Bench Scale Performance of Partitioning Electron Donors for TCE DNAPL Bioremediation

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Abstract

Prior to the implementation of an enhanced bioremediation pilot study for a trichloroethene (TCE) source area at an industrial site in the United Kingdom (the Site), laboratory microcosm and column studies were performed. The purpose of this column study was to determine if TCE removal rates could be increased with the addition of partitioning electron donors and bioaugmentation with KB-1® culture. Three 1-meter continuous flow columns were constructed using aquifer solids from the Site and artificial groundwater. A TCE dense non-aqueous phase liquid (DNAPL) zone was emplaced in each column. SRS™, a commercially available emulsified vegetable oil (EVO) product, and n-butyl acetate (nBA) were evaluated as partitioning electron donors, while the third column acted as an unamended control. Both nBA and SRS™ were successfully used in previous microcosm studies with high concentrations of TCE (400 and 800 mg/L) to successfully promote the reductive dechlorination of TCE to ethene.

Dechlorination of TCE to *cis*-1,2-dichloroethene (*cis*-DCE) with trace amounts of vinyl chloride (VC) and ethene, as well as sulfate reduction, were observed in the SRS™ column effluent while DNAPL was present. A dissolution enhancement factor of 2.1 was calculated. The TCE source zone was depleted after approximately 300 days of column operation. Following depletion of the TCE DNAPL, high concentration (~400 mg/L) of TCE amended artificial groundwater was pumped through the column to simulate high TCE concentrations in a plume down gradient from a source zone. Dechlorination of TCE via *cis*-DCE and VC to ethene was observed in the column effluent along with increases in *Dehalococcoides* (Dhc) counts. Sulfate concentrations increased during the plume phase while dechlorination to ethene still occurred indicating that complete dechlorination to ethene was possible in the presence of sulfate.

Dechlorination of TCE to *cis*-DCE was observed, but neither VC nor ethene was detected in the nBA Amended column. The nBA was observed to degrade in the column to butyl alcohol and acetate, neither of which partition as strongly as nBA, and were not retained in

the column. A continuous addition of nBA promoted the highest amount of *cis*-DCE production and sulfate reduction was also observed. Once the continuous addition was stopped, dechlorination and sulfate reduction halted indicating that electron donor retention in the column was not achieved. *Dehalococcoides* (Dhc) concentrations did not increase in the effluent of this column. A dissolution enhancement factor of 1.2 was calculated for the nBA column.

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Dedication

For Pam

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List of Abbreviations

AGW	artificial groundwater
cm	centimeter
cm/day	centimeter per day
CO_2	carbon dioxide
CHC	chlorinated hydrocarbon
cis-DCE	*cis*-1,2-dichloroethene
COC	contaminant of concern
Dhc	*Dehalococcoides*
^oC	degrees Celsius
^oC/min	degrees Celsius per minute
DNAPL	dense non aqueous phase liquid
DAP	diammonium phosphate
DHG	dissolved hydrocarbon gases
EVO	emulsified vegetable oil
GC	gas chromatograph
gene copies/L	gene copies per liter
g	grams
g/cm^3	grams per centimeter cubed
g/L	grams per liter
g/mol	grams per mole
H_2	hydrogen
IC	ion chromatograph
Kg	kilogram
LCFA	long chain fatty acid
MCL	maximum contaminant level
MCLG	maximum contaminant level goal
µg/L	micrograms per liter
µM	micromolar
mL	milliliter
mL/min	milliliters per minute

mg/L	milligram per liter
mm	millimeter
mm Hg	millimeters of mercury
mM	millimolar
mV	millivolt
min	minutes
nBA	n-butyl acetate
nM	nanomolar
PED	partitioning electron donor
pmol	picomoles
PCR	polymerase chain reaction
RPM	revolutions per minute
RPD	relative percent difference
rRNA	ribosomal RNA
PCE	tetrachloroethene
TOC	total organic carbon
TCE	trichloroethene
VC	vinyl chloride
*vcr*A	vinyl chloride reductase A gene
VFA	volatile fatty acid
VOC	volatile organic compound

Chapter 1
Introduction

1.1 Introduction

Chlorinated solvents, notably trichloroethene (TCE) and perchloroethene (PCE, also referred to as tetrachloroethene) are among the most common contaminants in soil and groundwater (Ferguson and Pietari, 2000; Cope and Hughes, 2001). The limited aqueous solubility of TCE and PCE often leads to TCE and PCE contaminated sites characterized by the presence of dense non-aqueous phase liquid (DNAPL) source zones. These source zones provide a long term source of groundwater contamination as dissolution of the source zone occurs for up to hundreds of years under natural conditions (Johnson and Pankow, 1992).

Most of the contaminant mass at a DNAPL site is found in the source zone and much attention has been given to explore ways to contain and/or remove the source zone. Typical remediation technologies used include pump and treat, vapor stripping, solvent extraction, thermal technologies, and chemical oxidation (Aulenta et al., 2007). These remedial options typically have high operating costs, prolonged timelines and are often ineffective at treating the DNAPL source zone. More recently there has been an interest in the use of enhanced anaerobic biodegradation to treat DNAPL source zones. This technology has the potential to be both less expensive and faster than other technologies in treating chlorinated solvent source zones (ITRC, 2005).

Bioremediation has been shown in many studies to be an effective remedial option for treating down gradient plume concentrations from a source zone, and more recently appears to be a promising remedial approach for source zones. Biostimulation involves the addition of electron donors and/or nutrients to the subsurface in order to stimulate indigenous anaerobic bacteria present at a contaminated site to transform the target compounds (ITRC, 2005), while bioaugmentation is the introduction of microorganisms capable of transforming a target compound in contaminated media (Adamson et al., 2003). Da Silva et al. (2006) concluded that bioaugmentation enhanced PCE mass removal 1.6 times over biostimulation alone in experimental controlled release system tanks, Yang and McCarty (2000) measured a 5-fold increase in PCE DNAPL dissolution in biological column

experiments and Cope and Hughes (2001) showed that biological activity could enhance the rate of PCE dissolution by up to 16 fold. These laboratory studies were all performed with PCE, which has a lower solubility value then TCE (180 mg/L versus 1,100 mg/L respectively). Although far fewer DNAPL studies have been performed with TCE, Neilson and Keasling (1999) previously demonstrated that an uncharacterized microbial consortium was capable of dechlorination of saturation levels of TCE in microcosm studies and Harkness et al., 1999 showed that TCE concentrations up to 170 mg/L were dechlorinated in bioaugmented columns.

Biodegradation does not act directly on the free phase DNAPL, but depletes the concentrations from groundwater near the DNAPL:water interface. This increases the concentration gradient, which enhances diffusion – driven mass transfer from the DNAPL to the aqueous phase where the degradation occurs (ABA, 2005). Reductive dechlorination of the parent compounds creates the more soluble daughter products *cis*-1,2-dichloroethene (*cis*-DCE) and vinyl chloride (VC). Although it would be ideal to have complete dechlorination to ethene enhanced dissolution of TCE and the production of cis-DCE and VC have advantages because they increase the effectiveness of down gradient treatment systems (pump and treat) and the daughter products are biodegradable through aerobic processes, such as cometabolism (Adamson et at., 2003 and Yang and McCarty 2000). The primary goal of bioenhanced DNAPL dissolution and source treatment is not typically to reduce contaminant concentration to regulatory levels but rather to achieve and maintain a high flux of contaminant from the DNAPL and sorbed phases to the aqueous phase (Aulenta et al., 2006).

With the use of biodegradation to treat DNAPL source zones being recognized, attention has been focused on the use of electron donors that partition into the DNAPL phase and provide a source of electron donor at the DNAPL:water interface. If these electron donors can be introduced into the subsurface and come in contact with the DNAPL, they have the potential to partition into the DNAPL phase and then slowly dissolve back into the water phase providing optimum conditions for dechlorination to occur at the DNAPL:water interface and enhance dissolution. These electron donors can also be cheaper to apply because they do not require continuous or batch additions in order to maintain their effectiveness (Harkness, 2000).

SABRE (source Area BioREmediation) is a public/private consortium of twelve companies, two government agencies, and three research institutions whose charter is to determine if enhanced

anaerobic bioremediation can result in effective and quantifiable treatment of chlorinated solvent DNAPL source areas. The focus of the 4-year, $5.7 million dollar research and development project is a field site in the United Kingdom containing a DNAPL source area with groundwater concentrations exceeding several hundred mg/L of TCE. Unique features of the SABRE study include a systematic attempt to quantify the effectiveness of bioremediation to treat DNAPL in the field, treatment of TCE (as opposed to PCE) DNAPL, and the consideration of slow release and partitioning electron donors such as emulsified vegetable oil (EVO), hexanol, and n butyl acetate (nBA). Prior to field application laboratory microcosm and column experiments were performed. Four laboratories (GE, Dupont, Terra systems, and SiREM) performed microcosm studies, while GE, Dupont, and SiREM also conducted column studies.

1.2 Research Objectives

The focus of this report is on a column study that was performed at the SiREM lab. Important information from the GE column study will be used as required to support observations from this study. The objectives of this study were to:

1. Determine if reductive dechlorination is inhibited by the presence of pure phase TCE when partitioning substrates are used as electron donors.
2. Compare 2 partitioning electron donors for (1) the extent of reductive dechlorination in the presence of TCE DNAPL (2) retention in column, and (3) ability to sustain activity over time.
3. Estimate the extent of DNAPL dissolution enhancement created by the bioremediation process.

This thesis is organized into 8 chapters.

Chapter 2 presents background information

Chapter 3 describes the materials and methods

Chapter 4 describes the batch studies that were performed

Chapter 5 presents the column study experimental design

Chapter 6 presents the results from the column study

Chapter 7 provides a discussion of the column study results

Chapter 8 states the conclusions from this study and planned future work

Chapter 2
Background Information

2.1 Trichloroethene and DNAPLS

TCE is a chlorinated hydrocarbon compound (CHC). The structures of TCE and other chlorinated ethenes are shown in Figure 2.1. Since the 1950s TCE has been used in many industrial processes as a degreasing agent for metal parts and textiles and many other general solvent purposes such as in paints, paint strippers, and adhesives (Agency for toxic Substance and Disease Registry, 1997).

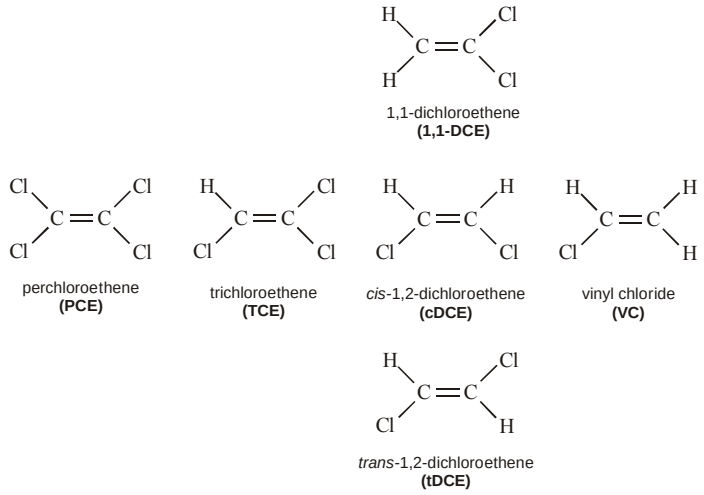

Figure 2.1 Structures of chlorinated ethenes

TCE contaminated soil and groundwater has resulted due to past disposal directly onto land, accidental spills, and leaking storage tanks. TCE is a contaminant of concern at over 500 National Priority List sites in the United States (EPA, 2004). The maximum contaminant level goal (MCLG) for TCE is set at zero, while the maximum contaminant level (MCL) is 0.005 mg/L. Exposure to high concentrations of TCE can cause headaches, drowsiness, and eye nose, or skin irritation and long-term exposure to TCE concentrations in drinking water can cause damage to the liver, kidney, nervous, and immune system (Prager, 1996). There is some evidence to suggest that exposure to TCE over many years may be linked to several types of cancer (Prager, 1996). The physical properties of interest of TCE and other chlorinated ethenes are shown in Table 2.1.

Table 2.1 Physical and Chemical Properties of chlorinated ethenes and ethene (From Montgomery, 2000 and Mackay *et al*., 1993)

	Molecular Weight (g/mol)	Aqueous solubility (mg/L)	Density (g/cm^3)	Vapor Pressure (mmHg)	Log K_{OC}
TCE	131.4	1,100	1.464	74	1.81
Cis-DCE	96.94	3,500	1.284	200	1.50
VC	62.5	2,700	0.9106	2,531	0.39
Ethene	28.5	131	--	22,800	--

The physical properties of TCE determine the fate of TCE in the environment. The solubility of TCE is relatively low, but because it is much higher then the MCL, large volumes of contaminated ground water can result from small volumes of TCE. Also, the solubility of TCE is several times higher than the drinking water limit of 0.005 mg/L set by the US EPA (Norris et al., 1994). With a relatively low partitioning coefficient into the organic phase of soil (K_{OC}), TCE is not strongly retarded relative to the rate of groundwater flow allowing plumes to travel long distances (Russel et al., 1992). TCE is denser and less viscous then water resulting in rapid rates of subsurface migration and eventually in the formation of DNAPLS, which can be extremely difficult to remediate due to their inaccessibility and insolubility, potentially leading to long term contamination of aquifers (Isalou and Sleep 1998).

When TCE is released it can move through the unsaturated zone, below the water table and migrate with groundwater flow. TCE will not migrate downwards uniformly, but will migrate along multiple pathways both vertically and laterally. Hysteretic capillary forces cause retention of a portion of the TCE within the pores as disconnected blobs and ganglia, which is referred to as residual DNAPL (Environment Agency, 2003). The blobs and ganglia are held in place by capillary forces that arise because the interface between the DNAPL and water is in a state of tension (Environment Agency, 2003). Residual DNAPL saturations have been observed in a sand aquifer below the water table at 1-15% (Kueper et al., 1993). TCE can also form pools, which contain TCE that is continuous between adjacent pores and have saturations up to approximately 70 percent of the pore space (Environment Agency, 2003). TCE pools tend to form above finer grained horizons such as clay or silt units.

Residual DNAPL and pooled DNAPL form what is commonly referred to as the source zone. DNAPL mass tends to dissolve slowly into flowing ground water, serving as a long term source of groundwater contamination (Aulenta et al., 2006). The main processes affecting the fate and transport of DNAPLs in groundwater are shown in Figure 2.2.

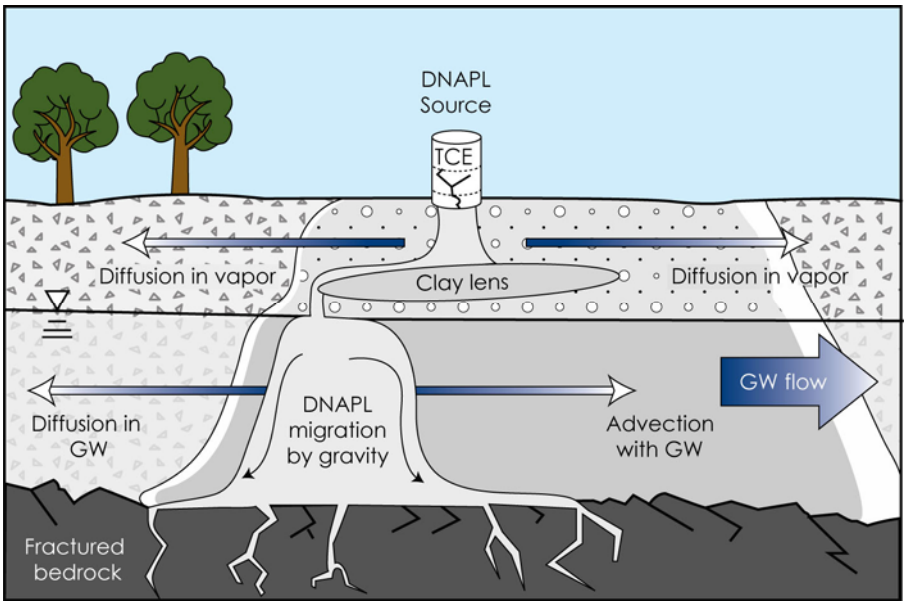

Figure 2.2 DNAPL Transport Processes (U.S. EPA, 2000)

2.2 Bioremediation

Bioremediation is the use of microorganisms to degrade contaminants in soil and groundwater. When the organisms capable of degrading the contaminants of concern (COCs) are present at a site biostimulation may be used to enhance degradation. Biostimulation involves the addition of electron donors and/or nutrients to the subsurface in order to stimulate indigenous anaerobic bacteria present at a contaminated site to transform the target compounds (ITRC, 2005). If the organisms required to carry out the degradation are not present at a contaminated site then bioaugmentation may be required. Bioaugmentation is the introduction of microorganisms capable of transforming a target compound in contaminated media (Adamson et al., 2003).

2.2.1 Reductive Dechlorination

Freedman and Gossett (1989) were the first to discover that PCE and TCE can be readily biodegraded anaerobically by reductive dechlorination to the non hazardous end product ethene (Figure 2.3)

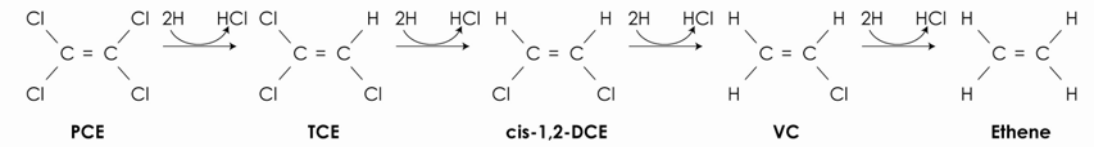

Figure 2.3 Pathway for the reductive dechlorination of chlorinated ethenes

It should be noted that TCE and dechlorination products can also be mineralized to carbon dioxide (CO_2) cometabolically by several organisms under aerobic conditions following a different pathway then reductive dechlorination (Duhamel, 2005). However, this will not be discussed in detail because several studies have shown that TCE degradation is most efficient following the reductive dechlorination pathway under anaerobic conditions.

In reductive dechlorination the chlorinated compounds serve as electron acceptors for microorganisms and hydrogen serves as the electron donor. In the reduction-oxidation (Redox) reaction the electron donor is oxidized and the electron acceptor is reduced. As seen in Figure 2.3 reductive dechlorination involves the stepwise replacement of chlorine atoms with hydrogen atoms thus releasing chloride at each step. The predominant intermediate formed is *cis*-DCE, although small quantities of *trans*-1,2-dichloroethene may be produced cometabolically (McCarty, 1994). Each step of the dechlorination sequence yields energy; some organisms are able to use this energy for growth, while others perform this function fortuitously (Simmonds, 2007). It is preferable to exploit growth-related pathways for bioremediation because this ensures the most efficient use of added nutrients (Duhamel, 2005). The microorganisms capable of obtaining growth from the reduction of chlorinated compounds are known as dehalorespiring bacteria and include members from a large number of genera, such as *Anaeromyxobacter, Desulfitobacterium, Trichlorobacter, and Dehalobacter* (Smidt and De Vos, 2004).

Several types of organisms have been shown to dechlorinate PCE and TCE to *cis*-DCE, including *Sulfurospirillum multivorans*, *Dehalobacter restrictus*, *Desulfuromonas michiganensis*, *Desulfitobacterium* sp. PCE-1 (Da Silva et, al 2006), and Geobacter strain SZ (Sung et al., 2006). The dechlorination of PCE and TCE to *cis*-DCE, which accumulates, is observed at many chlorinated solvent contaminated sites and is often referred to as "*cis*-DCE stall". *Dehalococcoides* spp. (Dhc) is the only group of organisms known to completely dechlorinate PCE and TCE to ethene (Da Silva et, al 2006 and Maymo-Gatell et al., 1999).

There have been five *Dehalococcoides* strains isolated to date, strain 195 (Maymo-Gatell et al., 1997), strain CBDB1 (Adrian et al., 2000), strain BAV1 (He et al., 2005), strain FL-2(He et al., 2003), and strain GT (Sung et al., 2006). These Dhc strains use hydrogen (H_2) as the electron donor and PCE and TCE as electron acceptor to produce VC. Of these five strains only two (BAV1 and GT) have been shown to be capable of growth on VC, while the others cometabolically dechlorinate VC to ethene (Da Silva et al., 2006). Different strains of Dhc have been shown to be specialized to different dechlorination steps (Amos et al, 2007) and since only two strains are known to metabolically reduce VC to ethene it is important to know what type of Dhc is present at a field site. If Dhc are not present, or if the wrong strain of Dhc is present, a contaminated site may require bioaugmentation to remove the contaminants. The vinyl chloride reductase A gene (*vcrA)* produces the corresponding enzyme which is capable of converting VC to ethene (Muller et al., 2004). *vcrA* or closely related genes with similar activity are found in many (but not all) Dhc bacteria. Hendrickson et al. (2002) tested samples from 24 chlorinated ethene contaminated sites for the presence of Dhc populations and observed a positive correlation between ethene formation and the presence of Dhc. Lu et al. (2006) collected samples from eight field sites and determined that if Dhc DNA is detected at a density of 1×10^7 Dhc gene copies per liter (gene copies/L) of groundwater then natural attenuation is likely occurring at a generally useful rate.

2.2.2 KB-1® Culture

KB-1® is a commercial dechlorinating culture produced and distributed by SiREM located in Guelph, Ontario. The culture originated from a former manufacturing site in South Western Ontario in 1996. The site was co-contaminated with TCE and methanol. High concentrations of ethene were also detected in the Site groundwater, suggesting that organisms capable of complete dechlorination to ethene were active in situ. A microcosm study was conducted which led to the development of

enrichment cultures maintained in Professor Elizabeth Edwards laboratory at the University of Toronto as described in Duhamel et al. 2002. In 2003 the culture was transferred to SiREM lab where the culture was scaled up to larger volumes for use as a bioaugmentation culture at contaminated sites. Over 100 sites have been bioaugmented with KB-1® to date. KB-1® is a Dhc dominated culture with approximately 10^{11} Dhc gene copies/L. The culture contains the following categories of organisms:

- Bacteria that reductively dechlorinate chlorinated ethenes (dechlorinators);
- Bacteria that ferment organic compounds;
- Methanogenic Archaea (methanogens);
- Sulfate reducing bacteria; and
- Relatively low proportion of facultative aerobic bacteria typically found in soil;

The microbial composition of KB-1® is relatively complex (i.e., it is not a pure culture) due to its origin as an enrichment from a diverse natural microbial community. Anaerobic dechlorinating consortia rely on a synergistic web of activities of different groups of microorganisms to ultimately achieve the reductive dechlorination of chlorinated ethenes.

2.2.3 Electron Donors

The presence of an electron donor is required for reductive dechlorination to occur. The most utilized electron donor for reductive dechlorination is H_2 and Dhc are dependent on H_2 as an electron donor (Yang and McCarty, 1998). Several studies have attempted to determine the thermodynamic threshold concentration of H_2 required for dechlorination to occur. Fennel and Gossett (1998) suggested it was at least as low as 1.5 nanomolar (nM); Yang and McCarty (1998) observed a threshold of 2.2 +/- 0.9 nM; and Smatlak et al. (1996) indicated a value of less than 2 nM. The H_2 needed for reductive dechlorination is often produced from fermentation of other substrates. Many electron donors suitable of supplying hydrogen for promoting reductive dechlorination of chlorinated solvents by anaerobic bacteria are available. Sugars (e.g., molasses), organic acids (e.g., lactate, formate, butyrate, propionate, and benzoate), alcohols (e.g., methanol, ethanol), and yeast extract have been most widely used in enhanced biodegradation applications to date. Fermentation of these organic compounds leads to the production of the necessary H_2 for dechlorination to occur. These

substrates are soluble in water and are highly biodegradable and therefore may need to be added periodically to maintain supply (Harkness 2000).

Insoluble electron donors have seen increasing application in enhanced biodegradation projects. These carbon sources biodegrade slowly over time and include substances like lactic acid polymers, soybean oil, chitin, and wood chips. These electron donors slowly hydrolyze, biotically or abiotically, into more soluble compounds (e.g. vegetable oils are hydrolyzed into soluble long chain fatty acids [LCFAs]) providing a slow-fermenting source of H_2 (Aulenta et al., 2006). They do not require continuous or batch additions in order to maintain their effectiveness and therefore can be cheaper to apply due to reduced substrate addition and system maintenance costs (Harkness, 2000).

2.2.3.1 Partitioning Electron Donors

Yang and McCarty (2002) compared different electron donors to bioenhance DNAPL dissolution in column studies. They found that olive oil exhibited the greatest conversion of PCE to ethene and was the most efficient substrate compared to pentanol and oleate. This led to more focus on partitioning electron donors (PEDS) for use in treating DNAPL zones. If PEDs can be effectively introduced into the subsurface near the DNAPL:water interface, these substrates will partition into the DNAPL phase and then slowly dissolve into the water phase with the DNAPL, providing a long-term source of electron donor to support the reductive dechlorination of the dissolving solvent. This will result in much higher and sustained concentrations of electron donor at the DNAPL:water interface than could be achieved with existing electron donor delivery methods and will promote the growth of dechlorinating biomass close to the DNAP and enhance DNAPL dissolution rates. The two PEDs tested in this study are n-butyl acetate (nBA) and slow release substrate (SRS^{TM}).

n-butyl acetate

The compound nBA (also known as butyl ethanonate) is readily available and costs 0.60 to 0.64 dollars per pound (Chemical Market Reporter, 2001). The solubility of nBA is reported to be 8,145 milligrams per liter (mg/L) (Montgemery, 2000), but was measured to be 6,000 mg/L by SiREM for this study, and has a log K_{OW} value of 1.82 (Montgemery, 2000). A specific TCE partitioning co-efficient of 458 was calculated for this study and is discussed in more detail in Section 4.1.2.

nBA is a clear, volatile, flammable organic solvent with a sweet odour (David et al., 2001). It is an important solvent in the chemical industry primarily in the manufacturing of paint and coatings and in the lacquer industry. Because of its lower impact on the environment, nBA is often used to replace the toxic and teratogenic ethoxy ethyl acetate (Steinigeweg and Gmehling 2002). It has been approved for use as a food additive by the FDA.

nBA is known to rapidly hydrolyze to n-butanol and acetic acid (David et al., 2001). Each mole of nBA produces one mole of n-butanol and one mole of acetic acid. The n-butanol produced can then be further broken down to 2moles of butyric acid, 2 additional moles of acetic acid, and 2 moles of H_2. The butyric acid produced can further be broken down to 2 moles acetic acid and 2 additional moles of H_2. If the acetic acid produced during these reactions is fully oxidized then 16 moles of H_2 is produced per mole of nBA. The reactions of interest are as follows:

$$C_6H_{12}O_2 + H_2O = C_4H_9OH + CH3COOH \quad (2.1)$$

$$C_4H_9OH + HCO_3 = 2C_3H_7COOH + 2CH3COOH + 2H_2 \quad (2.2)$$

$$C_3H_7COOH + 2H_2O = 2CH3COOH + 2H_2 \quad (2.3)$$

$$C_6H_{12}O_2 + 10H_2O = 6\,CO_2 + 16H_2 \quad (2.4)$$

The use of nBA as an electron donor for bioremediation could not be found in the literature. However, nBA was used in the microcosm phase of the Sabre project with successful results as is discussed in Chapter 4.

SRS

SRS™ is a commercially available EVO product manufactured by Terra Systems, Inc., Wilmington, Delaware. SRS™ is designed to release bio-available hydrogen over long periods of time (3 to 5 years). SRS contains the following: soybean oil (60%), sodium lactate (4%), food grade emulsifier package (6%), proprietary nutrient package (<1%), and water (30%).

Edible oils are relatively inexpensive, innocuous, food-grade substrates that have been used to stimulate in situ anaerobic bioremediation processes in both barriers and source area treatments (Zawtocki et al., 2004). As discussed above vegetable oils are relatively immobile and they do not require continuous or batch additions in order to maintain their effectiveness and therefore can be cheaper to apply (Harkness, 2000). Edible oils can be injected as pure oil, or as oil in water emulsions. Achieving effective distribution of pure oil is difficult because of the limited spread of the

oil and large amount of chase water needed to displace the oil (Zenker et al., 2000). Also, the oil tends to migrate upward due to buoyancy effects (Lee et al., 2005), and results in high residual saturations and high permeability loss (Long and Borden, 2006). To overcome these problems oil in water emulsions have been developed to (1) be stable for extended time periods; (2) have small, uniform droplets to allow transport in most aquifers; and (3) have a negative surface charge to reduce droplet capture by the solid surfaces (Long and Borden 2006).

Soybean oil initially hydrolyses releasing glycerol and LCFAs (Hanaki et al., 1981). It has been hypothesized that LCFAs initially sorb to sediment surfaces, and then are slowly fermented via beta oxidation to acetate and H_2 (Long and Borden, 2006). The main fatty acid found in soybean oil is linoleic acid (May, 2008). Therefore linoleic acid is often used to represent soybean oil in stoichiometric calculations for bioremediation studies. Linoleic acid is fermented to 9 moles of acetate and 14 moles of H_2. If acetate is completely oxidized to CO_2 an additional 28 moles of H_2 is produced. The reactions for linoleic acid are as follows:

$$C_{18}H_{32}O_2 + 16\ H_2O = 9CH_3COO^- + 14H_2 \quad (2.5)$$

$$9CH_3COO^- + 27H_2O = 9CO_2 + 9HCO_3 + 28H_2 \quad (2.6)$$

$$C_{18}H_{32}O_2 + 16\ H_2O = 9CO_2 + 9H_2CO_3 + 50H_2 \quad (2.7)$$

SRS has been used at many manufacturing sites throughout the USA and was used in the microcosm phase of the Sabre project with successful results as is discussed in Chapter 4.
It should be noted that although these equations show acetate being oxidized and releasing H_2, it has been shown that acetate is not likely an electron donor for dechlorination activity (Freedman and Gossett, 1989). However, acetate can be used directly by sulfate reducers (Widdel, 1988) and acetoclastic methanogens (Yang and McCarty 2002). The complete oxidation equations are shown to represent the maximum amount of H_2 available from these compounds.

2.2.4 Important Side Reactions

There are several other reactions that occur in the subsurface that are important to understand when biostimulation and/or bioaugmentation are chosen as a remedial technology. The addition of electron donor may stimulate the activity of dechlorinating microorganisms along with competing populations such as methanogens, acetogens, sulfate reducers, and nitrate reducers (Aulenta et al., 2007), the most important of these, in most situations, being the methanogens and sulfate reducers. The

competition for the fermentation products (H_2 or acetate) of the supplied electron donor is an important factor in determining the rate and extent of dechlorination, the amount of electron donor necessary for dechlorination to occur, and the success of the process (Aulenta et al., 2002).

Methane gas produced by methanogens is a problem in bioremediation systems because of the wastage of electron donor and clogging caused by significant biomass and methane gas production (Yang and McCarty 2002). Competition from methanogens for H_2 can potentially reduce the effectiveness of electron donor's added (Isalou and Sleep 1998), but are not actually detrimental to the dechlorinators (Adamson et al., 2003). Methane is produced either by hydrogen-utilizing (autotrophic) methanogens, or acetate-utilizing (acetoclastic) methanogens (Yang and McCarty, 2000). The H_2 threshold for methanogens is reported to be in the range of 5-95 nM (Aulenta et al., 2006), which is considerably higher then the H_2 threshold for dechlorination discussed in section 2.2.3 suggesting that dechlorinators have the potential to out compete methanogens when H_2 is present at low concentrations.

The role of sulfate is controversial primarily because both dechlorinators and sulfate reducers are able to thrive at very low and similar H_2 levels (Aulenta et al., 2007). Heimann et al. (2005) concluded that sulfate can negatively affect dechlorination at low H_2 concentrations, while Aulenta et al. (2007a) concluded that dechlorination can take place under sulfate reducing conditions and that dechlorinators may benefit from H_2 produced by sulfate reducing bacteria. Other studies have shown that sulfate had no inhibition effect on dechlorination and even that sulfate reducers were out competed by dechlorinators at low H_2 concentrations (Hoelen and Reinhard, 2004), partial inhibition (Cabirol et al., 1998), or complete inhibition (Nelson et al., 2002). Fennell and Gossett (2003) suggested that, when observed, the lack of dechlorination under sulfate-reducing conditions may be the result of (1) direct competition for supplied electron donor by sulfate-reducing microorganisms, (2) inhibition by sulfate enzymes involved in dechlorination, (2) preferential use of sulfate as terminal electron acceptor, instead of chlorinated compounds with in the same organism (e.g. *Desulfitobacterium* spp.), or (4) larger predominance and faster growth kinetics of sulfate-reducing bacteria compared with dechlorinators in sulfate-rich environments. Heimann et al. (2005) also summarized that apart from just outcompeting dechlorinators for reducing equivalents there are other mechanisms for sulfate impairing dechlorination including, dehalogenating enzyme repression, sulfide accumulation, and inhibition by potential intermediates of sulfate reduction such as sulfite and thiosulfate.

To date the typical approach for enhancing dechlorination in sulfate rich environments is to dose the system with excess electron donor to first deplete the sulfate present. This approach may result in several side effects due to the excessive consumption of electron donor including bioclogging of the aquifer, explosive hazards through excess methane production, and the accumulation of secondary contaminants (Fe(II) and Mn(II)) from the reduction of Fe(III) and Mn(IV)) with resulting deterioration of groundwater quality (Aulenta et al., 2007). Therefore, it would be beneficial if this excessive dosing of electron donor was not necessary.

2.2.5 Bioremediation of DNAPLs

DNAPLs dissolve slowly into groundwater and serve as long-term sources of groundwater contamination (Aulenta et al., 2006). In the past bioremediation methods focused only on plume treatment because concentrations associated with DNAPL source zones were believed to be toxic to micro-organisms. For example PCE dehalogenation by *Dehalospirillum multivorans* was inhibited when PCE concentration was higher than 0.3 millimolar (mM) (Yang and McCarty, 2000), which is well below the saturation concentration of about 0.9 mM for PCE. Yang and McCarty (2000) reported that only trace amount of *cis*-DCE was observed when TCE DNAPL was present, yielding a solution TCE concentration of 8.4 mM. Amos et al. (2007) reported that concentrations of TCE as high as 80 mg/L completely inhibited the activity of the tested dechlorinating isolates and Adamson et al. (2003) observed that PCE saturation concentrations severely inhibited dechlorination past *cis*-DCE in a mixed culture study.

In contrast, other studies have shown that reductive dechlorination of DNAPLs or at least of high concentrations of chlorinated solvents existing near DNAPL source zones can occur. Isalou and Sleep (1998) showed that ethene was produced in the lower portion of a column, where PCE and TCE were present. Adamson et al. (2003) showed strong evidence that inoculation successfully resulted in the growth of dechlorinating organisms in close proximity to the PCE-DNAPL, although dechlorination past *cis*-DCE was not observed. Nielsen and Keasling (1999) reported that a microbial culture enriched from a TCE contaminated groundwater aquifer could actually produce VC and ethene at a faster rate under saturation conditions than in a subsaturated system. In the study that Yang and McCarty (2000) reported a five times increase in PCE DNAPL dissolution rate and cis-DCE was the major dechlorination product, but significant amounts of VC and ethene were also formed. Also TCE concentrations up to 170 mg/L (a concentration suggesting the presence of

DNAPL) were dechlorinated after bioaugmentation in Dover soil columns (Harkness et al., 1999). In the microcosm phase of the Sabre project TCE concentrations as high as 800 mg/L were dechlorinated to cis-DCE and VC, and in a few cases completely to ethene.

Yang and McCarty (2000) list three benefits of the bioremediation of DNAPLs; (1) Enhanced dissolution of TCE and high concentrations of *cis*-DCE that results can reduced overall time for cleanup as well as increase the effectiveness of down gradient treatment systems, such as pump and treat, (2) dehalogenation products from PCE are biodegradable through aerobic processes, such as cometabolism, and (3) the problem of competitive utilization of added electron donor substrate is greatly alleviated with saturated solution PCE dehalogenation. The third benefit is because methanogens and other H_2 utilizers are often inhibited by high concentrations of PCE and TCE (Yang and McCarty 1998 and 2000, Nielsen and Keasling, 1999). This allows for more efficient utilization of H_2 produced from the biodegradation of organic substrates by dechlorinating organisms.

Although methanogens have been shown to be inhibited by high concentrations of PCE and TCE there are cases when methane production is observed in the presence of DNAPL. Methane generation was still occurring in a column in the presence of 600 micromolar (μM) PCE (Isalou and Sleep 1998). It was believed that methanogenesis was occurring in microenvironments not exposed to high concentrations of PCE. Yang and McCarty (2002) had a similar hypothesis for the observed methane production in columns with PCE DNAPL present. They believed that the heterogeneity of aquifer material in the columns and different spatial distribution of different organisms and substrates might play an important role in the observed reduced toxicity. This is further supported by the fact that a PCE gradient is likely to exist from the bottom of the column to the top of the column, and thus the PCE concentration in some parts of the column is likely to be below the saturation, or toxicity limit.

A similar hypothesis could be put forward for observed dechlorination in DNAPL zones in porous media. The amount of residual DNAPL retained by a typical porous medium is typically between 5 and 20 percent of the pore space in the particular lenses and laminations invaded by the DNAPL (Environment Agency, 2003), leaving much of the pore spaces not occupied by DNAPL and the opportunity for microenvironments to exist. Denis et al. (2003) observed high concentrations of *cis*-DCE and VC in a PCE DNAPL zone in columns, and suggested that some members of the microbial

community were able to withstand very high levels of PCE near the source zone, possibly in microenvironments exposed to lower concentrations of the compound.

There are complicating factors for the bioremediation of DNAPLs including (1) DNAPL exists as a separate phase and often as non uniform ganglia so donor substrate and nutrients must be delivered to near the DNAPL surface to enhance dissolution, (2) microbial growth near the DNAPL can cause a marked reduction in hydraulic conductivity over time, and (3) gas production and entrapment as a result of microbial activity can results in clogging and flow diversion around DNAPL (Yang and McCarty 2002). PEDs can be used to overcome many of these factors. PEDs will readily partition into the DNAPL phase and provide a source of electron donor near the DNAPL water interface. The conditions near the DNAPL water interface are not favorable for methanogens so gas production and clogging will be reduced as observed by Yang and McCarty (2002) when olive oil was mixed with PCE DNAPL. Other potential advantages of PEDs are (1) they are easily transported in the source area, which aids in their mixing throughout the source zone and contacting DNAPLs, (2) they are inexpensive on a per electron equivalent basis, and less expensive than other commercial electron donor products (eg., HRC^{TM}), and (3) they are slowly metabolized; therefore, they can be transported without significant loss and efficient distribution throughout the source zone becomes feasible.

Chapter 3
Materials and Methods

3.1 Equipment Used

Columns were custom made by Namdar Custom Glassblowing (Mississauga, Ontario) of borosilicate glass. The columns were 60 centimeters (cm) long with a 7.5 cm inside diameter and were fitted with Teflon end caps. The bottom end cap included a coarse fritted glass filter disk to ensure uniform distribution of the influent fluid across the cross-sectional area of the column. Three sampling ports were included spaced every 15 cm along length of column. However, it should be noted here that these ports were unreliable and collecting samples from these ports was not possible throughout the column study.

The pump used to regulate flow was a Master Flex L/S precision standard drive (1-100 rotations per minute [rpm]) equipped with a Master Flex L/S multi channel head capable of producing the desired flow rate. Influent water was pumped into the columns from glass and plastic bottles or tedlar bags depending on the phase of the study. Figure 3.1 shows a schematic of the column set-up.

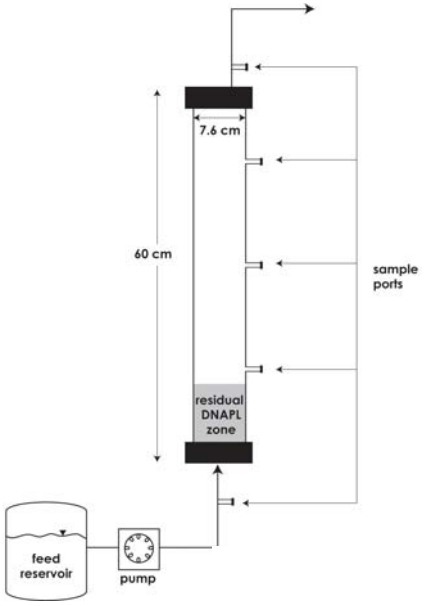

Figure 3.1 Schematic of Column Study Setup

All components were connected using 1/8th inch Teflon, viton, or stainless steel tubing to minimize sorption losses. Effluent from the columns was directed to a 20 milliliter (mL) VOA vial fitted with a stainless steel flow through apparatus to allow for collection of samples (Figure 3.2). This allowed the effluent to continually flow through the VOA vial and a sample could be collected at any time with minimal losses due to volatilization.

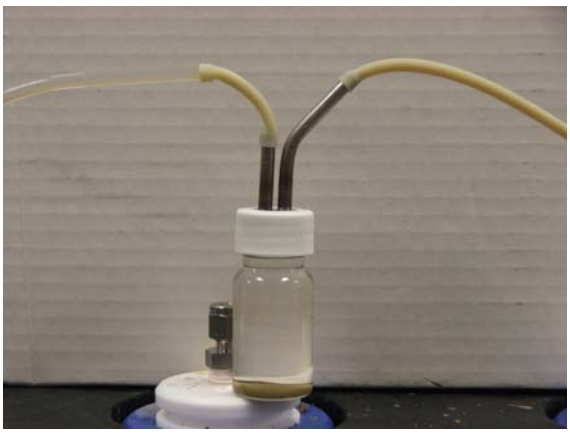

Figure: 3.2 Effluent collection vial

3.2 Analytical Procedures

3.2.1 Volatile Organic Compound and Dissolved Hydrocarbon Gas Analysis

This section describes the methods to quantify the chlorinated ethenes as well as methane, ethene and ethane (dissolved hydrocarbon gases [DHG]), nBA, and n-butanol. The Method Quantitation Limit (MQL) for the chlorinated ethenes, DHG's, and nBA ranged between 100 micrograms per liter (µg/L) and 1000 µg/L depending on the phase of the study and the sample volume analyzed.

Chlorinated ethenes, DHGs, and nBA concentrations were measured using a Hewlett-Packard (Hewlett Packard 5890 series II Plus) gas chromatograph (GC) equipped with a head-space auto sampler (Hewlett Packard 7684) programmed to heat each sample to 75 degrees Celsius (°C) for 45 minutes (min) prior to injection into a GSQ Plot column (0.53 millimeters x 30 meters, J&W) and a flame ionization detector. The injector temperature used is 200°C, and the detector temperature is 250°C. The specific headspace parameters are shown in Table 3.1. The oven temperature is programmed as follows: 35°C for 2 min, increase to 100°C at 50 degrees Celsius per minute (°C/min), then increased to 185°C at 25°C/min and held at 185°C for 6.80 min, followed by an

increase to 225°C at 25°C/min and held for 0 min. The carrier gas was helium at a flow rate of 11 milliliters per minute (mL/min).

Table 3.1 HP 7694 Parameters

Oven temperature	75^{oC}
Transfer line temperature	80^{oC}
Loop temperature	90^{oC}
Pressurization time	0.0 min
Loop fill time	0.2 min
Injection time	3.0 min
Vial equilibration time	45 min
GC Cycle time	21 min
Loop equilibration time	0.0 min

Chlorinated ethene, DHG, and nBA concentrations were measured by withdrawing a liquid sample from the effluent collection vial for the column effluent samples, or from the appropriate vial for batch tests, and injecting the sample into a 10-mL headspace vial containing acidified deionized water. The pH of the sample after acidification was approximately 2 to inhibit dechlorination and fermentation activity. The vial was sealed with an inert Teflon-coated septum and aluminum crimp-cap for automated injection onto the GC. Five-point calibrations were performed. Chlorinated ethene calibrations were performed using external standards purchased as standard solutions (Sigma St Louis, Missouri). The nBA standards were prepared gravimetrically in methanol using 99.5 % purity nBA (Fisher Scientific, Whitby, Ontario). DHG calibration was performed using standards that were prepared by injecting known volumes of ethene, ethane, and methane gases of greater than 99% purity (Scotty II, Alltech Associates Inc., Deerfield, IL) into 250 mL bottles containing 150 mL of water. The concentrations of DHGs were calculated using dimensionless Henry's law constants (27.20 for methane, 20.42 for ethane, and 8.76 for ethene). Standards were prepared along with samples and analyzed with each run to ensure recovery of the target analytes were within 15% of expected. Blanks were run every 20 samples to ensure there was no carry over of target analytes or instrument contamination. Data was integrated using Peak Simple Chromatography Data System Software (SRI Inc., Torrance, California).

n-butanol was analyzed by the Organic laboratory at the University of Waterloo using a 7673A Hewlett Packard Auto sampler and a Hewlett Packard 5890 gas chromatograph equipped with

a flame ionization detector and a packed column. Peaks were measured with a Hewlett Packard 3395 integrator. The method was calibrated using an external calibration mode. The column was 10 feet in length by 0.125 inches in diameter and packed with 3 % SPI500 on CaropackB (80/100) mesh. The carrier gas was helium at a flow rate of 20 ml/min. The injector temperature was 115°C, the detector was 230°C and the oven was isothermal at 145°C. The MQL for n-butanol was 0.075 mg/L.

3.2.2 Anions and Volatile Fatty Acids

This section describes the methods used to quantify anions and volatile fatty acids (VFAs).

Anions

Anion analysis was performed on a Dionex DX-600 ion chromatograph (IC) equipped with a Dionex AS-40 auto-sampler and an AS18 column. The sample loop volume was 25 μL. An isocratic separation was performed using 33 mM sodium hydroxide eluent for 13 min. Calibration was performed using external standards of known concentrations. Five-point calibrations were performed. Standards were prepared gravimetrically using purchased salts of the highest purity from Bioshop Canada Inc. (Burlington, Ontario). Standards were analyzed along with samples to ensure recovery of the target analytes is within 15% of expected. Blanks were run every 20 samples to ensure there was no carry over of target analytes or instrument contamination. Data were integrated using Dionex's Peaknet chromatography software. The MQLs were as follows: 0.03 mg/L chloride, 0.03 mg/L sulfate, and 0.39 mg/L bromide.

Anion concentrations were measured by withdrawing a liquid sample from the effluent collection vial for the column effluent samples, or from the appropriate vial for the batch tests, and injecting the sample into a 1.5 mL micro-centrifuge tube. Samples were centrifuged for five minutes to settle out solids. The supernatant was removed, diluted 10-fold in deionized water and placed in a Dionex auto-sampler vial with a filter cap for automated injection onto the IC.

VFAs

VFA analysis was performed on the same Dionex DX-600 IC equipped with a Dionex AS-40 auto-sampler. For VFA analysis an AS11 high capacity column was used. The sample loop volume was 25 μL. A gradient separation using sodium hydroxide was performed as follows; 0.5 mM from 0-2.5

minutes, increase to 5 mM from 2.5 – 6.0 minutes, hold at 5 mM from 6.0-10.5 minutes, increase to 33 mM from 10.5-11.1 minutes, hold at 33 mM from 11.1-25 minutes. Calibration was performed using external standards of known concentrations. Five-point calibrations were performed. Standards were prepared gravimetrically using purchased salts of the highest purity from Bioshop. Standards were prepared along with samples and analyzed with each run to ensure recovery of the target analytes was within 15% of expected. Blanks were run every 20 samples to ensure there was no carry over of target analytes or instrument contamination. Data were integrated using Dionex's Peaknet chromatography software. The QLs are as follows: lactate 0.40 mg/L, acetate 0.54 mg/L, propionate 0.31 mg/L, formate 0.23 mg/L, butyrate 0.41 mg/L, and pyruvate 0.69 mg/L.

VFA concentrations were measured by withdrawing a liquid sample from the effluent collection vial for the column effluent samples, or from the appropriate vial for batch tests, and injecting the sample into a 1.5 mL micro-centrifuge tube. Samples were centrifuged for five minutes to settle out solids. The supernatant was removed, diluted 10-fold in deionized water and placed in a Dionex auto-sampler vial with a filter cap for automated injection onto the IC.

3.2.3 pH and ORP

The pH measurements were performed using an Accumet AB15 pH meter with combination pH electrode. The pH meter was calibrated according to the manufacturer's instructions using pH standards. Calibrations of the probe were performed daily and standards were analyzed at each sampling event to ensure they were within the calibration range of the instrument at each sampling event.

The ORP measurements were performed using a Corning 313 meter with double junction ORP electrode (Ag/AgCl reference). A single point calibration of the meter was performed at each sampling event with Zobell ORP calibration solution.

3.2.4 Molecular Methods

Quantitative polymerase chain reaction (PCR) was performed at SiREM using commercially available Quantitative Gene-Trac-Dhc (16S ribosomal RNA [rRNA] gene) and Gene-Trac-VC methods (vcrA gene). These proprietary methods are subject to technology licensing agreements between SiREM and DuPont and Stanford University respectively. 16S rRNA primers are similar to

those described by Hendrickson et al. (2002) and are protected under US patent US6894156B2 (Hendrickson and Ebersole), use of vcrA gene (Müller et al, 2004) is subject to US Patent Application USSN 60/598459 (Spormann and McCarty).

Groundwater Filtration

Groundwater samples were stored at 4°C prior to concentration of biomass by vacuum filtration. Groundwater was decanted into a 0.20 micrometer disposable filter unit (Nalgene) and vacuum filtered. Groundwater volumes ranging from (100 ml to 500 ml) were used depending on the amount of biomass in the groundwater. Filters were removed from the housing, transferred into a sterile 50 mL centrifuge tubes and stored at -20°C until DNA extraction.

Genomic DNA Extraction

Extraction of DNA was performed using the PowerSoil™ DNA Isolation Kit (MO BIO Laboratories, Inc, Carlsbad, California). Up to 0.25 grams (g) of solids were used per isolation. Filters were placed into Bead Solution and pulverized using a sterile pipette tip. All subsequent steps of the DNA extraction were performed according to the manufacturer's instructions. Cell lyses were performed using a MiniBeadbeater-8™ (Biospec Products, Bartlesville, Oklahoma) at 50% of the maximum setting for 30 seconds. A negative control consisting of sterile water was filtered and extracted with each set of samples to rule out background DNA or cross contamination.

Quantitative PCR

40 µl PCR reactions consisted of 20 µl of 2X iQ™ SYBR Green Supermix, (Bio-Rad Laboratories Inc., Hercules, California) 1.6 µl of primer mix (10 picomoles (pmol) each primer) and 18.4 µl of template DNA. For quantification of total *Dehalococcoides*, primers targeting the 16S rRNA gene producing a 512-bp amplicon were used. Primers used for the quantification of the *vcrA* gene were rdhA14_642f GAAAGCTCAGCCGATGACTC and rdhA14_846r TGGTTGAGGTAGGGTGAAGG (Waller et al., 2005). Thermocycling was performed as follows for 16 S rRNA primers: initial denaturation of 94 ^{0}C for 2 min; 40 cycles of 94 ^{0}C for 1 min, 60 ^{0}C for 1 min and 72 ^{0}C for 1 min. with a final extension of 8 minutes, for *vcrA* primers: initial denaturation at 94 ^{0}C for 5 min with 36 cycles of 94 ^{0}C for 1 min, 58 ^{0}C for 1 min and 72 ^{0}C for 1 min with a final extension of 10 min at 72 ^{0}C.

Data collection and multi-component analysis were performed with the MyiQ™ Single-Color Real-Time PCR Detection System Software (Bio-Rad Laboratories Inc.). Standard curves of threshold fluorescence (C_t) versus $\log_{10}$ of the gene copy number were produced using cloned 16S rRNA and *vcrA* genes and were used to quantify the number of DNA targets in groundwater samples. In order to verify specificity and identity of the PCR products, melt curve analysis between 72 ^{0}C and 95 ^{0}C was performed.

Chapter 4
Batch Tests

4.1 Summary of Batch Tests

Prior to the start of the column study a large multi-laboratory microcosms study was performed. Three batch tests were also conducted prior to and along with the column study. The batch tests performed were to (1) determine a partitioning coefficient of nBA into TCE DNAPL (2) determine if there is a concentration of nBA that is toxic to dechlorinators in the KB-1® culture, and (3) determine the SRS loading percentage for columns. Batch tests one and two were performed by SiREM, while batch test three was performed by GE.

4.1.1 Summary of Sabre Microcosm Study

This section provides a brief review of the microcosm study that was performed prior to the column studies. A paper will be submitted for publication by the Sabre lab group of which I will be a co-author.

The objectives of the microcosm phase of the sabre program were to: (1) select the optimal electron donor for the column studies and field implementation; (2) determine if supplemental nutrients (nitrogen, phosphate, and trace minerals) are necessary or beneficial to the dechlorination process; (3) determine if bioaugmentation is necessary or beneficial to the same process; and (4) determine if the high levels of TCE present at the site will have a negative impact on the dechlorination process.

The microcosm study was designed as a fractional factorial experiment. The design consisted of 48 combinations of the levels of the experimental variables. These include four laboratories (DuPont, GE, Terra Systems, SiREM), six electron donors (Lactate, Acetate, Methanol, SRS™, Hexanol, and nBA), supplemental nutrients (With and Without), bioaugmentation with KB-1® (With and Without), and TCE (low level [100 mg/L] and high level [400 mg/L]).

The results showed that all of the electron donors promoted complete dechlorination of TCE to ethene in some microcosms during the incubation period. The classic reductive dechlorination sequence of TCE to *cis*-DCE to VC to ethene was observed in all cases. Figure 4.1 and 4.2 show examples of the

results obtained for SiREM microcosms, SRS™ amended high TCE plus nutrients plus KB-1® and nBA amended low TCE plus nutrients plus KB-1® respectively. The presence of sulfate did not inhibit TCE to *cis*-DCE dechlorination and was observed to be reduced concurrently with *cis*-DCE to VC. The pH in these microcosms was monitored throughout the incubation period and remained close to neutral indicating that the site material was capable of buffering the acid produced from the dechlorination process in the microcosm bottles.

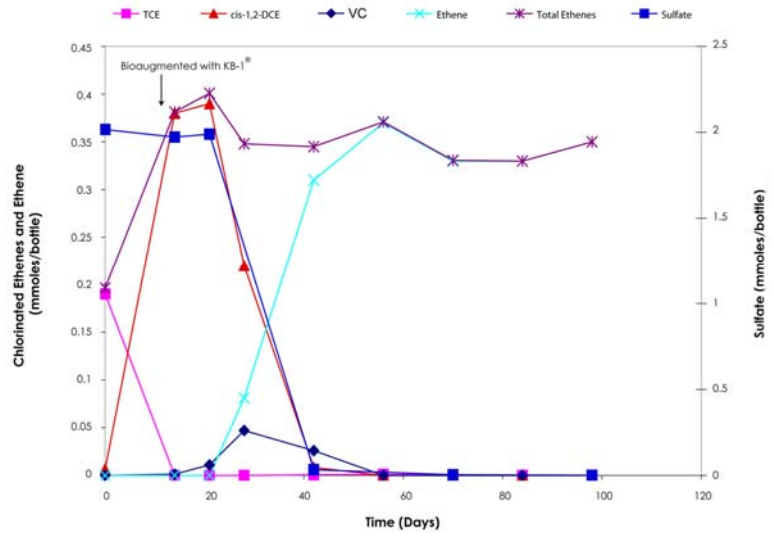

Figure 4.1 Chlorinated Ethenes, Ethene, and Sulfate Concentration trends in SRS™ amended high TCE plus nutrients plus KB-1® Microcosms

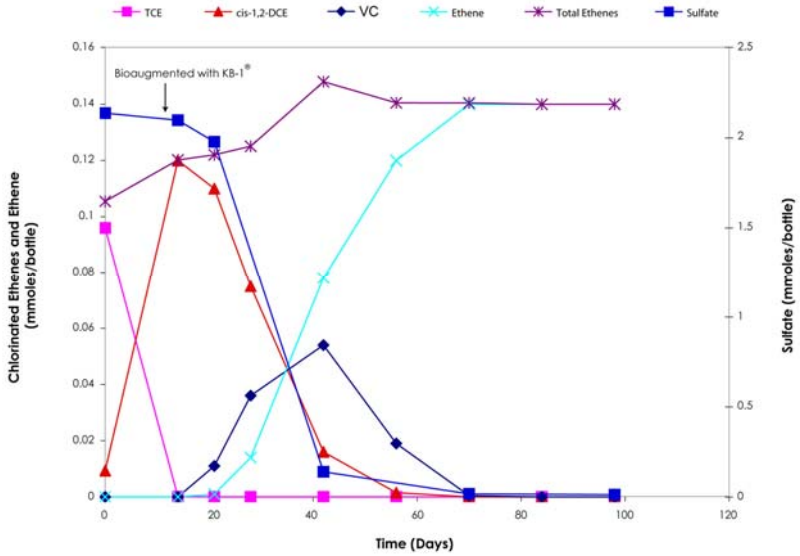

Figure 4.2 Chlorinated Ethenes, Ethene, and Sulfate Concentration trends in nBA amended low TCE plus nutrients plus KB-1® Microcosms.

A re-spike experiment was conducted on twenty-nine of the microcosms that went to completion in the main microcosm study. These microcosms were re-spiked with TCE to a concentration of 800 mg/L. The results indicated that more than half of these microcosms supported dechlorination of TCE to *cis*-DCE and VC after 210 days and a few microcosms went completely to ethene. In addition to spiking with TCE selected microcosm were re-spiked with 1,000 mg/L of sulfate. Interestingly the addition of sulfate appeared to enhance the rate of dechlorination in the re-spike experiment. In all cases sulfate was reduced concurrently with *cis*-DCE to VC.

The results of the microcosm study indicate that reductive dechlorination of TCE to ethene is feasible at high TCE concentrations (up to 800 mg/L) that will be encountered in DNAPL source areas. SRS™ supported the fastest dechlorination of TCE to ethene and bioaugmentation with KB-1® and nutrient addition were shown to benefit the speed of reductive dechlorination. Therefore SRS™, bioaugmentation, and nutrient addition were chosen as the treatment parameters of the column studies. Although nBA was not the best performing electron donor in the microcosm study complete dechlorination to ethene was achieved in many of the microcosms (e.g., Figure 4.2), and therefore nBA was chosen as an electron donor in the SiREM column study.

4.1.2 Partitioning Experiment

A variation of the shake flask method described in the OECD test guideline (107) was used to calculate TCE-DNAPL water partitioning co-efficients (P) for nBA. The partitioning coefficient is defined as the ratio of equilibrium concentration (C_i) of a dissolved substance in a two phase system consisting of two largely immiscible solvents. In this case a TCE and water system.

$$P = C_{i\text{-}TCE}/C_{(water)} \qquad (4.1)$$

Three ratios of TCE to water were tested (1:1, 1:2, and 2:1) in duplicate. Six 40 mL VOA vials were capped with septa caps and weighed. TCE was added gravimetrically to the six vials at the amounts specified in Table 4.1. A 4,000 mg/L nBA stock solution was created in dionized water with a measured concentration of 3,898 mg/L. The nBA solution was used to fill all six vials so that no headspace remained; the vials were capped and weighed again. The vials were placed on a New Brunswick Scientific shaker (Edison, New Jersey) at100 RPM for 6 days. The vials were removed from the shaker and the aqueous phase was sampled for nBA concentrations. The TCE phase was not sampled, but instead the concentration of nBA in the TCE phase was calculated as the difference in nBA concentrations from the measurements at day six and the original stock solution. The partition

coefficient was calculated as the concentration of nBA in TCE at day 6 divided by the concentration of nBA in water at day 6. An average partitioning co-efficient of 458 was calculated with a standard deviation of 32. Results are summarized in Table 4.1. Since the DNAPL phase was not analyzed directly for nBA duplicate control vials of aqueous nBA without TCE present were constructed to account for losses of nBA due to hydrolysis. The concentration of nBA in the control vials remained relatively stable over the incubation period with a decrease in nBA mass of less then 10% indicating that losses of nBA in the aqueous phase of the test vials containing DNAPL were due to partitioning of the nBA into the TCE DNAPL.

Table 4.1 Summary of nBA Partitioning Experiment Results

	empty vial (g)	Vial and TCE (g)	Filled with NBA (g)	TCE (g)	TCE (mL)	nBA (g)	nBA (mL)	nBA in water (mg/L) T=0	nBA in water (mg/L) T=6	nBA in water (mg) T=0	nBA in water (mg) T=6	nBA in TCE (mg) T=6	nBA in TCE (mg/L) T=6	Decrease in nBA mass (%)	P
TCE1:1	29.35	60.45	82.55	31.1	21	22.1	22	3989	9.6	88	0.21	88	4140	--	430
TCE1:1	28.70	59.60	81.90	30.9	21	22.3	22	3989	9.8	89	0.22	89	4204	--	430
TCE2:	29.30	71.50	85.90	42.2	29	14.4	14	3989	4.6	57	0.07	57	1990	--	436
TCE2:1	28.90	70.95	85.55	42.1	26	14.6	15	3989	4.4	58	0.06	58	2245	--	507
TCE1:2	28.90	49.55	79.45	20.7	13	29.9	30	3989	19.8	119	0.59	119	9328	--	471
TCE1:2	29.05	49.75	79.15	20.7	13	29.4	29	3989	19.2	117	0.56	117	9151	--	477
nBA Control-1	29.1	29.10	71.60	0.00	0.00	42.5	13	3989	3652	170	155	--	--	8.4	--
nBA Control-2	29.80	29.80	73.25	0.00	0.00	43.5	14	3989	3695	173	161	--	--	7.4	--
average	--	--	--	--	--	--	--	--	--	--	--	--	--	--	458
stdev	--	--	--	--	--	--	--	--	--	--	--	--	--	--	32

Notes: P = (nBA in TCE (mg/L) at T=6/ (nBA in water (mg/L) at T=6 days

4.1.3 nBA Toxicity Experiment

This batch test was conducted after the results were obtained from the first two nBA additions to the nBA column as discussed in Section 6.1.2. The objective of the nBA toxicity experiment was to determine if there was a concentration threshold of nBA that would inhibit reductive dechlorination of TCE by the KB-1® culture. Past work by Duhamel et al., (2002) showed that 1,1,1-trichloroethane and chloroform are potent inhibitors of chlorinated ethene dechlorination by the KB-1® culture, so it was decided to check if nBA would have a similar inhibitory effect at some level. The concentration of nBA used in the Sabre microcosm study was 500 mg/L and complete dechlorination of TCE to ethene was achieved, therefore 500 mg/L was used as the lowest concentration of nBA in this batch test. The ideal concentration used to load a DNAPL would be at the solubility limit of nBA (6,000mg/L). This corresponds to the maximum amount of nBA that could be injecting in a given volume of water and would be the most efficient way to load a DNAPL with nBA. Therefore concentrations from 500 to 6,000 mg/L of nBA were tested in this batch test.

Microcosms were constructed by filling sterile 40 mL (nominal volume) VOA vials with 35 mL of KB-1® culture. A sample was removed from the KB-1® growth vessel using a one liter transfer bottle. The culture was purged for 20 minutes with a nitrogen/carbon dioxide gas mixture to remove volatile organic compounds (VOCs) and DHGs from the culture. The culture was transferred to an anaerobic chamber (Coy Laboratory Products, Grass Lake, MI) filled with approximately 80 % nitrogen, 10 % carbon dioxide, and 10 % hydrogen (BOC Gases, Guelph, Ontario). The vials were capped with Mininert™ closures to allow repetitive sampling of the vials without VOC loss, and to allow nutrient amendment, as needed throughout the incubation period. Anaerobic conditions were maintained by constructing the microcosms in the anaerobic chamber; anaerobic microcosms were incubated and sampled in the anaerobic chamber. One replicate of each treatment was amended with resazurin to monitor redox conditions. Resazurin is clear under anaerobic conditions but turns pink when exposed to oxygen. Duplicate microcosms were prepared for a positive control (methanol and ethanol amended) and for the nBA amended microcosms. All microcosms were spiked with TCE to a target concentration of 50 mg/L. The nBA concentrations tested were 500 mg/L, 1,000 mg/L, 2,000 mg/L, 3,000 mg/L, 4,000 mg/L, 5,000 mg/L, and 6,000 mg/L.

Microcosms were sampled for chlorinated ethenes and ethene for up to 39 days. Figure 4.3 shows the chlorinated ethene and ethene profiles for the different treatments over the incubation period. Complete dechlorination of TCE to ethene with excellent mass balance was observed by day 2 in the methanol and ethanol control microcosms. Complete dechlorination of TCE to ethene with excellent mass balance was observed by day 7 in the 500, 1000, and 2000 mg/L nBA microcosms. These microcosms were no longer sampled after day 7. Partial dechlorination of TCE to ethene was observed in the 3,000 mg/L nBA amended microcosms by day 7, while dechlorination was limited in the 4,000 mg/L, 5,000 mg/L, and 6,000 mg/L amended microcosms. At day 21 the 3,000 mg/L and higher nBA amended microcosms were amended with methanol and ethanol to determine if the higher concentrations of nBA were actually inhibitory to the dechlorinators or if the dechlorinators were not able to use the nBA as an electron donor at these concentrations. TCE and *cis*-DCE concentrations decreased with corresponding increases in VC and ethene in the 3,000 mg/L amended treatment to day 39. TCE and *cis*-DCE remained relatively stable in the 4,000 mg/L nBA amended microcosms with slight increases in VC. TCE concentrations remained relatively stable in the 5,000 mg/L and 6,000 mg/L microcosms with low detects of *cis*-DCE and VC. Ethene production was not observed. The microcosm study was ended at day 39.

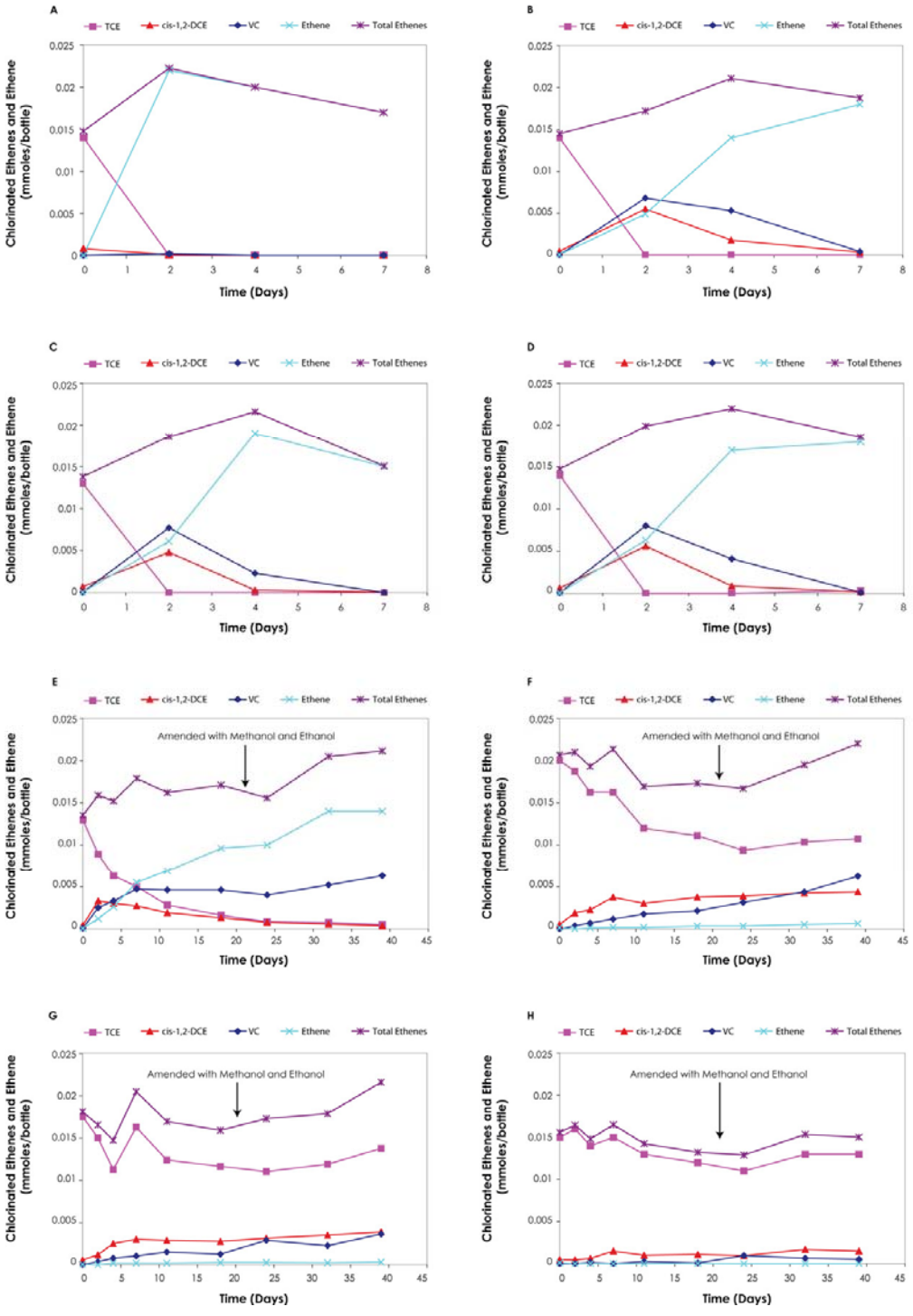

Figure 4.3 Chlorinated ethenes and ethene concentration trends in nBA toxicity test microcosms (A) Control; (B) 500 mg/L nBA; (C) 1,000 mg/L nBA;(D) 2,000 mg/L nBA; (E) 3,000 mg/L nBA; (F) 4,000 mg/L nBA; (G) 5,000 mg/L nBA; and (H) 6,000 mg/L nBA

4.1.4 SRS™ Loading Percentage Experiment.

The objective of the SRS™ loading batch test was to quantify the equilibrium partitioning behavior of TCE in the presence of site soil, a residual TCE DNAPL phase, and varying amount of SRS™. Equilibrium partition coefficients are not available for soybean oil in the neat or emulsified forms. Neat soybean oil has similar properties to octanol and may be modeled as a separate oil phase, but this may not be true of the emulsion phase as the emulsion phase is not stable. Total organic carbon (TOC) measurements were used as a surrogate for direct measurement of the soybean oil in the SRS™.

The experiments were performed in 120 mL glass serum bottles crimp-sealed with Teflon-lined butyl rubber septa. Six bottles were constructed with 50 g of Site soil and 75 mL of dionized water. TCE (1.5 g) was added to each bottle. SRS™ was added to each bottle to give different percentages of SRS™ ranging from 0 to 6.25% (v/v). The bottles were shaken well and allowed to stand over night to allow TCE to come to equilibrium between the soil and water phases. Figure 4.4 shows the reactor bottles with soil, water, TCE and increasing amounts of SRS™.

Figure 4.4 SRS™ Partitioning Experiment Reactor Bottles

The aqueous phase was measured for TCE on days 1, 3, 7, 15, and 21. The TCE profile for the 4.5 % SRS™ reactor is shown in Figure 4.5. At day one TCE concentrations were elevated slightly above the solubility limit of TCE followed by a decrease at Day 3 to concentrations lower than TCE saturation which remained stable through day 21. The elevated concentrations of TCE were only temporary indicating that loading rates of SRS™ close to 4.5 % are not likely to mobilize TCE DNAPL. Also, EVO loading rates of 2-10% are commonly used in field studies and therefore a loading rate of 5% was chosen for this study

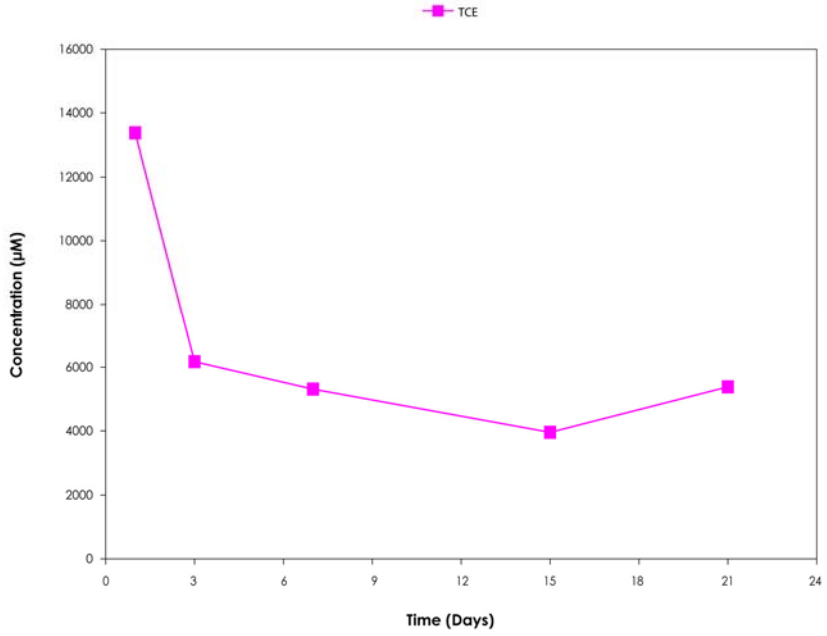

Figure 4.5 TCE Concentration Profile in the 4.5 % SRS™ Amended Reactors

4.2 Conclusions from Batch Tests

The following conclusions from the batch tests were made;

1) SRS™ will be used in the column study because it supported the fastest dechlorination of TCE to ethene in the Sabre microcosm study;
2) Bioaugmentation with KB-1® and nutrient addition will be used in the column study because they were shown to enhance the rate of reductive dechlorination in the Sabre microcosm study;
3) nBA supported complete dechlorination of TCE to ethene in the Sabre microcosm study and will be used as a partitioning electron donor in the SiREM column study;
4) nBA partitions readily into TCE DNAPL with a partitioning coefficient of 458+/-32;
5) Concentrations of nBA above 2,000mg/L appear to inhibit complete dechlorination of TCE to ethene with the KB-1® culture;
6) SRS™ will be added to the columns as a 5% (v/v) solution.

Chapter 5
Column Study Experimental Design

5.1 Column Set-up and Construction

Three soil columns were constructed to evaluate three conditions. One column was unamended and acted as the control column, the second column was amended with nBA, nutrients, and was bioaugmented with KB-1®, and the third was amended with SRS™, nutrients, and was bioaugmented with KB-1®. The following sections describe the set-up and construction of the columns.

5.1.1 Soil Collection and Artificial Groundwater

The soil used in this study was obtained from the field site in the UK. Soil samples were collected on 21 October 2005 several meters below ground surface inside the DNAPL source area using a direct push rig and 4-inch diameter, acetate sleeves. The acetate sleeves were capped and sealed with wax immediately upon retrieval. The soil was packed in iced coolers and sent by courier to SiREM and was received on 31 October 2005. The soil was stored in a cold room at 4°C until processing. The material was dominantly sandy gravel, with silty sandy gravel, gravel and minor clay and silt horizons.

Due to the expense of collecting and shipping the amount of ground water needed for the column studies an artificial ground water (AGW) was created in the lab that was designed to match the geochemistry of the site ground water. This allowed all three laboratories to make AGW as needed throughout the study. The procedure for making the AGW is described in Appendix A.

5.1.2 Column Packing

On 4 January 2006 the soil material was removed from the cold room and placed in a temporary anaerobic glove bag. The cores were opened and the material was sieved through a 12 millimeter (mm) screen to remove larger rocks and debris and then mixed by hand inside a large plastic bag to homogenize the contents. Figure 5.1 shows the material that was used to pack the columns and the larger material that was removed during the sieving process.

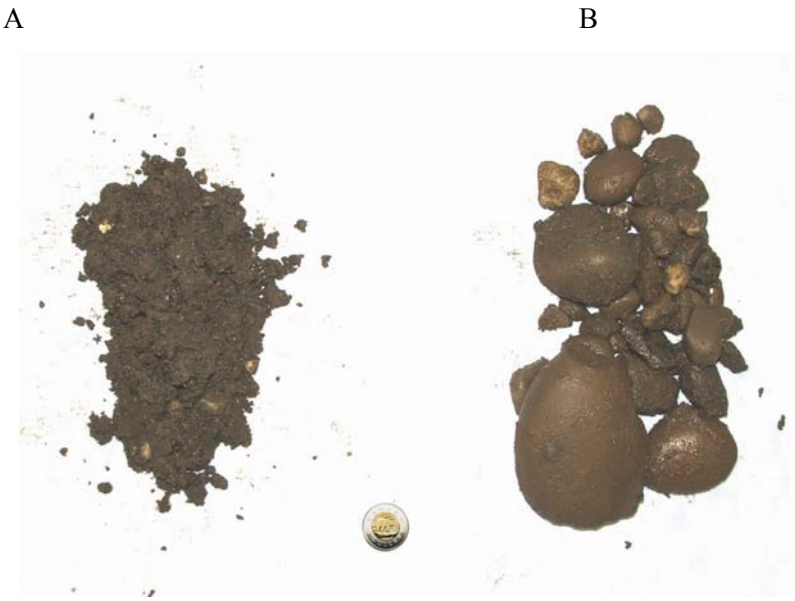

Figure 5.1 Sabre test cell aquifer solids. (A) Material that passed through a 12 mm screen used to pack the columns, and (B) material that was removed with the 12 mm screen and was not used in the columns.

The SRS™ amended and nBA amended columns were packed on 11 January 2006, while the control column was packed on 15 June 2006 because the original control column broke and was not used in the study. A 2 cm layer of clean, non-sterilized, Federal Fine Ottawa sand (30-140 mesh) was placed in the column immediately above the end cap to prevent the study soil from entering the disk and plugging the glass frit. The site soil was added to the column in 2 cm lifts. After each lift was added the soil was uniformly compacted with a compacting tool. During column packing a constant stream of CO_2 gas was passed through the column to remove oxygen and minimize residual air pockets, since CO_2 more readily dissolves into water than oxygen. The top portion of the column (approximately 2 cm) was packed tightly with inert wet glass wool. The end cap was installed and tightened. The weight or soil added to each column was recorded. Columns 1, 2, and 3 received 4.9, 5.1, and 5.3 kilograms (kg) of site material respectively.

5.1.3 DNAPL Emplacement

TCE was dyed with oil red-O at a concentration of 0.1 grams per liter (g/L) prior to adding TCE to the columns. The dye allowed visual observations of the TCE in the columns. A constant head tank containing dyed TCE connected to the bottom of the columns was used to add the TCE to the columns. The height of TCE in the constant head tank provided enough pressure at the bottom of the

column to force the TCE to displace water in the column and move upwards. The amount of TCE in the tank was recorded. The target was to create a TCE DNAPL zone in the bottom 20 cm of the column. TCE was visually observed to reach 30 cm in the nBA and SRS columns and 33 cm in the control column. After the TCE was added to a column the constant head tank was disconnected and the volume of TCE remaining in the tank was recorded. A tank of AGW was connected to the top of the column for approximately two hours to drain the free DNAPL phase and leave a residual DNAPL zone in the column. The DNAPL leaving the bottom of the column was collected in a graduated cylinder and the volume collected was recorded. The amount of TCE remaining in the column was calculated as the difference between the amount added from the constant head tank and the amount collected in the graduated cylinder. The procedure is graphically presented in Figure 5.2. The volume of TCE added to each column was different, which resulted in different saturations of the source zones of the three columns (Table 5.1).

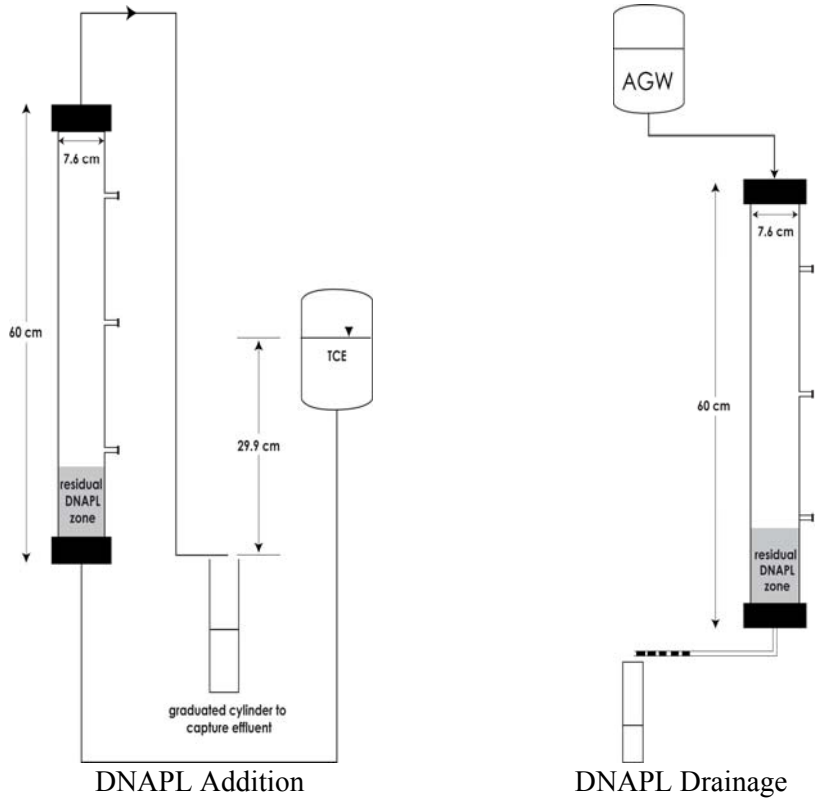

Figure 5.2 Schematic of DNAPL Addition and Drainage

Table 5.1 Summary of DNAPL Additions

Column ID	Volume TCE added (mL)	Volume TCE Retained (mL)	Volume of Source Zone (mL)	DNAPL Saturation (%)
Control	73	62	467	13.3
SRS™	35	21.5	397	5.4
nBA	70	40	451	8.9

Notes: DNAPL saturation (%) is equal to the volume of TCE retained / (porosity X volume of source zone (mL)) X 100
Volume of source zone is based on the observed height of DNAPL in the columns (33 cm, 30 cm, and 30 cm for control, SRS, and nBA columns respectively), a cross sectional area of 45.6 cm^2, and the porosity of the individual columns as calculated by a tracer test described in Section 6.1 below. (Volume of source = cross sectional area X length of source zone X porosity)

5.2 Electron Donor and Nutrient Addition and Bioaugmentation

5.2.1 nBA Column Amendments

nBA was amended to the nBA column four different times throughout the column study. Table 5.2 summarizes the nBA amendments. The first two additions were as saturated stocks added for approximately one pore volume. This allowed the greatest amount of mass possible to be loaded into the column in a given volume of water. The third addition was at a concentration of 2,000 mg/L based on the results of the toxicity test described in section 4.1.3. The fourth and final addition was as neat nBA in an attempt to directly load the nBA into the DNAPL phase of the column. The total amount of nBA added throughout the column study period was equal to 1.3 times the electron donor demand based on the amount of TCE in the column and the amount of sulfate that would be pumped through the column for one year of column operation. Refer to Appendix B for details of the nBA electron donor demand calculations and for the procedures for making the nBA solutions.

Table 5.2 Summary of nBA Amendments

Duration (Days)	Amendment	Amount nBA added (g)
47-53	6,000 mg/L	5.4
118-125	6,000 mg/L	4.9
209-246	2,000 mg/L	10.9
280	neat	5.3

A hole was drilled in the cap of a 1L Pyrex bottle containing the saturated nBA solution allowing a piece of Teflon tubing to fit through it tightly. The Teflon tubing was lowered to the bottom of the bottle. The Teflon tubing was connected to the pump tubing and the nBA solution was pumped through the column at the experimental flow rate. Due to the volatility of nBA there was the potential to have losses of the free phase nBA on top of the AGW. The saturated solution was visibly observed every day during the amendment phases to verify that the free phase of nBA was present. The solutions were also analyzed for nBA at the start and end of the amendment phases that confirmed the concentration of the solution. At the end of the saturated stock amendments the flow was stopped for 72 hours followed by the continuation of the AGW solution at the experimental flow rate.

The third nBA amendment phase used a concentrated stock solution of nBA at a concentration of approximately 2,000 mg/L. This solution was pumped through the column from days 209 to 215. On day 215 the concentration of nBA in the influent bag was measured and found to be at a concentration of 500 mg/L indicating that losses were occurring in the influent bag. On 6 November 2006 (Day 222) the bag was removed, cleaned, and a new 2,000 mg/L stock solution was made following the same procedure. On 7 November 2007 (Day 223) the new solution was pumped through the column. On 30 November 2006 (Day 246) the nBA solution was replaced with the regular AGW solution. Table 5.3 shows the concentration of nBA, acetate, and butyrate in the influent bags over time. Although only one data point was collected for acetate and butyrate the data indicate that degradation of nBA in the influent bag was occurring. The AGW contained a redox indicator, resazurin, which is blue in the presence of oxygen and turns to pink and then clear as oxygen is consumed. The AGW in the influent bag turned pink over the addition phase indicating that oxygen was being consumed by microorganisms and that the influent bag was not sterile. This microbial activity may have increased

the rate of nBA hydrolysis. Hydrolysis of nBA did not occur over the duration of the TCE partitioning batch test (Section 4.1.2) when sterile dionized water was used. This suggests that the rate of hydrolysis was faster in the influent bag, either due a component of the AGW or microbial activity. Butanol measurements were not taken, but since there was very little butyrate found, butanol would be expected to be present at an equilmolar amount as acetate (assuming acetate degradation was not occurring). This is because hydrolysis of nBA forms one mole of acetate and one mole of butanol (equation 2.1). If butanol degradation were occurring butyrate would be expected as a degradation product along with more acetate. Since, butyrate concentrations were very low, butanol degradation is minimal and the amount of butanol present will be equal to the moles of acetate.

Table 5.3 Concentrations of nBA, acetate, and butyrate in the influent bag during the 2,000 mg/L nBA amendment phase

Sample ID	Date	Day	nBA (mg/L)	Acetate (mg/L)	Butyrate (mg/L)
influent bag	20-Oct-06	205	2122	--	--
influent bag	30-Oct-06	215	500	--	--
Comment	6-Nov-06	222	bag removed, cleaned and re-amended with 2,000 mg/L of nBA		
influent bag	7-Nov-06	223	2038	--	--
influent bag	14-Nov-06	230	770	--	--
influent bag	17-Nov-06	233	267	--	--
influent bag	21-Nov-06	237	114	1691	4.0
influent bag	24-Nov-06	240	79	--	--
influent bag	27-Nov-06	243	88	--	--

The fourth and final nBA amendment was added as neat nBA directly to the column inlet. A volume of 6 mL of neat nBA was added slowly to the column inlet on 3 January 2007 (Day 280). This volume was chosen because it was similar to the amount added during the first two nBA additions. Immediately after the neat addition regular AGW was pumped through the column at the experimental flow rate. On 2 February 2007 (Day 310) a crack developed in the bottom of the nBA column that could not be fixed and the nBA column was discontinued.

5.2.2 SRS™ electron donor

SRS™ was amended to the column only once during the column operational period. The total amount of SRS™ added was equal to approximately 2.2 times the electron donor demand based on the amount of TCE in the column and the amount of sulfate that would be pumped through the column for one year of column operation. Refer to Appendix B for details on the SRS electron donor demand calculations and for the procedure for making the SRS™ solution.

A 5% solution of SRS™ was created in AGW to amend the column. A hole was drilled in the cap of the Pyrex bottle and a piece of Teflon tubing was lowered to the bottom of the bottle similar to the nBA set-up. The Teflon tubing was connected to the pump tubing and the SRS™ solution was pumped through the column at the experimental flow rate. The SRS™ solution was amended to the column from 12 May 2006 to 19 May 2006 (Days 47 to 54). The SRS™ solution was placed on a stir plate and continuously stirred for the amendment period to keep the emulsion together. If the emulsion were to break separate oil and water phases would be created leading to improper loading of the electron donor into the column. The SRS™ solution was observed daily during the amendment phase. A small amount of oil was observed at the top of the SRS™ solution, but the emulsion remained intact throughout the addition phase. At the end of the SRS™ amendment phase the flow was stopped for 72 hours followed by the continuation of the AGW solution at the experimental flow rate.

5.2.3 Nutrient Addition, Bioaugmentation, and Buffering

The microcosm results indicated that both nutrient addition and bioaugmentation were beneficial to the dechlorination process and therefore were used in the column study.

Bioaugmentation of both electron donor amended columns took place on 15 June 2006 (Day 78). The bioaugmentation culture used was the KB-1® culture grown and maintained at the SiREM lab. A sample was removed from the KB-1® growth vessel using a one liter transfer bottle. The culture was purged for 20 minutes with a nitrogen/carbon dioxide gas mixture to remove VOCs and DHGs from the culture. The culture was transferred to an anaerobic chamber (Coy Laboratory Products, Grass Lake, MI) filled with approximately 80 % nitrogen, 10 % carbon dioxide, and 10 % hydrogen (BOC Gases, Guelph, Ontario). For each column bioaugmentation, a 10 mL sample was removed from the transfer bottle using a 10 mL syringe that was stored in the anaerobic chamber for several days prior to use. The syringe was also rinsed with the culture three times to remove any trace amounts of

oxygen present in the syringe. The syringe filled with KB-1® was removed from the anaerobic chamber and 10 mL of KB-1® was injected directly into the column inlets over a time span of 10 minutes (flow rate of 1 mL/min). Immediately after bioaugmentation AGW was pumped through the column at the experimental flow rate. QPCR analysis performed directly on the KB-1® used to bioaugment the columns indicated that there were 1.8×10^{11} gene copies/L of Dhc in the anaerobic culture. This corresponds to a concentration of 2.1×10^{9} gene copies/L in the columns assuming the culture was distributed throughout the entire volume of the columns.

Nutrients were added to the treatment columns starting on 1 August 2006 (Day 125) and continued for the remainder of the column operation period. Reagent grade diammonium phosphate (DAP) (Fisher Scientific) was added to the influent AGW at a concentration of 25 mg/L. This concentration was chosen because concentrations higher then this caused precipitation to occur in the AGW solution. For comparison, the DAP used in the microcosm study was a one time addition at a concentration of 500 mg/L.

On 30 November 2006 (Day 246) additional sodium bicarbonate was added to the influent AGW of the nBA and SRS columns because the pH in the effluent was continually below a pH of 6.5. The optimum pH for dehalorespiring bacteria is 6.8-7.8 (Middledorp et al., 1999 and SiREM unpublished data). To address this it was decided to increase the pH of the influent AGW to a target pH of 8.0 to increase the pH throughout the columns. A volume of 3 mL of a saturated bicarbonate solution was needed to reach this target pH in 2L of AGW. This increased the concentration of bicarbonate in the influent AGW from 363 mg/L to 455 mg/L. The pH was not adjusted in AGW used in the control column.

Chapter 6
Column Study Results

6.1 Column Study Results

Prior to the addition of DNAPL to the columns bromide tracer tests were performed for each column. Breakthrough curves were obtained by continuous injection of a sodium bromide solution at a concentration of 91 mg/L at the experimental flow rate of 0.07 mL/min. In order to determine the soil properties of the columns, namely the porosity and dispersivity, modeling of the bromide tracer tests was performed by Kokkinaki (2007) as part of the University of Toronto's contribution to the Sabre project. The model used was the COMPSIM model developed by Sleep and Sykes (1993). The model is a finite difference groundwater fate and transport model. The porosity, dispersivity, velocity and residence time values calculated are summarized in Table 6.1 and the breakthrough curves and raw data from the tracer test is presented in Appendix C.

Table 6.1 Summary of Column Properties

Column	Porosity	Dispersivity (m)	Velocity (cm/day)	Residence Time (Days)
Control Column	0.31	0.08	7.6	7.97
SRS Amended Column	0.31	0.06	8.2	7.45
nBA Amended Column	0.32	0.099	7.4	8.29

The results indicate that the columns were all packed similarly, had similar properties, and that there were likely no preferential flow paths.

6.1.1 Control Column Results

The control column operational period discussed in this report was from 7 July 2006 (Day 0) to 22 October 2007 (Day 472). The VOC and ethene results of the effluent samples collected over the duration of the control column operational period are presented graphically in Figure 6.1. The first effluent samples were collected on day 3. The results showed TCE in the effluent at a concentration of 746 mg/L (5.7 mM) and *cis*-DCE at a concentration of 4.1 mg/L (0.043 mM), VC and ethene were not detected. TCE concentrations increased to day 17 reaching the near saturation concentration of 1,070 mg/L (8.1 mM). TCE concentrations remained relatively stable through day 255 with concentrations in the effluent ranging between 900 mg/L (6.85 mM) and 1,200 mg/L (9.1 mM). *cis*-DCE concentrations remained low up to day 52, after which concentrations decreased to non-detect values. There were low level detections of *cis*-DCE periodically throughout the incubation period, while VC and ethene remained non-detect. After day 255 more variability in the TCE effluent values was observed. Periodic values as low as 610 mg/L (4.6 mM) were measured, but values as high as in the first 255 days of column operation were still consistently observed. The reason for the increased variability is likely due to heterogeneity of the source as the DNAPL phase in the column shrinks due to dissolution. There were no detections of VC or ethene, and methane concentrations remained at or below the detection limit throughout the operation period.

The anion data is presented in Figure 6.2. Sulfate and chloride concentrations remained relatively stable throughout the operation period. Concentrations of VFAs were below the detection limit in the control column throughout the operation period (data not shown).

The pH and ORP data is presented in Figure 6.3. The pH in the control column initially increased to a maximum value of 7.4 on day 115, followed by a slow decrease throughout the remainder of the operational period, but the pH remained above 6.5 over the course of the experiment. The ORP initially slowly decreased to a value of -29 millivolts (mV) on day 213 followed by a rapid increase to 145 mV on day 227. The ORP remained mainly positive throughout the rest of the operational period with periodic decreases below zero observed.

The Dhc and vcrA concentration in the control column remained at or below the detection limit throughout the column operational period (data not shown).

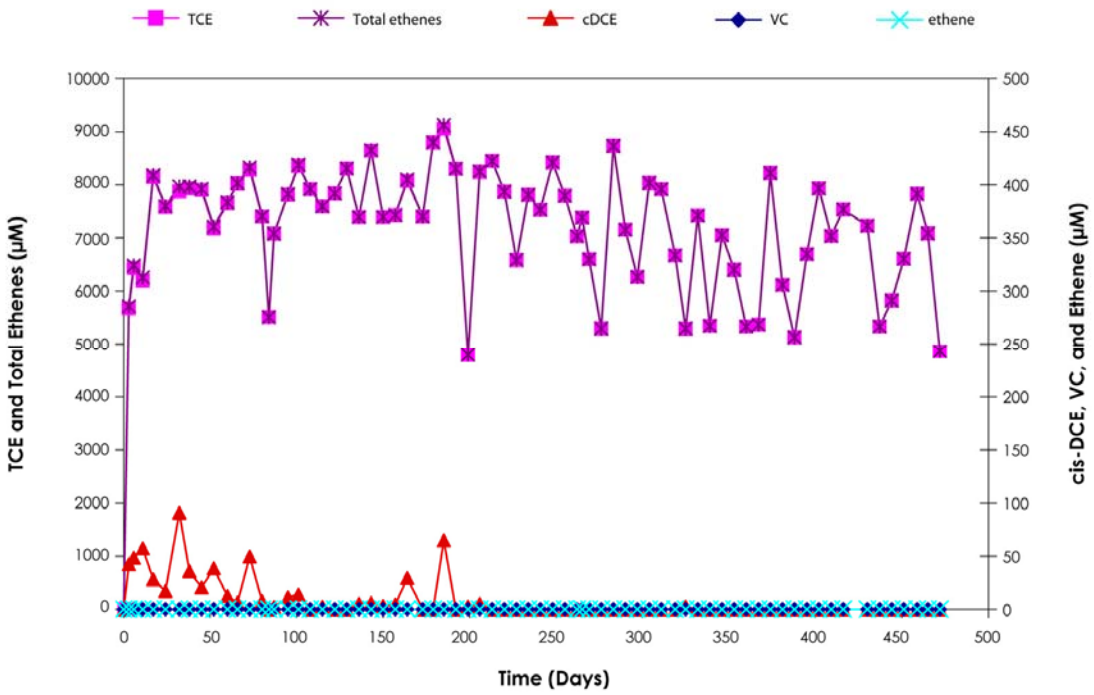

Figure 6.1 VOC and ethene concentration trends in the control column

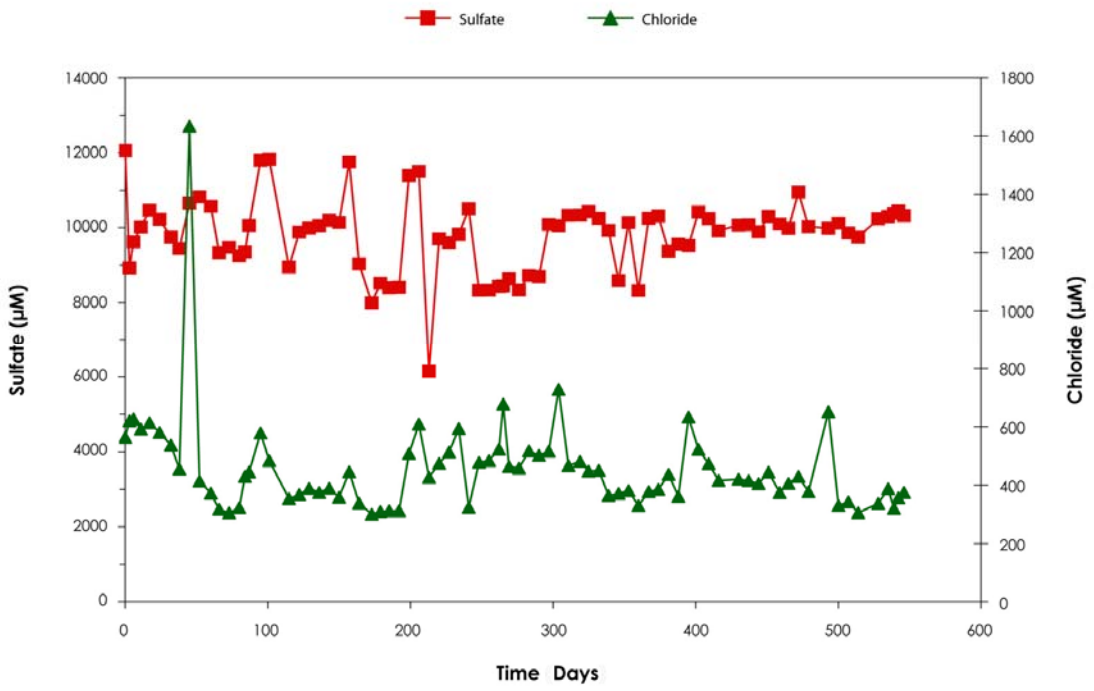

Figure 6.2 Anion concentration trends in the control column

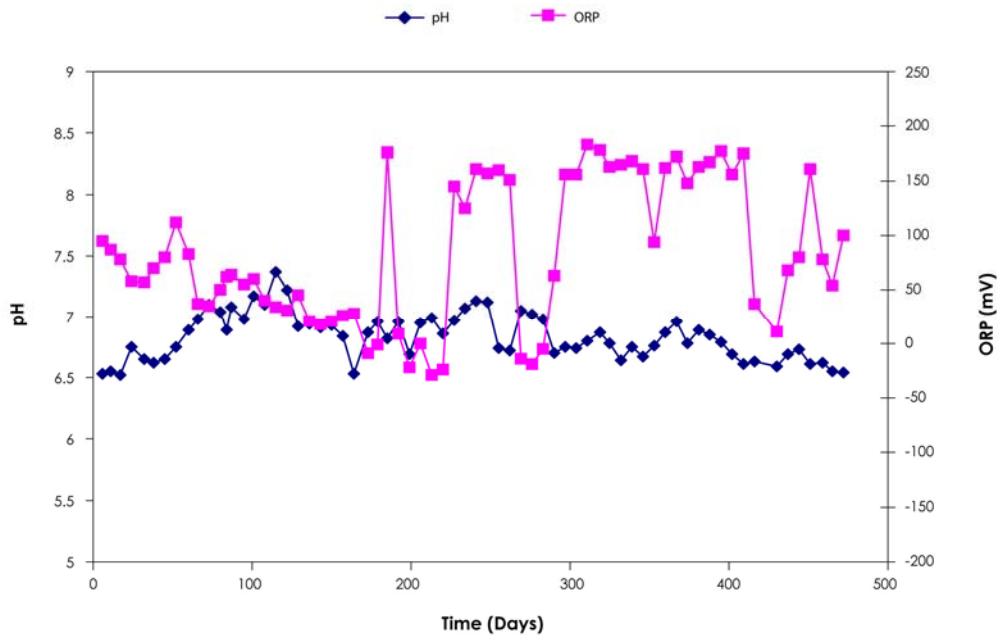

Figure 6.3 pH and ORP trends in the control column

6.1.2 nBA column results

The nBA column operational period was from 21 March 2006 (Day 0) to 29 January 2007 (Day 306). The VOC and ethene results of the effluent samples collected over the duration of the nBA column operation are graphically presented in Figure 6.4. Prior to the first nBA amendment TCE and *cis*-DCE concentrations reached 148 mg/L (1.1 mM) and 92 mg/L (0.95 mM) respectively. *cis*-DCE concentrations leveled off until day 32 and then decreased to 16 mg/L (0.17 mM) on day 47. TCE concentrations continued to increase to 601 mg/L (4.6 mM) on day 45. After the first nBA amendment on day 47 TCE concentrations continued to increase reaching 842 mg/L (6.4 mM) on day 75. *cis*-DCE concentrations initially decreased slightly followed by an increase to 35 mg/L (0.34 mM) on day 65 and then a decrease to 11 mg/L (0.12 mM) on day 75. After bioaugmentation on day 78 TCE concentrations continued to increase reaching 924 mg/L (7.4 mM) on day 92. TCE concentrations remained relatively stable through the second nBA addition, increasing only slightly to 1,060 mg/L (8.1 mM) prior to the third nBA addition on day 209. *cis*-DCE concentrations remained relatively stable after bioaugmentation until the second nBA addition, after which *cis*-DCE increased to 27 mg/L (0.28 mM) on day 145. *cis*-DCE decreased to 6.0 mg/L (0.062 mM) by day 173 and remained stable prior to the third nBA addition. TCE concentrations remained relatively stable during the 2,000 mg/L nBA addition from day 209 to day 246. However, *cis*-DCE began to increase

slowly to day 222 and then more rapidly to day 252 reaching a concentration of 430 mg/L (4.5 mM). After the 2,000 mg/L nBA addition phase TCE and *cis*-DCE concentrations decreased to 772 mg/L (5.9 mM) and 84 mg/L (0.87 mM) respectively by day 279 prior to the final nBA addition on day 280. Following the neat nBA addition on day 280, TCE continued to decrease slightly and reached 677 mg/L (5.1 mM) by the final sampling event on day 306. *cis*-DCE increased to 105 mg/L (1.1 mM) on day 290 followed by a decrease to 41 mg/L (0.42 mM) on day 306. There were no detections of VC or ethene throughout the column operation period and methane concentrations remained consistently at or below the detection limit.

The anion data for the nBA column is presented in Figure 6.5. Sulfate concentrations increased from day 0 to the first nBA addition on day 46 reaching a concentration of 1,041 mg/L (11 mM). Sulfate concentrations remained relatively stable after bioaugmentation and the second nBA addition prior to the third nBA addition on day 209. Chloride concentrations increased initially to day 13 reaching a concentration of 68 mg/L (1.9 mM), remained stable to day 29 and decreased to 25 mg/L (0.71 mM) on day 47. Chloride concentrations remained relatively stable after bioaugmentation and the second nBA addition prior to the third nBA addition on day 209. Sulfate concentrations remained stable to day 216, following the 2,000 mg/L nBA addition that began on day 209, and then decreased rapidly to 28 mg/L (0.29 mM) on day 249. The sulfate level remained at this low level to day 251. Following the end of the 2,000 mg/L nBA addition phase on day 246 sulfate rapidly increased to influent levels by day 263. Sulfate concentrations decreased slightly to 720 mg/L (7.6 mM) on day 279. Chloride concentrations increased following the 2,000 mg/L nBA addition reaching a maximum concentration of 162 mg/L (4.6 mM) on day 249 followed by a decrease to influent levels by day 280. Following the neat nBA addition on day 280 sulfate concentrations remained relatively stable to day 288 and then increased to influent levels by day 306. Chloride initially increased to 61 mg/L (1.7 mM) on day 289 followed by decrease to 14 mg/L (0.39 mM) on day 292. The chloride concentration was showing an increasing trend on the last sampling event on day 306 reaching 68 mg/L (1.9 mM).

The VFA data for the nBA column is presented in Figure 6.6. The acetate concentrations are displayed on a secondary axis because acetate was the dominant VFA and was present at concentrations much higher then the other VFAs. The time scale for this figure starts at the beginning of the first nBA amendment period (Day 47). All VFAs were below detection limits prior to electron

donor addition. After the nBA addition all VFAs remained below the detection limit to day 56 when a spike of butyrate was observed to reach 9.1 mg/L (0.10 mM), followed by a spike of acetate at 65 mg/L (1.1 mM) on day 58. Butyrate concentrations decreased and remained below the detection limit until the second nBA addition, while acetate concentrations decreased slowly from day 58 to day 120. The second nBA addition occurred from day 118 to 125. Acetate increased rapidly to 432 mg/L (7.3 mM) on day 127, followed by a decrease to non-detect on day 145. Butyrate concentrations also increased after the second nBA addition reaching 14 mg/L (0.16 mM) on day 130, followed by a decrease to below the detection limit on day 145. All VFAs remained near or below the detection limit prior to the 2,000 mg/L nBA addition starting at day 209. Acetate increased rapidly to 1,430 mg/L (24 mM) on day 240 followed by a rapid decrease after the 2,000 mg/L addition phase to below the detection limit on day 279. Butyrate concentrations also increased reaching 484 mg/L (5.5 mM) on day 245, followed by a decrease to below detection on day 264. All VFAs remained near or below detection prior to the neat nBA addition on day 280. Acetate concentrations increased slightly at day 286 and then increased rapidly to 879 mg/L (15 mM) on day 294, followed by a decrease to 193 mg/L (3.3 mM) at the end of the operational period on day 306. Acetate concentrations were showing a declining trend at the end of the incubation period. Butyrate increased only slightly after the neat nBA addition with concentrations of approximately 2.0 mg/L (0.022 mM) persisting in the effluent until the end of the operational period. The other VFAs (lactate, formate, and pyruvate) were below detection limits for the entire column operational period.

The nBA and butanol data is presented in Figure 6.7. There were no detections of nBA in the column effluent during the first three nBA addition phases. Following the neat nBA addition on day 280 nBA increased to 752 mg/L (6.5 mM) on day 294 followed by a decrease to 8.6 mg/L (0.073 mM) at the end of the operational period on day 306. Butanol measurements were not taken until the 2,000 mg/L nBA addition phase began on day 209. Butanol increased to 731 mg/L (9.9 mM) on day 222 followed by a rapid decrease to 97.4 mg/L (1.3 mM) on day 232. Butanol concentrations increased to 1,575 mg/L (21 mM) on day 294 followed by a decrease to 275 mg/L (3.7 mM) at the end of the operational period on day 306.

The pH and ORP data for the nBA column is presented in Figure 6.8. The pH in the nBA column initially decreased to 6.32 on day 78, followed by a slow increase to 7.42 on day 215. The pH then decreased to 6.30 on day 264 despite the increased bicarbonate addition to the AGW on day 236. The

pH increased slightly to 6.60 at the end of the operational period on day 306. ORP measurements were not taken in the nBA column until day 99. The ORP initially increased to a value of 112 on day 152 followed by a decrease throughout the operational period to -27mV on day 306.

The Dhc and vcrA concentrations in the nBA column were at concentrations of 1 X 10^6 gene copies/L and 4 X 10^5 gene copies/L respectively prior to electron donor addition. Both Dhc and vcrA decreased to near non-detect levels prior to bioaugmentation and then remained at this low level throughout the operational period (data not shown).

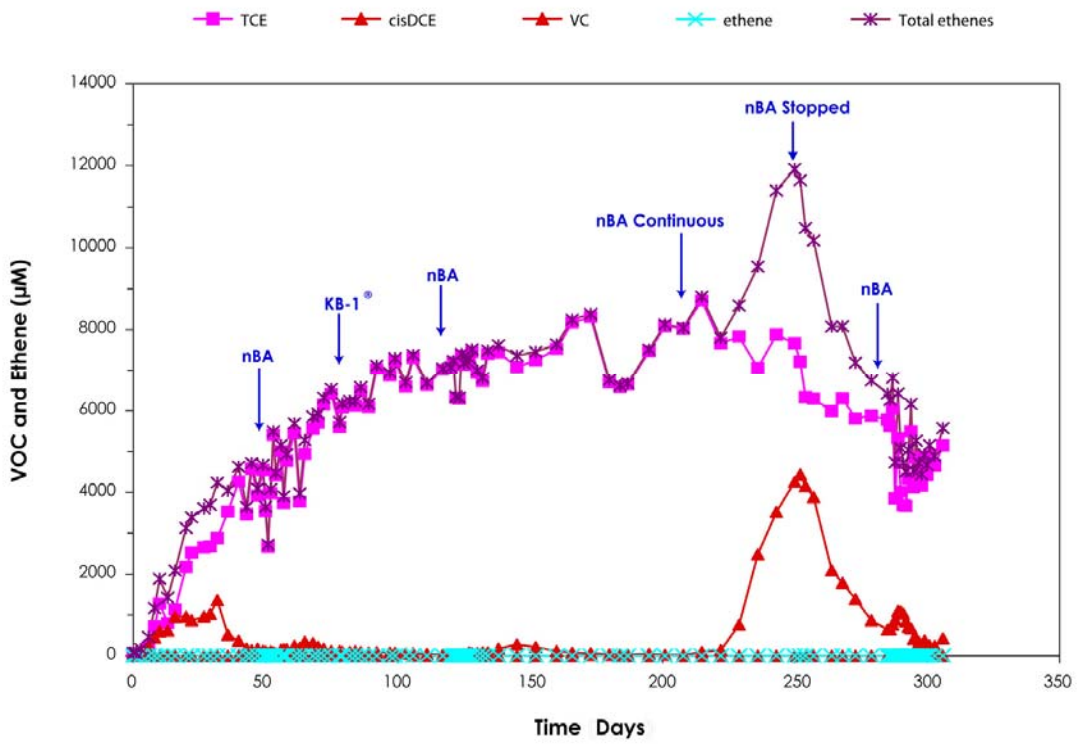

Figure 6.4 VOC and ethene concentration trends in the nBA Amended column

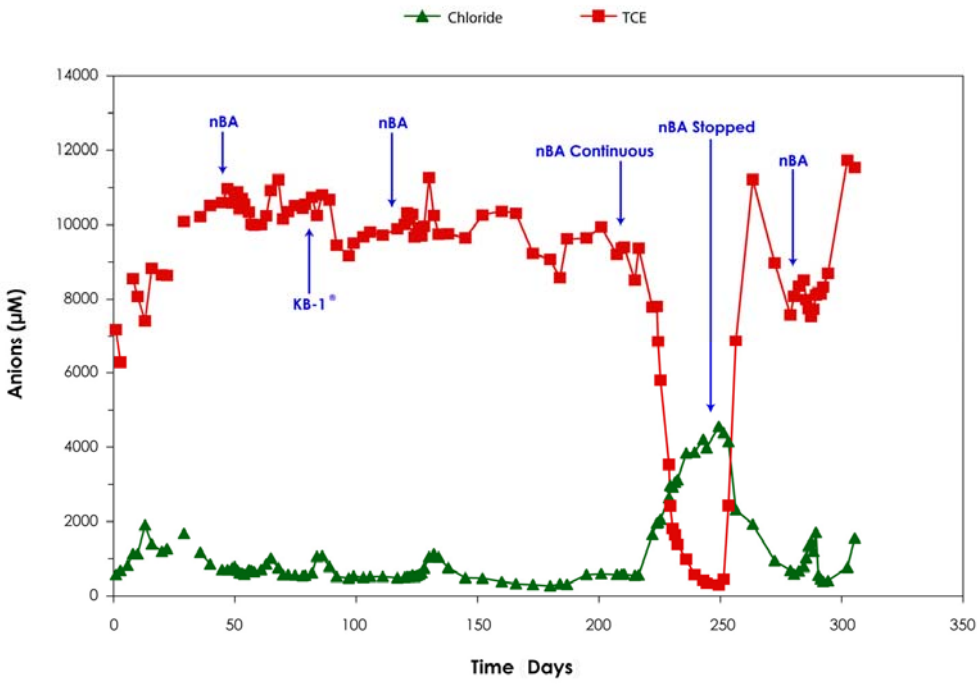

Figure 6.5 Anion concentration trends in the nBA Amended column

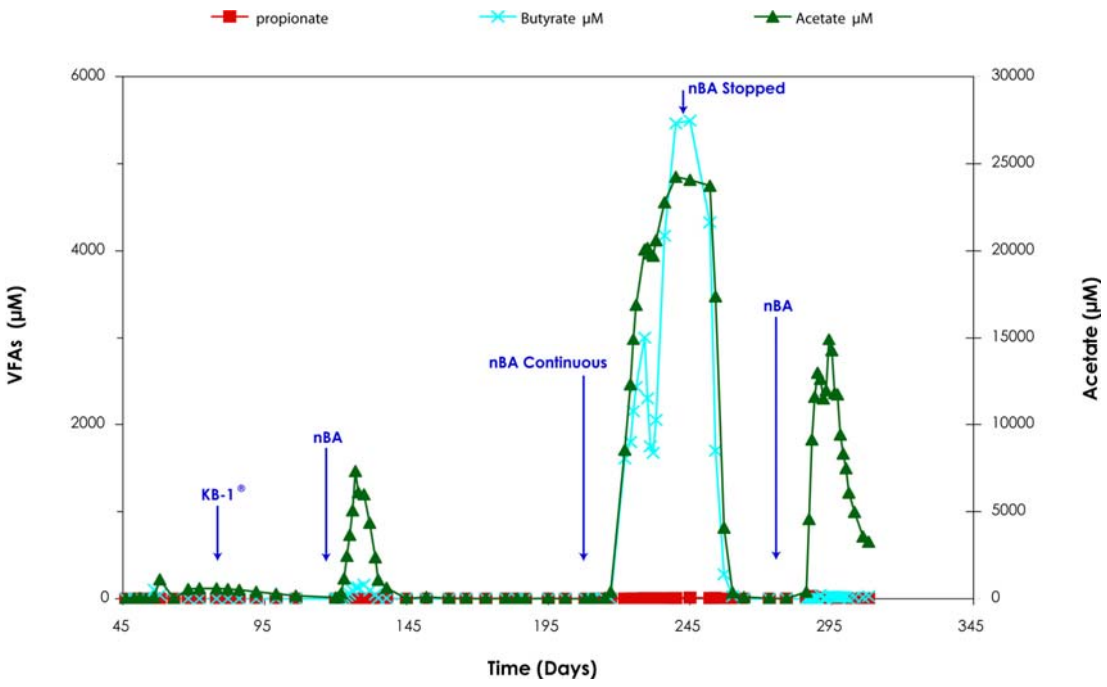

Figure 6.6 VFA concentration trends in the nBA Amended column

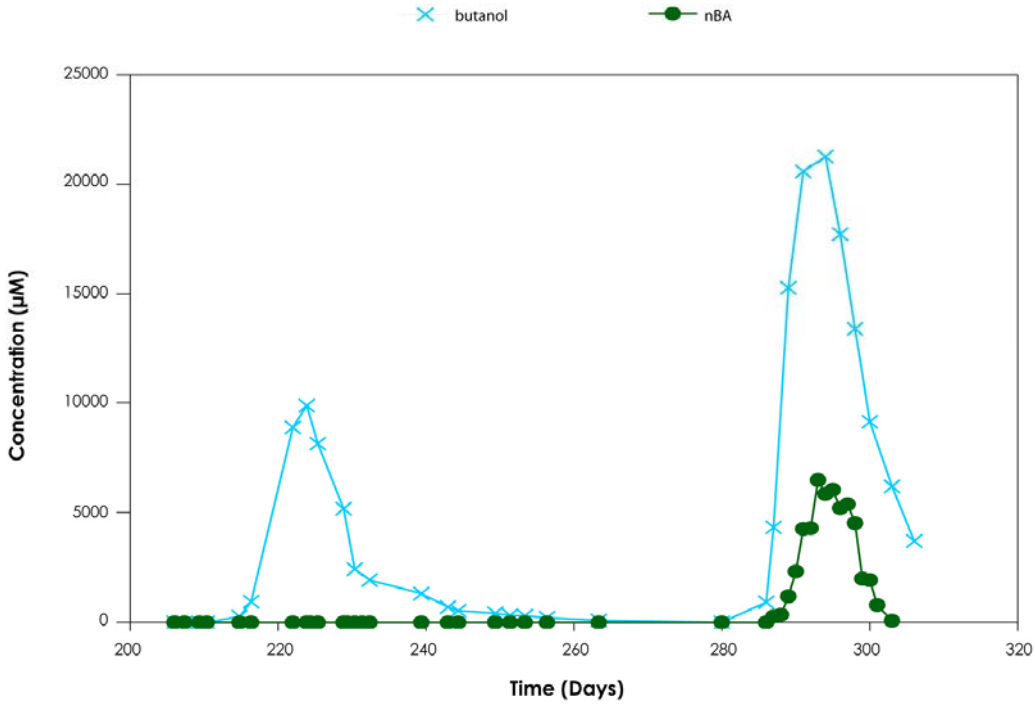

Figure 6.7 nBA and butanol concentration trends in the nBA Amended column

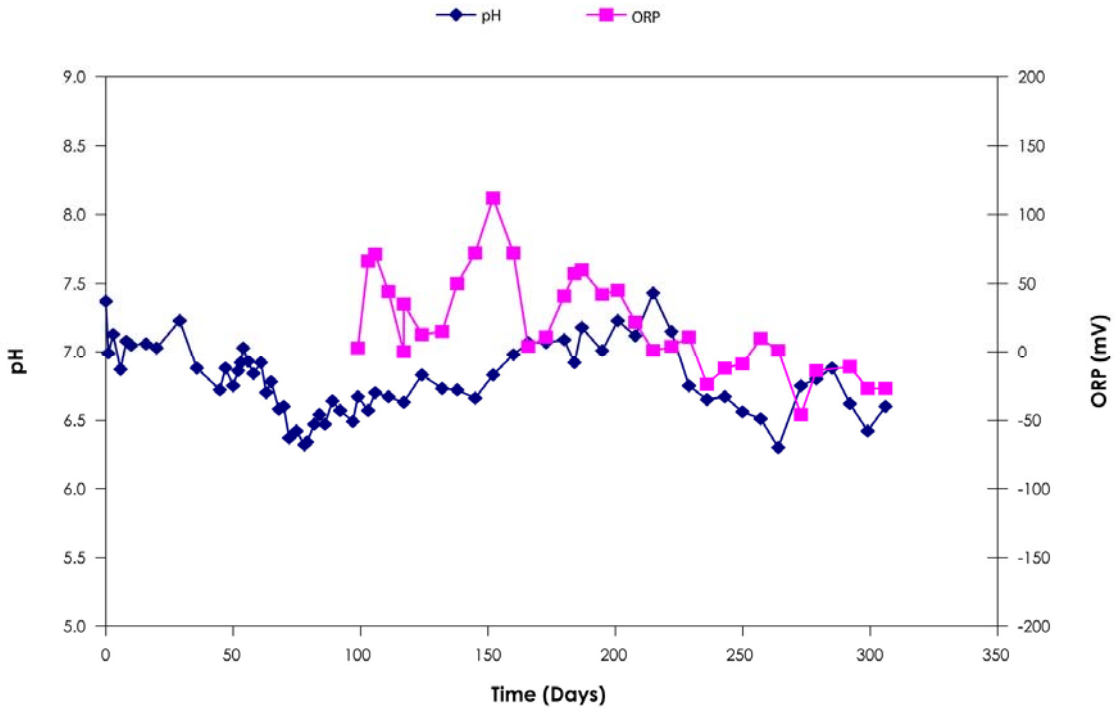

Figure 6.8 pH and ORP trends in the nBA amended column

6.1.3 SRS™ Column Results

The SRS™ column operational period discussed here was from 21 March 2006 (Day 0) to 22 October 2007 (Day 572). The operational period was divided into two phases; the DNAPL phase from day 0 to day 329, and the plume phase from day 329 to 572. The VOC and DHG results of the effluent samples collected over the duration of the SRS™ column operational period are presented in Figure 6.9. Prior to SRS™ amendment TCE and *cis*-DCE concentrations increased similarly to the trend observed in the nBA column. On day 16 TCE reached a concentration of 268 mg/L (2.0 mM) and cis-DCE reached 92 mg/L (0.95 mM). *cis*-DCE concentrations decreased after day 16 to 3.4 mg/L (0.035 mM) on day 47. TCE concentrations continued to increase to 785 mg/L (6.0 mM) on day 45. After the SRS™ amendment on day 47 TCE concentrations continued to increase reaching 913 mg/L (6.9 mM) on day 78. *cis*-DCE concentrations increased slightly to 14 mg/L (0.14 mM) on day 72 followed by a decrease to 4.2 mg/L (0. 043 mM) on day 78. After bioaugmentation on day 78 TCE concentrations continued to increase reaching 1,068 mg/L (8.1 mM) on day 89 followed by a slow decrease to a concentration of 549 mg/L (4.2 mM) on day 229 and a rapid decrease to 4.8 mg/L (0.036 mM) on day 257. TCE concentrations remained at or near the detection limit for the

remainder of the DNAPL phase. Following bioaugmentation on day 78 *cis*-DCE concentrations remained relatively stable to day 89 followed by an increase to 131 mg/L (1.3 mM) on day 145. *cis*-DCE concentrations increased slowly to a concentration of 154 mg/L (1.6 mM) on day 195 followed by a rapid increase to a concentration of 498 mg/L (5.1 mM) on day 243. The cis-DCE concentration decreased rapidly to near the detection limit on day 299 and remained near or below the detection limit for the remainder of the DNAPL phase. VC and ethene concentrations remained below detection limits for the first 138 days of the operational period. On day 145 low levels of VC and ethene were detected and slowly increased to day 243 to concentrations of 0.81 mg/L (0.013 mM) and 0.32 mg/L (0.011 mM) respectively. After day 243 VC concentrations increased corresponding to the decreasing concentration of *cis*-DCE reaching a maximum concentration of 24 mg/L (0.039 mM) on day 268, followed by a rapid decrease to below the detection limit on day 299. VC remained near or below the detection limit for the remainder of the DNAPL phase. Ethene concentrations remained relatively stable from day 243 to day 264 followed by an increase to 1.0 mg/L (0.036 mM) on day 306 corresponding to the decreasing concentration of VC. Ethene decreased slightly to 0.65 mg/L (0.023 mM) on day 327. Methane concentrations remained stable up to day 152, after which methane began to increase reaching concentration of 8.6 mg/L (0.54 mM) on day 320.

From day 306 to day 327 the main component measured in the column effluent was ethene. Since the DNAPL was depleted it was decided to amend the influent groundwater with high concentrations of TCE to simulate a TCE plume area down gradient of a TCE source zone. On day 329 AGW spiked with approximately 400 mg/L of TCE was pumped through the SRS™ column for the remainder of the operational period. Ethene began to increase almost immediately followed by detections of VC and *cis*-DCE on day 362. Ethene continued to increase to a maximum concentration of 35 mg/L (1.2mM) on day 509 followed by a decrease to 16 mg/L (0.56 mM) on day 572. VC increased rapidly from day 362 to day 390 reaching a concentration of 62 mg/L (0.99 mM). VC remained relatively stable to day 495 followed by a decrease to a concentration of 32 mg/L (0.52 mM) at the end of the operational period on day 572. *cis*-DCE increased from day 362 to day 404 reaching a concentration of 139 mg/L (1.4 mM). *cis*-DCE decreased to a concentration of 22 mg/L (0.23 mM) on day 460 and remained relatively stable to day 572. TCE concentrations remained below the detection limit over the plume phase of the study. Methane concentrations increased following the end of the DNAPL phase to a concentration of 12 mg/L (0.74 mM) on day 365 followed by a rapid

decrease to 1.8 mg/L (0.12 mM) on day 404 and remained relatively stable for the remainder of the plume phase.

The target TCE concentration in the influent AGW was 400 mg/L. Losses of TCE were observed in the influent AGW bag so the concentration of TCE added to the column varied with time. Figure 6.10 shows the fluctuations of TCE in the influent bag over time during the plume phase.

The anion data for the SRS™ column is presented in Figure 6.11. Sulfate concentrations increased from day 0 to day 47 reaching a concentration of 1,015 mg/L (11 mM). Sulfate concentrations decreased slightly after SRS addition to a concentration of 992 mg/L (10 mM) on day 79. Chloride concentrations increased initially to day 16 reaching a concentration of 48 mg/L (1.4 mM) followed by a slow decrease to 20 mg/L (0.56 mM) on day 79. After bioaugmentation on day 79 sulfate concentrations remained stable to day 86 followed by a rapid decrease to 31 mg/L (0.33 mM) on day 173. A rebound of sulfate to 242 mg/L (2.5 mM) on day 295 was observed followed by a decrease to 1.8 mg/L (0.019 mM) on day 264. The concentration of sulfate remained low at the start of the plume phase until day 348, after which the sulfate concentration began to increase reaching a maximum concentration of 562 mg/L (5.9 mM) on day 404. After day 404 sulfate decreased to 244 mg/L (2.6 mM) on day 460 and then slowly increased to the end of the operational period reaching a concentration of 514 mg/L (5.4 mM) on day 572. The concentration of chloride began to increase after bioaugmentation reaching 72 mg/L (2.0 mM) on day 103 and remained relatively stable to day 195. Chloride increased to a maximum concentration of 193 mg/L (5.4 mM) on day 243 followed by a decrease to 16 mg/L (0.46 mM) by day 285. The concentration of chloride remained stable to day 327 and began to increase at the start of the plume phase reaching a maximum concentration of 214 mg/L (6.0 mM) on day 488. Chloride showed a decreasing trend to the end of the operational period reaching a concentration of 112 mg/L (3.2 mM) on day 572.

The VFA data for the SRS™ column is presented in Figure 6.12. The acetate concentrations are displayed on a secondary axis because acetate was the dominant VFA measured and was present at concentrations much higher then the other VFAs. The time scale for this figure starts at the beginning of the SRS™ amendment period (Day 47). All VFAs were below detection limits prior to electron donor addition. After the SRS™ addition increases in lactate, butyrate, propionate, and acetate were observed. Lactate increased first reaching a maximum concentration of 363 mg/L (4.1 mM) by day

56 followed by a decrease to below the detection limit at day 78. Butyrate and propionate increases followed reaching maximum concentrations on day 58 of 421 mg/L (4.8 mM) and 153 mg/L (2.1 mM) respectively. Butyrate decreased to below detection limit on day 78, while propionate decreased to 41.5 mg/L (0.57 mM) on day 63 and remained relatively stable through to day 78. Acetate increased reaching 133 mg/L (2.3 mM) on day 58 followed by a decrease to near the detection limit on day 63. Low levels of acetate persisted through to day 78. After bioaugmentation on day 78 the concentration of propionate decreased to 12 mg/L (0.16 mM) on day 124 and remained relatively stable through day 292 followed by a decrease to below the detection limit on day 327. Propionate remained near or below the detection limit for the remainder of the operational period. Butyrate was detected sporadically between days 78 and 327 and remained below the detection limit to the end of the operational period. Acetate concentrations increased rapidly after bioaugmentation reaching a maximum concentration of 1,623 mg/L (28 mM) on day 184, followed by a decrease to non-detect on day 404. Acetate remained below detection limit to the end of the operational period on day 572.

The pH and ORP data is presented in Figure 6.13. The pH in the SRS^{TM} column remained stable up to day 58 after which it began to decrease reaching a value of 6.30 on day 236. Following the bicarbonate addition, which began on day 236, the pH increased rapidly to 6.77 on day 273 followed by a slow increase to 7.28 on day 467. The pH decreased slightly to 6.81 on day 572. ORP measurements were not taken in the SRS column until day 99. The initial ORP was slightly less then zero and initially increased to +50 mV on day 111, followed by a decrease reaching a value of -281 mV on day 432. The ORP remained stable to day 502, after which it increased to a value of 161 mV on day 551, followed by a decrease to -9 mV at the end of the operational period.

The molecular data is presented in Figure 6.14. The Dhc and vcrA concentrations in the SRS column were at concentrations of 1 X 10^5 gene copies/L and 2 X 10^5 gene copies/L respectively prior to electron donor addition. These concentrations were associated with the detection limit of the method. Both Dhc and vcrA remained at the detection limit up to day 230, after which a rapid increase in both values was observed reaching 1 X 10^8 and 8 X 10^7 gene copies/L respectively by day 324. The concentration of Dhc and vcrA remained at these high levels for the remainder of the column operational period.

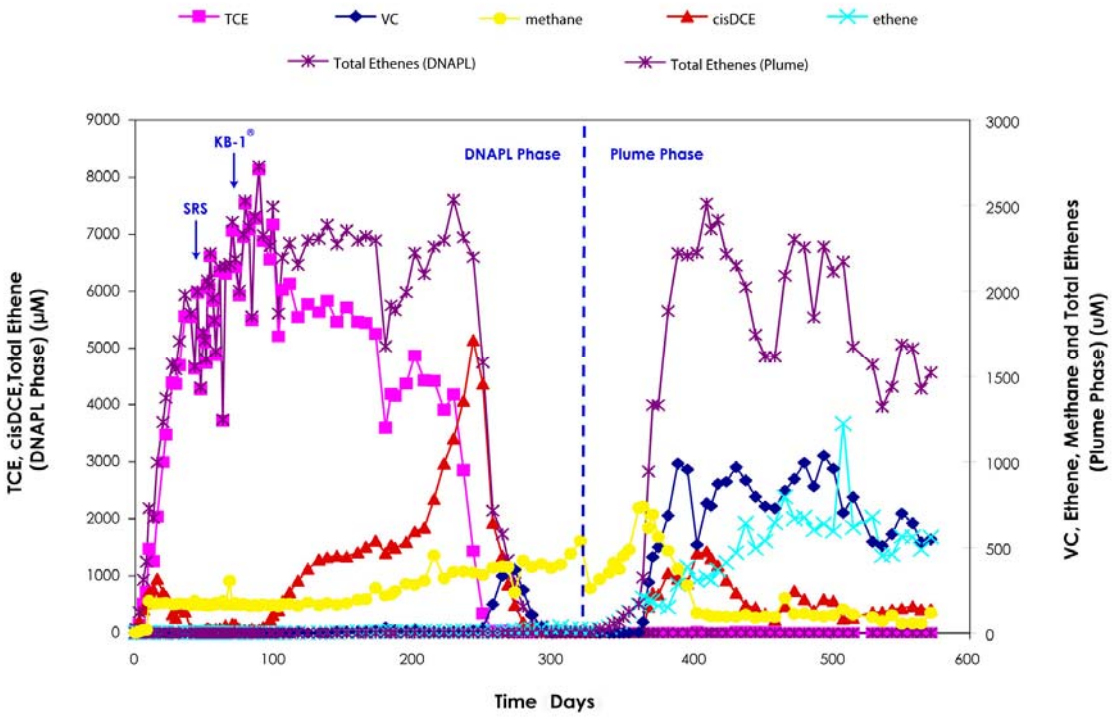

Figure 6.9 VOC, Ethene and Methane concentration trends in the SRS amended column

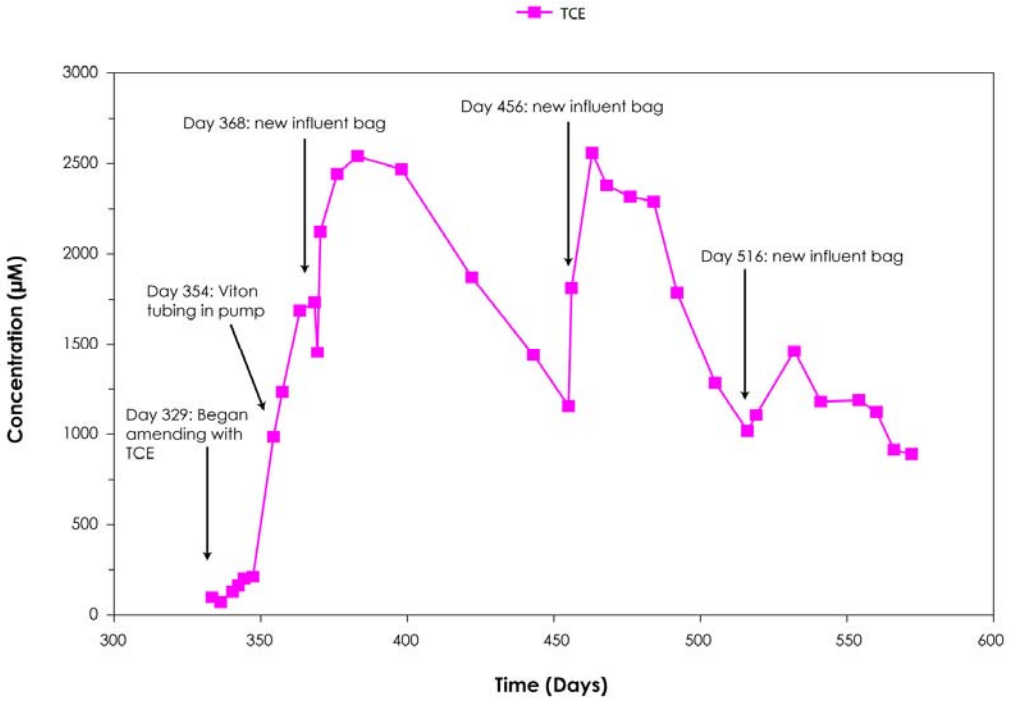

Figure 6.10 TCE concentration trends in the influent AGW bag

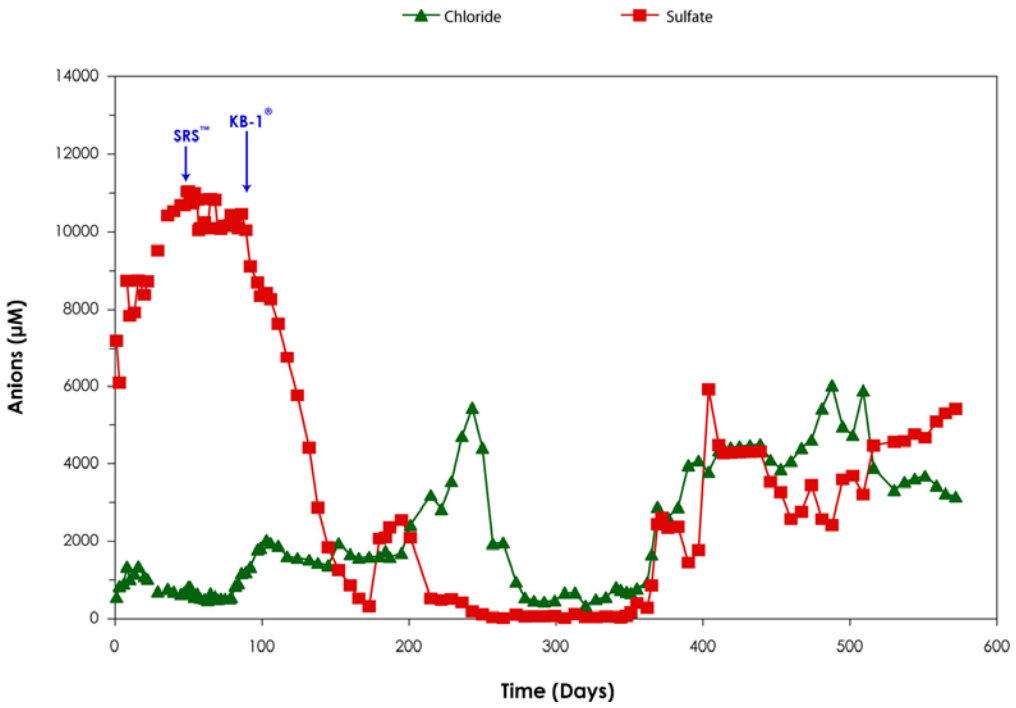

Figure 6.11 Anion concentration trends in the SRS amended column

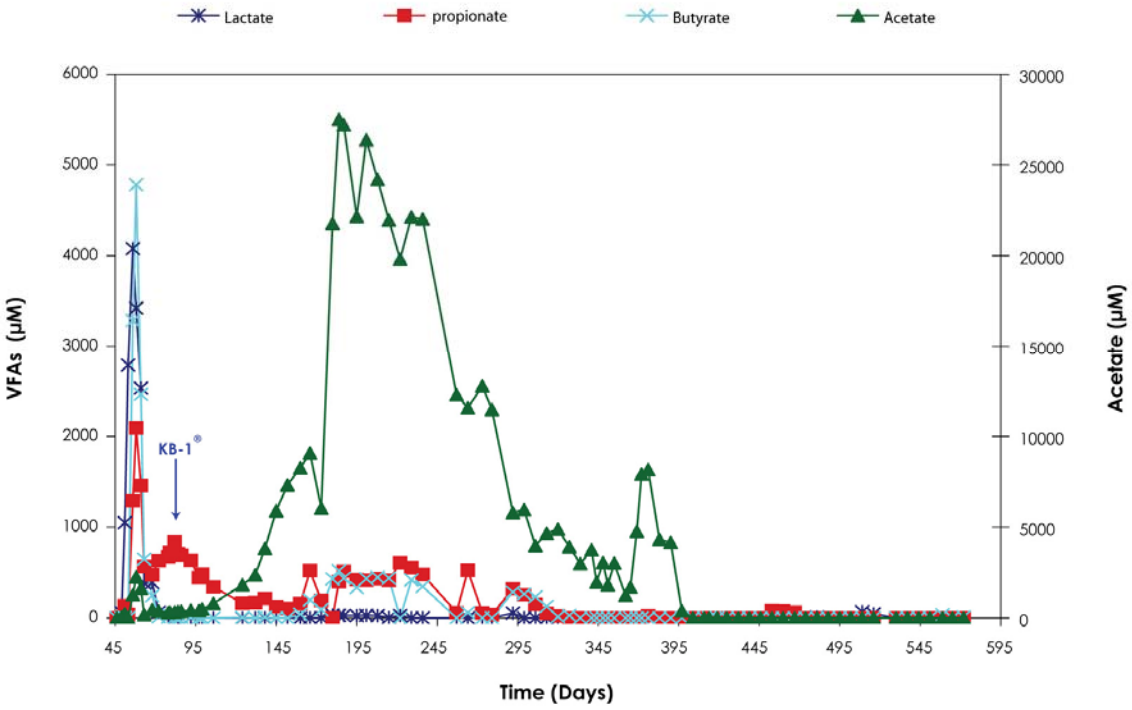

Figure 6.12 VFA concentration trends in the SRS amended column

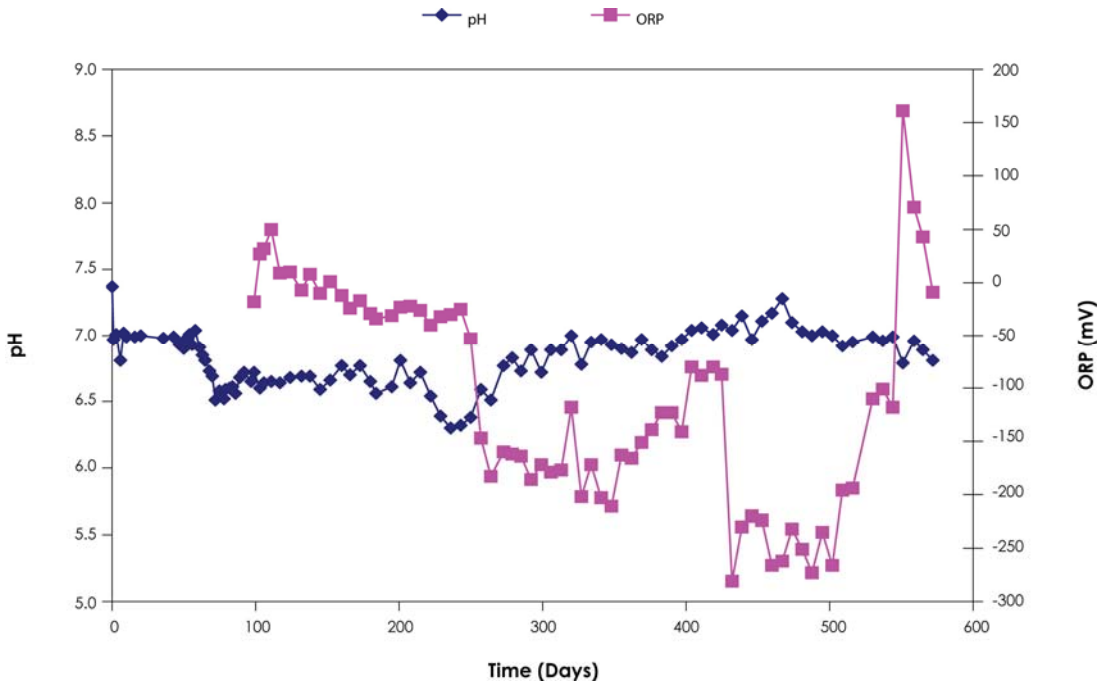

Figure 6.13 pH and ORP trends in the SRS amended column

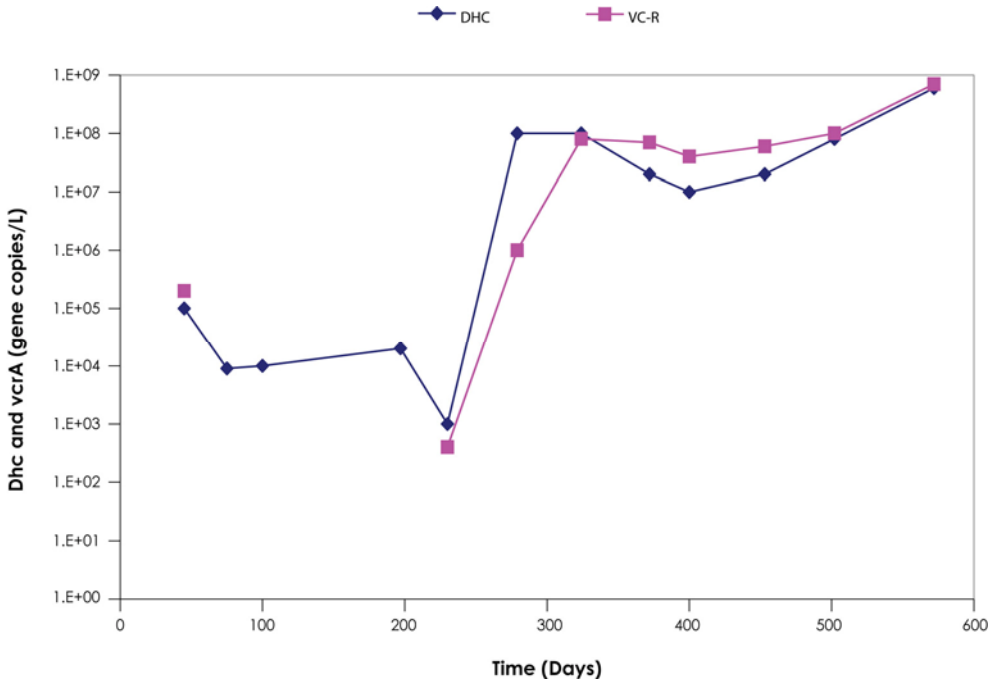

Figure 6.14 Dhc and vcrA concentration trends in the SRS^{TM} amended column

Chapter 7
Column Study Discussion

7.1 TCE DNAPL Distributions

The effluent TCE concentration profile for the control column over the first 47 days of column operation was different than the nBA and SRS^{TM} columns. TCE concentrations increased very rapidly in the control column to near saturation levels, whereas the increase in TCE was much more gradual in the nBA and SRS^{TM} amended columns. The COMPSIM fate and transport model was used to simulate the TCE breakthrough curves for the SRS and control columns. The results are presented in Figure 7.1. The results indicate that the reason for the different breakthrough profiles was primarily due to the greater amount of TCE retained in the control column compared to the treatment columns. This is evident by comparing the curves for each column that do not account for sorption effects because the amount of TCE retained is the only variable for those simulations. The simulated concentration of TCE increased much faster in the control column than in the SRS^{TM} column as was observed from the experimental data. Another factor that appears to add to the differences in TCE dissolution profiles is the sorption properties of the columns. The best fit for the experimental data from the control column was when sorption was not considered, while the best fit for the SRS^{TM} column was when a fraction of organic carbon (F_{oc}) of 0.45% was used. The aquifer material was homogenized prior to packing the columns, but it is difficult to completely homogenize soil and it is possible that the SRS^{TM} and nBA columns received a higher percentage of organic matter then the control column. Also, the control column was constructed several months after the treatment columns and it is possible that the organic matter in the material was degraded or changed during storage. A picture of the TCE distribution in the control column is shown in Figure 7.1. The TCE distributions in the nBA and SRS^{TN} columns looked similar to the control column.

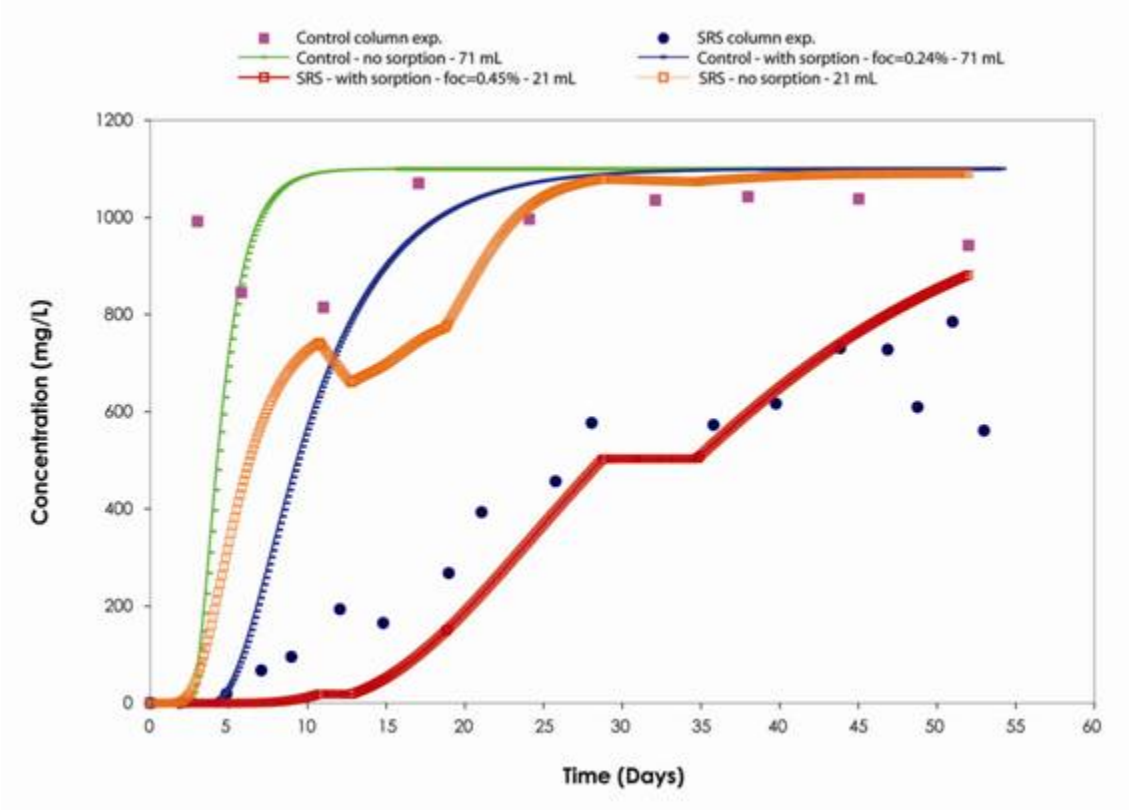

Figure 7.1 Experimental and Simulation Results for the TCE Breakthrough curves in the Control and SRS^{TM} Columns

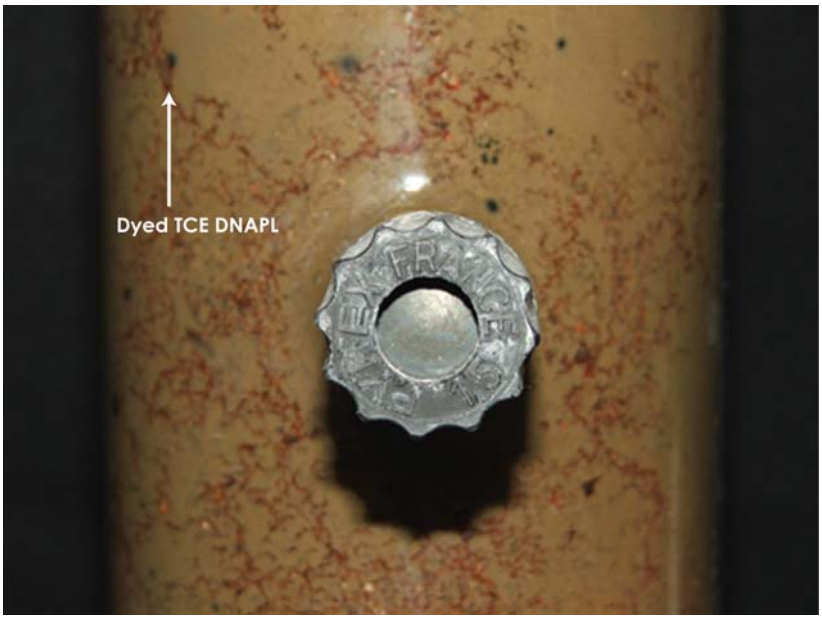

Figure 7.2 Dyed TCE distribution in the Control Column

7.2 Effect of TCE Concentrations on Indigenous Microorganisms

The *cis*-DCE concentration profiles increased similarly in the nBA and SRS™ amended columns, while *cis*-DCE was not observed to increase in the control column. The initial increase in *cis*-DCE in the nBA and SRS™ amended columns is likely from dechlorination of TCE to *cis*-DCE by indigenous microorganisms present in the aquifer material. Partial dechlorination of TCE to *cis*-DCE was observed in intrinsic control microcosms in the Sabre microcosm study indicating that the aquifer material did indeed contain dechlorinating organisms. The F_{oc} of the aquifer material was measured and found to be 0.6%, which may have served as electron donor for the dechlorination of TCE to cis-DCE. Once the TCE concentrations reached approximately 400 mg/L (3.0 mM) in the effluent of the nBA and SRS™ columns the concentration of *cis*-DCE began to decrease. This decrease in the dechlorination of TCE to *cis*-DCE could be due to: (1) the F_{oc} in the aquifer material that was providing electron donor was depleted, or (2) the concentration of TCE in the areas of the column where dechlorination was occurring became toxic to the indigenous microorganisms, and 3) nutrient levels had declined, slowing the biotransformation. The lack of *cis*-DCE production in the control column is likely due to inhibition of TCE to *cis*-DCE dechlorination by the initial high TCE concentrations; therefore the second explanation above is most likely the reason the *cis*-DCE concentrations declined in the treatment columns. This is also supported by previous reports that concentrations of TCE in this range are toxic to dechlorinators (Yang and McCarty, 2000).

7.3 Electron donor retention in columns

7.3.1 SRS™ retention in column

The amount of SRS™ added was based on the amount required to support sulfate reduction and complete dechlorination of TCE to ethene for one year of column operation. In order for the one time addition of SRS™ to support dechlorination over that period the SRS™ would need to be retained in the column. Visual observations were made during the SRS™ addition phase. The SRS™ material entered the column and followed similar pathways on the outside of the column as the TCE. The SRS™ appeared to surround the TCE DNAPL and the two phases appeared to mix as evident by the SRS™ turning a pinkish color. The SRS™ material was observed to move through the entire column by the end of the addition phase with a slight amount of visible SRS™ in the effluent collection vial on 19 May 2006 (Day 54). There was no flow through the SRS™ column for three days following the SRS™ addition and once the AGW flow continued visible SRS™ was not detected in the column

effluent for the remainder of the operational period. SRS™ breakdown products (VFAs) were detected in the effluent for the first 400 days of column operation indicating that SRS™ was retained in the column for at least that time frame.

GE was able to analyze for TOC and used TOC measurements as a surrogate for SRS™ measurements. The GE experiment consisted of two columns, one that contained TCE DNAPL and one that did not, and SRS™ was added in equal amounts to each column. They calculated the amount of TOC added to each column and compared it to the amount of TOC measured in the effluent of each column (Table 7.1). Almost all of the TOC added was retained in TCE DNAPL column versus 71% in the control column indicating that SRS partitioned into the TCE DNAPL resulting in enhanced retention of electron donor in the system.

Table7.1 Summary of TOC Retention in the GE Control and DNAPL Columns

Column	TOC In (g)	TOC Out (g)	Amount Retained (%)
Control	6.34	1.85	70.82
DNAPL	6.18	0.09	98.54

7.3.1.1 SRS™ mass balance

A mass balance was performed in an attempt to account for the fate of the SRS™ that was added to the SRS™ column. Because there was no direct measure of SRS™ in the effluent, the mass balance performed used effluent parameters that would consume electron donor and effluent acetate concentrations. For this mass balance the useable electron donor in SRS™ was assumed to be linoleic acid, which was 60% of the initial SRS™ mass (because SRS™ is 60 % soybean oil). First, the amount of H_2 consumed during dechlorination, sulfate reduction, and methanogenesis was calculated (H_2 consumed per electron acceptor). Then the amount of SRS™ consumed was estimated from acetate production because linoleic acid is fermented to acetate and hydrogen (equation 2.5) and acetate was easily measured in the column effluent. The amount of H_2 consumed during dechlorination, sulfate reduction and methanogenesis was greater than the amount of H_2 produced from linoleic acid fermentation to acetate (equation 2.5). Therefore the missing H_2 (H_2 required) was assumed to come from the complete oxidation of a portion of the linoleic acid (equation 2.7). The results are summarized in Table 7.2 and the calculations are provided in Appendix D.

The calculations were performed for two time periods. The first was from the day of SRS™ addition (Day 47) to day 404. This time period was chosen because after day 404 measurable VFA's (mainly acetate) were no longer detected in the effluent and it is likely that the SRS™ was completely consumed at this time. Sulfate reduction and dechlorination were observed to occur after day 404 to the end of the operational period on day 572, but it is possible that the electron donor used during this phase was not from the SRS™, but was from decaying biomass. However, the calculations were also performed for the entire operational phase because it is possible that there were pockets of SRS™ remaining in the column that were slowly fermenting providing the needed electrons for sulfate reduction, dechlorination, and methanogenesis. The results indicate that 58 % of the SRS™ was consumed by day 404 and 70 % by day 572. In either case the amount of SRS™ added to the column was not accounted for in the mass balance. There are several factors that may contribute to the missing mass in the mass balance calculations: (1) there was some visible oil observed in the effluent vial on the last day of SRS™ amendment that was not quantified, (2) acetate can be used directly by sulfate reducers (Widdel,1988) biasing the estimate of SRS consumed from acetate production to be lower than actual (3) other possible H_2 consuming reactions, such as iron and manganese reduction, that were not accounted for, (4) H_2 produced from SRS™ fermentation may have not been used and left the column directly and therefore would not have been used in the mass balance calculation, and (5) possible incorporation of carbon into biomass as suggested by Cope and Hughes, (2001). Long and Borden (2006) performed carbon mass balance equations to account for EVO that was amended to columns and obtained errors ranging from 2% to 67% indicating that these measurements are difficult and variability is high.

Even though the total SRS™ added to the column was not accounted for, the addition of SRS™ was able to promote dechlorination and sulfate reduction over the operational period (572 days) and possibly longer. Long and Borden (2006) reported good performance with no evidence of substrate depletion or reduced degradation rates after 14 months of column operation and calculated that all of the injected carbon would be released from the column in 6 to 7 years. In this case the SRS™ was likely depleted from the column after approximately 404 days (last measurable acetate in effluent), but dechlorinating activity and sulfate reduction continued indicating that SRS™ amendment was able to promote the appropriate conditions for these processes longer then anticipated.

Table7.2 Summary of SRS™ Mass Balance Results

	H_2 consumed per Electron Acceptor (mmoles)						Acetate Produced (mmoles)
Phase	TCE	*cis*-DCE	VC	methane	sulfate	Sum	
Day 47 - 404	33	2.3	0.59	49	1215	1300	330
Day 47 - 572	53	18	7.5	59	1687	1824	330

linoleic acid consumed to acetate and H_2 (mmoles)	H_2 produced (mmoles)	H_2 required (mmoles)	linoleic acid consumed to CO_2 and H_2 (mmoles)	Total linoleic consumed (mmoles)	Total linoleic consumed (g)	Mass SRS added (g)*	% SRS™ Consumed
37	513	787	16	52	15	25	58
37	513	1311	26	63	18	25	70

Notes: * corrected for mass of soybean oil in SRS™. SRS™ is 60 % soybean oil

7.3.2 nBA Retention in Column and Mass Balance

nBA was added to the nBA column four times throughout the operational period. nBA was not detected in the effluent until the final nBA addition, when it was added as a neat compound. It should be noted that butanol measurements were not taken during the saturated nBA additions, but were taken during the 2,000 mg/L and neat nBA addition phases. nBA is a colorless liquid and visual observations were not possible as with the SRS™ amendment. Mass balance calculations were performed by comparing the amount of nBA added to the column with the amount of nBA and breakdown products measured in the effluent for each amendment phase. The results are summarized in Table 7.3 and the data is presented graphically in Figure 7.3.

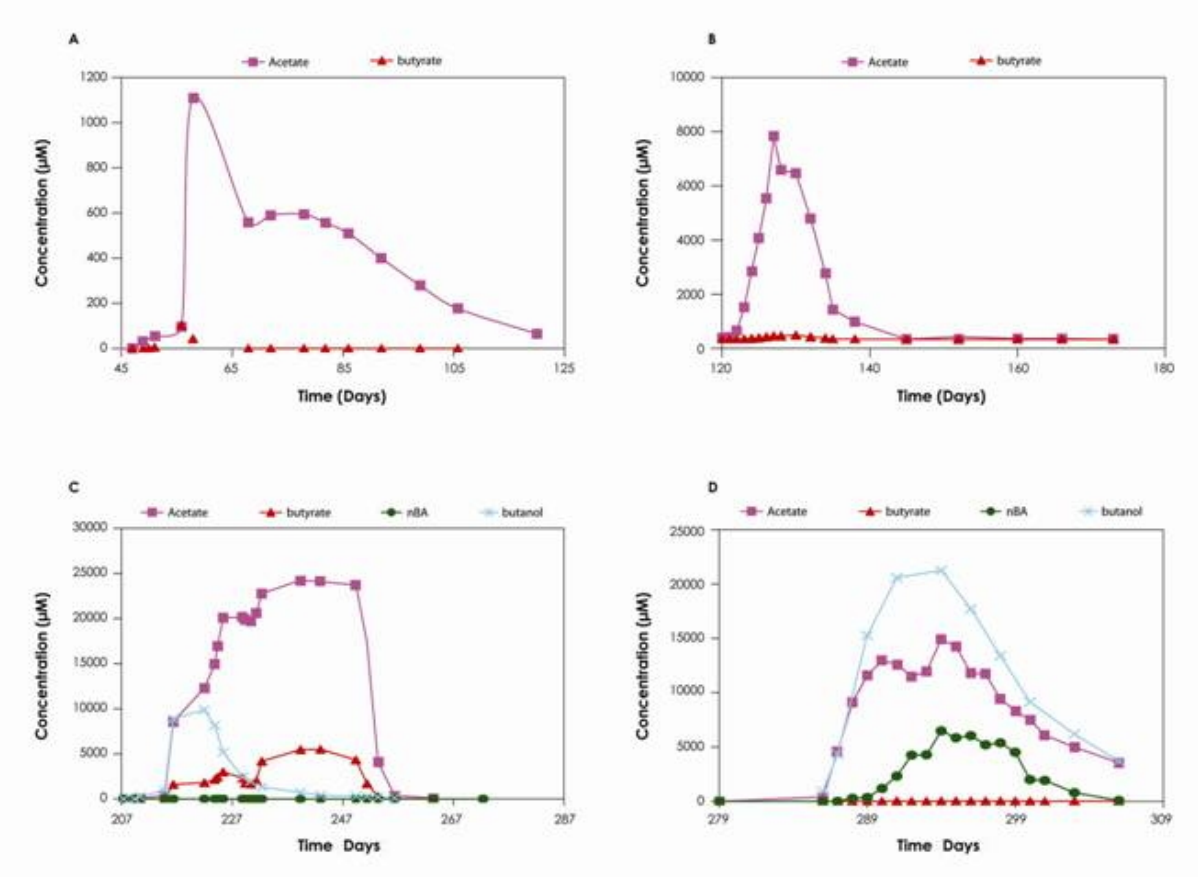

Figure 7.3 Effluent concentration trends of nBA, butanol, butyrate, and acetate. (A) first saturated stock addition. (B) second saturated stock addition. (C) 2,000 mg/L addition phase. (D) neat nBA addition.

Table7.3 Summary of nBA Amendments and Mass Recoveries

Days added	Concentration (mg/L)	nBA Mass Added (g)	nBA and Breakdown Products Mass Recovered (g)	Amount Recovered (%)
45-53	6,000	5.4	0.39	7.2*
118-125	6,000	4.9	0.89	18.1*
207-250	2,000	10.9	11.4	104
280	neat	5.3	5.7	108

Notes: * does not include n-butanol

The recoveries from the first two nBA additions were very poor. Butanol data was not available, but since one mole of butanol is produced for every one mole of acetate during nBA hydrolysis (equation 2.1), and there was very little butyrate measured, the butanol concentrations can be estimated from

the acetate data (assuming that acetate is not further transformed). Using estimated butanol concentrations the nBA recovery increases to 14.2% and 35.9% for the first and second additions respectively. The recoveries are still poor when butanol is included. Initially it was believed that the nBA had partitioned into the TCE DNAPL and the poor recoveries were due to the nBA mass being retained in the DNAPL as was expected to occur with a PED. However, the mass was not recovered over time as nBA or breakdown products, and with the lack of dechlorination and sulfate reduction the fate of nBA is unclear for the first two additions. It is possible that a portion of the nBA was completely oxidized to CO_2, which was not measured in the effluent, or there were losses of nBA from the influent bottle or tubing during the nBA amendment and the intended mass of nBA was not loaded into the column.

Recoveries for the 2,000 mg/L and neat nBA additions were much better. The recoveries were slightly greater then 100%, which is likely due to errors in the measurements and analytical analysis. The excellent recoveries from these two phases suggests that nBA was likely not completely oxidized during the first two nBA additions and further support the theory that the nBA mass from the first two additions was not sufficiently loaded into the column. The apparent losses of nBA during first two additions make if difficult to determine the partitioning behavior of saturated nBA under these conditions.

7.4 Effects of Biostimulation

Following electron donor addition on day 47 *cis*-DCE increased in both donor amended columns. The concentration of *cis*-DCE did not increase as high as the original increase at the beginning of the operational period, but do indicate that the indigenous microorganisms were able to dechlorinate at least a portion of the TCE to *cis*-DCE with the addition of nBA or SRS™ as electron donor, perhaps in microenvironments not exposed to high concentrations of TCE (Isalou and Sleep, 1998 and Dennis et al., 2003). Although the effluent TCE concentration was near saturation levels, the TCE concentration in portions of the column is likely lower. Sulfate reduction was not observed in the nBA or SRS™ columns after electron donor addition possibly due to toxic effects of the high TCE concentrations to sulfate reducers. Sulfate reduction was observed in SRS™ and nBA amended microcosms in the Sabre microcosm study indicating that the aquifer material did indeed contain organisms capable of sulfate reduction.

Acetate was present in the effluent after the first nBA addition indicating that nBA hydrolysis and/or fermentation occurred releasing electron donor available for sulfate reduction. There was a small amount of butyrate measured indicating that some H_2 may have been produced from fermentation of butanol (equation 2.2) The H_2 needed for the TCE to *cis*-DCE dechlorination likely came from here. The lack of mass balance from the first nBA addition makes it difficult to speculate on the fate of the electron donor and the amount of electron donor that was actually available for use in sulfate reduction and dechlorination during this initial phase. With only 7.2% of the added nBA recovered it is likely that electron donor was limited during this initial phase.

The initial increase in lactate, butyrate, and propionate in the effluent of the SRS™ column was attributed to the lactate component of the SRS™. The SRS™ electron donor contains 4% lactate to initially stimulate biological activity when added to the subsurface because lactate is readily available to many microorganisms. The initial propionate and acetate concentrations observed were likely due to fermentation of lactate. Aulenta et al. (2007a) observed that lactate was fermented to acetate and propionate in the absence of sulfate reduction. The lactate component of the SRS™ was not completely fermented as evident by the lactate measured in the effluent. This suggests that microbial activity in the column was limited initially. The lactate, propionate, and butyrate in the effluent represented a source of hydrogen that was not utilized and essentially wasted in the column effluent. Acetate only increased slightly and since LCFAs fermented from the oil initially sorb to sediment surfaces and then are slowly fermented (Long and Borden, 2006); it is likely that the acetate at this stage was from lactate fermentation to acetate and propionate rather than from fermentation of the oil component of the SRS. This suggests that H_2 production from the fermentation of LCFAs was not occurring, or occurring slowly. Also, given the likelihood that lactate fermentation followed the pathway to acetate and propionate, instead of acetate to H_2, (as indicated by the increase in propionate concentrations) the H_2 available for dechlorination may have been limited during this initial phase after donor addition and before bioaugmentation.

Biostimulation did not promote significant dechlorination or sulfate reduction in the time frame observed here. However, this phase is important to condition the columns prior to bioaugmentation with the KB-1® culture. The KB-1® culture requires reducing conditions, which are typically achieved by first amending the subsurface with electron donor and allowing the indigenous organisms to consume oxygen and created the reducing conditions.

7.5 Effects of Bioaugmentation

7.5.1 nBA column

Bioaugmentation with KB-1® promoted limited dechlorination of TCE to *cis*-DCE initially and after the second nBA amendment phase. The mass balance and availability of nBA was slightly better in the second addition than in the first, but it is still possible that there were limited amounts of electron donor available in this phase. During the 2,000 mg/L nBA amendment phase sulfate concentrations dropped rapidly and *cis*-DCE concentrations increased in the presence of high TCE concentrations indicating that sulfate reduction and dechlorination was possible in this column. Acetate, butanol, and butyrate were all present in the effluent and the nBA mass balance was excellent. Butanol and butyrate detected in the column effluent represented untapped H_2 sources, but there was likely more acetate and H_2 available than after the first two additions. The activity observed during this phase, along with the decrease in activity after the 2,000 mg/L nBA addition phase, indicate that there was sufficient electron donor available to promote dechlorination and sulfate reduction in this phase and that dechlorination of TCE to *cis*-DCE was possible with TCE DNAPL present.

VC and ethene concentrations did not increase throughout the operational period, even during the continuous addition phase. The concentrations of Dhc and vcrA did not increase in the effluent over the operational period indicating the conditions in the column were not favorable for the growth of the organisms responsible for the final dechlorination steps (i.e. cis-DCE to VC and ethene). Several other studies have observed similar results in the presence of DNAPL (Adamson et al., 2003, Carr et al., 2000, and Cope and Hughes, 2001), suggesting that complete dechlorination to TCE to ethene should not be expected in the immediate vicinity of the source zone. Bioaugmentation with KB-1® and the use of a PED as electron donor were used to over come this expectation, but were not able to promote complete dechlorination to ethene in this column scenario. The concentrations of Dhc and vcrA did not increase during the periods of *cis*-DCE production indicating that these organisms were not likely the organisms responsible for the TCE to *cis*-DCE dechlorination. Many organisms have been shown to be capable of PCE and TCE dechlorination to *cis*-DCE (Da Silva et, al 2006). It is likely that either intrinsic dechlorinators or dechlorinators in the KB-1® culture performed the observed dechlorination. The KB-1® culture contains Geobacter species, which is one possible candidate for the TCE to *cis*-DCE dechlorination. Duhamel et al., 2004 observed a Geobacter population increase during TCE to *cis*-DCE dechlorination suggesting that this organism grew from

the dechlorination of TCE to *cis*-DCE. Also, Sung et al. (2006) demonstrated that Geobacter strain SZ was capable of using PCE and TCE as metabolic electron acceptors and that 16srRNA gene sequences with high similarity to strain SZ were detected in the KB-1® culture.

The continuous addition of nBA during the third addition phase when the sulfate reduction and dechlorination were observed was more representative of a soluble electron donor delivery strategy rather then a PED addition. The nBA appeared to break down readily in the column influent bag (Table 5.3), and likely broke down readily once in the column so the nBA may not have made contact with the DNAPL phase and therefore could not partition into the DNAPL. The partitioning properties of the nBA breakdown products are less then nBA. Butanol is the closest with a log K_{ow} of 0.88 (Montgomery, 2000), butyric acid was estimated to be 0.79 +/-0.12 (Lyman et al, 1990), and acetic acid is negative with a log K_{ow} of -0.29 (Montgomery, 2000).

There was only limited data obtained after the neat nBA addition. The strategy for the neat nBA addition was to add the nBA, allow the nBA to partition into the DNAPL, and then re-bioaugment the column with KB-1®. Re-bioaugmentation would be needed because the neat nBA addition would have inhibited dechlorinating organisms present in the column. The nBA concentrations would be lower when partitioning out of the DNAPL back into the aqueous phase providing the needed electron donor to promote dechlorination. Unfortunately the column broke before it was re-bioaugmented with KB-1®. The limited data collected suggests that the neat nBA addition inhibited fermenting organisms in the column. High concentrations of butanol and only very low butyrate concentrations were measured in the effluent indicating that fermentation of butanol to butyrate was not a major process as it was during the 2,000 mg/L nBA addition phase.

7.5.2 SRS™ Column

During the DNAPL phase bioaugmentation with KB-1® promoted dechlorination of TCE to *cis*-DCE with trace amounts of VC and ethene. Sulfate reduction occurred almost immediately following bioaugmentation. TCE concentrations decreased slowly after bioaugmentation, but remained above 500 mg/L (consistent with concentrations representing the presence of DNAPL) with increases in *cis*-DCE production. Dhc and vcrA concentrations remained low during *cis*-DCE production indicating that other organisms were likely responsible for the TCE to *cis*-DCE dechlorination as discussed above for the nBA column. Following TCE decrease and the production of *cis*-DCE, VC, and ethene

after day 230 concentrations of Dhc and vcrA increased to 1 X 10^8 and 8 X 10^7 gene copies/L respectively. Figure 7.3 shows the increases in Dhc and vcrA with increases in VC and ethene over this time frame and to the end of the operational period. The concentrations of Dhc measured here are consistent with levels where ethene production is expected (Lu et al., 2006). The concentration of Dhc and vcrA remained consistent throughout the plume phase when high levels of VC and ethene continued to be measured in the effluent. These results indicate that the dechlorinating organisms were robust enough to recover from the stresses of high TCE concentrations and dechlorinate through to ethene once the DNAPL was depleted.

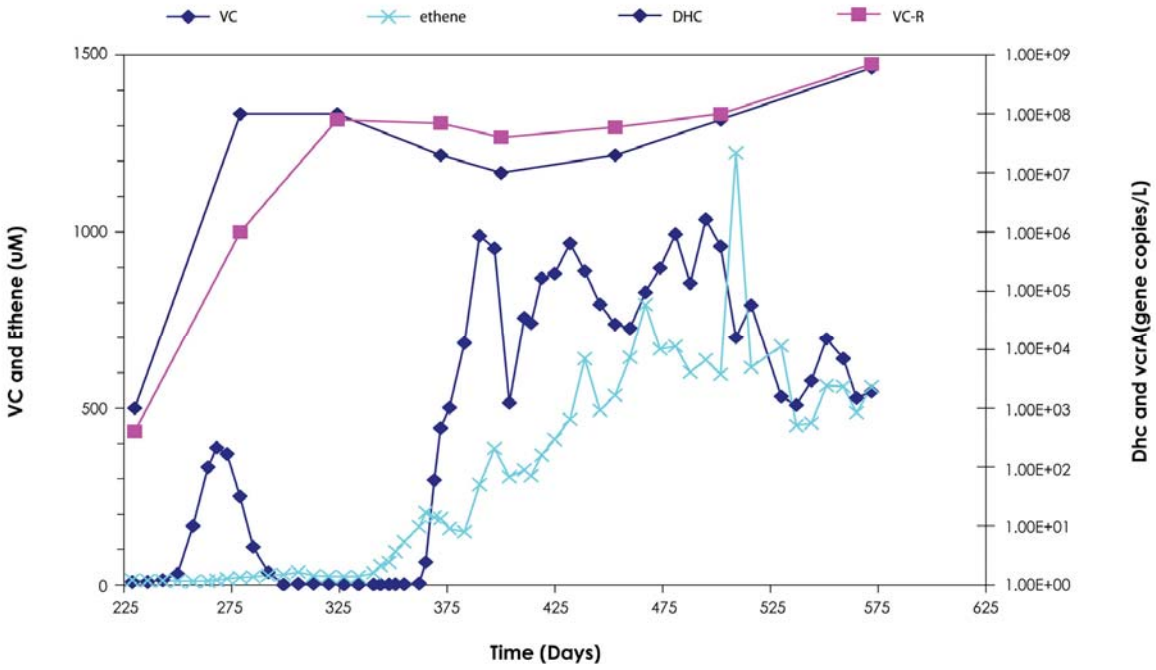

Figure 7.4 Dhc, vcrA, VC, and Ethene Concentration Trends in the SRS Column

Following bioaugmentation the concentration of acetate in the effluent increased rapidly indicating that the LCFA in the SRS^{TM} were being fermented and producing the needed H_2 and acetate for dechlorination and sulfate reduction. Dechlorination continued after acetate was no longer detected in the effluent from day 404 through day 572. This was an indication that the useable electron donor was consumed or fermentation of the LCFAs was no longer occurring. There was no noticeable change in dechlorination activity as TCE dechlorination products were continuously measured in the effluent. However, sulfate concentrations began to increase around the same time as the acetate was

no longer detected in the effluent. The sulfate concentrations measured in the effluent never reached as high as influent levels indicating that sulfate reduction was still occurring, which required a source of electron donor. It is possible that there were low flow zones in the column where a portion of the SRS™ was trapped and was slowly being fermented supplying the needed electron donor. Sulfate reducers can use acetate directly (Widdel, 1988) so even though acetate wasn't observed in the effluent it is possible that acetate was present in the column and was consumed by sulfate reducers somewhere in the column prior to reaching the effluent. If sulfate reducers were using acetate then it is possible that the dechlorinators benefited from the H_2 produced by the sulfate reducing bacteria as proposed by Aulenta et al. (2007a).

Methane concentrations began to increase in the DNAPL phase following day 150 when high concentrations of TCE and *cis*-DCE were present in the column at concentrations known to inhibit methanogenesis (Yang and McCarty (2000); perhaps in microsites. Methane concentrations continued to increase when chlorinated ethenes were not measured in the effluent. The methanogens benefited during this phase of the column operation, not only from the low chlorinated ethene concentrations, but also from the lack of competition for electron donor from dechlorinators. During this period acetate concentrations were high and it is possible that acetoclastic methanogens as well as hydrogenic methanogens were active. Methane concentrations decreased almost immediately following the start of the plume phase when the column was impacted by high TCE concentrations in the influent AGW. This suggests that methanogens present in the column were inhibited by TCE.

During the plume phase methanogens were at a disadvantage, not only from the high chlorinated ethene concentrations, but also from competition for electron donor by dechlorinators and sulfate reducers. Electron donor was likely limited during much of this phase as evident by the non-detect levels of VFAs in the effluent. Sulfate reducers and dechlorinators have a much lower hydrogen threshold then methanogens so it is possible that the H_2 concentrations were maintained below the threshold for methanogens. Therefore, even if microsites with low TCE concentrations existed, there may not have been enough H_2 available for the methanogens.

The ORP in the column effluent began to increase after day 502 and reached positive values (e.g. +161 mV) on day 551. This corresponds with the decrease in the breakdown products of the SRS™ and its apparent depletion indicating that conditions, at least in the column effluent, were not as

reducing as they were earlier in the operational phase. However, dechlorination products were measured in the effluent during this period and so it appears that reductive dechlorination was still active, perhaps in anaerobic microsites.

The pH in the SRS™ column decreased to near 6 during the period when *cis*-DCE production was occurring. This is below the optimum pH for reductive dechlorination. This suggests that the acid-buffering capacity of the site materials is not sufficient to maintain a neutral pH during acid production from dechlorination. The pH of the effluent was easily increased to near neutral with the addition of bicarbonate in the influent groundwater. This demonstrates that pH buffering may be required in the field to ensure optimal conditions for dechlorination are maintained.

7.5.3 Importance of Sulfate Reduction and Dechlorination in the SRS™ Column

The observed dechlorination of TCE and *cis*-DCE through to VC and ethene in the presence of high sulfate concentrations is a very important finding. There are reports in the literature that suggest dechlorination can take place with sulfate present (Aulenta et al., 2007a) and that sulfate had no inhibition effect on dechlorination (Hoelen and Reinhard, 2004). However, there are other studies that have shown sulfate can negatively affect dechlorination at low H_2 concentrations (Heimann et al., 2005) and that sulfate completely inhibited dechlorination (Nelson et al., 2002). The issue is still controversial and the typical approach used in bioremediation projects is to add enough electron donor to deplete the sulfate first (Aulenta et al., 2007) prior to expecting dechlorination to occur. This is significant because sulfate is often the main electron donor sink and drives the cost of electron donor required for bioremediation projects. It is likely in the plume phase of the SRS™ column that H_2 concentrations were low. The results here suggest that dechlorinators are able to compete with the sulfate reducers for H_2 under H_2 limiting conditions and that it is not necessary to deplete sulfate concentrations in order for dechlorination to proceed through to ethene. It is possible that sulfate reducers were inhibited by the high concentrations of TCE allowing the dechlorinating organisms to function in areas where sulfate reducers were not able to compete for electron donor. However, the results from the microcosm study showed that sulfate reducers were able to reduce sulfate in the presence of 800 mg/L of TCE so sulfate reducers and dechlorinators could have co-existed in the column and competed for available electron donor.

7.6 Mass balances

7.6.1 Chlorinated Ethene and Ethene Mass Balances

Throughout the column study operational period the chlorinated ethene and ethene concentrations in the effluent of the columns were summed to calculate the amount of chlorinated ethene and ethene mass being removed from the columns. The data is summarized in Table 7.4, an example calculation of cumulative mass removal is shown in Appendix D, and the raw data is provided in Appendix E. Over the operational period 57% of the TCE DNAPL in the control column was removed, mainly due to dissolution with 99.87% of the measured chlorinated ethenes removed as TCE. In the nBA column 50 % of the TCE DNAPL was removed in the 306 day operational period before the column broke. The removal was mainly as TCE dissolution (91 %) with 9 % *cis*-DCE, and trace VC measured. The DNAPL was believed to be depleted after about 300 days in the SRS^{TM} column as observed by the decrease in TCE and dechlorination products mass measured in the column effluent. The plume phase of the SRS^{TM} column did not begin until day 329 and all data up to day 327 was used in the DNAPL phase mass balance calculations. Only 76% of the TCE DNAPL retained in the column was accounted for in the effluent as TCE or dechlorination products. Again, the majority of the mass removed was as TCE (77%); *cis*-DCE accounted for 22% of the total mass removed, with VC and ethene making up the remaining 1%.

The chlorinated ethene and ethene concentrations in the effluent of the SRS^{TM} column during the plume phase were summed to compare with the mass of TCE added in the influent AGW. During this phase 94% of the added TCE was accounted for in the effluent with 0% as TCE, 27% as *cis*-DCE, 40% as VC, and 33% as ethene. The mass balance in this case was much better then in the DNAPL phase with only 6% of the added TCE unaccounted for.

The unaccounted for TCE mass in the SRS^{TM} column could be due to degradation of the chlorinated ethenes and ethene via a different pathway to end products that were not measured in this study. Anaerobic oxidation of VC to CO_2 by indigenous microorganisms has been demonstrated under redox conditions ranging from methanogenic to nitrate reducing (Bradley and Chapelle, 2000)). Also, Bradley and Chapelle (2002) demonstrated that under sulfate reducing conditions, bed sediment microorganisms completely oxidized ethene to CO_2. The mass balances obtained in the SRS^{TM} column during both the DNAPL and the plume phases did not account for all of the mass added.

Anaerobic oxidation of VC and/or ethene is a possible explanation for the missing mass. Mass loss was also observed in the GE column, which was attributed to anaerobic oxidation processes.

7.6.2 Chloride Mass Balances

Chloride is often used as a metric to verify measurements in dechlorination studies because it is a conservative ion (i.e., it does not degrade) and it is easy to measure. The concentration of chloride is expected to increase during the reductive dechlorination process. As seen in Figure 2.3 one mole of chloride is produced for each dechlorination step and if TCE is completely dechlorinated to ethene three moles of chloride will be produced. Mass balances were performed using the chloride measured in the effluent of the columns with the observed dechlorination products. A chloride mass balance was not performed on the control column because chloride concentrations were not observed to be higher then the background chloride levels in the AGW.

The measured chloride was slightly greater then the chloride expected from dechlorination in the nBA and SRS^{TM} columns. Differences were 6.0 %, 2.5 %, and 3.5 % for the nBA column, SRS^{TM} column DNAPL phase, and SRS column plume phase respectively (Table 7.5) and are not considered significantly different from 0%. This indicates that chloride is an excellent parameter to measure during the reductive dechlorination process and can be used to verify chlorinated ethene and ethene concentrations in bioremediation studies. Refer to Appendix D for an example calculation of cumulative mass removal and Appendix E for the raw data.

Table 7.4 Summary of Chlorinated Ethene and Ethene Mass Balance Results

Column	TCE added (mmoles)	TCE mmoles (% of total mmoles)	Cis-DCE mmoles (% of total mmoles)	VC mmoles (% of total mmoles)	Ethene mmoles (% of total mmoles)	Total mmoles	Amount Removed (%)
Control	691	394 (99.87)	0.51 (0.13)	0.00 (0.00)	0.00 (0.00)	394	57
nBA	446	201 (90.66)	21 (9.3)	0.097 (0.044)	0.00 (0.00)	222	50
SRS (DNAPL Phase)	240	140(77.21)	40 (22)	1.0(0.57)	0.31 (0.17)	182	76
SRS (Plume Phase)	52	0.00 (0.00)	13 (27)	19 (39)	16 (33)	49	94

Notes: Bracketed values are the percentage of the total mmoles measured for that compound

Table 7.5 Summary of Chloride Mass Balance Results

	Control column					nBA Column				
	Measured in effluent (mmoles)	mmoles of Cl released per mole	Cl released during dechlorination (mmoles)	Cl Measured (mmoles)	RPD	Measured in effluent (mmoles)	mmoles of Cl released per mole of VOC	Cl released during dechlorination (mmoles)	Cl Measured (mmoles)	RPD
TCE	394	0	0	--	--	201	0	0	--	--
cis-DCE	0.51	1	0.51	--	--	20.6	1	20.6	--	--
VC	0.00	2	0	--	--	0.097	2	0.19	--	--
Ethene	0.00	3	0	--	--	0	3	0	--	--
Total	395	--	0.51	ND	--	222	--	20.8	21.9	5.58

	SRS Column (DNAPL Phase)					SRS column (Plume Phase)				
	Measured in effluent (mmoles)	mmoles of Cl released per mole	Cl released during dechlorination (mmoles)	Cl Measured (mmoles)	RPD	Measured in effluent (mmoles)	mmoles of Cl released per mole of VOC	Cl released during dechlorination (mmoles)	Cl Measured (mmoles)	RPD
TCE	140	0	0	--	--	0	0	0	--	--
cis-DCE	40.1	1	40.1	--	--	13.3	1	13.1	--	--
VC	1.04	2	2.08	--	--	19.1	2	38.2	--	--
Ethene	0.31	3	0.94	--	--	16.1	3	48.4	--	--
Total	182	--	43.1	44.2	2.46	48.6	--	99.9	104	3.52

7.7 Evidence of Enhanced Dissolution

Several studies have demonstrated biologically induced enhanced dissolution of PCE DNAPL in column studies. Enhancement factors of 1.6 (Da Silva et al., 2006), 5.0 (Yang and McCarty, 2000), and 16 (Cope and Hughes, 2001) have been reported. Similar studies using TCE DNAPL could not be found in the literature. The solubility of PCE (140 mg/L) is much less then TCE (1,100 mg/L) and the K_{OW} of TCE is 9 times less than PCE (Adamson et al., 2003). Therefore, higher enhancement factors can be expected for PCE bioremediation as the difference in the solubility's and partitioning properties of dechlorination products is greater for PCE then for TCE. For example the solubility of cis-DCE (3,500 mg/L) is 23 times greater then PCE, but only 3 times greater then TCE. Nonetheless, the production of less chlorinated compounds from TCE DNAPL will increase the concentration gradient and allow more TCE to dissolve into the aqueous phase and increase the removal rate from a source zone relative to the dissolution of TCE alone.

Enhancement factors are typically calculated as the total moles removed in a treatment column divided by the total moles removed due to TCE dissolution only in a control column (Cope and Hughes, 2001). The cumulative mass recovery in the SRS™ column and control column was compared over the first 229 days of column operation (Figure 7.5). This time period was chosen because this was before the total mass in the SRS™ column dropped rapidly indicating that DNAPL was no longer present. The cumulative mass recovery in the nBA column and control column was compared over the entire 306 days of column operation (Figure 7.6). In both cases the mass removed due to dissolution alone in the control column was greater then the mass removed in the treatment columns. Enhancement factors of 0.71 and 0.77 were calculated for the SRS™ and nBA columns respectively. Enhancement factors less then one indicate the mass removal was actually greater in the control column then in the treatment columns. However, as discussed above, the amount of DNAPL added to each column was different and the dissolution profiles before any amendments were made to the treatment columns were not the same as the control column over the same time period. Therefore the dissolution profile from the control column is likely not a good indication of what the untreated dissolution profile would be in the treatment columns.

Non treated dissolution profiles representative of the treatment columns were not available so a different method of estimating enhanced dissolution was needed. The treatment columns were normalized to the control column by comparing the cumulative mass removed divided by the initial mass retained in the control column with the cumulative mass removed divided by the initial mass retained in the treatment columns. Refer to Appendix D for an example calculation of cumulative mass removal and Appendix E for the raw data. The normalized enhanced dissolution profiles for the SRS™ and nBA columns are shown in Figures 7.7 and 7.8 respectively.

Figure 7.7 shows that before biostimulation in the SRS™ column the normalized dissolution in the control column was slightly greater then in the SRS™ column. After biostimulation on day 47 the SRS™ profile began to increase relative to the control profile and this increased further after bioaugmentation on day 79 indicating that biostimulation and bioaugmentation increased the rate of mass removal relative to the control column. After 229 days of column operation 68% of the mass was removed from the SRS™ column versus only 33% of the mass in the control column, or 2.1 times more of the relative mass was removed from the SRS™ column compared to the control column.

The normalized dissolution in the control column was greater then in the nBA amended column up to the 2,000 mg/L nBA addition phase on day 209 (Figure 7.8). After day 209 the nBA dissolution increased above the control to the end of the operational period on day 306, although the differences weren't as great as in the SRS™ column. 50% of the mass was removed from the nBA column versus 42% in the control column, or 1.2 times more of the relative mass was removed from the nBA column compared to the control column.

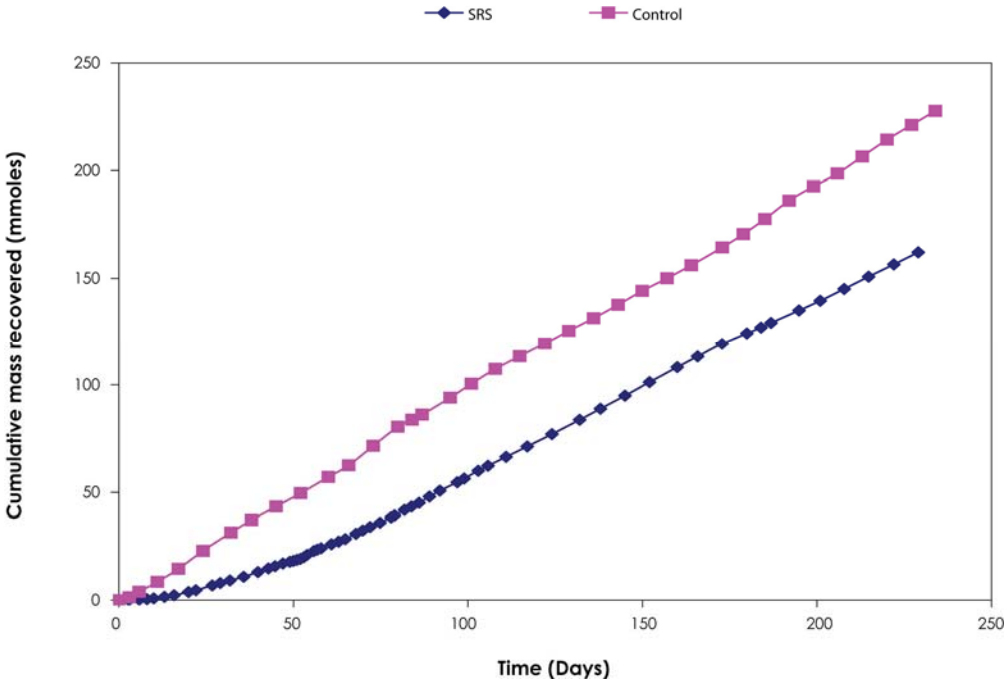

Figure 7.5 Cumulative Mass Recovered in the SRS™ and Control Columns

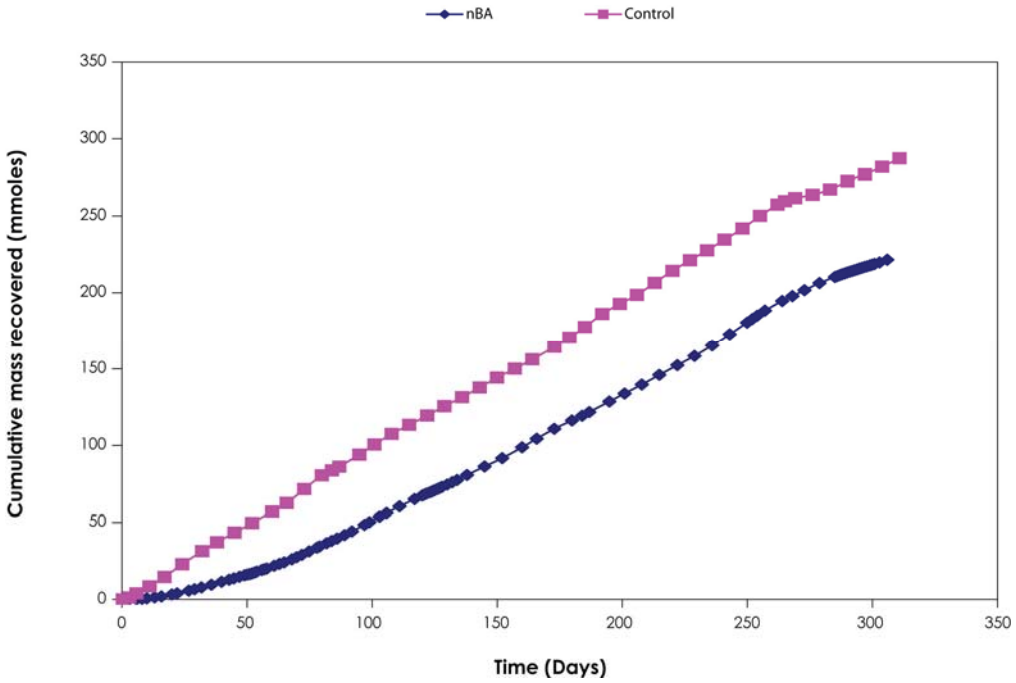

Figure 7.6 Cumulative Mass Recovered in the nBA and Control Columns

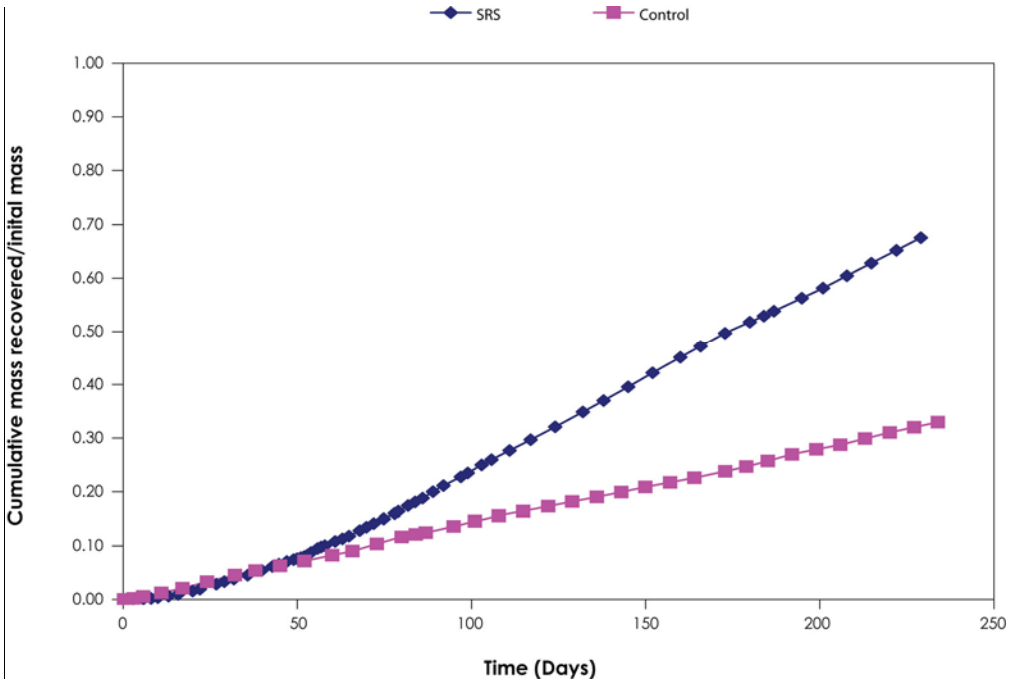

Figure 7.7 Normalized Enhanced Dissolution in the SRS^{TM} and Control Columns

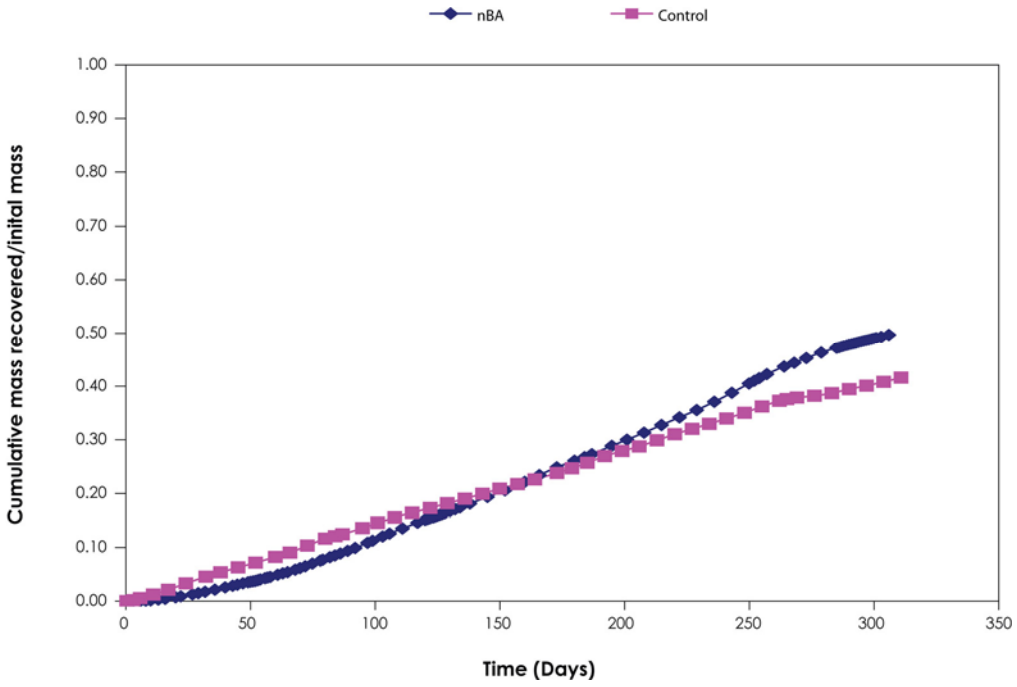

Figure 7.8 Normalized Enhanced Dissolution in the nBA and Control Columns

Chapter 8
Conclusions and Future Work

8.1 Conclusions

This research focused on enhancing the dissolution from TCE DNAPL source areas using bioremediation with partitioning electron donors and bioaugmentation as the remedial technology. The objectives of this research were to compare two partitioning electron donors in their ability to stimulate reductive dechlorination in the presence of TCE DNAPL and estimate the extent of DNAPL dissolution enhancement created by the bioremediation process. The following conclusions are drawn.

1. Both nBA and SRS™ electron donors were capable of supporting dechlorination of TCE to *cis*-DCE when TCE DNAPL was present in the column. The presence of DNAPL inhibited complete dechlorination to ethene.
2. Dhc were not responsible for the TCE to cis-DCE dechlorination in the presence of high TCE concentrations, the dechlorination was performed by other dechlorinating organisms. However, Dhc organisms were robust enough to recover from the stresses of the high TCE concentrations and dechlorinated TCE through to ethene following DNAPL depletion in the SRS™ column.
3. nBA was unstable in groundwater and flushed through the column rapidly. Activity was not maintained after the 2,000 mg/L nBA addition indicating limited electron donor retention within the column.
4. The addition of SRS™ promoted sulfate reduction and dechlorination for 1.5 years, which was longer than anticipated. Anaerobic activity was maintained after SRS™ breakdown products (VFAs) were not detected indicating that other metrics (dechlorination and sulfate reduction) are needed before reamending with electron donor.
5. Dechlorination to ethene was achieved in the presence of high sulfate concentrations. It may not be necessary to deplete sulfate prior to achieving complete dechlorination, which will decrease the amount of electron donor required.
6. The buffering capacity of the site material is not sufficient to buffer acid produced during dechlorination. pH needs to be carefully monitored during bioremediation studies and adjusted if required to ensure optimum dechlorinating conditions are maintained.

7. By normalizing the mass in the control column to the treatment columns enhancement factors of 2.1 and 1.2 were calculated for the SRS™ and nBA columns respectively.

8.2 Future Work

At the time this report was written the Sabre project was still underway and the following future work related to the SiREM column study is planned.

1. Perform a final tracer tests on the SRS™ column to compare the porosity and dispersivity values to the initial tracer test. This will be used to determine if the porosity decreased throughout the study due to the bioactivity in the column.
2. Analyze archived DNA samples collected from the nBA and SRS™ columns for Geobacter to verify the hypothesis that Geobacter was responsible for the TCE to *cis*-DCE dechlorination. It is expected that Geobacter counts will be high in the SRS™ column during the TCE to *cis*-DCE dechlorination and decrease once the Dhc concentrations increased during VC and ethene production.
3. Dismantle the SRS™ column and collect soil samples along the profile of the column. Extract DNA from different soil zones and analyze for Dhc, vcrA, and Geobacter counts to determine how these organisms are distributed in the column. Samples will also be submitted for denatured gradient gel electrophoresis (DGGE) to determine if there are changes in the microbial communities in different zones of the column.
4. Continue to run the control column at the experimental flow rate until the TCE DNAPL is depleted. This will be used to compare the dissolution curve as TCE is depleted from dissolution alone to the bioenhanced dissolution profile in the SRS™ column.

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Appendix A

Procedure For Making Artificial Ground Water

The artificial groundwater (AGW) used in this study was made in two liter amounts and stored for up to two months in the dark at room temperature. A bicarbonate solution, trace mineral mix solution, and a resazurin solution were made as concentrated solutions and were diluted to form the final AGW solution. Mineral mix and nutrients were added to the AGW solution immediately prior to use to minimize the chances of contamination due to microbial growth.

Bicarbonate Solution

The bicarbonate solution was made at 10 times the concentration required for the final AGW solution. Each chemical listed below was weighed out separately into a weigh boat and added to approximately 750 mL of dionized water in a 1 L volumetric flask. Dionized water was added to bring the total volume up to 1 L. The solution was mixed well on a stir plate until all components were dissolved, transferred into a 1 L sterile pyrex bottle, and stored in the dark at room temperature.

Chemical	Target amount
$NaHCO_3$	5.0 g
KCl	0.2 g
$MgSO_4 \cdot 7H_2O$	2.8 g

Trace Mineral Mix

The trace mineral mix solution was made at 500 times the concentration required for the final AGW solution. Each chemical listed below was weighed out separately into a weigh boat and added to approximately 750 mL of dionized water in a 1 L volumetric flask. A volume of 1 mL of 36 M H_2SO_4 was added to help dissolve all components. Once dissolved dionized water was added to bring the total volume up to 1 L. The solution was transferred into a 1 L pyrex bottle, autoclaved, and stored in the dark at room temperature.

Chemical	Target amount
H_3BO_3	0.3 g
$ZnCl_2$	0.1 g
$Na_2MoO_4 \cdot 2H_2O$	0.1 g
$NiCl_2 \cdot 6H_2O$	0.75 g
$MnCl_2 \cdot 4H_2O$	1.0 g
$CuCl_2 \cdot 2H_2O$	0.1 g
$CoCl_2 \cdot 6H_2O$	1.5 g
Na_2SeO_3	0.02 g
$Al_2(SO4)_3 \cdot 18H_2O$	0.1 g

Resazurin

The resazurin solution was made at 1000 times the concentration required for the final AGW solution. A target mass of one gram of resazurin was weighed into a weigh boat and added to approximately 750 mL of dionized water in a 1 L volumetric flask. Dionized water was added to bring the total volume up to 1 L. The solution was transferred into a 1 L pyrex bottle and stored in the dark at room temperature.

Preparing the Artificial Ground Water Solution

A target mass of 2.78 grams of calcium sulfate dihydrate was weighed into a weigh boat and added to approximately 1,600 mL of dionized water in a 2 L volumetric flask. The solution was heated and mixed on a stir plate until dissolved. The solution was allowed to cool to room temperature. A volume of 200 mL of the concentrated bicarbonate solution and 2 mL of the concentrated resazurin solution were added to the 2 L volumetric flask and dionized water was used to bring the total volume up to 2 L. The solution was mixed, transferred to a sterile 2 L Pyrex bottle, and stored in the dark at room temperature.

Immediately prior to use 4 mL of the concentrated trace mineral mix was added to the AGW and a target mass of 0.05 grams of diammonium phosphate was weighed into a weigh boat and added to the AGW. The AGW was mixed well and was ready for use.

Appendix B

Electron Donor Demand Calculations

The theoretical electron donor demand was calculated for the nBA and SRS™ columns. The SRS™ electron donor demand was used to determine how much SRS™ to add to the SRS™ column. The nBA electron donor demand was calculated to compare the actual nBA added with the theoretical demand. Calculations used are outlined below.

nBA

nBA Electron Donor Calculations

Calculation to determine the amount of sulfate added to the nBA column over one year of column operation:

Sulfate concentration in AGW = 1,000 mg/L
Experimental flow rate = 0.07 ml/min
Time = 365 days

Sulfate added (mg/column) =
1,000 mg/L X (0.07mL/min/1000mL/L) X 365days X 24hours/day X 60 min/hour = 36,792

Balanced chemical equations for electron acceptor with nBA to determine molar ratio:

TCE: $3C_6H_{12}O_2 + 16C_2HCl_3 + 30H_2O = 18CO_2 + 16C_2H_4 + 48H+ + 48Cl^-$
Sulfate: $C_6H_{12}O_2 + 4SO_4^{2-} + 8H^+ = 6CO_2 + 4H_2S + 6H_2O$

Calculation for the nBA demand needed to reduce the amount of sulfate added:

nBA demand (mg/column) = 36,792 (mg sulfate/column)/ 96 mg/mmol X ¼ X 116.16 mg/mmol) = 11,130

Calculation for the nBA demand needed to reduce the amount of TCE added:

nBA demand (mg/column) = 59,000 (mg TCE/column)/ 131.4 mg/mmol X 3/16 X 116.16 mg/mmol) = 9,779

Table B1: Summary of nBA demand calculations

	Sulfate	TCE
Initial Concentration (mg/column)	36,792[a]	59,000
Molecular Weight (mg/mmol)	96	131.4
Molar Ratio[b]	1/4	3/16
nBA Demand (mg/column)	11,130	9,779
Total nBA Demand (mg/column)	20,909	
First nBA addition (mg/column)	5,400	
Second nBA addition (mg/column)	4,900	
Third nBA addition (mg/column)	10,900	
Fourth nBA addition (mg/column)	5,300	
Total nBA added (mg/column)	26,500[c]	
Safety Factor	1.3	

Notes: [a]based on the amount of sulfate added to the column for one year of operation at the experimental flow rate
[b]Molar ratio is the number of moles of electron donor consumed per mole of electron acceptor
[c] sum of nBA amended to the column over the operational period

nBA Amendment Solutions

Procedure used to make nBA saturated stocks for first and second nBA amendments:

nBA solubility = 6,000 mg/L
nBA density = 0.882 mg/µL

The amount of nBA required to make an 800 mL nBA saturated stock in AGW is

Mass nBA needed (mg) = 6,000 mg/L X 0.8L = 4,800 mg
Volume nBA needed (µL) = 4,800 mg / 0.882 mg/µL = 5,442 µL

A one liter glass Pyrex bottle was filled with 800 mL of AGW. A volume of 100 mL of nBA was poured into the AGW. This amount of nBA was well above the theoretical amount of nBA needed. This procedure was used so that there was a visible phase of nBA above the AGW to ensure that the saturated stock concentration was maintained throughout the addition phase. The bottle was capped and the solution was shaken well and allowed to equilibrate over night prior to use.

Procedure used to make the 2,000 mg/L nBA solutions for the third nBA amendment phase:

The solution was made in a 10L tedlar bag containing 6L of AGW.

Mass nBA needed (mg) = 2,000 mg/L X 6.0 L = 12,000 mg
Volume nBA needed (µL) = 12,000 mg / 0.882 mg/µL = 14,000 µL

A 25 mL syringe was used to inject the 14 mL of nBA through the inlet septa on the tedlar bag. The solution was shaken well and allowed to equilibrate over night prior to use.

Procedure used for the fourth (neat nBA) addition phase:

It was decided to add 6 mL of nBA because this was similar to the mass of nBA added during the first and second nBA additions.

Mass nBA added (mg) = 6 mL X 0.882 mg/µL X 1000 mL/µL = 5,300 mg

A 10 mL syringe was used to inject the nBA directly into the column inlet. The nBA was injected at a rate of 1 mL/min.

SRS™

SRS™ Electron Donor Calculations

Calculation to determine the amount of sulfate added to the SRS™ column over one year of column operation:

Sulfate concentration in AGW = 1,000 mg/L
Experimental flow rate = 0.07 ml/min
Time = 365 days

Sulfate added (mg/column) =
1,000 mg/L X (0.07mL/min/1000mL/L) X 365days X 24hours/day X 60 min/hour = 36,792

SRS is 60% soybean oil. Soybean oil is composed of:

53.3% Linoleic Acid
23.8% Oleic Acid
10.8% Palmitic Acid
4.0% Stearic Acid
7.1% Gamma-Linoleic

Balanced chemical equations for electron acceptor with SRS™ to determine molar ratio:

TCE:
$3C_{18}H_{32}O_2 + 50C_2HCl_3 + 129H_2O = 50C_2H_4 + 27CO_2 + 27HCO_3^- + 177H^+ + 150Cl^-$
$C_{18}H_{34}O_2 + 17C_2HCl_3 + 43H_2O = 17C_2H_4 + 9CO_2 + 9HCO_3^- + 60H^+ + 51Cl^-$
$3C_{16}H_{32}O_2 + 46C_2HCl_3 + 114H_2O = 46C_2H_4 + 24CO_2 + 24HCO_3^- + 162H^+ + 138Cl^-$
$3C_{18}H_{36}O_2 + 52C_2HCl_3 + 129H_2O = 52C_2H_4 + 27CO_2 + 27HCO_3^- + 183H^+ + 156Cl^-$
$3C_{18}H_{30}O_2 + 49C_2HCl_3 + 129H_2O = 49C_2H_4 + 27CO_2 + 27HCO_3^- + 174H^+ + 147Cl^-$

Actual molar ratio used is the sum of the molar ratio of each component of soybean oil multiplied by the percentage of that component in soybean oil as follows:

(0.533X3/50) + (0.238X 1/17) + (0.108X3/46) + (0.04X3/52) + (0.071X3/49) = 4/67

Sulfate:
$2C_{18}H_{32}O_2 + 25SO_4^{2-} + 32H^+ = 25H_2S + 18CO_2 + 18HCO_3^- + 14H_2O$
$4C_{18}H_{34}O_2 + 51SO_4^{2-} + 66H^+ = 51H_2S + 36CO_2 + 36HCO_3^- + 32H_2O$
$2C_{16}H_{32}O_2 + 23SO_4^{2-} + 30H^+ = 23H_2S + 16CO_2 + 16HCO_3^- + 16H_2O$
$C_{18}H_{36}O_2 + 13SO_4^{2-} + 17H^+ = 13H_2S + 9CO_2 + 9HCO_3^- + 9H_2O$
$4C_{18}H_{30}O_2 + 49SO_4^{2-} + 62H^+ = 49H_2S + 36CO_2 + 36HCO_3^- + 24H_2O$

Actual molar ratio used is the sum of the molar ratio of each component of soybean oil multiplied by the percentage of that component in soybean oil as follows:

(0.533X2/25) + (0.238X 4/51) + (0.108X2/23) + (0.04X1/13) + (0.071X4/49) = 7/88

Calculation for the SRS™ demand needed to reduce the amount of sulfate added:

Molecular weight used is that of linoleic acid because linoleic acid is the main component in soy bean oil.

SRS™ demand (mg/column) = 36,792 (mg sulfate/column)/ 96 mg/mmol X 7/88 X 280 mg/mmol) = 8,536

Calculation for the SRS™ demand needed to reduce the amount of TCE added

SRS™ demand (mg/column) = 24,000 (mg TCE/column)/ 131.4 mg/mmol X 4/67 X 280 mg/mmol) = 3,053

Table B2: Summary of SRS™ demand calculations

	Sulfate	TCE
Initial Concentration (mg/column)	36792[a]	24000
Molecular Weight (mg/mmol)	96	131.4
Molar Ratio[b]	7/88	4/67
Soybean Oil Demand (mg/column)	8536	3053
Total Soybean Oil Demand (mg/column)	11589	
Total SRS Demand (mg/column)	19315[c]	
Total SRS added (mg/column)	42200[d]	
Safety Factor	2.2	

Notes: [a]based on the amount of sulfate added to the column for one year of operation at the experimental flow rate
[b]Molar ratio is the number of moles of electron donor consumed per mole of electron acceptor
[c] soybean oil demand multiplied by 60% because SRS™ is 60% soybean oil
[d] Amount of SRS™ added to the column

SRS™ Amendment Solution

SRS™ was added to the column as a 5% (w/v) solution based on the results of the batch test described in Section 4.1.4.

5% = 5 parts per 100
Mass SRS (g) = 50g/L X 1L = 50g

A one liter glass Pyrex bottle was partially filled with AGW. 50 g of SRS™ was weighed on a weigh boat and added to the AGW. A syringe with AGW was used to rinse the SRS™ into the bottle. AGW was added to the bottle to bring the total volume of the solution to 1 L. The bottle was capped and the solution was shaken well and allowed to equilibrate over night prior to use. During addition the solution was continually stirred using a magnetic stir bar and stir plate.

Appendix C

Bromide Tracer Test

The tracer tests were conducted using AGW amended with sodium bromide to a measured concentration of 91 mg/L. The solution was pumped through all three columns at a target flow rate of 0.07 mL/min. Flow rate measurements were taken throughout the tracer tests and are shown in Table C1. The breakthrough data were fit using the COMPSIM fate and transport model by Kokkinaki (2007) to estimate porosity and dispersivity values. Also, calculations for velocity and residence time were performed for all three columns.

Sample Calculations for velocity and residence time using the SRS™ column:

Pore water velocity

$V = Q/(nXA)$

Average Q = 0.079 cm^3/min / 60 sec/min/1000/1000 = 1.32 X 10^{-9} m^3/sec
n = 0.31 estimated from COMPSIM
column radius (r) = 3.8 cm = 0.038 m
$A = \pi r^2 = 0.0045\ m^2$
v = 1.32 X 10^{-9} m^3/sec/(0.31 X 0.0045 m^2) = 9.43 X 10^{-7} m/sec X 60 sec/min X 60 min/hour X 24 hour/day X 100 cm/m = 8.2 cm/day

Residence Time

$\tau = n\ X\ (V/Q)$

V = A X L
V = 0.0045 m^2 X 0.6 m = 0.0027 m^3
τ= 0.31 X 0.0027 m^3 / 1.32 X 10^{-9} m^3/sec /60 sec/min / 60 min/hour / 24 hour/day = 7.45 days

Table C1: Bromide Tracer Test Data

Control Column				nBA Column				SRS™ Column			
Time (Days)	Br. Conc. (mg/L)	Simulated Br. Conc. (mg/L)	flow rate (cm^3/min)	Time (Days)	Br. Conc. (mg/L)	Simulated Br. Conc. (mg/L)	flow rate (cm^3/min)	Time (Days)	Br. Conc. (mg/L)	Simulated Br. Conc. (mg/L)	flow rate (cm^3/min)
0.00	0.67	0.00	0.09	0.00	<0.39	0.00	0.09	0.00	<0.39	0.00	0.10
1.00	<0.39	0.00	0.07	1.00	<0.39	0.01	0.06	1.00	<0.39	0.00	0.07
2.06	2.5	0.91	0.08	2.06	0.83	1.4	0.09	2.06	1.7	0.80	--
3.02	11	5.9	0.07	3.02	7.4	7.1	0.07	3.02	7.8	6.0	0.08
4.76	28	25	0.07	4.76	26	26	0.07	4.76	28	28	0.09
5.23	34	32	0.07	5.23	36	31	0.07	5.23	36	34	0.08
5.77	38	38	0.08	5.77	42	38	0.07	5.77	42	42	0.07
6.09	44	42	0.07	6.09	40	41	0.07	6.09	49	46	0.08
6.81	49	50	0.07	6.81	45	48	0.07	6.81	55	55	0.07
7.14	51	54	0.08	7.14	46	52	0.08	7.14	59	58	0.08
7.78	58	60	0.07	7.78	54	57	0.07	7.78	65	64	0.08
8.11	61	63	0.08	8.11	55	60	0.08	8.11	65	67	0.08
8.81	66	68	0.07	8.81	65	65	0.07	8.81	72	72	0.08
9.14	68	70	0.08	9.14	65	67	0.08	9.14	74	74	0.09
9.77	69	73	0.07	9.77	66	70	0.07	9.77	75	77	0.08
10.14	77	75	0.07	10.14	72	72	0.07	10.14	82	79	0.08
10.91	84	79	--	10.91	81	75	--	10.91	87	82	--
11.93	85	82	--	11.93	85	79	--	11.93	88	85	--
12.83	88	84	0.07	12.83	87	82	0.07	12.83	87	87	0.08
13.13	88	85	0.09	13.13	80	82	0.08	13.13	89	87	0.08
13.80	89	86	0.07	13.80	75	84	0.07	13.80	90	88	0.08
14.77	90	87	0.07	15.78	89	87	0.07	14.77	91	89	0.08
15.78	90	88	0.07	--	--	--	--	15.78	92	90	0.08

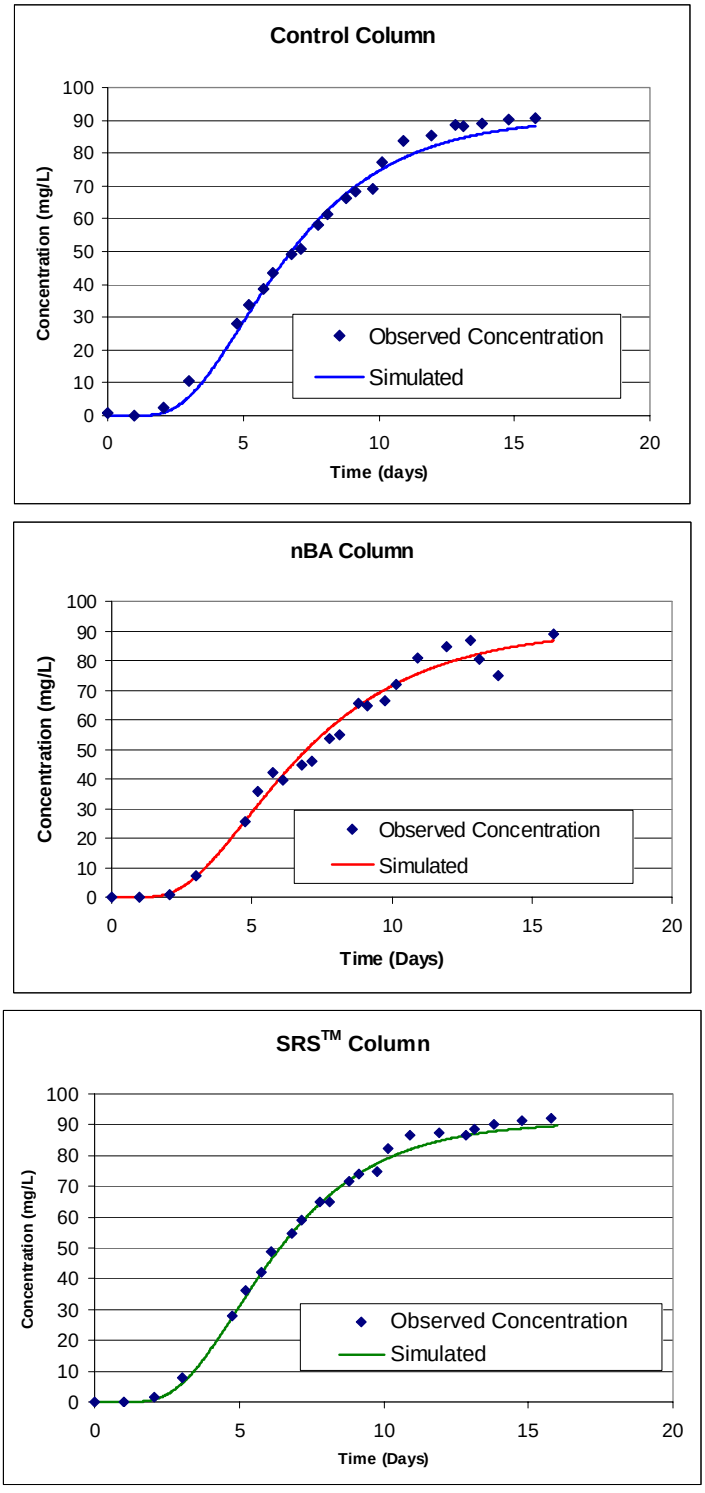

Figure C1: Bromide Breakthrough Curves for control, nBA and SRS™ Columns

Appendix D

Mass Balance Calculations

In order to perform electron donor, chlorinated ethene and ethene, and chloride mass balance calculations the mass of chlorinated ethenes, ethene, methane, sulfate, chloride, and acetate removed from the column were needed. After each sampling event the cumulative masses of these compounds exiting the column were calculated. The following example shows the method used to determine the cumulative mass of a compound removed from a column after day 50. Day 50 was chosen randomly. The same method was used for all other mass removal calculations. Refer to Appendix E for the raw data sheets.

Example Calculation for mass removed from a column:

Mass removed (mg) = (average of current and previous compound concentration [mg/L]) X (current day – previous day [day]) X (average of current and previous flow rate [ml/min]) /(1000 [ml/L] X 60 [min/hour] X 24 [hours/day]) + (previous day cumulative compound mass [mg])

For TCE in the SRS column after 50 days of column operation:

Mass TCE removed (mg) = (average of 670 mg/L and 689 mg/L) X (50 days – 49 days) X (average of 0.062 ml/min and 0.046 ml/min) / 1000 ml/L X 60 min/hour X 24 hour/day + 2,082 mg
Mass TCE removed (mg) = (679 mg/L) X (1 day) X (0.054 ml/min) / (1000 ml/L X 60 min/hour X 24 hour/day) + 2,082 mg

Mass TCE removed (mg) = 2,134 mg

Chlorinated Ethene Consumption:

In order to determine the amount of electron donor used, the mass of chlorinated ethenes consumed was needed. Using the reductive dechlorination sequence the mass of TCE consumed is equal to the mass of *cis*-DCE, VC, and ethene produced. Similarly the mass of *cis*-DCE consumed is equal to the mass of VC and ethene produced and the mass of VC consumed is equal to the mass of ethene produced. Using the masses of chlorinated ethenes and ethenes exiting the column after 572 days (refer to Appendix E):

TCE consumed = 5,178 mg + 1,259 mg + 468 mg = 6,906 mg
cis-DCE consumed = 1,259 mg + 468 mg = 1, 729 mg
VC consumed = 468 mg

Methane Production:

Amount methane produced is equal to the cumulative mass of methane removed from the column = 240 mg

Sulfate Reduction:

The mass of sulfate pumped through the column from day 89 to 572 was calculated. This time frame was chosen because before day 89 there was no measurable sulfate reduction and the sulfate exiting the column was assumed to have not consumed any electron donor.

Sulfate concentration in AGW = 1,000 mg/L
Experimental flow rate = 0.07 ml/min
Time = 572 – 89 = 483 days

Sulfate added (mg/column) =
1,000 mg/L X (0.07mL/min/1000mL/L) X 483 days X 24hours/day X 60 min/hour = 48,686

Mass of sulfate removed from day 89 to 572 is equal to the cumulative mass of sulfate exiting the column over this time frame = 8,190 mg

The amount of sulfate reduced is equal to the amount of sulfate pumped through the column minus the mass of sulfate removed in the effluent.

Mass sulfate reduced = 48,686 mg – 8,190 mg = 40,496 mg

Acetate production:

Amount acetate produced is equal to the cumulative mass of acetate removed from the column = 19,472 mg

Calculation for the amount of SRS™ consumed during reductive dechlorination, sulfate reduction and methane production:

The calculation shown here is for the entire operational period (up to day 572). The same method was used to calculate the amount of SRS™ consumed over the shorter time period up to day 404.

Balanced chemical equations for chlorinated ethenes, sulfate and methane with hydrogen were used to determine the molar ratio, hydrogen demand, and the amount of hydrogen consumed for each reaction (Table D1).

The initial amount of SRS™ added was = 42,200 mg
SRS™ is composed of 60% soybean oil and soybean oil is assumed to be 100% linoleic acid for the purposes of this calculation. Therefore the amount of linoleic acid added was = 42,2000 mg X 60% = 25,320 mg

Table D1: Summary of Hydrogen Consumption Calculations

Reaction	Balanced Equation	Amount (mg)	Amount (mmol)	H_2 demand (mmol/mmol)	H_2 consumed (mmol)
TCE to cis-DCE	$C_2HCl_3 + H_2 = C_2H_2Cl_2 + H^+ + Cl^-$	6,906	53	1	53
cis-DCE to VC	$C_2H_2Cl_2 + H_2 = C_2H_3Cl + H^+ + Cl^-$	1, 729	18	1	18
VC to ethene	$C_2H_3Cl + H_2 = C_2H_4 + H^+ + Cl^-$	468	7.5	1	7.5
Sulfate reduction	$SO_4^{2-} + 4H_2 + H^+ = HS^- + 4H_2O$	40,496	422	4	1,687
Methane production	$CO_2 + 4H_2 = CH_4 + 2H_2O$	240	15	4	60
Total hydrogen consumed					1,823

First the mmoles of linoleic acid consumed was calculated from the amount of acetate produced.
mmoles acetate produced = 19,472 mg / 59mg/mmole = 330 mmoles.
Using the balanced equation for linoleic acid fermentation to acetate.
$C_{18}H_{32}O_2 + 16\ H_2O = 9CH_3COOH + 14H_2$
mmoles of linoleic acid consumed = 330 / 9 = 36.67 mmoles
and the mmoles of hydrogen produced = 36.67 X 14 = 514

The amount of hydrogen consumed is greater then the amount of hydrogen produced.
1,826-513 = 1,312 mmoles
Therefore the missing amount of hydrogen (1,312 mmoles) is assumed to come from complete oxidation of linoleic acid.
$C_{18}H_{32}O_2 + 16\ H_2O = 9CO_2 + 9H_2CO_3 + 50H_2$
Hydrogen produced from complete oxidation of linoleic acid = 1,312 / 50 = 26 mmoles
The total mmoles of linoleic acid consumed is equal to the mmoles of linoleic acid consumed from acetate production plus the mmoles of linoleic acid consumed from complete oxidation = 37 +26 = 63 mmoles

The mass of linoleic acid consumed = 63 mmoles X 280 mg/mmol = 17,616 mg
The percent of linoleic acid consumed = 17,616 / 25,320 = 70%

Appendix E
Raw Data Sheets

VOC and DHG Data for Control Column

Date	Day	Sample ID	Flow Rate (mL/Min)	Total TCE Mass Removed (mg)	Total cisDCE Mass Removed (mg)	Total VC Mass Removed (mg)	Total Ethene Mass Removed (mg)	Total Ethane mass removed (mg)	PCE (mg/L)	PCE (uM)	TCE (mg/L)	TCE (µM)	cis-DCE mg/L	cis-DCE (µM)	VC (mg/L)	VC (µM)	Ethene (mg/L)	Ethene (µM)	Ethane (mg/L)	Ethane (uM)	Methane (mg/L)	Methane (uM)	Total Ethenes (µM)
7/7/2006 14:10	0	7-July-06-2		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
7/10/2006 14:10	3	10-July-06-2	0.11	339	1.88	0.00	0.00	0.00	0.00	0.00	746	5675	4.1	43	0.00	0.00	0.00	0.00	0.00	0.00	2.4	149	5717
7/13/2006 9:00	6	13-July-06-2	0.11	676	3.7	0.00	0.00	0.00	0.00	0.00	846	6436	4.7	48	0.00	0.00	0.00	0.00	0.00	0.00	2.6	161	6484
7/18/2006 14:10	11	18-July-06-2	0.09	1278	7.4	0.00	0.00	0.00	0.00	0.00	815	6203	5.5	57	0.00	0.00	0.00	0.00	0.00	0.00	2.6	160	6260
7/24/2006 15:15	17	24-July-06-2	0.11	2072	11	0.00	0.00	0.00	0.00	0.00	1071	8148	2.7	28	0.00	0.00	0.00	0.00	0.00	0.00	2.4	147	8177
7/31/2006 16:15	24	31-July-06-2	0.10	3163	13	0.00	0.00	0.00	0.00	0.00	997	7585	1.7	17	0.00	0.00	0.00	0.00	0.00	0.00	2.7	165	7602
8/8/2006 16:30	32	8-August-06-2	0.09	4272	19	0.00	0.00	0.00	0.00	0.00	1036	7882	8.8	91	0.00	0.00	0.00	0.00	0.00	0.00	2.4	151	7973
8/14/2006 13:45	38	14-August-06-2	0.08	5021	23	0.00	0.00	0.00	0.00	0.00	1043	7936	3.5	36	0.00	0.00	0.00	0.00	0.00	0.00	2.6	164	7972
8/21/2006 14:45	45	21-August-06-2	0.07	5841	26	0.00	0.00	0.00	0.00	0.00	1038	7903	2.0	21	0.00	0.00	0.00	0.00	0.00	0.00	2.4	150	7923
8/28/2006 15:30	52	28-August-06-2	0.09	6652	28	0.00	0.00	0.00	0.00	0.00	943	7175	3.7	39	0.00	0.00	0.00	0.00	0.00	0.00	2.3	145	7214
9/5/2006 14:15	60	5-Sept-06-2	0.09	7626	30	0.00	0.00	0.00	0.00	0.00	1006	7658	1.2	12	0.00	0.00	0.00	0.00	0.00	0.00	2.5	158	7670
9/11/2006 10:15	66	11-Sept-06-2	0.08	8342	31	0.00	0.00	0.00	0.00	0.00	1055	8028	0.61	6.3	0.00	0.00	0.00	0.00	0.00	0.00	2.4	148	8034
9/18/2006 10:30	73	18-Sept-06-2	0.14	9527	34	0.00	0.00	0.00	0.00	0.00	1088	8284	4.8	50	0.00	0.00	0.00	0.00	0.00	0.00	3.1	195	8333
9/25/2006 13:00	80	25-Sept-06-2	0.08	10695	37	0.00	0.00	0.00	0.00	0.00	973	7404	0.74	7.6	0.00	0.00	0.00	0.00	0.00	0.00	2.2	136	7411
9/29/2006 14:00	84	29-Sept-06-2	0.09	11122	37	0.00	0.00	0.00	0.00	0.00	724	5511	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.3	140	5511
10/2/2006 11:00	87	02-Oct-06-2	0.09	11432	37	0.00	0.00	0.00	0.00	0.00	930	7081	0.20	2.1	0.00	0.00	0.00	0.00	0.00	0.00	2.2	140	7083
10/10/2006 11:40	95	10-Oct-06-2	0.09	12466	38	0.00	0.00	0.00	0.00	0.00	1027	7814	1.1	11	0.00	0.00	0.00	0.00	0.00	0.00	2.9	182	7826
10/16/2006 13:30	101	16-Oct-06-2	0.09	13327	39	0.00	0.00	0.00	0.00	0.00	1099	8361	1.4	14	0.00	0.00	0.00	0.00	0.00	0.00	2.7	169	8375
10/23/2006 10:15	108	23-Oct-06-2	0.08	14235	40	0.00	0.00	0.00	0.00	0.00	1041	7921	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.9	180	7921
10/30/2006 10:15	115	30-Oct-06-2	0.07	15016	40	0.00	0.00	0.00	0.00	0.00	998	7597	0.22	2.3	0.00	0.00	0.00	0.00	0.00	0.00	4.8	297	7599
11/6/2006 15:00	122	06-Nov-06-2	0.08	15812	40	0.00	0.00	0.00	0.00	0.00	1030	7838	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.1	193	7838
11/13/2006 11:55	129	13-Nov-06-2	0.07	16606	40	0.00	0.00	0.00	0.00	0.00	1092	8307	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.1	191	8307
11/20/2006 14:15	136	20-Nov-06-2	0.07	17380	40	0.00	0.00	0.00	0.00	0.00	971	7393	0.49	5.1	0.00	0.00	0.00	0.00	0.00	0.00	3.1	193	7398
11/27/2006 14:30	143	27-Nov-06-2	0.08	18207	40	0.00	0.00	0.00	0.00	0.00	1136	8644	0.56	5.8	0.00	0.00	0.00	0.00	0.00	0.00	2.8	175	8649
12/4/2006 12:30	150	04-DEC-06-2	0.08	19059	41	0.00	0.00	0.00	0.00	0.00	971	7393	0.30	3.1	0.00	0.00	0.00	0.00	0.00	0.00	2.8	175	7396
12/11/2006 15:30	157	11-DEC-06-2	0.07	19832	41	0.00	0.00	0.00	0.00	0.00	976	7428	0.43	4.4	0.00	0.00	0.00	0.00	0.00	0.00	2.9	178	7432
12/18/2006 14:15	164	18-DEC-06-2	0.08	20630	42	0.00	0.00	0.00	0.00	0.00	1061	8073	2.9	30	0.00	0.00	0.00	0.00	0.00	0.00	2.9	182	8103
12/27/2006 11:00	173	27-DEC-06-2	0.08	21716	44	0.00	0.00	0.00	0.00	0.00	973	7404	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.6	161	7404
1/2/2007 11:30	179	2-JAN-07-2	0.09	22524	44	0.00	0.00	0.00	0.00	0.00	1156	8799	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.6	163	8799
1/8/2007 15:45	185	8-JAN-07-2	0.09	23447	46	0.00	0.00	0.00	0.00	0.00	1190	9058	6.3	65	0.00	0.00	0.00	0.00	0.00	0.00	2.6	161	9123
1/15/2007 14:30	192	15-JAN-07-2	0.11	24564	49	0.00	0.00	0.00	0.00	0.00	1091	8304	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.8	171	8304
1/22/2007 14:30	199	22-JAN-07-2	0.09	25427	49	0.00	0.00	0.00	0.00	0.00	629	4785	0.23	2.4	0.00	0.00	0.00	0.00	0.00	0.00	2.6	160	4788
1/29/2007 11:00	206	29-JAN-07-2	0.09	26198	50	0.00	0.00	0.00	0.00	0.00	1083	8245	0.49	5.1	0.00	0.00	0.00	0.00	0.00	0.00	2.5	153	8250
2/5/2007 14:00	213	5-feb-07-2	0.09	27237	50	0.00	0.00	0.00	0.00	0.00	1110	8448	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.6	161	8448
2/12/2007 16:00	220	12-feb-07-2	0.10	28266	50	0.00	0.00	0.00	0.00	0.00	1035	7874	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.5	279	7874
2/19/2007 16:30	227	19-feb-07-2	0.09	29167	50	0.00	0.00	0.00	0.00	0.00	865	6584	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.1	196	6584
2/26/2007 12:00	234	26-feb-07-2	0.09	30024	50	0.00	0.00	0.00	0.00	0.00	1026	7812	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.8	175	7812
3/5/2007 11:30	241	5-March-07-2	0.09	30933	50	0.00	0.00	0.00	0.00	0.00	989	7528	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.7	169	7528
3/12/2007 15:30	248	12-March-07-2	0.09	31882	50	0.00	0.00	0.00	0.00	0.00	1106	8418	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.0	186	8418
3/19/2007 16:30	255	19-March-07-2	0.11	32968	50	0.00	0.00	0.00	0.00	0.00	1024	7795	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.8	175	7795
3/26/2007 16:00	262	26-March-07-2	0.09	33929	50	0.00	0.00	0.00	0.00	0.00	924	7032	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.8	174	7032
3/29/2007 16:00	265	29-March-07-2	0.06	34221	50	0.00	0.00	0.00	0.00	0.00	970	7385	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.7	166	7385
4/2/2007 17:15	269	2-April-07-2	0.04	34486	50	0.00	0.00	0.00	0.00	0.00	867	6597	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.2	138	6597
4/9/2007 16:50	276	9-April-07-2	0.03	34769	50	0.00	0.00	0.00	0.00	0.00	696	5297	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.9	178	5297
4/16/2007 16:00	283	16-April-07-2	0.07	35228	50	0.00	0.00	0.00	0.00	0.00	1147	8730	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.8	173	8730
4/23/2007 16:00	290	23-April-07-2	0.06	35917	50	0.00	0.00	0.00	0.00	0.00	940	7156	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.6	164	7156
4/30/2007 14:00	297	30-April-07-2	0.07	36502	50	0.00	0.00	0.00	0.00	0.00	824	6268	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.7	165	6268
5/7/2007 11:00	304	7-May-07-2	0.06	37131	50	0.00	0.00	0.00	0.00	0.00	1056	8038	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.5	157	8038
5/14/2007 9:45	311	14-May-07-2	0.07	37856	50	0.00	0.00	0.00	0.00	0.00	1041	7919	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.5	158	7919
5/22/2007 11:30	319	22-May-07-2	0.07	38664	50	0.00	0.00	0.00	0.00	0.00	877	6674	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.5	157	6674
5/28/2007 11:00	325	28-May-07-2	0.06	39113	50	0.00	0.00	0.00	0.00	0.00	695	5292	0.24	2.5	0.00	0.00	0.00	0.00	0.00	0.00	2.5	156	5294
6/4/2007 15:00	332	04-June-07-2	0.05	39596	50	0.00	0.00	0.00	0.00	0.00	976	7424	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.6	159	7424
6/11/2007 12:00	339	11-June-07-2	0.07	40075	50	0.00	0.00	0.00	0.00	0.00	702	5346	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.8	176	5346
6/18/2007 12:00	346	18-June-07-2	0.05	40569	50	0.00	0.00	0.00	0.00	0.00	927	7054	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.5	156	7054
6/25/2007 13:00	353	25-June-07-2	0.21	41733	50	0.00	0.00	0.00	0.00	0.00	842	6405	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.6	160	6405
7/2/2007 11:00	360	2-July-07-2	0.05	42728	50	0.00	0.00	0.00	0.00	0.00	701	5334	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.4	150	5334
7/9/2007 15:30	367	9-July-07-2	0.04	43083	50	0.00	0.00	0.00	0.00	0.00	706	5369	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.4	150	5369
7/16/2007 10:00	374	16-July-07-2	0.07	43562	50	0.00	0.00	0.00	0.00	0.00	1080	8222	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.5	153	8222
7/23/2007 14:00	381	23-July-07-2	0.06	44183	50	0.00	0.00	0.00	0.00	0.00	804	6117	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.5	157	6117
7/30/2007 10:00	388	30-July-07-2	0.07	44650	50	0.00	0.00	0.00	0.00	0.00	674	5130	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.8	171	5130
8/6/2007 14:30	395	6-Aug-07-2	0.05	45127	50	0.00	0.00	0.00	0.00	0.00	880	6697	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.3	145	6697
8/13/2007 12:00	402	13-Aug-07-2	0.08	45730	50	0.00	0.00	0.00	0.00	0.00	1043	7937	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.3	205	7937
8/20/2007 17:00	409	20-Aug-07-2	0.07	46445	50	0.00	0.00	0.00	0.00	0.00	925	7036	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.8	175	7036
8/27/2007 16:00	416	27-Aug-07-2	0.08	47137	50	0.00	0.00	0.00	0.00	0.00	990	7536	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.0	188	7536
9/10/2007 16:00	430	10-sep-07-2	0.08	48672	50	0.00	0.00	0.00	0.00	0.00	950	7230	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.9	182	7230
9/17/2007 16:00	437	17-sep-07-2	0.07	49272	50	0.00	0.00	0.00	0.00	0.00	701	5332	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.4	148	5332
9/24/2007 16:00	444	24-sep-07-2	0.06	49730	50	0.00	0.00	0.00	0.00	0.00	765	5823	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.9	241	5823
10/1/2007 16:00	451	1-oct-07-2	0.05	50186	50	0.00	0.00	0.00	0.00	0.00	868	6606	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.6	100	6606
10/9/2007 11:30	459	9-oct-07-2	0.07	50835	50	0.00	0.00	0.00	0.00	0.00	1029	7830	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.5	95	7830
10/15/2007 15:00	465	15-oct-07-2	0.05	51361	50	0.00	0.00	0.00	0.00	0.00	931	7087	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.7	108	7087
10/22/2007 14:00	472	22-oct-07-2	0.08	51878	50	0.00	0.00	0.00	0.00	0.00	639	4861	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.9	241	4861

Anion Data for Control Column

Date	Day	Sample ID	Fow Rate (mL/Min)	Chloride (mg/L)	Chloride (µM)	Sum Chloride (µM)	Nitrite-N (mg/L)	Nitrate-N (mg/L)	Sulfate (mg/L)	Sulfate (µM)	Bromide (mg/L)	Phosphate (mg/L)
7/7/2006 14:10	0	7-July-06-2	0.00	--	--	--	--	--	--	--	--	--
7/10/2006 14:10	3	10-July-06-2	0.11	20	563	256	0.00	0.00	1146	12060	0.00	0.00
7/13/2006 9:00	6	13-July-06-2	0.11	22	620	507	0.00	0.00	848	8924	0.00	0.00
7/18/2006 14:10	11	18-July-06-2	0.09	22	627	915	0.00	0.00	914	9625	0.00	0.00
7/24/2006 15:15	17	24-July-06-2	0.11	21	592	1480	0.00	0.00	951	10016	0.00	0.00
7/31/2006 16:15	24	31-July-06-2	0.10	22	614	2101	0.00	0.00	994	10467	0.00	0.00
8/8/2006 16:30	32	8-August-06-2	0.09	21	580	2704	0.00	0.00	971	10219	0.00	0.00
8/14/2006 13:45	38	14-August-06-2	0.08	19	537	3094	0.00	0.00	926	9747	0.00	0.00
8/21/2006 14:45	45	21-August-06-2	0.07	16	455	3461	0.00	0.00	897	9444	0.00	0.00
8/28/2006 15:30	52	28-August-06-2	0.09	58	1634	4398	0.00	0.00	1012	10653	0.00	0.00
9/5/2006 14:15	60	5-Sept-06-2	0.09	15	414	5407	0.00	0.00	1029	10829	0.00	0.00
9/11/2006 10:15	66	11-Sept-06-2	0.08	13	372	5668	0.00	0.00	1004	10571	0.00	0.00
9/18/2006 10:30	73	18-Sept-06-2	0.14	11	317	6155	0.00	0.00	887	9333	0.00	0.00
9/25/2006 13:00	80	25-Sept-06-2	0.08	11	305	6415	0.00	0.00	901	9480	0.00	0.00
9/29/2006 14:00	84	29-Sept-06-2	0.09	11	322	6581	0.00	0.00	879	9250	0.00	0.00
10/2/2006 11:00	87	02-Oct-06-2	0.09	15	429	6721	0.00	0.00	889	9353	0.00	0.00
10/10/2006 11:40	95	10-Oct-06-2	0.09	16	445	7190	0.00	0.00	956	10061	0.00	0.00
10/16/2006 13:30	101	16-Oct-06-2	0.09	21	578	7603	0.00	0.00	1121	11796	0.00	0.00
10/30/2006 10:15	115	30-Oct-06-2	0.08	17	484	8445	0.00	0.00	1123	11825	0.00	0.00
11/6/2006 15:00	122	06-Nov-06-2	0.07	13	353	8760	0.00	0.00	850	8947	0.00	0.00
11/13/2006 11:55	129	13-Nov-06-2	0.08	13	367	9041	0.00	0.00	939	9880	0.00	0.00
11/20/2006 14:15	136	20-Nov-06-2	0.07	14	389	9321	0.00	0.00	949	9990	0.00	0.00
11/27/2006 14:30	143	27-Nov-06-2	0.07	13	375	9608	0.00	0.00	955	10055	0.00	0.00
12/4/2006 12:30	150	04-DEC-06-2	0.08	14	389	9916	0.00	0.00	968	10192	0.00	0.00
12/11/2006 15:30	157	11-DEC-06-2	0.08	13	358	10228	0.00	0.00	963	10140	0.00	0.00
12/18/2006 14:15	164	18-DEC-06-2	0.07	16	445	10523	0.00	0.00	1117	11759	0.00	0.00
12/27/2006 11:00	173	27-DEC-06-2	0.08	12	338	10939	0.00	0.00	858	9036	0.00	0.00
1/2/2007 11:30	179	2-JAN-07-2	0.08	11	300	11171	0.00	0.00	759	7992	0.00	0.00
1/8/2007 15:45	185	8-JAN-07-2	0.09	11	310	11418	0.00	0.00	809	8515	0.00	0.00
1/15/2007 14:30	192	15-JAN-07-2	0.09	11	312	11685	0.00	0.00	797	8393	0.00	0.00
1/22/2007 14:30	199	22-JAN-07-2	0.11	11	312	12031	0.00	0.00	798	8404	0.00	0.00
1/29/2007 11:00	206	29-JAN-07-2	0.09	18	508	12392	0.00	0.00	1082	11393	0.00	0.00
2/5/2007 14:00	213	5-feb-07-2	0.09	22	609	12927	0.00	0.00	1093	11506	0.00	0.00
2/12/2007 16:00	220	12-feb-07-2	0.09	15	426	13408	0.00	0.00	583	6140	0.00	0.00
2/19/2007 16:30	227	19-feb-07-2	0.10	17	474	13849	0.00	0.00	922	9705	0.00	0.00
2/26/2007 12:00	234	26-feb-07-2	0.09	18	513	14289	0.00	0.00	912	9604	0.00	0.00
3/5/2007 11:30	241	5-March-07-2	0.09	21	594	14812	0.00	0.00	933	9823	0.00	0.00
3/12/2007 15:30	248	12-March-07-2	0.09	11	324	15216	0.00	0.00	998	10507	0.00	0.00
3/19/2007 16:30	255	19-March-07-2	0.09	17	478	15583	0.00	0.00	791	8331	0.00	0.00
3/26/2007 16:00	262	26-March-07-2	0.11	17	484	16118	0.00	0.00	792	8334	0.00	0.00
3/29/2007 16:00	265	29-March-07-2	0.09	19	523	16304	0.00	0.00	801	8431	0.00	0.00
4/2/2007 17:15	269	2-April-07-2	0.06	24	677	16503	0.00	0.00	802	8443	0.00	0.00
4/9/2007 16:50	276	9-April-07-2	0.04	16	464	16745	0.00	0.00	821	8637	0.00	0.00
4/16/2007 16:00	283	16-April-07-2	0.03	16	458	16882	0.00	0.00	792	8339	0.00	0.00
4/23/2007 16:00	290	23-April-07-2	0.07	18	517	17224	0.00	0.00	828	8719	0.00	0.00
4/30/2007 14:00	297	30-April-07-2	0.06	18	502	17536	0.00	0.00	826	8697	0.00	0.00
5/7/2007 11:00	304	7-May-07-2	0.07	18	516	17898	0.00	0.00	958	10083	0.00	0.00
5/14/2007 9:45	311	14-May-07-2	0.06	26	728	18292	0.00	0.00	955	10054	0.00	0.00
5/22/2007 11:30	319	22-May-07-2	0.07	17	467	18813	0.00	0.00	981	10331	0.00	0.00
5/28/2007 11:00	325	28-May-07-2	0.07	17	481	19098	0.00	0.00	982	10336	0.00	0.00
6/4/2007 15:00	332	04-June-07-2	0.06	16	448	19398	0.00	0.00	991	10431	0.00	0.00
6/11/2007 12:00	339	11-June-07-2	0.05	16	450	19618	0.00	0.00	973	10246	0.00	0.00
6/18/2007 12:00	346	18-June-07-2	0.07	13	364	19889	0.00	0.00	943	9928	0.00	0.00
6/25/2007 13:00	353	25-June-07-2	0.05	13	371	20091	0.00	0.00	816	8590	0.00	0.00
7/2/2007 11:00	360	2-July-07-2	0.21	14	381	20860	0.00	0.00	963	10136	0.00	0.00
7/9/2007 15:30	367	9-July-07-2	0.05	12	330	21058	0.00	0.00	791	8321	0.00	0.00
7/16/2007 10:00	374	16-July-07-2	0.04	13	377	21209	0.00	0.00	973	10247	0.00	0.00
7/23/2007 14:00	381	23-July-07-2	0.07	14	385	21470	0.00	0.00	980	10312	0.00	0.00
7/30/2007 10:00	388	30-July-07-2	0.06	16	437	21718	0.00	0.00	890	9372	0.00	0.00
8/6/2007 14:30	395	6-Aug-07-2	0.07	13	361	21996	0.00	0.00	908	9560	0.00	0.00
8/13/2007 12:00	402	13-Aug-07-2	0.05	22	633	22249	0.00	0.00	905	9523	0.00	0.00
8/20/2007 17:00	409	20-Aug-07-2	0.08	19	522	22699	0.00	0.00	990	10419	0.00	0.00
8/27/2007 16:00	416	27-Aug-07-2	0.07	17	473	23023	0.00	0.00	973	10240	0.00	0.00
9/10/2007 16:00	430	10-sep-07-2	0.08	15	416	23733	0.00	0.00	942	9915	0.00	0.00
9/17/2007 16:00	437	17-sep-07-2	0.08	15	420	24061	0.00	0.00	957	10069	0.00	0.00
9/24/2007 16:00	444	24-sep-07-2	0.07	15	415	24341	0.00	0.00	957	10078	0.00	0.00
10/1/2007 16:00	451	1-oct-07-2	0.06	14	405	24579	0.00	0.00	940	9891	0.00	0.00
10/9/2007 11:30	459	9-oct-07-2	0.05	16	444	24832	0.00	0.00	978	10299	0.00	0.00
10/15/2007 15:00	465	15-oct-07-2	0.07	13	375	25081	0.00	0.00	959	10095	0.00	0.00
10/22/2007 14:00	472	22-oct-07-2	0.05	14	406	25286	0.00	0.00	948	9983	0.00	0.00

VOC and DHG Data for nBA Column

Date	Day	Sample ID	Flow Rate (mL/Min)	Total TCE Mass Removed (mg)	Total cis-DCE Mass Removed (mg)	Total VC Mass Removed (mg)	Total Ethene Mass Removed (mg)	Total Ethane Mass Removed (mg)	PCE (mg/L)	PCE (uM)	TCE (mg/L)	TCE (μm)	cis-DCE (mg/L)	cis-DCE (μM)	VC (mg/L)	VC (μM)	Ethene (mg/L)	Ethene (μM)	Ethane (mg/L)	Ethane (μM)	Ethane (mg/L)	Methane (μM)	Total Ethenes (μM)	n-Butyl Acetate (mg/L)	n-Butyl Acetate (μM)
3/21/2006 15:15	0	21-mar-06-1	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	1.6	7.0	72	0.02	0.32	0.00	0.00	0.00	0.00	0.03	1.9	74	0.00	0.00
3/22/2006 14:40	1	22-mar-06-1	0.08	0.06	0.81	0.0	0.00	0.00	0.00	0.00	0.80	6.1	6.8	71	0.32	5.1	0.00	0.00	0.00	0.00	0.03	2.1	82	0.00	0.00
3/24/2006 12:00	3	24-mar-06-1	0.08	0.5	3.0	0.1	0.00	0.00	0.00	0.00	3.4	26	13	133	0.49	7.8	0.00	0.00	0.00	0.00	0.13	8.3	167	0.00	0.00
3/27/2006 11:00	6	27-mar-06-1	0.08	5.8	8.9	0.26	0.00	0.00	0.00	0.00	28	216	23	235	0.45	7.2	0.00	0.00	0.00	0.00	0.29	18	458	0.00	0.00
3/29/2006 16:00	8	29-Mar-06-1	0.08	21	17	0.35	0.00	0.00	0.00	0.00	94	716	43	444	0.26	4.1	0.00	0.00	0.00	0.00	0.30	19	1164	0.00	0.00
3/31/2006 14:00	10	31-Mar-06-1	0.08	51	29	0.40	0.00	0.00	0.00	0.00	169	1283	58	597	0.20	3.2	0.00	0.00	0.00	0.00	3.0	188	1883	0.00	0.00
4/3/2006 16:00	13	03-Apr-06-1	0.09	104	51	0.48	0.00	0.00	0.00	0.00	105	803	60	616	0.19	3.0	0.00	0.00	0.00	0.00	2.7	170	1422	0.00	0.00
4/6/2006 10:00	16	06-apr-06-1	0.09	149	79	0.58	0.00	0.00	0.00	0.00	149	1130	92	951	0.37	5.9	0.00	0.00	0.00	0.00	2.4	151	2087	0.00	0.00
4/10/2006 14:00	20	10-apr-06-1	0.08	257	124	0.67	0.00	0.00	0.00	0.00	286	2173	93	955	0.00	0.00	0.00	0.00	0.00	0.00	2.8	173	3128	0.00	0.00
4/12/2006 16:00	22	12-apr-06-1	0.07	323	143	0.68	0.00	0.00	0.00	0.00	331	2521	84	865	0.08	1.3	0.00	0.00	0.00	0.00	2.8	175	3388	0.00	0.00
4/17/2006 9:00	27	17-apr-06-1	0.08	495	188	0.70	0.00	0.00	0.00	0.00	348	2650	93	960	0.00	0.00	0.00	0.00	0.00	0.00	2.7	168	3610	0.00	0.00
4/19/2006 16:00	29	19-apr-06-1	0.08	585	213	0.70	0.00	0.00	0.00	0.00	351	2670	99	1025	0.00	0.00	0.00	0.00	0.00	0.00	2.7	168	3694	0.00	0.00
4/27/2006 10:00	32	27-apr-06-1	0.07	690	246	0.70	0.00	0.00	0.00	0.00	378	2880	132	1358	0.00	0.00	0.00	0.00	0.00	0.00	2.8	174	4238	0.00	0.00
5/1/2006 9:00	36	1-may-06-1	0.08	868	284	0.70	0.00	0.00	0.00	0.00	463	3526	50	516	0.00	0.00	0.00	0.00	0.00	0.00	2.7	169	4042	0.00	0.00
5/5/2006 11:00	40	5-may-06-1	0.07	1096	304	0.72	0.00	0.00	0.00	0.00	560	4258	36	367	0.09	1.4	0.00	0.00	0.00	0.00	2.6	164	4627	0.00	0.00
5/8/2006 11:30	43	8-may-06-1	0.08	1260	312	0.73	0.00	0.00	0.00	0.00	455	3463	17	178	0.00	0.00	0.00	0.00	0.00	0.00	3.1	191	3641	0.00	0.00
5/10/2006 9:00	45	10-may-06-1	0.08	1372	315	0.73	0.00	0.00	0.00	0.00	602	4579	13	137	0.00	0.00	0.00	0.00	0.00	0.00	2.6	164	4715	0.00	0.00
5/12/2006 14:30	47	12-may-06-1	0.08	1511	319	0.73	0.00	0.00	0.00	0.00	515	3917	16	170	0.00	0.00	0.00	0.00	0.00	0.00	2.6	159	4087	0.00	0.00
5/14/2006 14:30	49	14-may-06-1	0.07	1625	322	0.73	0.00	0.00	0.00	0.00	598	4548	12	121	0.00	0.00	0.00	0.00	0.00	0.00	2.6	164	4668	0.00	0.00
5/15/2006 14:30	50	15-may-06-1	0.07	1679	323	0.73	0.00	0.00	0.00	0.00	465	3538	10	105	0.00	0.00	0.00	0.00	0.00	0.00	2.7	166	3642	0.00	0.00
5/16/2006 15:00	51	16-may-06-1	0.08	1726	324	0.73	0.00	0.00	0.00	0.00	349	2657	6.0	62	0.00	0.00	0.00	0.00	0.00	0.00	2.6	161	2718	0.00	0.00
5/17/2006 14:00	52	17-may-06-1	0.08	1776	325	0.73	0.00	0.00	0.00	0.00	522	3974	10	105	0.00	0.00	0.00	0.00	0.00	0.00	2.6	159	4079	0.00	0.00
5/18/2006 14:00	53	18-may-06-1	0.09	1853	326	0.73	0.00	0.00	0.00	0.00	710	5406	8.5	88	0.00	0.00	0.00	0.00	0.00	0.00	2.6	159	5494	0.00	0.00
5/19/2006 13:00	54	19-may-06-1	0.08	1930	327	0.73	0.00	0.00	0.00	0.00	581	4422	5.4	56	0.00	0.00	0.00	0.00	0.00	0.00	2.6	160	4478	0.00	0.00
5/24/2006 11:00	56	24-may-06-1	0.07	2063	329	0.73	0.00	0.00	0.00	0.00	658	5009	14	145	0.00	0.00	0.00	0.00	0.00	0.00	2.7	170	5154	0.00	0.00
5/25/2006 11:00	57	25-may-06-1	0.07	2125	331	0.73	0.00	0.00	0.00	0.00	492	3742	15	159	0.00	0.00	0.00	0.00	0.00	0.00	2.6	163	3901	0.00	0.00
5/26/2006 13:30	58	26-may-06-1	0.08	2193	332	0.73	0.00	0.00	0.00	0.00	627	4773	16	161	0.00	0.00	0.00	0.00	0.00	0.00	2.6	163	4934	0.00	0.00
5/29/2006 12:00	61	29-may-06-1	0.08	2418	339	0.73	0.00	0.00	0.00	0.00	715	5444	23	241	0.00	0.00	0.00	0.00	0.00	0.00	2.7	170	5685	0.00	0.00
5/31/2006 14:00	63	31-may-06-1	0.08	2568	344	0.73	0.00	0.00	0.00	0.00	496	3772	19	199	0.00	0.00	0.00	0.00	0.00	0.00	3.0	188	3971	0.00	0.00
6/2/2006 11:30	65	02-June-06-1	0.08	2696	350	0.73	0.00	0.00	0.00	0.00	649	4938	33	338	0.00	0.00	0.00	0.00	0.00	0.00	2.6	163	5276	0.00	0.00
6/5/2006 13:15	68	05-June-06-1	0.08	2945	361	0.73	0.00	0.00	0.00	0.00	729	5549	30	307	0.00	0.00	0.00	0.00	0.00	0.00	2.9	178	5856	0.00	0.00
6/7/2006 11:30	70	07-June-06-1	0.08	3112	367	0.73	0.00	0.00	0.00	0.00	749	5702	21	221	0.00	0.00	0.00	0.00	0.00	0.00	2.6	161	5923	0.00	0.00
6/9/2006 14:00	72	09-June-06-1	0.08	3307	372	0.73	0.00	0.00	0.00	0.00	807	6143	17	173	0.00	0.00	0.00	0.00	0.00	0.00	2.6	163	6316	0.00	0.00
6/12/2006 10:30	75	12-June-06-1	0.09	3593	377	0.79	0.00	0.00	0.00	0.00	842	6409	11	116	0.32	5.1	0.00	0.00	0.00	0.00	2.6	162	6530	0.00	0.00
6/15/2006 14:20	78	15-June-06-1	0.09	3908	381	0.91	0.00	0.00	0.00	0.00	736	5598	11	112	0.27	4.3	0.00	0.00	0.00	0.00	2.6	162	5715	0.00	0.00
6/16/2006 14:45	79	16-June-06-1	0.08	4005	383	0.95	0.00	0.00	0.00	0.00	798	6073	9.3	96	0.32	5.1	0.00	0.00	0.00	0.00	2.7	166	6174	0.00	0.00
6/19/2006 10:40	82	19-June-06-1	0.08	4276	386	1.1	0.00	0.00	0.00	0.00	806	6132	8.8	91	0.63	10	0.00	0.00	0.00	0.00	2.5	157	6233	0.00	0.00
6/21/2006 11:00	84	21-June-06-1	0.08	4465	388	1.2	0.00	0.00	0.00	0.00	805	6124	11	110	0.00	0.00	0.00	0.00	0.00	0.00	2.5	158	6234	0.00	0.00
6/23/2006 15:00	86	23-June-06-1	0.08	4670	390	1.2	0.00	0.00	0.00	0.00	851	6478	9.1	94	0.17	2.7	0.00	0.00	0.00	0.00	2.6	161	6574	0.00	0.00
6/26/2006 14:00	89	26-June-06-1	0.08	4959	393	1.2	0.00	0.00	0.00	0.00	800	6086	7.8	81	0.00	0.00	0.00	0.00	0.00	0.00	2.5	155	6166	0.00	0.00
6/29/2006 14:00	92	29-June-06-1	0.08	5269	396	1.2	0.00	0.00	0.00	0.00	923	7028	8.4	87	0.00	0.00	0.00	0.00	0.00	0.00	2.7	166	7115	0.00	0.00
7/4/2006 13:30	97	04-July-06-1	0.09	5820	401	1.2	0.00	0.00	0.00	0.00	902	6863	7.3	75	0.00	0.00	0.00	0.00	0.00	0.00	2.5	155	6939	0.00	0.00
7/6/2006 13:30	99	06-July-06-1	0.08	6049	403	1.2	0.00	0.00	0.00	0.00	950	7230	6.7	69	0.00	0.00	0.00	0.00	0.00	0.00	2.5	157	7299	0.00	0.00
7/10/2006 13:40	103	10-July-06-1	0.09	6498	405	2.0	0.00	0.00	0.00	0.00	866	6594	4.4	46	3.3	52	0.00	0.00	0.00	0.00	0.00	0.00	6692	0.00	0.00
7/13/2006 9:00	106	13-July-06-1	0.08	6813	407	2.7	0.00	0.00	0.00	0.00	961	7310	5.9	61	0.67	11	0.00	0.00	0.00	0.00	2.6	162	7382	0.00	0.00
7/18/2006 13:30	111	18-July-06-1	0.08	7373	410	3.0	0.00	0.00	0.00	0.00	871	6632	4.4	45	0.19	3.0	0.00	0.00	0.00	0.00	2.5	158	6681	0.00	0.00
7/24/2006 14:30	117	24-July-06-1	0.08	7990	413	3.1	0.00	0.00	0.00	0.00	922	7015	2.5	26	0.16	2.6	0.00	0.00	0.00	0.00	2.4	148	7043	0.00	0.00
7/27/2006 15:00	120	27-July-06-1	0.07	8286	414	3.1	0.00	0.00	0.00	0.00	926	7047	3.0	31	0.00	0.00	0.00	0.00	0.00	0.00	2.5	157	7078	0.00	0.00
7/28/2006 15:00	121	28-July-06-1	0.07	8380	414	3.1	0.00	0.00	0.00	0.00	946	7197	3.3	34	0.00	0.00	0.00	0.00	0.00	0.00	2.4	151	7231	0.00	0.00
7/29/2006 13:30	122	29-July-06-1	0.07	8464	414	3.1	0.00	0.00	0.00	0.00	829	6311	3.4	35	0.00	0.00	0.00	0.00	0.00	0.00	2.4	148	6346	0.00	0.00
7/30/2006 19:15	123	30-July-06-1	0.07	8568	415	3.1	0.00	0.00	0.00	0.00	827	6295	3.1	32	0.00	0.00	0.00	0.00	0.00	0.00	2.4	147	6327	0.00	0.00
7/31/2006 16:00	124	31-July-06-1	0.07	8646	415	3.2	0.00	0.00	0.00	0.00	968	7363	3.1	31	0.71	11	0.00	0.00	0.00	0.00	2.6	162	7406	0.00	0.00
8/1/2006 14:00	125	1-August-06-1	0.07	8734	415	3.2	0.00	0.00	0.00	0.00	938	7136	4.5	46	0.00	0.00	0.00	0.00	0.00	0.00	2.5	154	7182	0.00	0.00
8/2/2006 15:00	126	2-August-06-1	0.07	8833	416	3.2	0.00	0.00	0.00	0.00	945	7192	3.7	38	0.00	0.00	0.00	0.00	0.00	0.00	2.4	148	7230	0.00	0.00
8/3/2006 13:30	127	3-August-06-1	0.07	8922	416	3.2	0.00	0.00	0.00	0.00	948	7213	7.9	82	0.51	8.2	0.00	0.00	0.00	0.00	2.6	161	7303	0.00	0.00
8/4/2006 14:00	128	4-August-06-1	0.07	9021	417	3.3	0.00	0.00	0.00	0.00	979	7453	5.9	61	0.38	6.1	0.00	0.00	0.00	0.00	2.5	156	7520	0.00	0.00
8/6/2006 15:30	130	6-August-06-1	0.07	9218	418	3.3	0.00	0.00	0.00	0.00	911	6935	6.5	67	0.00	0.00	0.00	0.00	0.00	0.00	2.4	150	7003	0.00	0.00
8/8/2006 15:00	132	8-August-06-1	0.08	9408	420	3.3	0.00	0.00	0.00	0.00	883	6723	8.1	84	0.00	0.00	0.00	0.00	0.00	0.00	2.4	151	6807	0.00	0.00
8/10/2006 14:00	134	10-August-06-1	0.07	9604	422	3.3	0.00	0.00	0.00	0.00	973	7407	8.1	84	0.00	0.00	0.00	0.00	0.00	0.00	2.5	154	7491	0.00	0.00
8/14/2006 13:45	138	14-August-06-1	0.08	10021	427	3.3	0.00	0.00	0.00	0.00	978	7442	17	177	0.00	0.00	0.00	0.00	0.00	0.00	2.7	168	7619	0.00	0.00
8/21/2006 14:45	145	21-August-06-1	0.07	10721	443	3.3	0.00	0.00	0.00	0.00	931	7086	27	277	0.00	0.00	0.00	0.00	0.00	0.00	2.4	150	7362	0.00	0.00
8/28/2006 15:30	152	28-August-06-1	0.08	11414	461	3.3	0.00	0.00	0.00	0.00	952	7244	21	213	0.00	0.00	0.00	0.00	0.00	0.00	2.3	145	7457	0.00	0.00
9/5/2006 14:15	160	5-Sept-06-1	0.08	12321	475	3.3	0.00	0.00	0.00	0.00	989	7529	11	114	0.00	0.00	0.00	0.00	0.00	0.00	2.5	158	7643	0.00	0.00
9/11/2006 10:15	166	11-Sept-06-1	0.08	13046	482	3.3	0.00	0.00	0.00	0.00	1074	8172	7.4	77	0.00	0.00	0.00	0.00	0.00	0.00	2.4	148	8249	0.00	0.00
9/18/2006 10:30	173	18-Sept-06-1	0.07	13888	487	3.7	0.00	0.00	0.00	0.00	1092	8307	6.1	62	1.0	16	0.00	0.00	0.00	0.00	3.2	197	8386	0.00	0.00
9/25/2006 13:00	180	25-Sept-06-1	0.07	14594	490	4.5	0.00	0.00	0.00	0.00	880	6700	3.4	35	1.2	19	0.00	0.00	0.00	0.00	2.2	137	6754	0.00	0.00
9/29/2006 14:00	184	29-Sept-06-1	0.09	14993	492	4.9	0.00	0.00	0.00	0.00	865	6582	2.9	30	0.51	8.2	0.00	0.00	0.00	0.00	2.2	140	6621	0.00	0.00
10/2/2006 11:00	187	02-Oct-06-1	0.09	15309	493	5.0	0.00	0.00	0.00	0.00	873	6641	2.9	30	0.00	0.00	0.00	0.00	0.00	0.00	2.2	140	6671	0.00	0.00
10/10/2006 11:40	195	10-Oct-06-1	0.08	16208	497	5.0	0.00	0.00	0.00	0.00	981	7467	4.9	50	0.00	0.00	0.00	0.00	0.00	0.00	2.9	183	7517	0.00	0.00
10/16/2006 13:30	201	16-Oct-06-1	0.07	16883	499	5.5	0.00	0.00	0.00	0.00	1062	8083	2.2	23	1.5	24	0.00	0.00	0.00	0.00	2.7	170	8130	0.00	0.00
10/23/2006 10:15	208	23-Oct-06-1	0.08	17653	501	6.0	0.00	0.00	0.00	0.00	1055	8027	1.9	19	0.00	0.00	0.00	0.00	0.00	0.00	2.9	178	8046	0.00	0.00
10/30/2006 10:15	215	30-Oct-06-1	0.07	18484	505	6.0	0.00	0.00	0.00	0.00	1145	8712	9.2	94	0.00	0.00	0.00	0.00	0.00	0.00	4.8	300	8807	0.00	0.00
11/6/2006 15:00	222	06-Nov-06-1	0.07	19306	513	6.0	0.00	0.00	0.00	0.00	1007	7667	13	137	0.00	0.00	0.00	0.00	0.00	0.00	3.1	193	7804	0.00	0.00
11/13/2006 11:55	229	13-Nov-06-1	0.08	20064	545	6.0	0.00	0.00	0.00	0.00	1029	7834	73	757	0.00	0.00	0.00	0.00	0.00	0.00	3.0	186	8590	0.00	0.00
11/20/2006 14:15	236	20-Nov-06-1	0.07	20807	665	6.0	0.00	0.00	0.00	0.00	928	7061	241	2481	0.00	0.00	0.00	0.00	0.00	0.00	3.2	201	9542	0.00	0.00
11/27/2006 14:30	243	27-Nov-06-1	0.07	21509	873	6.0	0.00	0.00	0.00	0.00	1035	7876	341	3517	0.00	0.00	0.00	0.00	0.00	0.00	3.4	211	11393	0.00	0.00
12/4/2006 12:30	250	04-DEC-06-1	0.06	22183	1121	6.0	0.00	0.00	0.00	0.00	1008	7668	412	4254	0.00	0.00	0.00	0.00	0.00	0.00	4.3	270	11922	0.00	0.00
12/6/2006 14:30	252	06-DEC-06-1	0.07	22377	1205	6.0	0.00	0.00	0.00	0.00	948	7216	430	4436	0.00	0.00	0.00	0.00	0.00	0.00	4.5	280	11652	0.00	0.00
12/8/2006 13:30	254	08-DEC-06-1	0.07	22552	1287	6.0	0.00	0.00	0.00	0.00	832	6333	402	4149	0.09	1.4	0.00	0.00	0.00	0.00	4.7	292	10484	0.00	0.00
12/11/2006 15:30	257	11-DEC-06-1	0.08	22821	1413	6.0	0.00	0.00	0.00	0.00	827	6294	377	3884	0.00	0.00	0.00	0.00	0.00	0.00	4.7	295	10177	0.00	0.00
12/18/2006 13:30	264	18-DEC-06-1	0.06	23380	1614	6.0	0.00	0.00	0.00	0.00	786	5985	203	2093	0.00	0.00	0.00	0.00	0.00	0.00	3.6	223	8078	0.00	0.00
12/22/2006 15:00	268	22-DEC-06-1	0.07	23696	1687	6.0	0.00	0.00	0.00	0.00	828	6303	173	1781	0.00	0.00	0.00	0.00	0.00	0.00	3.1	192	8084	0.00	0.00
12/27/2006 11:00	273	27-DEC-06-1	0.08	24102	1765	6.0	0.00	0.00	0.00	0.00	763	5804	135	1388	0.00	0.00	0.00	0.00	0.00	0.00	2.8	174	7192	0.00	0.00
1/2/2007 11:30	279	2-JAN-07-1	0.08	24612	1838	6.0	0.00	0.00	0.00	0.00	772	5873	84	867	0.00	0.00	0.00	0.00	0.00	0.00	2.6	164	6740	0.00	0.00
1/8/2007 15:15	285	8-JAN-07-1	0.06	25074	1882	6.0	0.00	0.00	0.00	0.00	759	5777	62	639	0.00	0.00	0.00	0.00	0.00	0.00	2.6	161	6416	0.00	0.00
1/9/2007 14:30	286	9-JAN-07-1	0.07	25141	1888	6.0	0.00	0.00	0.00	0.00	738	5620	62	643	0.00	0.00	0.00	0.00	0.00	0.00	2.9	181	6263	0.00	0.00
1/10/2007 14:00	287	10-JAN-07-1	0.07	25217	1894	6.0	0.00	0.00	0.00	0.00	795	6049	73	756	0.00	0.00	0.00	0.00	0.00	0.00	2.8	174	6805	0.00	0.00
1/11/2007 11:30	288	11-JAN-07-1	0.07	25276	1902	6.0	0.00	0.00	0.00	0.00	506	3851	85	878	0.00	0.00	0.00	0.00	0.00	0.00	2.9	178	4730	32	272
1/12/2007 13:30	289	12-JAN-07-1	0.07	25341	1912	6.0	0.00	0.00	0.00	0.00	700	5326	106	1095	0.10	1.60	0.00	0.00	0.00	0.00	2.9	178	6423	40	348
1/13/2007 13:30	290	13-JAN-07-1	0.07	25403	1923	6.0	0.00	0.00	0.00	0.00	527	4009	105	1080	0.00	0.00	0.00	0.00	0.00	0.00	2.7	170	5089	138	1184
1/14/2007 14:00	291	14-JAN-07-1	0.07	25455	1933	6.0	0.00	0.00	0.00	0.00	484	3686	100	1035	0.00	0.00	0.00	0.00	0.00	0.00	2.7	171	4720	269	2320
1/15/2007 13:30	292	15-JAN-07-1	0.08	25507	1943	6.0	0.00	0.00	0.00	0.00	482	3668	81	839	0.00	0.00	0.00	0.00	0.00	0.00	2.8	175	4507	494	4249
1/16/2007 11:30	293	16-JAN-07-1	0.07	25559	1950	6.0	0.00	0.00	0.00	0.00	569	4330	68	705	0.00	0.00	0.00	0.00	0.00	0.00	2.8	174	5035	498	4287
1/17/2007 11:30	294	17-JAN-07-1	0.07	25624	1957	6.0	0.00	0.00	0.00	0.00	722	5492	65	671	0.00	0.00	0.00	0.00	0.00	0.00	2.8	172	6162	753	6479
1/18/2007 11:30	295	18-JAN-07-1	0.07	25687	1962	6.0	0.00	0.00	0.00	0.00	541	4115	40	410	0.00	0.00	0.00	0.00	0.00	0.00	2.7	168	4525	679	5848
1/19/2007 11:30	296	19-JAN-07-1	0.07	25747	1966	6.0	0.00	0.00	0.00	0.00	638	4852	40	411	0.00	0.00	0.00	0.00	0.00	0.00	2.7	171	5263	701	6038
1/20/2007 11:30	297	20-JAN-07-1	0.07	25808	1970	6.0	0.00	0.00	0.00	0.00	577	4392	32	328	0.00	0.00	0.00	0.00	0.00	0.00	2.6	161	4720	604	5199
1/21/2007 11:30	298	21-JAN-07-1	0.07	25865	1973	6.0	0.00	0.00	0.00	0.00	547	4165	27	275	0.00	0.00	0.00	0.00	0.00	0.00	2.6	160	4440	625	5380
1/22/2007 14:00	299	22-JAN-07-1	0.08	25933	1977	6.0	0.00	0.00	0.00	0.00	598	4548	36	376	0.00	0.00	0.00	0.00	0.00	0.00	2.6	159	4924	525	4517
1/23/2007 11:30	300	23-JAN-07-1	0.07	25989	1979	6.0	0.00	0.00	0.00	0.00	582	4426	24	243	0.00	0.00	0.00	0.00	0.00	0.00	2.5	155	4669	231	1993
1/24/2007 11:30	301	24-JAN-07-1	0.07	26051	1982	6.0	0.00	0.00	0.00	0.00	644	4902	25	253	0.00	0.00	0.00	0.00	0.00	0.00	2.5	155	5155	223	1923
1/26/2007 11:30	303	26-JAN-07-1	0.07	26178	1987	6.0	0.00	0.00	0.00	0.00	611	4652	23	237	0.00	0.00	0.00	0.00	0.00	0.00	2.5	155	4889	92	792
1/29/2007 13:15	306	29-JAN-07-1	0.08	26390	1997	6.0	0.00	0.00	0.00	0.00	676	5148	41	424	0.00	0.00	0.00	0.00	0.00	0.00	2.5	155	5572	8.6	74

Anion Data for nBA Column

Date	Day	Sample ID	Flow Rate (mL/Min)	Chloride (mg/L)	Chloride (µM)	Sum Chloride (µM)	Nitrite-N (mg/L)	Nitrate-N (mg/L)	Sulfate (mg/L)	Sulfate (µM)	Bromide (mg/L)	Phosphate (mg/L)
3/21/2006 15:15	0	21-mar-06-1	0.080	--	--	--	--	--	--	--	--	--
3/22/2006 14:40	1	22-Mar-06-1	0.083	20	571	68	0.00	0.04	682	7177	46	0.00
3/24/2006 12:00	3	24-Mar-06-1	0.081	24	689	205	0.00	0.04	597	6280	51	0.00
3/27/2006 11:00	6	27-Mar-06-1	0.075	29	818	446	0.00	0.04	0.00	0.00	26	0.00
3/29/2006 16:00	8	29-Mar-06-1	0.082	40	1131	699	0.00	0.06	812	8546	7.5	0.00
3/31/2006 14:00	10	31-Mar-06-1	0.084	40	1129	961	0.00	0.00	767	8072	0.9	0.00
4/3/2006 16:00	13	03-Apr-06-1	0.091	68	1907	1573	0.00	0.00	704	7409	2.2	0.00
4/6/2006 10:00	16	06-apr-06-1	0.089	49	1393	2155	0.00	0.00	838	8822	2.4	0.00
4/10/2006 14:00	20	10-apr-06-1	0.076	43	1198	2742	0.00	0.00	822	8652	0.00	0.00
4/12/2006 16:00	22	12-apr-06-1	0.068	45	1274	2994	0.00	0.00	821	8639	0.00	0.00
4/19/2006 16:00	29	19-apr-06-1	0.075	60	1681	4116	0.00	0.00	959	10093	0.00	0.00
5/1/2006 9:00	36	1-may-06-1	0.078	42	1172	5190	0.00	0.00	970	10215	0.00	0.00
5/5/2006 11:00	40	5-may-06-1	0.073	30	855	5628	0.00	0.00	999	10515	0.00	0.00
5/10/2006 9:00	45	10-may-06-1	0.080	25	710	6071	0.00	0.00	1007	10599	0.00	0.00
5/12/2006 14:30	47	12-may-06-1	0.075	25	707	6242	0.00	0.00	1041	10959	4.0	0.00
5/14/2006 14:30	49	14-may-06-1	0.067	27	760	6382	0.00	0.00	1006	10585	0.00	0.00
5/15/2006 14:30	50	15-may-06-1	0.075	28	786	6465	0.00	0.00	1020	10740	0.00	0.00
5/16/2006 15:00	51	16-may-06-1	0.082	25	699	6555	0.00	0.00	1034	10886	4.6	0.00
5/17/2006 14:00	52	17-may-06-1	0.085	22	621	6632	0.00	0.00	990	10420	33	0.00
5/18/2006 14:00	53	18-may-06-1	0.089	22	612	6711	0.00	0.00	1016	10696	67	0.00
5/19/2006 13:00	54	19-may-06-1	0.083	21	578	6780	0.00	0.00	1002	10552	87	0.00
5/24/2006 11:00	56	24-may-06-1	0.073	25	705	6909	0.00	0.00	983	10345	104	0.00
5/25/2006 11:00	57	25-may-06-1	0.075	24	686	6984	0.00	0.00	951	10015	103	0.00
5/26/2006 13:30	58	26-may-06-1	0.078	23	653	7067	0.00	0.00	949	9987	113	0.00
5/29/2006 12:00	61	29-may-06-1	0.081	25	712	7300	0.00	0.00	950	10004	79	0.00
5/31/2006 14:00	63	31-may-06-1	0.084	30	857	7497	0.00	0.00	972	10237	34	0.00
6/2/2006 11:30	65	02-June-06-1	0.081	36	1023	7705	0.00	0.00	1038	10923	1.0	0.00
6/5/2006 13:15	68	05-June-06-1	0.082	27	759	8028	0.00	0.00	1065	11208	1.9	0.00
6/7/2006 11:30	70	07-June-06-1	0.082	20	568	8178	0.00	0.00	964	10149	0.00	0.00
6/9/2006 14:00	72	09-June-06-1	0.083	20	574	8322	0.00	0.00	984	10358	0.00	0.00
6/12/2006 10:30	75	12-June-06-1	0.086	20	560	8522	0.00	0.00	998	10510	0.00	0.00
6/15/2006 14:20	78	15-June-06-1	0.090	19	541	8748	0.00	0.00	991	10432	0.00	0.00
6/16/2006 14:45	79	16-June-06-1	0.082	20	553	8814	0.00	0.00	1002	10552	0.00	0.00
6/19/2006 10:40	82	19-June-06-1	0.083	22	619	9012	0.00	0.00	1019	10731	0.00	0.00
6/21/2006 11:00	84	21-June-06-1	0.079	38	1066	9204	0.00	0.00	974	10248	0.00	0.00
6/23/2006 15:00	86	23-June-06-1	0.080	38	1078	9472	0.00	0.00	1026	10798	0.00	0.00
6/26/2006 14:00	89	26-June-06-1	0.085	28	795	9810	0.00	0.00	1014	10669	0.00	0.00
6/29/2006 14:00	92	29-June-06-1	0.082	18	520	10042	0.00	0.00	898	9451	0.00	0.00
7/4/2006 13:30	97	04-July-06-1	0.087	17	483	10354	0.00	0.00	871	9167	0.00	0.00
7/6/2006 13:30	99	06-July-06-1	0.085	19	537	10478	0.00	0.00	903	9509	0.00	0.00
7/10/2006 13:40	103	10-July-06-1	0.087	18	500	10738	0.00	0.00	919	9670	0.00	0.00
7/13/2006 9:00	106	13-July-06-1	0.083	19	522	10910	0.00	0.00	932	9810	0.00	0.00
7/18/2006 13:30	111	18-July-06-1	0.081	19	524	11225	0.00	0.00	924	9721	0.00	0.00
7/24/2006 14:30	117	24-July-06-1	0.077	17	492	11567	0.00	0.00	939	9884	0.00	0.00
7/27/2006 15:00	120	27-July-06-1	0.070	18	506	11719	0.00	0.00	951	10011	0.00	0.00
7/28/2006 15:00	121	28-July-06-1	0.070	18	518	11771	0.00	0.00	981	10323	0.00	0.00
7/29/2006 13:30	122	29-July-06-1	0.070	18	514	11820	0.00	0.00	962	10130	0.00	0.00
7/30/2006 19:15	123	30-July-06-1	0.070	20	563	11887	0.00	0.00	977	10281	0.00	0.00
7/31/2006 16:00	124	31-July-06-1	0.070	18	520	11934	0.00	0.00	918	9668	0.00	0.00
8/1/2006 14:00	125	1-August-06-1	0.070	20	552	11984	0.00	0.00	927	9762	0.00	0.00
8/2/2006 15:00	126	2-August-06-1	0.070	21	581	12043	0.00	0.00	942	9914	0.00	0.00
8/3/2006 13:30	127	3-August-06-1	0.070	22	625	12100	0.00	0.00	921	9695	0.00	0.00
8/4/2006 14:00	128	4-August-06-1	0.070	27	749	12171	0.00	0.00	946	9955	0.00	0.00
8/6/2006 15:30	130	6-August-06-1	0.070	37	1054	12358	0.00	0.00	1069	11257	0.00	0.00
8/8/2006 15:00	132	8-August-06-1	0.079	40	1132	12605	0.00	0.00	974	10249	0.00	0.00
8/10/2006 14:00	134	10-August-06-1	0.070	37	1049	12820	0.00	0.00	926	9748	0.00	0.00
8/14/2006 13:45	138	14-August-06-1	0.079	27	762	13230	0.00	0.00	927	9758	0.00	0.00
8/21/2006 14:45	145	21-August-06-1	0.066	17	489	13648	0.00	0.00	916	9641	0.00	0.00
8/28/2006 15:30	152	28-August-06-1	0.080	17	478	14037	0.00	0.00	975	10258	0.00	0.00
9/5/2006 14:15	160	5-Sept-06-1	0.084	14	382	14449	0.00	0.00	985	10365	0.00	0.00
9/11/2006 10:15	166	11-Sept-06-1	0.084	12	326	14698	0.00	0.00	979	10307	0.00	0.00
9/18/2006 10:30	173	18-Sept-06-1	0.070	11	305	14922	0.00	0.00	877	9234	0.00	0.00
9/25/2006 13:00	180	25-Sept-06-1	0.070	9.5	266	15125	0.00	0.00	861	9064	0.00	0.00
9/29/2006 14:00	184	29-Sept-06-1	0.087	11	323	15275	0.00	0.00	814	8572	0.00	0.00
10/2/2006 11:00	187	02-Oct-06-1	0.089	11	309	15391	0.00	0.00	914	9618	0.00	0.00
10/10/2006 11:40	195	10-Oct-06-1	0.079	20	575	15795	0.00	0.00	916	9638	0.00	0.00
10/16/2006 13:30	201	16-Oct-06-1	0.072	21	598	16164	0.00	0.00	944	9935	0.00	0.00
10/23/2006 0:00	207	23-Oct-06-1	0.075	21	578	16575	0.00	0.00	874	9205	0.00	0.00
10/25/2006 0:00	209	25-Oct-06-1	0.070	21	579	16691	0.00	0.00	890	9364	0.92	0.00
10/26/2006 0:00	210	26-Oct-06-1	0.070	21	588	16750	0.00	0.00	893	9396	0.49	0.00
10/30/2006 10:15	215	30-Oct-06-1	0.075	20	550	17020	0.00	0.00	808	8504	0.00	0.00
11/1/2006 0:00	216	1-Nov-06-1	0.070	20	563	17108	0.00	0.00	890	9363	64	0.00
11/6/2006 15:00	222	06-Nov-06-1	0.073	59	1650	17763	0.00	0.00	740	7788	44	0.00
11/8/2006 12:00	224	08-Nov-06-1	0.070	69	1956	18103	0.00	0.00	742	7806	73	0.00
11/9/2006 0:00	224	09-Nov-06-1	0.070	70	1974	18202	0.00	0.00	650	6845	90	0.00
11/10/2006 0:00	225	10-Nov-06-1	0.070	73	2063	18406	0.00	0.00	550	5795	94	0.00
11/13/2006 11:55	229	13-Nov-06-1	0.077	94	2645	19323	0.00	0.00	335	3531	97	0.00
11/14/2006 0:00	229	14-Nov-06-1	0.070	105	2970	19465	0.00	0.00	230	2423	95	0.00
11/15/2006 0:00	230	15-Nov-06-1	0.070	104	2930	19763	0.00	0.00	173	1819	93	0.00
11/16/2006 0:00	231	16-Nov-06-1	0.070	108	3053	20064	0.00	0.00	155	1636	97	0.00
11/17/2006 0:00	232	17-Nov-06-1	0.070	111	3121	20376	0.00	0.00	131	1379	94	0.00
11/20/2006 14:15	236	20-Nov-06-1	0.071	136	3836	21658	0.00	0.00	94	993	86	0.00
11/24/2006 0:00	239	24-Nov-06-1	0.070	137	3857	22979	0.00	0.00	54	568	94	0.00
11/27/2006 14:30	243	27-Nov-06-1	0.071	149	4207	24455	0.00	0.00	41	427	93	0.00
11/29/2006 0:00	244	29-Nov-06-1	0.070	141	3980	25031	0.00	0.00	32	340	91	0.00
12/4/2006 0:00	249	04-DEC-06-1	0.062	162	4559	26935	0.00	0.00	28	293	94	0.00
12/6/2006 0:00	251	06-DEC-06-1	0.070	156	4381	27836	0.00	0.00	43	457	84	0.00
12/8/2006 0:00	253	08-DEC-06-1	0.070	147	4143	28695	0.00	0.00	231	2431	47	0.00
12/11/2006 0:00	256	11-DEC-06-1	0.076	82	2319	29751	0.00	0.00	652	6861	8.6	0.00
12/18/2006 0:00	263	18-DEC-06-1	0.064	68	1924	31113	0.00	0.00	1065	11214	0.00	0.00
12/27/2006 0:00	272	27-DEC-06-1	0.077	34	953	32543	0.00	0.00	853	8979	0.00	0.00
1/2/2007 11:30	279	2-JAN-07-1	0.077	24	690	33130	0.00	0.00	720	7580	0.00	0.00
1/4/2007 14:30	281	4-JAN-07-1	0.070	21	586	33267	0.00	0.00	768	8080	0.00	0.00
1/6/2007 14:30	283	6-JAN-07-1	0.070	24	674	33394	0.00	0.00	793	8350	0.00	0.00
1/8/2007 15:15	285	8-JAN-07-1	0.059	28	797	33521	0.00	0.00	808	8504	0.00	0.00
1/9/2007 14:30	286	9-JAN-07-1	0.070	37	1029	33610	0.00	0.00	758	7984	0.00	0.00
1/10/2007 14:00	287	10-JAN-07-1	0.070	48	1344	33728	0.00	0.00	735	7741	0.00	0.00
1/11/2007 11:30	288	11-JAN-07-1	0.070	52	1456	33854	0.00	0.00	716	7535	0.00	0.00
1/12/2007 13:30	289	12-JAN-07-1	0.070	43	1202	33999	0.00	0.00	734	7724	0.00	0.00
1/13/2007 13:30	290	13-JAN-07-1	0.070	61	1710	34146	0.00	0.00	771	8114	0.00	0.00
1/14/2007 14:00	291	14-JAN-07-1	0.070	20	556	34262	0.00	0.00	776	8172	0.00	0.00
1/15/2007 13:30	292	15-JAN-07-1	0.080	16	463	34320	0.00	0.00	774	8145	0.00	0.00
1/16/2007 11:30	293	16-JAN-07-1	0.070	14	393	34360	0.00	0.00	791	8325	0.00	0.00
1/18/2007 11:30	295	18-JAN-07-1	0.070	15	412	34441	0.00	0.00	826	8697	0.00	0.00
1/26/2007 11:30	303	26-JAN-07-1	0.070	27	772	34918	0.00	0.00	1115	11738	0.00	0.00
1/29/2007 13:15	306	29-JAN-07-1	0.079	55	1560	35325	0.00	0.00	1096	11532	0.00	0.00

VFA Data for nBA Column

Date	Day	Sample ID	Flow Rate (mL/Min)	Lactate (mg/L)	Lactate (µm)	Acetate (mg/L)	Acetate (µM)	Sum Acetate (µM)	Propionate (mg/L)	Propionate (µM)	Formate (mg/L)	Formate (µM)	Butyrate (mg/L)	Butyrate (µM)	Sum Butyrate (µM)	Pyruvate (mg/L)	Pyruvate (µM)
22-Mar	1	22-Mar-06-1	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11-May	46	11-May-06-1	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00
14-May	49	14-may-06-1	0.07	0.00	0.00	1.9	33	4.7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
16-May	51	16-may-06-1	0.08	0.00	0.00	3.2	54	15	0.00	0.00	0.00	0.00	0.5	5.6	0.67	0.00	0.00
18-May	53	18-may-06-1	0.09	0.00	0.00	0.00	0.00	22	0.00	0.00	0.00	0.00	0.00	0.00	1.4	0.00	0.00
24-May	56	24-may-06-1	0.07	0.00	0.00	5.6	94	37	0.57	7.8	0.00	0.00	9.1	104	18	0.00	0.00
26-May	58	26-may-06-1	0.08	0.00	0.00	65	1108	172	1.1	15	0.00	0.00	3.8	44	34	0.00	0.00
31-May	63	31-may-06-1	0.08	0.00	0.00	0.00	0.00	506	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
5-Jun	68	05-June-06-1	0.08	0.00	0.00	33	558	670	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
9-Jun	72	09-June-06-1	0.08	0.00	0.00	35	591	945	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
15-Jun	78	15-June-06-1	0.09	0.00	0.00	35	594	1406	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
19-Jun	82	19-June-06-1	0.08	0.00	0.00	33	557	1682	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
23-Jun	86	23-June-06-1	0.08	0.00	0.00	30	509	1927	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
29-Jun	92	29-June-06-1	0.08	0.00	0.00	24	400	2248	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
6-Jul	99	06-July-06-1	0.08	0.00	0.00	16	279	2539	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
13-Jul	106	13-July-06-1	0.08	0.00	0.00	10	177	2730	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
27-Jul	120	27-July-06-1	0.07	0.00	0.00	3.8	65	2901	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
28-Jul	121	28-July-06-1	0.07	0.00	0.00	5.4	91	2909	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
29-Jul	122	29-July-06-1	0.07	0.00	0.00	19	314	2929	0.00	0.00	0.00	0.00	0.00	0.00	47	0.00	0.00
30-Jul	123	30-July-06-1	0.07	0.00	0.00	68	1159	3004	0.00	0.00	0.00	0.00	1.1	12	48	0.00	0.00
31-Jul	124	31-July-06-1	0.07	0.00	0.00	145	2458	3186	0.00	0.00	0.00	0.00	2.9	33	50	0.00	0.00
1-Aug	125	1-August-06-1	0.07	0.00	0.00	216	3658	3494	0.00	0.00	0.00	0.00	4.8	55	55	0.00	0.00
2-Aug	126	2-August-06-1	0.07	0.00	0.00	299	5073	3934	0.00	0.00	0.00	0.00	8.4	95	62	0.00	0.00
3-Aug	127	3-August-06-1	0.07	0.00	0.00	432	7323	4559	0.00	0.00	0.00	0.00	11.5	130	74	0.00	0.00
4-Aug	128	4-August-06-1	0.07	0.00	0.00	360	6103	5236	0.00	0.00	0.00	0.00	11.3	128	87	0.00	0.00
6-Aug	130	6-August-06-1	0.07	0.00	0.00	353	5986	6454	0.00	0.00	0.00	0.00	14.2	161	116	0.00	0.00
8-Aug	132	8-August-06-1	0.08	0.00	0.00	257	4353	7632	0.00	0.00	0.00	0.00	8.3	94	145	0.00	0.00
10-Aug	134	10-August-06-1	0.07	0.00	0.00	140	2378	8310	0.00	0.00	0.00	0.00	4.2	47	159	0.00	0.00
11-Aug	135	11-Aug-06-1	0.08	0.00	0.00	64	1080	8506	0.00	0.00	0.00	0.00	0.66	7.5	162	0.00	0.00
14-Aug	138	14-August-06-1	0.08	0.00	0.00	37	628	8797	0.00	0.00	0.00	0.00	0.56	6.3	164	0.00	0.00
21-Aug	145	21-August-06-1	0.07	0.00	0.00	0.00	0.00	9006	0.00	0.00	0.00	0.00	0.00	0.00	167	0.00	0.00
28-Aug	152	28-August-06-1	0.08	0.00	0.00	5.7	97	9045	0.00	0.00	0.00	0.00	0.00	0.00	167	0.00	0.00
5-Sep	160	5-Sept-06-1	0.08	0.00	0.00	1.5	25	9104	0.00	0.00	0.00	0.00	0.00	0.00	167	0.00	0.00
11-Sep	166	11-Sept-06-1	0.08	0.00	0.00	1.3	22	9121	0.00	0.00	0.00	0.00	0.00	0.00	167	0.00	0.00
18-Sep	173	18-Sept-06-1	0.07	0.00	0.00	0.00	0.00	9128	0.00	0.00	0.00	0.00	0.00	0.00	167	0.00	0.00
25-Sep	180	25-Sept-06-1	0.07	0.00	0.00	1.4	24	9137	0.00	0.00	1.0	23	0.00	0.00	167	0.00	0.00
29-Sep	184	29-Sept-06-1	0.09	2.8	31	1.2	20	9148	0.00	0.00	1.2	26	0.00	0.00	167	0.00	0.00
2-Oct	187	02-Oct-06-1	0.09	4.9	55	0.00	0.00	9152	0.00	0.00	1.8	40	0.00	0.00	167	0.00	0.00
10-Oct	195	10-Oct-06-1	0.08	3.1	34	1.4	24	9163	0.00	0.00	1.2	27	0.00	0.00	167	0.00	0.00
16-Oct	201	16-Oct-06-1	0.07	4.0	44	0.00	0.00	9170	0.00	0.00	0.91	20	0.00	0.00	167	0.00	0.00
23-Oct	208	23-Oct-06-1	0.08	3.8	42	0.00	0.00	9170	0.00	0.00	2.1	46	0.00	0.00	167	0.00	0.00
25-Oct	210	25-Oct-06-1	0.07	2.6	29	0.00	0.00	9170	0.00	0.00	1.0	21	0.00	0.00	167	0.00	0.00
26-Oct	211	26-Oct-06-1	0.07	3.0	34	0.00	0.00	9170	0.00	0.00	1.2	28	0.00	0.00	167	0.00	0.00
30-Oct	215	30-Oct-06-1	0.07	0.00	0.00	3.3	56	9182	1.5	21	4.7	105	0.00	0.00	167	0.00	0.00
1-Nov	217	1-Nov-06-1	0.07	0.00	0.00	23	398	9228	2.2	30	20	455	0.00	0.00	167	0.00	0.00
6-Nov	222	06-Nov-06-1	0.07	1.5	17	504	8545	11577	2.3	31	1.1	24	142	1607	589	0.00	0.00
8-Nov	224	08-Nov-06-1	0.07	2.3	26	726	12299	13678	3.2	43	2.0	44	158	1799	932	0.00	0.00
9-Nov	225	09-Nov-06-1	0.07	0.00	0.00	880	14910	15050	2.0	27	84	1859	190	2153	1131	0.00	0.00
10-Nov	226	10-Nov-06-1	0.07	0.00	0.00	997	16904	16653	3.9	54	94	2098	214	2430	1362	0.00	0.00
13-Nov	229	13-Nov-06-1	0.08	0.00	0.00	1185	20078	22834	5.8	80	2.4	52	265	3004	2270	0.00	0.00
14-Nov	230	14-Nov-06-1	0.07	4.4	50	1190	20164	24862	5.9	81	2.9	64	203	2299	2538	0.00	0.00
15-Nov	231	15-Nov-06-1	0.07	0.00	0.00	1171	19847	26879	5.9	81	68	1510	154	1749	2742	0.00	0.00
16-Nov	232	16-Nov-06-1	0.07	2.9	33	1163	19717	28873	5.5	76	2.7	59	148	1674	2914	0.00	0.00
17-Nov	233	17-Nov-06-1	0.07	2.3	26	1216	20606	30905	6.4	87	2.8	62	181	2050	3102	0.00	0.00
20-Nov	236	20-Nov-06-1	0.07	0.00	0.00	1344	22786	37584	7.4	101	162	3604	368	4174	4060	0.00	0.00
24-Nov	240	24-Nov-06-1	0.07	1.9	22	1430	24244	47066	8.1	111	4.0	90	481	5463	6003	0.00	0.00
29-Nov	245	29-Nov-06-1	0.07	5.6	63	1420	24073	59241	13	173	3.4	75	484	5494	8764	0.00	0.00
6-Dec	252	06-DEC-06-1	0.06	1.9	21	1400	23734	74163	7.8	106	2.9	65	381	4328	11830	0.00	0.00
8-Dec	254	08-DEC-06-1	0.07	2.2	25	1026	17384	78308	8.9	122	2.9	64	150	1699	12437	0.00	0.00
11-Dec	257	11-DEC-06-1	0.08	3.2	36	241	4077	81816	1.8	25	1.5	33	25	280	12761	2.3	0.03
14-Dec	260	14-Dec-06-1	0.06	3.6	41	21	359	82426	0.00	0.00	4.0	89	2.6	30	12803	1.8	0.02
18-Dec	264	18-DEC-06-1	0.06	1.8	21	5.6	94	82509	0.00	0.00	1.3	29	0.00	0.00	12809	0.00	0.00
27-Dec	273	27-DEC-06-1	0.08	2.9	32	1.4	24	82568	0.00	0.00	1.6	35	0.00	0.00	12809	0.00	0.00
2-Jan	279	2-JAN-07-1	0.08	0.00	0.00	0.00	0.00	82576	1.5	21	0.00	0.00	0.00	0.00	12809	0.00	0.00
9-Jan	286	9-JAN-07-1	0.07	0.00	0.00	24	398	82716	0.00	0.00	0.00	0.00	0.00	0.00	12809	0.00	0.00
10-Jan	287	10-JAN-07-1	0.07	2.3	26	269	4564	82966	0.00	0.00	22	488	0.00	0.00	12809	0.00	0.00
11-Jan	288	11-JAN-07-1	0.07	0.00	0.00	539	9132	83657	30	416	0.00	0.00	0.00	0.00	12809	0.00	0.00
12-Jan	289	12-JAN-07-1	0.07	0.00	0.00	683	11582	84701	14	191	0.00	0.00	0.00	0.00	12809	0.00	0.00
13-Jan	290	13-JAN-07-1	0.07	0.00	0.00	765	12965	85938	6.0	82	0.00	0.00	0.00	0.00	12809	0.00	0.00
14-Jan	291	14-JAN-07-1	0.07	1.0	11	744	12607	87227	0.00	0.00	0.33	7.3	3.8	43	12811	0.00	0.00
15-Jan	292	15-JAN-07-1	0.08	0.00	0.00	678	11488	88622	1.6	22	0.00	0.00	0.00	0.00	12813	0.00	0.00
16-Jan	293	16-JAN-07-1	0.07	0.00	0.00	705	11953	89804	0.00	0.00	0.28	6.2	0.00	0.00	12813	0.00	0.00
17-Jan	294	17-Jan-08	0.07	0.00	0.00	880	14908	91158	0.00	0.00	0.87	19	2.4	27	12815	0.00	0.00
18-Jan	295	18-JAN-07-1	0.07	0.00	0.00	841	14255	92627	0.00	0.00	0.62	14	2.5	28	12817	0.00	0.00
19-Jan	296	29-JAN-07-1	0.07	0.00	0.00	696	11793	93940	0.00	0.00	0.32	7.1	2.2	25	12820	0.00	0.00
20-Jan	297	20-Jan-06-1	0.07	0.00	0.00	692	11724	95125	4.8	65	0.43	10	2.0	23	12823	0.00	0.00
21-Jan	298	21-Jan-06-1	0.07	0.00	0.00	556	9417	96191	0.00	0.00	0.42	9.3	1.7	20	12825	0.00	0.00
22-Jan	299	22-Jan-06-1	0.07	0.00	0.00	491	8325	97085	0.00	0.00	0.45	10	1.8	20	12827	0.00	0.00
23-Jan	300	23-Jan-06-1	0.07	0.00	0.00	442	7483	97882	1.3	18	0.42	9.4	1.7	19	12829	0.00	0.00
24-Jan	301	24-Jan-06-1	0.07	0.00	0.00	359	6088	98566	0.00	0.00	0.48	11	0.00	0.00	12830	0.00	0.00
26-Jan	303	26-JAN-07-1	0.07	0.00	0.00	294	4979	99681	1.3	18	0.41	9.2	1.5	17	12831	0.00	0.00
29-Jan	306	29-JAN-07-1	0.08	0.00	0.00	211	3569	101138	0.71	10	0.34	7.5	1.5	17	12837	0.00	0.00

VOC and DHG Data for SRS™ Column

Date	Day	Sample ID	Flow Rate (mL/Min)	Total TCE Mass Removed (mg)	Total cis-DCE Mass Removed (mg)	Total VC Mass Removed (mg)	Total Ethene Mass Removed (mg)	Total Ethane Mass Removed (mg)	Total Methane Mass Removed (mg)	PCE (mg/L)	PCE (uM)	TCE (mg/L)	TCE (μM)	cis-DCE (mg/L)	cis-DCE (μM)	VC (mg/L)	VC (μM)	Ethene (mg/L)	Ethene (μM)	Ethane (mg/L)	Ethane (uM)	Methane (mg/L)	Methane (μM)	Total Ethenes (μM)
3/21/2006 15:15	0	21-mar-06-3	--	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.15	1.1	6.6	68	0.0	0.37	0.00	0.00	0.00	0.00	0.03	1.9	70
3/22/2006 14:40	1	22-mar-06-3	0.07	0.02	0.61	0.01	0.00	0.00	0.00	0.01	0.06	0.32	2.4	6.3	65	0.09	1.5	0.00	0.05	0.00	0.00	0.03	1.9	69
3/24/2006 12:00	3	24-mar-06-3	0.08	1.9	3.2	0.05	0.00	0.00	0.02	0.01	0.06	19	144	20	210	0.38	6.1	0.03	0.95	0.00	0.00	0.14	8.5	361
3/27/2006 11:00	6	27-mar-06-3	0.06	15	12	0.15	0.01	0.00	0.08	0.03	0.16	67	512	40	412	0.30	4.7	0.05	1.7	0.00	0.00	0.29	18	931
3/29/2006 16:00	8	29-Mar-06-3	0.07	32	22	0.21	0.03	0.00	0.15	0.03	0.16	95	724	50	519	0.20	3.2	0.05	1.8	0.00	0.00	0.30	19	1248
3/31/2006 14:00	10	31-Mar-06-3	0.07	62	34	0.24	0.04	0.00	0.49	0.00	0.00	193	1471	69	710	0.12	1.9	0.08	2.8	0.00	0.00	3.0	186	2186
4/3/2006 16:00	13	03-Apr-06-3	0.07	120	57	0.28	0.06	0.00	1.4	0.00	0.00	165	1255	73	755	0.11	1.8	0.06	2.1	0.00	0.00	2.7	171	2013
4/6/2006 10:00	16	06-apr-06-3	0.08	185	82	0.29	0.08	0.00	2.2	0.00	0.00	268	2036	92	948	0.00	0.00	0.07	2.5	0.00	0.00	2.8	172	2986
4/10/2006 14:00	20	10-apr-06-3	0.07	333	118	0.29	0.11	0.00	3.5	0.00	0.00	393	2991	68	700	0.00	0.00	0.07	2.5	0.00	0.00	2.8	174	3693
4/12/2006 16:00	22	12-apr-06-3	0.07	422	132	0.29	0.12	0.00	4.1	0.00	0.00	457	3474	62	645	0.00	0.00	0.00	0.00	0.00	0.00	2.8	176	4119
4/17/2006 9:00	27	17-apr-06-3	0.08	688	156	0.29	0.13	0.00	5.5	0.00	0.00	577	4392	32	326	0.00	0.00	0.05	1.8	0.00	0.00	2.7	167	4720
4/19/2006 16:00	29	19-apr-06-3	0.06	825	163	0.29	0.14	0.00	6.1	0.00	0.00	573	4360	26	265	0.00	0.00	0.04	1.4	0.00	0.00	2.7	168	4626
4/27/2006 10:00	32	27-apr-06-3	0.06	969	171	0.29	0.16	0.00	6.8	0.00	0.00	617	4692	41	427	0.00	0.00	0.06	2.1	0.00	0.00	2.8	172	5121
5/1/2006 9:00	36	1-may-06-3	0.05	1179	183	0.29	0.18	0.00	7.6	0.00	0.00	731	5562	36	373	0.00	0.00	0.07	2.5	0.00	0.00	2.7	170	5938
5/5/2006 11:00	40	5-may-06-3	0.08	1456	191	0.29	0.20	0.00	8.7	0.00	0.00	728	5540	6.9	72	0.00	0.00	0.05	1.8	0.00	0.00	2.6	162	5613
5/8/2006 11:30	43	8-may-06-3	0.07	1674	193	0.31	0.21	0.00	10	0.00	0.00	609	4638	3.0	31	0.09	1.4	0.04	1.4	0.00	0.00	3.0	187	4672
5/10/2006 9:00	45	10-may-06-3	0.07	1812	193	0.32	0.22	0.00	10	0.00	0.00	785	5975	2.0	21	0.00	0.00	0.04	1.4	0.00	0.00	2.6	164	5997
5/12/2006 14:30	47	12-may-06-3	0.08	1972	194	0.32	0.23	0.00	11	0.00	0.00	561	4270	3.4	35	0.00	0.00	0.04	1.4	0.00	0.00	2.7	167	4307
5/14/2006 14:30	49	14-may-06-3	0.05	2082	194	0.32	0.24	0.00	11	0.00	0.00	689	5242	3.5	36	0.00	0.00	0.05	1.8	0.00	0.00	2.6	163	5280
5/15/2006 14:30	50	15-may-06-3	0.06	2134	195	0.32	0.24	0.00	11	0.00	0.00	670	5098	3.7	39	0.00	0.00	0.04	1.4	0.00	0.00	2.7	170	5138
5/16/2006 15:00	51	16-may-06-3	0.06	2192	195	0.32	0.25	0.00	12	0.00	0.00	623	4740	6.1	63	0.00	0.00	0.05	1.8	0.00	0.00	2.6	161	4805
5/17/2006 14:00	52	17-may-06-3	0.07	2255	196	0.32	0.25	0.00	12	0.00	0.00	803	6108	7.8	80	0.00	0.00	0.04	1.4	0.00	0.00	2.6	159	6190
5/18/2006 14:00	53	18-may-06-3	0.11	2355	196	0.32	0.25	0.00	12	0.00	0.00	796	6056	6.0	61	0.00	0.00	0.04	1.4	0.00	0.00	2.5	158	6118
5/19/2006 13:00	54	19-may-06-3	0.13	2495	197	0.32	0.26	0.00	13	0.00	0.00	869	6611	5.6	58	0.00	0.00	0.04	1.4	0.00	0.00	2.6	160	6671
5/24/2006 11:00	56	24-may-06-3	0.07	2728	199	0.32	0.27	0.00	13	0.00	0.00	767	5840	4.2	43	0.00	0.00	0.03	1.1	0.00	0.00	2.7	170	5884
5/25/2006 11:00	57	25-may-06-3	0.08	2808	199	0.32	0.28	0.00	14	0.00	0.00	720	5476	1.3	13	0.00	0.00	0.04	1.4	0.00	0.00	2.6	164	5490
5/26/2006 13:30	58	26-may-06-3	0.08	2894	200	0.32	0.29	0.00	14	0.00	0.00	640	4871	6.7	69	0.00	0.00	0.13	4.6	0.00	0.00	2.8	175	4944
5/29/2006 12:00	61	29-may-06-3	0.08	3135	202	0.32	0.31	0.00	15	0.00	0.00	835	6351	7.3	76	0.00	0.00	0.03	1.1	0.00	0.00	2.7	170	6428
5/31/2006 14:00	63	31-may-06-3	0.08	3291	203	0.32	0.32	0.00	16	0.00	0.00	488	3717	2.1	21	0.00	0.00	0.02	0.70	0.00	0.00	3.0	185	3738
6/2/2006 11:30	65	02-June-06-3	0.09	3446	205	0.32	0.33	0.00	16	0.00	0.00	828	6304	13	131	0.00	0.00	0.04	1.4	0.00	0.00	2.6	164	6436
6/5/2006 13:15	68	05-June-06-3	0.08	3766	208	0.32	0.34	0.00	18	0.00	0.00	845	6431	5.2	53	0.00	0.00	0.03	1.1	0.00	0.00	4.9	304	6485
6/7/2006 11:30	70	07-June-06-3	0.08	3961	210	0.32	0.35	0.00	19	0.00	0.00	928	7060	15	156	0.00	0.00	0.03	1.1	0.00	0.00	2.6	164	7217
6/9/2006 14:00	72	09-June-06-3	0.08	4168	214	0.32	0.35	0.00	19	0.00	0.00	844	6422	14	144	0.00	0.00	0.03	1.1	0.00	0.00	2.8	175	6567
6/12/2006 10:30	75	12-June-06-3	0.08	4427	217	0.36	0.36	0.00	20	0.00	0.00	780	5934	6.9	71	0.25	4.0	0.00	0.00	0.00	0.00	2.6	162	6009
6/15/2006 14:20	78	15-June-06-3	0.09	4745	219	0.45	0.36	0.00	21	0.00	0.00	913	6947	4.2	43	0.23	3.7	0.00	0.00	0.00	0.00	2.7	170	6994
6/16/2006 14:45	79	16-June-06-3	0.08	4863	220	0.46	0.36	0.00	21	0.00	0.00	991	7540	4.5	46	0.00	0.00	0.00	0.00	0.00	0.00	2.7	165	7586
6/19/2006 10:40	82	19-June-06-3	0.09	5191	221	0.5	0.36	0.00	22	0.00	0.00	931	7083	4.4	46	0.45	7.2	0.00	0.00	0.00	0.00	2.5	158	7136
6/21/2006 11:00	84	21-June-06-3	0.09	5399	223	0.6	0.36	0.00	23	0.00	0.00	722	5494	6.6	68	0.00	0.00	0.00	0.00	0.00	0.00	2.5	158	5562
6/23/2006 15:00	86	23-June-06-3	0.08	5620	224	0.6	0.36	0.00	24	0.00	0.00	955	7271	4.1	43	0.00	0.00	0.00	0.00	0.00	0.00	2.6	163	7314
6/26/2006 14:00	89	26-June-06-3	0.09	5996	226	0.6	0.36	0.00	25	0.00	0.00	1069	8132	5.6	58	0.00	0.00	0.00	0.00	0.00	0.00	2.5	156	8190
6/29/2006 14:00	92	29-June-06-3	0.07	6351	229	0.6	0.36	0.00	25	0.00	0.00	904	6883	10	101	0.00	0.00	0.00	0.00	0.00	0.00	2.7	166	6983
7/4/2006 13:30	97	04-July-06-3	0.08	6851	238	0.6	0.36	0.00	27	0.00	0.00	862	6560	23	233	0.00	0.00	0.00	0.00	0.00	0.00	2.6	160	6793
7/6/2006 13:30	99	06-July-06-3	0.09	7071	244	0.6	0.36	0.00	28	0.00	0.00	942	7170	31	317	0.00	0.00	0.00	0.00	0.00	0.00	2.6	163	7487
7/10/2006 13:40	103	10-July-06-3	0.11	7520	263	0.6	0.36	0.00	29	0.00	0.00	685	5212	39	398	0.19	3.0	0.00	0.00	0.00	0.00	2.5	154	5613
7/13/2006 9:00	106	13-July-06-3	0.08	7800	281	0.7	0.36	0.00	30	0.00	0.00	792	6031	54	552	0.15	2.4	0.00	0.00	0.00	0.00	2.7	170	6585
7/18/2006 13:30	111	18-July-06-3	0.08	8293	319	0.8	0.36	0.00	32	0.00	0.00	806	6135	69	712	0.00	0.00	0.00	0.00	0.00	0.00	2.7	170	6847
7/24/2006 14:45	117	24-July-06-3	0.08	8851	376	0.9	0.37	0.00	34	0.00	0.00	729	5544	89	914	0.46	7.4	0.04	1.4	0.00	0.00	2.5	157	6467
7/31/2006 16:15	124	31-July-06-3	0.08	9491	461	1.1	0.39	0.00	36	0.00	0.00	759	5774	109	1122	0.00	0.00	0.00	0.00	0.00	0.00	2.9	178	6896
8/8/2006 15:15	132	8-August-06-3	0.08	10217	574	1.1	0.42	0.00	38	0.00	0.00	741	5637	125	1286	0.00	0.00	0.06	2.1	0.00	0.00	2.6	161	6925
8/14/2006 13:45	138	14-August-06-3	0.09	10764	666	1.1	0.46	0.00	40	0.00	0.00	767	5840	128	1324	0.00	0.00	0.07	2.5	0.00	0.00	2.8	174	7167
8/21/2006 14:45	145	21-August-06-3	0.09	11413	779	1.3	0.5	0.00	43	0.00	0.00	718	5463	131	1348	0.50	8.0	0.11	3.9	0.00	0.00	2.6	165	6823
8/28/2006 15:30	152	28-August-06-3	0.09	12082	897	1.8	0.7	0.00	45	0.00	0.00	752	5722	129	1334	0.48	7.7	0.16	5.6	0.00	0.00	2.8	173	7069
9/5/2006 14:15	160	5-Sept-06-1	0.08	12820	1031	2.3	0.8	0.00	48	0.00	0.00	718	5463	137	1413	0.52	8.3	0.19	6.7	0.00	0.00	3.1	193	6891
9/11/2006 10:15	166	11-Sept-06-3	0.09	13335	1133	2.7	1.0	0.00	50	0.00	0.00	715	5441	146	1508	0.61	10	0.21	7.4	0.00	0.00	3.2	196	6966
9/18/2006 10:30	173	18-Sept-06-3	0.08	13945	1264	3.3	1.2	0.00	54	0.00	0.00	690	5254	157	1618	0.82	13	0.28	10	0.00	0.00	4.2	262	6895
9/25/2006 13:00	180	25-Sept-06-3	0.08	14433	1387	4.5	1.4	0.00	57	0.00	0.00	472	3595	135	1398	2.0	32	0.26	9.1	0.00	0.00	3.5	216	5034
9/29/2006 14:00	184	29-Sept-06-3	0.09	14691	1459	5.3	1.6	0.00	59	0.00	0.00	551	4190	149	1542	0.95	15	0.25	8.8	0.00	0.00	3.6	224	5756
10/2/2006 11:00	187	02-Oct-06-3	0.09	14903	1516	5.6	1.7	0.00	60	0.00	0.00	546	4154	144	1489	0.96	15	0.27	9.5	0.00	0.00	3.9	244	5667
10/10/2006 11:40	195	10-Oct-06-3	0.08	15466	1666	6.5	1.9	0.00	64	0.00	0.00	574	4371	154	1593	0.74	12	0.26	9.1	0.00	0.00	4.6	287	5985
10/16/2006 13:30	201	16-Oct-06-3	0.08	15897	1782	7.2	2.1	0.00	68	0.00	0.00	640	4868	172	1778	1.3	21	0.27	9.5	0.00	0.00	4.5	281	6676
10/23/2006 10:15	208	23-Oct-06-3	0.09	16418	1932	8.0	2.4	0.00	72	0.00	0.00	582	4432	179	1846	0.50	8.0	0.30	11	0.00	0.00	4.9	304	6296
10/30/2006 10:15	215	30-Oct-06-3	0.08	16926	2109	8.4	2.6	0.00	77	0.00	0.00	581	4423	227	2344	0.39	6.2	0.34	12	0.00	0.00	7.3	453	6786
11/6/2006 15:00	222	06-Nov-06-3	0.08	17382	2324	8.7	2.9	0.00	82	0.00	0.00	513	3905	288	2971	0.31	5.0	0.29	10	0.00	0.00	5.1	319	6891
11/13/2006 11:55	229	13-Nov-06-3	0.08	17795	2564	9.0	3.2	0.00	86	0.00	0.00	549	4181	330	3403	0.49	7.8	0.37	13	0.00	0.00	5.7	358	7606
11/20/2006 14:15	236	20-Nov-06-3	0.07	18148	2841	9.3	3.4	0.00	91	0.00	0.00	375	2855	394	4069	0.50	8.0	0.34	12	0.00	0.00	5.8	360	6944
11/27/2006 14:30	243	27-Nov-06-3	0.07	18345	3152	10	3.7	0.00	95	0.00	0.00	188	1434	498	5142	0.81	13	0.32	11	0.00	0.00	5.7	353	6600
12/4/2006 12:30	250	04-DEC-06-3	0.07	18425	3468	11	3.9	0.00	98	0.00	0.00	44	336	423	4367	1.9	31	0.29	10	0.00	0.00	5.4	337	4744
12/11/2006 15:30	257	11-DEC-06-3	0.07	18442	3687	15	4.1	0.00	103	0.00	0.00	4.8	36	187	1930	10	167	0.26	9.1	0.00	0.00	6.1	380	2142
12/18/2006 14:00	264	18-DEC-06-3	0.06	18446	3791	25	4.2	0.00	107	0.00	0.00	5.6	43	131	1347	21	333	0.29	10	0.00	0.00	6.2	388	1732
12/22/2006 15:00	268	22-DEC-06-3	0.06	18447	3829	33	4.4	0.00	109	0.00	0.00	3.3	25	82	849	24	388	0.36	13	0.00	0.00	6.2	385	1274
12/27/2006 11:00	273	27-DEC-06-3	0.06	18448	3856	43	4.5	0.00	111	0.00	0.00	0.76	5.8	47	488	23	370	0.48	17	0.00	0.00	3.8	237	880
1/2/2007 11:30	279	2-JAN-07-3	0.06	18448	3873	54	4.8	0.00	114	0.00	0.00	0.00	0.00	18	190	16	250	0.58	20	0.00	0.00	6.8	421	461
1/8/2007 15:00	285	8-JAN-07-3	0.07	18448	3882	60	5.2	0.00	118	0.00	0.00	0.00	0.00	8.5	87	6.7	107	0.63	22	0.00	0.00	6.2	385	216
1/15/2007 14:00	292	15-JAN-07-3	0.08	18450	3886	64	5.7	0.00	123	0.00	0.00	4.7	36	2.3	24	2.2	35	0.74	26	0.00	0.00	6.5	403	121
1/22/2007 17:00	299	22-JAN-07-3	0.08	18452	3887	65	6.4	0.00	128	0.00	0.00	0.00	0.00	0.8	8.5	0.00	0.00	0.80	28	0.00	0.00	6.1	380	37
1/29/2007 11:45	306	29-JAN-07-3	0.08	18452	3887	65	7.1	0.00	133	0.00	0.00	0.00	0.00	0.00	0.00	0.17	2.7	1.02	36	0.00	0.00	6.4	400	39
2/5/2007 14:00	313	5-feb-07-3	0.08	18452	3888	65	7.8	0.00	139	0.00	0.00	0.00	0.00	0.33	3.4	0.19	3.0	0.72	25	0.00	0.00	7.4	463	32
2/12/2007 16:00	320	12-feb-07-3	0.08	18452	3888	65	8.4	0.00	145	0.00	0.00	0.00	0.00	0.29	3.0	0.16	2.6	0.67	24	0.00	0.00	8.6	537	29
2/19/2007 16:30	327	19-feb-07-3	0.07	18452	3888	65	8.9	0.00	150	0.00	0.00	0.00	0.00	0.01	0.14	0.03	0.42	0.65	23	0.00	0.00	4.2	260	23
2/26/2007 12:00	334	26-feb-07-3	0.06	18452	3888	65	9.3	0.00	153	0.00	0.00	0.00	0.00	0.01	0.08	0.01	0.21	0.65	23	0.00	0.00	5.0	314	23
3/5/2007 11:30	341	5-March-07-3	0.07	18452	3888	65	10	0.00	157	0.00	0.00	0.00	0.00	0.01	0.07	0.01	0.23	0.94	33	0.00	0.00	5.7	353	33
3/8/2007 15:30	344	8-March-07-3	0.07	18452	3888	65	10	0.00	159	0.00	0.00	0.00	0.00	0.01	0.11	0.02	0.29	1.5	54	0.00	0.00	6.6	409	55
3/12/2007 15:00	348	12-March-07-3	0.08	18452	3888	65	11	0.00	162	0.00	0.00	0.00	0.00	0.02	0.16	0.03	0.44	1.8	64	0.00	0.00	6.0	373	64
3/15/2007 15:00	351	15-March-07-3	0.07	18452	3888	65	12	0.00	164	0.00	0.00	0.00	0.00	0.06	0.62	0.07	1.1	2.7	94	0.00	0.00	7.2	450	95
3/19/2007 15:30	355	19-March-07-3	0.06	18452	3888	65	13	0.00	167	0.00	0.00	0.00	0.00	0.08	0.86	0.08	1.3	3.5	122	0.00	0.00	7.8	485	124
3/26/2007 15:00	362	26-March-07-3	0.07	18452	3888	65	16	0.00	173	0.00	0.00	0.00	0.00	0.20	2.1	0.22	3.6	4.7	164	0.00	0.00	12	731	170
3/29/2007 15:30	365	29-March-07-3	0.08	18452	3889	66	17	0.00	177	0.00	0.00	0.00	0.00	5.4	56	4.0	64	5.8	204	0.00	0.00	12	738	324
4/2/2007 15:30	369	2-April-07-3	0.09	18452	3901	72	20	0.00	182	0.00	0.00	0.28	2.1	44	453	19	296	5.5	191	0.00	0.00	10	613	943
4/5/2007 14:00	372	5-April-07-3	0.06	18452	3919	79	22	0.00	186	0.00	0.00	0.00	0.00	68	701	28	443	5.3	187	0.00	0.00	11	692	1331
4/9/2007 16:50	376	9-April-07-3	0.07	18452	3945	91	24	0.00	190	0.00	0.00	0.14	1.1	65	670	31	501	4.5	159	0.00	0.00	9.0	560	1331
4/16/2007 16:00	383	16-April-07-3	0.04	18452	3991	111	26	0.00	194	0.00	0.00	0.36	2.8	102	1047	43	685	4.3	150	0.00	0.00	7.7	480	1884
4/23/2007 16:00	390	23-April-07-3	0.05	18452	4037	136	29	0.00	198	0.00	0.00	0.00	0.00	92	951	62	989	8.1	283	0.00	0.00	6.0	374	2223
4/30/2007 14:00	397	30-April-07-3	0.04	18452	4076	163	33	0.00	200	0.00	0.00	0.19	1.5	84	868	60	954	11	385	0.00	0.00	4.5	278	2209
5/7/2007 11:00	404	7-May-07-3	0.06	18453	4129	185	38	0.00	201	0.00	0.00	1.5	12	135	1394	32	515	8.7	305	0.00	0.00	1.9	115	2226
5/14/2007 9:45	411	14-May-07-3	0.06	18453	4209	208	43	0.00	202	0.00	0.00	0.16	1.2	139	1430	47	757	9.3	325	0.00	0.00	1.7	107	2513
5/17/2007 13:30	414	17-May-07-3	0.06	18453	4245	221	46	0.00	203	0.00	0.00	0.00	0.00	127	1312	46	742	8.8	308	0.00	0.00	1.6	98	2362
5/22/2007 11:30	419	22-May-07-3	0.09	18453	4310	248	51	0.00	204	0.00	0.00	0.00	0.00	115	1183	54	870	10	367	0.00	0.00	1.6	97	2419
5/28/2007 11:00	425	28-May-07-3	0.04	18453	4364	277	57	0.00	205	0.00	0.00	0.16	1.2	89	922	55	882	12	411	0.00	0.00	1.5	96	2217
6/4/2007 15:00	432	04-June-07-3	0.07	18454	4405	307	63	0.00	205	0.00	0.00	1.8	14	68	701	61	968	13	468	0.00	0.00	1.5	95	2151
6/11/2007 12:00	439	11-June-07-3	0.07	18455	4445	347	74	0.00	206	0.00	0.00	1.7	13	47	481	56	890	18	640	0.00	0.00	1.7	106	2024
6/18/2007 12:00	446	18-June-07-3	0.07	18456	4478	387	86	0.00	208	0.00	0.00	1.8	14	43	442	50	796	14	494	0.00	0.00	1.4	89	1746
6/25/2007 13:00	453	25-June-07-3	0.08	18458	4507	423	98	0.00	209	0.00	0.00	1.4	10	32	330	46	739	15	536	0.00	0.00	1.5	97	1616
7/2/2007 11:00	460	2-July-07-3	0.05	18459	4524	453	109	0.00	210	0.00	0.00	1.9	14	22	230	45	728	18	644	0.00	0.00	1.5	93	1616
7/9/2007 15:30	467	9-July-07-3	0.06	18459	4545	483	121	0.00	211	0.00	0.00	0.00	0.00	45	468	52	829	23	795	0.00	0.00	3.3	204	2092
7/16/2007 10:00	474	16-July-07-3	0.06	18459	4579	515	133	0.00	213	0.00	0.00	0.00	0.00	71	737	56	899	19	668	0.00	0.00	1.8	110	2304
7/23/2007 14:00	481	23-July-07-3	0.04	18459	4612	544	143	0.00	214	0.00	0.00	0.00	0.00	57	588	62	994	19	676	0.00	0.00	1.8	112	2258
7/30/2007 10:00	488	30-July-07-3	0.08	18459	4639	577	153	0.00	215	0.00	0.00	0.00	0.00	38	390	53	855	17	602	0.00	0.00	1.7	103	1847
8/6/2007 14:30	495	6-Aug-07-3	0.07	18459	4675	623	167	0.00	216	0.00	0.00	0.00	0.00	57	590	65	1036	18	637	0.00	0.00	1.6	97	2262
8/13/2007 12:00	502	13-Aug-07-3	0.06	18459	4713	665	179	0.00	217	0.00	0.00	0.00	0.00	54	559	60	960	17	595	0.00	0.00	1.7	104	2114
8/20/2007 14:30	509	20-Aug-07-3	0.67	18459	4861	861	277	0.00	224	0.00	0.00	0.00	0.00	24	250	44	701	35	1223	0.00	0.00	2.2	138	2173
8/27/2007 16:00	516	27-Aug-07-3	0.06	18459	4954	1036	375	0.00	232	0.00	0.00	0.00	0.00	26	266	50	793	18	616	0.00	0.00	1.7	107	1675
9/10/2007 16:00	530	10-sep-07-3	0.08	18459	4997	1094	401	0.00	234	0.00	0.00	0.00	0.00	35	360	33	533	19	676	0.00	0.00	1.5	92	1569
9/17/2007 16:00	537	17-sep-07-3	0.07	18459	5023	1118	412	0.00	235	0.00	0.00	0.00	0.00	35	362	32	508	13	450	0.00	0.00	1.1	69	1321
9/24/2007 16:00	544	24-sep-07-3	0.08	18459	5051	1143	422	0.00	236	0.00	0.00	0.00	0.00	39	405	36	578	13	457	0.00	0.00	1.7	104	1440
10/1/2007 16:00	551	1-oct-07-3	0.06	18459	5080	1172	433	0.00	237	0.00	0.00	0.00	0.00	41	427	44	698	16	564	0.00	0.00	0.90	56	1689
10/9/2007 11:30	559	9-oct-07-3	0.08	18459	5115	1206	446	0.00	237	0.00	0.00	0.00	0.00	45	464	40	640	16	561	0.00	0.00	0.92	57	1665
10/15/2007 15:00	565	15-oct-07-3	0.08	18459	5145	1232	456	0.00	238	0.00	0.00	0.00	0.00	40	411	33	529	14	487	0.00	0.00	0.91	57	1427
10/22/2007 14:00	572	22-oct-07-3	0.08	18459	5178	1259	468	0.00	239	0.00	0.00	0.00	0.00	40	414	34	546	16	560	0.00	0.00	1.9	116	1521

Anion Data for SRS™ Column

Date	Day	Sample ID	Flow Rate (ml/min)	Chloride (mg/L)	Chloride (µM)	Sum Chloride (µm)	Nitrite-N (mg/L)	Nitrate-N (mg/L)	Sulfate (mg/L)	Sulfate (µM)	Sum Sulfate (µM)	Bromide (mg/L)	Phosphate (mg/L)
3/21/2006 15:15	0	--	--	--	--	--	--	--	--	--	--	--	--
3/22/2006 14:40	1	22-Mar-06-3	0.07	20	563	53	0.00	0.00	684	7203	679	62	0.00
3/24/2006 12:00	3	24-Mar-06-3	0.08	30	843	202	0.00	0.00	579	6096	2084	45	0.00
3/27/2006 11:00	6	27-Mar-06-3	0.06	32	900	429	0.00	0.00	--	--	3676	14	0.00
3/29/2006 16:00	8	29-Mar-06-3	0.07	48	1346	697	0.00	0.00	831	8745	5761	10	0.00
3/31/2006 14:00	10	31-Mar-06-3	0.07	36	1017	938	0.00	0.00	745	7841	7450	1.0	0.00
4/3/2006 16:00	13	03-Apr-06-3	0.07	41	1164	1293	0.00	0.00	753	7929	10017	1.5	0.00
4/6/2006 10:00	16	06-apr-06-3	0.08	48	1352	1685	0.00	0.00	831	8752	12618	2.3	0.00
4/10/2006 14:00	20	10-apr-06-3	0.07	39	1093	2197	0.00	0.00	796	8382	16208	0.00	0.00
4/12/2006 16:00	22	12-apr-06-3	0.07	36	1025	2422	0.00	0.00	829	8730	18025	0.00	0.00
4/17/2006 9:00	27	17-apr-06-3	0.08	--	--	2983	0.00	0.00	--	--	22797	0.00	0.00
4/19/2006 16:00	29	19-apr-06-3	0.06	25	706	3133	0.00	0.00	904	9520	24827	0.00	0.00
4/27/2006 10:00	32	27-apr-06-3	0.06	20	563	3276	0.00	0.00	--	--	26975	0.00	0.00
5/1/2006 9:00	36	1-may-06-3	0.05	27	772	3476	0.00	0.00	990	10421	30088	1.8	0.00
5/5/2006 11:00	40	5-may-06-3	0.08	25	699	3809	0.00	0.00	1001	10535	34835	0.00	0.00
5/8/2006 11:30	43	8-may-06-3	0.07	--	--	4031	0.00	0.00	--	--	38177	0.00	0.00
5/10/2006 9:00	45	10-may-06-3	0.07	23	638	4157	0.00	0.00	1015	10684	40283	0.00	0.00
5/12/2006 14:30	47	12-may-06-3	0.08	24	679	4317	0.00	0.00	1015	10688	42883	0.00	0.00
5/14/2006 14:30	49	14-may-06-3	0.05	27	765	4412	0.00	0.00	1049	11039	44314	0.00	0.00
5/15/2006 14:30	50	15-may-06-3	0.06	29	829	4483	0.00	0.00	1050	11053	45300	1.6	0.00
5/16/2006 15:00	51	16-may-06-3	0.06	29	823	4556	0.00	0.00	1029	10830	46269	14	0.00
5/17/2006 14:00	52	17-may-06-3	0.07	23	639	4623	0.00	0.00	1025	10790	47254	36	0.00
5/18/2006 14:00	53	18-may-06-3	0.11	23	637	4723	0.00	0.00	1020	10736	48944	57	0.00
5/19/2006 13:00	54	19-may-06-3	0.13	20	562	4835	0.00	0.00	1045	11003	50964	84	0.00
5/24/2006 11:00	56	24-may-06-3	0.07	23	646	4954	0.00	0.00	1029	10837	53119	94	0.00
5/25/2006 11:00	57	25-may-06-3	0.08	20	577	5023	0.00	0.00	954	10044	54302	92	0.00
5/26/2006 13:30	58	26-may-06-3	0.08	19	539	5094	0.00	0.00	959	10090	55575	91	0.00
5/29/2006 12:00	61	29-may-06-3	0.08	18	516	5261	0.00	0.00	973	10246	58804	75	0.00
5/31/2006 14:00	63	31-may-06-3	0.08	17	474	5383	0.00	0.00	959	10090	61307	24	0.00
6/2/2006 11:30	65	02-June-06-3	0.09	23	654	5523	0.00	0.00	1030	10847	63907	6.4	0.00
6/5/2006 13:15	68	05-June-06-3	0.08	20	577	5745	0.00	0.00	1029	10828	67817	2.6	0.00
6/7/2006 11:30	70	07-June-06-3	0.08	18	502	5860	0.00	0.00	959	10092	70048	0.00	0.00
6/9/2006 14:00	72	09-June-06-3	0.08	19	525	5981	0.00	0.00	957	10074	72424	0.00	0.00
6/12/2006 10:30	75	12-June-06-3	0.08	19	522	6148	0.00	0.00	965	10154	75649	0.00	0.00
6/15/2006 14:20	78	15-June-06-3	0.09	18	521	6356	0.00	0.00	966	10173	79693	0.00	0.00
6/16/2006 14:45	79	16-June-06-3	0.08	20	555	6420	0.00	0.00	992	10443	80920	0.00	0.00
6/19/2006 10:40	82	19-June-06-3	0.09	30	855	6668	0.00	0.00	982	10340	84586	0.00	0.00
6/21/2006 11:00	84	21-June-06-3	0.09	32	909	6890	0.00	0.00	958	10088	87159	0.00	0.00
6/23/2006 15:00	86	23-June-06-3	0.08	42	1176	7158	0.00	0.00	994	10464	89794	0.00	0.00
6/26/2006 14:00	89	26-June-06-3	0.09	43	1201	7624	0.00	0.00	954	10045	93820	0.00	0.00
6/29/2006 14:00	92	29-June-06-3	0.07	48	1340	8032	0.00	0.00	866	9112	96894	0.00	0.00
7/4/2006 13:30	97	04-July-06-3	0.08	64	1790	8970	0.00	0.00	826	8699	102234	0.00	0.00
7/6/2006 13:30	99	06-July-06-3	0.09	65	1829	9418	0.00	0.00	793	8346	104341	0.00	0.00
7/10/2006 13:40	103	10-July-06-3	0.11	72	2033	10592	0.00	0.00	801	8437	109443	0.00	0.00
7/13/2006 9:00	106	13-July-06-3	0.08	69	1956	11257	0.00	0.00	786	8273	112230	0.00	0.00
7/18/2006 13:30	111	18-July-06-3	0.08	67	1885	12439	0.00	0.00	726	7638	117126	0.00	0.00
7/24/2006 14:45	117	24-July-06-3	0.08	57	1614	13729	0.00	0.00	642	6759	122434	0.00	0.00
7/31/2006 16:15	124	31-July-06-3	0.08	56	1569	15101	0.00	0.00	548	5768	127832	0.00	0.00
8/8/2006 15:15	132	8-August-06-3	0.08	54	1524	16591	0.00	0.00	419	4413	132739	0.00	0.00
8/14/2006 13:45	138	14-August-06-3	0.09	51	1438	17678	0.00	0.00	272	2868	135411	0.00	0.00
8/21/2006 14:45	145	21-August-06-3	0.09	49	1379	18913	0.00	0.00	175	1846	137477	0.00	0.00
8/28/2006 15:30	152	28-August-06-3	0.09	69	1952	20485	0.00	0.00	119	1254	138941	0.00	0.00
9/5/2006 14:15	160	5-Sept-06-1	0.08	59	1666	22189	0.00	0.00	82	866	139939	0.00	0.00
9/11/2006 10:15	166	11-Sept-06-3	0.09	56	1573	23395	0.00	0.00	50	529	140459	0.00	0.00
9/18/2006 10:30	173	18-Sept-06-3	0.08	57	1602	24732	0.00	0.00	31	326	140819	0.00	0.00
9/25/2006 13:00	180	25-Sept-06-3	0.08	57	1608	26056	0.00	0.00	196	2067	141806	0.00	0.00
9/29/2006 14:00	184	29-Sept-06-3	0.09	62	1743	26960	0.00	0.00	200	2101	142931	0.00	0.00
10/2/2006 11:00	187	02-Oct-06-3	0.09	57	1594	27611	0.00	0.00	224	2361	143801	0.00	0.00
10/10/2006 11:40	195	10-Oct-06-3	0.08	60	1694	29126	0.00	0.00	242	2548	146064	0.00	0.00
10/16/2006 13:30	201	16-Oct-06-3	0.08	86	2422	30608	0.00	0.00	199	2095	147735	0.00	0.00
10/30/2006 10:15	215	30-Oct-06-3	0.08	113	3193	35240	0.00	0.00	50	525	149896	0.00	0.00
11/6/2006 15:00	222	06-Nov-06-3	0.08	100	2827	37680	0.00	0.00	46	484	150305	0.00	0.00
11/13/2006 11:55	229	13-Nov-06-3	0.08	126	3545	40177	0.00	0.00	49	514	150696	8.1	0.00
11/20/2006 14:15	236	20-Nov-06-3	0.07	167	4714	43142	0.00	0.00	40	420	151031	5.6	0.00
11/27/2006 14:30	243	27-Nov-06-3	0.07	193	5445	46620	0.00	0.00	18	189	151239	6.2	0.00
12/4/2006 12:30	250	04-DEC-06-3	0.07	157	4413	50054	0.00	0.00	11	112	151344	6.6	0.00
12/11/2006 15:30	257	11-DEC-06-3	0.07	69	1941	52337	0.00	0.00	3.6	37	151398	3.6	0.00
12/18/2006 14:00	264	18-DEC-06-3	0.06	70	1965	53526	0.00	0.00	1.8	19	151415	0.00	0.00
12/27/2006 11:00	273	27-DEC-06-3	0.00	34	953	53526	0.00	0.00	10	106	151415	0.00	0.00
1/2/2007 11:30	279	2-JAN-07-3	0.06	20	550	53920	0.00	0.00	5.2	54	151457	0.00	0.00
1/8/2007 15:00	285	8-JAN-07-3	0.06	16	463	54203	0.00	0.00	5.4	57	151488	0.00	0.00
1/15/2007 14:00	292	15-JAN-07-3	0.07	16	441	54538	0.00	0.00	5.4	56	151530	0.00	0.00
1/22/2007 17:00	299	22-JAN-07-3	0.08	17	469	54916	0.00	0.00	6.4	67	151581	0.00	0.00
1/29/2007 11:45	306	29-JAN-07-3	0.08	24	673	55366	0.00	0.00	1.8	19	151615	1.6	0.00
2/5/2007 14:00	313	5-feb-07-3	0.08	24	674	55941	0.00	0.00	11	120	151674	5.1	0.00
2/12/2007 16:00	320	12-feb-07-3	0.08	12	335	56370	0.00	0.00	3.4	36	151740	15	0.00
2/19/2007 16:30	327	19-feb-07-3	0.08	18	505	56697	0.00	0.00	3.5	37	151769	0.54	0.00
2/26/2007 12:00	334	26-feb-07-3	0.07	20	560	57083	0.00	0.00	5.0	53	151801	0.00	0.00
3/5/2007 11:30	341	5-March-07-3	0.06	29	813	57531	0.00	0.00	4.6	49	151834	0.00	0.00
3/8/2007 15:30	344	8-March-07-3	0.07	26	746	57786	0.00	0.00	2.4	25	151846	0.00	0.00
3/12/2007 15:00	348	12-March-07-3	0.07	25	692	58075	0.00	0.00	6.5	68	151865	0.00	0.00
3/15/2007 15:00	351	15-March-07-3	0.08	23	661	58310	0.00	0.00	16	168	151906	0.00	0.00
3/19/2007 15:30	355	19-March-07-3	0.07	28	782	58602	0.00	0.00	38	405	152022	0.00	0.00
3/26/2007 15:00	362	26-March-07-3	0.06	33	938	59115	0.00	0.00	27	288	152228	0.00	0.00
3/29/2007 15:30	365	29-March-07-3	0.07	59	1659	59524	0.00	0.00	82	863	152410	0.00	0.00
4/2/2007 15:30	369	2-April-07-3	0.08	102	2886	60603	0.00	0.00	232	2442	153194	0.00	0.00
4/5/2007 14:00	372	5-April-07-3	0.09	95	2665	61666	0.00	0.00	249	2617	154163	0.00	0.00
4/9/2007 16:50	376	9-April-07-3	0.06	93	2621	62632	0.00	0.00	223	2346	155070	0.00	0.00
4/16/2007 16:00	383	16-April-07-3	0.07	102	2873	64549	0.00	0.00	226	2376	156717	0.00	0.00
4/23/2007 16:00	390	23-April-07-3	0.04	141	3962	65961	0.00	0.00	138	1448	157507	0.00	0.00
4/30/2007 14:00	397	30-April-07-3	0.05	145	4078	68053	0.00	0.00	168	1770	158345	0.00	0.00
5/7/2007 11:00	404	7-May-07-3	0.04	134	3787	69498	0.00	0.00	562	5917	159757	0.00	0.00
5/14/2007 9:45	411	14-May-07-3	0.06	154	4346	71954	0.00	0.00	426	4484	162897	0.00	0.00
5/17/2007 13:30	414	17-May-07-3	0.06	156	4389	73084	0.00	0.00	406	4270	164030	0.00	0.00
5/22/2007 11:30	419	22-May-07-3	0.06	157	4417	75025	0.00	0.00	407	4281	165914	0.00	0.00
5/28/2007 11:00	425	28-May-07-3	0.09	158	4446	78377	0.00	0.00	408	4291	169156	0.00	0.00
6/4/2007 15:00	432	04-June-07-3	0.04	159	4474	79998	0.00	0.00	409	4302	170718	0.00	0.00
6/11/2007 12:00	439	11-June-07-3	0.07	160	4502	82968	0.00	0.00	410	4312	173568	0.00	0.00
6/18/2007 12:00	446	18-June-07-3	0.07	146	4099	86150	0.00	0.00	335	3531	176470	0.00	0.00
6/25/2007 13:00	453	25-June-07-3	0.07	137	3858	89135	0.00	0.00	310	3261	179018	0.00	0.00
7/2/2007 11:00	460	2-July-07-3	0.08	144	4068	92164	0.00	0.00	244	2571	181247	0.00	0.00
7/9/2007 15:30	467	9-July-07-3	0.05	156	4404	94520	0.00	0.00	262	2757	182729	0.00	0.00
7/16/2007 10:00	474	16-July-07-3	0.06	164	4614	97369	0.00	0.00	328	3451	184690	0.00	0.00
7/23/2007 14:00	481	23-July-07-3	0.06	192	5422	100279	0.00	0.00	244	2570	186436	0.00	0.00
7/30/2007 10:00	488	30-July-07-3	0.04	214	6022	102560	0.00	0.00	230	2422	187431	0.00	0.00
8/6/2007 14:30	495	6-Aug-07-3	0.08	176	4964	106846	0.00	0.00	342	3596	189778	0.00	0.00
8/13/2007 12:00	502	13-Aug-07-3	0.07	168	4741	110430	0.00	0.00	351	3695	192472	0.00	0.00
8/20/2007 14:30	509	20-Aug-07-3	0.06	209	5889	113805	0.00	0.00	305	3206	194662	0.00	0.00
8/27/2007 16:00	516	27-Aug-07-3	0.67	138	3897	147384	0.00	0.00	425	4471	221007	0.00	0.00
9/10/2007 16:00	530	10-sep-07-3	0.06	118	3320	151929	0.00	0.00	434	4570	226700	0.00	0.00
9/17/2007 16:00	537	17-sep-07-3	0.08	125	3530	154551	0.00	0.00	436	4585	230205	0.00	0.00
9/24/2007 16:00	544	24-sep-07-3	0.07	128	3618	157106	0.00	0.00	453	4768	233548	0.00	0.00
10/1/2007 16:00	551	1-oct-07-3	0.08	131	3692	160022	0.00	0.00	444	4673	237313	0.00	0.00
10/9/2007 11:30	559	9-oct-07-3	0.06	122	3439	162597	0.00	0.00	484	5094	240841	0.00	0.00
10/15/2007 15:00	565	15-oct-07-3	0.08	115	3231	164971	0.00	0.00	504	5305	244542	0.00	0.00
10/22/2007 14:00	572	22-oct-07-3	0.08	112	3152	167538	0.00	0.00	514	5414	248852	0.00	0.00

VFA Data for SRS™ Column

Date	Day	Sample ID	Flow Rate (ml/min)	Lactate (mg/L)	Lactate (µm)	Acetate (mg/L)	Acetate (µm)	Sun Acetate (µm)	Propionate (mg/L)	Propionate (µM)	Formate (mg/L)	Formate (µM)	Butyrate (mg/L)	Butyrate (µM)	Pyruvate (mg/L)	Pyruvate (µM)
3/21/2006	0	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3/22/2006	1	22-Mar-06-3	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/11/2006	46	11-May-06-3	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5/14/2006	49	14-may-06-3	0.05	5.3	59	3.4	58	5.7	0.52	7.1	0.00	0.00	0.00	0.00	0.00	0.00
5/16/2006	51	16-may-06-3	0.06	93	1049	14	231	31	9.7	133	0.00	0.00	0.46	5.2	0.24	2.8
5/18/2006	53	18-may-06-3	0.11	248	2787	0.00	0.00	67	2.7	37	0.00	0.00	0.00	0.00	29	336
5/24/2006	56	24-may-06-3	0.07	363	4079	75	1272	264	94	1291	0.60	13	289	3286	3.7	43
5/26/2006	58	26-may-06-3	0.08	305	3422	133	2260	668	153	2092	1.0	23	421	4782	1.2	14
5/29/2006	61	29-may-06-3	0.08	225	2532	96	1620	1297	107	1459	0.00	0.00	217	2463	0.00	0.00
5/31/2006	63	31-may-06-3	0.08	35	388	11	183	1510	41	568	0.24	5.3	57	647	0.00	0.00
6/5/2006	68	5-June-6-3	0.08	35	391	26	445	1695	35	476	0.00	0.00	21	243	0.00	0.00
6/9/2006	72	9-June-6-4	0.08	5.6	62	22	376	1879	46	631	0.00	0.00	1.1	12	0.33	3.8
6/15/2006	78	15-June-6-5	0.09	0.67	7.5	18	298	2133	49	671	0.00	0.00	0.64	7.3	0.00	0.00
6/16/2006	79	16-June-6-6	0.08	2.6	29	19	315	2170	53	724	0.00	0.00	2.8	32	0.00	0.00
6/19/2006	82	19-June-6-7	0.09	0.00	0.00	19	327	2290	61	838	0.00	0.00	0.51	5.8	0.00	0.00
6/21/2006	84	21-June-6-8	0.09	0.00	0.00	20	345	2374	52	707	0.00	0.00	0.00	0.00	0.00	0.00
6/23/2006	86	23-June-6-9	0.08	0.47	5.3	22	369	2458	50	688	0.00	0.00	0.49	5.5	0.00	0.00
6/29/2006	92	29-June-6-10	0.07	0.70	7.8	25	418	2711	46	634	1.36	30	0.42	4.8	0.00	0.00
7/4/2006	97	4-jul-06-3	0.08	0.00	0.00	24	405	2959	32	443	0.00	0.00	0.00	0.00	0.00	0.00
7/6/2006	99	6-Jul-06-3	0.09	0.00	0.00	29	487	3069	35	482	0.00	0.00	0.00	0.00	0.00	0.00
7/13/2006	106	13-Jul-06-3	0.08	0.00	0.00	47	791	3601	25	341	0.00	0.00	0.00	0.00	0.00	0.00
7/31/2006	124	31-july-06-3	0.08	0.00	0.00	108	1825	6474	12	162	0.00	0.00	0.50	5.6	0.00	0.00
8/8/2006	132	8-Aug-06-3	0.08	0.00	0.00	140	2377	8511	12	167	0.00	0.00	0.00	0.0	0.00	0.00
8/14/2006	138	14-Aug-06-3	0.09	0.00	0.00	226	3823	10809	16	214	0.00	0.00	0.83	9.4	0.00	0.00
8/21/2006	145	21-Aug-06-3	0.09	0.00	0.00	348	5899	15047	9.0	124	1.1	25	0.00	0.0	0.00	0.00
8/28/2006	152	28-Aug-06-3	0.09	0.00	0.00	432	7326	21262	7.4	102	0.00	0.00	0.00	0.0	0.00	0.00
9/5/2006	160	5-sept-06-3	0.08	0.00	0.00	487	8257	28651	11	156	0.00	0.00	3.7	42	0.00	0.00
9/11/2006	166	11-sept-06-3	0.09	0.00	0.00	536	9080	35294	38	520	0.00	0.00	17.4	197	0.00	0.00
9/18/2006	173	18-sept-06-3	0.08	0.00	0.00	357	6044	41655	14	192	0.00	0.00	8.0	90	0.00	0.00
9/25/2006	180	25-sept-06-3	0.08	2.6	30	1285	21779	52962	0.00	0.00	1.2	27	38	430	1.6	18
9/29/2006	184	29-sept-06-3	0.09	2.4	28	1623	27510	66121	29	401	2.7	60	46	520	2.2	26
10/2/2006	187	2-oct-06-3	0.09	2.4	27	1605	27206	77257	38	514	1.4	31	39	438	1.3	15
10/10/2006	195	10-oct-06-3	0.08	2.3	26	1307	22160	99934	31	424	1.0	21	30	336	1.4	17
10/16/2006	201	16-oct-06-3	0.08	2.5	28	1556	26374	117181	30	416	1.2	26	38	434	2.0	23
10/23/2006	208	23-oct-06-3	0.08	2.3	26	1428	24197	138147	32	433	0.91	20	40	448	3.0	34
10/30/2006	215	30-oct-06-3	0.08	0.27	3.1	1296	21963	157373	30	416	0.82	18	39	439	3.3	38
11/6/2006	222	6-nov-06-3	0.08	2.4	27	1169	19816	173837	44	606	1.7	38	0.00	0.00	5.9	68
11/13/2006	229	13-nov-06-3	0.08	0.00	0.00	1306	22132	190581	41	555	0.97	22	37	419	4.0	46
11/20/2006	236	20-nov-06-3	0.07	0.00	0.00	1299	22023	206217	35	479	1.0	23	30	346	2.9	33
12/11/2006	257	11-dec-06-3	0.07	0.00	0.00	725	12292	242566	4.3	59	2.0	44	0.00	0.00	2.0	23
12/18/2006	264	18-dec-06-3	0.06	0.00	0.00	682	11565	249891	38	524	9.0	199	5.2	58	0.00	0.00
12/27/2006	273	27-dec-06-3	0.00	0.00	0.00	754	12777	249891	4.1	56	1.9	42	0.00	0.00	1.9	22
1/2/2007	279	2-Jan-07-3	0.06	0.00	0.00	677	11476	256227	2.6	36	0.98	22	0.00	0.00	0.00	0.00
1/15/2007	292	15-Jan-07-3	0.06	4.8	54	342	5796	266449	23	321	1.0	22	25	284	0.00	0.00
1/22/2007	299	22-Jan-07-3	0.07	0.00	0.00	351	5954	270820	19	255	0.97	21	23	265	2.5	28
1/29/2007	306	29-Jan-07-3	0.08	0.00	0.00	235	3980	274880	11	148	0.86	19	20	232	1.4	16
2/5/2007	313	5-Feb-07-3	0.08	0.00	0.00	275	4658	278396	3.8	52	0.83	18	11	127	0.00	0.00
2/12/2007	320	12-Feb-07-3	0.08	0.00	0.00	288	4890	282438	1.6	22	1.7	39	1.3	15	0.00	0.00
2/19/2007	327	19-Feb-07-3	0.08	0.00	0.00	231	3919	286148	0.00	0.00	0.44	10	2.5	28	0.00	0.00
2/26/2007	334	26-Feb-07-3	0.08	0.00	0.00	176	2991	288756	0.00	0.00	0.33	7.3	0.00	0.00	0.00	0.00
3/5/2007	341	5-Mar-07-3	0.07	0.00	0.00	221	3751	291260	0.00	0.00	0.25	5.5	0.00	0.00	0.00	0.00
3/8/2007	344	8-Mar-07-3	0.06	0.00	0.00	117	1975	292108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/12/2007	348	12-Mar-07-3	0.07	0.00	0.00	180	3043	293141	0.00	0.00	0.27	6.0	0.00	0.00	0.00	0.00
3/15/2007	351	15-Mar-07-3	0.07	0.00	0.00	108	1823	293877	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/19/2007	355	19-Mar-07-3	0.08	0.00	0.00	178	3017	295004	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/26/2007	362	26-Mar-07-3	0.07	0.00	0.00	73	1238	296500	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3/29/2007	365	29-Mar-07-3	0.06	0.00	0.00	100	1696	296879	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/2/2007	369	2-Apr-07-3	0.07	0.00	0.00	281	4771	298227	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4/5/2007	372	5-Apr-07-3	0.08	0.00	0.00	467	7920	300440	0.00	0.00	0.48	11	0.00	0.00	0.00	0.00
4/9/2007	376	9-Apr-07-3	0.09	0.00	0.00	482	8168	304757	1.8	24.3	0.46	10	0.00	0.00	0.00	0.00
4/16/2007	383	16-Apr-07-3	0.06	0.00	0.00	255	4324	308621	0.00	0.0	0.00	0.00	0.00	0.00	0.00	0.00
4/23/2007	390	23-Apr-07-3	0.07	0.00	0.00	245	4156	311595	0.00	0.0	0.00	0.00	0.00	0.00	0.00	0.00
4/30/2007	397	30-Apr-07-3	0.04	0.00	0.00	23	393	312523	0.00	0.0	0.27	6.0	0.00	0.00	0.00	0.00
5/7/2007	404	7-May-07-3	0.05	0.00	0.00	0.00	0.00	312625	0.00	0.0	0.00	0.00	0.00	0.00	0.00	0.00
5/14/2007	411	14-May-07-3	0.04	0.00	0.00	0.00	0.00	312625	0.00	0.0	0.00	0.00	0.00	0.00	0.00	0.00
5/17/2007	414	17-May-07-3	0.06	0.00	0.00	0.00	0.00	312625	0.00	0.0	0.00	0.00	0.00	0.00	0.00	0.00
5/22/2007	419	22-May-07-3	0.06	0.00	0.00	0.00	0.00	312625	0.00	0.0	0.00	0.00	0.00	0.00	0.00	0.00
5/28/2007	425	28-May-07-3	0.06	0.00	0.00	0.00	0.00	312625	0.00	0.0	0.00	0.00	0.00	0.00	0.00	0.00
6/4/2007	432	4-june-07-3	0.09	0.00	0.00	0.00	0.00	312625	0.00	0.0	0.00	0.00	0.00	0.00	0.00	0.00
6/11/2007	439	11-june-07-3	0.04	0.00	0.00	0.00	0.00	312625	0.00	0.0	0.57	13	0.00	0.00	0.00	0.00
6/18/2007	446	18-june-07-3	0.07	0.00	0.00	0.00	0.00	312625	0.00	0.0	2.4	53	0.00	0.00	0.00	0.00
6/25/2007	453	25-june-07-3	0.07	0.00	0.00	0.00	0.00	312625	5.7	79	0.00	0.00	0.00	0.00	0.00	0.00
7/2/2007	460	2-July-07-3	0.08	0.00	0.00	0.00	0.00	312625	5.6	76	0.00	0.00	0.00	0.00	0.00	0.00
7/9/2007	467	9-July-07-3	0.05	0.00	0.00	0.00	0.00	312625	4.6	63	0.00	0.00	0.00	0.00	0.00	0.00
7/16/2007	474	16-July-07-3	0.06	0.00	0.00	0.00	0.00	312625	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7/23/2007	481	23-July-07-3	0.06	0.88	9.9	0.00	0.00	312625	0.00	0.00	0.82	18	0.00	0.00	0.00	0.00
7/30/2007	488	30-July-07-3	0.04	0.00	0.00	0.00	0.00	312625	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8/6/2007	495	6-Aug-07-3	0.08	0.00	0.00	0.00	0.00	312625	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8/13/2007	502	13-Aug-07-3	0.07	0.00	0.00	0.00	0.00	312625	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8/20/2007	509	20-Aug-07-3	0.06	5.9	67	0.00	0.00	312625	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8/27/2007	516	27-Aug-07-3	0.67	4.0	45	0.00	0.00	312625	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9/10/2007	530	10-Sep-07-3	0.06	0.00	0.00	0.00	0.00	312625	0.00	0.00	0.52	12	0.00	0.00	0.00	0.00
9/17/2007	537	17-Sep-07-3	0.08	0.00	0.00	0.00	0.00	312625	0.00	0.00	0.47	11	0.00	0.00	0.00	0.00
9/24/2007	544	24-Sep-07-3	0.07	0.00	0.00	0.00	0.00	312625	0.00	0.00	0.39	8.71	0.00	0.00	0.00	0.00
10/1/2007	551	1-Oct-07-3	0.08	0.00	0.00	0.00	0.00	312625	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10/9/2007	559	9-Oct-07-3	0.06	0.00	0.00	0.00	0.00	312625	0.00	0.00	1.1	24	3.0	35	0.00	0.00
10/15/2007	565	15-Oct-07-3	0.08	0.00	0.00	0.00	0.00	312625	0.00	0.00	0.29	6.4	0.00	0.00	0.00	0.00
10/22/2007	572	22-Oct-07-3	0.08	0.00	0.00	0.00	0.00	312625	0.00	0.00	1.4	31	1.01	11	0.00	0.00

pH and ORP Data for Control Column

Date	Time (Days)	pH	ORP
7/13/2006	6	6.53	95
7/18/2006	11	6.55	87
7/24/2006	17	6.52	78
7/31/2006	24	6.75	58
8/8/2006	32	6.65	57
8/14/2006	38	6.62	70
8/21/2006	45	6.65	80
8/28/2006	52	6.75	112
9/5/2006	60	6.89	83
9/11/2006	66	6.98	37
9/18/2006	73	7.10	35
9/25/2006	80	7.04	50
9/29/2006	84	6.89	62
10/2/2006	87	7.08	64
10/10/2006	95	6.98	55
10/16/2006	101	7.17	60
10/23/2006	108	7.10	40
10/30/2006	115	7.37	34
11/6/2006	122	7.22	31
11/13/2006	129	6.92	45
11/20/2006	136	6.94	21
11/27/2006	143	6.91	18
12/4/2006	150	6.93	21
12/11/2006	157	6.84	26
12/18/2006	164	6.53	28
12/27/2006	173	6.87	-9
1/2/2007	179	6.96	-1
1/8/2007	185	6.82	176
1/15/2007	192	6.96	9
1/22/2007	199	6.69	-22
1/29/2007	206	6.95	0
2/5/2007	213	6.99	-29
2/12/2007	220	6.86	-24
2/19/2007	227	6.97	145
2/26/2007	234	7.07	125
3/5/2007	241	7.13	161
3/12/2007	248	7.12	157
3/19/2007	255	6.74	160
3/26/2007	262	6.72	151
4/2/2007	269	7.05	-14
4/9/2007	276	7.02	-19
4/16/2007	283	6.98	-5
4/23/2007	290	6.70	63
4/30/2007	297	6.75	156
5/7/2007	304	6.74	156
5/14/2007	311	6.80	183
5/22/2007	319	6.87	178
5/28/2007	325	6.78	163
6/4/2007	332	6.64	165
6/11/2007	339	6.75	168
6/18/2007	346	6.67	161
6/25/2007	353	6.76	94
7/2/2007	360	6.87	162
7/9/2007	367	6.96	172
7/16/2007	374	6.78	148
7/23/2007	381	6.89	163
7/30/2007	388	6.85	167
8/6/2007	395	6.79	177
8/13/2007	402	6.69	156
8/20/2007	409	6.61	175
8/27/2007	416	6.63	37
9/10/2007	430	6.59	11
9/17/2007	437	6.69	68
9/24/2007	444	6.73	80
10/1/2007	451	6.61	161
10/9/2007	459	6.62	78
10/15/2007	465	6.55	54
10/22/2007	472	6.54	100

pH and ORP Data for nBA Column

Date	Time (Days)	pH	ORP
3/22/2006	1	6.99	--
3/24/2006	3	7.13	--
3/27/2006	6	6.87	--
3/29/2006	8	7.08	--
3/31/2006	10	7.05	--
4/6/2006	16	7.06	--
4/10/2006	20	7.03	--
4/19/2006	29	7.23	--
5/1/2006	36	6.88	--
5/10/2006	45	6.72	--
5/12/2006	47	6.88	--
5/15/2006	50	6.75	--
5/17/2006	52	6.86	--
5/18/2006	53	6.92	--
5/19/2006	54	7.03	--
5/24/2006	56	6.93	--
5/26/2006	58	6.84	--
5/29/2006	61	6.92	--
5/31/2006	63	6.70	--
6/2/2006	65	6.78	--
6/5/2006	68	6.58	--
6/7/2006	70	6.60	--
6/9/2006	72	6.37	--
6/12/2006	75	6.42	--
6/15/2006	78	6.32	--
6/16/2006	79	6.34	--
6/19/2006	82	6.47	--
6/21/2006	84	6.54	--
6/23/2006	86	6.47	--
6/26/2006	89	6.64	--
6/29/2006	92	6.57	--
7/4/2006	97	6.49	--
7/6/2006	99	6.67	3
7/10/2006	103	6.57	66
7/13/2006	106	6.70	71
7/18/2006	111	6.67	44
7/24/2006	117	6.63	35
7/31/2006	124	6.83	13
8/8/2006	132	6.73	15
8/14/2006	138	6.72	50
8/21/2006	145	6.66	72
8/28/2006	152	6.83	112
9/5/2006	160	6.98	72
9/11/2006	166	7.07	4
9/18/2006	173	7.07	11
9/25/2006	180	7.09	41
9/29/2006	184	6.92	57
10/2/2006	187	7.18	60
10/10/2006	195	7.01	42
10/16/2006	201	7.23	45
10/23/2006	208	7.12	22
10/30/2006	215	7.43	1
11/6/2006	222	7.15	4
11/13/2006	229	6.75	11
11/20/2006	236	6.65	-24
11/27/2006	243	6.67	-12
12/4/2006	250	6.56	-9
12/11/2006	257	6.51	10
12/18/2006	264	6.30	1
12/27/2006	273	6.75	-46
1/2/2007	279	6.80	-14
1/8/2007	285	6.88	--
1/15/2007	292	6.62	-11
1/22/2007	299	6.42	-27
1/29/2007	306	6.60	-27

pH and ORP Data for SRS™ Column

Date	Time (Days)	pH	ORP
3/21/2007	0	7.37	--
3/22/2006	1	6.97	--
3/24/2006	3	7.01	--
3/27/2006	6	6.81	--
3/29/2006	8	7.02	--
3/31/2006	10	6.99	--
4/6/2006	16	6.99	--
4/10/2006	20	7.00	--
5/1/2006	36	6.98	--
5/8/2006	43	6.99	--
5/12/2006	47	6.93	--
5/15/2006	50	6.90	--
5/17/2006	52	6.98	--
5/18/2006	53	6.93	--
5/19/2006	54	7.01	--
5/24/2006	56	6.93	--
5/26/2006	58	7.04	--
5/29/2006	61	6.91	--
5/31/2006	63	6.85	--
6/2/2006	65	6.81	--
6/5/2006	68	6.73	--
6/7/2006	70	6.69	--
6/9/2006	72	6.51	--
6/12/2006	75	6.58	--
6/15/2006	78	6.52	--
6/16/2006	79	6.59	--
6/19/2006	82	6.60	--
6/21/2006	84	6.61	--
6/23/2006	86	6.56	--
6/26/2006	89	6.68	--
6/29/2006	92	6.72	--
7/4/2006	97	6.65	--
7/6/2006	99	6.72	-18
7/10/2006	103	6.60	27
7/13/2006	106	6.64	32
7/18/2006	111	6.65	50
7/24/2006	117	6.64	9
7/31/2006	124	6.68	10
8/8/2006	132	6.69	-7
8/14/2006	138	6.69	8
8/21/2006	145	6.59	-10
8/28/2006	152	6.66	1
9/5/2006	160	6.77	-12
9/11/2006	166	6.70	-24
9/18/2006	173	6.77	-17
9/25/2006	180	6.65	-29
9/29/2006	184	6.56	-34
10/10/2006	195	6.61	-31
10/16/2006	201	6.81	-23
10/23/2006	208	6.64	-22
10/30/2006	215	6.72	-26
11/6/2006	222	6.54	-40
11/13/2006	229	6.39	-32
11/20/2006	236	6.30	-30
11/27/2006	243	6.32	-25
12/4/2006	250	6.38	-53
12/11/2006	257	6.59	-147
12/18/2006	264	6.51	-183
12/27/2006	273	6.77	-160
1/2/2007	279	6.83	-162
1/8/2007	285	6.73	-164
1/15/2007	292	6.89	-186
1/22/2007	299	6.72	-172
1/29/2007	306	6.89	-179
2/5/2007	313	6.89	-177
2/12/2007	320	7.00	-118
2/19/2007	327	6.78	-202
2/26/2007	334	6.95	-172
3/5/2007	341	6.97	-203
3/12/2007	348	6.93	-211
3/19/2007	355	6.90	-163
3/26/2007	362	6.87	-166
4/2/2007	369	6.97	-151
4/9/2007	376	6.89	-139
4/16/2007	383	6.84	-123
4/23/2007	390	6.92	-123
4/30/2007	397	6.97	-141
5/7/2007	404	7.04	-80
5/14/2007	411	7.06	-88
5/22/2007	419	7.01	-80
5/28/2007	425	7.08	-87
6/4/2007	432	7.04	-281
6/11/2007	439	7.15	-230
6/18/2007	446	6.97	-220
6/25/2007	453	7.11	-224
7/2/2007	460	7.17	-266
7/9/2007	467	7.28	-262
7/16/2007	474	7.10	-232
7/23/2007	481	7.03	-251
7/30/2007	488	7.00	-273
8/6/2007	495	7.03	-235
8/13/2007	502	7.00	-266
8/20/2007	509	6.92	-196
8/27/2007	516	6.95	-194
9/10/2007	530	6.99	-110
9/17/2007	537	6.96	-101
9/24/2007	544	6.99	-118
10/1/2007	551	6.79	161
10/9/2007	559	6.96	71
10/15/2007	565	6.89	43
10/22/2007	572	6.81	-9

Microbial Data for All Columns

Control Column						
Sample ID	**Sample Date**	**DAY**	***Dehalococcoides* 16S Gene Copies/L**	**QL**	***Dehalococcoides* VC Reductase Gene Copies/L**	**QL**
Control Column	October 2 to October 12 2006	97	Not detected	1 x 10^4/liter	--	--
Control Column	January 22 to February 2 2007	210	Not detected	4 x 10^3/liter	--	--
Control Column	April 19 to May 2 2007	300	6 x 10^3/liter(1)	2 x 10^4/liter	2 x 10^4/liter	2 x 10^4/liter
Control Column	July 27 to August 13 2007	402	2 x 10^4/liter(1)	2 x 10^4/liter	--	--
Control Column	Sept 24 07 - Oct 12 07	472	Not detected	4 x 10^3/liter	--	--

nBA Column						
Sample ID	**Sample Date**	**DAY**	***Dehalococcoides* 16S Gene Copies/L**	**QL**	***Dehalococcoides* VC Reductase Gene Copies/L**	**QL**
nBA Column	May 10, 2006	45	1 x 10^6	1 x 10^5/liter	4 x 10^5/liter	1 x 10^5/liter
nBA Column	June 2 - June 12 2006	75	Not detected	1 x 10^4/liter	--	--
nBA Column	June 28 to July 7 2006	100	Inconclusive	9 x 10^3/liter	2 x 10^5/liter	9 x 10^3/liter
nBA Column	October 2 to October 12 2006	197	Inconclusive	1 x 10^4/liter	--	--
nBA Column	December 4 to December 15 2006	261	9 x 10^3/liter	9 x 10^3/liter	1 x 10^4/liter	9 x 10^3/liter
nBA Column	January 22 to January 29 2007	306	5 x 10^2/liter(1)	9 x 10^3/liter	7 x 10^3/liter	9 x 10^3/liter

SRS™ Column						
Sample ID	**Sample Date**	**DAY**	***Dehalococcoides* 16S Gene Copies/L**	**QL**	***Dehalococcoides* VC Reductase Gene Copies/L**	**QL**
SRS™ Column	May 10, 2006	45	Inconclusive	1 x 10^4/liter	2 x 10^5/liter	1 x 10^5/liter
SRS™ Column	June 2 - June 12	75	Not detected	1 x 10^4/liter	--	--
SRS™ Column	June 28 to July 7	100	Not detected	1 x 10^4/liter	--	--
SRS™ Column	October 2 to October 12	197	2 x 10^4/liter	1 x 10^4/liter	--	--
SRS™ Column	November 3 to November 14 2006	230	1 x 10^3/liter	4 x 10^3/liter	4 x 10^2/liter	4 x 10^3/liter
SRS™ Column	December 22 2006 to January 2 2007	279	1 x 10^8/liter	4 x 10^3/liter	1 x 10^6/liter	4 x 10^3/liter
SRS™ Column	February 2 to February 16 2007	324	1 x 10^8/liter	4 x 10^3/liter	8 x 10^7/liter	4 x 10^3/liter
SRS™ Column	March 19 to April 5 2007	372	2 x107/liter	2 x 10^4/liter	7 x 10^7/liter	2 x 10^4/liter
SRS™ Column	April 19 to May 2 2007	400	1 x107/liter	2 x 10^4/liter	4 x 10^7/liter	2 x 10^4/liter
SRS™ Column	June 15 to June 29 2007	453	2 x107/liter	2 x 10^4/liter	6 x 10^7/liter	2 x 10^4/liter
SRS™ Column	July 27 to August 13 2007	502	8 x107/liter	2 x 10^4/liter	1 x 10^8/liter	2 x 10^4/liter
SRS™ Column	October 12 to October 25 2007	572	6 x 10^8/liter	4 x 10^3/liter	7 x 10^8/liter	4 x 10^3/liter