the contaminant concentrations in an area are known and we can use the mathematical model to estimate the travel time and associated treatment efficiency. The amount of carbon required is determined based on an expected utilization rate and the design life of the barrier. Once the amount of carbon is known, it is simply a matter of injecting the organic substrate to form the required barrier. The remainder of this section will deal with the modeling results and the resulting first order decay rates. It should be noted that the estimated decay rates in modeling this work will be slightly higher than those in the field because of the higher temperature of the laboratory studies. Groundwater temperatures often range from 10 to 13^o C and laboratory columns were maintained at a constant temperature of 21^o C.

5.3 Biological/Mathematical Modeling Methods

For simulation purposes, each column was represented as a 1 x 1 x 102 array of cells. Each cell was 9.285 cm wide x 9.285 cm tall x 1.0 cm in the direction of water flow for a total of 102 cells in the x-direction. The two extra cm were included to simulate the model inlet and outlet drain. A simulation was then run using MODFLOW within the GMS modeling system to simulate the head distribution for each of the columns. Stress periods were set to match the sample periods for all columns. Flow rates over the sample periods were input for the injection well located in the first cell of the column. The columns were modeled as confined aquifers with a starting head of 6 cm. The permeability was chosen based on the experimental results after the 10 month permeability test. The drain was put in with a high conductivity so it would maintain a constant head in the outlet cell.

The RT3D simulation used the MODFLOW results for the head distribution and had the same stress periods. A minimum of 4 time steps per stress period were used. This was decided to be valid after the default setting of 10 time steps was used for modeling column 2 and compared to that of 4 time steps per stress period. The results from the different simulations varied little, were easier to manage, and the program ran faster when 4 time steps per stress period were used. Contaminant biodegradation was simulated using the sequential decay reactions included in RT3D under the chemical reaction package. The effective porosity of each column was estimated from the bromide tracer test. The Modified Incomplete Choleski solver in the GCG solver package was selected for its rapid solution and close match to other solvers. A constant dispersivity of 10 cm was used for all columns. The observation coverage for the inlet, outlet, and three sample port cells (1, 101, 26, 51, and 76 respectively) was used for comparison of

model results with the experimental data. Sorption to the entrapped oil was simulated as a linear isotherm. The bulk density was estimated from the column 1 effective porosity and assuming a sediment specific gravity of 2.65. The sorption coefficients were based on the octanol-water partition coefficient and the fraction of oil injected into the columns. All physical parameters that were used in modeling can be seen in Table 9.

5.4 Modeling Parameters

The sediment-water partition coefficients (K_p) for PCE, TCE, DCE, and VC are presented in Table 10. K_p was calculated as the product of the octanol-water partition coefficient (K_{ow}) and the sediment organic fraction (f_{oc}). f_{oc} was assumed to be equal to the carbon present in the injected oil for columns 1, 2, and 3. For column 4, the background organic carbon content of the sediment was used. For TCE, DCE, and VC, the published K_{ow} values were used without further calibration. However for PCE, published values of K_{ow} vary between 400 and 3500. In this work, a K_{ow} of 400 was found to provide the best fit for the PCE breakthrough curve in column 1. This best-fit value was then used in simulations for columns 2, 3, and 4.

Table 9: Physical Parameters used in Model Simulations

Physical Parameters	**Column #**			
	1	**2**	**3**	**4**
Bulk Density (g/cc)	1.49	1.49	1.49	1.49
Effective Porosity	0.44	0.42	0.35	0.38
Ave. Flow Rate (mL/d)	100	107	148	108
Background f_{oc} (g/g)	0.000245	0.000245	0.000245	0.000245

Oil Content f_{oc} (g/g)	0.002781	0.002781	0.002781	N/A
Total f_{oc} (g/g)	0.003025	0.003025	0.003025	0.000245
Dispersivity (cm)	10	10	10	10

Table 10: Partition Coefficients used in Model Simulations

	PCE	**TCE**	**DCE**	**VC**
Octanol-Water Partition, K_{ow}	400	263	72	4
Column 1 K_p (g/mL)	1.112	0.731	0.200	0.011
Column 2 K_p (g/mL)	1.112	0.731	0.200	0.011
Column 3 K_p (g/mL)	1.112	0.731	0.200	0.011
Column 4 K_p (g/mL)	0.098	0.064	0.018	0.001

Table 11: Biotransformation Kinetic Coefficients used in Model Simulations

Kinetic Coefficients	**Column #**			
Stoichiometry Yield Coefficients	**1**	**2**	**3**	**4**
PCE -> TCE (g/g)	0.792	0.792	0.792	0.792
TCE -> DCE (g/g)	0.738	0.738	0.738	0.738
DCE -> VC (g/g)	0.644	0.644	0.644	0.644
Decay Rates (0-322 days)				
PCE (d^{-1})	0	1	1	1

TCE (d^{-1})	0	4	4	4
DCE (d^{-1})	0	0	0	0.1
VC (d^{-1})	0	0	0	0.15
Decay Rates (322-435 days)				
PCE (d^{-1})	0	1	1	1
TCE (d^{-1})	0	4	4	4
DCE (d^{-1})	0	1	0.005	0.1
VC (d^{-1})	0	0.75	0.3	0.15

5.5 Modeling Results

5.5.1 *Column 1 – Low pH*

Low pH column 1 had little biological activity and was modeled assuming all first order decay rates were equal to zero. Using a K_{ow} for PCE of 400, PCE reached a concentration of half the average influent concentration on day 400. Figure 16A and 16B show the simulated column influent and effluent PCE concentrations. During the experimental period, there were four times when extremely high PCE concentrations were detected in the influent samples. These very high concentrations are thought to have occurred due to pumping non-aqueous phase PCE into the sample lines when the flow rates were increased for sample collection. These very high concentrations are not believed to be representative of what actually entered the column and were not included when simulating the inflow concentration for the numerical model.

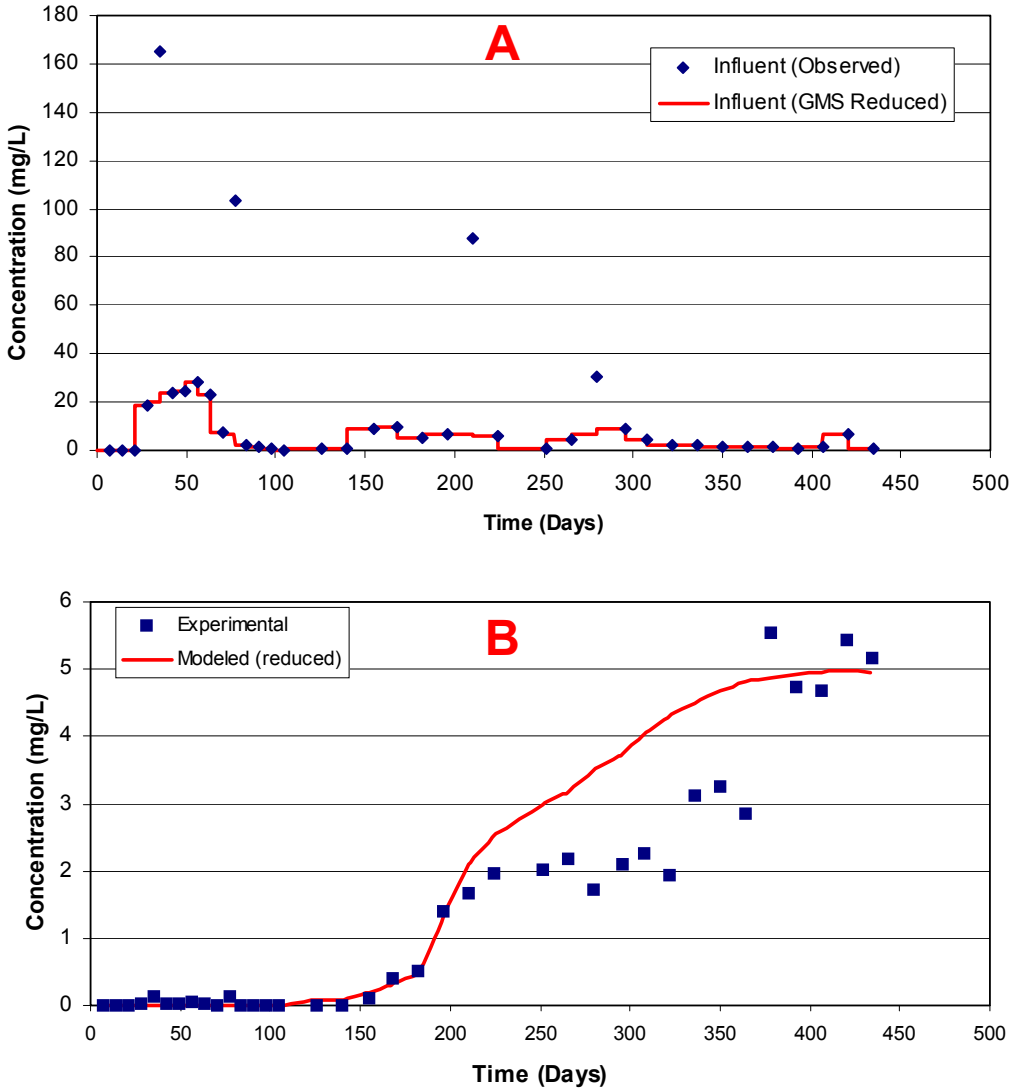

Figure 16: Simulated and observed concentrations in the low pH - column 1: (A) PCE in influent and (B) PCE in effluent.

As seen in Figure 16B, the simulated PCE breakthrough curve closely matches the observed PCE breakthrough. As previously mentioned, this fit was obtained with a K_{ow} for PCE of 400. This best-fit value for the PCE K_{ow} was then used in the column 2, 3, and 4 simulations.

5.5.2 *Column 2*

Significant levels of PCE and TCE were not detected in the effluent of any live columns. As a consequence, the discussion in this section will focus on modeling the breakthrough and subsequent removal of DCE and VC. Modeling of column 2 included biological activity and required first order decay rates to simulate the degradation of the chlorinated solvents. Once simulations began, it became clear due to the lack of DCE degradation until approximately day 320, that two successive simulations would be needed to model the observed biodegradation. The first simulation covered the first 322 days, with the DCE degradation rate assumed to be equal to zero and PCE and TCE decay rates equal to 1 and 4 day^{-1}, respectively. After day 322 the decay rates were changed to 1, 4, 1, and .75 day^{-1} for PCE, TCE, DCE, and VC. The influent PCE concentrations used in the column 2 simulation are shown in Figure 17A. As with column 1, there were 3 times when very high PCE concentrations were detected in the column 2 influent, presumably due to a sampling error. However, these high concentrations were included in the model input since they did not appear to have a significant impact on the model simulation results. Simulated breakthrough curves for DCE and VC are shown in Figures 17B and 17C. The model over estimates the DCE concentrations during the first 322 days, but closely matches DCE concentrations during the later portions of the experiment. The over prediction could be due to the model predicting more PCE degradation and less sorption than actually occurred. The model appears to provide a good match with observed VC concentrations throughout the experiment.

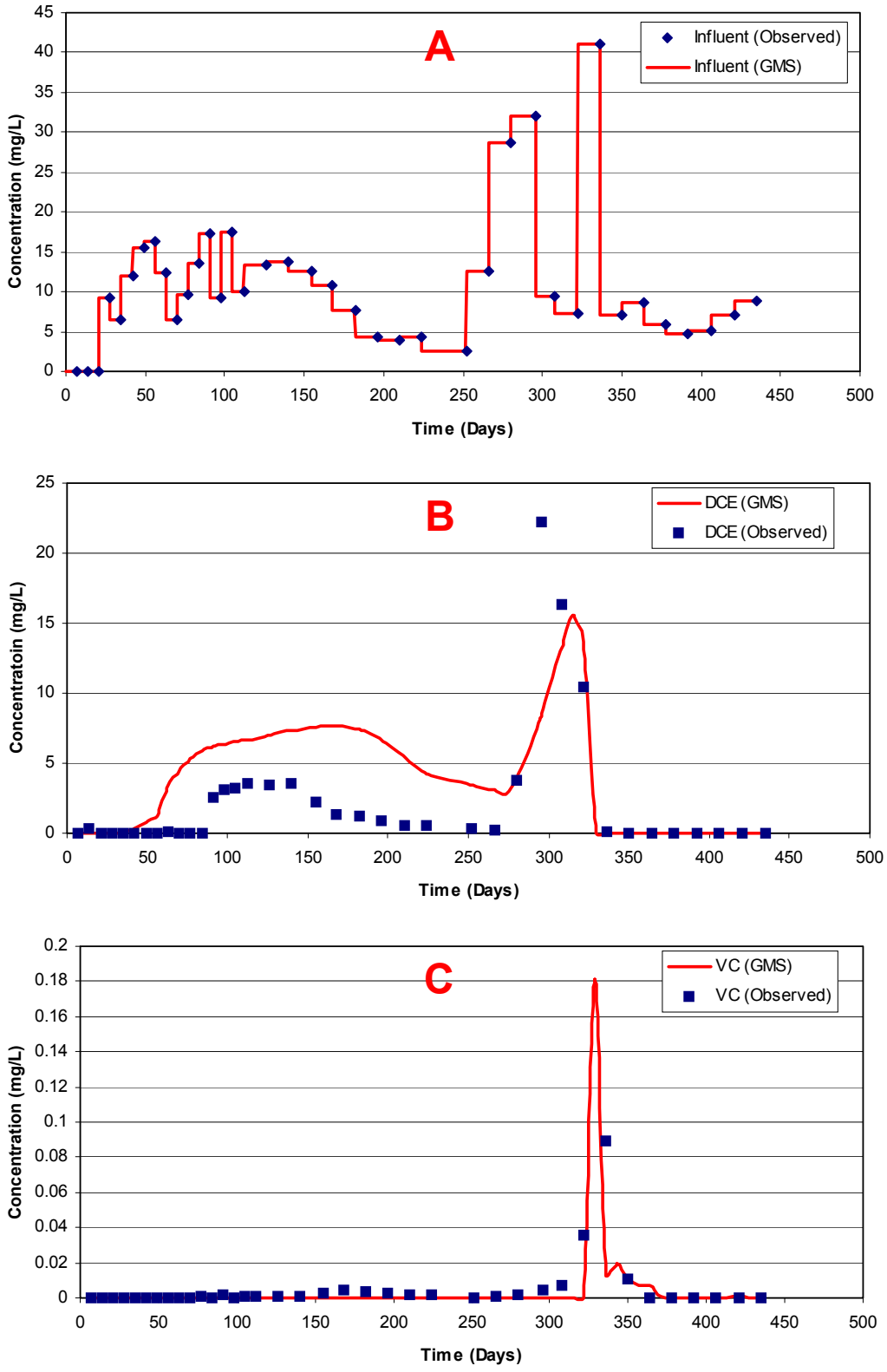

Figure 17: Simulated and observed concentrations in the emulsion treated - column 2 effluent: (A) PCE in influent (B) DCE in effluent (C) VC in effluent.

5.5.3 *Column 3*

Column 3 was also modeled using different kinetic parameters for the time periods 0 – 322 days and 322 to 435 days. Little if any PCE or TCE was observed in the effluent so simulation results are only presented for DCE and VC. The observed versus simulated results for DCE and VC are shown in Figure 18B and 18C. The result is not as close of a match as column 2. However, the mass balance is better and the peaks are apparent just shifted in time by about two weeks. The shape being shifted could be due to an inaccurate estimate of porosity, incorrect partition coefficients, or slightly different first order decay rates. The decay rates used for PCE, TCE, DCE, and VC were 1, 4, 0, and 0 day^{-1} respectively for 0 – 322 days and 1, 4, 0.005, and 0.3 day^{-1} for 322 – 435 days. The lower decay rates for DCE and VC during the second time period were used because DCE and VC degradation was not as efficient in column 3 as in column 2. The exact values themselves were used because they provided the best fit to the data.

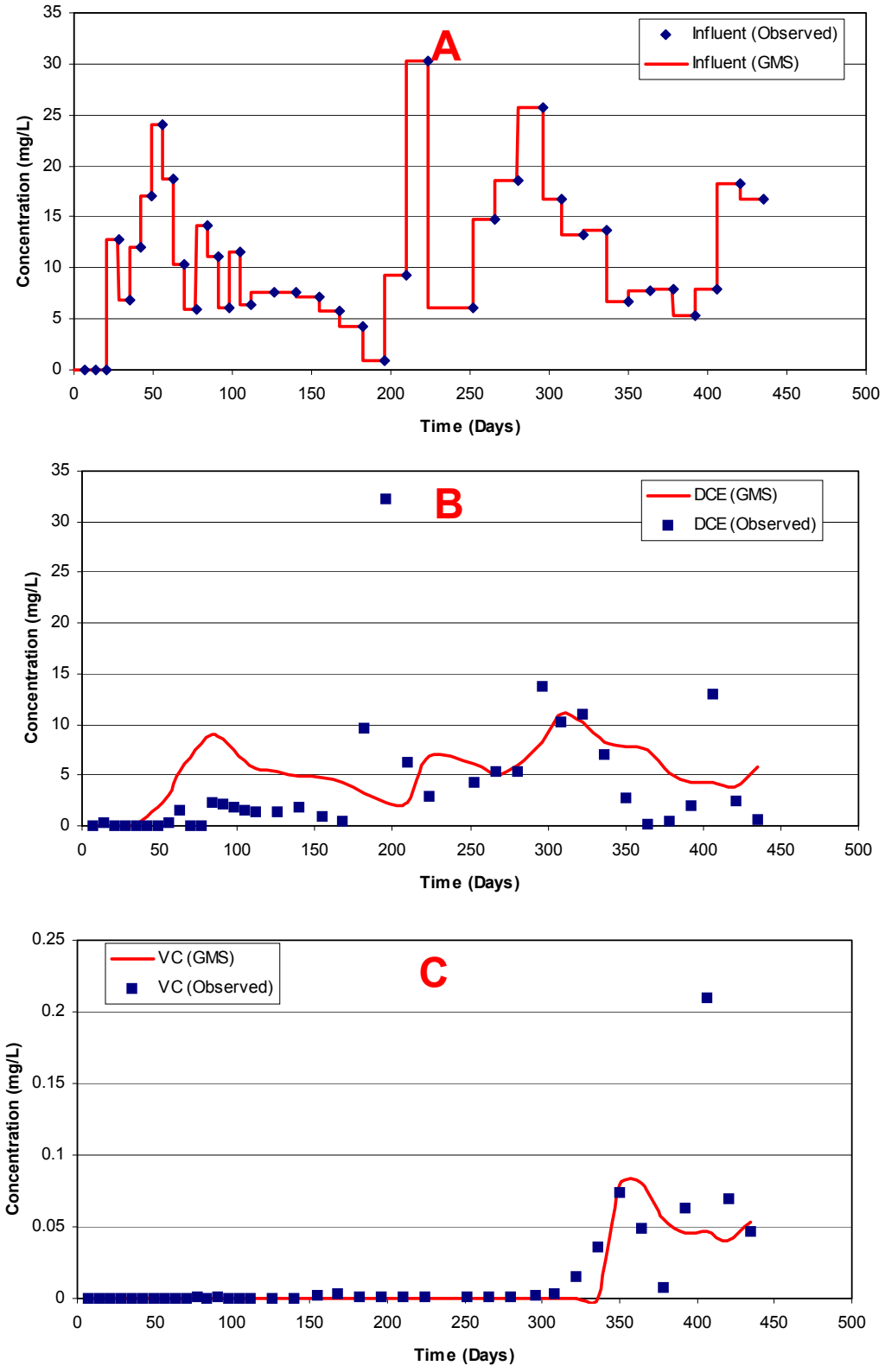

Figure 18 Simulated and observed concentrations in the emulsion/sludge treated - column 3 effluent: (A) PCE in influent (B) DCE in effluent (C) VC in effluent.

5.5.4 *Column 4*

Column 4 could not be modeled with any accuracy. Unlike columns 2 and 3, the DCE and VC degradation patterns could not be matched to the observed values. As with the previous modeled columns, PCE and TCE were below detection throughout the experiment and had little impact on model calibration. DCE, VC, and ethene were observed in the effluent of column 4 earlier than the two emulsion treated columns. A single simulation period from 0 – 435 days was used with degradation rates for PCE, TCE, DCE, and VC set at 1, 4, 0.1, and 0.15 day^{-1}. Attempts were made to better match the observed results using two simulation periods with different decay rates (Figure 19D). However, this approach did not significantly improve the model fit. The poor modeling results may be because of the limited ability to predict sorption in column 4. Without the emulsion inject the fraction of organic carbon was more difficult to establish, which made the sorption coefficient more difficult to predict.

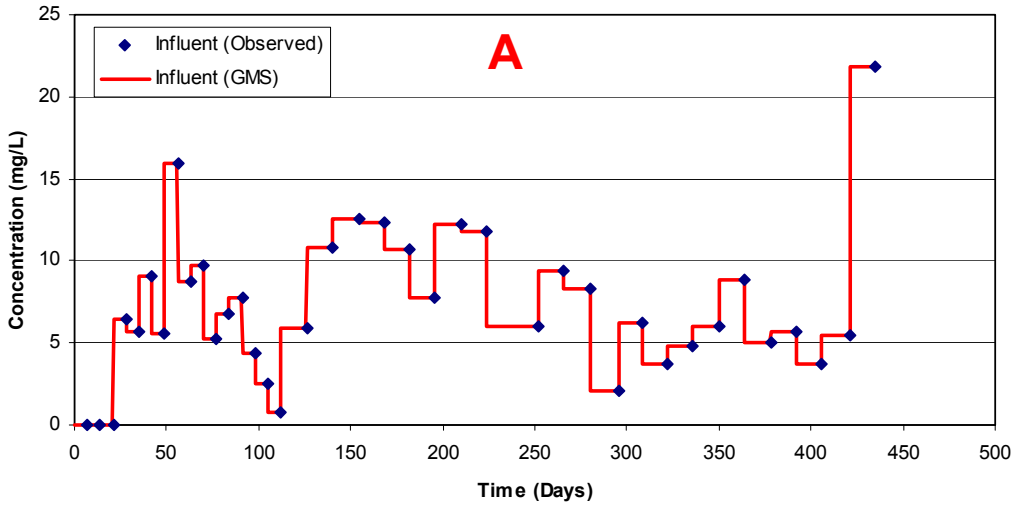

Figure 19A: Simulated and observed PCE concentrations in the soluble substrate - column 4 influent.

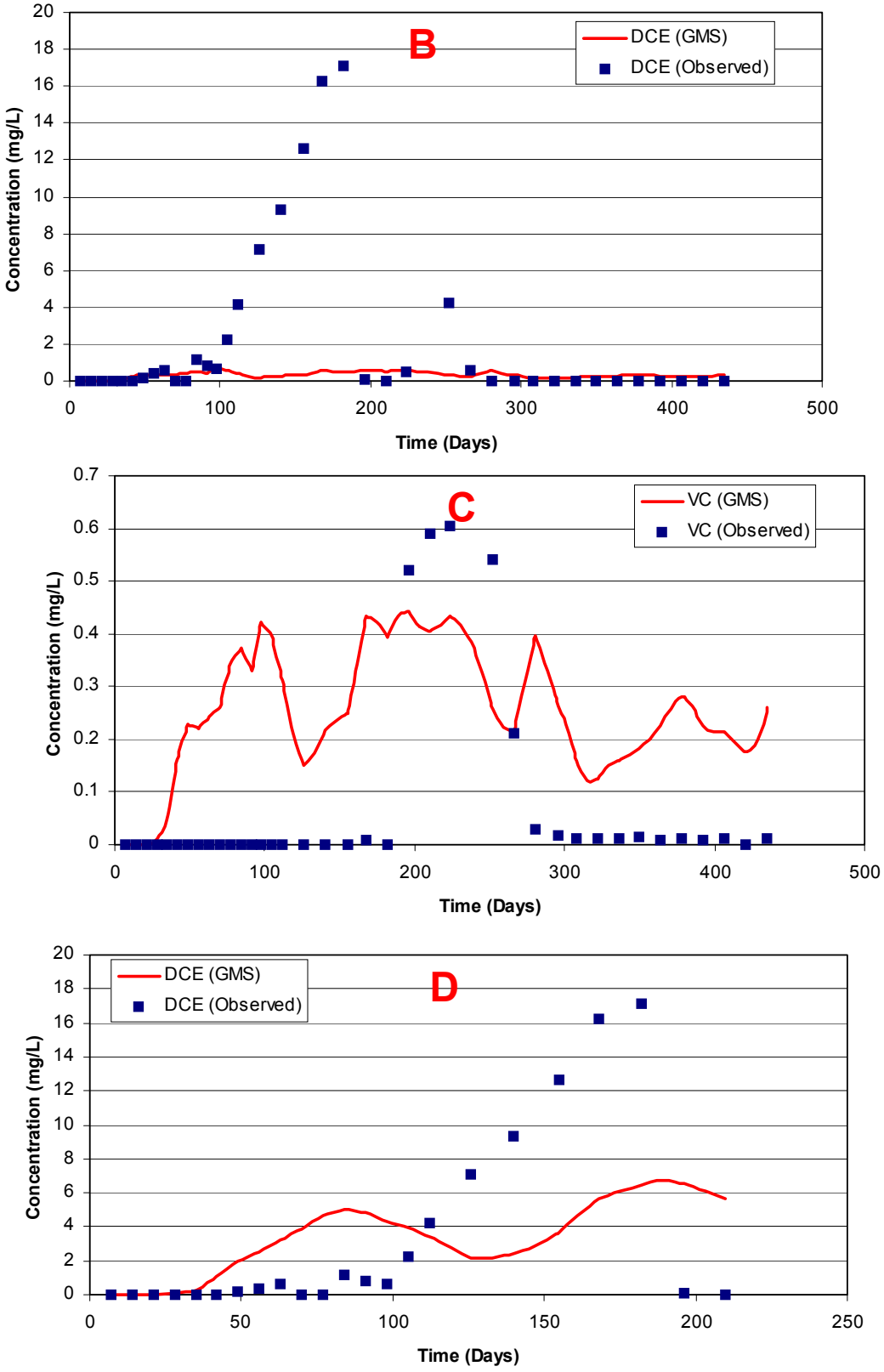

Figure 19: Simulated and observed concentrations in the soluble substrate - column 4 effluent: (B) DCE in effluent – single simulation period; (C) VC in effluent – single simulation period; and (D) DCE in effluent – two modeling periods.

5.6 Modeling Mass Balance

Overall mass balance results for each of the model simulations are presented in Table 12. In column 1, total mass of PCE discharged in the model effluent closely matched observed. Since all decay rates were set to zero for column 1, no TCE, DCE or VC was present in the effluent, which closely matched experimental results. In columns 2 and 3, overall mass balance results for the model closely matched simulated values for PCE, TCE, DCE, and VC. As discussed previously, the match between simulated and observed for column 4 was poor.

Table 12: Modeling mass balance summary table in milligrams (mg) of each chloroethene.

PCE Effluent	**Column 1**	**Column 2**	**Column 3**	**Column 4**
Modeled	113	<5	<5	<5
Experimental	88	1.1	15	3.5
TCE Effluent				
Modeled	0	< 1	< 1	< 1
Experimental	12	< 1	5	<1
DCE Effluent				
Modeled	0	186	356	15.4
Experimental	< 1	117	362	106
VC Effluent				
Modeled	0	0.50	0.95	11.8
Experimental	< 1	0.39	1.48	4.60

6.0 OVERALL EVALUATION OF TREATMENT PERFORMANCE

Experimental results from column 2 show that permeable reactive barriers created using edible oil emulsions have the potential for providing very effective treatment of high concentrations of chlorinated ethenes with a reasonable contact time (~ 1 month). Given that the project was carried out at 21^{o} C, a more conservative contact time is recommended for field scale systems. A contact time of greater than one-month should be used. This allows for the potential of slower degradation at the lower temperature observed in groundwater.

Sorption of the more hydrophobic contaminants (e.g. PCE) can be significant. However, once an active microbial population is established, PCE and/or TCE that has partitioned into the residual soybean oil will be released and degraded. The sorption observed from PCE and associated degradation products can be predicted by using the octanol water partitioning coefficient and the fraction of oil injected. Results from Column 3 suggest that competition between dechlorinators and methanogens for substrate/hydrogen may, in some cases, limit complete dechlorination of DCE to ethene. Column 3 may also have lagged behind column 2 in complete dechlorination because it had a shorter average retention time at ~20 days than the estimated 33 day retention time for column 2. Soluble substrate column 4, which exhibited the fastest removal rate, also had the recommended estimated retention time of 30 days. A one-month retention time appears to be ideal for reductive dechlorination under the experimental conditions of this project.

Columns 2 and 3 were bioaugmented on three separate dates to ensure complete dechlorination. At this point, it is unclear if the dechlorination that followed resulted from the actual bioaugmentation culture or the yeast extract loading that preceded the bioaugmentation.

Circumstantial results from this project suggest that the addition of yeast extract may be beneficial for stimulating complete dechlorination of PCE to ethene.

In columns 2 and 4, a substantial portion of the injected PCE was not recovered in the column effluent and sediment. These columns were also observed to completely dechlorinate PCE through DCE and VC to ethene. This suggests that some process may be degrading the ethene further, possibly producing methane or carbon dioxide and is consistent with the work of Bradley (1999).

Results from this study showed that a one-time injection of an edible oil emulsion supported reductive dechlorination for over 435 days. Gradual use of the substrate over time should allow for one-time injections that can last up to 10 years. The projected carbon lifetime in columns 2 and 3 are 1.2 yrs and 8.5 years respectively. The longer lifetime of carbon in column 3 could be attributed to the less efficient dechlorination in this column or simply due to uncertainties in the amount of carbon remaining at the end of the experiment. As degradation rates increase, so will the carbon usage. Overall the reductive dechlorination process is a relatively inefficient one with only 0.5% to 1.7% of the inorganic carbon produced as a result of dechlorination.

Permeability loss associated with biomass growth and/or gas production can be significant in columns treated with emulsified soybean oil. However, the permeability losses in the emulsion-treated columns were no worse than in the soluble substrate column. While permeability loss is an important consideration in any anaerobic bioremediation process, our results indicate that permeability loss in edible oil emulsion barriers will probably not be excessive. In most cases, it should be possible to design an effective permeable reactive barrier using edible oil emulsion by increasing the barrier length to account for the anticipated permeability reduction.

The modeling results indicate that PCE breakthrough and dechlorination can be reasonably simulated when a soybean oil emulsion is used as the carbon source. There appeared to be two phases in the dechlorination process. During the first phase, only PCE and TCE degraded. Then after the third bioaugmentation event around day 322, DCE started to degrade to VC and further to ethene. Mathematical model results showed that DCE and VC were the byproducts that could be simulated most effectively. PCE and TCE were degraded rapidly and as a result they were not very useful in the modeling process.

The lack of a mass balance made it impossible to model any column exactly. As a result, columns 2 and 3 were modeled more for the general shape of the contaminant breakthrough curve than actual chloroethene concentration. Although column 3 exhibited less DCE degradation, the model provided a fairly good match between the simulated and observed masses. It may be possible to improve the match between simulated and observed concentrations through minor adjustments of the contaminant degradation rates. Overall simulation of DCE is reasonably straight forward and accurate. However, simulating further degradation to VC and ethene becomes more difficult. For future modeling purposes, other programs that simulate DCE and VC degradation with multiple pathways should be explored. Improving our understanding of these processes will allow development of more accurate models of chloroethene degradation. Overall RT3D was useful in fitting the observed results for emulsion treated columns, but is unable to be used to predict the degradation that will take place in the field. As a result, any predictions of in-situ biodegradation generated using RT3D should be viewed with caution.

7.0 CONCLUSIONS

- Permeable reactive barriers (PRB) installed with emulsified edible oils can be effective at enhancing reductive dechlorination.
- A conservative hydraulic retention time (HRT) for enhancing reductive dechlorination in an edible oil emulsion PRB is greater than 1 month.
- Addition of yeast extract to the emulsion before injection in the field should be considered to enhance complete reductive dechlorination.
- More research is needed to understand the pathways of DCE and VC degradation and the ultimate fate of these compounds in strongly reducing environments.
- Results from column 3 indicate that a single injection of emulsified edible oil into sandy sediments could potentially last for up to 8 years providing a long-term source of organic substrate to stimulate in-situ biodegradation of chlorinated solvents. Results from column 2 indicate that the substrate lifetime may be considerably shorter. However, the carbon balance for column 2 was only able to account for 33% of the injected carbon suggesting that substrate lifetime estimated from this column may not be reliable.
- The reductive dechlorination process is relatively inefficient with respect to carbon use. Other compounds including dissolved oxygen, iron, sulfate, and nitrate need to be considered when estimating the actual carbon required for enhancing reductive dechlorination.

- Permeability loss is significant with an edible oil substrate. However, permeability loss is also significant with soluble substrates. The potential impacts of permeability loss need to be carefully considered when designing any anaerobic bioremediation system.
- Modeling dechlorination for the edible oil substrate columns with first order kinetics is possible, especially to the point of DCE and in some cases to VC.

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9.0 APPENDIX – ANALYSIS OF SEDIMENT SAMPLES AFTER COMPLETION OF COLUMN EXPERIMENTS

Chlorinated Solvent Results			
Distance from Inlet (cm)	PCE (ug/g)	TCE (ug/g)	DCE (ug/g)
Column 1			
10	13.4721	0.0084	0.055
20	7.6589	0.0041	0.019
30	0.3483	0.0002	0.018
40	0.5885	0.0003	0.019
50	0.9227	0.0002	0.019
60	12.2095	0.0027	0.024
70	0.0171	0.0203	0.019
80	6.5425	0.0005	0.021
90	12.8343	0.0036	0.019
Column 2			
0	0.0102	0.0222	0.019
50	0.0006	0	0.018
60	0.0005	0	0.016
70	0.0004	0	0.014
80	0.0006	0	0.001
90	0.0004	0	0.016
100	0.0002	0	0.019
Column 3			
0	0.62	0.0001	4.025
80	0.0004	0	0.018
90	0	0	0.022
100	0	0	0
Column 4			
0	1.4018	0.2049	0.029
30	0.0066	0.0005	0.001
40	0.0001	0	0.005
50	0	0	0.021
60	0	0	0.019
70	0.0001	0.0001	0.001
80	0	0	0.013
90	0.0001	0	0
100	0.0001	0.0001	0.019

Total Carbon Results			
Distance from Inlet (cm)	ID	Lab ID	% C
Column 1			
20-30	C1-1	Z3419	0.14
30-40	C1-2	Z3420	0.12
40-50	C1-3	Z3421	0.17
50-60	C1-4	Z3422	0.17
60-70	C1-5	Z3423	0.18
70-80	C1-6	Z3424	0.1
80-90	C1-7	Z3425	0.48
90-100	C1-8	Z3426	0.19
Column 2			
0	C2-IN	Z3432	0.23
40-50	C2-1	Z3427	0.04
50-60	C2-2	Z3450	0.05
60-70	C2-3	Z3428	0.05
70-80	C2-4	Z3429	0.06
80-90	C2-5	Z3430	0.08
90-100	C2-6	Z3431	0.12
100	C2-OUT	Z3433	0.08
Column 3			
0	C3-IN	Z3440	1.61
40-50	C3-1	Z3434	0.1
50-60	C3-2	Z3435	0.07
60-70	C3-3	Z3436	0.06
70-80	C3-4	Z3437	0.05
80-90	C3-5	Z3438	0.08
90-100	C3-6	Z3439	0.18
100	C3-OUT	Z3441	0.16
Column 4			
0	C4-IN	Z3448	0.06
40-50	C4-1	Z3442	0.06
50-60	C4-2	Z3443	0.07
60-70	C4-3	Z3444	0.06
70-80	C4-4	Z3445	0.05
80-90	C4-5	Z3446	0.23
90-100	C4-6	Z3447	0.26
100	C4-OUT	Z3449	0.13
Background Carbon			
	FS1		0.0221
	FS2		0.0262
	FS3		0.0252
	Average		0.0245

Any questions about research or methods used can be directed to Dr. R.C. Borden at North Carolina State University. A thanks to everyone that was involved.