SETH BULLOCK RAMALEY
Feasibility Investigation for Natural Attenuation of a Shallow Chlorinated Solvent Plume at the Former Naval Training College, Orlando, Florida
(Under the Direction of VALENTINE NZENGUNG)

A two layer site-conceptual model is proposed to explain the attenuation of chlorinated solvents at the NTC, Orlando site. Microcosm biodegradation experiments investigated the rates and extent of Perchloroethylene (PCE), Trichloroethylene (TCE), and Dichloroethylene (DCE) degradation by indigenous microbial communities in NTC, Orlando site sediments. Microcosms amended with different carbon substrates (acetate, lactate, corn oil, molassess, a polylactate ester HRC®, and yeast extract) were used to determine if in-situ biodegradation could be enhanced and implemented in the clean up plan for the site. The biodegradation experiments consisted of both batch vials and continuously stirred bioreactor vessels containing site sediment and site groundwater. Provided with extra carbon sources, the chloroethenes were dehalogenated to ethene. Degradation patterns suggest dehalorespirating processes are responsible for biodegradation in the source zone and co-metabolic processes exist away from the source zone. Biodegradation was enhanced by the additions of carbon sources in both the surface and deep sediments, with the best results obtained by using amendments of acetate or lactate with yeast extract. The results of this laboratory feasibility study warrant a scale up field test for enhanced bioremediation as a remedial technology for the site.

INDEX WORDS: Natural Attenuation, Enhanced Bioremediation, Perchloroethylene, Trichloroethylene

FEASIBILITY INVESTIGATION FOR MONITORED NATURAL ATTENUATION OF A SHALLOW CHLORINATED SOLVENT PLUME AT THE FORMER NAVAL TRAINING CENTER, ORLANDO, FLORIDA

by

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DEDICATION

This thesis is dedicated to

Meredith Anne Jackson

for her unconditional love and support.

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CHAPTER 1

INTRODUCTION

Widespread usage, historic disposal practices, accidental spills, and a poor understanding of the fate of chlorinated organic solvents and petroleum hydrocarbons in the environment have led to widespread contamination at United States Department of Defense (DOD) and industrial facilities (ESTCP. 1998). The Environmental Protection Agency (EPA) has estimated that groundwater contamination has occurred at approximately 330,000 sites: including 2000 Superfund national priority sites, between 1500 and 3000 Resource Compensation and Recovery Act (RCRA) sites, 295,000 leaking underground fuel tank sites, 7300 Department of Defense (DOD) sites, 4000 Department of Energy (DOE) sites, 350 other federal sites, and 20,000 state sites (U.S. EPA, 1993). It is estimated that 373 billion to 1.694 trillion dollars needs to be spent in the next three decades to clean up hazardous waste sites in the United States of America (Russell et al., 1991). Chlorinated solvents, primarily tetrachloroethene (PCE) and trichlorethene (TCE), are the most frequently detected contaminants in groundwater at these sites. PCE and TCE are among the top ten contaminants on EPA's list of priority pollutants. Both compounds are suspected carcinogens (National Research Council, 1994). PCE and TCE are also among fourteen volatile organic compounds regulated under the Safe Drinking Water Act Amendments of 1986.

Field and laboratory biodegradation of chlorinated ethenes (PCE and TCE) in anaerobic environments has been well documented. Technologies and regulatory

approaches that stress managing contaminants in place by taking advantage of natural attenuation processes have resulted in remediation costs that are lower than those associated with traditional pump and treat systems and soil vapor extraction systems. As a result, monitored natural attenuation (also referred to as intrinsic bioremediation) has received much attention as an effective, low-cost, remedial technology (Brady et al. 1998). Natural attenuation is defined as, "The biodegradation, dispersion, dilution, sorption, volatilization, and /or chemical and biochemical stabilization of contaminants to effectively reduce contaminant toxicity, mobility, or volume to levels that are protective of human health and the ecosystem"(United States Environmental Protection Agency, U.S. EPA, 1997). The processes of natural attenuation can reduce the risk posed by site contaminants in three ways: 1) the contaminant can be converted to a non-toxic form through destructive processes such as biodegradation or abiotic transformations, 2) groundwater concentration levels can be reduced by dilution or dispersion, and 3) contaminant mobility and bioavailability can be reduced by sorption to the aquifer matrix (U.S. EPA, 1997). At most hazardous waste sites, natural attenuation occurs to varying degrees depending on the site-specific physical, chemical, and biological characteristics of the soil and groundwater. However, at circumneutral pH, microbial induced aerobic and anaerobic biodegradation of the chlorinated aliphatics account for the most significant processes of natural attenuation (Lovely et al., 1994; Schwarzenbach, 1993; Dominico and Schwartz, 1998; EPA, 1997; Wiedemeier et al., 1999).

Monitored natural attenuation is defined as, "The use of natural attenuation processes within the context of a carefully controlled and monitored site cleanup approach that will reduce the contaminant concentrations to levels that are protective of

human health and the environment within a reasonable time frame" (U.S. E.P.A., 1997). The time frame to cleanup the site should not be excessive compared to that required for other remedies and ensures that sensitive receptors are not affected. Monitored natural attenuation is estimated to be implemented as the sole remedial technology at twenty-percent of all chlorinated solvent sites and will possibly serve as a part of the remedy at an additional fifty-percent of all chlorinated solvent sites (Ellis et al. 1996).

Three types of site-specific data are needed to evaluate the efficiency of monitored natural attenuation as a remedial technology because of the site-specific nature of in-situ processes (US EPA, 1997). The first type of evidence used is historical data showing plume stabilization and/or observed reduction in contaminant concentrations along the flow path down gradient from the source of contamination. This information shows that the contaminant plume is being attenuated but does not indicate that the contaminant mass is being destroyed (Weidemeier et al, 1999). A second type of evidence is used to determine that the contaminant mass is being destroyed and not just diluted or sorbed to the aquifer matrix. This involves a documented loss of the contaminant mass at the field scale by either chemical, geochemical data, or biological decay rate data. Biogeochemical indicators such as electron acceptors and donors are measured to support this second type of evidence. If the first two types are inadequate, a third type consisting of microbial laboratory data supporting degradation and decay rates can be used. In addition to the three types of evidence, solute transport models can be used to illustrate evidence that supports natural attenuation (Wiedemeier, et al., 1999).

Monitored natural attenuation is considered inadequate or limited if the three types of evidence show that degradation rates are slow and incomplete. Insufficient

levels of nutrients, fermentable substrates, or electron acceptors limit biodegradation. Enhanced in-situ biodegradation is one way to overcome this limitation. Supplying excess nutrients and substrates to the subsurface can stimulate biodegradation by the microbial consortia to effectively degrade contaminants. Enhanced biodegradation is a promising in-situ technology for the bioremediation of chlorinated solvents (ESTCP. 1998).

Study Site

The study area within Area C (also referred to as Operable Unit 4, OU4) of the former Naval Training Center (NTC) is located in Orange County, Orlando, Florida (Figure 1-1, 1-2,1-3). Ground water investigations in 1996 and 1997 revealed concentrations of chlorinated ethenes above Florida environmental protection department (EPD) maximum contaminant levels (MCLs). The site is characterized by a chlorinated solvent plume that extends from four to forty-five feet below land surface and a type II environment (systems that are anaerobic due to naturally occurring organic carbon; Wiedemeier et al., 1999). The plume originates near building 1100 and flows toward Lake Druid with anaerobic degradation products of PCE, such as TCE, cis- 1,2-Dichloroethene (cDCE), and vinyl chloride (VC) present within the plume.

Research Objectives

The identification of anaerobic degradation products of PCE provide evidence that natural attenuation is occurring at OU4. However, installation of two recirculating wells near the lake in 1998 complicated the interpretation of the ground

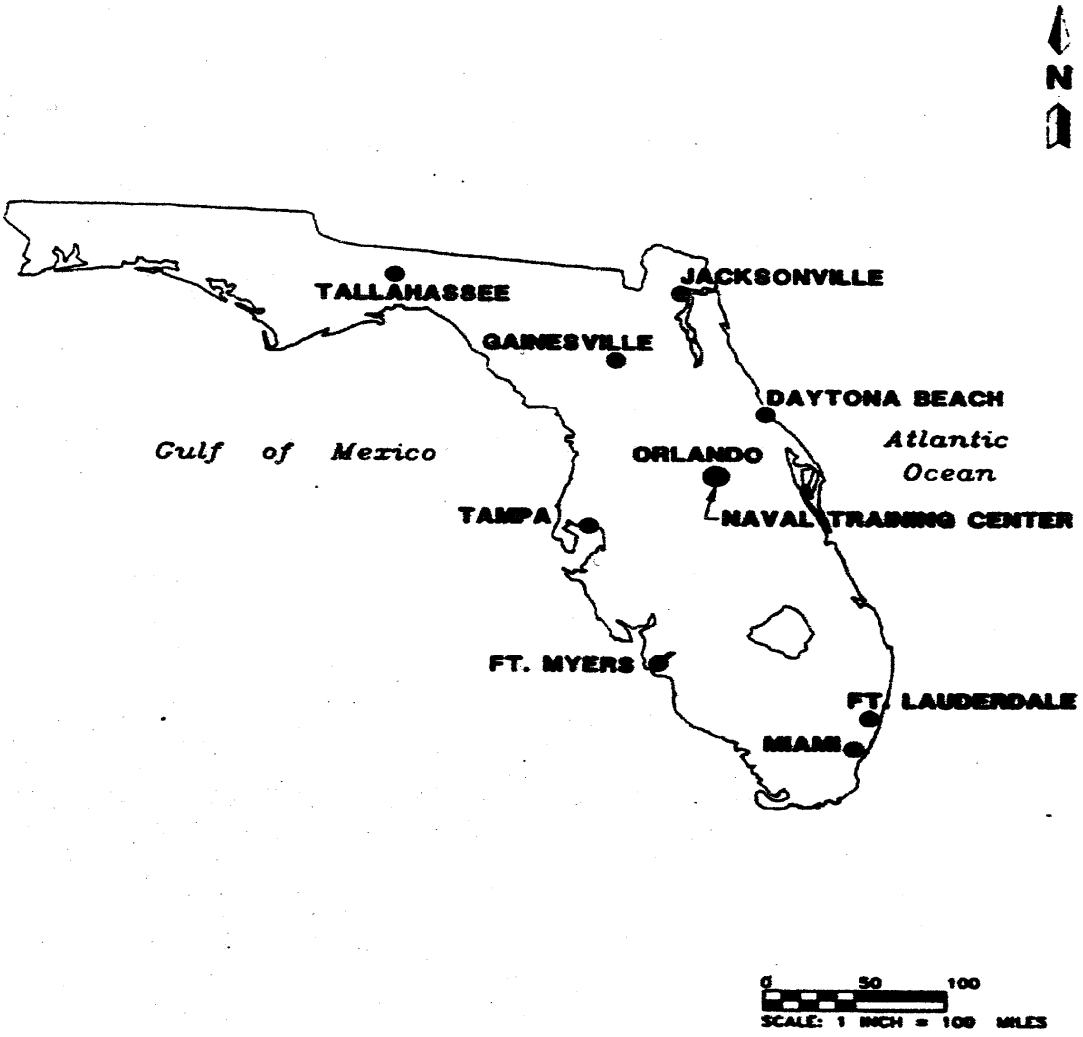


Figure 1.1. Location of the former Naval Training Center (NTC), Orlando, Florida (Figure from Harding Lawson & Associates (HLA), 1998).

Figure 1.2. Location of Area C within the former NTC complex

(Figure from HLA, 1998).

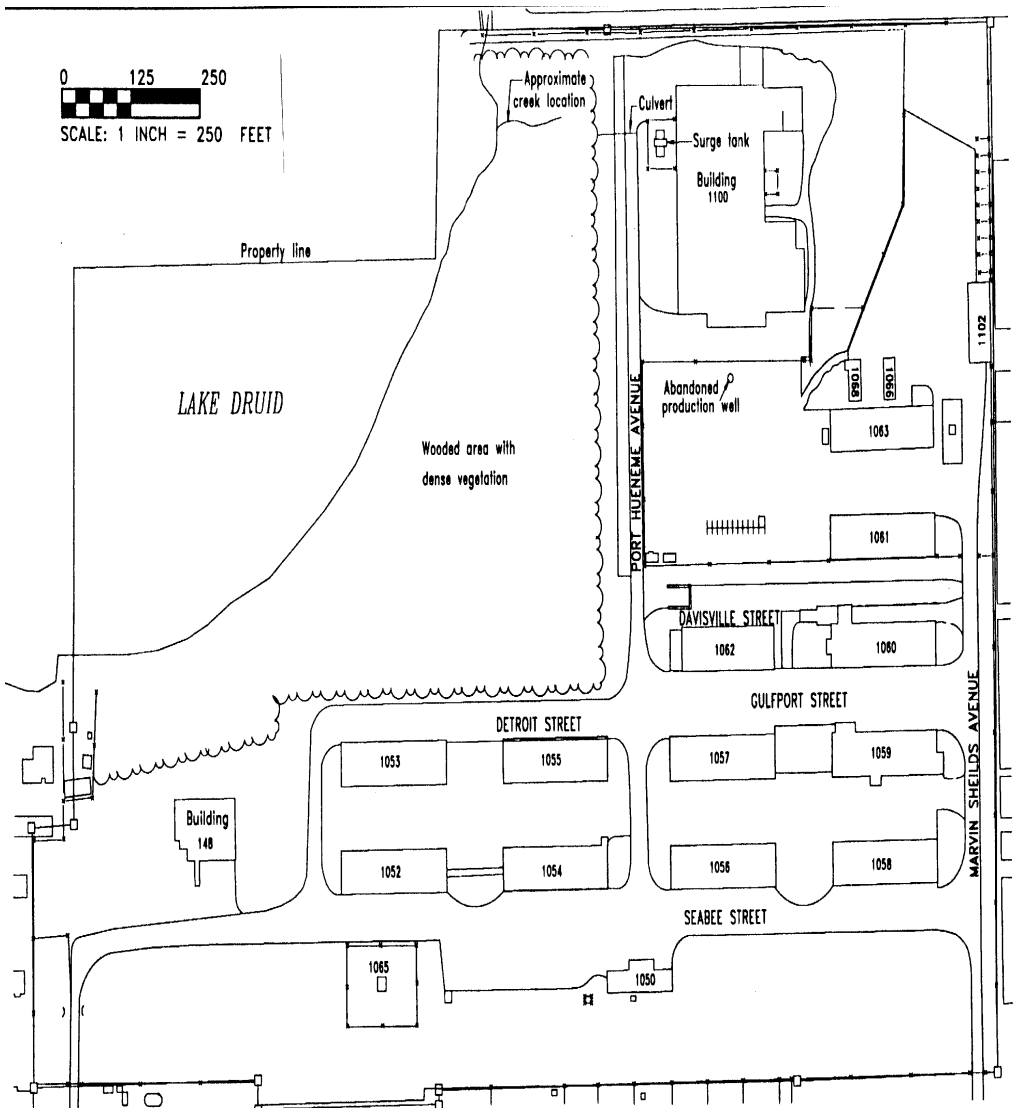


Figure 1.3. Detailed map of Area C of the former NTC, Orlando, Florida.

water data. The treatment system obscured the extent to which natural attenuation has decreased the ground water contaminant concentrations. Hence, field data demonstrating decay rates for long-term predictions of the efficacy of monitored natural attenuation (MNA) cannot be obtained from the existing site monitoring data.

This research determined if favorable geochemical conditions and significant biodegradation exist to support monitored natural attenuation as a remedial technology for the OU4 at the former NTC site in Orlando. Laboratory biodegradation experiments were conducted using sediment from site cores and site groundwater. This feasibility study involved the determination of biodegradation rates of PCE and its byproducts, biodegradation pathways, and investigation of which electron donors and nutrient combination that can enhance biodegradation. Sorption coefficients were determined for the purpose of refining the input parameters to the ground water model of OU4 being developed by the EPA/NERL-Athens as part of this research project.

CHAPTER 2

LITERATURE REVIEW

Naturally occurring biological processes can degrade organic contaminates in situ or during transport in the subsurface under aerobic and/or anaerobic conditions. Microorganisms catalyze the degradation reactions to obtain energy for growth, reproduction and cell maintenance (Schwarzenbach et al., 1993; Wiedemeier, 1999; Sewell and Gibson, 1997). Useable energy is recovered through a series of redox reactions where the microorganisms act as "electron transport mediators" (Figure 2.1; Schwarzenbach et al., 1993). Biologically mediated electron transfer couples the oxidation of an electron donor (organic compound) with the reduction of an electron

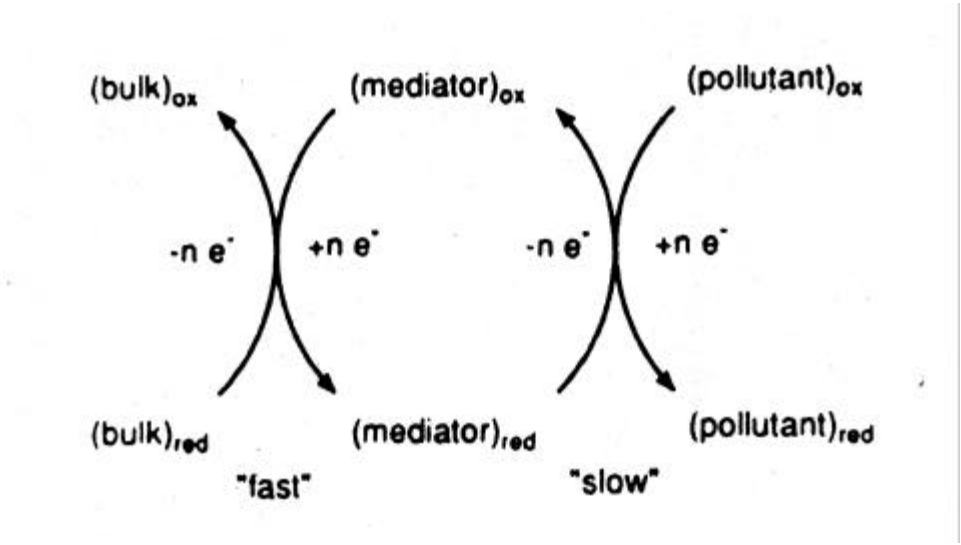


Figure 2.1. Illustration of Microorganisms acting as electron transport mediators (Figure from Shwarzenbach et al., 1993).

acceptor (inorganic or organic) and results in the production of useable energy for microbial consortia. The bulk electron donor acts as a fuel source for the reactions and the reactions proceed as long as there is a source of electrons. Fuel sources can be native organic carbon, co-contaminants such as fuel hydrocarbons, or organic compounds such as acetate and lactate. In aerobic environments, the chlorinated solvents act as electron donors and under anaerobic environments the chlorinated solvents act as electron acceptors.

There are two primary mechanisms involved in the biodegradation of chlorinated organic solvents (Table 1). First, biodegradation may be growth-linked and provides carbon and energy to support growth when the compound is used as primary substrate and directly oxidized via Mechanism 1. When the chlorinated solvent is used as a primary substrate for energy, it can be aerobically mineralized or anaerobically dechlorinated by halorespiration (Hollinger and Schumacher, 1994). Secondly, biodegradation may not be growth linked but rather maybe used to provide energy for the cells to maintain their viability when the compound is degraded by fortuitous co-metabolic reactions via Mechanism 2 (Suthersan, 1997; Adriaens and Vogel, 1995). Co-metabolism is a process where the organism receives no direct benefit from the degradation of the organic compound (McCarty and Semprini, 1994). There are two types of co-metabolic reactions: Co-oxidation and reductive dechlorination. Co-metabolic reactions tend to be incomplete and can possibly lead to an accumulation of more toxic daughter products. To date, vinyl chloride (VC) and dichloethene (cis/trans) are the only chlorinated solvents that can be degraded by all aerobic and anaerobic pathways (Wiedemeier et al. 1999).

Table 2.1 Summary of the degradation pathways for selected chlorinated organics (Wiedemeier et al., 1999; Young and Cerniglia, 1995).

		Mechanism 1			Mechanism 2	
Compound	Acronym	Halorespiration	Direct Aerobic Oxidation	Direct Anaerobic Oxidation	Aerobic Cometabolism	Cometabolic Reduction
Tetrachloroethene	PCE	X				X
Trichloroethene	TCE	X			X	X
Dichloroethene	DCE	X	X	X	X	X
Vinyl Chloride	VC	X	X	X	X	X

Reductive Dechlorination

The predominant mechanism for the biodegradation of chlorinated solvents in anaerobic environments is reductive dechlorination, whether the organic compound is a primary electron acceptor (haleorespiration) or is co-metabolized. Before 1994, reductive dechlorination was thought to be 'strictly' a co-metabolic process (Hollinger and Schumacher, 1994: Wiedemeier et al., 1999). However, metabolic energy can be produced when the chlorinated solvents are used as a primary electron acceptor. During reductive dechlorination, the chlorinated solvents act as an electron acceptor and a chlorine atom is replaced with a hydrogen atom (Figure 2.2; RTDF, 1997; Wiedemeier et al., 1999).

The oxidation-redox potential (ORP) affects the thermodynamics of reductive dechlorination. Microorganisms will facilitate only those oxidation-reduction reactions that have a net yield of energy. For reductive dechlorination to be thermodynamically favorable the redox potential of the environment must be sufficiently low, thereby

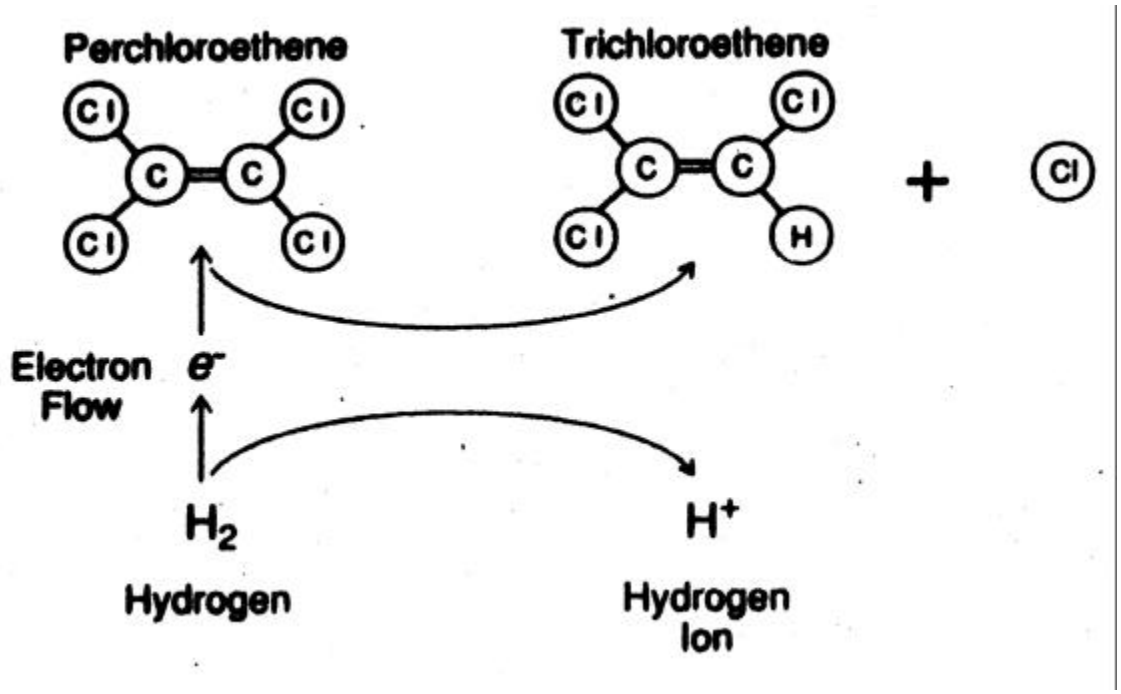


Figure 2.2. Reductive dechlorination of PCE to TCE

(Wiedemeier et al. 1998).

excluding the presence of oxygen and nitrate as terminal electron acceptors (EPA, 1997). Further, the presence of nitrate may have an inhibitory effect on PCE dechlorination (Luijten et al., 2000). The redox potential range for reductive dechlorination is shown in figure 2.3

Research has shown that PCE can be sequentially degraded to ethene (Figure 2.4; Freedman and Gossett, 1989; Vogel et al., 1987; McCarty and Semprini, 1994: Barrio-Lage et al., 1986; De Bruin et al., 1992). Of the three possible DCE isomers formed as metabolites, cis-1, 2-DCE predominates over trans-1, 2-DCE and 1,1-DCE in biodegradation reactions (RTDF, 1997). Although specific single strains of bacteria have been shown to sequentially degrade PCE to ethene in laboratory settings, microorganisms in the subsurface are believed to exist as a very tightly linked symbiotic microbial

consortium (Cabirol et al., 1998; Sewell and Gibson, 1997). Degradation of PCE is often not attributed to a single type of microorganism, rather different populations in a consortium perform different steps along the pathway from PCE to ethene (Flynn et al., 2000). The more chlorinated the organic compound is, the more susceptible it is to reduction. Further, the rate of the reaction slows as each chlorine atom is removed and the intermediate daughter products may persist longer in the environment than the parent compound (Suthersan, 1997). Studies have indicated that the final dehalogenation reaction of VC is rate limiting and may result in the accumulation of VC.

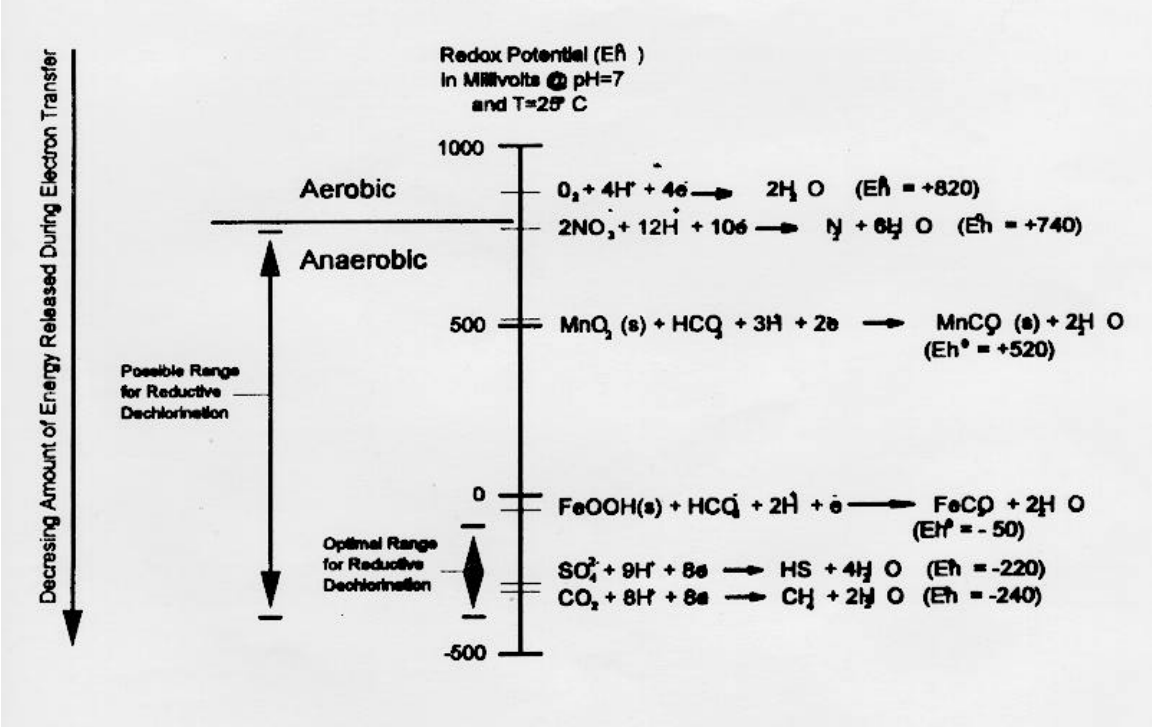


Figure 2.3. Optimal redox range for reductive dechlorination and redox ranges for the important electron donors and electron acceptors (RTDF, 1997).

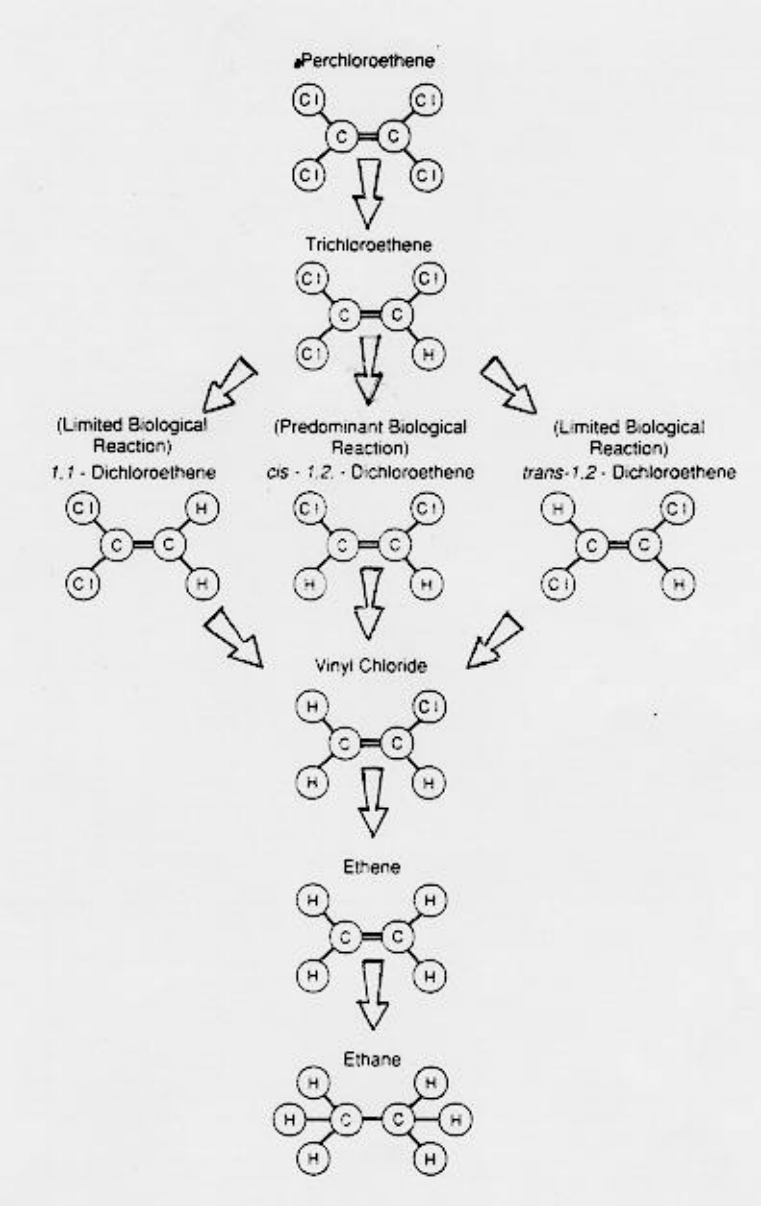


Figure 2.4. Illustration of the possible degradation pathway of PCE to ethane (Vogel et al., 1987).

DIRECT AEROBIC/ANAEROBIC OXIDATION

The most significant biological mechanism for the degradation of chlorinated solvents is when they are used as a primary substrate. In direct oxidation reactions, the chlorinated solvent acts as an electron donor and the microorganism uses molecular oxygen as an electron acceptor. Microorganisms obtain energy and organic carbon from the degraded chlorinated solvent. The more chlorinated compounds, PCE, carbon tetrachloride (CT), and hexachloroeethane (HCA), are neither susceptible to aerobic oxidation nor are they degraded under anaerobic oxidizing conditions when used as a primary substrate (Weidemeier et al., 1999). TCE undergoes slow aerobic degradation to trichloroethanol and then to acetic acid, but the reaction is not thermodynamically favorable. Therefore, discussion of aerobic oxidation and mineralization will focus on DCE and VC.

Rates of aerobic oxidation are more rapid for the less chlorinated organics (DCE and VC) when compared to their reductive dechlorination rates. It has been well documented in literature that VC is oxidized directly to carbon dioxide and water (Bradley and Chappelle, 1998; McCarty and Semprini, 1994; Hartmans and de Bont, 1992; Davis and Carpenter, 1990). Aerobic oxidation of cDCE has been speculated by Bradley and Chappelle (1998). However, Bradley and Chappelle (1998) could not ascertain whether DCE was reduced to VC and then direct oxidization of VC produced carbon dioxide or if direct oxidation of DCE occurred to produce carbon dioxide.

Microorganisms can anaerobically mineralize VC and DCE in the presence of a complexed, bioavailable electron acceptor such as FE-EDTA (Bradley and Chapelle 1996 and 1997). Studies by Bradley and Chapelle (1996,1997,1998) have focused on the

possible oxidation of VC and DCE when they are used as a primary growth substrate under anaerobic environments. Their results show VC and DCE mineralization under methanogenic and iron reducing conditions in anaerobic streambed sediments without the accumulation of ethene or ethane and a build up of carbon dioxide. Decreases of VC and DCE concentrations corresponded quantitatively to the production of carbon dioxide.

HALORESPIRATION

Halorespiration, also referred to as dehalorespiration, occurs when the organic compound acts as an electron acceptor (primary growth substrate) during reductive dechlorination. During halorespiration, the chlorinated organic compounds are used directly by microorganisms, termed halorespirators, as an electron acceptor while dissolved hydrogen serves as an electron donor (Wiedemeier et al, 1999; DiStefano et al., 1992):

$$H_2 + C\text{-}Cl = C\text{-}H + H^+ + Cl^-$$

where C-Cl represents the chlorinated compound. Halorespiration occurs as a two-step process which results in the interspecies hydrogen transfer by two distinct strains of bacteria. In the first step, bacteria ferment organic compounds to produce hydrogen. During primary or secondary fermentation, the organic compounds are transformed to compounds such as acetate, water, carbon dioxide, and dissolved hydrogen. Fermentation substrates are either biodegradable, nonchlorinated contaminants (i.e., BTEX- benzene, toluene, ethyl benzene, and xylenes; or acetone) or naturally occurring organic compounds. In the second step, the non-fermenting microbial consortia utilize the hydrogen produced by fermentation for halorespiration (Wiedemeier et al., 1999; Fennel et al., 1997). Denitrifiers, iron reducers, sulfate reducers, methanogens, and

halorepirators can all utilize hydrogen as an electron donor (Weidemeier et al., 1999). Figure 2.5 shows which reducing environment is favored depending on the hydrogen concentration. Although compounds produced during fermentation other than hydrogen have been demonstrated to drive halorespiration (Gibson and Sewell, 1992), hydrogen appears to be the most important electron donor for this process (Maymo-Gatell et al., 1997; Fennell et al., 1997). H_2 is able to serve as an electron donor for reductive dechlorination of PCE to VC and eventually to ethene in cultures provided with the proper nutritional supplements (Maymo-Gatell et al., 1995; DiStefano et al., 1992).

COMETABOLIC CO-OXIDATIONS

The widespread occurrence of chlorinated aliphatics, such as PCE and TCE, in groundwater environments reflects their relative resistance to microbial degradation under aerobic conditions (Chapelle, 1993). Highly chlorinated compounds such as PCE and TCE exist in very oxidized states and further oxidation under aerobic environments is thermodynamically unfavorable. Therefore, chlorinated solvents like PCE and TCE can persist and accumulate in aerobic groundwater environments. The chlorinated solvents contain "little useful energy" for microorganisms to exploit via oxidation (Wiedemeier et al., 1999). However, microorganisms are able to catalyze the reactions by cometabolism, the fortuitous oxidation of the chlorinated solvent (Adrains and Vogel , 1995).

A well studied co-metabolic pathway where the growth substrate is unrelated to the chlorinated compound is the methane monooxygenase (MMO) enzyme system. Oxidation of TCE, DCE, and VC via the MMO system has been demonstrated (Wilson and Wilson, 1985; Adriaens and Vogel, 1995; Fox et al., 1990). Of the two types of MMO, membrane bound MMO and soluble MMO, expression of the latter is

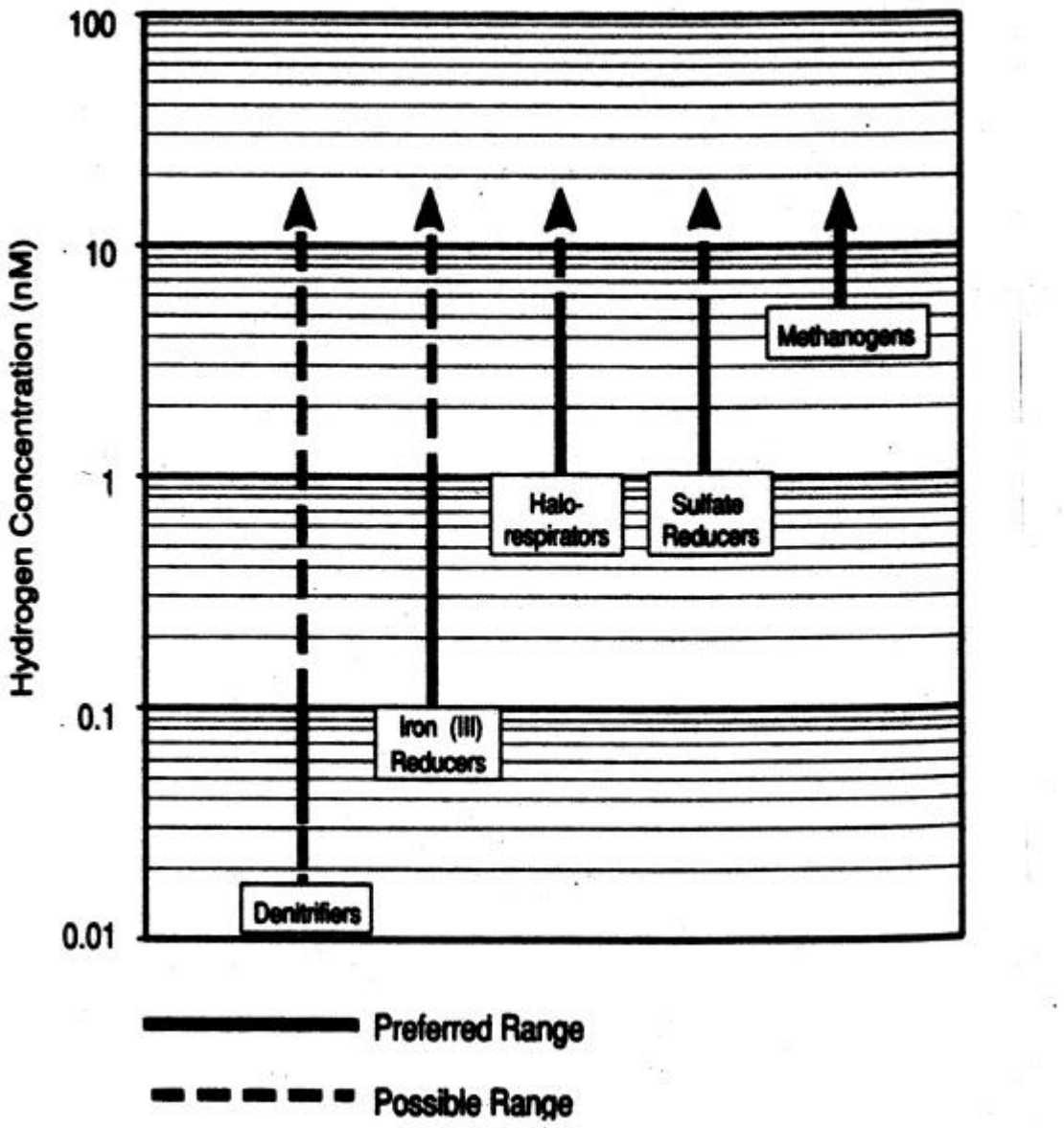


Figure 2.5. Range of hydrogen concentrations for the different reducing environments (Modified from Wiedemeier et al. 1998).

required for high rates of TCE oxidation (Tsien et al., 1989). The aerobic co-metabolic biodegradation of these compounds proceeds via an unstable epoxide intermediate that spontaneously decomposes to water, carbon dioxide, and chloride or other organic by-products such as acetate (Roberts et al., 1989). However, because methane availability in aerobic aquifers is limited, metaoxidates are too low to affect TCE degradation in most aquifers (Chappelle, 1999). Another oxygenase, toluene dioxygenase, has a broad substrate specificity (over 40 known substrates) and has been used for TCE, cis-1,2-DCE, trans-1,2,DCE, and 1,1-DCE oxidation (Nelson et al., 1988; Wackett and Gibson, 1988). Data shows oxidation by toluene dioxygenase proceeds via a symmetrical iron bridged dioxygen intermediate that yields formate and glyoxylate and argues against an epoxide or dihydroxy intermediate (Miller and Guengrich, 1982).

Taking advantage of the broad substrate oxygenase enzymes, studies have shown degradation of the chlorinated aliphatics by aerobic microorganisms using methane or natural gas (Wilson and Wilson, 1985), propane (Wackett et al., 1989), toluene or phenol (Nelson et al., 1987; Nelson et al., 1986), and ammonia (Arciero et al., 1989). Microcosm and pilot field studies at Moffet Air field by Hopkins et al.(1993) demonstrated phenol and toluene amended microcosms were 90 % effective in reducing 1,2-cis-DCE concentrations in groundwater and 60 to 70 % effective in removing TCE from groundwater. Methane fed microcosms were the most effective in removing 1,2-trans-DCE while ammonia amended microcosm were the least effective. McCarty et al. (1998) provided a field scale study of aerobic co-metabolism of TCE. Injections of toluene, oxygen, and hydrogen peroxide resulted in 98 % removal efficiency of TCE. A problem arises with bacterial oxygenases when dealing with highly chlorinated aliphatics

such as PCE. Soluble MMO and toluene dioxygenase do not oxidize PCE (Arciero et al., 1989). Special considerations and monitoring have to take place when using aerobic co-metabolic processes as remedial technologies because co-metabolic processes sometimes only partially transform the parent chemical and toxic daughter products accumulate, such as chloral or vinyl chloride (Suthersan, 1997).

COMETABOLIC REDUCTIVE DECHLORINATION

Cometabolic reduction of the chlorinated solvents is catalyzed by the reductive dehalogenase and reductase enzymes produced by microorganisms (Neumann et al., 1996; Schwarzenbach et al., 1993). Cometabolic degradation occurs under iron reducing, manganese reducing, sulfate reducing, and methanogenic environments (EPA. 1997). Anaerobic bacteria have enzymes that use a variety of electron acceptors: Fe(III) to Fe(II), Mn (IV) to Mn (II), sulfate to sulfide or hydrogen sulfide, and carbon dioxide to methane (Reactions are summarized in Figure 2.4). Electrons are transferred to dissolved contaminants coincidentally during the reduction processes. These degradation reactions are often incomplete resulting an accumulation of toxic daughter products.

CHAPTER 3

SITE BACKGROUND, GEOLOGY, HYDROGEOLOGY, AND NATURAL ATTENUATION ASSESSMENT

Site Background

The former Naval Training College (NTC) in Orlando, Florida was constructed in 1940 as part of the Orlando Municipal Airport. The U.S. Army Air Corps conducted operations at the Main Base and Area C from 1940 to 1947. In 1947, the U.S. Air force assumed command of the facilities as the Orlando Air Force Base (OAFB). The base was deactivated in 1949 until the Military airlift Command took full jurisdiction of the base in 1953. The base was designated as a naval training college in 1968 after the Navy ceased it operations at OAFB, Area C, and Herndon Annex. Area C, the focus of the investigations, served as a supply center for the NTC, Orlando, and includes Study Area (SA) 12, SA 13, and SA 14. The laundry cleaning facility of SA 13 remained active until the fall of 1994.

Historical records show that SA 12 has been used to store scrap items such as transformers and vehicles. SA 12 was also used to store small quantities of hazardous waste between 1959 and 1985. Wastes that were stored include the following: paints, insecticides, asbestos, solvents (including trichloroethene [TCE] and methyl-ethyl ketone [MEK]), ammonium hydroxide, sodium sulfate, and mercury. SA 13 includes building 1100 and building 1101. Building 1101 was a boiler house and was completely removed in the mid-1980's. Building 1100 is a 54,916 square foot building and has been used as

an industrial laundry and dry-cleaning facility. From 1958 to 1967, the dry-cleaning operations at building 1100 generated approximately 25 gallons per month of tetrachloroethene (PCE) and were allegedly disposed of in the North Grinder Landfill. All the dry-cleaning chemicals (Petroleum based solvents and PCE) were stored in the above ground storage tanks outside building 1100. The Environmental Baseline Survey (EBS) reported two notable spills/releases of 20 gallons of PCE northeast of Building 1100 and 55 gallons of PCE along the north side of building 1100 in October of 1994. Engineering drawings indicate a possible production well located north of Area C. There is also a deep drainage well (over 500 feet deep) near the shore of Lake Druid. Dry cleaning operations ceased in the fall of 1994 and the building has been cleared out. SA 14 includes building 1102 and the surrounding paved and grassy area. This area has been used for indoor and outdoor storage of salvageable equipment and materials as well as a storage of scrap and salvage yard in the northwest part. A release of 3 gallons of PCE was reported in 1989 followed by the removal of and disposal of approximately 20 drums of contaminated soil and asphalt. The exact location of this release was not indicated in the EBS report.

Results of BRAC and IRA Investigations

ABB Environmental Services (ABB-ES) conducted the first remedial investigations of the OU 4 area. An initial investigation was conducted in 1994 during the Base Realignment and Closure (BRAC) Environmental Baseline Survey (EBS), with follow up studies in January 1995, May 1996, March and April of 1997, and the implementation of an Interim Remedial Action (IRA). Harding Lawson Associates (HLA), formerly ABB-ES, conducted their Remedial Investigation (RI) of the OU 4 area

to fill in the data gaps from ABB-ES' site conceptual model in 1998. As a follow up to the RI, a natural attenuation assessment by Harding Lawson Associates was also conducted in 1998.

Site Screening Investigation

The findings of initial investigation of the OU4 site in 1994 during the BRAC EBS recommended further site screening for the IR program. The BRAC site screening included a geophysical survey, a soil gas survey, surface and subsurface soil sampling, and the installation of monitoring wells to evaluate groundwater contamination (Figure 3-1). Site screening in 1995 detected chlorinated solvents in all four shallow monitoring wells above Florida Department of Environmental Protection (FDEP) maximum contaminant levels (MCLs). Groundwater samples collected in between the building 1100 and Lake Druid by TerraProbe contained PCE, TCE, and cis-1-2-DCE. Surface water samples of Lake Druid contained PCE, cis-1,2-DCE, 1-1-DCE, and VC. Sediment samples of Lake Druid also contained PCE and TCE. At SA14, PCE was detected in one soil gas survey near the corner of building 1102. PCE and TCE were detected above their respective FDEP MCLs in one groundwater sample and antimony was detected above its FDEP MCL in three groundwater samples.

Based on these findings, further investigations to delineate the source and extent of PCE and TCE at SA12, SA13, and SA14 were conducted in May of 1996 and May and April of 1997. Site delineation revealed PCE and TCE were at concentrations of 1 to 3 milligrams per liter, which suggested the presence of a residual non-aqueous phase liquid (NAPL) source area beneath the former laundry facility. ABB-ES proposed immobile ganglia below the former laundry facility that slowly dissolves into groundwater

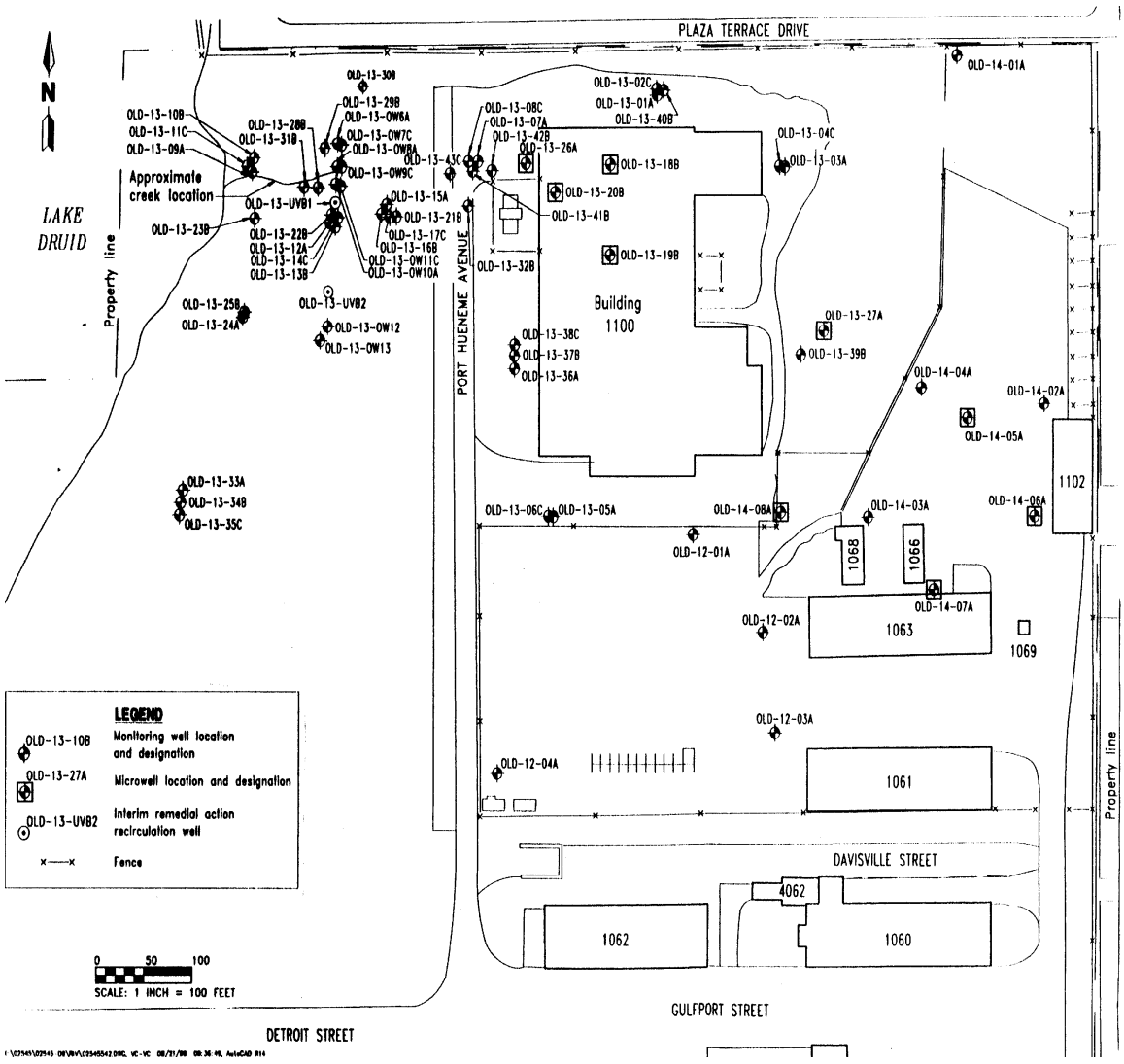


Figure 3.1. Location of the monitoring wells installed during the site investigations by HLA (Figure from HLA, 1998).

as another possible source area for the chlorinated solvents. Further investigations during the IRA indicated that source areas appear to be multiple and located near building 1100. The IRA consisted of two in-situ air-stripping recirculation wells to intercept the contaminant before it reaches the lake. The IRA included delineation of the southern, western, and northern extent of contamination to evaluate the possible off-site contamination and clarify transport parameters. The results of this delineation are shown on the groundwater plume contour map (Figure 3-2) and plume cross sections (Figures 3-3 and 3-4). The plume appears to be contained within the site. ABB-ES recognized PCE as the parent product at the OU4 site and TCE, cis-1-2-DCE, and VC as degradation daughter products as the plume moves from the suspected source area of building 1100 to Lake Druid (Figure 3.5).

Geology

This section is a review of the regional geology followed by a detailed description of the site geology. The information for this section comes from the remedial investigation report for the NTC site by Harding Lawson Associates and regional literature (Lichter er al., 1968). The regional geology (upper 2,000 feet) can be divided into three lithographic units: Holocene to Pliestocene surficial deposits approximately 100 feet thick, Miocene clastic sediment and unconsolidated carbonates (Hawthorn Group) approximately 100 feet thick, and an Eocene sequence of marine carbonates approximately 1200 feet thick (Figure 3.6). The site geology description will focus on the sediments to a depth of 60 feet (region of contamination and local groundwater flow) and comprises the Holocene/Pleistocene deposits.

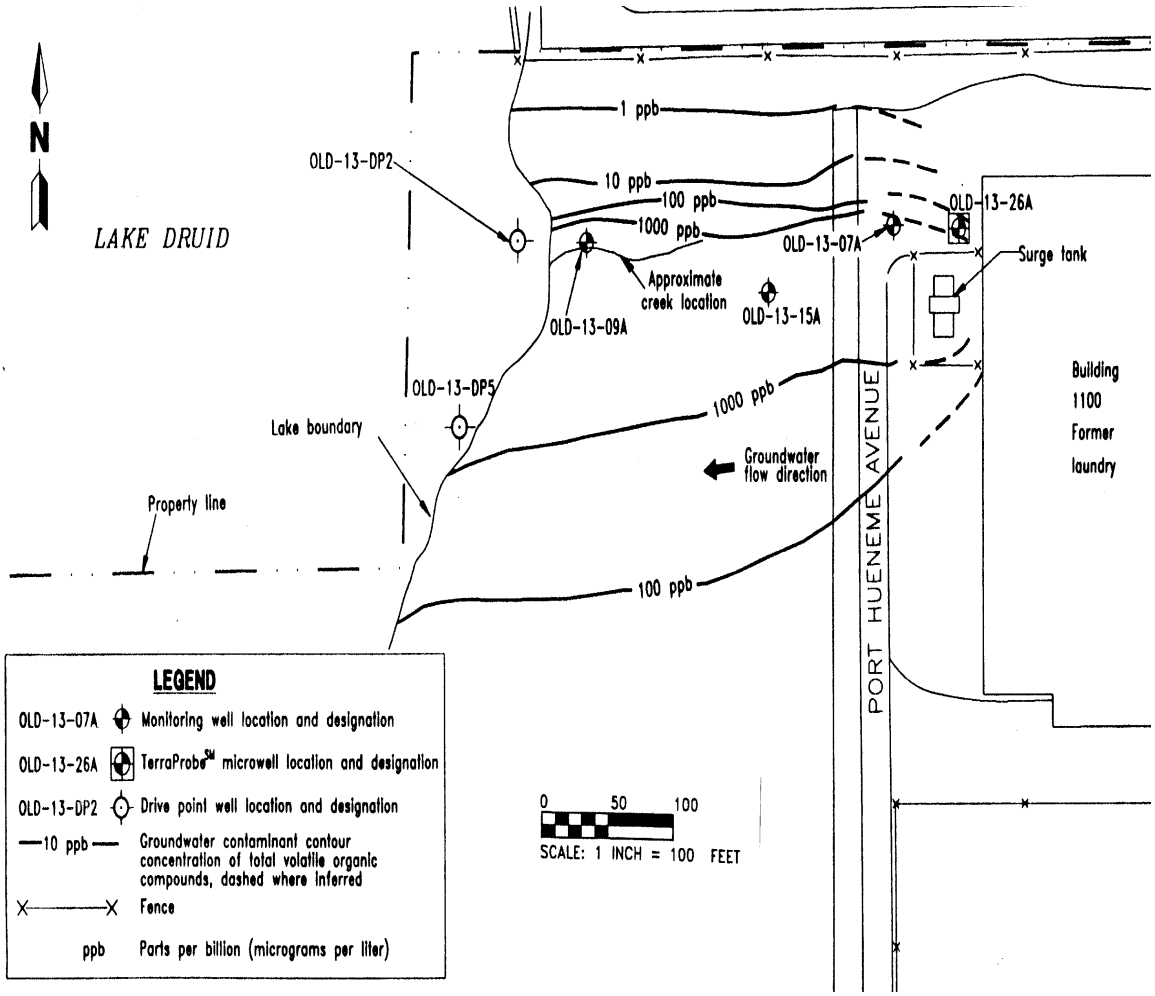


Figure 3.2. Groundwater contamination contour map for total volatile organics compounds (VOCs) (HLA, 1998).

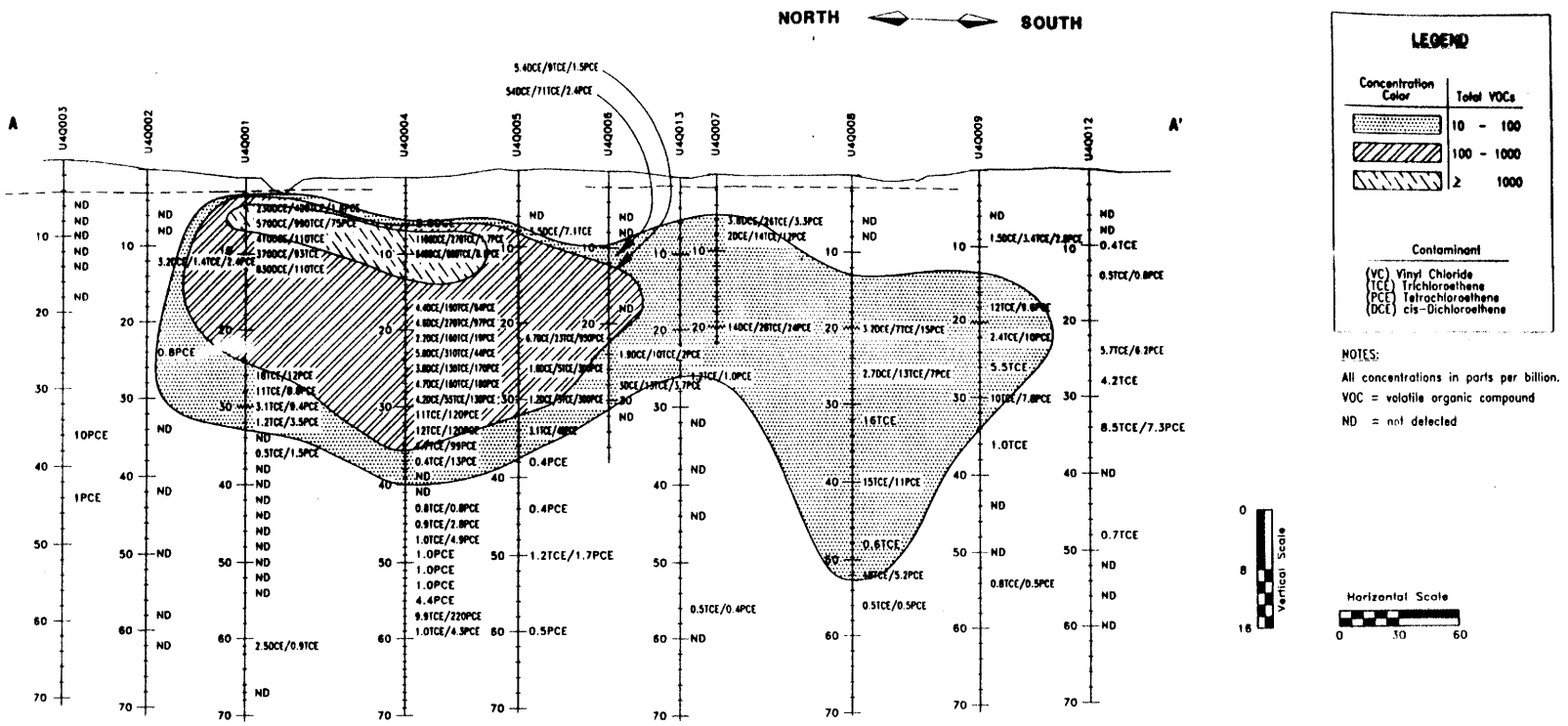


Figure 3.3. North-South cross-section of the plume. Shaded areas represent total VOCs and detected levels of PCE, TCE, and cDCE are shown.

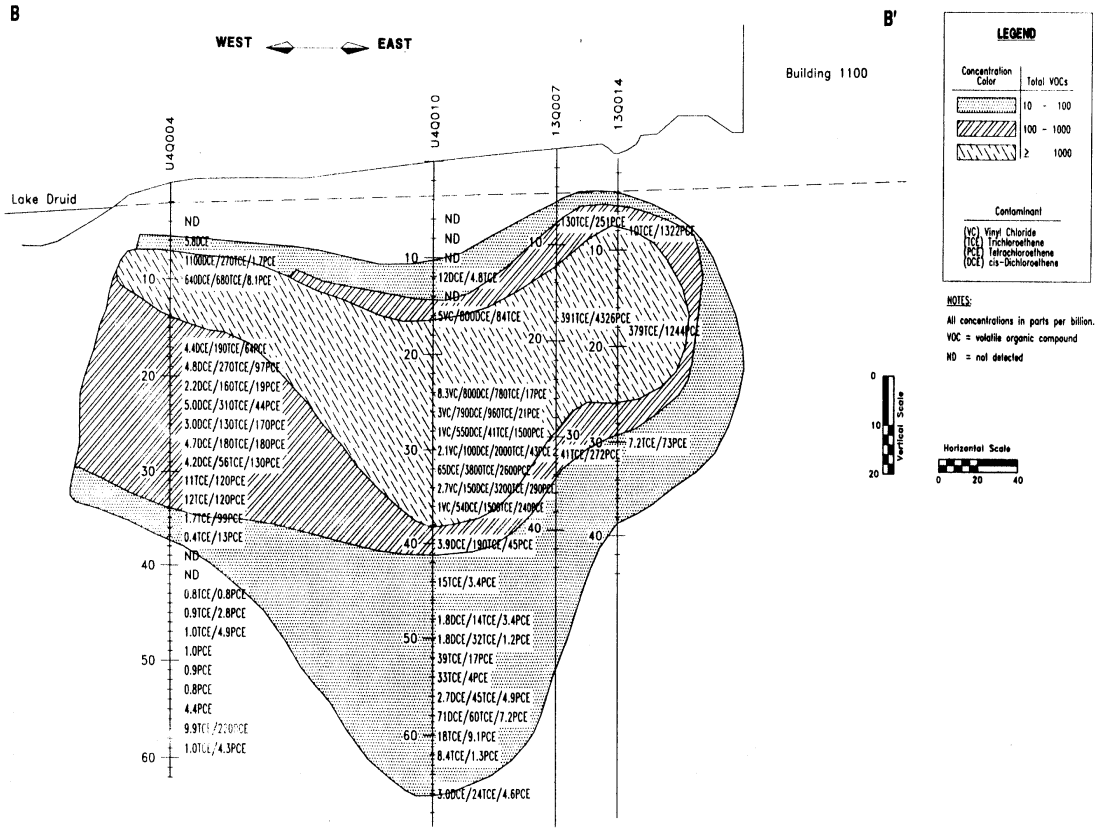


Figure 3.4. East-West cross-section of the plume.

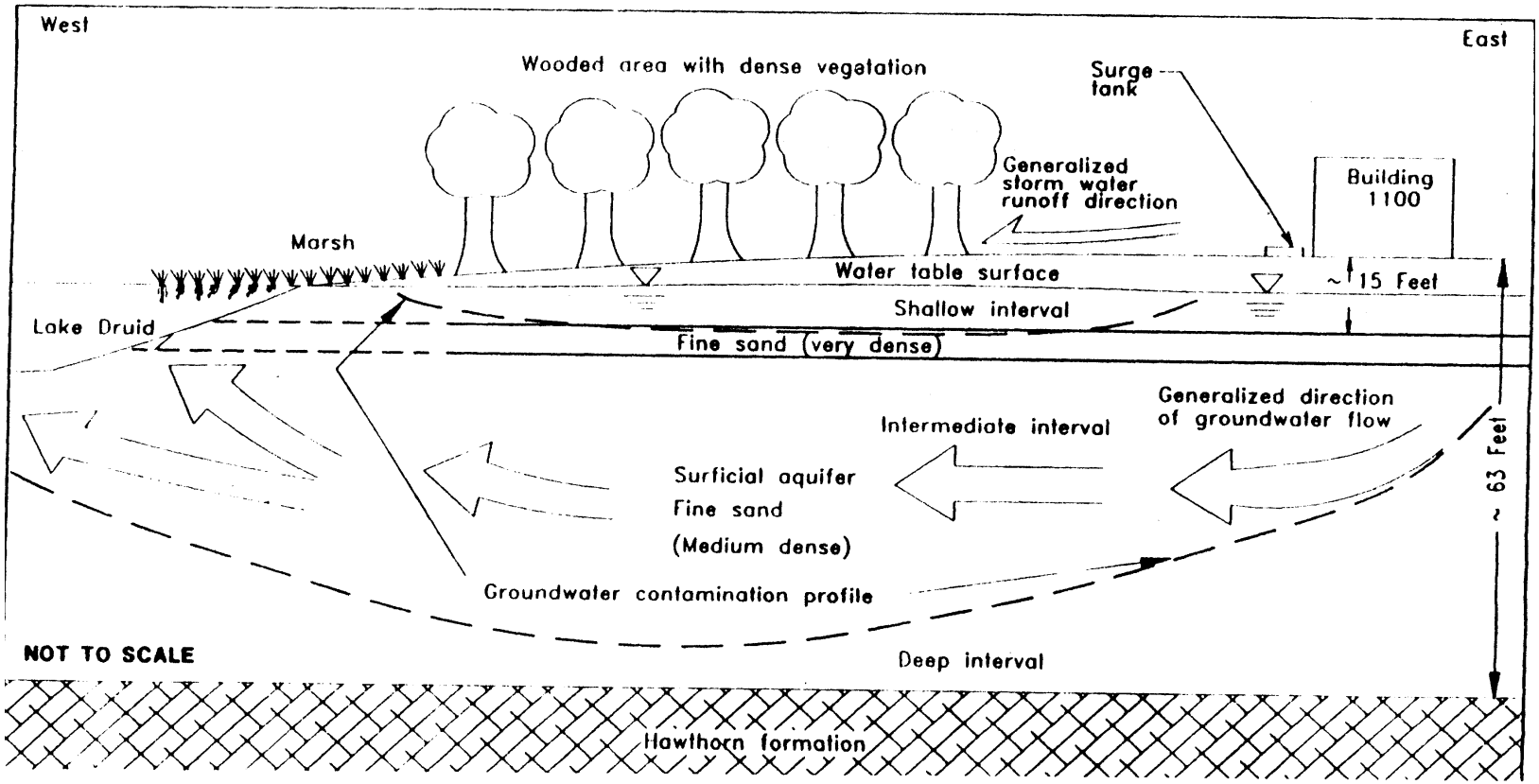


Figure 3. 5. Site Conceptual model developed by HLA (HLA, 1998).

Regional Geology

The youngest lithographic unit is a sequence of Eocene-age marine carbonates. This sequence is divided into three units: the Ocala Group, the Avon Park Limestone, and the Lake City Limestone. The Ocala Group consists of fine to medium grained limestone that is locally dolomitic. The Ocala Group is further divided into the Crystal River Formation, the Williston Formation, and the Inglis Formation. The Avon Park Limestone, of late middle Eocence age, underlies the Ocala Group. The Avon Park Limestone consists of granular limestone with cone-shaped formanifera and a lower section of crystalline dolomite. The Lake City Limestone underlies the Avon Park Limestone and is early middle Eocene in age. The Lake City limestone consists of an alternating crystalline dolomite and fossiliferous limestone.

The middle lithographic unit consists of the Hawthorn Group, a sequence of mixed unconsolidated clastic material and carbonates of Miocene age. This unit is composed of gray-green calcareous, phosphatic sandy clay, and clayey sand interbedded with thin discontinuous lenses of phosphatic sand, phosphatic sandy limestone, limestone, and dolostones. The most common carbonate components of the Hawthorn Group are dolomite and dolosilt. The Hawthorn Group averages 100 feet in thickness over central Florida. The unit thickens southward and measures over 600 feet in thickness in south Florida. The oldest lithographic unit is a thin sequence of undifferentiated clastic terrace deposits of Holocene and Pleistocene age. The surficial deposits consist predominantly of quartz sand with varying amounts of silt and clay sized grains. The sediment ranges from 50 to 100 feet thick with the thickest accumulation of sediment along the ridge of the Florida peninsula.

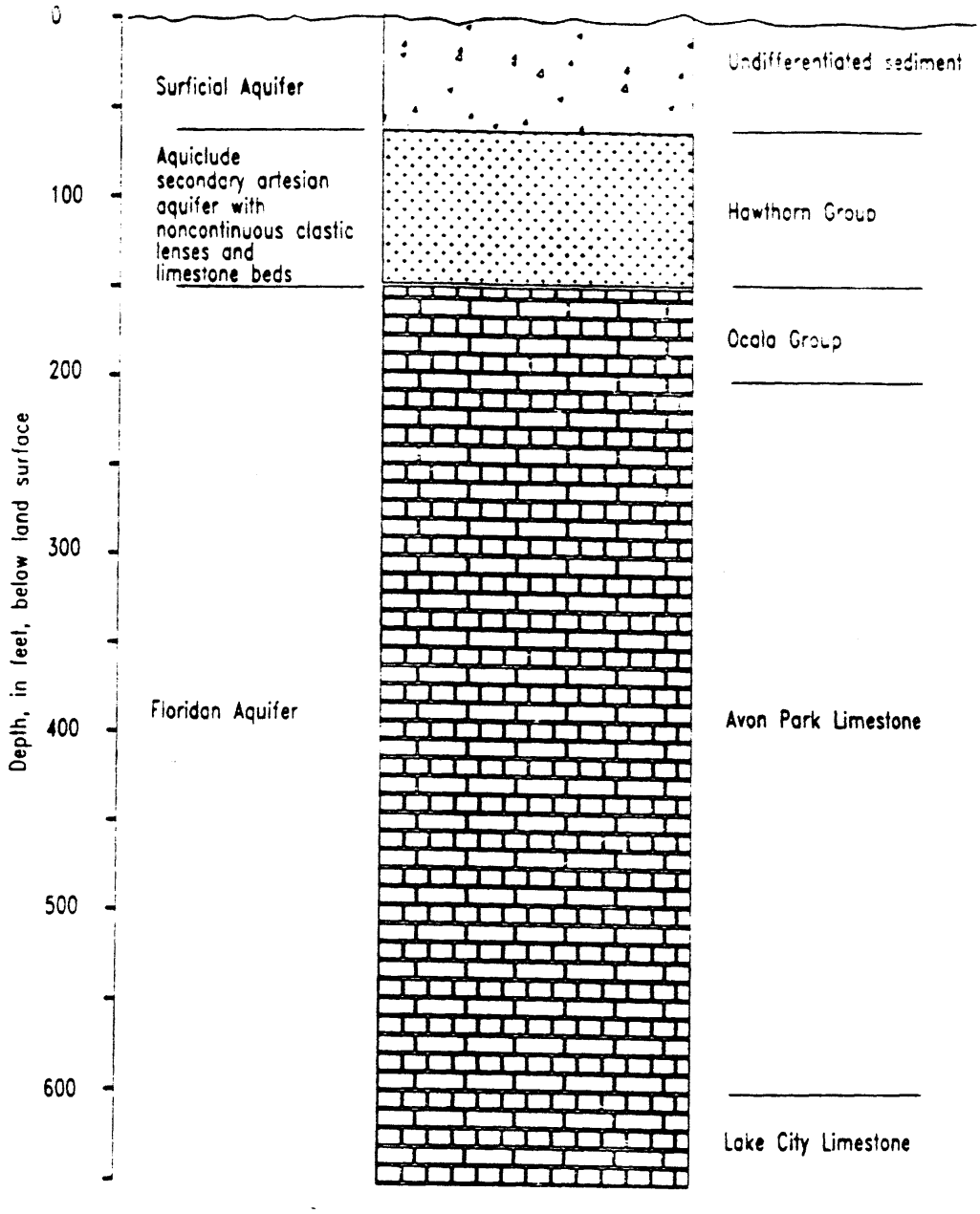


Figure 3.6. Regional geology of the OU4 Site, Orlando, Florida (HLA, 1998).

Site Geology

Subsurface exploration by HLA extended approximately 30 feet into the Hawthorn Formation. The surficial deposits are divided into three separate units based on texture and color characteristics. The shallowest sub-unit (0-4 feet) and middle sub-unit (4-14 feet) are composed of light gray to light brown silty, fine grained sand. The deepest sub-unit (16 - 40 feet) is a yellow to white silty, fine-grained sand with interlayered gray clayey silt. All three sub-units are laterally continuous and of uniform thickness across the site. The Hawthorn sediments are divided into two units within the study area. The upper 10 to 20 feet are composed of greenish-gray silty fine to coarse sand with phosphate nodules and shell fragments. The lower unit consists of greenish gray, silty clayey sand with interfingered layers of clay. The upper surface of the Hawthorn Formation is irregularly shaped and dips generally westward across the site, top surface is 40-50 below land surface (bls) near Lake Druid and 50-60 feet bls on the east side.

The lithologic data collected at the selected soil boring locations were used to construct two geologic cross sections. Cross section A-A' (Figure 3.7) provides a west to east profile and cross section B-B' (Figure 3.9) provides a north to south profile. As evident in the cross-sections, the surficial deposits range in thickness 40 to 50 feet and thin gradually westward in the direction of Lake Druid.

Hydrogeology

This section is a review of the regional hydrogeology followed by a detailed description of the site hydrogeology. The information for this section comes from the remedial investigation report for the NTC site by HLA and Lichter et al. (1968). The

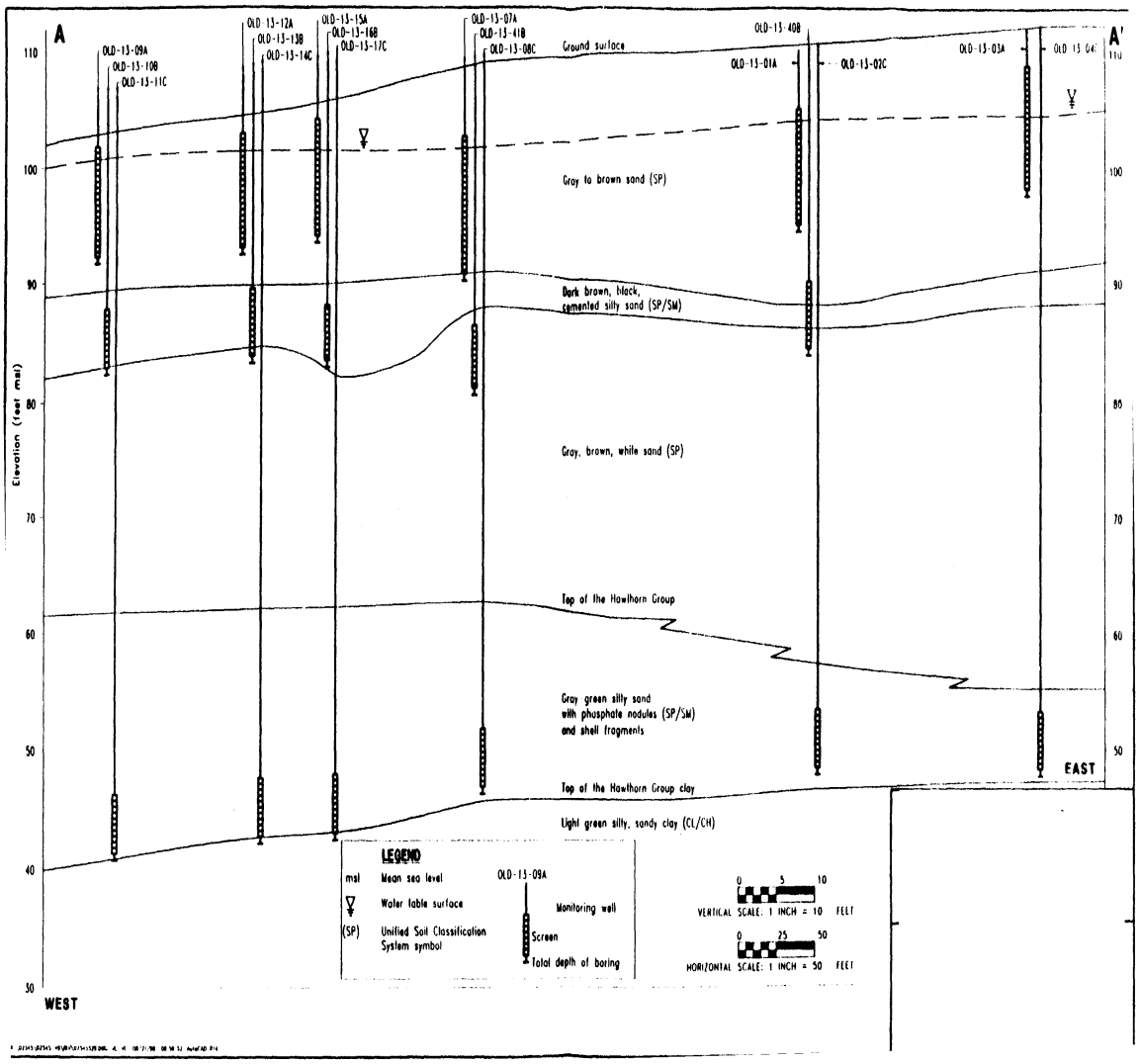
regional hyrdogeology is composed of a three aquifer system (A surficial aquifer, an intermediate 'Hawthorn' aquifer, and the Floridan aquifer system) that correspond to the three major lithographic units found in central Florida. The local hydrogeology description will encompass the surface hydrology and is limited to the surficial unconfined aquifer.

Regional Hydrogeology

The surficial aquifer is an unconfined flow system within the unconsolidated surficial deposits. In some areas the surficial aquifer extends into the top of the Hawthorn due to coarse-grained sediment overlying a confining clay layer. The water table ranges from 5 to 15 feet below land surface (bls). The surficial aquifer is recharged by precipitation and there is a limited amount of exchange between the surficial aquifer and the underlying intermediate and Floridan aquifers. Discharge of the surficial aquifer occurs by evapotranspiration, seepage into surface water bodies, and downward leakage into the Hawthorn aquifer.

The Hawthorn aquifer occurs within the clastic deposits of the Hawthorn Group. Groundwater is contained within these clastic lenses and limestone deposits. The Hawthorn Group generally acts as an aquitard to the downward leakage from the surficial aquifer and acts as a confining layer to the Floridan aquifer.

The principal source of fresh water in central Florida is the Floridan aquifer. Groundwater is contained within the sequence of Eocene carbonates: The Ocala Group, the Avon Park Limestone, and the Lake City Limestone. Lichter et al. (1968) reports transmissivities greater than 150,000 gallons per day per foot. The units of the Floridan aquifer dip to the south due to megascopic folding. Recharge to the Floridan



Figrue 3.7. West-East (A-A') geologic cross-section of the OU4 site constructed from well boring logs (HLA, 1998).

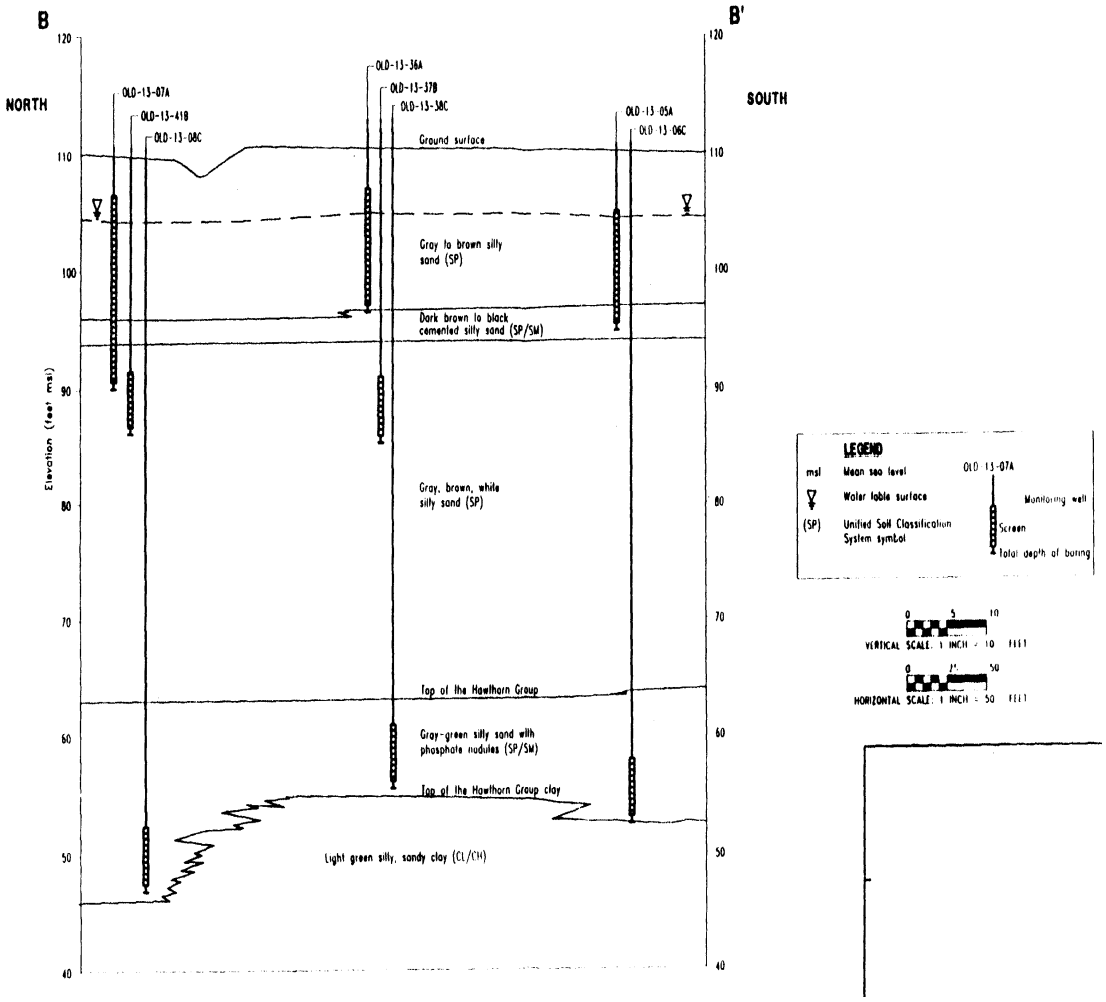


Figure 3.9. North-South (B-B') geologic cross-section of the OU4 site constructed from well boring logs (HLA, 1998).

occurs by precipitation where the units outcrop to the north and by downward leakage due to the net downward gradient from the surficial aquifer to the Floridan aquifer. Discharge occurs by pumping from supply wells and leakage to the Hawthorn aquifer because of the net upward gradient from the Floridan aquifer to the Hawthorn aquifer.

Site Hydrogeology

The overall hydraulic effect of the Hawthorn group as a confining layer is to restrict the vertical flow of groundwater in the surficial aquifer. This restriction produces an overall horizontal movement of groundwater flow. Even though the potential exists for the downward migration through the Hawthorn 'aquitard', the low permeability of the Hawthorn clay-rich sediment results in negligible vertical hydraulic conductivites relative to the horizontal conductivies. Therefore, all previous groundwater investigations have been limited to the surficial aquifer and surface water bodies.

Lake Druid is the major surface water feature of the NTC area, covering 800,000 square feet and reaching a maximum depth of 15 feet. This lake captures runoff from a 150 acre drainage basin comprised of the surrounding neighborhood storm drainage system and intermittent streams. A weir on the northwest shoreline maintains the lake level. Overflow from the weir is piped to Lake Rowena, approximately 0.75 miles to the northwest. Drainage from Lake Rowena flows to the Little Econlockhatchee River, which eventually drains to the St. Johns River.

Water levels for the surficial aquifer were recorded at all of the monitoring wells. Staff gauges and piezometers were used to determine the relationships between Lake Druid and the surficial aquifer. Water level measurements performed by HLA indicate groundwater of the surficial aquifer flows from the west side of OU4 to Lake druid

(Figure 3.10). The water table is relatively flat and has an overall average gradient of 0.008. An evaluation of the hydraulic potential of the surficial aquifer at depth shows that distinct downward and upward gradients exist.

Downward gradients are prevalent in the area of building 1100 at 0.008 indicating a recharge area. Toward Lake Druid, upward gradients exist at 0.025 indicating discharge to the surface water body. HLA performed hydraulic conductivity tests at nine monitoring wells, two shallow, five intermediate, and two deep. The hydraulic conductivity tests were composed of falling head (slug-in) and rising head (slug-out) hydraulic tests. The data was analyzed using the Aqtesolv software program, which utilizes the Bouwer and Rice method to calculate hydraulic conductivity. The mean hydraulic conductivity for the shallow, intermediate, and deep wells were 1.1×10^{-3} cm/sec, 1.5×10^{-3} cm/sec, and 4.2×10^{-3} cm/sec respectively (HLA, 1998).

Natural Attenuation Assessment

With the biodegradation products of PCE present at the site and the well-documented ability of chlorinated solvents to be biodegraded, natural attenuation was selected as a potential remedial alternative at the OU4 site. For natural attenuation to be an effective remedial alternative, it has to be demonstrated that the processes of natural attenuation are significant enough to reduce the concentrations of the anthropogenic contaminants below the respective state MCLs. The site assessment included screening the OU4 site for electron donors, electron acceptors, and other parameters (Oxidation-reduction potential (ORP), pH, chloride, alkalinity, and dissolved gases). The results of this study will be presented by examining each parameter.

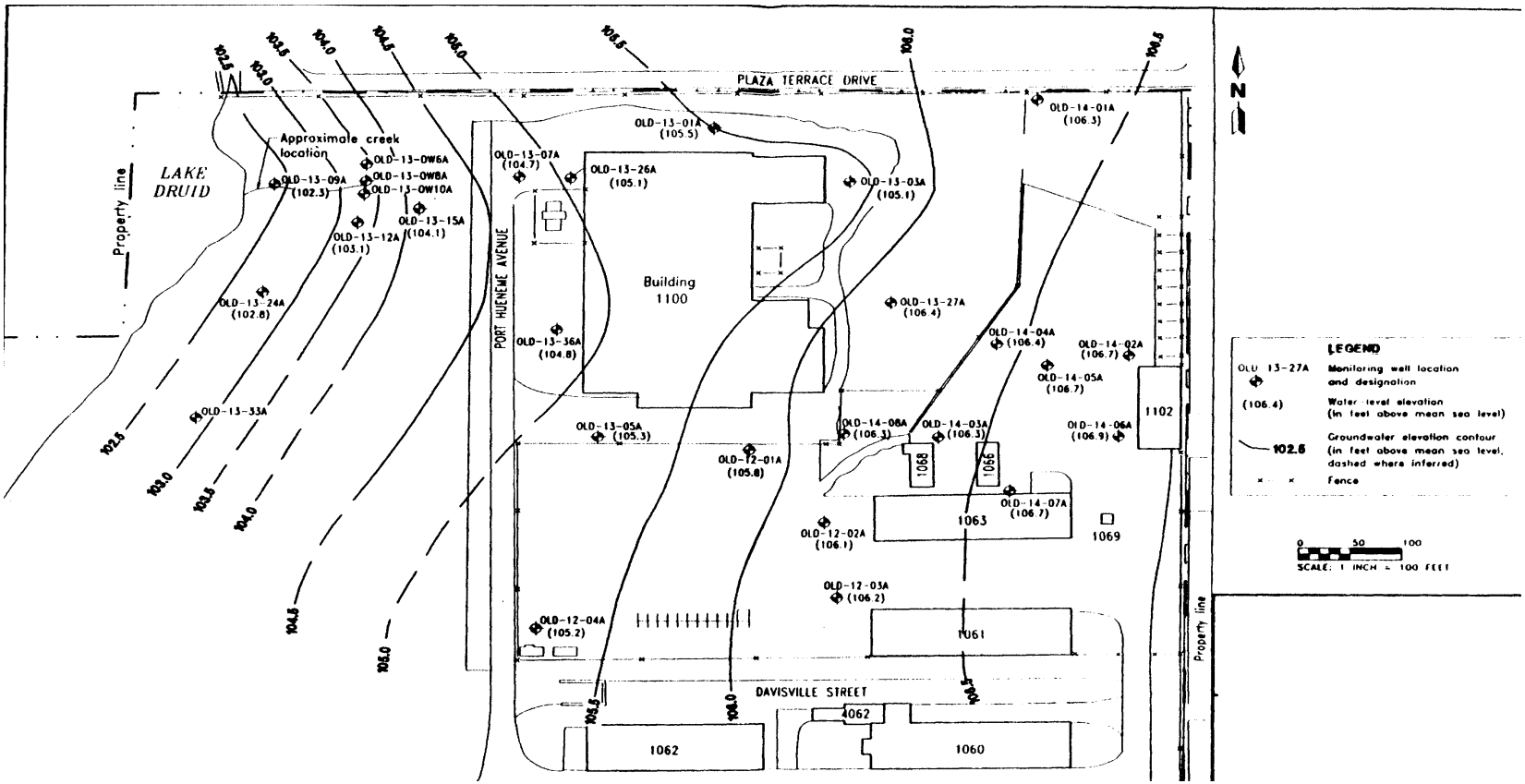


Figure 3.10. Water table contour map measured by HLA in January1997 (HLA, 1998).

(Table 3-1 summarizes the analytical results). The hydrogen data collected at the site was invalid because of the inconsistency of duplicate samples and the lack of correlation with the ORP values.

Electron Acceptors

The concentrations of terminal electron acceptors (TEAs) in groundwater are used to determine the predominant biodegradation pathway occurring *in-situ*. The TEAs measured were oxygen, nitrate, manganese, iron, and sulfate. Analysis of groundwater dissolved oxygen revealed concentrations of less than 1 mg/L, which shows that oxygen has been depleted within the groundwater plume. Background conditions are also observed to be low and anoxic before the groundwater reaches the contaminant plume. Nitrate was not detected in any of the groundwater samples indicating that denitrification is not the predominant metabolic pathway. Ferrous iron, the reduced form of ferric iron, and manganese were measured at only one well across at the site and indicated that manganese reducing or iron reducing conditions are not favored at the site for biodegradation of PCE. Sulfate was present at all locations and ranged from 4.1 mg/l to 31.7 mg/l. Sulfide, the reduced form of sulfate, was measured at only one location. The detection of sulfide indicates that limited sulfate reducing zones may exist, but the persistence of sulfate and absence of sulfide indicated that sulfate reduction might not be the predominant reducing conditions at the site. Carbon dioxide was detected in groundwater ranging from 20 mg/l to 65 mg/l. Methane, the reduction product of carbon dioxide, has been detected in groundwater across the site. This data indicates that methanogenisis is important as a biodegradation pathway at OU4.

Table 3.1. Summary of the natural attenuation parameters (HLA, 1998).

WELL	DEPTH OF SAMPLE	VOCs (ug/L)				ETHANE/						REDOX COUPLES (mg/L)				
		PCE	TCE	DCE	VC	ETHENE(ng/L	Cl(mg/L)	TOC(mg/L)	DO(mg/L)	CO2(mg/L)	CH4(mg/L)	NITRATE	NITRITE	IRON III	IRON II	SULFATE
	(ft bls)															
DP-2	7	10	2400	75	<5	84.6	19.5	4.3	0.61	47.89	<.002	<.5	<.5	<.5	<.5	12.6
OLD-13-9A	6	<5	360	2526	69	1889.9	15.3	2.28	0.82	67.25	<.002	<.5	<.5	<.5	<.5	10.5
OLD-13-23B	20	23	1900	544	<5	20.7	24.9	2.25	0.26	55.7	0.002	<.5	<.5	<.5	<.5	14.1
OLD-13-10B	20	<5	82	5140	<5	113.5	10.6	0	1.8	23.77	<.002	<.5	<.5	<.5	<.5	13.6
OLD-13-15A	7	7	35	42	<5	<6	5.08	6.7	0.73	20.53	0.006	<.5	<.5	<.5	<.5	5.83
OLD-13-13B	20	<5	<5	51	<5	9	6.66	7.7	2.17	22.08	0.011	<.5	<.5	<.5	<.5	4.14
OLD-13-16B	20	<5	720	1550	16	177.4	14.7	9.57	0.74	32.71	0.002	<.5	<.5	<.5	<.5	6.85
OLD-13-21B	30	20	1200	1671	<5	<6	35.1	3.2	0.64	47.52	<.002	<.5	<.5	<.5	<.5	11.1
OLD-13-26A	7	13000	200	99	<5	13.4	12.4	8.19	0.63	31.78	<.002	<.5	<.5	<.5	<.5	31.7
OLD-13-7A	7	12300	830	260	<5	15.4	6.25	5.4	2.62	22.97	<.002	<.5	<.5	<.5	<.5	13.2
OLD-13-20B	20	650	640	14	<5	26.6	7.85	5.14	0.34	47.32	0.003	<.5	<.5	<.5	<.5	24.1
OLD-13-7A	18	11000	770	330	<5	28.4	10.4	5.59	0.98	46.44	<.002	<.5	<.5	<.5	<.5	12.2
DP-5	3	15	530	1741	<5	63.4	94	4.95	0.39	52.5	<.002	<.5	<.5	<.5	<.5	12.3
OLD-13-5A	12	5	<5	<5	<5	<6	4.55	14.3	0.38	40.77	<.002	<.5	<.5	<.5	<.5	8.06

Oxidation-Reduction Potential

Anaerobic dechlorination is possible when the reduction potential is less than 50 millivolts (mV). However, the optimal range lies between -50 to -240 mV (RTDF, 1997). Dechlorination is a redox reaction, during which the chlorinated solvent is reduced. When oxygen is depleted the reduction potential decreases making it more favorable for the redox reactions, such as the degradation of the oxidized organic contaminant. Evaluation of the ORP in the contaminant plume compared to background levels gives evidence that favorable conditions exist for anaerobic degradation of the chlorinated solvents. ORP values were measured at shallow, mid-depth, and deep intervals. Shallow measurements ranged from 150 to 20 mV, mid-depth measurement ranged form 50 to -100 mV, and deep measurements ranged from -40 to -130 mV with the lower values downgradient from the source. These measurements indicate that conditions at the mid-depth and deep intervals are favorable for anaerobic dechlorination

Alkalinity

Microbial respiration results in elevated levels of carbon dioxide, which leads to an increase of the alkalinity relative to background conditions. Elevated alkalinity levels, compared to background levels, were not detected.

Chloride

Dechlorination of the chlorinated solvents causes an increase of chloride concentrations within the contaminant plume. The areas with contaminants showed elevated chloride concentrations in all three groundwater depth levels. Chloride concentrations at the source are 2 to 3 times greater than background and downgradient from the source are 5 to 50 times greater than background.

Dissolved gases

The dissolved gas of impacted (Contaminated Areas) and non-impacted (Background) locations can be compared to qualitatively evaluate the presence or absence of in-situ biodegradation processes. The dissolved gases analyzed for were methane, ethane, ethene, and carbon dioxide. Dissolved carbon dioxide in groundwater is the result of microbial respiration. Methane is the result of the reduction of carbon dioxide during methanogenesis. Ethane and ethene are produced during reductive dechlorination of the chlorinated compounds and reduction of other natural oxidized organic compounds. Methane was detected in wells across the site and ethene was present in almost all water samples except background and were greatest midplume. Carbon dioxide was detected in groundwater, but there were no changes in alkalinity when compared to background levels. The dissolved gas analysis provided direct evidence that microbial reductive processes are occurring at the site.

Assessment from Natural Attenuation Parameters

The data collected provides evidence that anaerobic dechlorination of the parent contaminant, PCE, is occurring *in-situ*. The concentrations of PCE in the source area range from 650 ug/l to 12,300 ug/l. Downgradient locations had a concentration of less than 25 ug/l. The majority of downgradient locations contained the daughter products, TCE and cis-1-2-DCE. VC was detected in only one shallow, middle, and deep well. There does not appear to be a widespread reducing environment across the plume. Sulfate-reducing, iron-reducing, and methanogenesis conditions were detected across the site. Biodegradation appears to be limited because of the accumulation of VC and cis-1, 2-DCE down-gradient of the source area. It appears that the limited biodegradation of

the contaminants at the OU4 site is due to depleted levels of DOC within the chlorinated solvent plume and the high rate of discharge from the site into lake Druid.

CHAPTER 4

MATERIALS AND METHODS

Materials

Soil Core Samples

A total of 8 cores samples were collected from the NTC site in Orlando, Florida (Figure 4.1). Mud rotary drilling and split spoon sampling procedures were used in the sampling. A detailed description of the samples collected is included below:

- **Locations 1, 6 and 7 (at the shores of lake Druid):** Samples were collected from shallow depths of 0–5 feet. Rooted soil was collected from the first one foot of the topsoil and unrooted soil was collected from 2 – 5 feet. These samples were collected in shelby tubes, stored in coolers and transported to the University of Georgia (UGA).
- **Locations 2, 3, 4 and 5:** Location 3 is behind the building. Locations 2, 4, and 5 are about midway between the road behind Building 1100 and Lake Druid. Cores were taken from shallow depth (0 – 5 feet), medium depth (10 – 20 feet) and deep in the aquifer (20 – 40 feet).
- **Location 8:** An intact core was obtained at 0 –5 feet in a shelby tube from the small creek that empties into Lake Druid on the study site

Each shelby tube contained about one to one-half gallon of the site sediment or aquifer material. The core samples were not dewatered before being capped for shipment. All

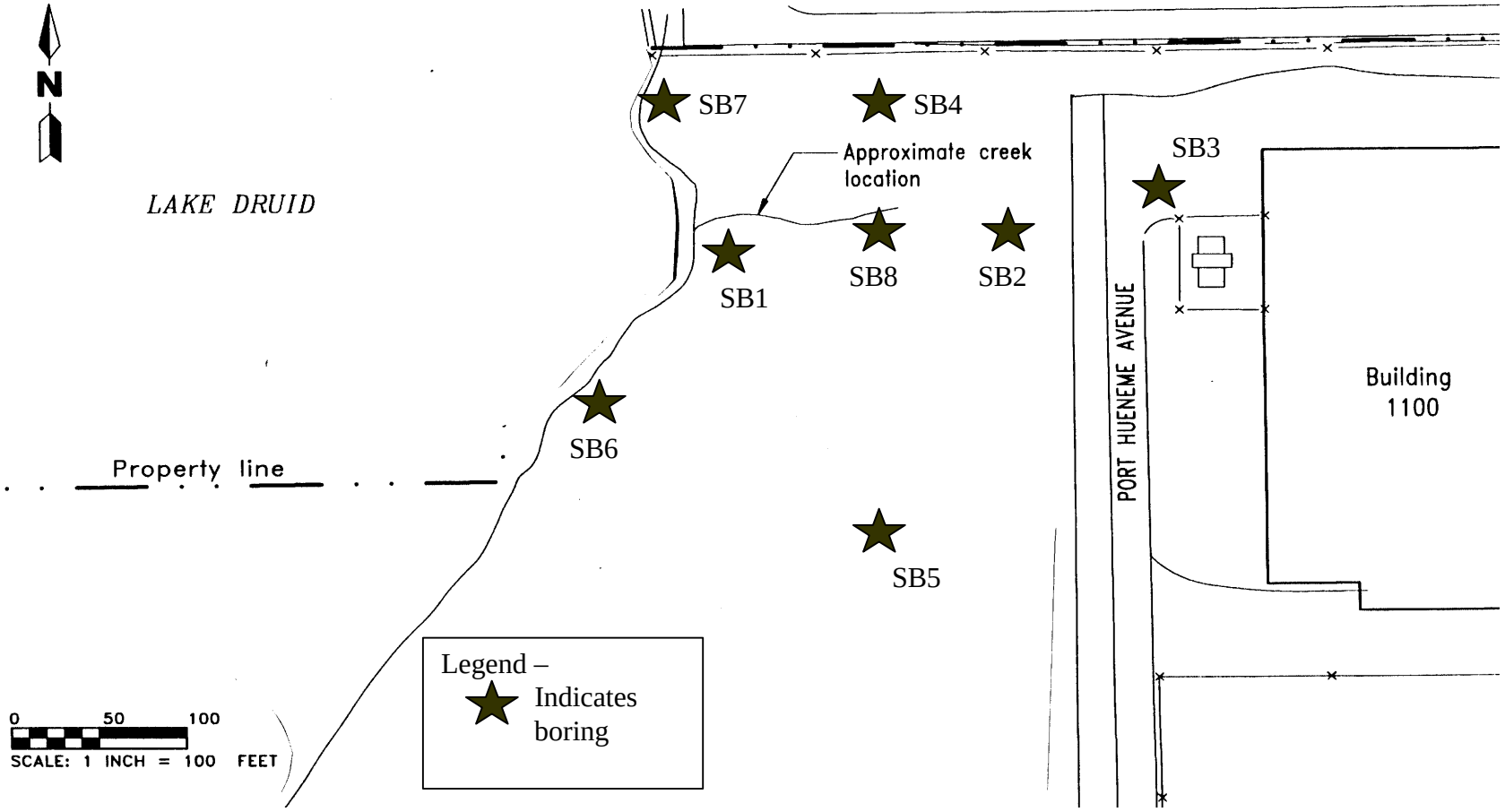


Figure 4.1. Location of sediment borings (SB) used for the feasibility study (Map from HLA, 1998)

samples were stored and transported in thin-walled shelby tubes (2 ft in length with an internal diameter of 4 inches) in coolers. Upon arrival at UGA the samples were stored in the dark in an environmental room maintained below 4^{o}C. About 200 gallons of Lake Druid water was collected for use in the feasibility studies.

Lake Core Samples

Two samples were collected from the shores of Lake Druid by Tetratech NUS, Inc using a Wildco Hand Corer without a core catcher (Figure 4.2). Sample DRUIDO2 was collected at a water depth of 7 feet, while sample DRUID01 was collected at a water depth of 4 feet. The lake cores were prepared by decanting free water, sawing off the excess liner and capping for shipment. The sediment cores were packaged in foot-long plastic sleeves (two sleeves per sample) with an internal diameter of 1 inch. After collection, the cores were sent to UGA via an overnight courier and stored in a dark environmental room maintained at 4^{o}C.

Groundwater Samples

Ground-water samples were collected from monitoring well OLD-13-09 at a depth of 10 feet (Figure 3.1). Sampling was conducted in accordance with a method developed by Olson et al.(1981). Sterile Teflon® tubing was inserted into the well, and the well was purged using a peristaltic pump connected to a Horiba flow-through cell. The Horiba flow-through cell enabled continuous collection of water quality sample parameters. Purging was stopped when the parameters stabilized indicating that the site water was representative of the formation and was not free water of the borehole. The

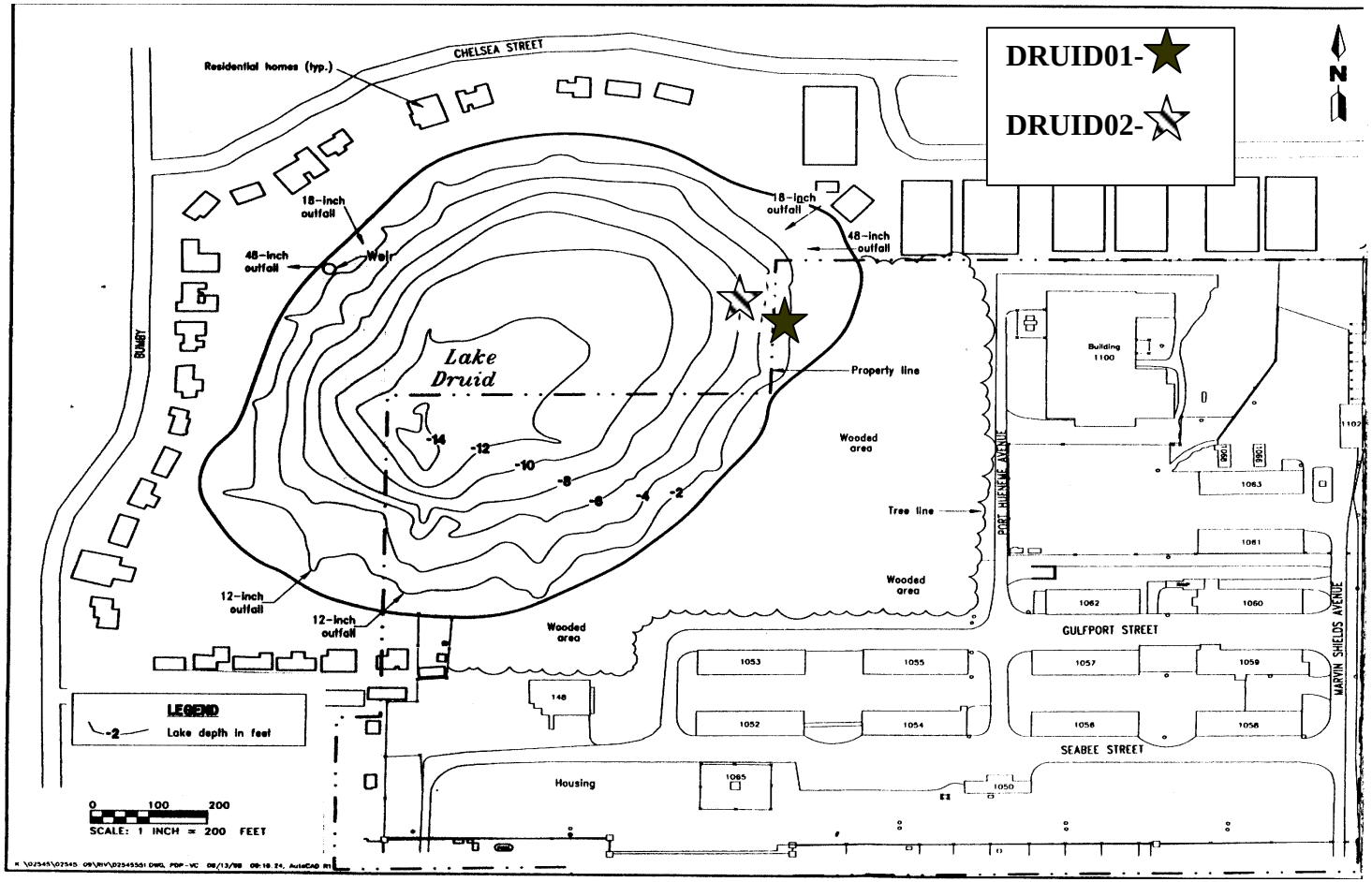


Figure 4.2. Location of the lake sediment cores collected for the feasibility study (Map from HLA, 1998).

well was purged for 27 minutes at an average flow rate of 189 ml/min. The water quality sample parameters at the time of collection were: Color=Clear, pH=5.14, Specific Conductivity =12.0 mS/cm, Temp=22.0 ^{o}C, Turbidity=0 NTU, DO=1.58 mg/L, and ORP=19 mV. Ten gallons of unpreserved groundwater were collected from well OLD-13-09 and sealed in 5 amber one-gallon glass jugs and 5 one-gallon polyethylene cubitainers. Groundwater was then shipped by overnight courier and stored in the dark in a temperature controlled environmental room until used.

Reagents and Chemicals

PCE and TCE were obtained from Aldrich Chemical Company (Milwaukee, WI). Radiolabeled PCE and TCE were obtained from Sigma Chemical Co. (St. Louis, MO). Prepared standards of trans-1,2-DCE, cis-1,2-DCE, and VC stock solutions in methanol were obtained from Supelco (Chicago, Illinois). Analytical grade methanol (Fisher Scientific Co., Pittsburgh, PA) was used to prepare stock solutions of PCE and TCE. All chemicals were greater than 99% purity, as confirmed by analysis using a gas chromatograph/mass spectrometer (GC/MS). Chemicals were used as obtained without further purification.

Resazurin and strontium carbonate was purchased form Aldrich Chemical Company (Miwaukee, WI). Lactic acid (sodium salt) was purchased from Sigma Chemical Company (St. Louis, Mo). ACS reagent grade sodium acetate (trihydrate crystal) was purchased from J. T. Baker (Phillipsburg, NJ). Yeast extract (Bacto yeast extract "Difco Certified") was obtained from Difco Laboratories (Detroit, Michigan). Unsulphured "Blackstrap" molasses and corn oil were purchased from Earth Fare (Athens, Georgia). Hydrogen release compound (HRC®) was provided by Regenisis

(San Clemente, California) for this study. Hionic-Fluor scintillation counting cocktail was purchased from Packard Instruments (Meridan, Conneticut). ScintiSafe 30% scintillation cocktail was purchased form Fisher Scientific, Co. (Pittsburgh, Pa).

Methods

Sorption experiments

Batch sorption experiments were conducted using ^{12}C-PCE and analyzed using a gas chromatograph with a micro electron capture detector (GC/uECD). Initial sorption experiments conducted with 5 g of sediment from the core samples and 18 mL of DI water showed no measurable sorption. As a result, the mass of solids was doubled to 10 g in subsequent sorption experiments to increase the fraction of initial PCE removed from solution due to sorption. Also, radiolabeled [^{14}C] PCE was used in the latter experiments. The [^{14}C] PCE experiments generally provide better sensitivity and accuracy than GC analysis of unlabeled PCE (Nzengung et al, 1996 and 1997). It was not necessary to determine sorption isotherms of TCE because low amounts of PCE sorbed to the core samples and the solubility of TCE is higher than that of PCE by about an order of magnitude. Thus, PCE sorption results indicated that sorption of TCE to the cores was not a significant fate process.

Sorption isotherms were performed in 20 mL vials (nominal volume). 10 g of sediment, 17 mL of dionized water with a 5 mM $CaCl_2$ as an electrolyte were added to each vial (Kile et al., 1995). The vials were dosed with five different concentrations of ^{14}C-labeled PCE stock in methanol to achieve initial concentrations of 0.5 ppm, 1 ppm, 3 ppm, 5 ppm and 10 ppm in the soil/sediment slurries. The amount of methanol added to the slurries (22-45 ìL) was assumed to have a negligible effect on solute sorption

behavior (Kile et al., 1995). Each sample vial was dosed with a PCE tracer having an initial specific activity of approximately 20,000 disintegrations /minute (dpm) in 1 ml of liquid. Vials were sealed immediately with aluminum-faced septa, placed on an end-over-end mechanical shaker at an ambient temperature $25^{o}C \pm 2^{o}C$. Triplicate samples and sediment free control vials were prepared at each concentration and headspace was minimized in all vials. After a 48-hours equilibration period, the vials were centrifuged for 20 minutes at 2500 rpm (Rutherford et al., 1992). Two mLs of liquid was removed from each vial and added to a separate vial containing 15 ml of ScintiSafe 30% scintillation cocktail (Fisher Scientific Co., Pittsburgh, PA). The sample and cocktail mixture was agitated for one minute and analyzed on a Beckman 5801 liquid scintillation (LS) counter and rerun after 24 hours. The LS data were used to quantify the PCE concentrations in the liquid phases and to prepare sorption isotherms.

Sorption Data Analysis

The difference method was used to calculate the concentrations of PCE sorbed to the sediment. This involved subtracting the equilibrium liquid phase concentrations (Ce in mg/l) from the initial concentrations (C_0 in mg/l) and attributing this difference to sorption. The sorbed phase concentration was calculated using the following equation:

$$Se = (Co - Ce) \cdot \left(\frac{V}{m} \right)$$

where Se is the sorbed concentration (mg/Kg), Co is the initial aqueous concentration (mg/L), Ce is the equilibrium aqueous concentration (mg/L), V is the volume of the aqueous phase in each vial (mL), and m is the mass of soil in the vial (mg). This method assumes that the difference in the initial and final aqueous phase concentrations is

primarily due to sorption of the hydrophobic organic contaminant (HOC) onto the solid phase.

The sorption data was described by three sorption models to determine the sorption mechanism of PCE to the OU4 core sediments. The model with the best regression coefficient (r^2) was used to describe the data for that experiment. The linear model is given by:

$$Se = K_p\, Ce$$

Where Ce and Se are described above and K_p is the partition coefficient. The simplest model is the linear sorption model, which assumes that sorption is reversible. Partition coefficients (Kp in mL/g) were determined by regression analyses of the sorbed concentrations (Se) versus the equilibrium solution concentration (Ce). The Freundlich model is described by the non-linear relationship:

$$Se = K_f \cdot Ce^N$$

where ^{N} is the degree of non-linearity (referred to as 1/n; unitless) and K_f is the Freundlich partition coefficient $\left(\frac{L^3}{mass}\right)^{\frac{1}{n}}$. K_f was determined by regression of log Se vs. log Ce. The Langmuir model is described by the equation:

$$\frac{Ce}{Se} = \frac{1}{(b \cdot Q)} + \frac{Ce}{Q}$$

Where b is an adsorption constant related to the binding energy (L/mg) and Q is the maximum amount of solute that can be adsorbed by the solid (mg/kg). The adsorption maximum (slope = 1/Q) was determined by regression of Ce/Se vs Ce.

The organic carbon-normalized sorption coefficient (Koc) of the solute was obtained by normalization of the slope of the linear isotherm (Kp) with the organic carbon fraction (foc) of the solid *(Kp = Koc· foc).* Retardation coefficients (R) were determined from the equation:

$$R = 1 + \frac{K_p \cdot r_b}{n_e}$$

where ρ_b is the bulk density (assumed value of 2.1 g/ml), n is the effective porosity (assumed value of 0.4 for sandy sediments), and K_p is the linear partition coefficient.

BET Surface Area Measurements

Twelve samples of core sediment (seven surface samples, two mid-depth samples, and three deep samples) were analyzed for specific surface area. A Gemini II 2375(Micromeretics) Surface Area Analyzer was used to measure the surface area of the sediment samples. The analyzer measures surface areas as low as 0.01 m^2/g. The external surface area was determined by measuring the amount of adsorbed N_2 gas at temperatures near the boiling point of liquid N (77K). The BET equation used was:

$$\frac{P}{V(Po - P)} = \frac{1}{Vm \cdot C} + \frac{P(C-1)}{Vm \cdot C \cdot Po}$$

Where Vm is the volume of gas required that forms a mono-layer of gas over the entire surface, V is the total volume of gas adsorbed at partial pressure P, Po is the saturated pressure, and C is a constant. If P/V(Po – P) vs. P/Po is plotted, the slope is 1/Vm and the specific surface can be calculated by the equation:

$$SA_{BET} = Vm \cdot \left(\frac{A \cdot N}{M} \right)$$

Where A is the Avogadro's number, N is the area of each absorbed molecule, and M is the molar volume of the gas.

Preparation of sediment for the surface area analysis involved air-drying the sample, weighing of the sample in a test tube, and purging the sample with nitrogen. Because of the high sand content of the aquifer sediments, 0.5 g of sample was used.

Particle Size Distribution (PSD) Analysis

The particle size pipette method was used to calculate the texture of thirteen sediment samples of the OU4 aquifer sediments (seven surface samples, 3 mid-depth samples, and 4 deep samples). Ten grams of sediment were added to 500 mL bottles. After adding 5mL of sodium metaphosphate to each bottle, dionized water was added to bring the total volume up to 400 mL. The bottles were sealed with a stopper and placed on a shaker for 24 hours. After 24 hours the bottles were removed from the shaker and placed on a stirring plate. At three-minute intervals the bottles were placed in a water bath at room temperature ($25^{o}C$).

Stoke's law was used to calculate the settling velocity of the clay fraction (i.e. <2 microns). The time to sample with the pipette before the clay fraction had settled was calculated for a depth of 5 cm in the bottles at a temperature of $25^{o}C$ based on the settling velocity. A time of three hours and 30 minutes after the bottle was taken off the stirrer and placed in the water bath was needed for the 20 micron fraction to settle but not the 2 micron fraction. The sample that was extracted with the pipette at the predetermined time was dried in an oven overnight at $105^{o}C$. After the 2 micron sampling had been completed the remaining solution was poured through a 300 mesh sieve (American Standard and Testing Materials, ASTM). The bulk sand fraction collected by the sieve

was baked overnight in the oven and weighed. The amount of clay was determined by subtracting the salting out factor from the weight of the dried clay in the crucible and then multiplying by the dilution factor (dividing the volume of the bottle by the volume of the pipetted amount). The sand and clay weights were transformed to percentages by dividing these numbers by the total weight of the initial bulk sample added, 10 grams. The amount of silt was calculated by subtracting the clay and sand percentages from 100.

Cation Exchange Capacity

The cation exchange capacity was determined by saturating a soil with an index cation, Ammonium Oxalate (NH_4Oac) at pH 7. The next step involved removing the excess salts of the index cation, and then displacing the index cation, NH_4, with another cation. The amount of displaced NH_4 was then used to determine the exchange capacity per gram of sediment.

Organic Carbon and Metals

The organic carbon and metals analysis were performed by Dr. Sayad Hassan and Marrie Hagan of Whitehall Environmental Laboratories at the University of Georgia. The metals analysis was performed by the digestion method (USEPA 3051a - microwave digestion). A Perkin Elmer Elan 6000 ICP-MS was used to analyze the metals content of the digestions. For the organic carbon analysis, 1 gram of sample was treated with 2 mL of 10 % HCL to get rid of the inorganic carbon and then the acid was evaporated. Organic carbon was measured with a LECO C, N,S 2000 determinator.

Gas Chromatography (GC/µECD) Methods for PCE, TCE, trans-1,2-DCE and cis-1,2-DCE

A Hewlett Packard gas chromatograph (GC) 6890 with a micro-electron capture detector (GC-µECD) was used for quantitative analysis of the PCE, TCE, cis-1,2-DCE, and trans-1,2-DCE in extracted aqueous and solid phase samples. The GC-µECD configuration used a splitless injection of 1 µL hexane extract using a Hewlett-Parkard-7863 series automatic injector. The splitless injection had a hold time of 0.5 minutes and the purge flow was set at 40 mL/min to maximize sensitivity. The separation column was a 75 m DB-VRX^{TM} (J & W Scientific) * 0.45 mm * 2.55 µm film. The DB-VRX^{TM} column temperature was programmed at 35^{o}C and held for 12 minutes, followed by a temperature increase of 5^{o}C/min to 65^{o}C and held for 1 minute, and a subsequent temperature increase at 17 ^{o}C /min to 200 ^{o}C which was maintained for 3 minutes, resulting in a total run time of 29.94 minutes per a sample. Helium was used as the carrier gas with an in-column flow rate of 3.3 mL/min and nitrogen was used as the makeup gas with a 60 mL/min flow rate. The inlet was held in the constant flow mode because of the tendency of the carrier gas to become more viscous at high temperatures. The initial inlet pressure was set at 9.57 Psi and increased during the run to maintain a column flow rate of 3.3 mL/ min (linear velocity of 27 cm/min). The injector and detector temperatures were 250^{o}C and 310^{o}C, respectively. One mg/L dichlorobenzene samples were analyzed as an external standard. To ensure accurate quantitative results, PCE, TCE, cis-1,2-DCE, and trans-1,2-DCE standards were prepared in-house and used to construct calibration curves each week or whenever GC conditions changed as

indicated by the external standard. Detection limits for TCE and PCE were 1 ppb, 10-15 ppb for cis-1, 2-DCE, and 30-40 ppb for trans-1,2-DCE

Gas Chromatography (GC/FID) Method

A Hewlett Packard GC-5890 gas chromatograph with a flame ionization detector (GC-FID) was used for headspace analysis of PCE, TCE, DCE, VC, ethane, ethene, and methane. All analyses were by manual splitless injection of vapor samples collected from the headspace of the batch vials using a Hamilton Gas-Lock syringe (Reno, Nevada). The splitless injection had a hold time of 0.5 min, a septum purge flow of 3 mL/min, and the purge flow was set at 50 mL/ min. A 25 m PLOT Fused Silica CP-PoraPLOT megabore * 0.53 mm ID * 20 µm film separation column was used in all analyses (Hewlett Packard). The initial column temperature was programmed at 40^{o}C for 5 minutes, followed by a temperature increase of 10^{o}C/min to 200^{o}C which was maintained for 10 minutes (28 min total run time). Helium was used as the carrier gas with an in-column flow rate of 5 mL/min. The injector temperature was 250^{o}C and the detector temperature 220^{o}C (20 ^{o}C above final column operating temperature) to maximize sensitivity and prevent condensation in the detector. Retention times for VC, ethane, ethene, and methane were confirmed by injecting standard gases in Scotty II gas cylinders obtained from Supelco (Chicago, Illinois). Retention times for PCE, TCE, and DCE were confirmed by headspace sampling from the neat chemicals. Headspace concentrations were determined using published Henry's Law constants (Gossett, 1987).

Hydrogen Analysis

Hydrogen was analyzed using a Trace Analytical RGA3 Reduction Gas Analyzer Menlo Park, CA) with a RGD2 detector at the United States Environmental Protection

laboratories in Athens, Ga. Air was used as the carrier gas and the column temperature was held isothermal at 105 ^{O}C with a detector temperature of 265 ^{o}C. The method has a detection limit of 10 ppb.

Liquid Scintillation Assay

For each ^{14}C measurement, three 1 mL liquid samples were collected from a sample vial (Packard, 2000; Rapkin 1962; and Vogel and McCarty, 1985). One mL of the liquid was injected into a glass counting vial containing 1 mL of 1 N HCL, another 1 mL of liquid was injected into 1 mL 1 M NaOH, and a third 1 mL of liquid into a vial containing 15 mL of liquid scintillation counting solution (Hionic-Fluor- Packard Instruments). The first two samples were then purged with argon for 10 minutes, and then 15 mL of scintillation fluid was added to each. This method allowed for the quantification of [^{14}C] PCE converted to [^{14}C] CO_2. Carbon dioxide reacted with NaOH to form bicarbonate, which allowed for [^{14}C] CO_2 to be quantified because all other volatile metabolites were stripped from the purged acidified samples. The presence of [^{14}C] CO_2 was confirmed by adding 0.5 mL 1 M strontium chloride to a 1 mL aqueous phase sample in a plastic 2 mL microfuge tube. Strontium chloride reacts with $^{14}CO_2$ and precipitates the $^{14}CO_2$ as $Sr^{14}CO_3$ (Rapkin, 1962; and Connell et al., 1997). The samples were centrifuged for 30 minutes, then the supernatant was decanted, and the precipitated pellets were resuspended in 1 mL of pH 10 dionized water. The resuspended pellets were added to15 mL of scientsafe cocktail for counting.

The [^{14}C] distribution (volatile, hydrophilic, and [^{14}C] CO_2 components) were calculated from the following equations:

% Volatile = ((Total Counts of 1mL sample in Cocktail – Total Counts in Acidified Samples) / Total Activity) x 100

% Hydrophilic = (Activity in Acidified Samples / Total Activity) x 100

% [^{14}C] CO_2 = ((Total Counts of Base Treated Sample – Total Counts of Acidified Samples)/ Total Activity) x 100

Microcosm Experiments

Microcosm degradation experiments were performed to determine the degradation rates of PCE, TCE, and cis-1, 2-DCE and to determine if the degradation can be enhanced by different electron/carbon sources. Batch microcosm studies allowed for multiple experiments composed of different sediments and carbon/nutrient combinations to be conducted simultaneously. The sediment plus groundwater microcosms were prepared by mixing ten grams (wet weight) of site sediment from the collected cores with 18 mL of site groundwater in 20 mL ICHEM borosilicate screw top vials. This was done in a glovebag under an argon environment (I2R Inflatable Glove bag Chamber; Cole Parmer Instruments). Prior to assembly, the site sediment and groundwater were purged with argon inside the glovebag. After purging was completed, the bag was evacuated and refilled with argon. The vials were sealed inside the glove bag with Teflon® lined septum and screw caps.

All vials were incubated in the dark for one week after preparation before spiking to ensure that the samples were completely anaerobic. After the one-week acclimation period, the vials were spiked with either PCE, TCE, or cDCE inside the argon filled glove bag, recapped, and wrapped with aluminum foil. Aluminum foil covering was necessary to prevent any photo-chemical degradation of the volatile organic compounds. All batch

vials in the experiments contained the same solids to solution ratio (10g sediment and 18 mL site groundwater) and were spiked with the same initial solute concentration. Amendments with corn oil, molasses, and HRC were based on volume / volume percentages. The other amendments were based on an initial micromolar concentration.

The samples were incubated by shaking continuously on a rotary end-over-end shaker (4 rpm) at a temperature of 25 ^{o}C. Repeated sampling of the same vial results in contamination and headspaces losses of the more volatile components (Barrio-Lage et al, 1986), therefore, duplicate microcosms were set up for each scheduled test period so that each pair of sample vials and a control were sacrificed for analysis. The aqueous phase was separated from the solid phase by centrifugation (2000 rpm for 30 min). The concentration of the initial solute and its degradation products in solution were measured by both direct aqueous sampling and hexane extracts on the GC/μECD. After removal of the aqueous sample, a 1 mL headspace sample was analyzed by GC-FID to independently confirm the chlorinated ethenes and ethanes measured by GC/μECD, as well as to qualitatively determine VC, ethene, and methane production.

Killed controls were used to differentiate between the biotic and abiotic processes of degradation. The killed controls contained no live microbes and any degradation was assumed to be abiotic. Two types of killed controls were used in these experiments because of the limitations associated with each method. One set of killed controlled controls consisted of gamma irradiated batch vials containing the sediment plus site water. The second set of killed controls was made up of autoclaved site sediment and groundwater. Autoclaving sediment can change the structure of carbon and underestimate the effects of sorption. Although radiation treatments do not change the

structure of carbon, radiation does not kill spores. Accordingly, radiation killed controls show the magnitude of sorption and autoclaved killed controls provide a sterile soil to assess any abiotic chemical or organo-metallic degradation reactions. The radiated controls were prepared by dosing a 400 g sediment sample with 400,000 rads of gamma radiation and the autoclaved controls was prepared by autoclaving a 600 g sediment for 2 hours at 125^{o}C on three consecutive days. Groundwater samples used in the killed control experiments were sterilized by autoclaving at 110^{o}C for 1 hour on two consecutive days.

Bioreactor Experiments

The bioreactor experiments were conducted in a sealed, continuous mixing three-liter fermentation vessels equipped with dissolved oxygen, redox probes, and pH probes (Figure 4.3 and 4.4; Cole Parmer Instruments, Vernon Hills, IL). The same solid to water ratio used in the microcosm experiments was used for the bioreactor experiments, 2 Ls of site groundwater to 1100 grams of sediment. Although headspace was minimized in the microcosm studies, a headspace of 500 mL was maintained in each of these bioreactors. The bioreactor was assembled in an argon-filled glovebag in the same manner as the microcosms. After an acclimation period of 1 week, the chambers were spiked with PCE from stock solutions of PCE and DI water. DI water stock solutions were prepared by purging DI with argon and adding neat PCE. A magnetic stirrer was used to mix the solution and increase dissolution of the non-aqueous phase liquid (NAPL) into the aqueous phase. Two sampling ports, one for headspace sampling and one for aqueous sampling, were used to measure the parent compound (PCE) and daughter products

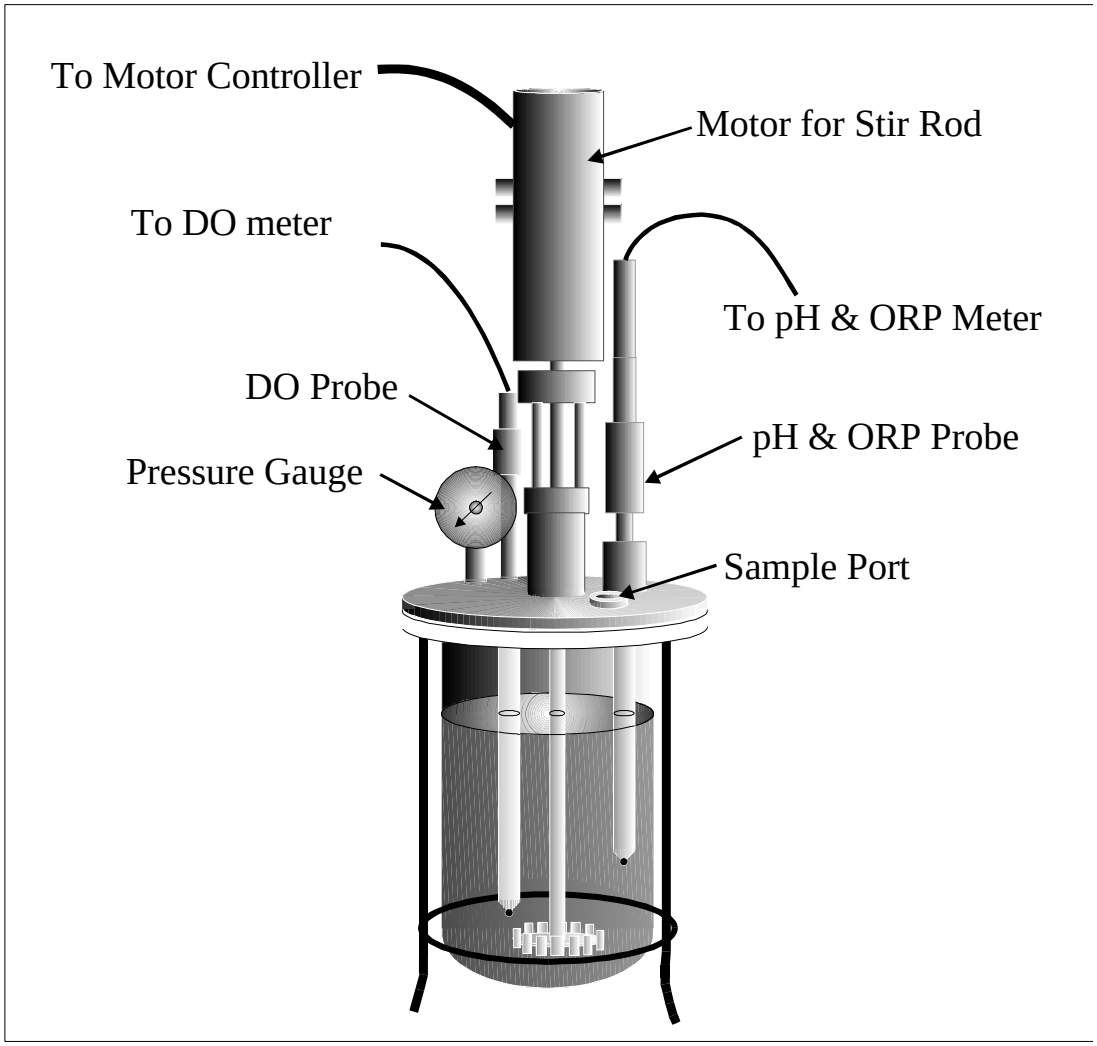


Figure 4.3. Diagram of a continuously stirred bioreactor chamber.

Figure 4.4. Picture of continuously stirred bioreactor experiments.

(TCE, DCE, VC, ethene, ethane, and methane) during the experiments. Loss of organic compounds due to sorption to the vessel O-rings and seals were determined by a control experiment composed of spiked DI water in a chamber.

Natural Attenuation Kinetic Data Analysis

First-order biodegradation rates for the batch microcosm experiments were determined by the method of least squares optimization. For each kinetic experiment, the parameter measured was the amount of compound left in solution at a given time t (C_t) relative to the concentration present at time t = 0 (C_0).

Zero-order biodegradation rates were modeled by the following equation:

$$\frac{d[A]}{dt} = -k[A]^0 = -k$$

Integration of the zero order equation yields:

$$[A] = [A]_0 - k \cdot t$$

Plotting the C_t vs time yields the zero-order rate constant k$\left(\frac{mg}{L \cdot d}\right)$. The half-life of disappearance for the zero-order reactions was calculated from the equation:

$$t_{\frac{1}{2}} = \frac{0.5[A]_0}{Co}$$

The first-order reaction rates were modeled by the following equation:

$$\frac{d[A]}{dt} = -k[A]$$

Rearranging and integrating the first order equation yields:

$$[A] = [A]_0 \cdot e^{-kt}$$

Plotting ln (C_t/C_0) verse time yields the first order rate constant k (d^{-1}).

The half-life of disappearance for the first order reactions was calculated from the following equation:

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

Degradation rates are reported within the 95 % confidence level, ($k * SE * t_{\alpha}$; where SE is the standard error and t_{α} is the critical t value).

CHAPTER 5

RESULTS OF NTC SITE SEDIMENT CHARACTERIZATION

Site characterization data was used to refine the preliminary conceptual model and development of an accurate three-dimensional representation of the hydrogeologic and contaminant transport system. Accordingly, the key to determining the fate of hydrophobic compounds lies in the understanding of the sediment-related processes (Karickhoff et al., 1978), because advection, dispersion, and retardation are significant processes that work to reduce the dissolved concentrations of contaminants and influence the fate of contaminants in the subsurface. Further, this analysis is necessary to better understand the abiotic influences and possible limitations of monitored natural attenuation.

The results of the sediment characterization are presented for three different depth intervals. Sediments from 0 to 4 feet below ground surface (bgs) will be referred to as surface sediments, sediments from 10 to 14 feet bgs will be referred to as mid-depth sediments, and sediments form 20 to 40 feet bgs will be referred to as deep sediments. The results for the site sediment characterization are summarized in Table 5.1.

Cation Exchange Capacity

The cation exchange capacity (CEC) of sediments affects their retention of inorganic and organic species. The CEC is defined as the ability to attract cations close to Electrostatic attraction brings dissolved cations to the surface to balance the charge. The CEC is dependent on both the organic carbon fraction and the secondary clay mineral

Table 5.1. Summary of results of sorption isotherm studies and characterization of NTC Orlando, Florida, core samples.

Soil Boring	Depth	Carbon Content % TOC	foc	$K_f(L^3/m)^{1/n}$	1/N	K_p(L/Kg)	r^2	Koc	Retardation Factor (R)	Texture %Sand	% Silt	% Clay	BET Surface Area (m^2/g)	CEC (meq/100g)
SB1	0-4	3.750	0.038	4.699	1.080	5.05	0.981	134.7	27.5	80.76	2.00	17.24	0.98	129.60
SB-2	0-4	1.800	0.018	2.300	0.999	2.39	0.97	132.6	13.5	91.12	1.91	6.98	2.51	27.93
	10-14	1.110	0.011	0.266	0.936	0.23	0.96	20.8	2.2	89.56	2.16	8.28	0.28	55.42
	25-29	0.890	0.009	0.241	1.180	0.34	0.99	38.2	2.8	91.41	1.99	6.60	1.07	64.54
	38-40	0.480	0.005							93.79	2.03	4.18	1.34	19.73
SB3	0-4	0.820	0.008	1.443	0.917	1.26	0.99	153.7	7.6	64.14	1.11	34.75	1.45	36.81
	10-14	0.270	0.003	0.293	1.039	0.32	0.98	118.5	2.7	94.33	2.32	3.34	0.99	8.02
	25-29	1.030	0.010	0.539	0.918	0.51	0.98	49.0	3.7					69.82
	38-40	0.250	0.003	0.240	0.630	0.08	0.45	32.0	1.4					13.11
SB4	0-4	2.300	0.023	2.157	0.883	1.79	0.98	77.7	10.4	91.13	2.49	6.38	2.02	72.30
	10-14	1.190	0.012											34.76
	25-29	0.450	0.005							93.54	2.22	4.25	0.98	39.28
	38-40	0.560	0.006	0.242	0.633					93.06	1.98	4.96		24.96
SB5	0-4	1.800	0.018	7.110	0.839	6.09	0.97	338.4	33.0	86.30	3.50	10.21	1.52	96.32
	10-14													78.01
	25-29													38.60
	38-40													13.68
SB6	0-4	2.550	0.026	4.950	0.886	3.86	0.88	151.5	21.3	72.29	2.84	24.87	1.12	21.11
SB7	0-4	1.770	0.018	3.440	0.878	2.52	0.84	142.1	14.2	93.94	1.97	4.09	0.20	27.31

fraction (Langmuir, 1997; Sparks, 1995). The net negative charge on the surface of the clay minerals is the result of isomorphic substitution of lower charged elements for higher charged elements in tetrahedral and octahedral lattice sites. The major source of negative charge on the surface of the organic matter (humic substances) is carboxylic (-COOH) and phenolic (R-OH) groups associated with a central unit of the organic solid (Deutsch,).

The CEC of the surface sediments ranged from 21.11 meq /100 g to 129 meq/100g with a mean of 58.77 meq/100g. The CEC of the mid-depth sediments ranged from 8.02 meq /100 g to 78.01 meq/100g with a mean of 44.05 meq/100 g. The CEC of the deep sediments ranged 13.11 meq/100g to 69.82 meq/100 g with a mean of 35.47 meq/100 g. Research by Stevenson (1982) and Toth and Ott (1970) estimated that up to 80 percent of the CEC in sediment is due to organic matter, even in sediments where the organic carbon content is low. Smectite was identified as the most predominant clay mineral in the aquifer sediments. Although the average clay percentage of the Orlando sediments is less than 10 percent, attributing the majority of the CEC to the organic carbon fraction could be misleading because of the high CEC attributed to smectite (Table 5.2).

The pooled data presented in figures 5.1 and 5.2 show that the CEC generally increased with an increase in both the percent of total organic carbon (TOC) and the clay fraction. A linear increase in the CEC with increasing percent TOC was observed at TOC values less than one percent (Figure 5.1). For TOC <1 %, the correlation weakens, presumably due to the influence of the clay content. There is a significant trend in figure 5.2 with several outliers to the data. The two outliers to the data could be a result of a

Table 5.2. Cation exchange capacities of secondary clay minerals and organic matter (Sparks, 1995; and Langmuir, 1997).

	CEC (meq/100g)
Kaolinite	2-15
Halloysite	10-40
Talc	<1
Montmorilonite	80-150
Dioctahedral Vermiculite	10-150
Trioctahedral Vermiculite	100-200
Muscovite	10-40
Biotite	10-40
Organic Matter	150-300

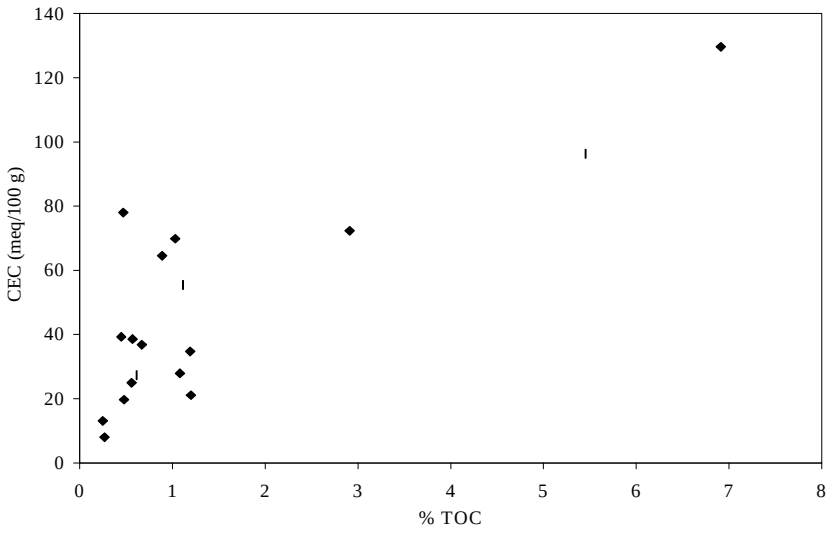


Figure 5.1. Comparison of the CEC values to the total organic fraction (TOC = foc * 100).

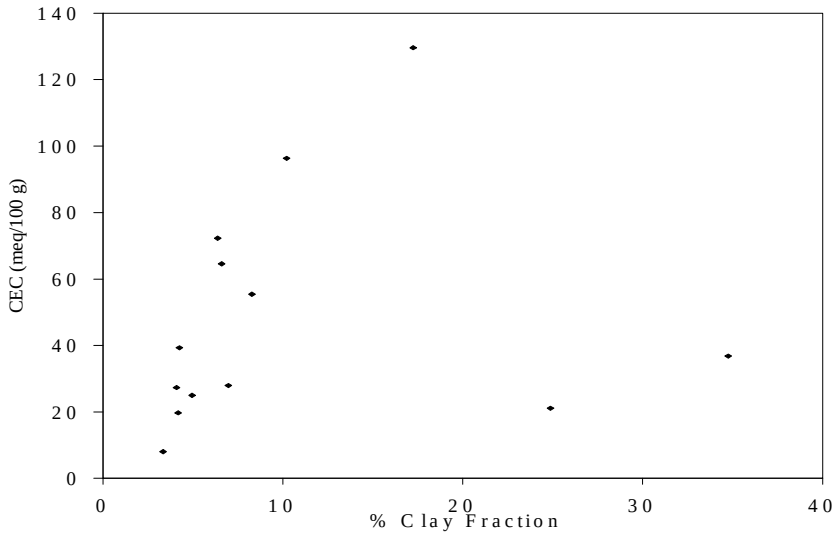


Figure 5.2. Comparison of the CEC values to the clay fraction.

percent TOC was greater than with increasing clay fraction. The poor correlation kaolin.component to the clay fraction. The rate of increase in CEC with increasing between the SSA and the CEC and the overall low surface area of the Orlando sediment suggested that the majority of the CEC was contributed by the organic carbon fraction (Suthersan, 1997).

Metals Analysis

Metals are an important mineralogical and compositional feature. The redox sensitive metals exist as complexes in the form of oxides and hydro-oxides and act as terminal electron acceptors during biodegradation. Iron (III) and Manganese (IV) oxides and oxyhyroxides are the most prominent metals in the subsurface involved in biodegradation processes. These metals have the tendency to act as terminal electron

acceptors during reductive dehalogenation. The bioavailable distribution of Iron (II) and Iron (III) and Mn (II) and Mn (IV) in the aquifer dissolved and solid phases is very difficult to determine due to the numerous subsurface sinks for these metals. The ICP metals analysis can determine the total iron and manganese concentrations of aquifer sediment. These concentrations are directly related to the abundance of the oxides and hydroxides of the sediment. The results are summarized in Table 5.3. Surface sediment generally contained the highest solid phase iron concentration and the concentration of most metals decreased with depth. The heterogeneous distribution of the quantified metals is clear from Table 5.3.

Particle Size Distribution

The surficial sediment averaged 16 percent clay, 2 percent silt, and 82 percent sand. The mid-depth to deep sediment averaged 5 percent clay, 2 percent silt, and 93 percent sand. Clay percentages of the surface sediments are possibly misleading because the analytical method includes the final weight of a pipetted portion that includes both colloidal organic matter and clay. The surface sediments have a loamy sand texture, and mid-depth to deep sediments have a sand texture (Based on textural triangle from Skopp, 1999). The particle size distribution (PSD) of an unconsolidated water table aquifer such as the surficial aquifer at the OU-4 site governs the hydraulic properties of the aquifer. PSD is the most fundamental physical property of sediment (Skopp, 1999). The PSD. determines the permeability and the porosity of an unconfined aquifer and is a way of distinguishing between two aquifer systems. Porosity and permeability determine the magnitude of the processes that affect the transport of contaminants in the subsurface.

Table 5.3. Concentration (µg/kg) of selected metals in OU4 Sediments. Nickel, arsenic, titanium, and cadmium were below the detection limit (BDL) of the analysis.

Soil Boring	Depth (ft)	Al	Mn	Fe	Cu	Zn	Se	Mo	Ag	Hg	Pb
SB-2	0-4	1,059,954	15,484	400,894	7,335	49,050	27	149	69,590	560	21,846
	10-14	349,329	296	11,845	577	bdl	bdl	45	116	97	3,092
	25-27	1,962,739	997	207,135	733	1,369	267	77	0	12	1,891
	38-40	925,278	228	19,731	5,342	121	365	103	26	243	672
SB-3	0-4	413,103	4,385	233,449	5,552	15,960	bdl	102	1,800	288	4,460
	10-14	97,667	1,376	24,006	260	bdl	bdl	4	42	262	495
	25-27	851,974	356	50,800	124	347	128	23	bdl	56	1,027
	38-40	327,619	1,563	54,336	330	1,779	87	37	77	170	1,439
SB-4	0-4	3,524,074	7,625	761,873	3,731	8,361	604	79	bdl	84	14,750
	10-14	2,620,284	2,317	296,208	1,891	15,644	76	181	100	215	12,243
	25-27	1,313,906	1,289	91,003	338	78	369	66	bdl	34	1,412
SB-5	0-4	1,309,712	662	107,454	279	670	122	6	bdl	97	2,775
	10-14	507,902	553	24,578	719	632	8	34	bdl	30	4,671
	25-27	958,734	316	49,191	249	bdl	455	87	bdl	54	1,092
SB-6	0-4	570,792	61	17,584	418	bdl	174	16	bdl	162	2,293
SB-7	0-4	553,054	588	58,536	54,937	2,843	70	91	bdl	104	2,356
LOD		0.234	0.213	2.89	0.129	0.528	0.609	0.021	0.054	0.009	0.015

The most important processes affecting contaminant transport are dispersion, advection, and retardation. The higher clay percentages of the surface sediments (low permeability) increase dispersion and retardation while decreasing the influence of advection. Conversely, the high sand percentages of the deep sediments (high permeability) increase the influence of advection and decrease the processes of dispersion and retardation.

Surface Area

The importance of surface properties on the fate and transport of organic chemicals in groundwater increases in proportion to the specific surface area (SSA) of the aquifer material. An increase in SSA results in a higher sorptive capacity (higher retardation factors) and a greater number of sites for surface catalyzed abiotic transformation reactions.

With soil organic matter and montmorillonite the predominant clay, a SSA of 600-800 m^2g^{-1} would be expected if the sample is composed entirely of organic matter and montmorillonite (Table 5.4). However, the average SSA for the OU-4 sediments is 1.1 m^2g^{-1}. The reported values of 560-800 m^2g^{-1} for the surface area of organic matter were determined using the retention of ethylene glycol (EG) at room temperature. Since surface area measurements based on the retention of EG are primarily due to monolayer absorption (Sparks, 1995), similar monolayer adsorption of nitrogen at liquid nitrogen temperature would be expected. Research by Chiou et al. (1990) examined the reported EG determined SSA values (560-800 m^2g^{-1}) for organic matter using the standard BET method based on nitrogen adsorption at liquid nitrogen temperature. Their measured BET values averaged less than 1 m^2g^{-1}. The high EG SSA values result from the creation of an interlamellar surface caused by lattice swelling that did not exist before the liquid

uptake (Chiou et al., 1990). Further, the high retention of EG by organic matter at room temperature is proposed to be a result of partitioning and not surface adsorption (Chiou et al., 1990).

The tendency of organic matter to coil into globular units further reduces the BET measured surface area. Organic matter coils to minimize its hydrophobic surface area exposed to the aqueous solution (Schwarzenbach et al., 1993). The low SSA of the OU-4 sediment is a product of both the low clay percentage (<10 %) and the lack of surface area of the organic matter determined by the standard BET method.

Table 5.4. Ranges of specific surface areas (SSA) of clay minerals, soil components, and soil textures (Sparks, 1995; and Skopp, 1999).

	SSA (m^2g^{-1})
Kaolinite	7-30
Halloysite	10-45
Montmorillionite	600-800
Dioctahedral Vermiculite	50-800
Trioctahedral Vermiculite	600-800
Muscovite	60-100
Biotite	40-100
Organic Matter	560-800
Iron-Oxides	116-184
Sands	<10
Sandy loams	5-20
Clay loams	15-40
Clay	>25

Organic Carbon

Organic carbon percentages were greatest at the surface and separated into two zones. The organic rich swamp portion of the surface averaged 2.49 % TOC and 1.6 %

TOC near building 1100. Organic carbon in the mid-depth to deep sediments averaged 0.6 % TOC. Dissolved organic matter of the site groundwater averaged around 9mg/L, 2 to 9 mg/l within the chlorinated solvent plume and background levels of 14 mg/l (Harding Lawson and Associates, 1998).

The amount of organic carbon controls sorption, biodegradation, and enhances physical properties such as CEC and sediment pH. Organic carbon can be either in the form of dissolved or particulate organic matter and includes organic residues, soil biomass, humic substances, humin or kerogen substances, humic acids, hymatomelanic acids, and fulvic acids (Sparks, 1995). Knowing the composition of the total organic carbon (TOC) of sediments is essential in assessing the biodegradation capacity at a contaminated site because TOC availability is often a limiting factor of monitored natural attenuation. Low DOC values within the plume and TOC values less than 1 % in the mid-depth and deep sediments of the OU4 soil cores suggest possible TOC limitations to biodegradation. The low levels of TOC in the mid-depth and deep sediments could be a result of low initial TOC concentrations or depletion by *in-situ* microbial activity.

Sorption

Chlorinated solvents are removed from groundwater by sorption onto to the aquifer matrix. Favorable thermodynamics cause hydrophobic contaminants to partition from groundwater to the aquifer matrix (Schwarzenbach et al., 1993). Sorption of the organic contaminant to the aquifer matrix results in a reduction of the aqueous contaminant concentration, retards the contaminant relative to the seepage velocity, and reduces the amount of dissolved contaminant in groundwater. Sorption consists of three main mechanisms: 1) physical sorption due to Van der Waals forces, 2) chemisorption

due to chemical bonding or surface coordination reactions such as adsorption to mineral surfaces, and 3) partitioning of the organic chemical into the organic carbon phase of sediments and soils. The influence of a given sorption mechanisms is primarily controlled by the fraction of organic carbon and clay mineral components of the aquifer matrix.

Results of PCE sorption experiments using NTC Orlando site sediment from various locations and depths are summarized in Table 5.1. The raw sorption data including the linear, Freundlich, and Langmuir isotherms are presented in Appendix 1. The Freundlich and linear sorption models were used in the data analysis of the surface and mid-depth sediments. The linear model best described the surface and mid-depth sorption data which displayed a high degree of linearity with a r^2 of 0.90 or better (Figure 5.4). The Langmuir model or the Freundlich model (1/n less than 1) more accurately characterized the deep sediment sorption data. The Langmuir model had a r^2 of 0.9 or better and an adsorption maximum (Q) of 0.678 mg/kg. Sorption was greatest with the surface sediments and decreased significantly with depth. The higher organic carbon partition coefficients (Koc) were obtained with the surface sediment (average Koc 295) and decreased by over eighty percent in the deep sediments (average 40).

The sorption isotherms fell into three groups corresponding to the fraction of organic carbon (Figure 5.5). Group I has an average TOC of 2.5 % and includes the surface sediments of SB1, SB5, SB6 and SB7. Group II averages 1.6 % TOC and includes the surface sediments of SB2, SB3, and SB4. Group III averages 0.6 % TOC and includes the mid-depth and deep sediments of SB2 and SB3.

The dominance of organic carbon on sorption of organic contaminants has been well-documented (Wiedemeier et al., 1999; Karickhoff et al., 1979; Schwarzenbach and Westail, 1981; Allen-King et al., 1997). Organic matter functions as a partition medium and the mechanism of sorption can be treated in a similar manner to that between an organic solvent phase and water (Chiou et al., 1983). Non-polar contaminants penetrate the chains of the coiled organic carbon particle and are absorbed into the organic carbon phase (Figure 5.6).

The Langmuir shape (Freundlich where 1/n <1) of the mid-depth and deep sediment isotherms indicates an adsorption maximum. This maximum could be a result of a significant depletion in the fraction of organic matter with depth of the OU4 sediments rather than the limits of mineral surface sites available to sorption. The standard rule is that mineral sorption may dominate if the fraction of organic carbon (foc) is less than .001 (Fetter, 1999; Schwarzenbach and Westall, 1981). McCarty et al. (1981) developed an equation that incorporates the SSA and hydrophobicity of the contaminant (Kow) to determine at what level of foc the sorption to minerals and organic carbon is equal. This level of foc is termed the critical level of foc and designated by f*oc. The comparison of measured foc and f*oc values indicates that sorption to mineral surfaces and organic carbon of the OU4 sediments are not equal. Further, sorption to organic carbon is greater than that to mineral surfaces because the measured foc is not below the standard of 0.001 and is two to three orders of magnitude higher than empirical f*oc (Table 5.5). Karickoff (1984) developed a semi-quantitative threshold to determine the contribution of mineral sorption to total sorption. The threshold is the ratio of the clay

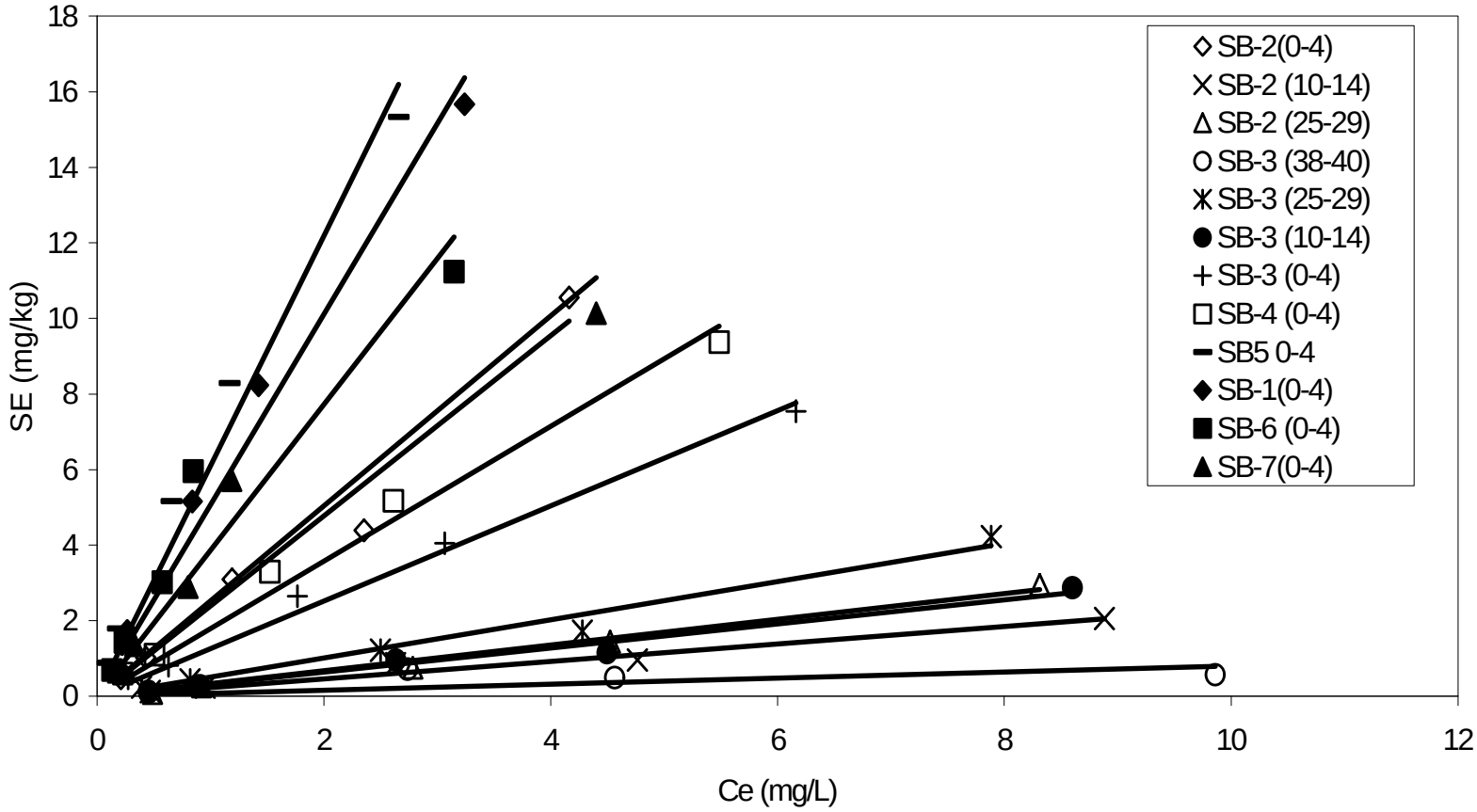


Figure 5.4. Linear sorption isotherms of PCE to the sediments of OU4 soil cores.

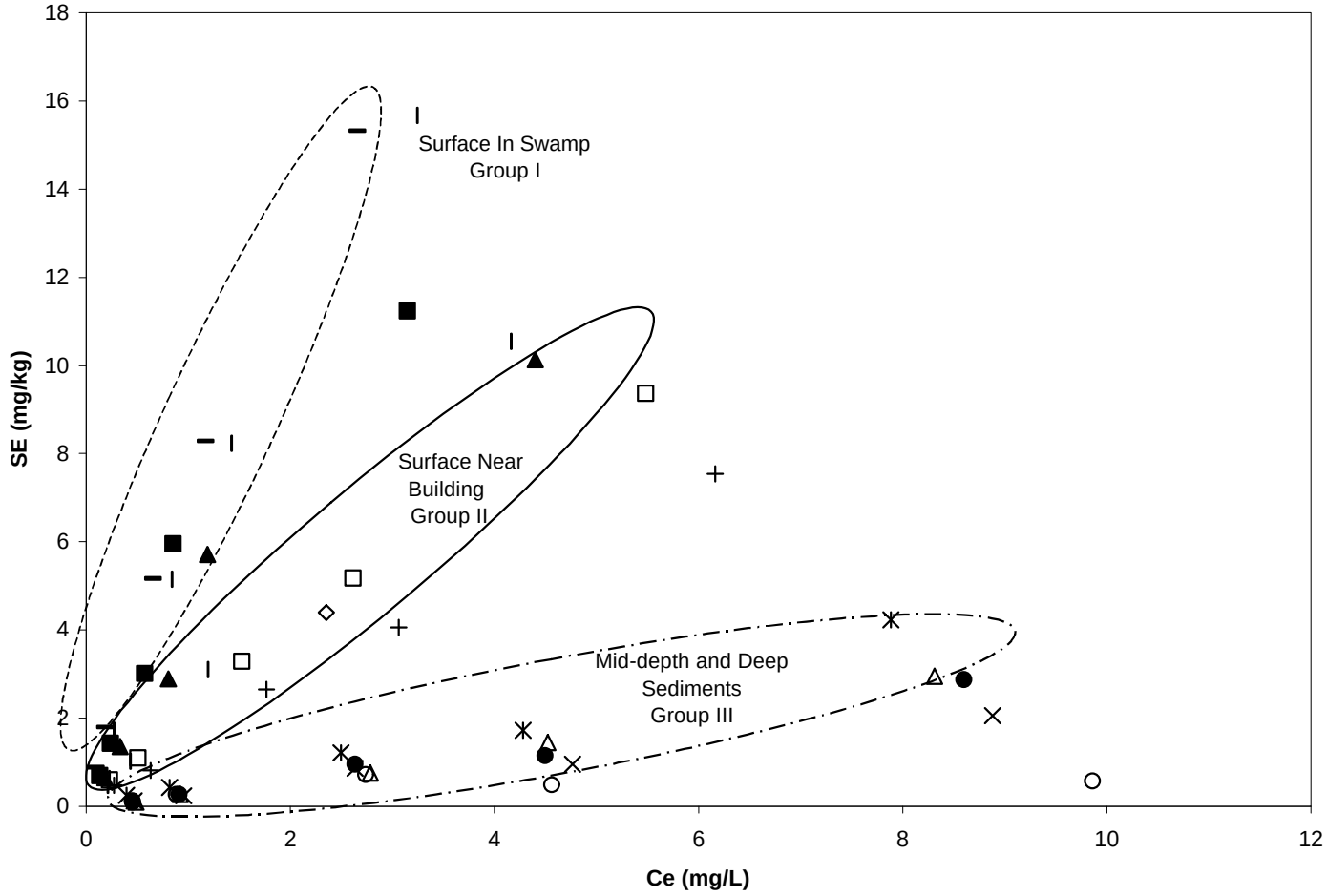


Figure 5.5. Grouping of the linear trendlines of sorption isotherms of PCE to sediments of the OU4 soil cores.

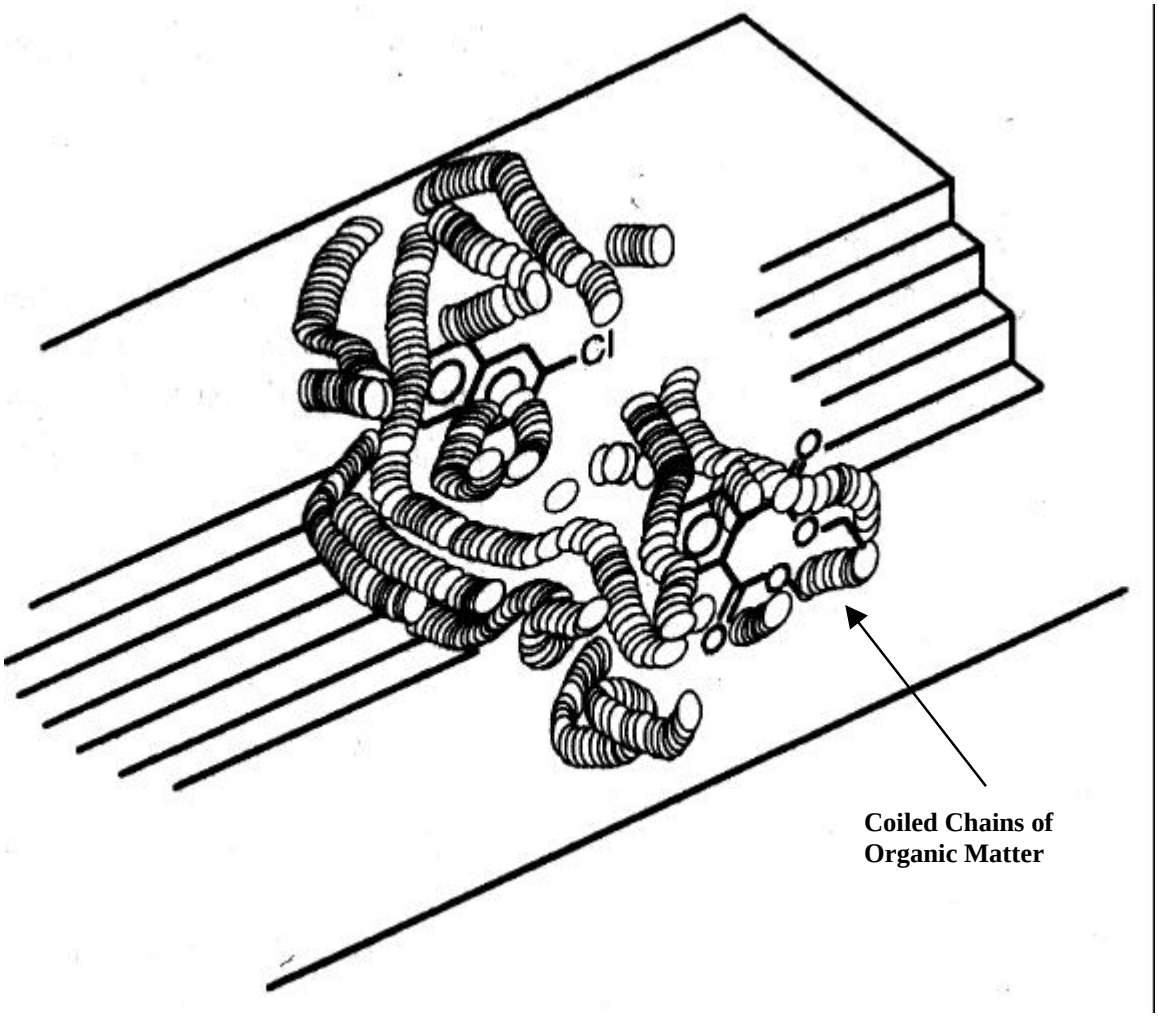


Figure 5.6. Illustration of the partitioning of organic molecules into the coiled chains of organic matter (pictured here is a chloro-benzene molecule, chloro-ethenes follow suit; from Schwarzenbach et al. 1993).

fraction (cm) to the foc at the onset of mineral contributions to enhance Koc with increasing mineral content. For non-polar organics, the threshold for mineral contribution is 60. The deep sediments do not plot in accordance with the cm/foc threshold of 60 on figure 5.7; rather, the data plots close to the origin far below the threshold and below the average Koc for the OU4 sediments. By applying this method by Karickhoff (1984), the mineral contribution to the adsorption maximum of the Langmuir isotherms can be considered negligible. The low BET surface areas, the linear sorption isotherms (figure 5.4), and a good correlation between the partition coefficients and the fraction of organic carbon (figure 5.8) confirms the dominance of organic carbon in sorption of PCE by the aquifer sediment. Retardation factors (R) calculated by assuming a linear sorption model for the surface sediments ranged between 17 to 35 and 3.1 to 1.6 for the mid-depth and deep sediments (Table 5.1).

Table 5.5. Comparison of the measured fraction of organic carbon coefficients (foc) and the critical level of foc (f*oc) defined by McCarty et al. (1981; $f^*oc = Sa / 200\ (Kow)^{0.84}$ where Sa is the surface area and Kow is the octanol-water partition coefficient).

Soil Boring	Depth(ft)	foc	Sa (m^2/g)	f*oc
SB1	0-4	3.75E-02	0.98	1.86E-05
SB-2	0-4	1.80E-02	2.51	4.77E-05
	10-14	1.10E-02	0.28	5.36E-06
	25-29	8.90E-03	1.07	2.03E-05
	38-40	4.80E-03	1.34	2.55E-05
SB3	0-4	8.20E-03	1.45	2.76E-05
	10-14	1.50E-03	0.99	1.88E-05
SB4	0-4	2.30E-02	2.02	3.84E-05
	25-29	4.60E-03	0.98	1.86E-05
SB5	0-4	1.80E-02	1.52	2.89E-05
SB6	0-4	2.55E-02	1.12	2.14E-05
SB7	0-4	1.77E-02	0.20	3.76E-06

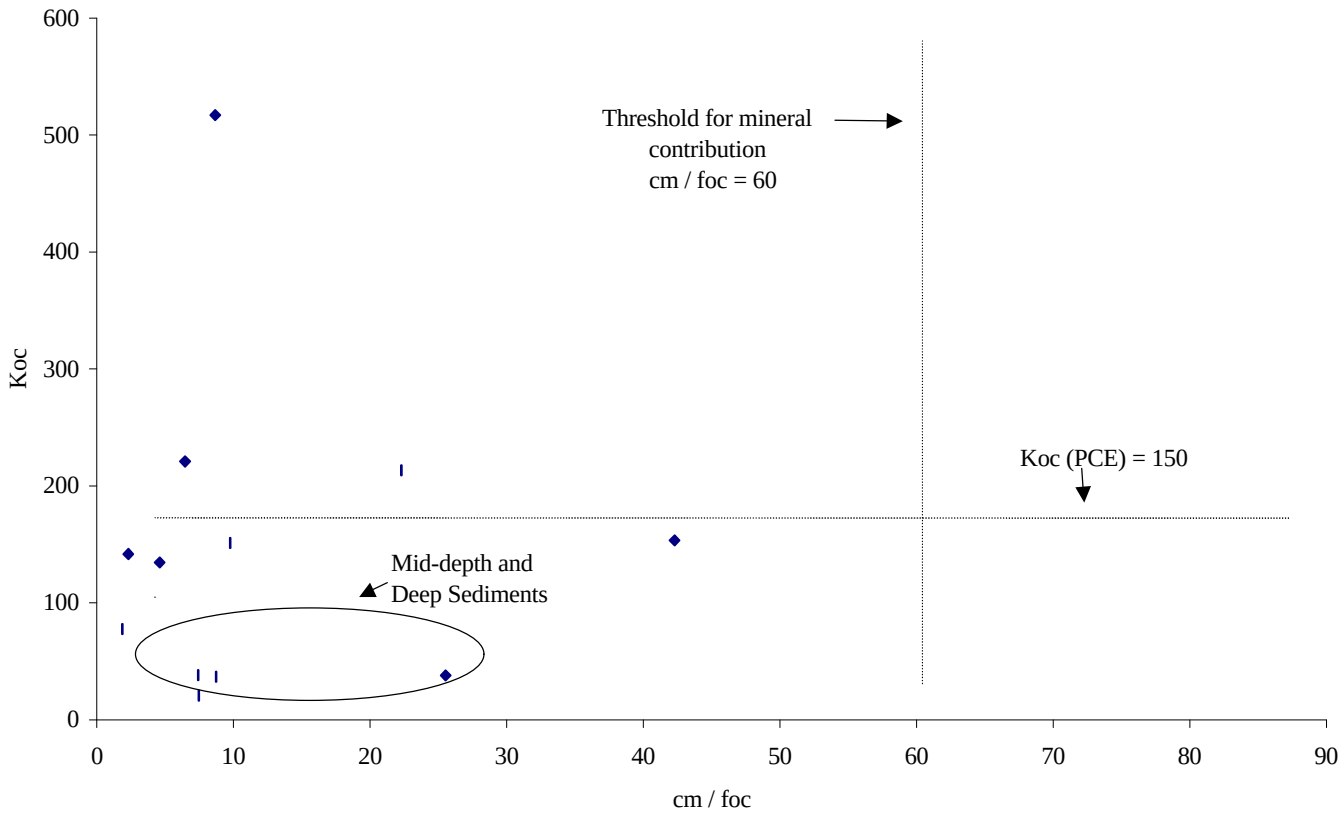


Figure 5.7. Mineral contributions to sorption of tetrachloroethene expressed as the organic carbon normalized sorption coefficient verses clay mineral fraction (cm) normalized by the foc.

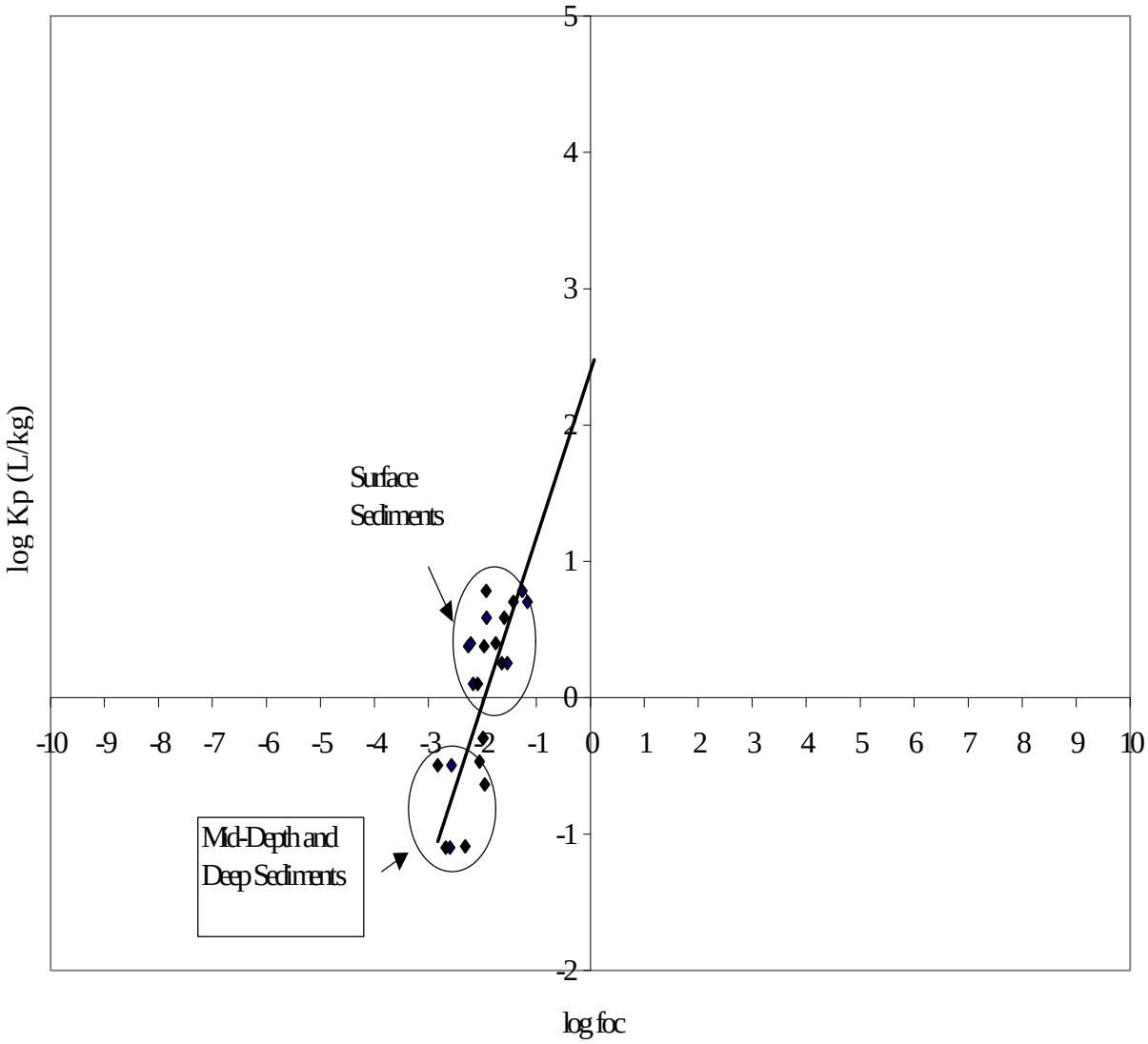


Figure 5.8. Linear partition coefficient (Kp) values of the OU4 sediments for PCE as a function of the fraction of organic carbon coefficient (foc).

CHAPTER 6

RESULTS OF BIODEGRADATION EXPERIMENTS

Laboratory degradation experiments were designed to determine the potential for in-situ biodegradation. These experiments used site sediment and groundwater to ascertain if indigenous microbial communities can degrade xenobiotic organic compounds at NTC, Orlando. Both batch microcosm and continuously stirred (CSTR) bioreactor vessels were used in this study. Unamended experiments provided degradation rates to assess background microbial activity. Experiments amended with different carbon source/nutrient combinations demonstrated whether in-situ biodegradation was limited by a lack of nutrients or an electron donor. Molasses, corn oil, Na-acetate, Na-lactate, and a HRC® compound were the electron donors used in this study. Yeast extract was used as both a carbon source and a nutrient source of B-complex vitamins.

Degradation pathways were studied in experiments using both the [^{12}C] PCE and [^{14}C] PCE forms of the chemicals. The formation of daughter products was used to confirm that sequential dehalogenation occurred, and to determine the final degradation products of PCE. The sequential dehalogenation of PCE yielded products at concentrations less than ten percent of the initial parent compound concentration. The lower concentration of the dehalogenation products made it difficult to determine degradation rates for these compounds. Therefore, different experiments were set up with PCE, TCE, and cDCE as the parent compound to determine their

biodegradation rates. Due to the large number of experiments (greater than 70) performed for the feasibility study, selected graphs and tables will be used to present the results. Detailed graphs of each experiment showing the depletion of the parent compound and production of the dehalogenation by-products are provided in appendices B, C and D. The graphs in the appendix show the concentration of the compounds in both parts per million (ppm) and micromoles (ìM) and was used to illustrate the percentage of the parent compound dehalogenated to the daughter products. Error bars on the graphs represent the variation in the activity of the vial pairs measured on each sampling event.

Biotic vs Abiotic Reactions

The question of whether the degradation reactions are biologically or abiotically mediated was investigated by performing degradation reactions with two types of kill controls; autoclaved and gamma irradiated microcosms. Both [^{14}C] PCE and [^{12}C] PCE were used to verify if there was any activity in the killed controls. Neither killed control produced any detectable levels of degradation products nor did any of the autoclaved radiolabeled experiments produce any detectable $^{14}CO_2$; determined by both the acid-base method and the strontium precipitate method. The live samples (trials 1, 2, and 3) showed a significant degradation of the chlorinated ethenes (Figure 6.1). The higher decrease in the solution concentration of the parent compound and the corresponding increase in degradation products in the live samples indicated that biological degradation was responsible for the activity observed with the OU4 sediments. The decrease in concentration of the parent compound in the two killed control experiments was

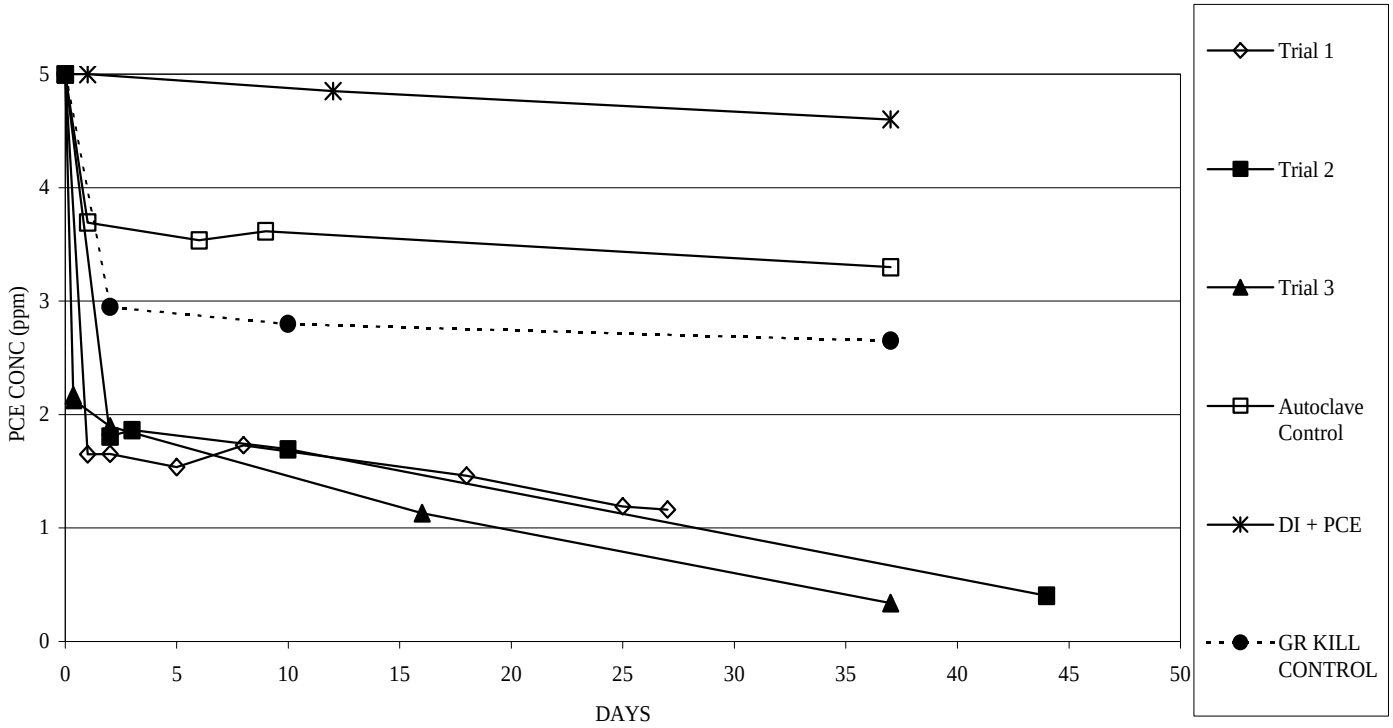


Figure 6.1. Biodegradation of PCE in live and killed controls of SB3 surface sediment batch microcosm studies.

attributed to sorption. The sorption experiment using SB3 surface sediment confirmed this conclusion. When the initial PCE concentration was 5 mg/L, the resulting equilibrium solution concentration after sorption ranged from 3.2 to 2.9 mg/L, which was similar to the fraction sorbed in the sorption isotherm experiments. Autoclaving sediment is believed to change the structure of carbon from soft to hard carbon and changes the sorption affinity of the sediment. The sorption kinetics of hard carbon is slower than that of soft carbon (Chiou et al., 2000).

Acclimation Time

Microbial acclimation time (lag time) is a result of either a genetic change, induction of reductase or oxidase enzymes, exhaustion of a substrate, or growth of an active population from very low initial numbers (Chapelle, 1993; and Mohn and Tiedje, 1992). To test for this, an experiment was performed where samples were spiked after 2 days of incubation (trial 1), 1 week of incubation (trial 2), and 2 weeks of incubation (trial 3). Samples that had incubation periods of 1 week and 2 weeks showed a slightly faster and quantitative conversion of PCE to cDCE (Figure 6.1 and Appendix B). Based on this experiment, samples were incubated for 1 week before spiking to allow microbial acclimation and to ensure anaerobic conditions.

Degradation Rates

A pseudo-first order kinetic model within the 95 % confidence limit described the bulk of the biodegradation data. Thus, half-lives are given in the range from the upper and lower 95 confidence level. The regression coefficients (r^2) for the experiments ranged from 0.2 to 0.9 and reflect the heterogeneity of the batch microcosms. The heterogeneity is attributed to differences in the organic carbon content that influenced

sorption, the onset of dehalogenation (Gibson and Sewell, 1992), and differences in the microbial biomass of the sediment (Farone et al., 2000). Even with the variability, ANOVA p values for the least squares analyses were less than 0.01, which indicate that the rates determined by the regression are statistically significant, and are not a product of random variation (Glantz and Slinker, 1990; Swan, 1995).

PCE removal in the batch microcosm experiments was attributed to the combined effects of sorption and biodegradation. Thus, the removal kinetics was divided into two segments (Figure 6.2): An initial rapid decrease due to sorption and the slow decrease there after due to biodegradation. Sorption was of minimum significance in the removal of the lesser-chlorinated ethenes, TCE and cDCE, which are more soluble than PCE. Biodegradation kinetics for TCE and cDCE were described by pseudo-first order degradation kinetic model.

Biodegradation Pathways

The primary degradation pathway for the chlorinated ethenes (PCE, TCE, and cDCE) in the OU4 site sediments was by sequential reductive dechlorination. When amended with extra carbon sources, PCE was completely transformed by reductive dechlorination to ethene and ethane (Figure 2.4). TCE and cDCE were the major intermediates of PCE dechlorination. The concentration of tDCE was below the method detection limits and none of the chlorinated ethanes produced by abiotic reactions were detected. Significant cDCE dechlorination did not proceed until PCE and TCE concentrations were below detection (1 ppb). VC did not accumulate in the samples and low levels of ethene and ethane were detected. As would be predicted from

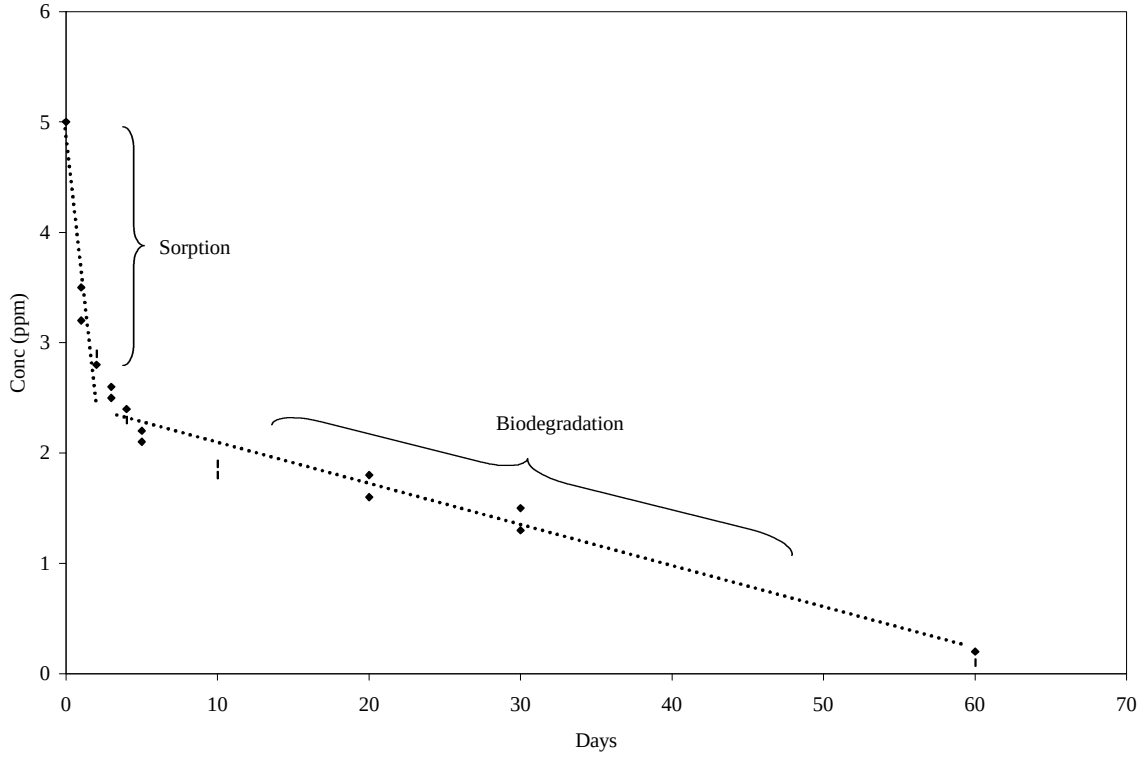


Figure 6.2. Illustration of the combined effects of sorption and biodegradation on PCE removal.

thermodynamics, the dechlorination rate of the chlorinated ethenes decreased in the following order: PCE > TCE > cDCE. In most experiments, the dechlorination rate of the chlorinated ethenes dropped as much as an order of magnitude with the removal of each chlorine atom. Radiolabeled experiments with [^{14}C] PCE indicated 3-6 % conversion to $^{14}CO_2$ (Table 6.1). Confirmation of $^{14}CO_2$ as a degradation product and the low concentrations of VC, ethene, and ethane detected suggested that more than one pathway could be involved in these biodegradation reactions. Bradley and Chapelle (1996 and 1997) showed that cDCE and VC are converted to$^{14}CO_2$ under iron reducing

conditions, and Buchanan et al (1995) showed rapid biological kinetics were responsible for the production of $^{14}CO_2$. However, it is unclear at which step mineralization to CO_2 occurred. Radiolabeled experiments by Freedman and Gossett (1989) demonstrated that ethene was the major degradation product of PCE. Increasing amounts of ethene with time would explain the decrease in mass balance percentages during the radiotracer experiments because mass balance percentages of Table 6.1 do not include [^{14}C] ethane. Because of the large Henry's law constant associated with ethene, if it were present it would reside mainly in the headspace of the vial and not in the scintillation cocktail. Ethene and ethane were detected in the microcosm and bioreactor experiments at low levels and did not stoichiometrically equate with the initial PCE molar concentration. The low concentration of ethene observed in these experiments was attributed to methanogens since high concentrations of ethene are toxic to methanogens (Schink, 1985). Methanogenic bacteria remove ethene by reducing it with molecular hydrogen and forming ethane (Oremland, 1981). The hydrophilic activity measured during the radiolabeled experiments could result form the transformation of the parent compound (PCE) to TCE and oxidation to chloroacetic acids or incorporation of the $^{14}CO_2$ into the microbial biomass as carbon. No direct determination of oxidative transformation products was carried out.

Surface Sediment Microcosm Experiments

Degradation rates for the unamended and amended surface experiments are summarized in Table 6.2 and 6.3. Microcosm experiments with surface sediment samples from SB3 had the highest PCE, TCE, and cDCE degradation rates. PCE had a half-life in the range of 8 to 20 days in the SB3 surface sediment microcosm experiments.

Table 6.1. Mass balance results of radiolabeled PCE biodegradation experiments

Experiment (Incubation Period-Days)	^{14}C (% Distribution)					
	Solid Phase	Aqeous Phase	Volatile	Hydrophilic	$[^{14}C]C0_2$	Mass Balance
Unamended SB3 Surface Sediment						
7	19	50	46.12	3.88	2.18	71.2
41	37	34.63	33.12	1.51	1.43	73.1
68	28.4	59	54.05	4.95	1	88.4
97	27.4	57.5	50.5	7	3	87.9
140	35	51	48	3	3.5	89.5
SB3 Surface Sediment Amended with Acetate						
1	21.6	68	63.4	4.6	2.5	92.1
30	24.8	56	52.4	3.6	0.79	81.6
45	28.8	44	42.8	1.2	2.14	74.9
SB3 Surface Sediment Amended with Acetate and Yeast Extract						
1	25.27	64.2	58.5	5.7	3.52	93.0
30	15.42	54	47.6	6.4	2.45	71.9
45	16.4	37	35.4	1.6	2.58	56.0
Unamended Deep SB3 Sediment						
30	7.5	77.1	76.9	0.27	0.86	85.5
Deep SB3 Sediment Amended with Acetate						
30	5.4	76.4	76	0.45	0.57	82.4
Deep SB3 Sediment Amended with Acetate and Yeast Extract						
30	6.8	74.13	72.73	1.4	1.1	82.0

*Deep samples were taken from core depths fo 28-40 ft

TCE had a half-life range of 3.4-7 days and cDCE had a half-life range of 44-110 days. More than seventy percent of the parent compounds were degraded to daughter products when the SB3 experiments were terminated. VC, ethene, and methane were qualitatively detected in all of the SB3 and SB2 microcosm experiments. PCE had a half-life range of 19-170 days in the microcosm experiments with surface sediment samples from SB1, SB2, SB4, SB5, SB6, SB7, and SB8. All showed degradation of PCE but the concentration of the dehalogenation products TCE and cDCE were less than ten percent of the initial parent PCE concentration. Experiments with sediment from SB5, SB6, and SB7 spiked with TCE alone showed no degradation products until after 80 days of incubation.

Microcosm experiments amended with additional carbon sources increased the rate of PCE dechlorination in the SB3 microcosm experiments. Amendments with a carbon source (Na-acetate or Na-lactate) and yeast extract showed the most rapid degradation of PCE with half-lives less than 1 day. The rate of degradation of PCE in SB3 surface sediments with different amendments followed the order: acetate or lactate + yeast extract > acetate or lactate > yeast extract only > molasses. Amended SB1 batch microcosms dosed with PCE produced a higher concentration of degradation products than the unamended samples. Degradation of PCE to detectable levels of cDCE, VC, ethane, methane occurred only with amended experiments. Surface sediments amended with acetate/lactate plus yeast extract and 10 % molasses produced extremely high levels of methane (>100 μM).

The removal of the PCE from the aqueous phase in the surface OU4 sediment microcosms is attributed to the combined effects of sorption and biodegradation.

Table 6.2. Summary results of SB3 core sediments (surface) batch microcosm experiments indicating degradation rates and the presence (+) or absence (-) of dehalogenation products of PCE, TCE, and cDCE, respectively.

Experiment	k (day^{-1}) **	$t^{1/2}$(days)***	r^2	TCE	cDCE	VC	Ethene	Ethane	Methane
PCE Degradation									
Unamended									
A	0.015 ± 0.003	37.6-59.2	0.77	+	+	-	+	-	+
B	0.061 ± 0.026	7.9-19.8	0.68	+	+	+	+	+	+
C	0.065 ± 0.026	7.6-17.8	0.69	+	+	+	+	+	+
Amended									
Molasses (3%)	0.019 ± 0.010	24-79	0.55	+	+	-	-	-	-
Yeast Extract(3%)	0.124 ± 0.055	4-10	0.72	+	+	-	+	-	+
Acetate (3mM)	0.345 ± 0.041	1.8-2.3	0.97	+	+	+	+	+	-
Acetate(3mM) + Yeast extract (3%)	1.20 ± 0.150	0.51-0.66	0.98	+	+	+	+	+	+
Lactate (3mM)	0.192 ± 0.078	2.5-6.3	0.72	+	+	+	+	-	+
Lactate (3mM) + Yeast extract (3%)	1.22 ± 0.091	0.615-0.53	0.99	+	+	+	+	+	+
TCE Degradation									
Unamended	0.152 ± 0.051	3.4-7	0.73		+	+	+	-	+
cDCE Degradation									
Unamended	0.011 ± 0.005	44-110	0.62			+	+	-	+

*- Analytes were qualitatively determined by GC-FID headspace analysis after removal of the aqeous sample
**- First order degradation rates +/- the 95 percent confidence level
***- Half-lives are given in the range of the upper and lower 95 percent confidence interval

Table 6.3. Summary results of SB1, SB2, SB4, SB5, SB6, SB7, and SB8 core sediment (surface) batch microcosm experiments indicating degradation rates and the presence (+) or absence (-) of dehalogenation products of PCE.

Experiment	k (day^{-1})**	$t^{1/2}$(days)***	r^2	Daughter Products TCE	cDCE	VC	Ethene	Ethane	Methane
PCE Degradation									
Unamended									
SB1	0.013 ± 0.002	47-62	0.91	+	-	-	+	-	-
SB2A	0.010 ± 0.002	58-87	0.79	+	+	+	+	-	+
SB2B	0.0241 ± 0.013	19-30	0.89	+	+	+	+	-	+
SB4	0.006 ± 0.002	95-171	0.53	+	+	-	-	-	-
SB5	0.009 ± 0.004	56-145	0.55	+	-	-	+	-	-
SB6	0.009 ± 0.002	69-99	0.84	+	-	-	+	-	+
SB7	0.007 ± 0.002	83-139	0.73	+	+	-	-	-	-
SB8	0.007 ± 0.002	74-148	0.62	+	-	-	+	-	-
Amended SB1 Microcosms									
Molasses (3%)	0.003 ± 0.001	164-417	0.78	+	-	-	-	-	-
Yeast Extract(3%)	0.003 ± 0.003	110-1742	0.72	+	+	-	+	-	-
Acetate (3mM)	0.013 ± 0.007	35-120	0.19	+	-	-	-	-	-
Acetate(3mM) + Yeast Extract (3%)	0.016 ± 0.006	31-73	0.60	+	+	+	+	+	+
Lactate (3mM)	0.004 ± 0.006	76-344	0.86	+	-	-	-	-	-
Lactate (3mM) + Yeast Extract (3%)	0.040 ± 0.013	13-25	0.77	+	+	+	+	+	+
Molasses (10 %)	0.021 ± 0.012	21-83	0.39	+	+	+	+	-	+
Acetate (10mM)	0.013 ± 0.003	44-69	0.89	+	+	-	-	-	-
Acetate(10mM) + Yeast Extract (10%)	0.012 ± 0.002	51-73	0.89	+	-	-	+	-	+

*-Analytes were qualitatively determined by GC-FID headspace analysis after removal of aqueous sample

**- First order degradation rates +/- the 95 percent confindence level

***- Half-lives are given in the range of the upper and lower 95 percent confidence interval

Biodegradation patterns in the surface sediments can be separated into two groups. The first group consists of source area (SB2 and SB3) sediment where biodegradation is the dominant removal mechanism and occurs under methanogenic conditions (methane concentration greater than 100 ìM). The second group consists of non-source area (SB1, SB4, SB5, SB6, SB7, SB8, and lake sediment) sediment where both sorption and biodegradation were important removal mechanisms under either sulfate or iron reducing conditions (methane production less than 1 ìM).

The kinetic data showed that the highest rate of dechlorination of chlorinated ethenes occurred in the source zone sediment with near stoichiometric dehalogenation to by-products with one to two less chlorine atoms (TCE and cDCE). Stoichiometric dehalogenation of PCE to cDCE indicates that sorption of PCE was insignificant compared to biodegradation. Sorption of PCE may be important initially, but PCE may be desorbed by the natural biosurfactants produced by the microorganisms (Hansen et al., 2000). If sorption of PCE were irreversible, then only 60 % of the initial PCE concentration would be available to the microorganisms for dehalogenation based on estimates from sorption data. The production of natural biosurfactants should enhance desorption of PCE from the solid phase to the aqueous phase. The latter should make available the PCE for biodegradation. It is speculated that the biosurfactant effect accounts for the greater than 70 % conversion of PCE to cDCE and further dehalogenation to ethene.

Relatively less degradation of the chlorinated ethenes was observed with core samples collected away from the source. Specifically, microcosms with non-source area sediment degraded PCE an order of magnitude slower and produced by-products less

than ten percent of the original parent compound concentration (Figure 6.3). The non-source area kinetic data is characterized by a rapid decrease in concentration due to sorption followed by a continued decrease in concentration due to biodegradation. In the lake sediment bioreactor experiment, a similar biodegradation trend was observed and hydrogen concentrations were indicative of Fe-reducing conditions.

These trends suggest that activity in the source zone sediments is probably the result of microorganisms that have adapted to utilize the chlorinated ethenes and suggests dehalorespiring process are working to degrade the chlorinated solvents (Carr et al., 2000; and Yager et al, 1997). The slow degradation of PCE and the poor quantitative dechlorination of PCE to cDCE suggest that co-metabolic processes are responsible for the observed reactions in the non-source area sediments (Tandol et al., 1994). Experiments performed using surface sediment from source area (SB3) and non-source area (SB1) supports this theory. Given the same percentages of amendments, the source area sediments degraded PCE faster and better stoichiometric product recoveries were obtained.

Source zone microbial communities represent an ecological niche and have been shown to posses the enzymes to degrade high concentrations of contaminants (Carr et al., 2000; and Yager et al., 1997). The source zone microbial consortia should be well adapted to utilize the chlorinated ethenes as electron acceptors since they have been exposed to the contaminants for decades. By using the chlorinated ethenes as electron acceptors, the consortium has an abundant source of electron acceptors.

Different carbon sources stimulated dechlorination in the surface sediment experiments. The wide substrate specificity can be explained because hydrogen is the

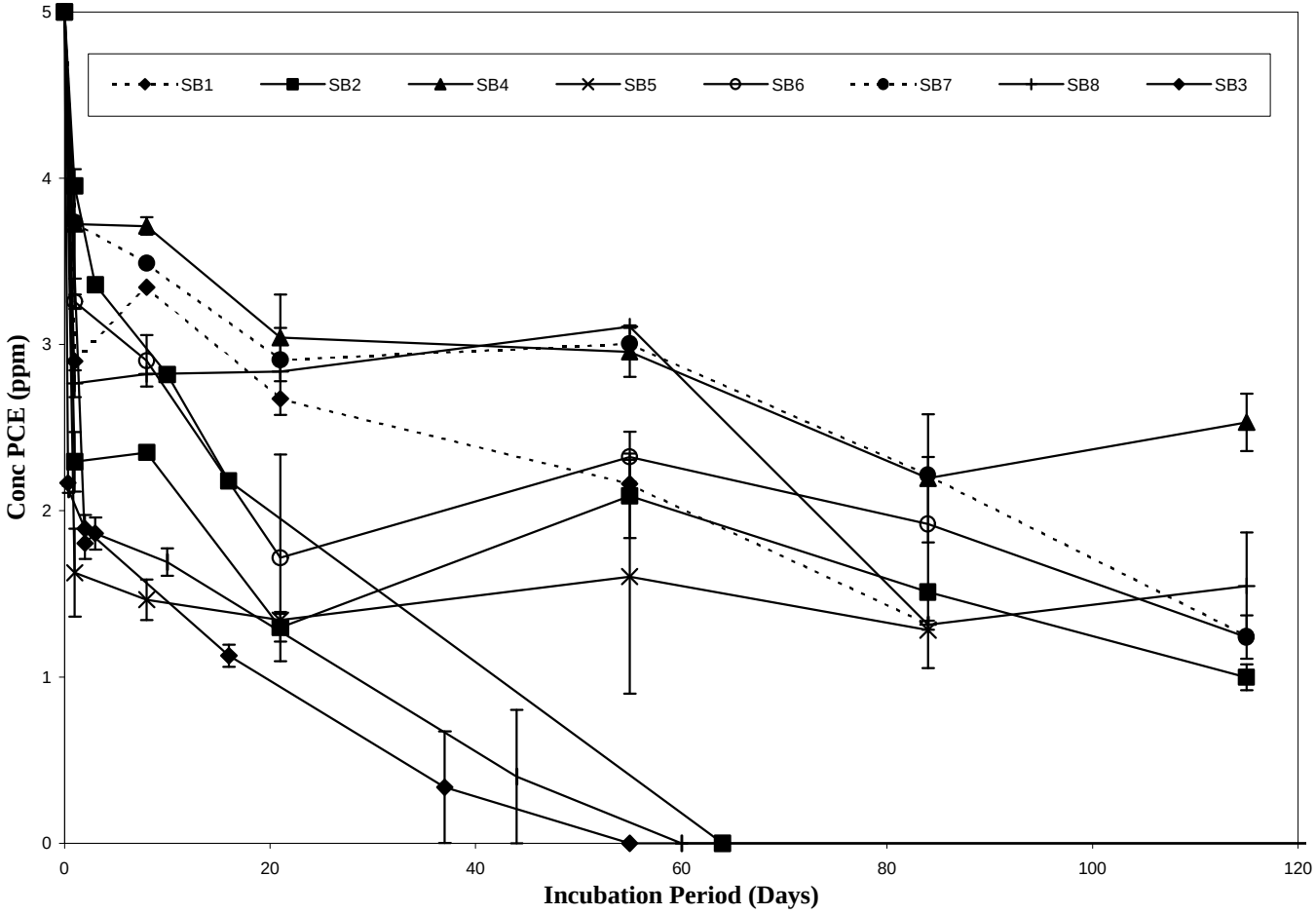


Figure 6.3. Change in concentration of PCE in unamended batch microcosms of surface sediment.

actual electron donor for dechlorination of the chlorinated ethenes (DiStefano et al., 1992; Newell et al., 1998). These compounds are directly fermented to produce hydrogen for the microbial consortia to use during the dechlorination reactions. Iron reducing, sulfate reducing, methanogenic, and dechlorinators can all use hydrogen (Wiedemeier et al., 1999). The wide range of reducing environments able to use hydrogen for dechlorination is a major benefit of this approach.

Acetate and lactate have been employed in field scale tests to provide the carbon source, which often limits biodegradation (Fam et al., 2000). Amendments to surface sediments with acetate produced slightly better results than amendments with lactate (Table 6.2 and Table 6.3). PCE was dechlorinated to VC and ethene in the surface sediments with amendments of acetate and lactate.

The best results for the amended surface experiments were with the addition of a carbon source and yeast extract combination (Figure 6.4.). This combination has also proven effective in enhancing dehalogenation and produced the best results in studies on the dechlorination of aromatic hydrocarbons (Coons et al., 2000). Yeast extract is used as a catchall nutrient because it contains B-vitamins (that act as transition-metal coenzymes; Wackett, 1995), and contains a mixture of different types of electron donors and still others are produced when it is fermented. Yang and McCarty (1998) reported that the decay of biomass produced from yeast extract fermentation provides an additional source of reducing equivalents and its slow decay could provide a continued source of carbon. Yeast extract by itself promoted dechlorination in this study and has been used successfully in field remediation of PCE (Buchanan et al., 1995). When

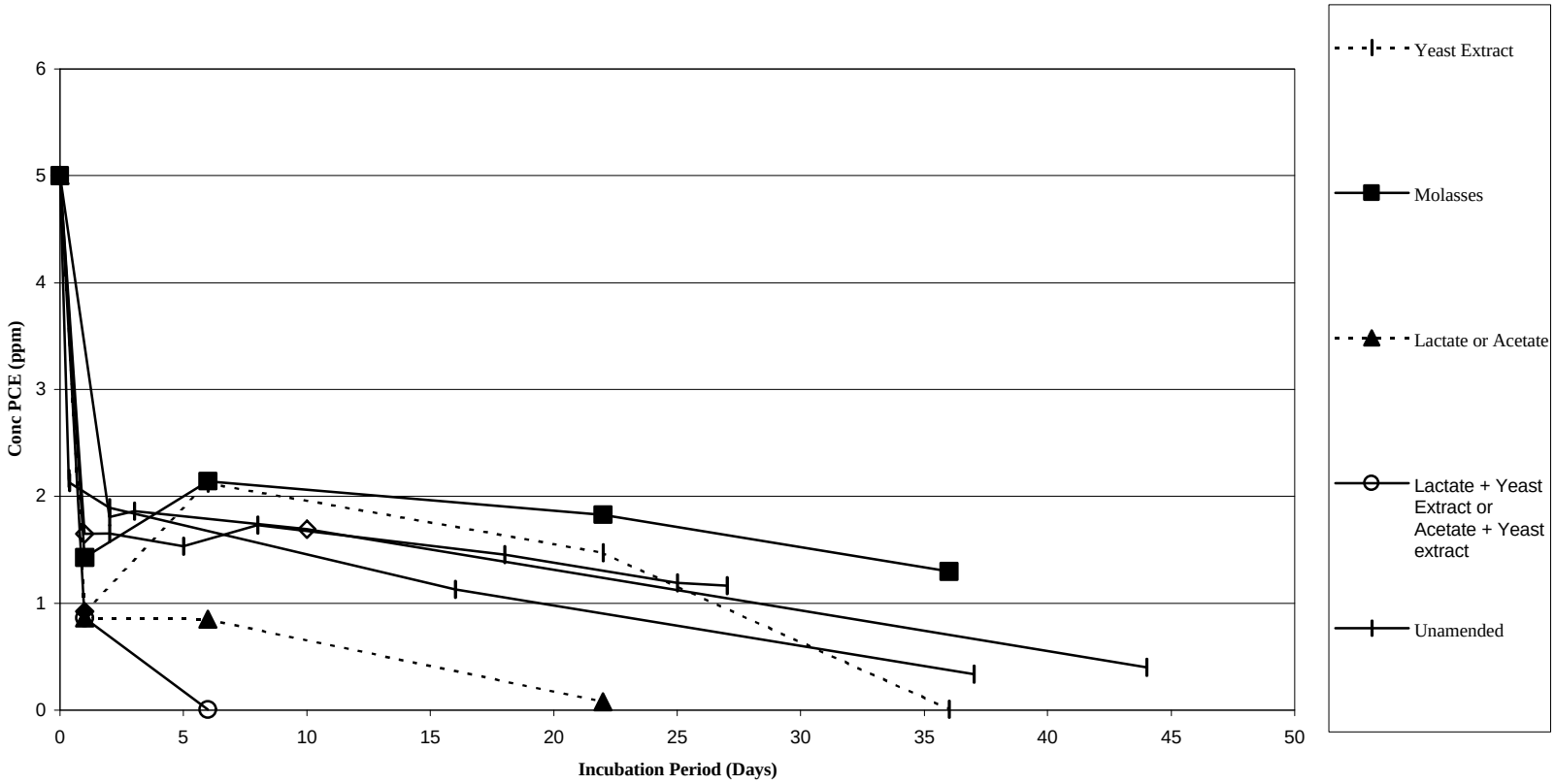


Figure 6.4. Change in concentration of PCE in amended ( ) and unamended ( ) batch microcosms of SB3 surface sediment.

combined with yeast extract, both lactate and acetate stimulated dechlorination. However, the lactate combination induced greater activity in the microcosms than the acetate combination.

The success with mixed substrates (two different carbon sources together, i.e. yeast extract and lactate) implies that methanogenic bacteria together with lactate fermenting bacteria are responsible for dechlorination or the microbial population includes methanogenic bacteria with different substrate ranges (Schollhorn et al., 1991; Maymo-Gatell et al., 1995). Acetate and hydrogen produced from the lactate fermentation could possibly be used by the methanogenic bacteria to produce CH_4 and CO_2 (Cabirol et al., 1998; and McInerney and Bryant, 1981). Methane production would be expected because acetate is a direct substrate for methanogens (Ferry, 1993). The proposed symbiotic relationship could explain the increased methanogenic activity in the microcosms amended with lactate and yeast extract and might explain the increased overall microbial degradation observed in the lactate and yeast extract amended microcosm experiments

Amended SB3 Surface Sediment Bioreactor

The bioreactor experiment consisted of SB3 surface sediment and site groundwater amended with 3 % Na-Acetate and 3 % Yeast Extract. The SB3 surface sediments were selected for this experiment because it showed the highest activity of all the cores in the microcosm study. The purpose of conducting the bioreactor experiment was to monitor disappearance of the parent compound, dissolved oxygen, pH, and redox potential simultaneously. The bioreactor was dosed with PCE three separate times. For the first two dosings the bioreactor was dosed with PCE to obtain an initial concentration

of 5 mg/L. The third time the bioreactor was dosed with PCE to obtain an initial concentration of 15 mg/L. In each case PCE was dehalogenated stoichiometrically to cDCE, which was further reductively transformed to VC, ethene, and ethane (Figure 6.5 and 6.6). At the concentration used in the amended bioreactor experiments, degradation followed zero-order kinetics for PCE and TCE and pseudo first-order kinetics for cDCE (all r^2 greater than 0.9). Zero-order rate constants for the depletion of PCE were 0.227, 2.22, and 2.83 mg L^{-1} day^{-1} for the first, second and third cycles, respectively. Zero-order rate constants for the depletion of TCE were greater than 5.1 mg L^{-1} day^{-1}. First-order rate constants for the depletion of cDCE were 0.073 day^{-1} and 0.011 day^{-1} for the second and third cycles, respectively. The amendments promoted methanogenic conditions in the bioreactor (Figure 6.7). Re-amending the bioreactor after methane production decreased appeared to cause a rebound in the methane production to higher levels than those detected after the initial amendment (greater than 80 mg/L). Hydrogen measurements were taken when the methane production leveled off. The dissolved hydrogen levels ranged from 5-6 nm and are indicative of methanogenic conditions.

Deep Sediment Microcosm Experiments

Degradation rates for PCE, TCE, and cDCE in the core sediments obtained from depths of 25-40 feet from SB2 and SB3 are summarized in Table 6.4. These experiments showed degradation of PCE with transformation products at concentrations less than ten percent of the parent compound concentration. First-order rate constants for the unamended experiments ranged from 0.010 $\pm$ 0.007 to 0.012 $\pm$ 0.008 day^{-1}. However, degradation of PCE in the unamended experiments was slower after 60 days of incubation. The addition of amendments increased the rate of biodegradation and

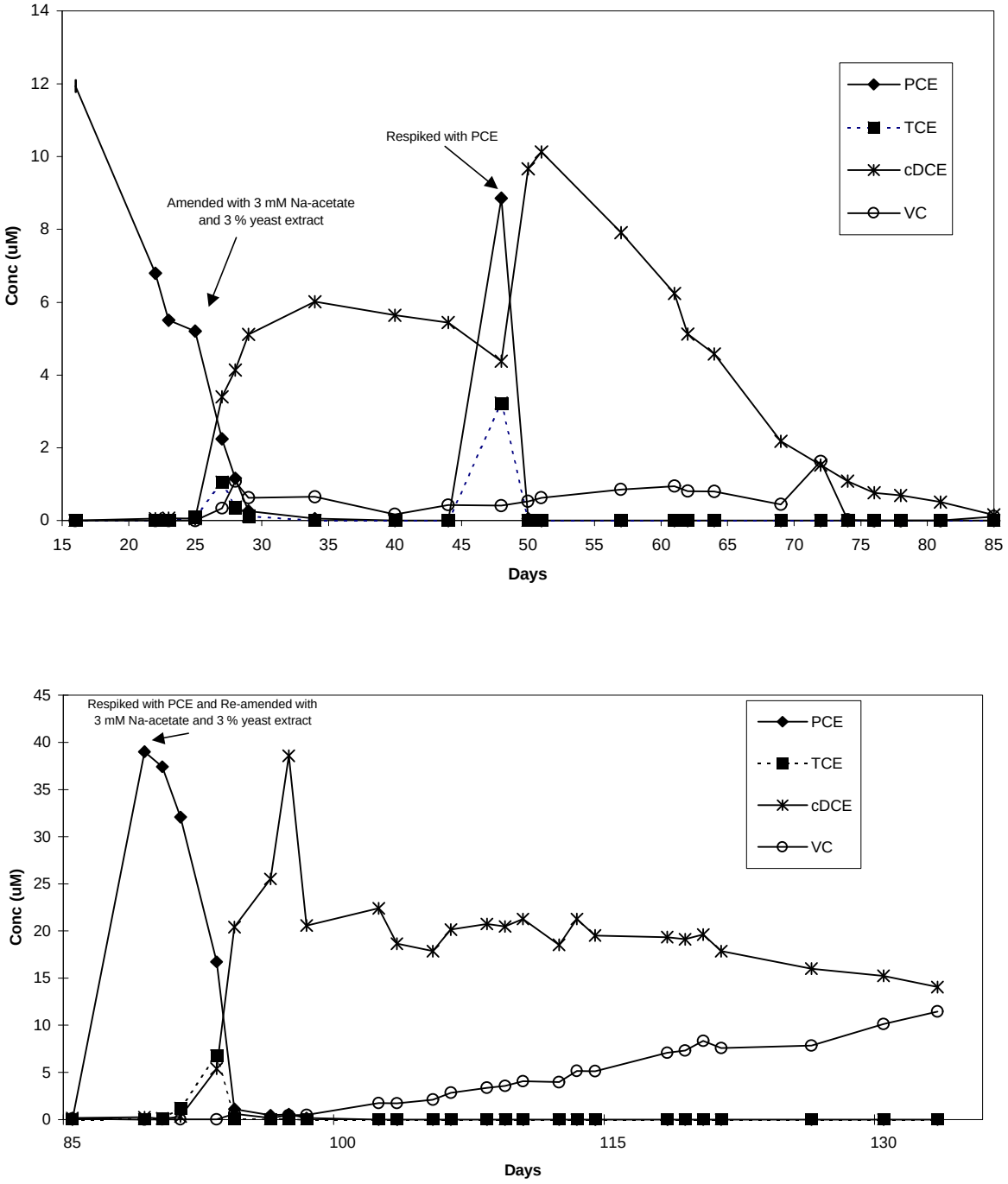


Figure 6.5. GC/FID analysis of headspace gases in SB3 surface sediment bioreactor dosed with PCE amended with 3 mM Na-acetate and 3 % yeast extract.

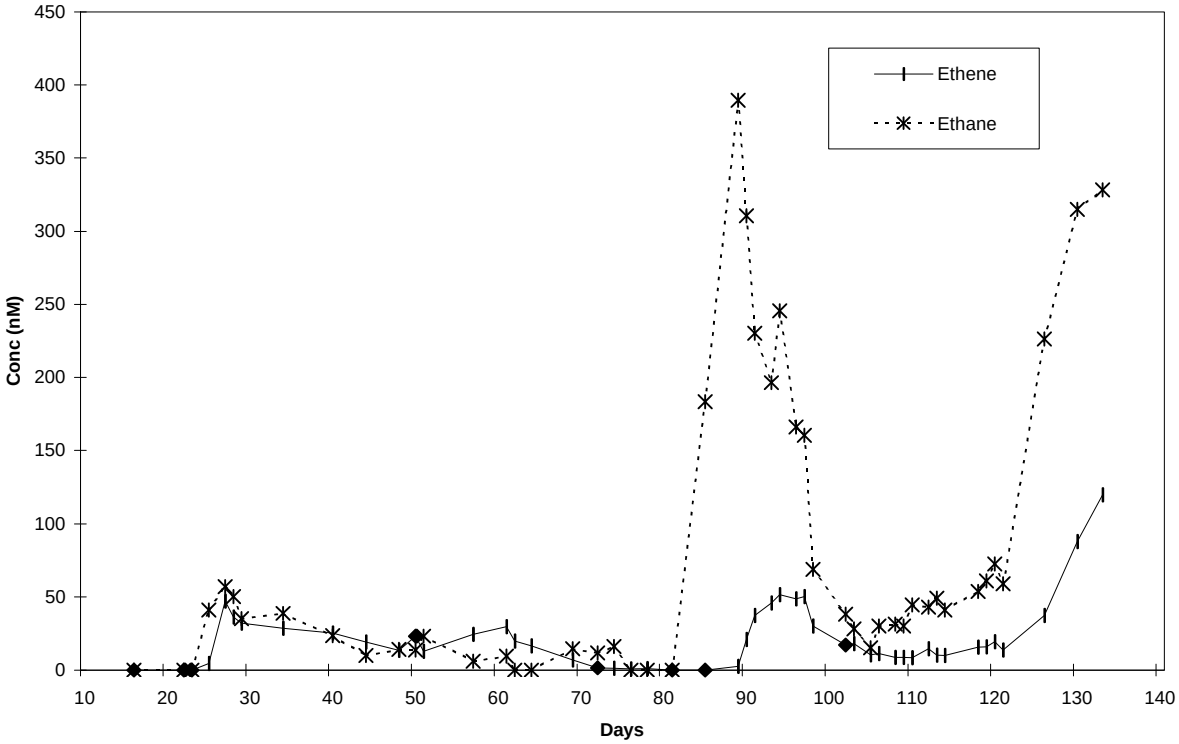


Figure 6.6. Production of ethene and ethane in the SB3 surface sediment bioreactor dosed with PCE and amended with 3 mM Na-acetate and 3 % yeast extract

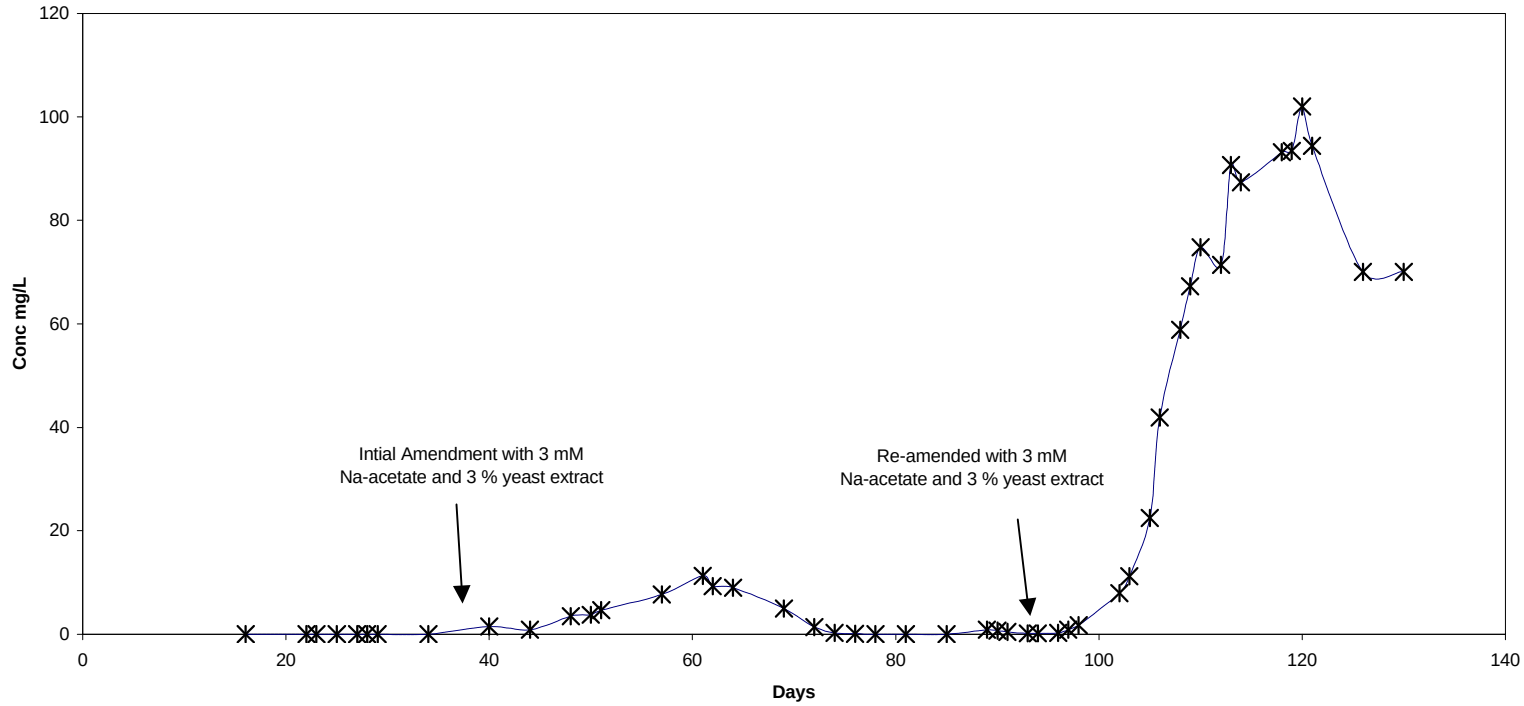


Figure 6.7. Production of methane in the SB3 surface sediment bioreactor dosed with PCE and amended with 3 mM Na-acetate and 3 % yeast extract.

increased the concentration of dehalogenation products (Table 6.5). Microcosms amended with 15 % Molasses showed the fastest kinetics with k_1 values of 0.017 $\pm$ 0.005. The greatest production of methane (> 100 ìM) was obtained in samples amended with molasses; while methane production in samples amended with acetate or lactate and yeast extract combination was 5- 25ìM. Degradation of PCE to VC and ethene was observed only in the amended samples. Unlike PCE and TCE, degradation of cDCE did not appear to be enhanced by the addition of amendments (figure 6.8). The k_1 ranged for cDCE from 0.003 to 0.007 $\pm$ 0.002 day^{-1}, which corresponded to a half-life range of 75-388 days.

The biodegradation pattern in the deep sediment was least influenced by sorption (confirmed by sorption studies) and the biodegradation under sulfate or iron reducing conditions (methane production less than 1 ìM). These results confirmed that degradation in deep sediments at NTC was slower than in surface or mid-depth microcosms. In sediments such as the deep sediments of the NTC where the TOC was less than one percent, biodegradation of the chlorinated ethenes is most likely limited by the availability of a suitable electron donor (Gibson and Sewell, 1992). Consequently, biodegradation of PCE and TCE in the unamended deep sediment microcosm experiments was mostly incomplete as higher levels of cDCE accumulated in those vials. The addition of carbon sources to the deep sediment microcosms sustained dehalogenation of PCE to ethene. Figure 6.9 shows that biodegradation in amended and unamended samples composed of SB2 deep sediment were similar. However, with a longer experiment duration, the best results for the amended surface and deep sediment

Table 6.4. Summary results of deep sediment (25-40 ft) batch microcosm experiments indicating degradation rates and the presence (+) or absence (-) of dehalogenation

Experiment		k (day^{-1})**	$t^{1/2}$ (days)	r^2	Daughter Products TCE	cDCE	VC	Ethene	Ethane	Methane
PCE Degradation										
	Unamended									
(SB2)		0.010 ± 0.007	38-195	0.39	+	+	-	-	-	-
(SB3)		0.012 ± 0.008	35-178	0.19	+	+	-	-	-	-
	Amended									
(SB3)	Acetate (3mM)	0.011 ± 0.003	49-82	0.77	+	+	-	+	-	-
	Acetate(3mM) + Yeast Extract (3%)	0.013 ± 0.003	44-66	0.89	+	-	+	+	+	+
	Lactate (3mM)	0.017 ± 0.004	36-47	0.95	+	+	-	-	-	-
	Lactate (3mM) + Yeast Extract (3%)	0.012 ± 0.004	43-83	0.74	+	+	-	+	+	+
	Corn Oil (10 %)	NA	NA	NA	+	+	-	-	+	-
(SB2)	Acetate (3mM)	0.012 ± 0.002	50-64	0.97	+	+	-	+	-	-
	Acetate(3mM) + Yeast Extract (3%)	0.017 ± 0.005	32-58	0.83	+	+	-	+	-	+
	Molasses (15 %)	0.015 ± 0.006	32-80	0.25	+	+	+	+	+	+
	HRC Compound (15 %)	0.009 ± 0.003	60-122	0.42	+	+	-	+	-	-
(SB3)	Acetate (10 mM)	0.010 ± 0.002	59-83	0.85	+	+	-	+	-	-
	Acetate (10mM) + Yeast Extract (10%)	0.013 ± 0.002	46-68	0.78	+	+	-	-	+	+
	Lactate (10mM) + Yeast Extract (10%)	0.008 ± 0.003	61-131	0.1	+	-	+	+	+	
	Molasses (15 %)	0.011± 0.004	46-94	0.47	+	+	+	+	+	+
	HRC Compound (15 %)	0.011 ± 0.003	51-88	0.75	+	+	-	+	-	-
TCE Degradation										
	Amended									
(SB3)	Corn Oil (10%)	NA	NA	NA		+	-	-	+	-
cDCE Degradation										
(SB3)	**Unamended**	0.003 ± 0.001	178-239	0.88			-	+	-	-
(SB2)	**Amended**									
	Acetate (3mM)	0.007 ± 0.002	75-123	0.69			-	+	-	-
	Acetate (3mM) + Yeast Extract (3%)	0.004 ± 0.001	145-212	0.8			+	+	-	+
	Lactate (3mM) + Yeast Extract (3%)	0.003 ± 0.001	159-388	0.3			+	+	-	+
	Corn Oil (10 %)	NA	NA	NA			-	+	+	-

* - Analytes were qualitatively determined by GC-FID headspace analysis after removal of aqueous sample

**- First order degradation rates +/- the 95 percent confindence level

Half-lives are given in the range of the upper and lower 95 percent confidence interval

Table 6.5. Comparison of the concentrations (mg/L) of PCE dehalogenation products measured in amended and unamended deep sediment (25-40 ft) batch microcosms.

Sediment Boring	Treatment	Concentration of PCE Dehalogenation Products (ppb)			
		< 30 Days TCE	> 30 Days	< 30 Days cDCE	> 30 Days
SB2	Unamended	7-10	6-7	BD	64-66
	Acetate (3mM) + Yeast Extract (3%)	2-9		BD-26	
	Molasses (15%)	2-6		28-53	
	Acetate (3mM)	2-8		18-58	
	HRC (15%)	3		BD-27	
SB3	Unamended	1-10	1-6	BD	48-55
	Lactate (3mM)	1-5	2-5.3	BD-14	30-31
	Acetate (3mM)	2-3	3-10	BD	24-27
	Lactate (3mM)+ Yeast Extract (3%)	5-28	12-18	BD-27	26-27
	Acetate (3mM) + Yeast Extract (3%)	3-11	49-108	BD	BD
	HRC (15 %)	1-9		BD-38	
	Molasses (15 %)	6-8		17-60	
	Acetate	2-11		BD	
	Acetate (10mM) + Yeast Extract(10%)	2-14		BD-22	
	Lactate(10mM) + Yeast Extract(10%)	3-26		BD	

BD-below detection,
Black areas indicate that the experiment did not extend to that duration

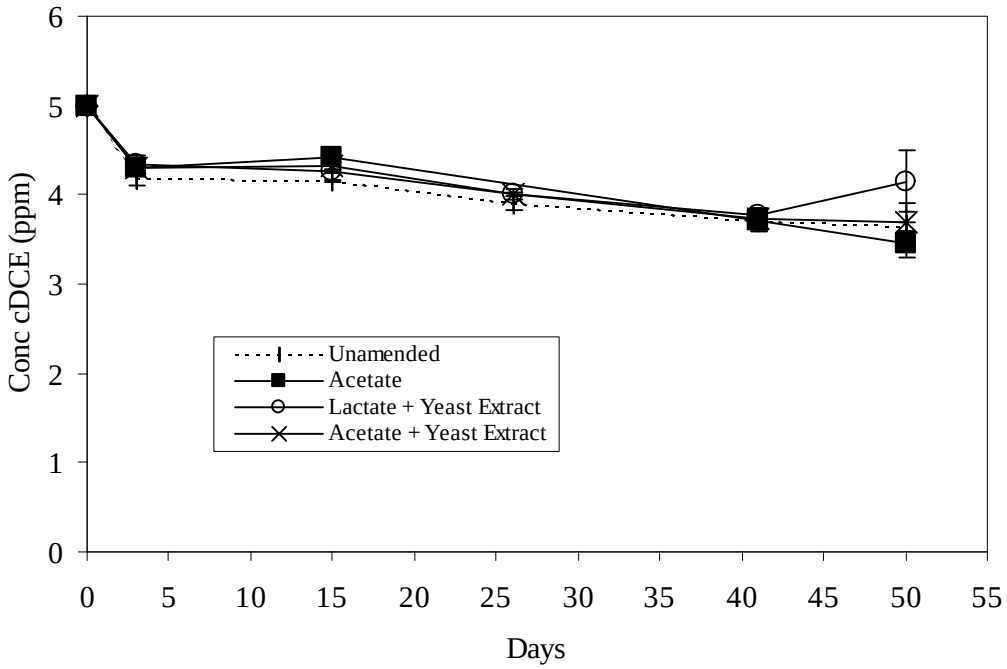


Figure 6.8. cDCE biodegradation in unamended and amended SB2 (25-40 ft) deep sediment microcosm studies.

experiments composed of SB3 deep sediment were observed with the addition of a mixture of acetate plus yeast extract (Figure 6.10).

Recently, edible oils such as corn oil, soybean, and olive oil have been used in studies to enhance dechlorination (Boulicault et al., 2000; and Zenker et al., 2000). The edible oil provides an insoluble substrate that would serve as a continuous source of carbon for many years as it slowly degrades. Microcosm studies amended with corn oil were inconclusive. Corn oil formed white globules believed to be hydrolyzed oil, which sorbed or enhanced sorption of the chlorinated ethene leading to random variation between the batch vials. However, dechlorination of PCE, TCE, and cDCE to ethane was

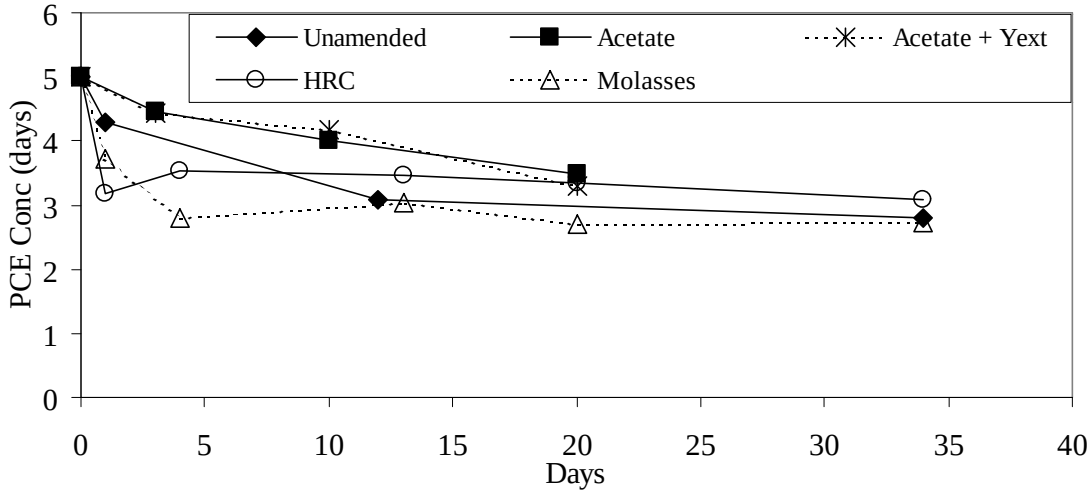


Figure 6.9. Biodegradation of PCE in deep SB2 sediment in batch microcosms (amended and unamended).

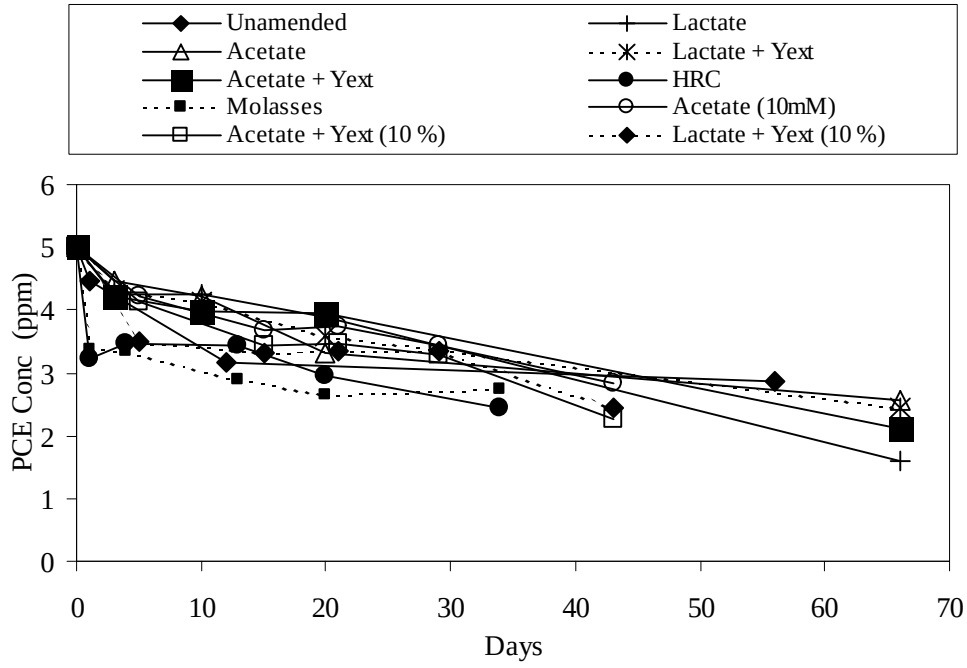


Figure 6.10. Biodegradation of PCE in deep SB3 sediment in batch microcosms (amended and unamended).

detected in the batch microcosms. The sorbent nature of the oil could be a problem for other removal techniques if dechlorination is ineffective (e.g., vapor extraction or pump and treat) and should be investigated further prior to field implementation.

Lake Sediment Microcosm and Bioreactor Experiments

Degradation rates for the lake sediment experiments are summarized in Table 6.6. Lake sediment microcosm experiments showed degradation under methanogenic conditions (>100 ìM). The pseudo first-order degradation constant for the dechlorination of PCE was 0.106 + 0.047 day^{-1}, 0.011 + 0.008 day^{-1} for TCE, and .006 + 0.002 day^{-1} for cDCE. Thus there was an order of magnitude decrease of the chlorinated aliphatics with one less chlorine. Degradation to VC and ethene was observed in the lake sediment microcosm experiments.

The pseudo first-order biodegradation rate of PCE in the bioreactor was 0.04 ± 0.009 (half-life of 14-22 days). The degradation products of PCE identified in the headspace were TCE, cDCE, VC, and ethane (Figure 6.11). The maximum amount of the detected products did not exceed 10 percent of the initial mass of the parent compound. Dissolved hydrogen concentrations of 0.5-nm indicate iron-reducing microorganisms prevailed during PCE degradation. The lake sediment bioreactor did not produce methane above 1 ìM.

The methanogenic conditions of the lake sediment microcosm experiments contrasted with the lake sediment bioreactor. The lake sediment microcosms showed significant degradation of PCE after the initial decrease due to sorption. Generally, the sorption of PCE to the organic rich lake sediments was an important removal mechanism

Table 6.6. Summary of lake sediment microcosm and bioreactor experiments indicating degradation rates and the presence (+) or absence (-) of dehalogenation products.

Experiment	k (day^{-1})**	$t^{1/2}$ (days)***	r^2	Daughter Products TCE	cDCE	VC	Ethene	Ethane	Methane
PCE Degradation									
Unamended Microcosm	0.106 ± 0.047	4.6-11	0.6	+	+	+	+	-	+
Unamended Bioreactor	0.040 ± 0.009	14-22	0.76	+	+	+	+	-	-
TCE Degradation									
Unamended Microcosm	0.011± 0.008	39-244	0.26		+	+	+	-	+
cDCE Degradation									
Unamended Microcosm	0.006 ± 0.002	96-156	0.81			+	+	-	+

*-VC, ethene, and ethane were qualitatively determined by GC-FID headspace analysis after removal of aqueous sample

** - First Order degradation Rates +/- the upper and lower 95 % confidence level

***- Half-lives are given in the range of upper and lower 95 percent confidence interval

because only 50 percent of the parent PCE concentration was dehalogenated to cDCE with further dehalogenation to VC and ethene. The lake sediment showed higher activity than similarly organic carbon rich sediment. The higher activity of the lake sediment could be a result of the higher clay content, which provides more surface area for biological reactions.

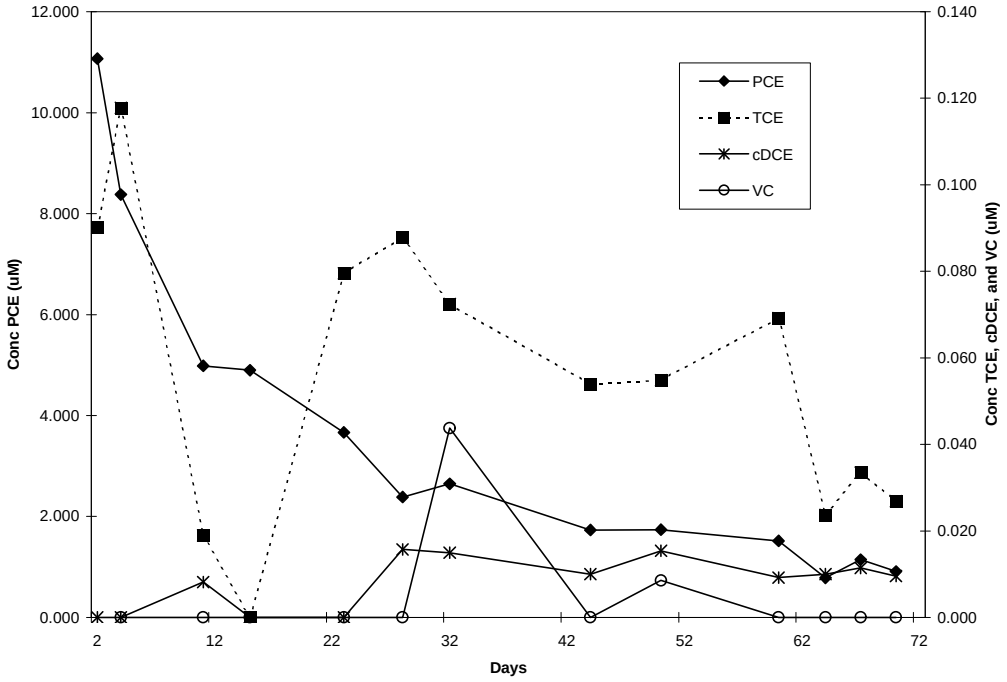


Figure 6.11. GC/FID analysis of PCE degradation products in headspace of the lake sediment bioreactor.

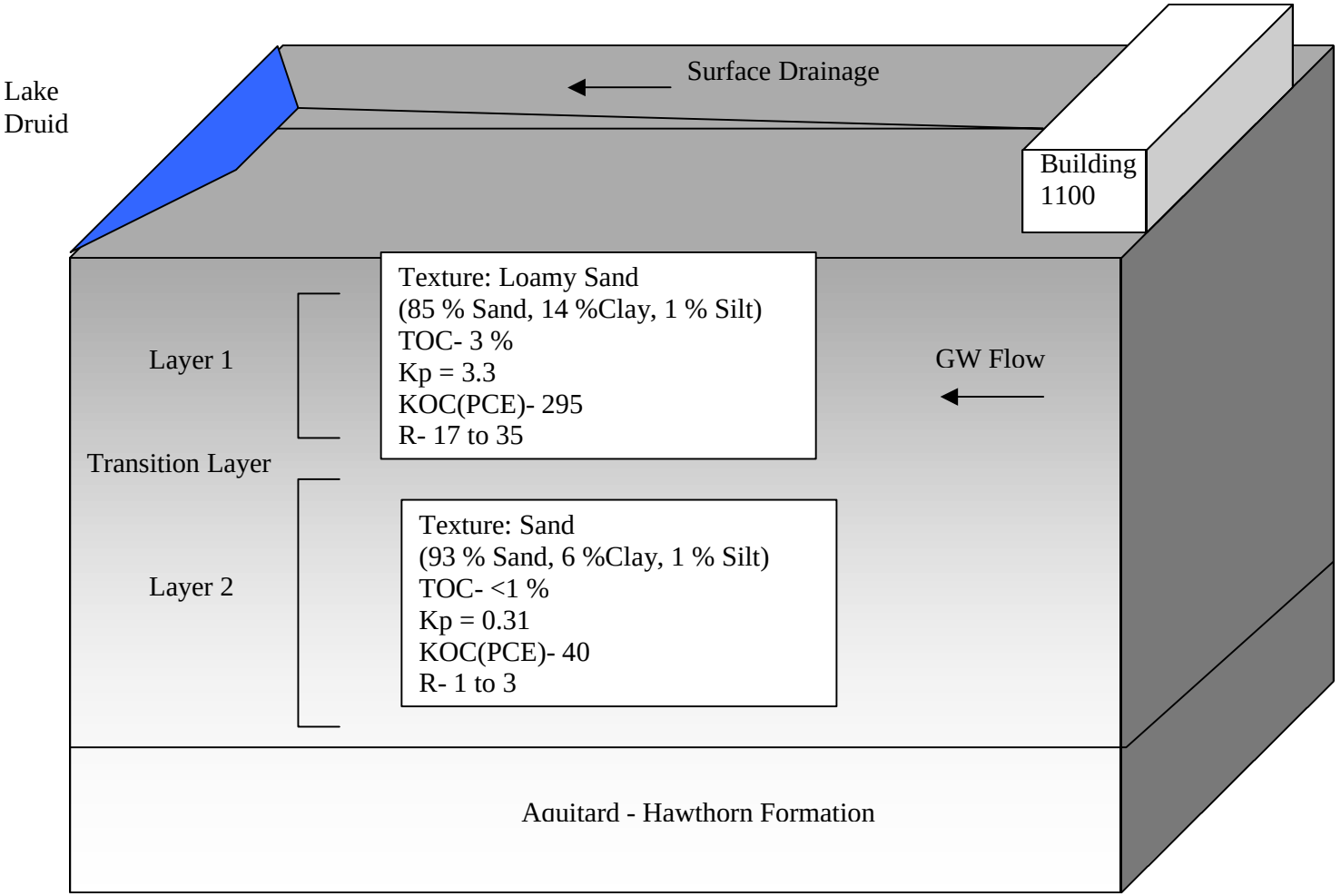
CHAPTER 7

CONCLUSIONS

Site Conceptual Model

The stratigraphy of OU4 consists of two layers with a transition zone between the two. The horizontal layers are delineated by TOC, texture, and organic carbon partition coefficients (Koc) (Figure 7.1). The first layer consists of surficial sediments to a depth of 10 feet. This layer has a loamy sand texture and averages 3 percent TOC, Koc of 295, and has an estimated retardation factor range of 17 to 35 for PCE. The **t**ransition layer has a sandy texture, TOC of 1 %, and a Koc of 70. The third layer has a sandy texture, TOC < 1%, Kp <0.5, Koc of 40, and an estimated retardation factor range of 1 to 3. BET SSA measurements averaged 1 m^2/g for all surface, mid-depth, and deep sediments. There was not a clear difference between the CEC values for surface and deep sediments; however, there was a general decrease in CEC with depth.

The hydrostratigraphy of the OU4 site consists of two main layers based on the site sediment analysis: layer 1 and layer 2. The hydraulic conductivity of the OU4 site does not vary with depth. The hydraulic conductivity of the shallow, mid-depth, and deep wells is 10^{-3} cm/sec (Harding Lawson and Associates, 1998). Because of the similarity of hydraulic conductivity values and texture of the OU4 sediments, the processes of advection and dispersion would be expected to be similar for both layers. The higher organic content of the surficial sediments is the main difference between



the

Figure 7.1. Cross-section of the site illustrating the two main stratigraphic layers based on the site sediment analysistwo hydrostratigraphic units of the OU4 site.

The higher organic content results in higher Koc values and retardation of the contaminant in the surficial sediments. The first would have a high residual non-aqueous phase (NAPL) concentration (especially in the smear zone) and would have a retarded contaminant velocity of 9.01 m/yr relative to the advective groundwater velocity of 315 m/yr. Due to the low retardation values, the second layer would transport the contaminant at the advective velocity of groundwater. With higher retardation values resulting in longer residence times the potential for biodegradation is increased.

Natural Attenuation

The removal of PCE from groundwater in the OU4 sediments is primarily due to both sorption and biodegradation and can be separated into three different groups (figure 7.2). Field and laboratory data shows that active biodegradation of the chlorinated ethenes occurs in the surface layer (0-14 ft) with halorespiration processes responsible for degradation in the source area sediments (group I) and co-metabolic processes responsible for degradation in the non-source area sediments (group II). Sorption is an important removal mechanism in the organic rich sediments (foc > 2.5%) of group II. The lack of organic carbon (<1%) in the deep sediments (group III) appears to limit biodegradation and sorption of PCE. Group III is characterized by incomplete biodegradation of PCE is and the sequential biodegradation of PCE does not proceed past cDCE within the incubation period of the laboratory experiments.

Monitored natural attenuation alone as remedial technology of the OU4 site does not appear to be feasible given the incomplete dehalogenation of PCE in the non-source

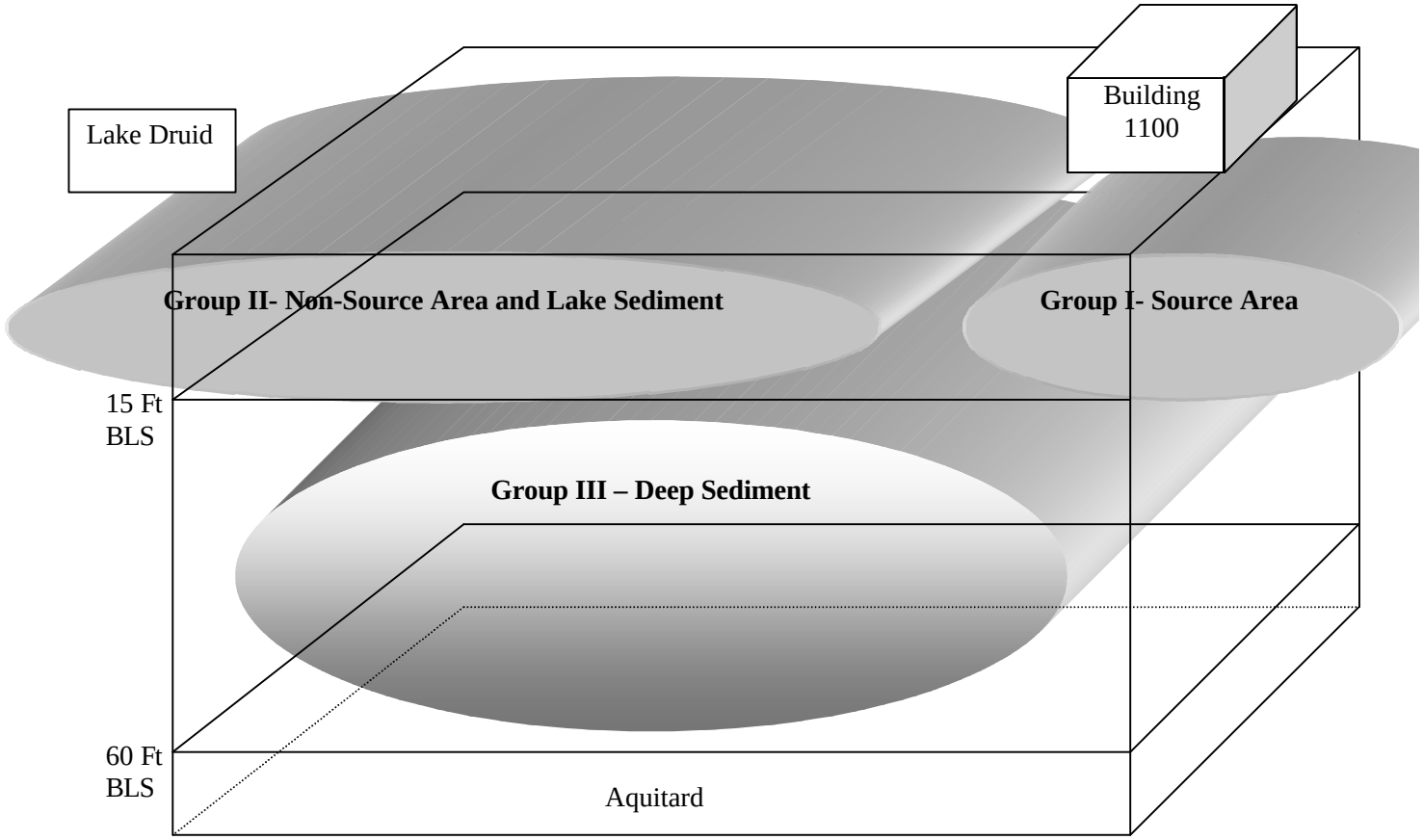


Figure 7.2. Biodegradation trends of the OU4 sediment separated into three groups.

area and deep sediments. Further limitations to using monitored natural attenuation are the lack of a wide spread reducing environment and low retention of the contaminants in the shallow groundwater system. The lack of the wide spread reducing environment could be due to the shallow water table and high hydraulic conductivity of the OU4 sediments (10^{-3} cm/sec). The oxygen flux through the site could be high enough to prevent the depletion of oxygen and the development of an anaerobic environment.

Enhanced Reductive Dechlorination (ERD)

The addition of amendments to stimulate reductive dechlorination at the OU4 site has the potential to accelerate dechlorination of the chlorinated ethene plume and serve as an effective remedial technology for OU4 at NTC Orlando, Florida. First, ERD can aggressively alter the redox state of ground water in a short time period (Hansen et al., 2000). Increased microbial activity speeds up the exhaustion of naturally occurring electron acceptors (e.g., oxygen and nitrate) and creates a highly reducing zone in an otherwise aerobic/anoxic groundwater system associated with shallow groundwater flow systems. Second, the relatively homogenous hydrostratigraphy allows for areas of constant and predictable groundwater flow. The ability to predict and control groundwater movement is crucial for an effective distribution of electron donors and nutrient throughout the subsurface.

The amended laboratory experiments with OU4 sediment demonstrated degradation of PCE and TCE to ethene and ethane. Deep sediment dehalogenation of PCE to VC and ethene occurred only with the addition of carbon sources. The OU4 sediment appears to have a wide range of substrate specificity and responded favorably to all amendments. The results of the laboratory feasibility study warrant a carefully

designed field scale test for enhanced biodegradation in the deep sediments. Care must be taken to ensure that the dechlorination of PCE with injection of amendments does not result in an accumulation of cDCE and VC.

Further Recommendations

Coupling phytoremediation and natural attenuation has great potential to enhance bioremediation in the surface sediments of OU4. Green plants have been shown to take up and metabolize these chlorinated organic solvents; their root exudates would also provide natural carbon and electron sources to enhance biodegradation within the rhizosphere. Thus, the coupling of natural attenuation and phytoremediation is recommended for OU4 at NTC, Orlando.

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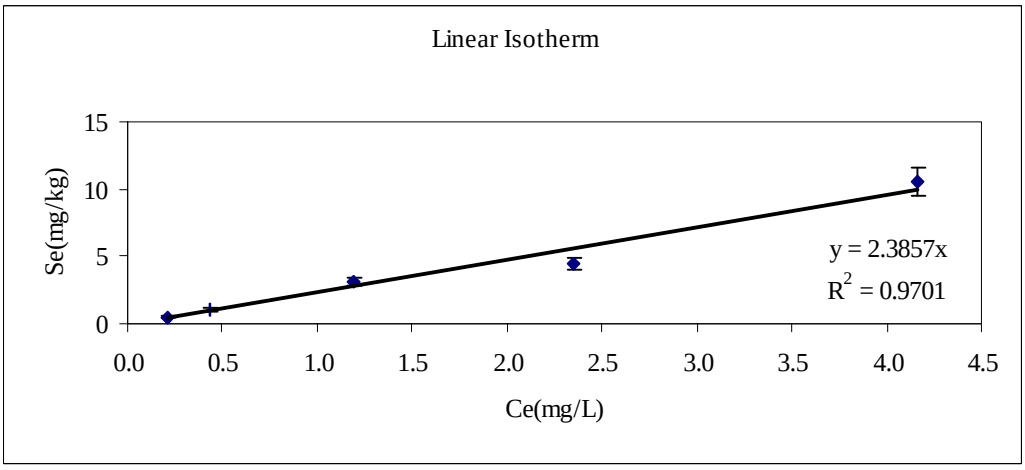
APPENDIX A

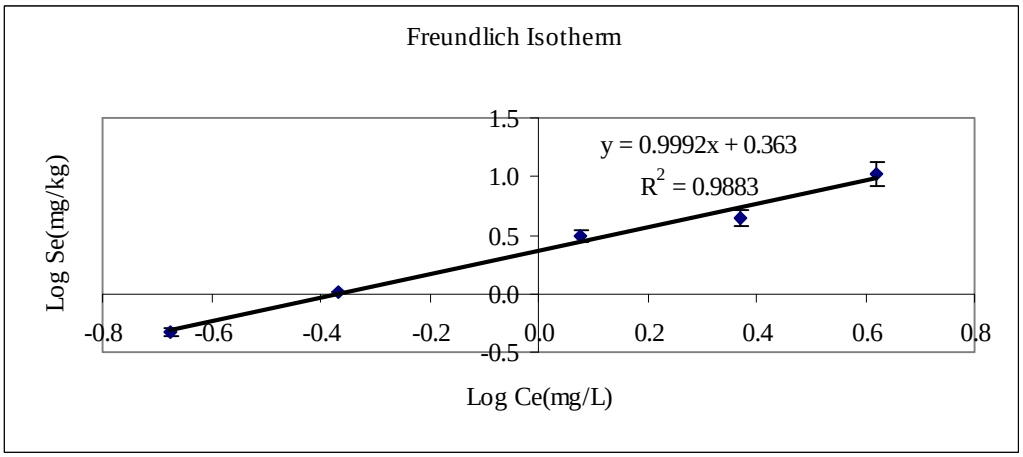
SORPTION DATA AND LINEAR, FREUNDLICH, AND LANGMUIR ISOTHERMS

SB-2(0-4)

	Co(mg/L)	Ce(mg/L)	V(mL)	V(L)	M(g)	SE(mg/g)	SE(mg/kg)
1A	0.46	0.20	17.06	0.0171	8.820	0.0005	0.498
1B	0.46	0.21	17.06	0.0171	8.820	0.0005	0.477
1C	0.45	0.22	17.39	0.0174	8.820	0.0004	0.447
2A	0.93	0.42	17.79	0.0178	8.820	0.0010	1.025
2B	0.95	0.47	17.48	0.0175	8.820	0.0009	0.933
2C	0.97	0.40	17.09	0.0171	8.820	0.0011	1.106
3A	2.72	1.27	17.70	0.0177	8.820	0.0029	2.915
3B	2.77	1.11	17.37	0.0174	8.820	0.0033	3.267
3C	2.79	1.20	17.22	0.0172	8.820	0.0031	3.115
4A	4.58	2.06	17.12	0.0171	8.820	0.0049	4.890
4B	4.83	2.56	16.22	0.0162	8.820	0.0042	4.165
4C	4.55	2.44	17.22	0.0172	8.820	0.0041	4.115
5A	9.37	3.84	17.81	0.0178	8.820	0.0112	11.182
5B	9.52	4.38	17.55	0.0175	8.820	0.0102	10.223
5C	9.32	4.27	17.91	0.0179	8.820	0.0103	10.250

Sample	Ce(mg/L)	log Ce(mg/L)	log Se	Se (mg/g)	Se (mg/kg)
1	0.21166	-0.674	-0.324	0.00047	0.474
2	0.43030	-0.366	0.009	0.00102	1.021
3	1.19249	0.076	0.491	0.00310	3.099
4	2.35346	0.372	0.642	0.00439	4.390
5	4.16257	0.619	1.023	0.01055	10.552

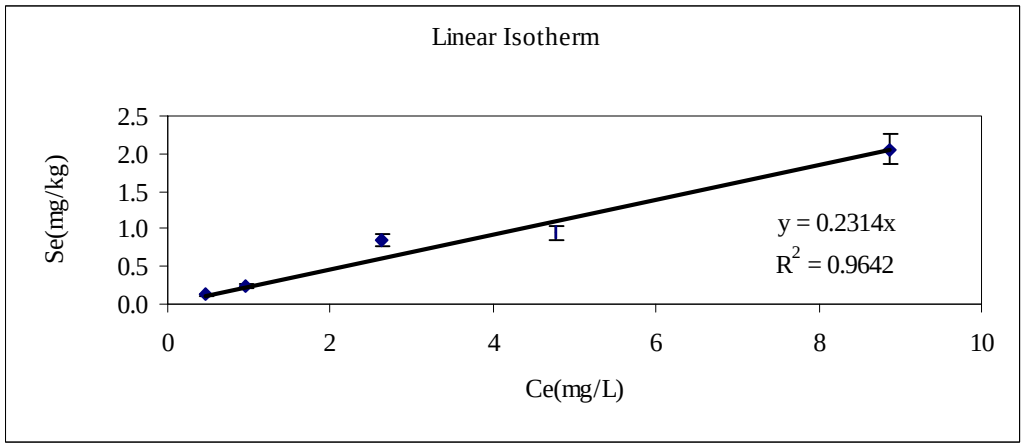


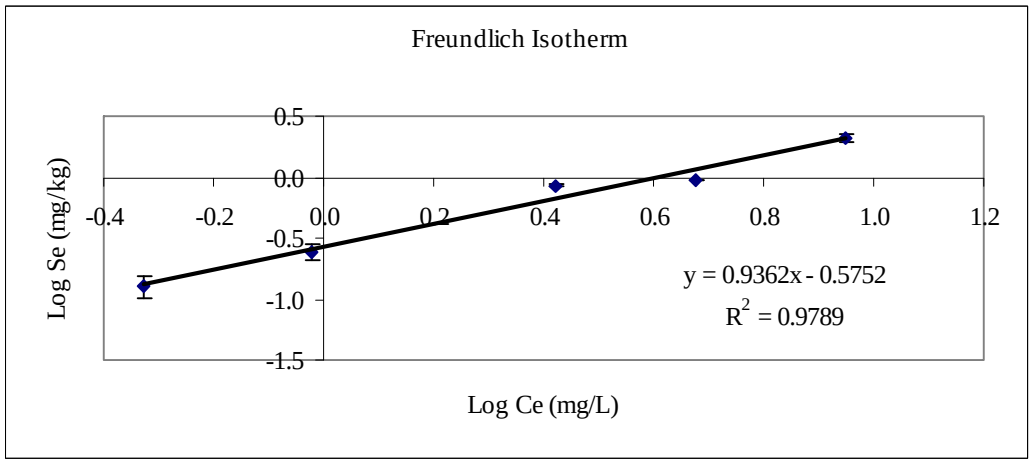


SB-2 (10-14)

	Co(mg/L)	Ce(mg/L)	V(mL)	V(L)	M(g)	SE(mg/g)	SE(mg/kg)
1 A	0.536	0.476	16.889	0.017	10.00	0.0001	0.1014
1 B	0.553	0.457	16.354	0.016	10.00	0.0002	0.1578
1 C	0.549	0.476	16.484	0.016	10.00	0.0001	0.1202
2 A	1.119	0.946	16.236	0.016	10.00	0.0003	0.2809
2 B	1.101	0.988	16.514	0.017	10.00	0.0002	0.1858
2 C	1.086	0.929	16.733	0.017	10.00	0.0003	0.2630
3 A	3.215	2.651	15.967	0.016	10.00	0.0009	0.9013
3 B	3.193	2.658	16.078	0.016	10.00	0.0009	0.8606
3 C	3.080	2.593	16.670	0.017	10.00	0.0008	0.8110
4 A	5.368	4.737	16.675	0.017	10.00	0.0011	1.0521
4 B	5.325	4.780	16.808	0.017	10.00	0.0009	0.9170
4 C	5.310	4.780	16.858	0.017	10.00	0.0009	0.8931
5 A	10.189	8.937	16.386	0.016	10.00	0.0021	2.0528
5 B	10.133	8.705	16.477	0.016	10.00	0.0024	2.3533
5 C	10.068	9.003	16.583	0.017	10.00	0.0018	1.7665

Sample	Ce(mg/L)	log Ce(mg/L)	log Se	Se (mg/g)	Se (mg/kg)
1	0.4697	-0.3282	-0.8980	0.0001	0.1265
2	0.9544	-0.0203	-0.6139	0.0002	0.2433
3	2.6338	0.4206	-0.0667	0.0009	0.8576
4	4.7656	0.6781	-0.0204	0.0010	0.9541
5	8.8816	0.9485	0.3133	0.0021	2.0575

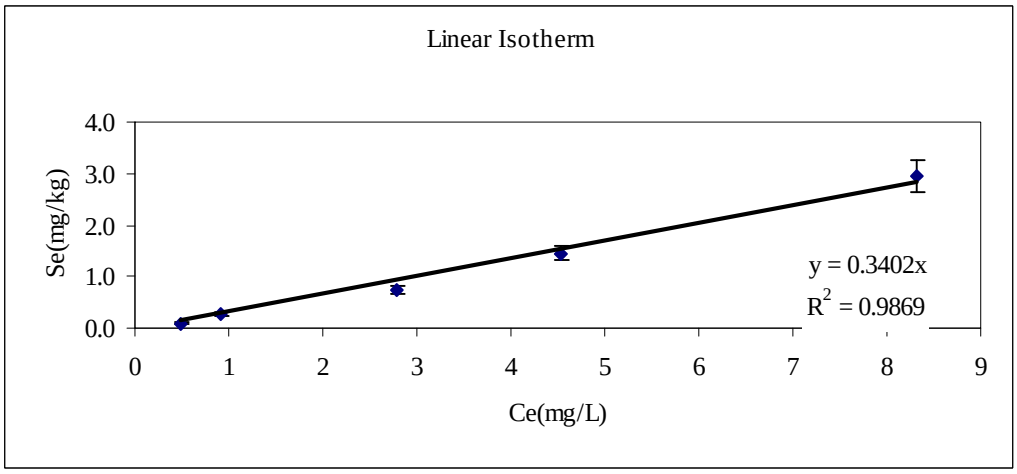


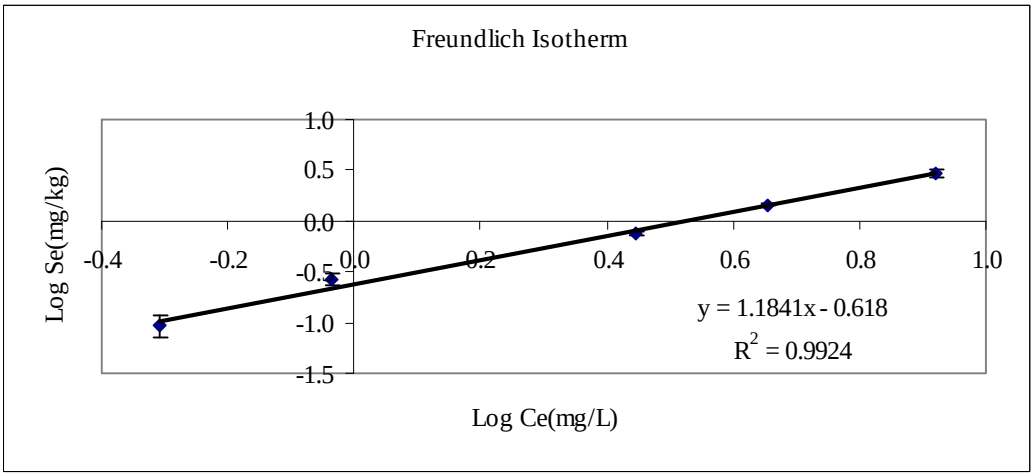


SB-2 (25-29)

	Co(mg/L)	Ce(mg/L)	V(mL)	V(L)	M(g)	SE(mg/g)	SE(mg/kg)
1A	0.5342	0.4824	16.9450	0.0169	10.0	0.0001	0.0877
1B	0.5378	0.5098	16.8310	0.0168	10.0	0.0000	0.0471
1C	0.5678	0.4797	15.9410	0.0159	10.0	0.0001	0.1405
2A	1.0658	0.8671	17.0510	0.0171	10.0	0.0003	0.3389
2B	1.0930	0.9381	16.6270	0.0166	10.0	0.0003	0.2576
2C	1.0789	0.9605	16.8450	0.0168	10.0	0.0002	0.1994
3A	3.2243	2.7425	16.9170	0.0169	10.0	0.0008	0.8149
3B	3.2924	2.7281	16.5670	0.0166	10.0	0.0009	0.9348
3C	3.1810	2.8839	17.1470	0.0171	10.0	0.0005	0.5095
4A	5.3821	4.7243	16.6310	0.0166	10.0	0.0011	1.0941
4B	5.2715	4.5084	16.9800	0.0170	10.0	0.0013	1.2957
4C	5.5473	4.3401	16.1360	0.0161	10.0	0.0019	1.9478
5A	10.2811	7.3241	16.2400	0.0162	10.0	0.0048	4.8021
5B	9.8603	8.7669	16.9330	0.0169	10.0	0.0019	1.8514
5C	10.1895	8.8426	16.3860	0.0164	10.0	0.0022	2.2070

Sample	Ce(mg/L)	log Ce(mg/L)	log Se	Se (mg/g)	Se (mg/kg)
1	0.4906	-0.3092	-1.0373	0.0001	0.0918
2	0.9219	-0.0353	-0.5762	0.0003	0.2653
3	2.7848	0.4448	-0.1232	0.0008	0.7531
4	4.5243	0.6555	0.1601	0.0014	1.4459
5	8.3112	0.9197	0.4703	0.0030	2.9535

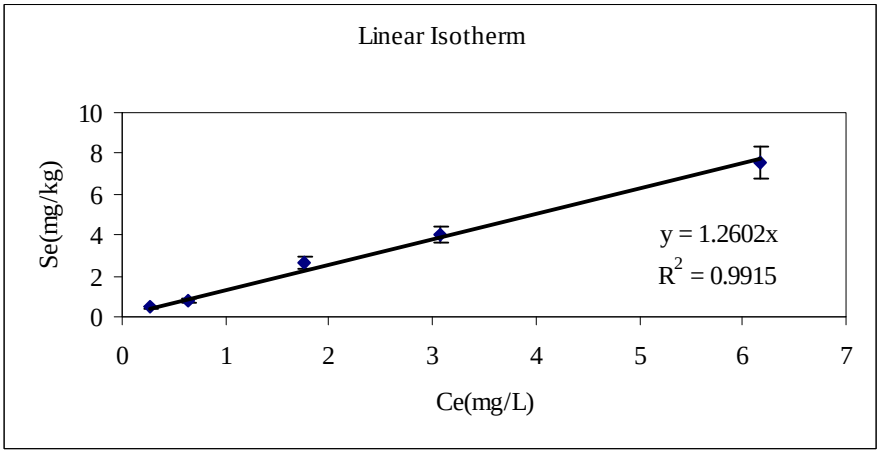


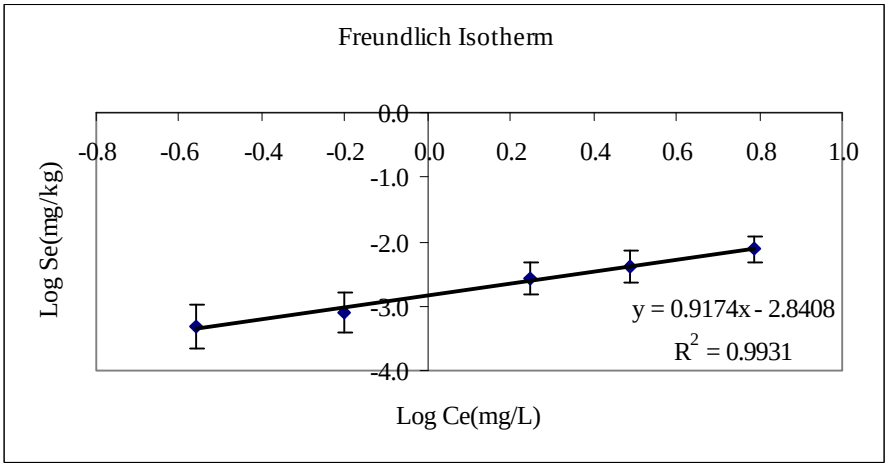


SB-3 (0-4)

	Co (mg/L)	Ce (mg/L)	V (mL)	V (L)	M (g)	Se (mg/g)	Se(mg/kg)
1A	0.519	0.2982	17.44	0.0174	8.81	0.0004	0.44
1B	0.510	0.2728	17.74	0.0177	8.81	0.0005	0.48
1C	0.507	0.2536	17.84	0.0178	8.81	0.0005	0.51
2A	1.037	0.6549	17.52	0.0175	8.81	0.0008	0.76
2B	1.034	0.6141	17.58	0.0176	8.81	0.0008	0.84
2C	1.044	0.6210	17.40	0.0174	8.81	0.0008	0.84
3A	3.039	1.7971	17.95	0.0179	8.81	0.0025	2.53
3B	3.115	1.6465	17.51	0.0175	8.81	0.0029	2.92
3C	3.115	1.8604	17.51	0.0175	8.81	0.0025	2.49
4A	5.115	3.2118	17.50	0.0175	8.81	0.0038	3.78
4B	5.051	3.0105	17.72	0.0177	8.81	0.0041	4.10
4C	5.138	2.9735	17.42	0.0174	8.81	0.0043	4.28
5A	9.710	6.0275	18.01	0.0180	8.81	0.0075	7.53
5B	10.086	6.3553	17.34	0.0173	8.81	0.0073	7.34
5C	10.021	6.1061	17.45	0.0175	8.81	0.0078	7.76

Sample	Ce(mg/L)	Log Ce(mg/L)	Log Se	Se (mg/g)	Se (mg/kg)
1	0.27488	-0.561	-3.322	0.00048	0.47630
2	0.62999	-0.201	-3.091	0.00081	0.81129
3	1.76802	0.247	-2.577	0.00265	2.64743
4	3.06529	0.486	-2.392	0.00406	4.05510
5	6.16297	0.790	-2.122	0.00754	7.54334

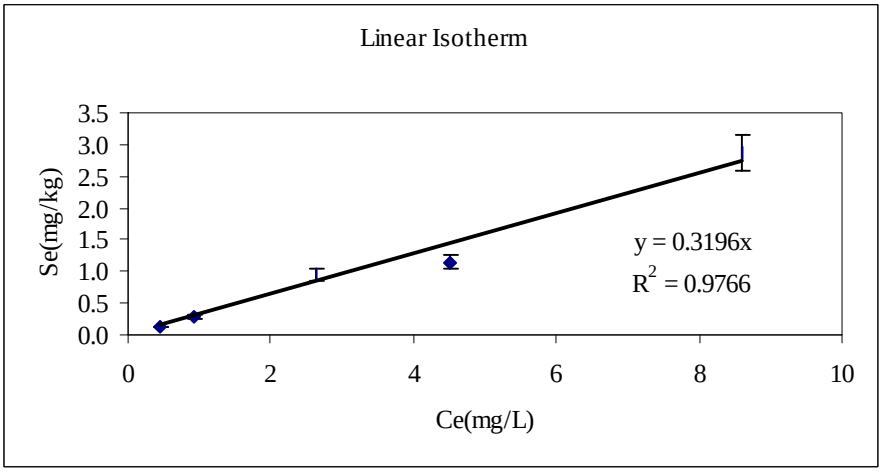


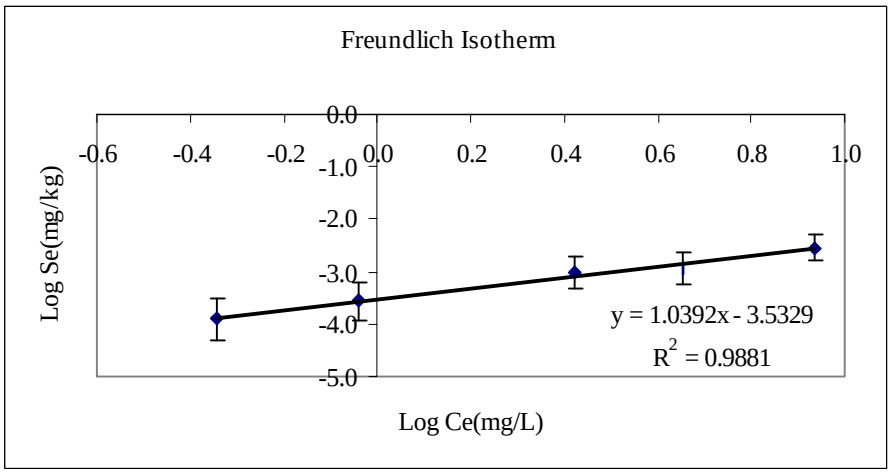


SB-3 (10-14)

	Co (mg/L)	Ce (mg/L)	V (mL)	V (L)	M (g)	Se (mg/g)	Se(mg/kg)
1A	0.506	0.4543	17.88	0.0179	8.90	0.0001	0.10
1B	0.519	0.4474	17.45	0.0174	8.90	0.0001	0.14
1C	0.522	0.4574	17.35	0.0174	8.90	0.0001	0.13
2A	1.035	0.9090	17.56	0.0176	8.90	0.0002	0.25
2B	1.065	0.9255	17.07	0.0171	8.90	0.0003	0.27
2C	1.060	0.9026	17.15	0.0171	8.90	0.0003	0.30
3A	3.078	2.6150	17.72	0.0177	8.90	0.0009	0.92
3B	3.108	2.6061	17.55	0.0175	8.90	0.0010	0.99
3C	3.177	2.6837	17.17	0.0172	8.90	0.0010	0.95
4A	5.070	4.4998	17.66	0.0177	8.90	0.0011	1.13
4B	5.141	4.4321	17.41	0.0174	8.90	0.0014	1.39
4C	5.021	4.5593	17.83	0.0178	8.90	0.0009	0.92
5A	10.155	8.4116	17.23	0.0172	8.90	0.0034	3.37
5B	10.088	8.6675	17.34	0.0173	8.90	0.0028	2.77
5C	9.977	8.7236	17.53	0.0175	8.90	0.0025	2.47

Sample	Ce(mg/L)	log Ce(mg/L)	log Se	Se (mg/g)	Se (mg/kg)
1	0.45303	-0.344	-3.909	0.00012	0.12322
2	0.91235	-0.040	-3.564	0.00027	0.27278
3	2.63495	0.421	-3.020	0.00095	0.95447
4	4.49706	0.653	-2.940	0.00115	1.14712
5	8.60089	0.935	-2.542	0.00287	2.86963

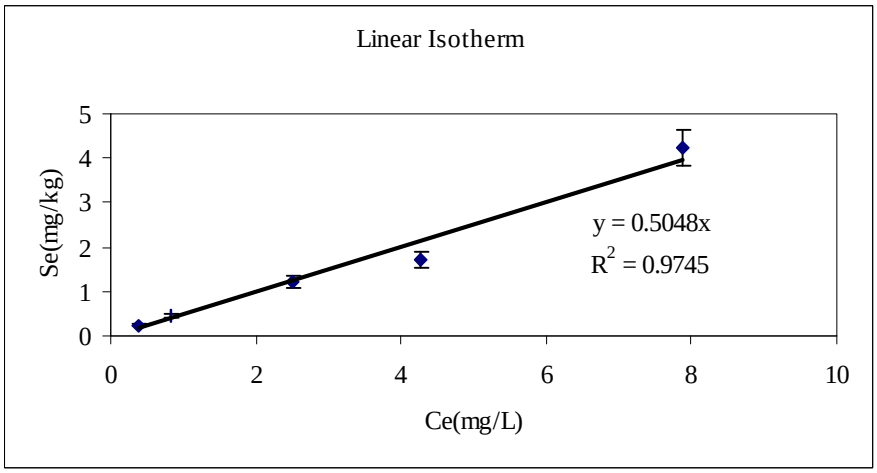


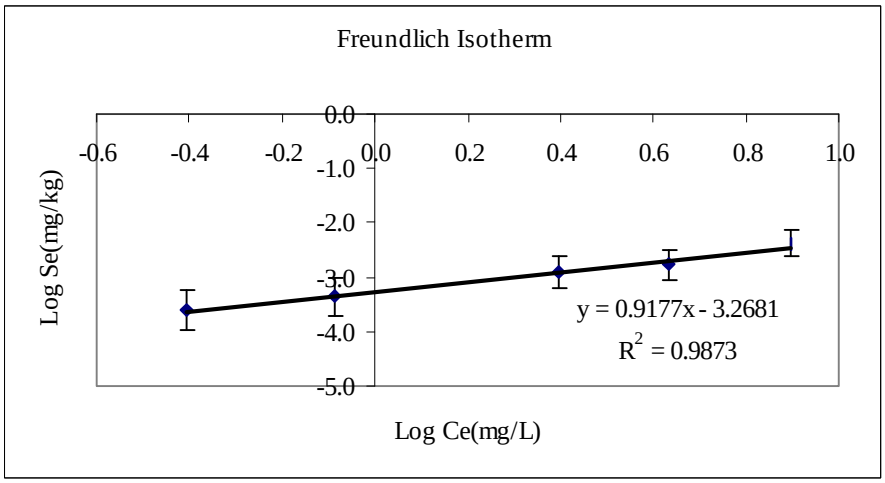


SB3 (25-27)

	Co (mg/L)	Ce (mg/L)	V (mL)	V (L)	M (g)	Se (mg/g)	Se(mg/kg)
1A	0.514	0.3738	17.61	0.0176	8.81	0.0003	0.28
1B	0.513	0.3684	17.65	0.0177	8.81	0.0003	0.29
1C	0.521	0.4362	17.37	0.0174	8.81	0.0002	0.17
2A	1.039	0.8182	17.49	0.0175	8.81	0.0004	0.44
2B	1.030	0.8131	17.64	0.0176	8.81	0.0004	0.43
2C	1.051	0.8301	17.30	0.0173	8.81	0.0004	0.43
3A	3.084	2.5794	17.68	0.0177	8.81	0.0010	1.01
3B	3.098	2.4787	17.61	0.0176	8.81	0.0012	1.24
3C	3.153	2.4422	17.30	0.0173	8.81	0.0014	1.40
4A	5.201	4.3935	17.21	0.0172	8.81	0.0016	1.58
4B	5.181	4.3774	17.28	0.0173	8.81	0.0016	1.58
4C	5.075	4.0731	17.64	0.0176	8.81	0.0020	2.01
5A	10.118	7.7179	17.29	0.0173	8.81	0.0047	4.71
5B	9.981	8.2028	17.52	0.0175	8.81	0.0035	3.54
5C	9.967	7.7359	17.55	0.0175	8.81	0.0044	4.44

Sample	Ce(mg/L)	log Ce(mg/L)	log Se	Se (mg/g)	Se (mg/kg)
1	0.39281	-0.406	-3.610	0.00025	0.24561
2	0.82047	-0.086	-3.361	0.00044	0.43550
3	2.50012	0.398	-2.915	0.00122	1.21601
4	4.28132	0.632	-2.765	0.00172	1.71980
5	7.88553	0.897	-2.374	0.00423	4.23063

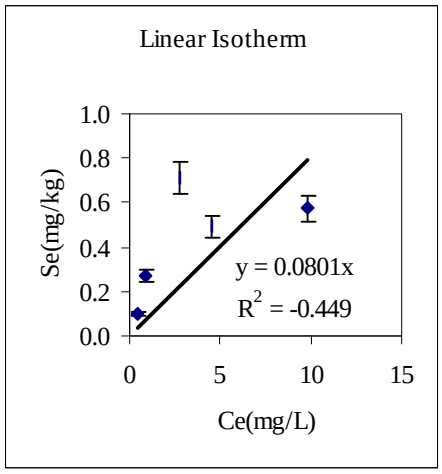


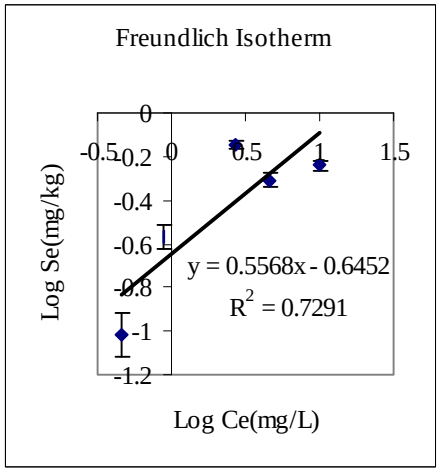


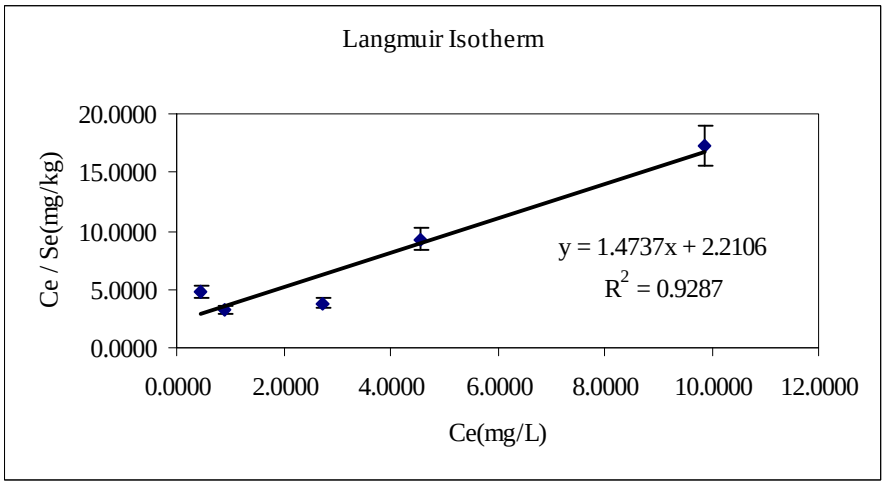
SB-3 (38-40)

	Co(mg/L)	Ce(mg/L)	V(mL)	V(L)	M(g)	SE(mg/g)	SE(mg/kg)
1A	0.4949	0.4585	18.2880	0.0183	8.6400	0.0001	0.0772
1B	0.5069	0.4657	17.8580	0.0179	8.6400	0.0001	0.0850
1C	0.5066	0.4455	17.8682	0.0179	8.6400	0.0001	0.1262
2A	1.0167	0.8703	17.8752	0.0179	8.6400	0.0003	0.3029
2B	1.0175	0.9335	17.8612	0.0179	8.6400	0.0002	0.1737
2C	1.0161	0.8547	17.8852	0.0179	8.6400	0.0003	0.3341
3A	3.0698	2.7335	17.7682	0.0178	8.6400	0.0007	0.6915
3B	3.1342	2.7938	17.4032	0.0174	8.6400	0.0007	0.6855
3C	3.0593	2.6876	17.8292	0.0178	8.6400	0.0008	0.7670
4B	5.0411	4.8799	17.7562	0.0178	8.6400	0.0003	0.3313
4C	5.0252	4.7084	17.8122	0.0178	8.6400	0.0007	0.6531
5A	9.9620	9.6821	17.9572	0.0180	8.6400	0.0006	0.5817
5B	9.9316	9.6042	18.0122	0.0180	8.6400	0.0007	0.6827
5C	10.5266	10.2946	16.9942	0.0170	8.6400	0.0005	0.4563

Sample	Ce(mg/L)	Ce/Se (kg/L)	Log Ce (mg/L)	Se (mg/g)	Se (mg/kg)	Log Se (mg/kg)
1	0.4566	4.7485	-0.340487684	0.0001	0.0962	-1.017040272
2	0.8862	3.2797	-0.052475451	0.0003	0.2702	-0.568314711
3	2.7383	3.8316	0.437485129	0.0007	0.7147	-0.145889778
4	4.5645	9.2743	0.659393974	0.0005	0.4922	-0.307884862
5	9.8603	17.1915	0.993889939	0.0006	0.5736	-0.241423597

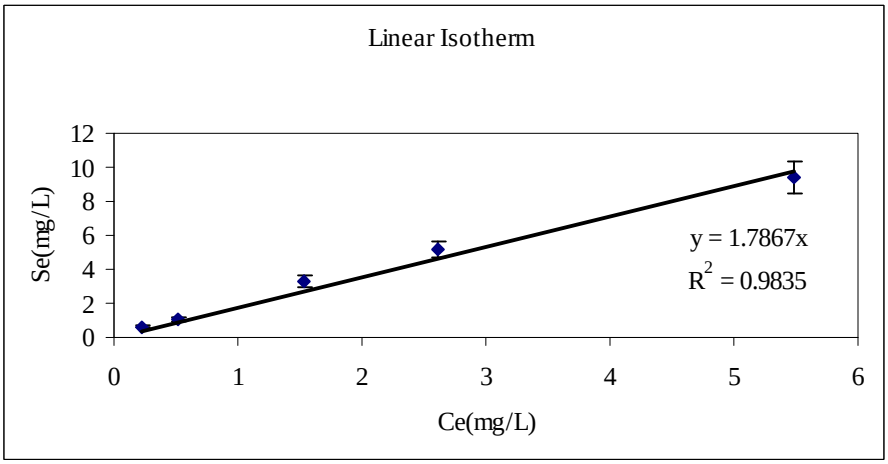


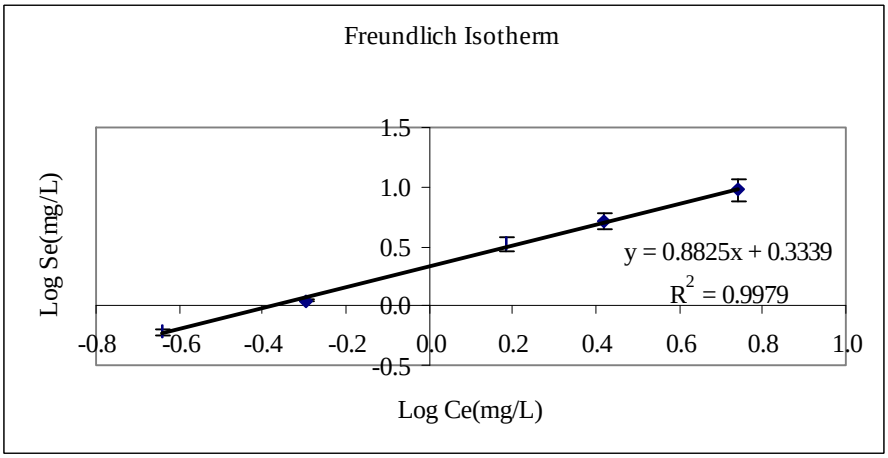




SB-4 (0-4)	Co(mg/L)	Ce(mg/L)	V(mL)	V(L)	M(g)	SE(mg/g)	SE(mg/kg)
1A	0.517	0.1878	17.519	0.0175	8.27	0.0007	0.70
1B	0.508	0.2502	17.819	0.0178	8.27	0.0006	0.56
1C	0.504	0.2475	17.964	0.0180	8.27	0.0006	0.56
2A	1.020	0.5412	17.820	0.0178	8.27	0.0010	1.03
2B	1.008	0.4105	18.034	0.0180	8.27	0.0013	1.30
2C	1.032	0.5737	17.619	0.0176	8.27	0.0010	0.98
3A	3.027	1.6973	18.020	0.0180	8.27	0.0029	2.90
3B	3.064	1.4354	17.802	0.0178	8.27	0.0035	3.51
3C	3.060	1.4452	17.827	0.0178	8.27	0.0035	3.48
4A	4.942	2.5694	18.113	0.0181	8.27	0.0052	5.20
4B	5.029	2.6113	17.800	0.0178	8.27	0.0052	5.20
4C	5.058	2.6596	17.697	0.0177	8.27	0.0051	5.13
5A	9.477	5.2687	18.457	0.0185	8.27	0.0094	9.39
5B	9.700	5.7963	18.033	0.0180	8.27	0.0085	8.51
5C	10.419	5.3877	16.789	0.0168	8.27	0.0102	10.21

Sample	Ce(mg/L)	Log Ce (mg/L)	Log Se (mg/L)	Se (mg/g)	Se (mg/kg)
1	0.22847	-0.641	-0.220	0.00060	0.60307
2	0.50845	-0.294	0.043	0.00110	1.10308
3	1.52597	0.184	0.518	0.00329	3.29439
4	2.61345	0.417	0.714	0.00518	5.17718
5	5.48425	0.739	0.972	0.00937	9.37235

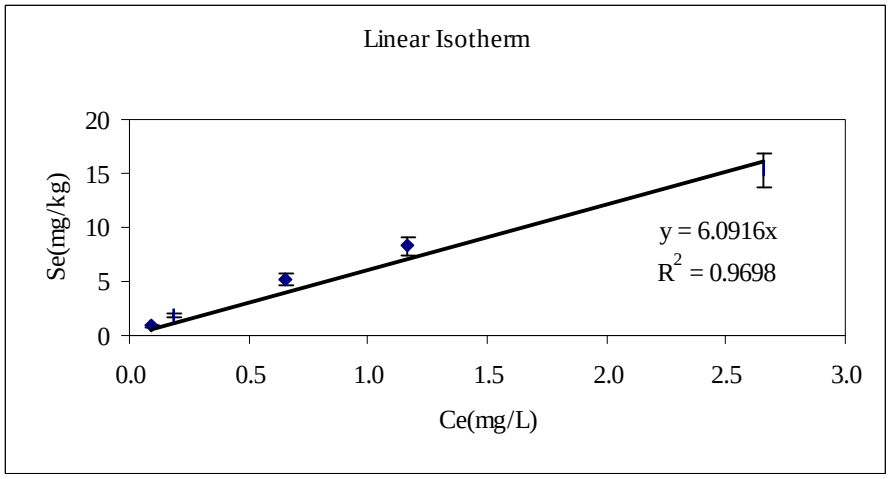


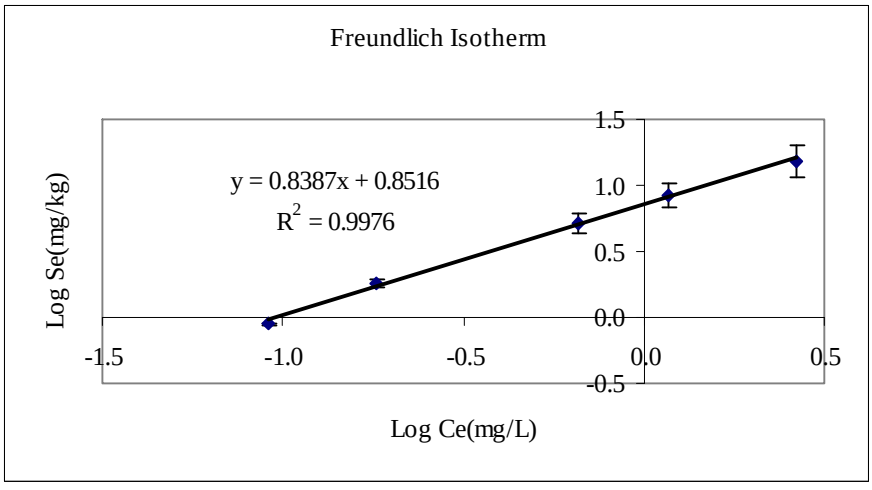


SB5 0-4

	Co(mg/L)	Ce(mg/L)	V(mL)	V(L)	M(g)	SE(mg/g)	SE(mg/kg)
1A	0.535	0.0819	16.905	0.0169	8.36	0.0009	0.92
1B	0.511	0.0883	17.705	0.0177	8.36	0.0009	0.90
1C	0.528	0.1044	17.142	0.0171	8.36	0.0009	0.87
2A	1.058	0.1784	17.176	0.0172	8.36	0.0018	1.81
2B	1.084	0.1371	16.761	0.0168	8.36	0.0019	1.90
2C	1.041	0.2288	17.465	0.0175	8.36	0.0017	1.70
3A	3.187	0.7431	17.117	0.0171	8.36	0.0050	5.00
3B	3.188	0.6103	17.107	0.0171	8.36	0.0053	5.28
3C	3.068	0.6103	17.781	0.0178	8.36	0.0052	5.23
4A	5.137	1.2332	17.424	0.0174	8.36	0.0081	8.14
4B	5.101	1.1656	17.546	0.0175	8.36	0.0083	8.26
4C	5.290	1.1060	16.921	0.0169	8.36	0.0085	8.47
5A	9.891	2.6153	17.684	0.0177	8.36	0.0154	15.39
5B	10.005	2.6669	17.482	0.0175	8.36	0.0153	15.35
5C	9.913	2.6916	17.644	0.0176	8.36	0.0152	15.24

Sample	Ce(mg/L)	Log Ce (mg/L)	Log Se (mg/L)	Se (mg/g)	Se (mg/kg)
1	0.09152	-1.038	-0.049	0.00089	0.89386
2	0.18146	-0.741	0.255	0.00180	1.80070
3	0.65457	-0.184	0.713	0.00517	5.16832
4	1.16826	0.068	0.918	0.00829	8.28857
5	2.65794	0.425	1.185	0.01533	15.32616

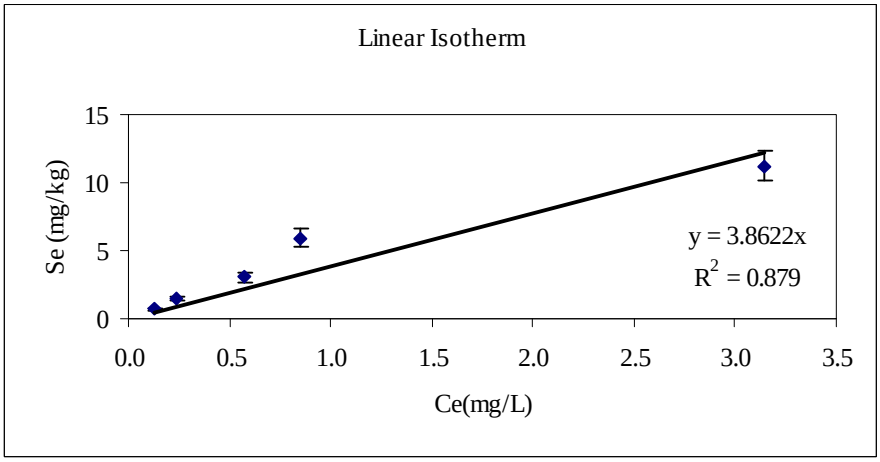


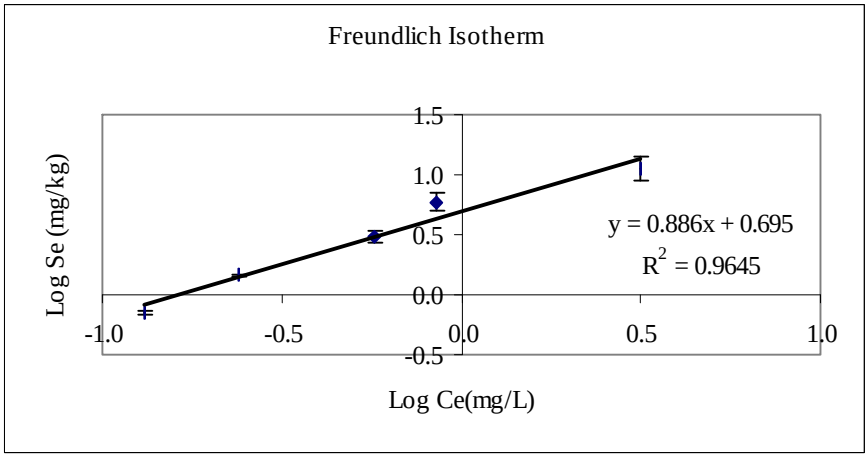


SB-6 (0-4)

	Co(mg/L)	Ce(mg/L)	V(mL)	V(L)	M(g)	SE(mg/g)	SE(mg/kg)
1A	0.5450	0.1311	16.6090	0.0166	10.00	0.0007	0.6875
1B	0.5692	0.1674	15.9010	0.0159	10.00	0.0006	0.6389
1C	0.6156	0.0949	14.7040	0.0147	10.00	0.0008	0.7656
2A	1.1646	0.2280	15.6050	0.0156	10.00	0.0015	1.4616
2B	1.1532	0.2394	15.7590	0.0158	10.00	0.0014	1.4401
2C	1.1317	0.2468	16.0590	0.0161	10.00	0.0014	1.4211
3A	1.1317	0.4247	16.8500	0.0169	10.00	0.0012	1.1912
3B	3.0467	0.4733	15.5950	0.0156	10.00	0.0040	4.0131
3C	3.2918	0.8284	15.5950	0.0156	10.00	0.0038	3.8418
4A	3.1190	0.6711	16.4590	0.0165	10.00	0.0040	4.0291
4B	5.5985	0.9858	14.9890	0.0150	10.00	0.0069	6.9140
4C	5.5161	0.8941	14.9800	0.0150	10.00	0.0069	6.9237
5A	10.1801	3.4106	15.2130	0.0152	10.00	0.0103	10.2985
5B	10.5022	2.6723	15.8980	0.0159	10.00	0.0124	12.4481
5C	9.8197	3.3604	17.0030	0.0170	10.00	0.0110	10.9828

Sample	Ce(mg/L)	log Ce(mg/L)	log Se (mg/kg)	Se (mg/g)	Se (mg/kg)
1	0.1311	-0.8822	-0.1566	0.0007	0.6973
2	0.2381	-0.6233	0.1586	0.0014	1.4409
3	0.5755	-0.2400	0.4793	0.0030	3.0154
4	0.8503	-0.0704	0.7749	0.0060	5.9556
5	3.1478	0.4980	1.0509	0.0112	11.2431

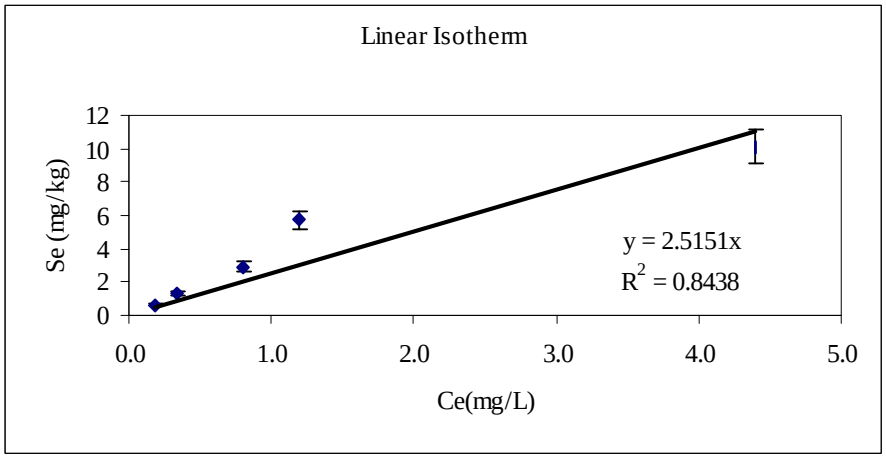


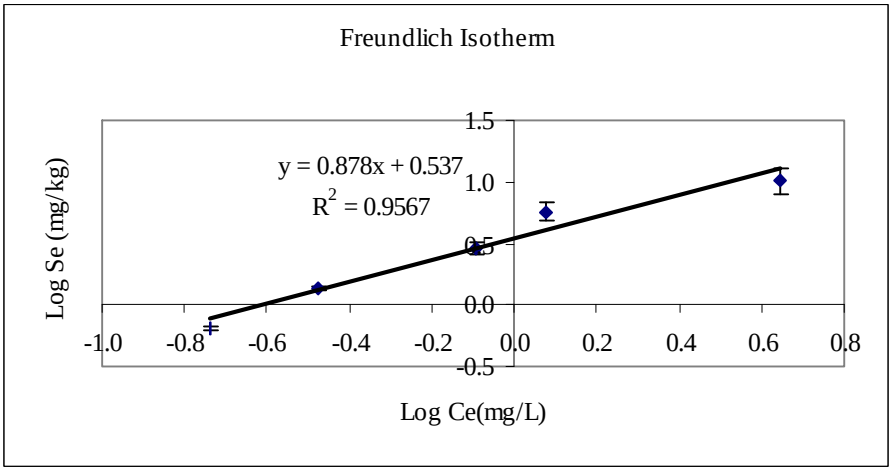


SB-7(0-4)

	Co(mg/L)	Ce(mg/L)	V(mL)	V(L)	M(g)	SE(mg/g)	SE(mg/kg)
1A	0.533	0.183	16.970	0.017	9.170	0.0006	0.6478
1B	0.541	0.234	16.735	0.017	9.170	0.0006	0.5596
1C	0.524	0.133	17.261	0.017	9.170	0.0007	0.7371
2A	1.045	0.319	17.395	0.017	9.170	0.0014	1.3769
2B	1.068	0.335	17.022	0.017	9.170	0.0014	1.3602
2C	1.045	0.345	17.390	0.017	9.170	0.0013	1.3273
3A	1.045	0.594	16.960	0.017	9.170	0.0008	0.8340
3B	3.027	0.662	17.060	0.017	9.170	0.0044	4.3996
3C	3.009	1.159	17.060	0.017	9.170	0.0034	3.4426
4A	2.990	0.939	17.168	0.017	9.170	0.0038	3.8409
4B	4.850	1.379	17.301	0.017	9.170	0.0065	6.5495
4C	4.947	1.251	16.752	0.017	9.170	0.0068	6.7536
5A	9.862	4.771	16.961	0.017	9.170	0.0094	9.4181
5B	9.803	3.738	17.031	0.017	9.170	0.0113	11.2655
5C	10.076	4.700	16.570	0.017	9.170	0.0097	9.7140

Sample	Ce(mg/L)	log Ce(mg/L)	log Se (mg /kg)	Se (mg/g)	Se (mg/kg)
1	0.183	-0.736	-0.188	0.001	0.648
2	0.333	-0.478	0.132	0.001	1.355
3	0.805	-0.094	0.461	0.003	2.892
4	1.189	0.075	0.757	0.006	5.715
5	4.403	0.644	1.006	0.010	10.133

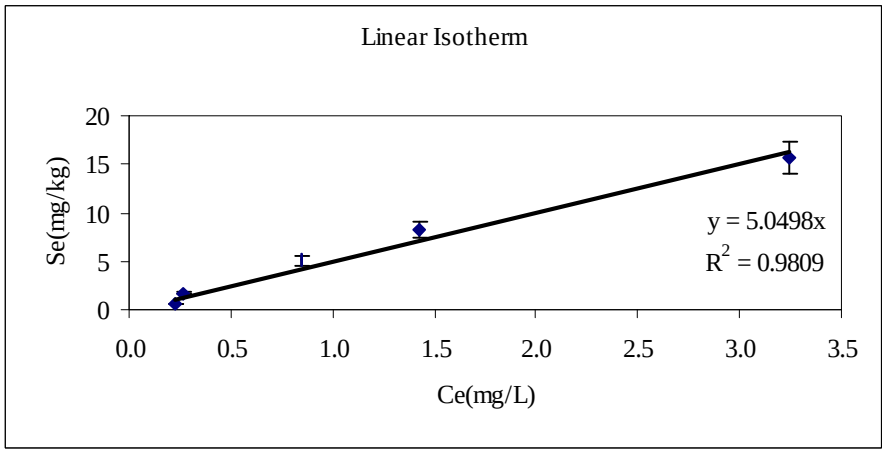


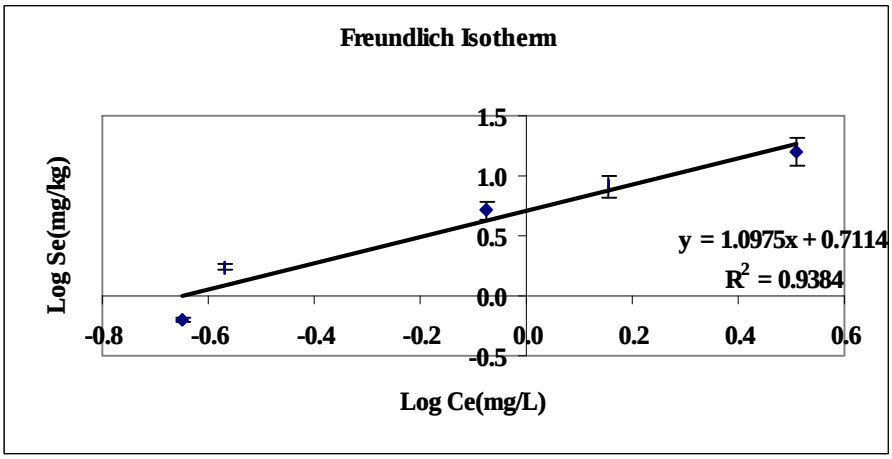


SB-1(0-4)

	Co(mg/L)	Ce(mg/L)	V(mL)	V(L)	M(g)	SE(mg/g)	SE(mg/kg)
1A	0.505	0.159	17.933	0.018	7.800	0.001	0.795
1B	0.485	0.225	18.650	0.019	7.800	0.001	0.624
1C	0.492	0.287	18.406	0.018	7.800	0.000	0.482
2A	1.031	0.303	17.626	0.018	7.800	0.002	1.646
2B	1.061	0.235	17.129	0.017	7.800	0.002	1.813
2C	1.055	0.269	17.233	0.017	7.800	0.002	1.736
3B	3.329	0.841	16.384	0.016	7.800	0.005	5.227
3C	3.078	0.841	17.722	0.018	7.800	0.005	5.082
4A	5.018	1.603	17.837	0.018	7.800	0.008	7.809
4B	5.036	1.370	17.775	0.018	7.800	0.008	8.354
4C	5.062	1.297	17.682	0.018	7.800	0.009	8.536
5A	10.365	2.863	17.259	0.017	7.800	0.017	16.601
5B	10.053	3.301	17.795	0.018	7.800	0.015	15.404
5C	10.297	3.558	17.373	0.017	7.800	0.015	15.011

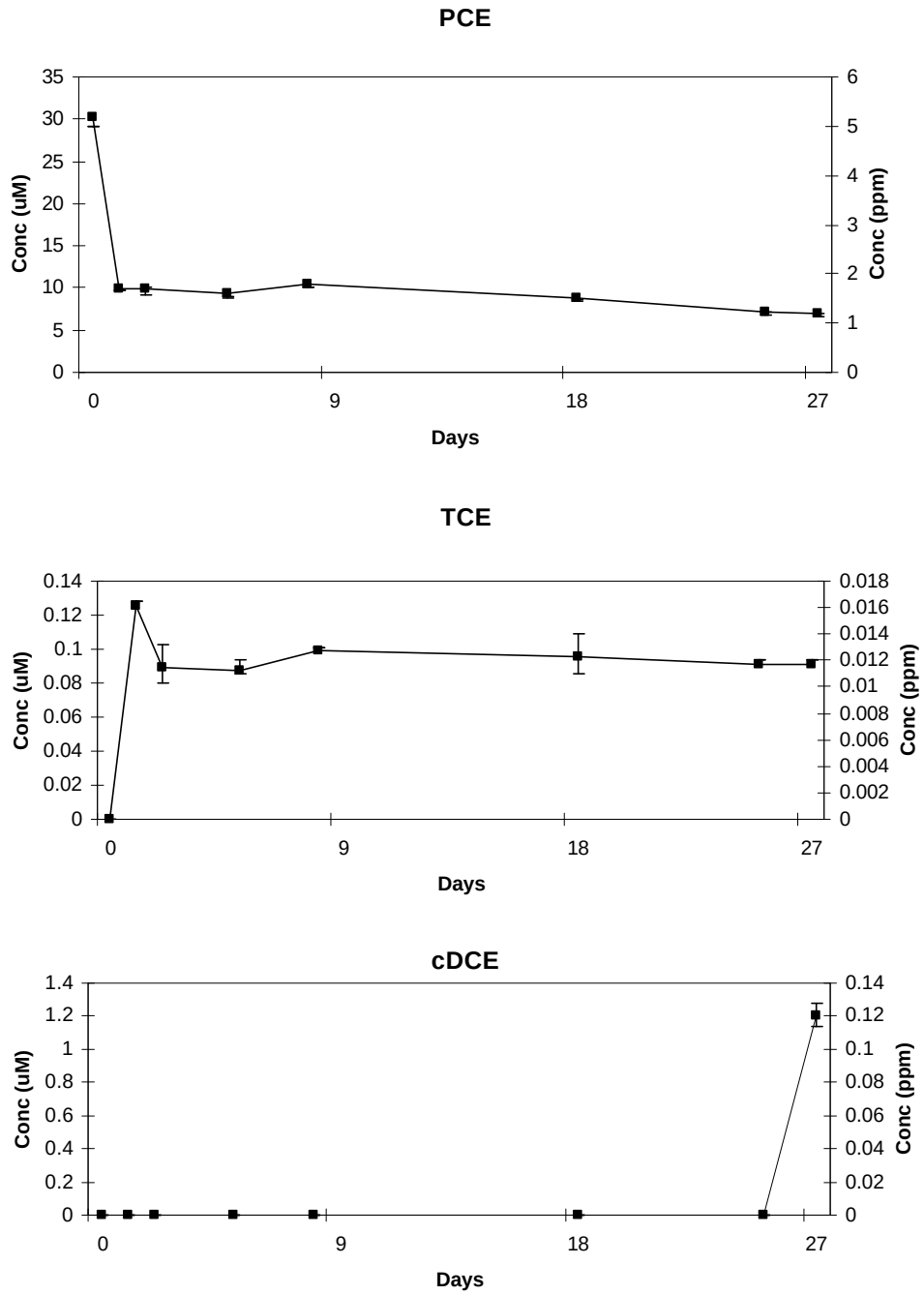
Sample	Ce(mg/L)	Log Ce (mg/L)	Log Se (mg/kg)	Se (mg/g)	Se (mg/kg)
1	0.22359	-0.651	-0.198	0.00063	0.63371
2	0.26889	-0.570	0.239	0.00173	1.73187
3	0.84094	-0.075	0.712	0.00515	5.15442
4	1.42343	0.153	0.916	0.00823	8.23287
5	3.24038	0.511	1.195	0.01567	15.67189



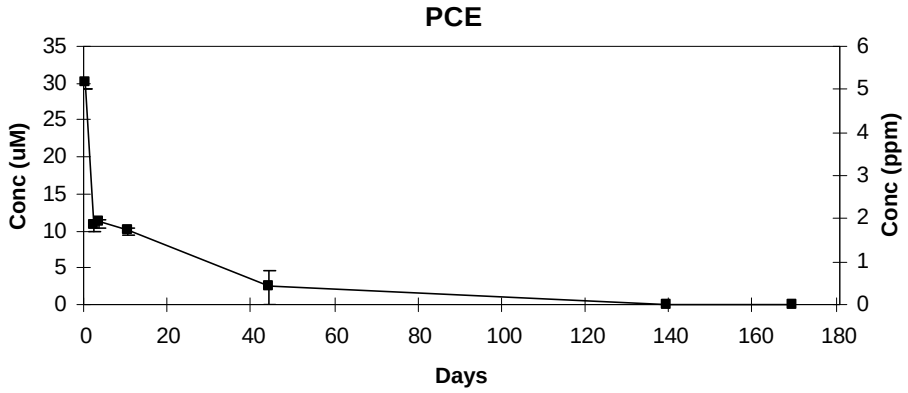


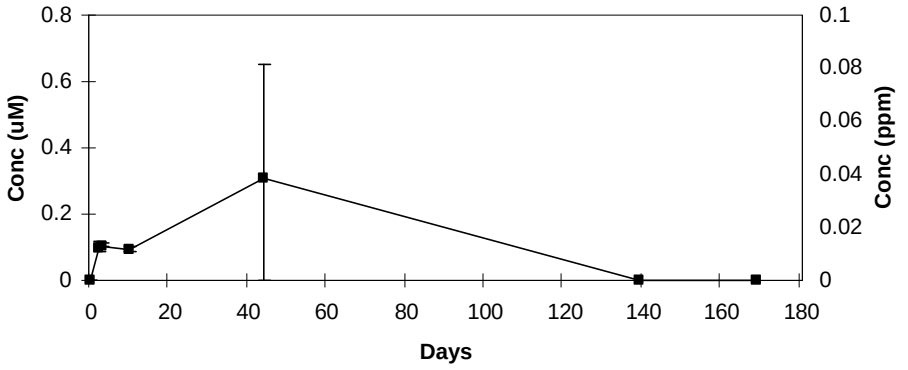
APPENDIX B

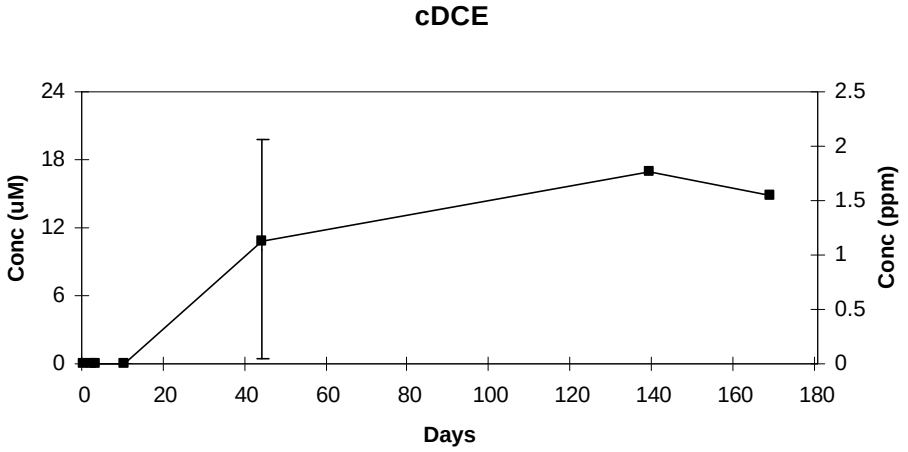
INDIVIUAL RESULTS OF SURFACE CORE (0-4 FT) MICROCOSM STUDIES



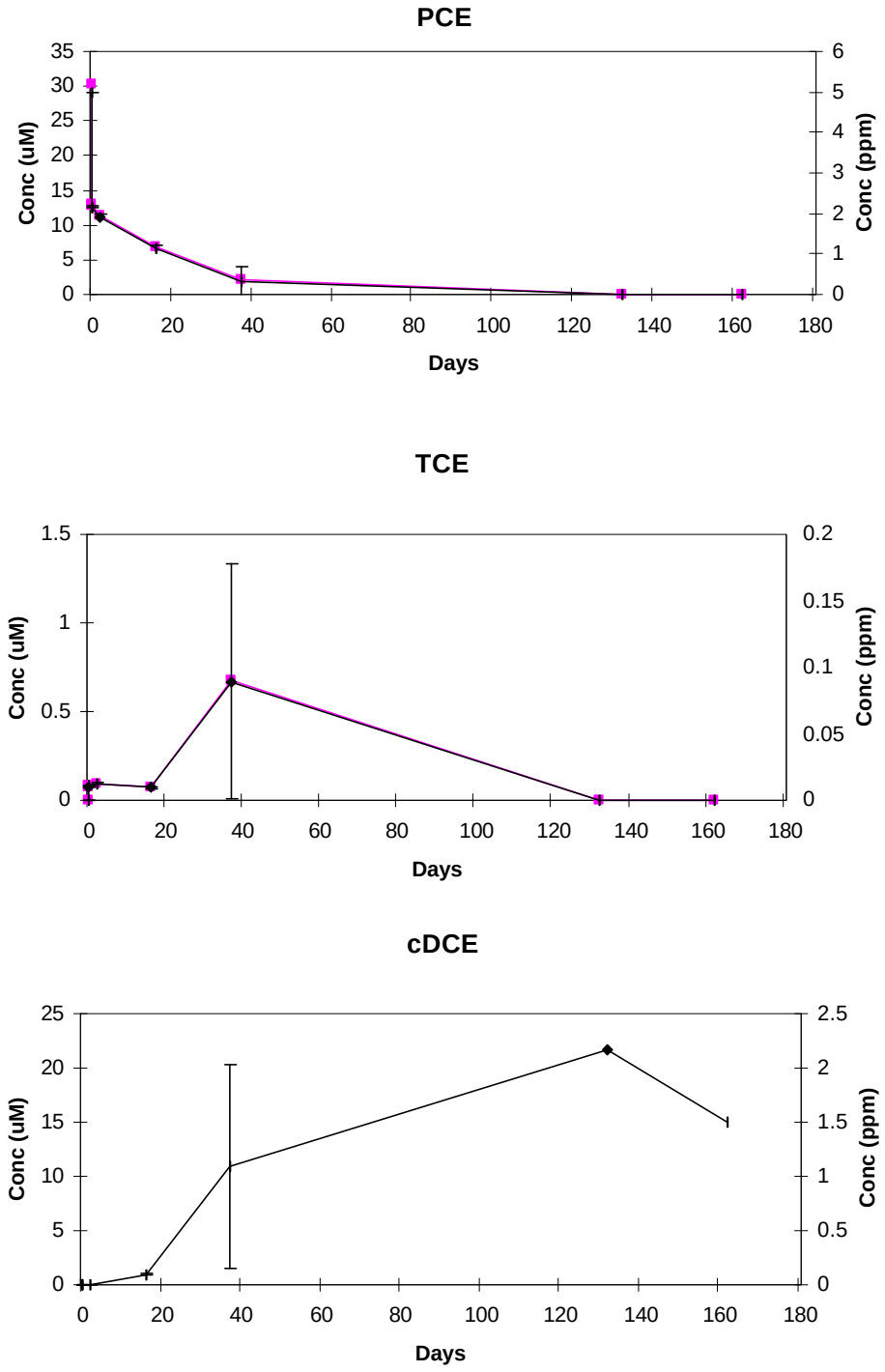
SB3 (0-4ft) Batch PCE Biodegradation, Spiked After a 2 Day Acclimation Period



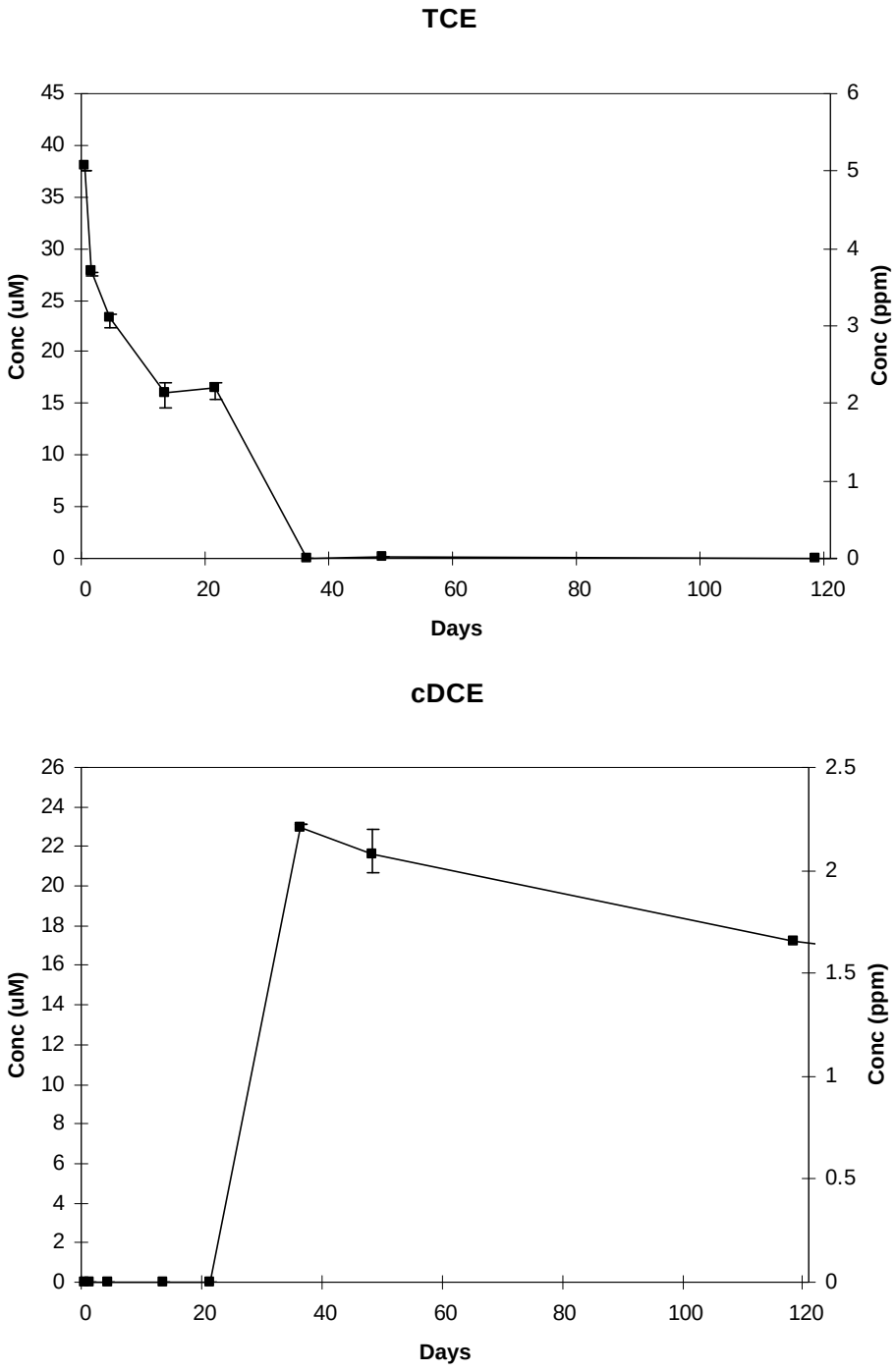




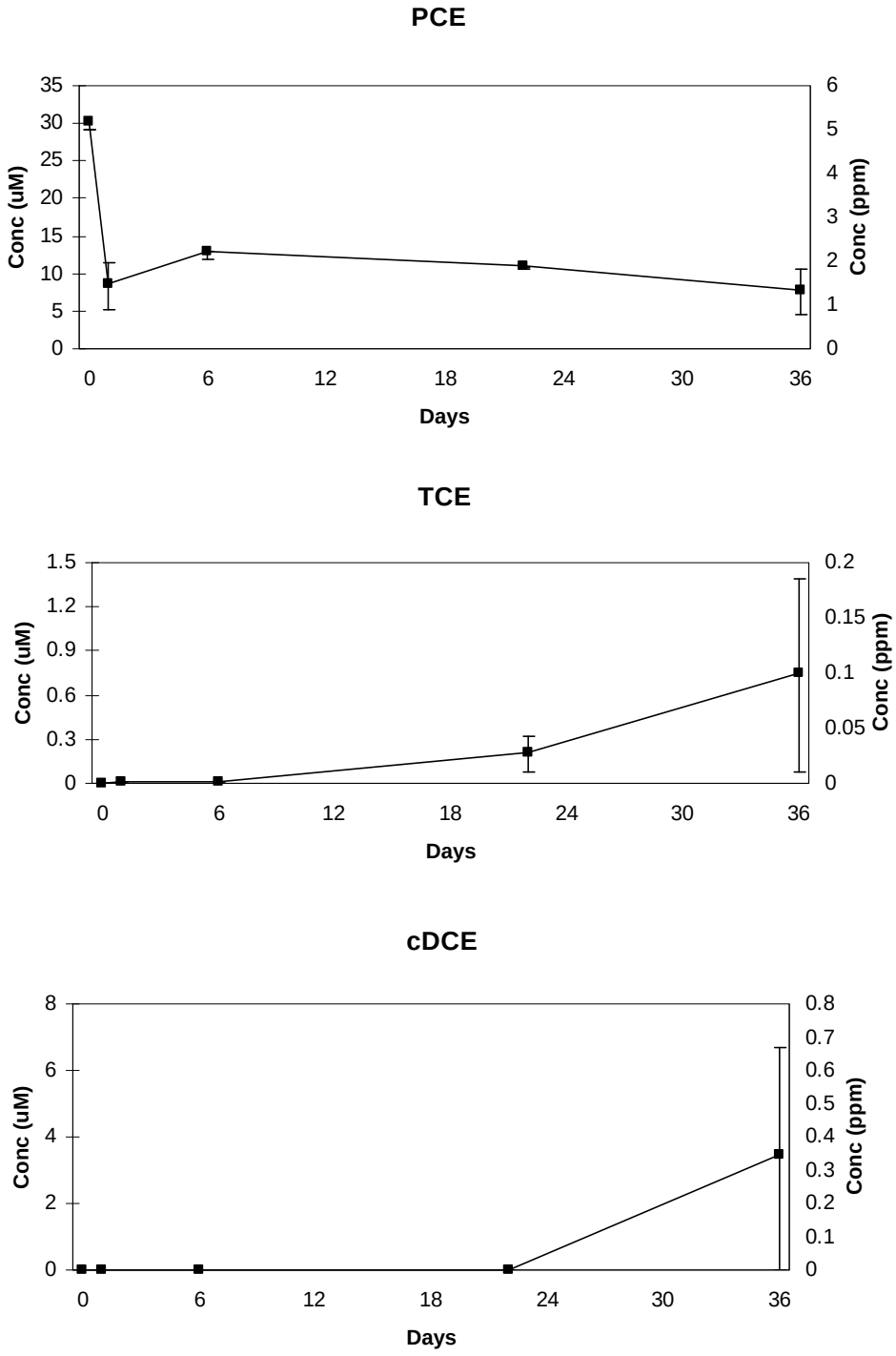
SB3 (0-4ft) Batch PCE Biodegradation, Spiked After a 1 week Acclimation Period



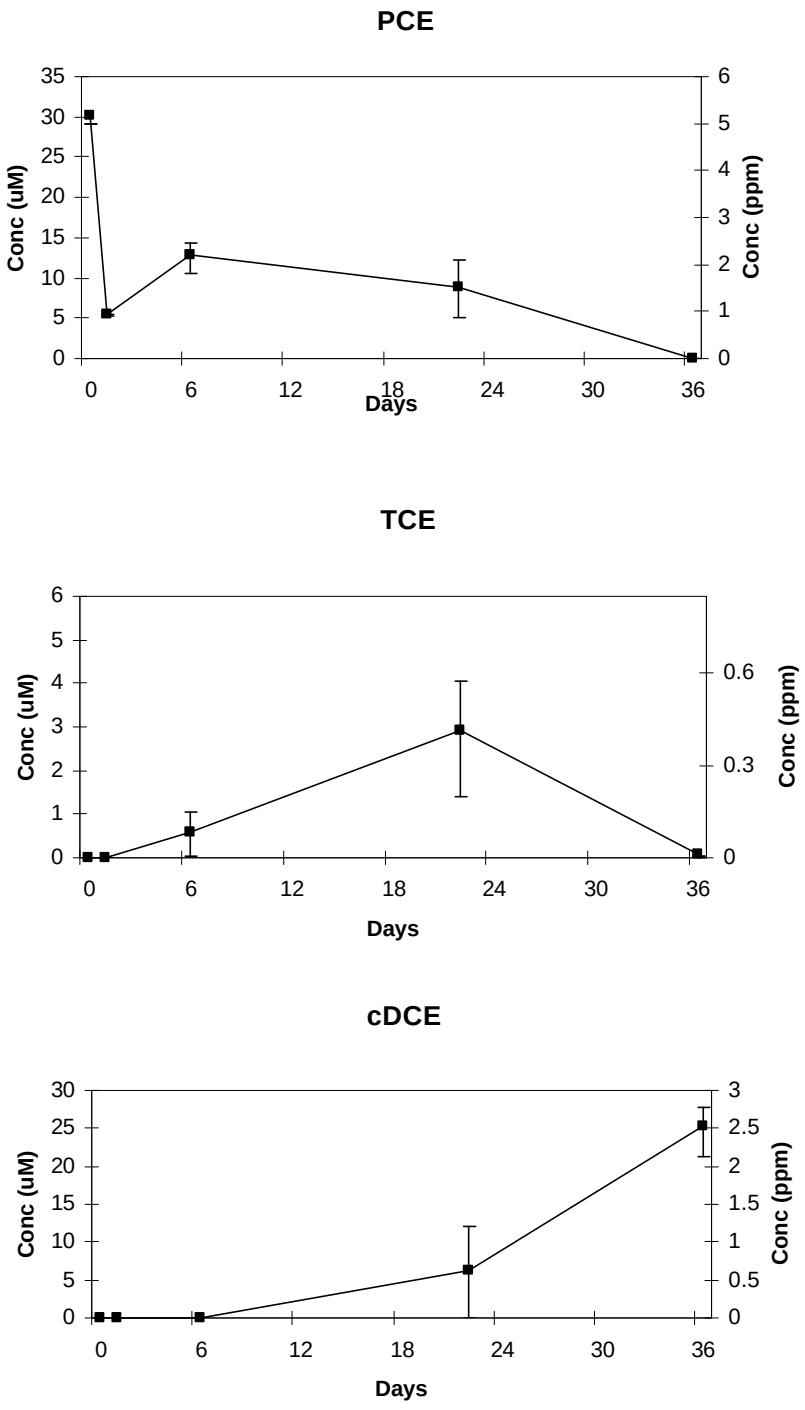
SB3 (0-4ft) Batch PCE Biodegradation, Spiked After a 2 week Acclimation Period



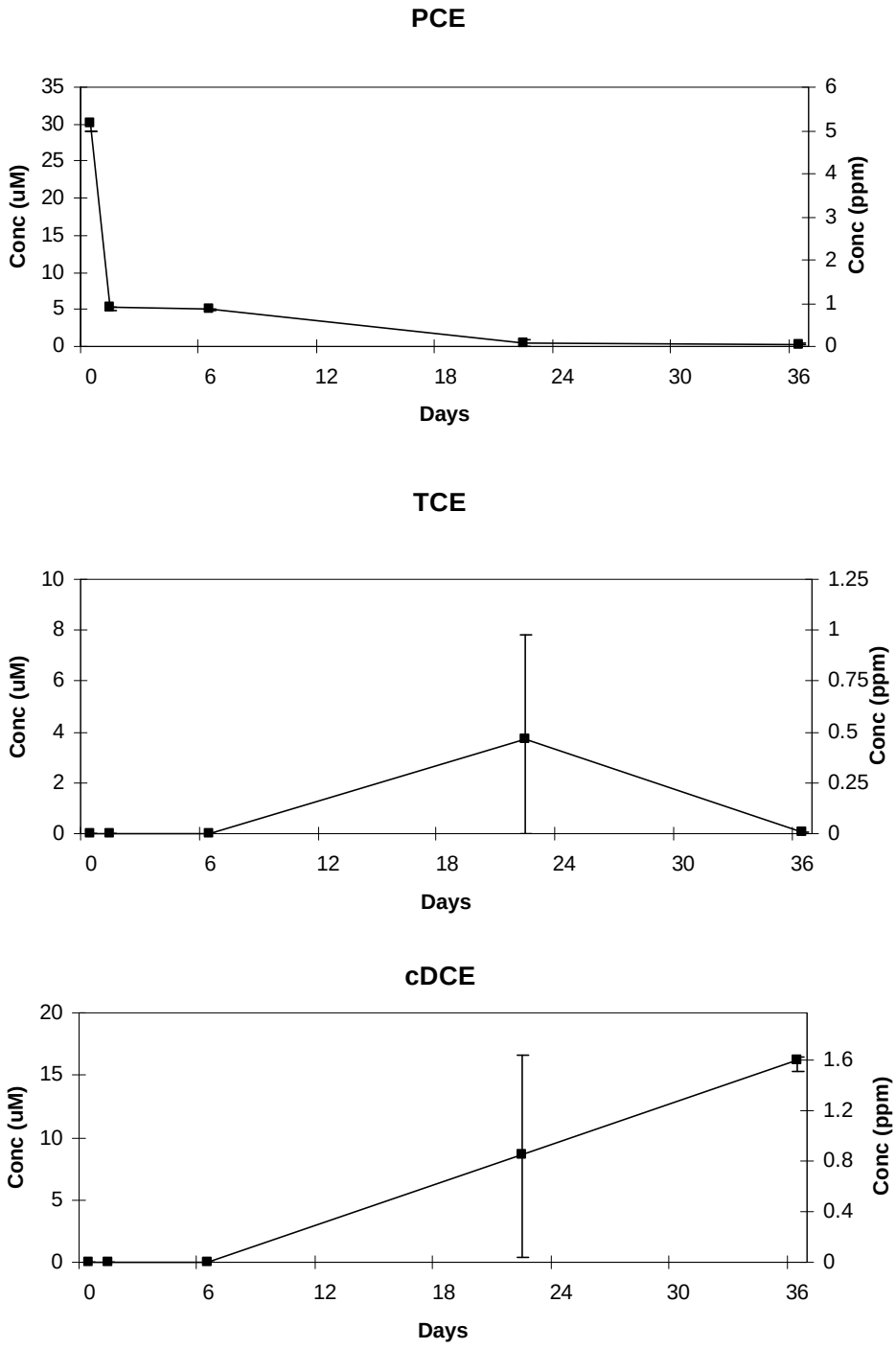
SB3 (0-4ft) Batch TCE Biodegradation, Spiked After a 1 week Acclimation Period



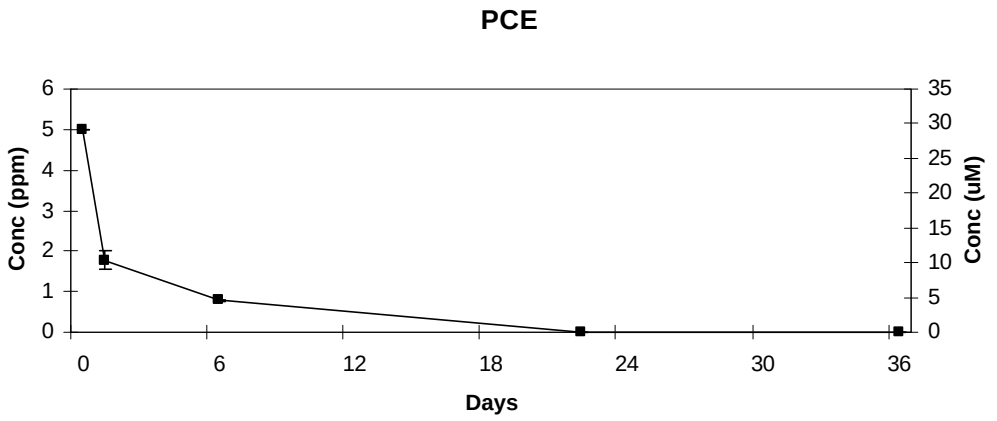
SB3 Surface Sediment (0-4ft) Amended with 3 % Molasses and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period

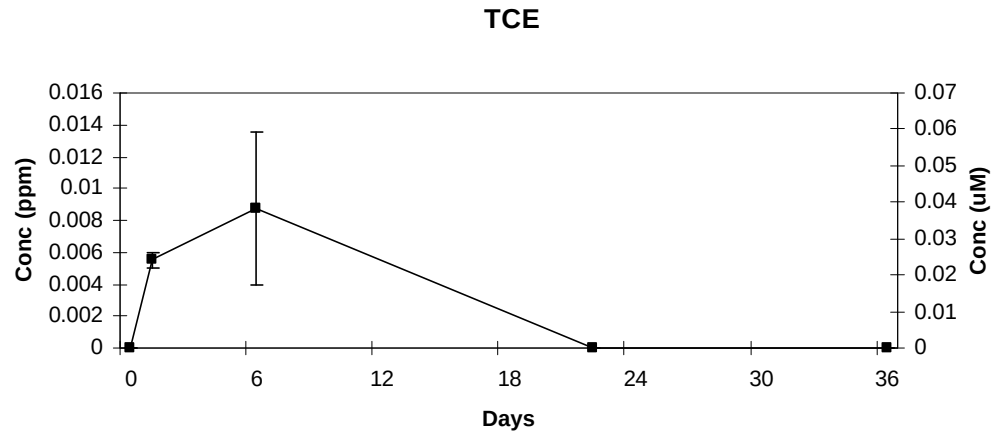


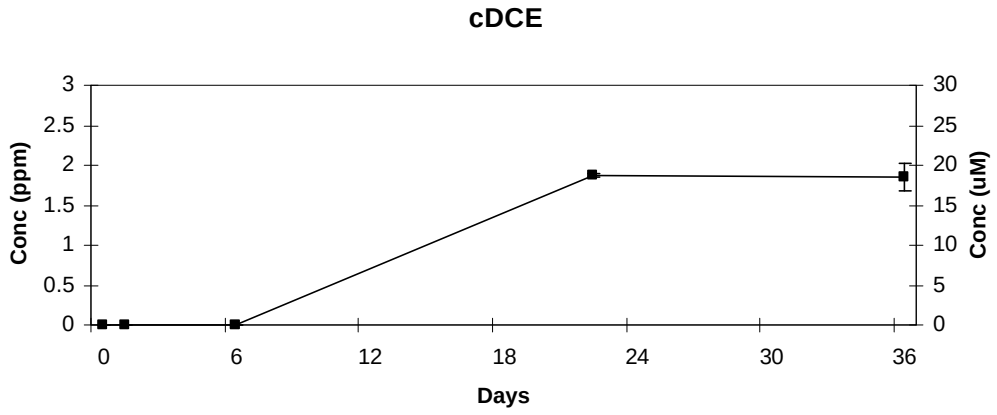
SB3 Surface Sediment (0-4ft) Amended with 3 % Yeast Extract and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



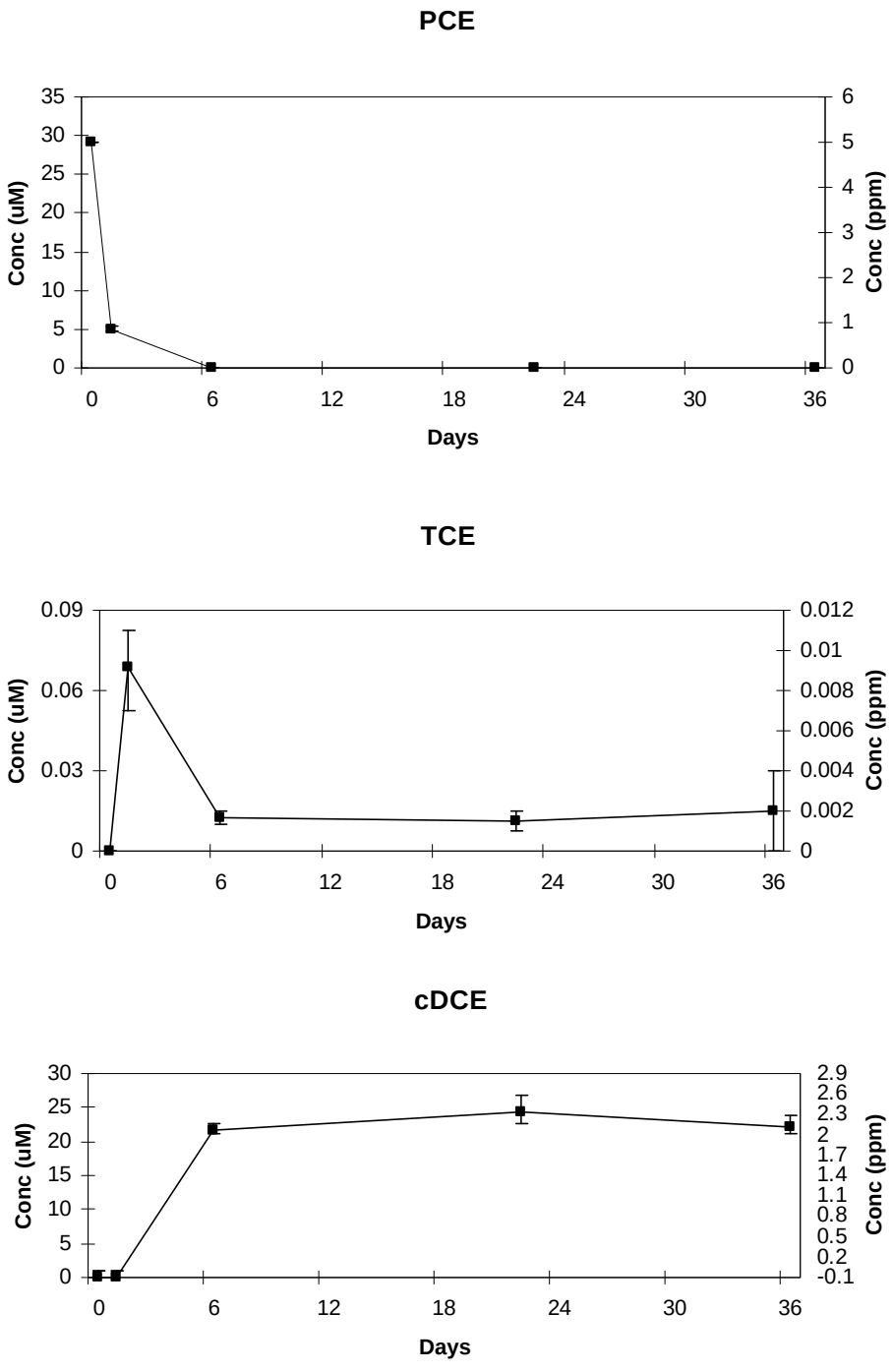
SB3 Surface Sediment (0-4ft) Amended with 3 mM Na-Lactate and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



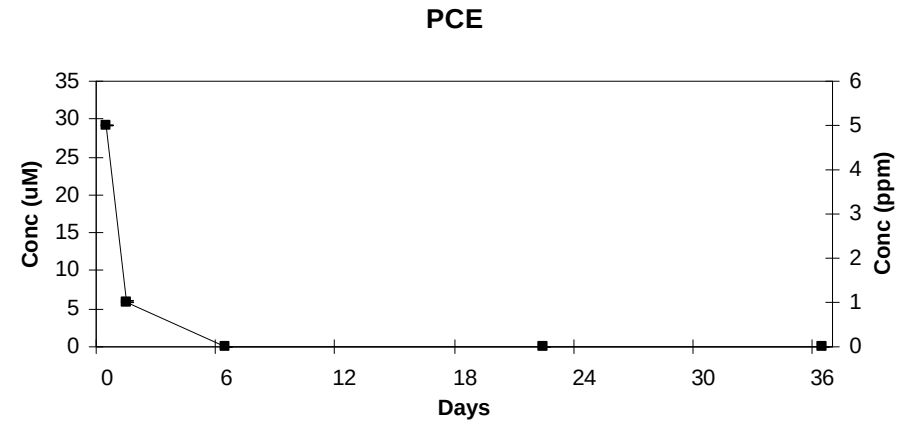


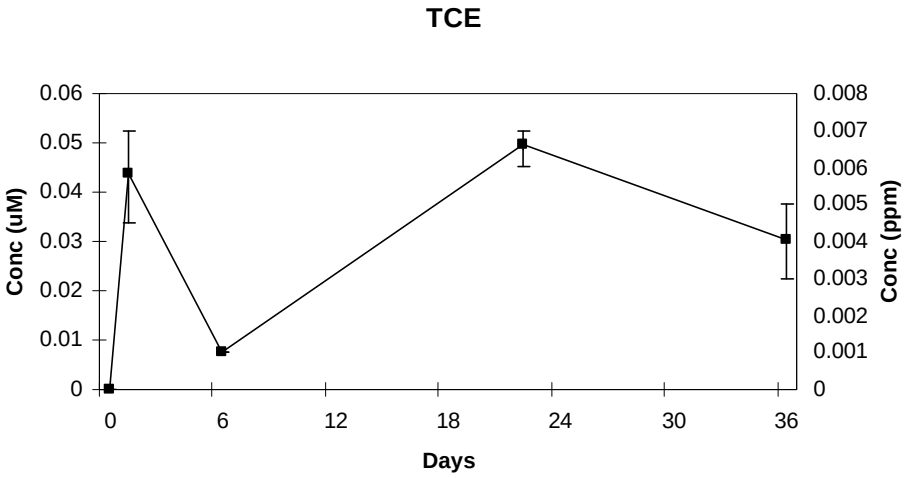


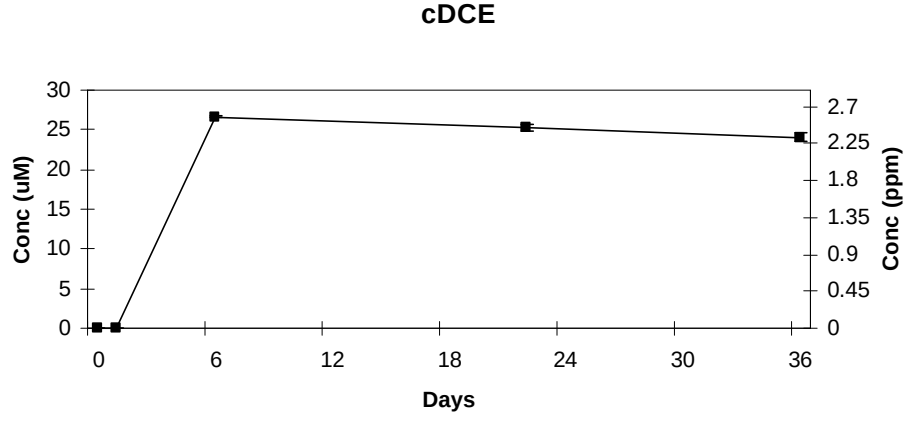
SB3 Surface Sediment (0-4ft) Amended with 3 mM Na-Acetate and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



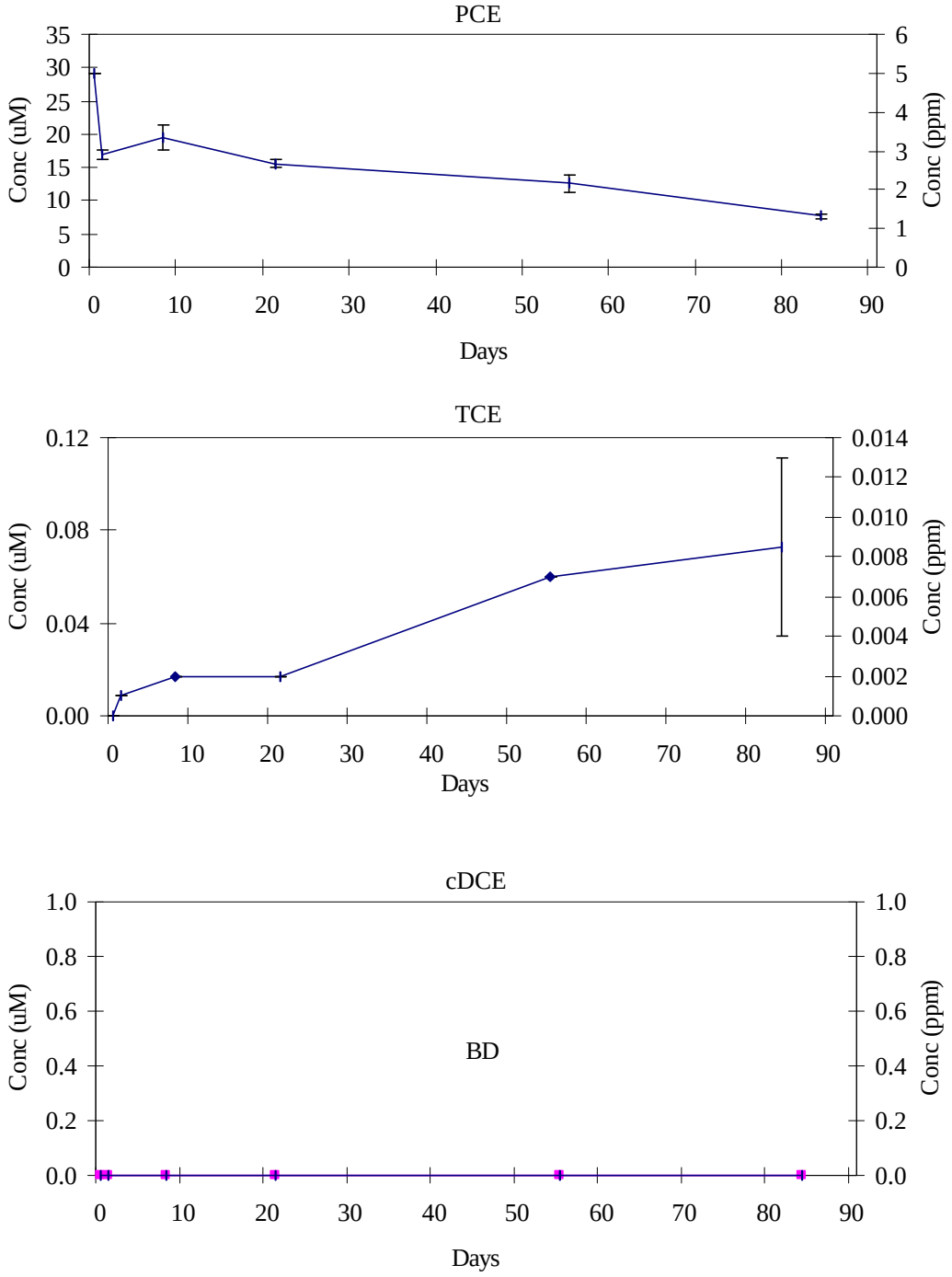
SB3 Surface Sediment (0-4ft) Amended with 3 mM Na-Acetate and 3 % Yeast Extract and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



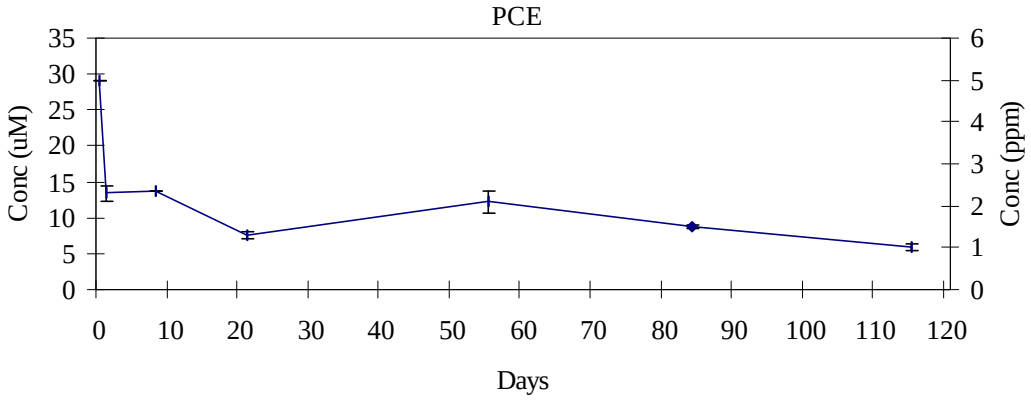


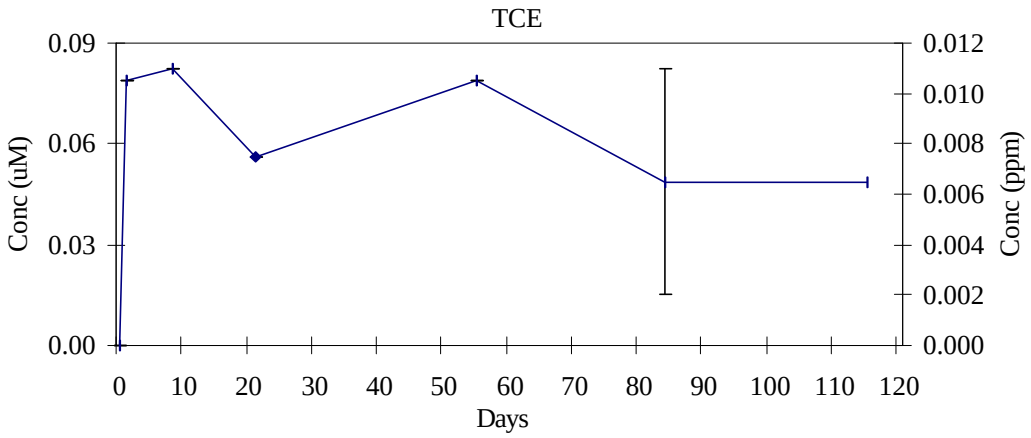


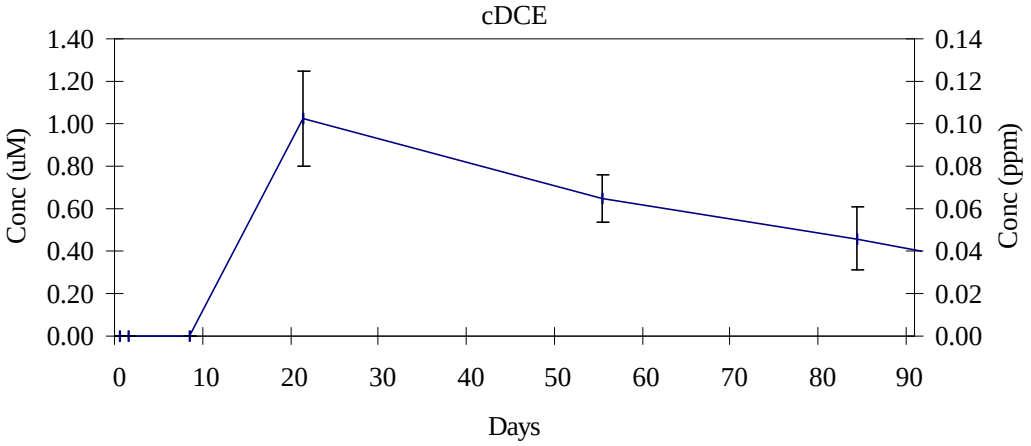
SB3 Surface Sediment (0-4ft) Amended with 3 mM Na-Lactate and 3 % Yeast Extract and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



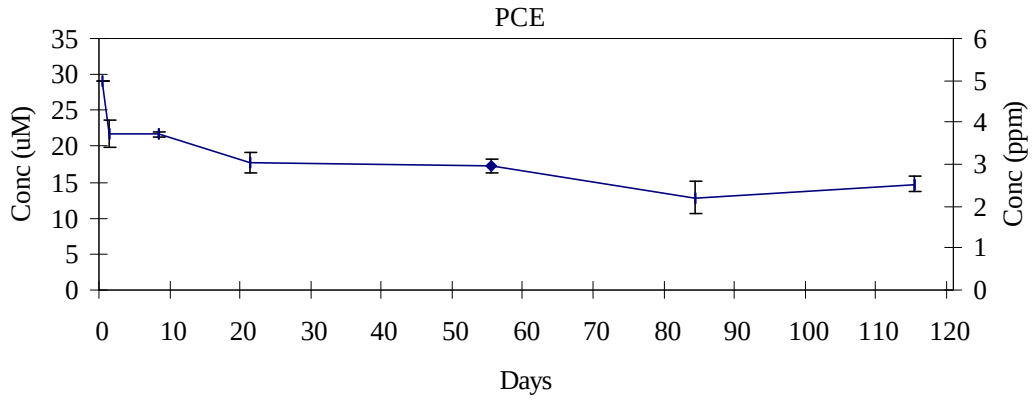
Unamended SB1 Surface Sediment (0-4ft) Dosed With 5 mg/L PCE After a 1 week Acclimation Period

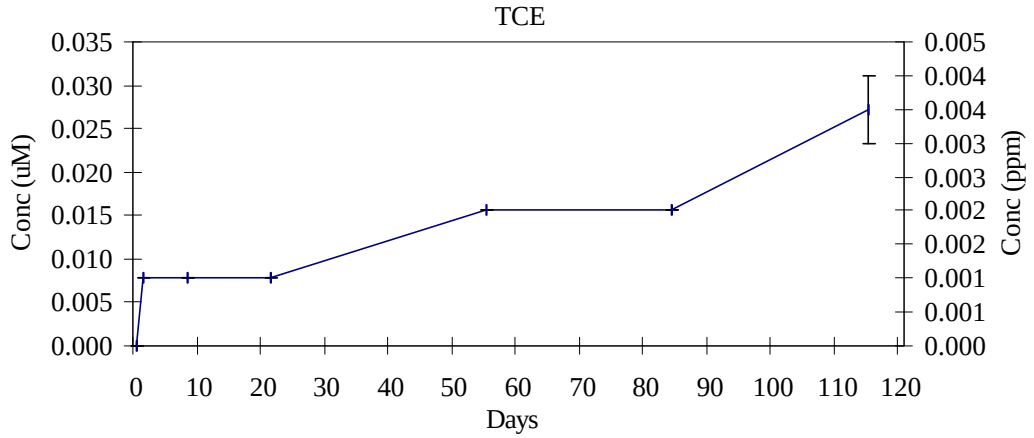


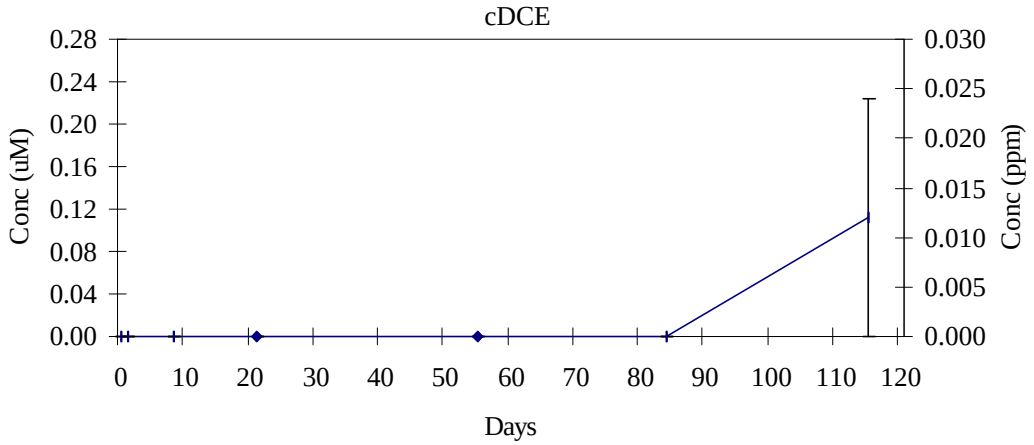




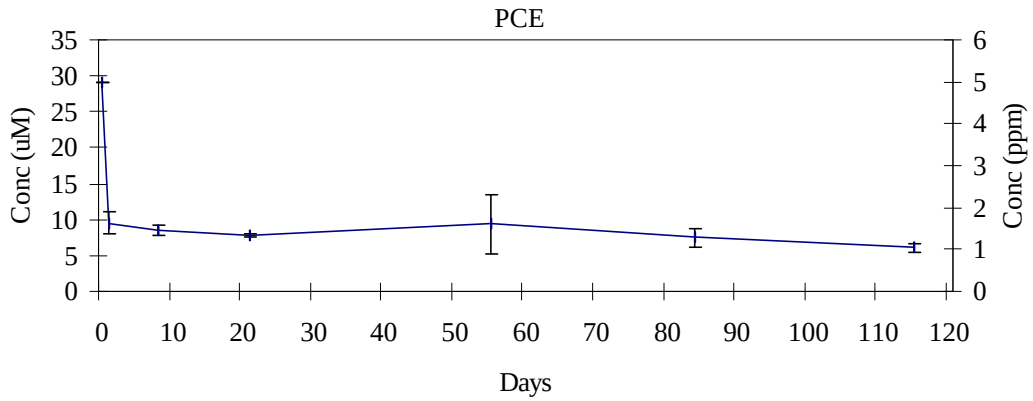
Unamended SB2 Surface Sediment (0-4ft) Dosed with 5 mg/L PCE After a 1 week Acclimation Period

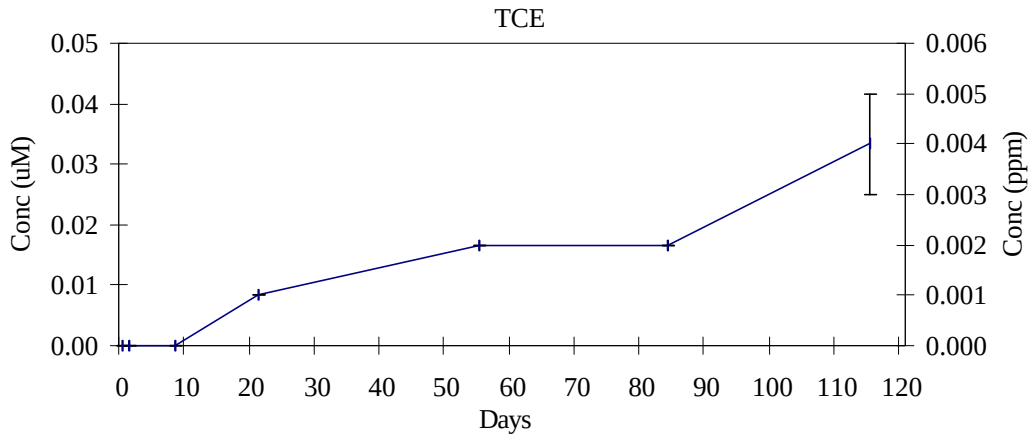


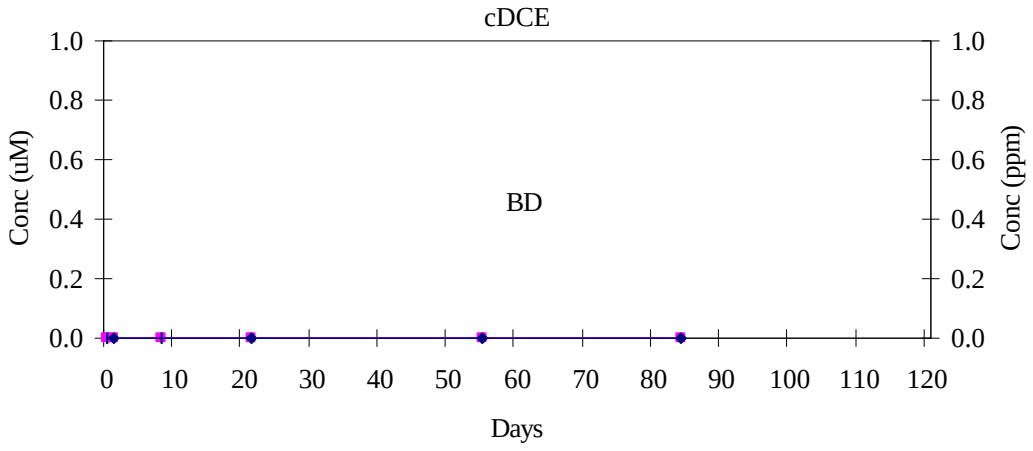




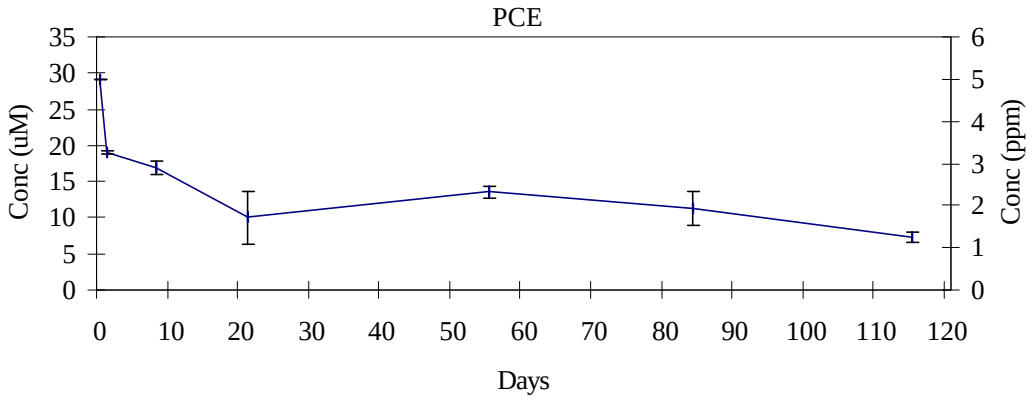
Unamended SB4 Surface Sediment (0-4ft) Dosed With 5mg/L PCE After a 1 week Acclimation Period

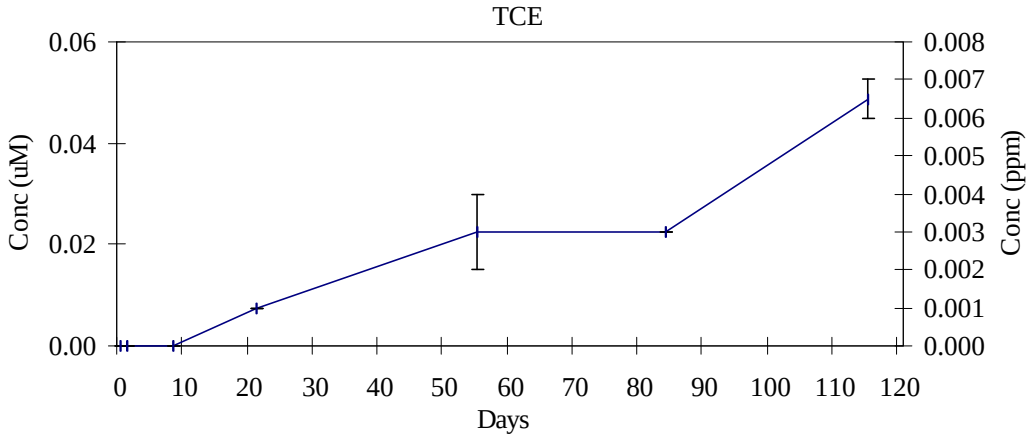


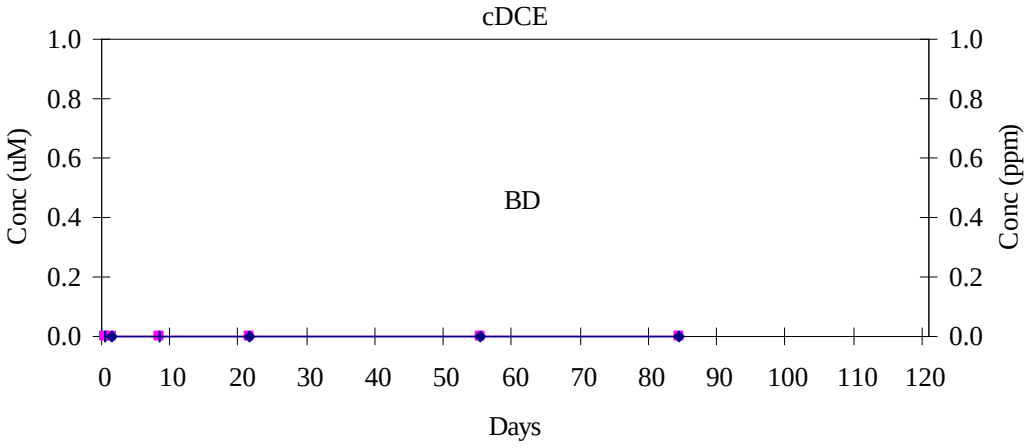




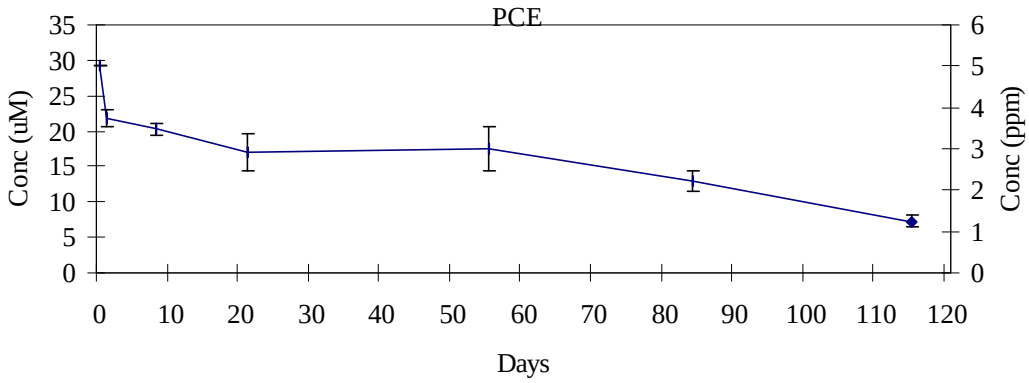
Unamended SB5 Surface Sediment (0-4ft) Dosed With 5 mg/L PCE After a 1 week Acclimation Period

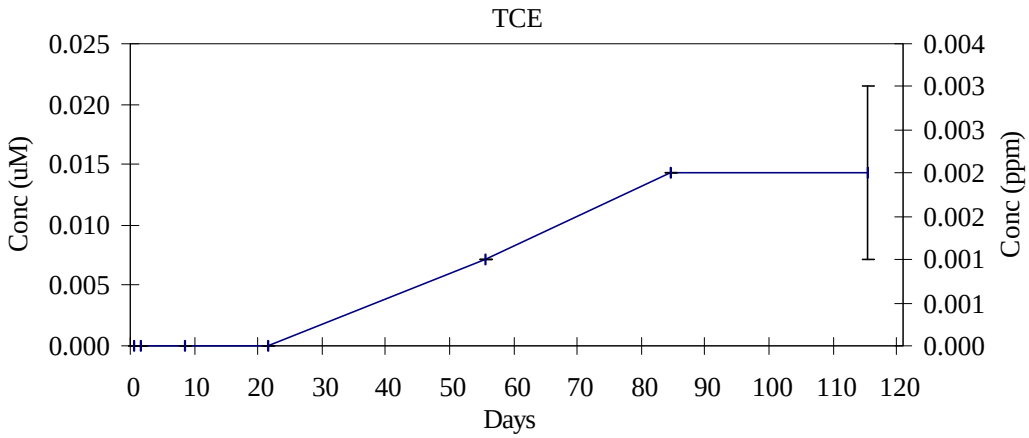


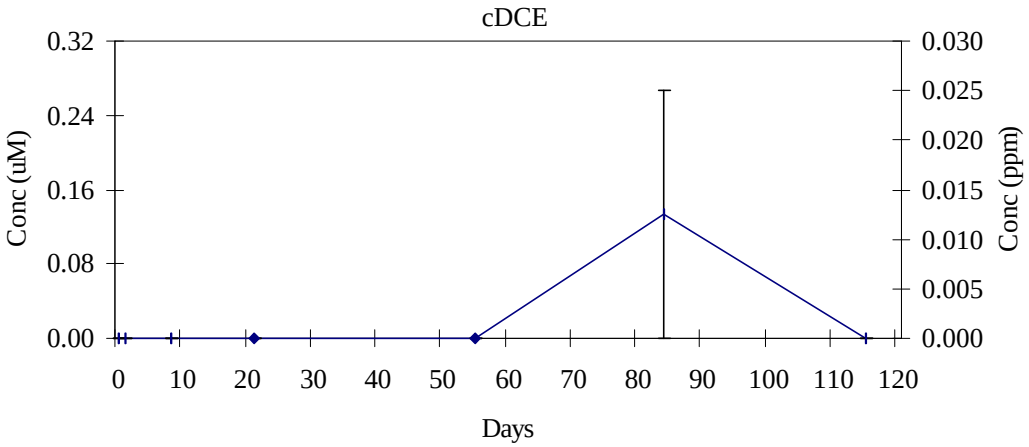




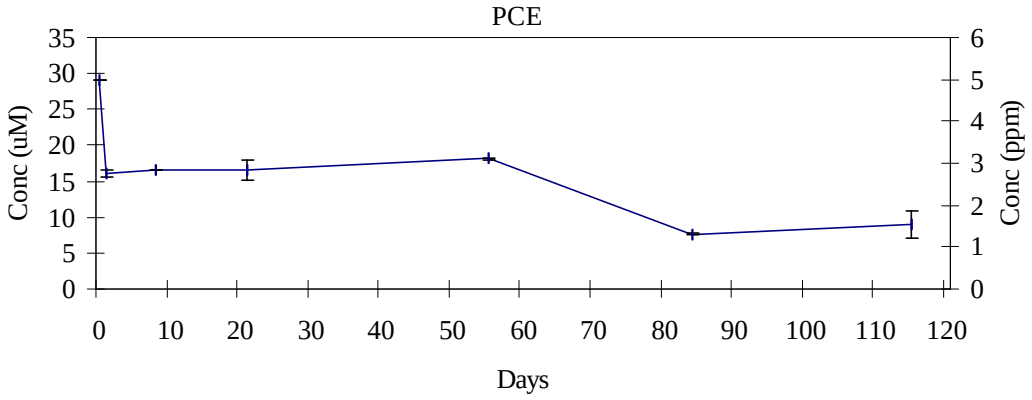
Unamended SB6 Surface Sediment (0-4ft) Dosed With 5 mg/L PCE After a 1 week Acclimation Period

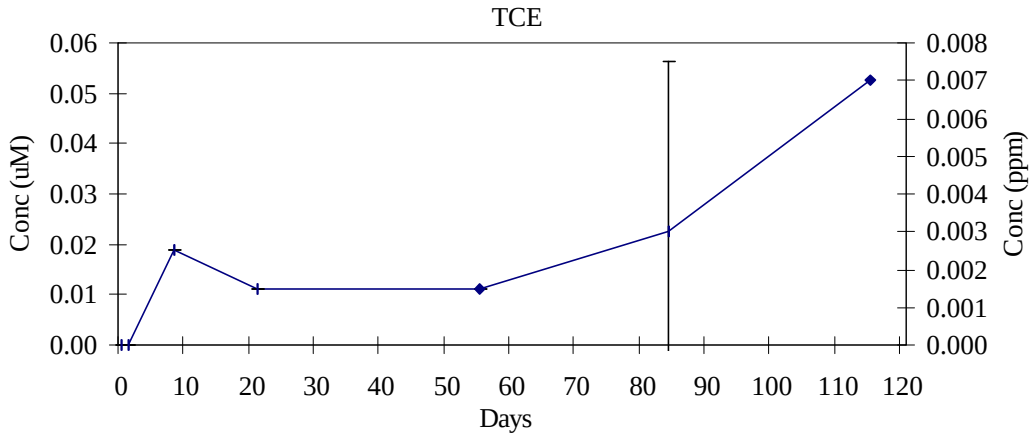


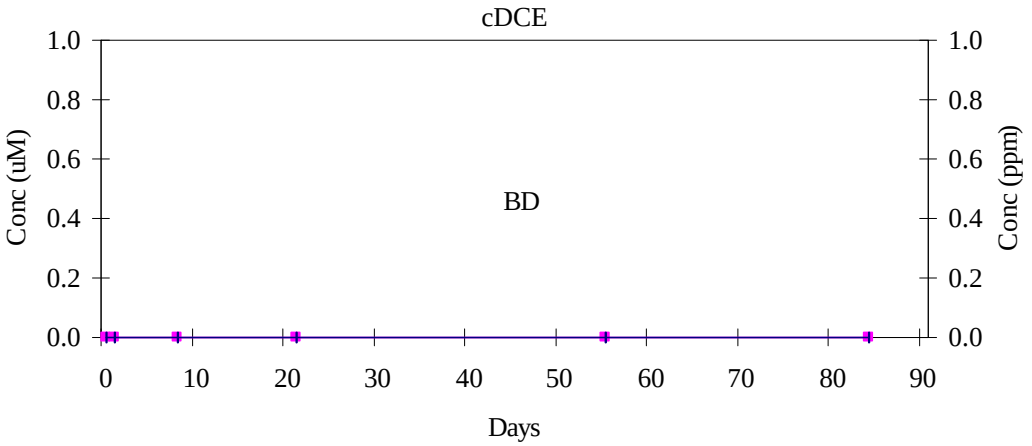




Unamended SB7 Surface Sediment (0-4ft) Dosed With 5mg/L PCE After a 1 week Acclimation Period



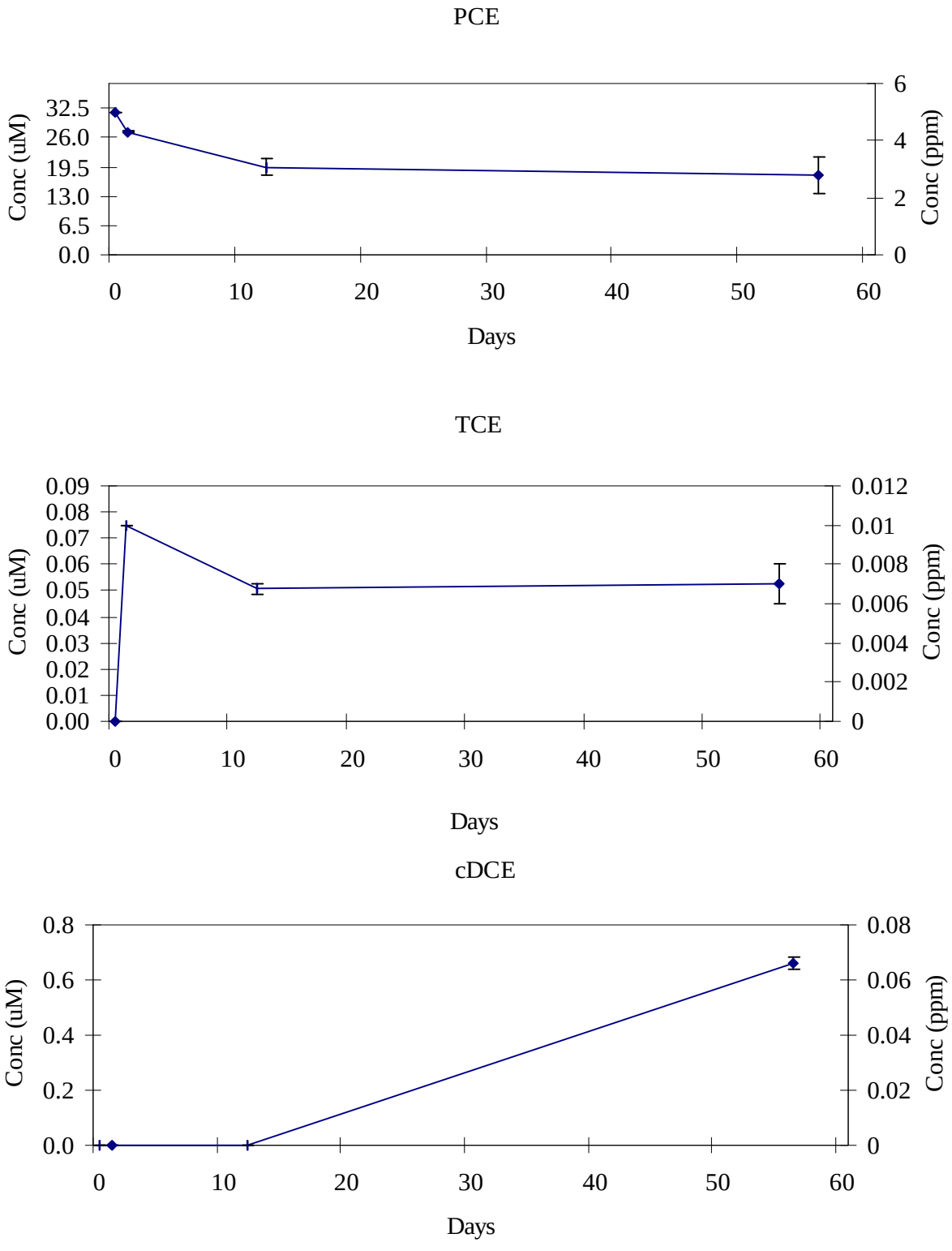




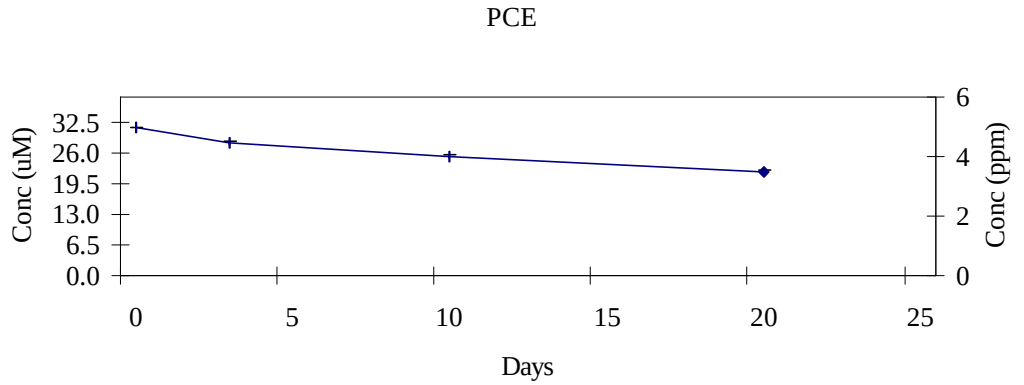
Unamended SB8 Surface Sediment (0-4ft) Dosed With 5 mg/L PCE After a 1 week Acclimation Period

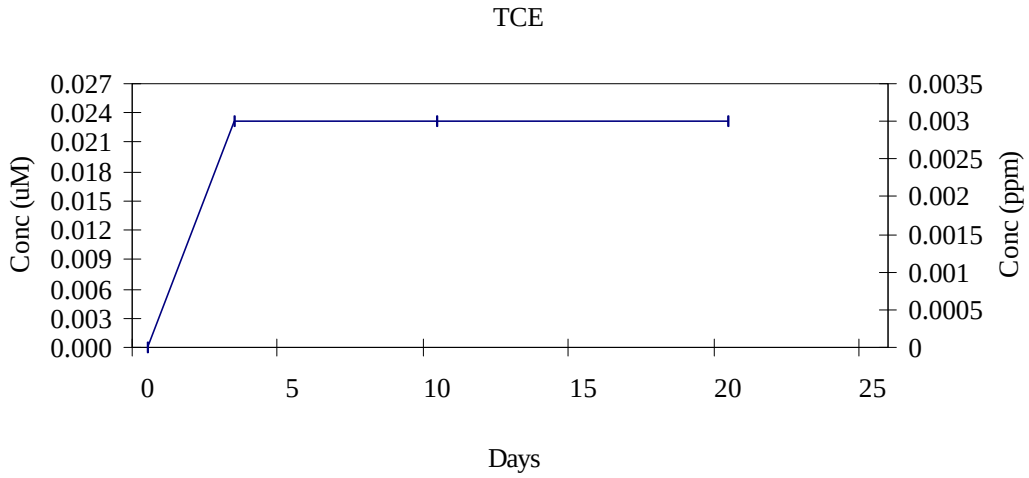
APPENDIX C

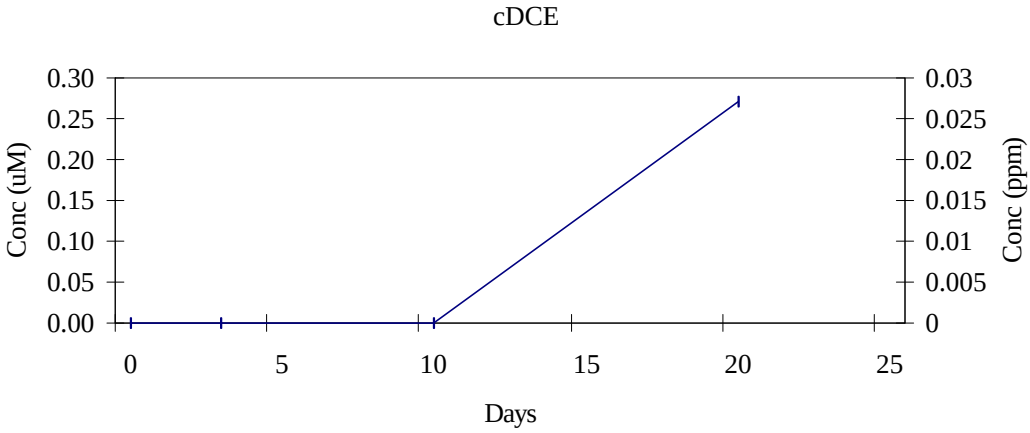
INDIVIDUAL RESULTS OF DEEP SEDIMENT (25-40 FT) MICROCOSM STUDIES



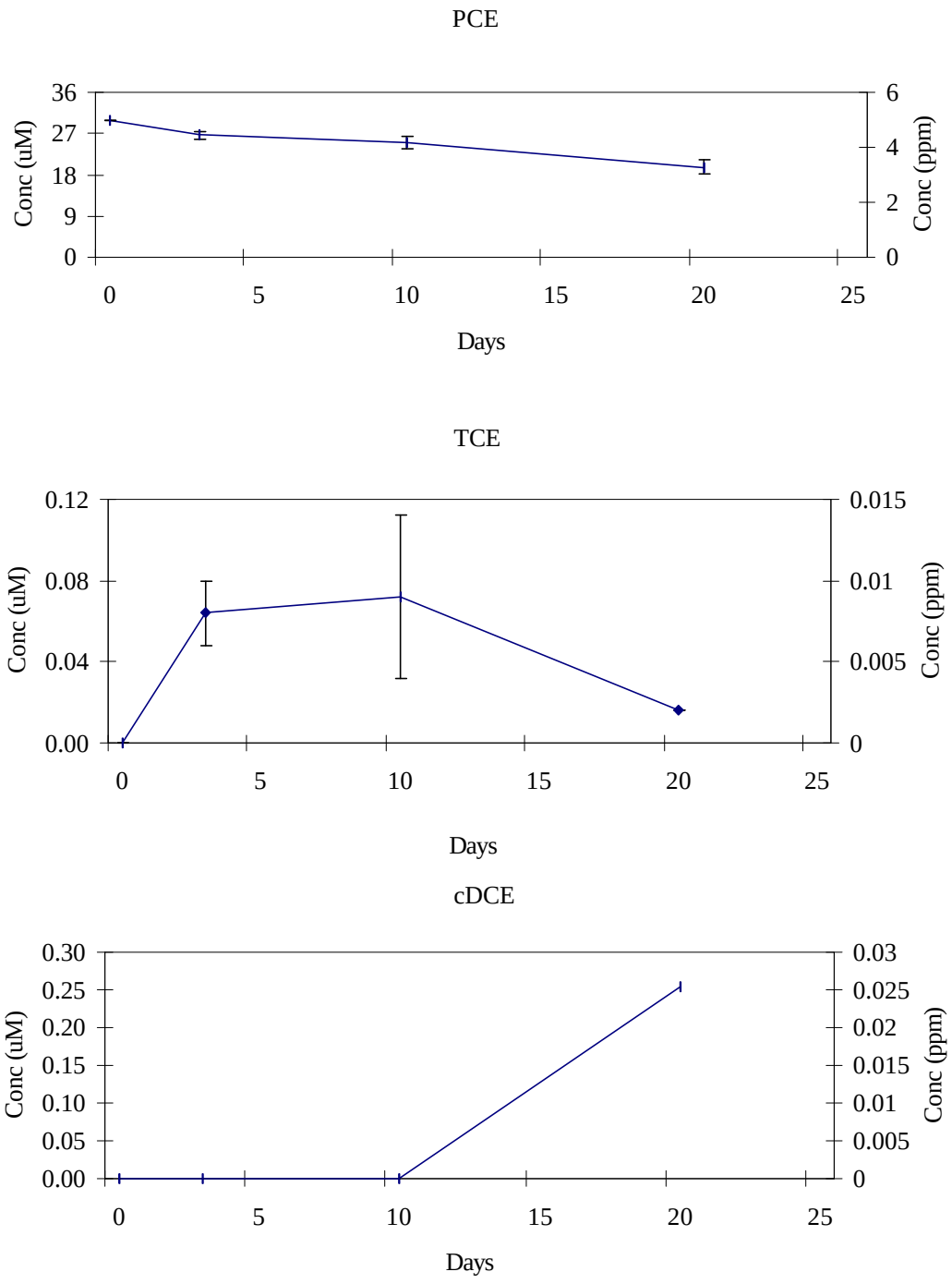
Unamended SB2 Deep Sediment (25-40 ft) Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



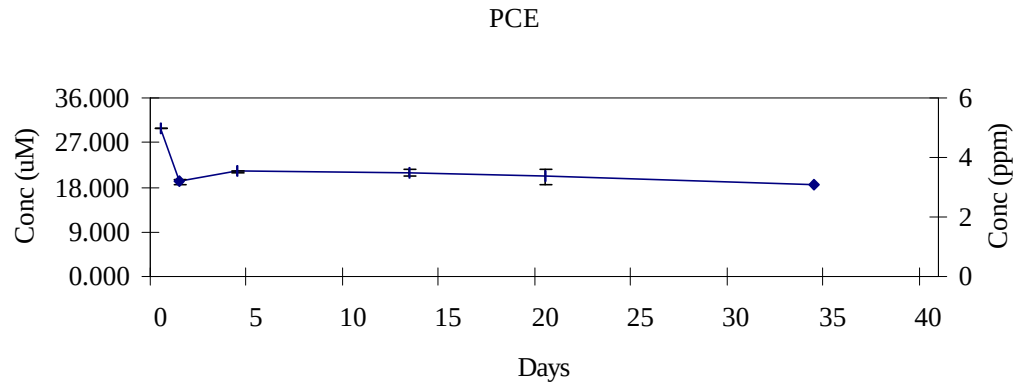


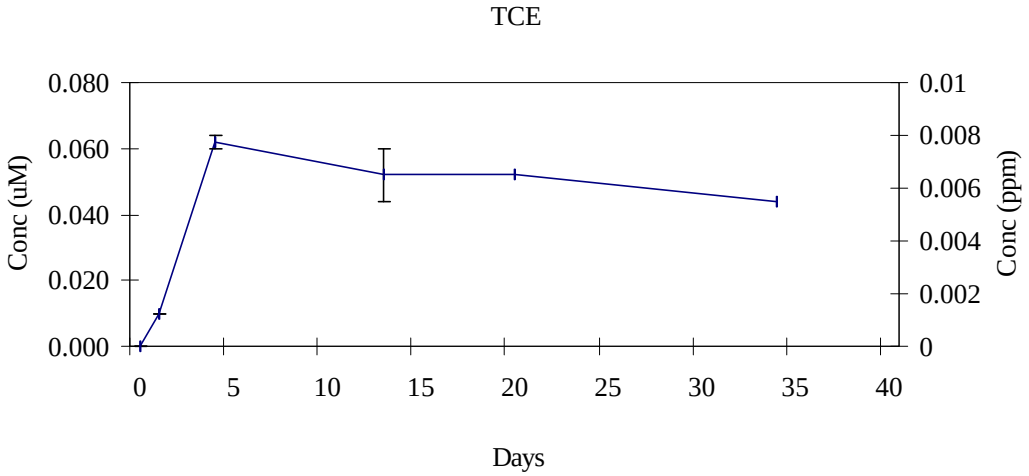


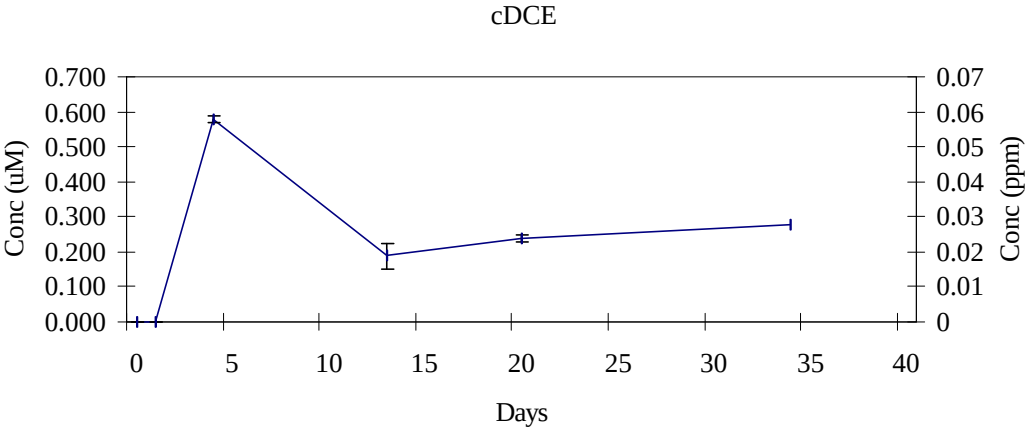
SB2 Deep Sediment (25-40 ft) Amended With 3 mM Na-Acetate and Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



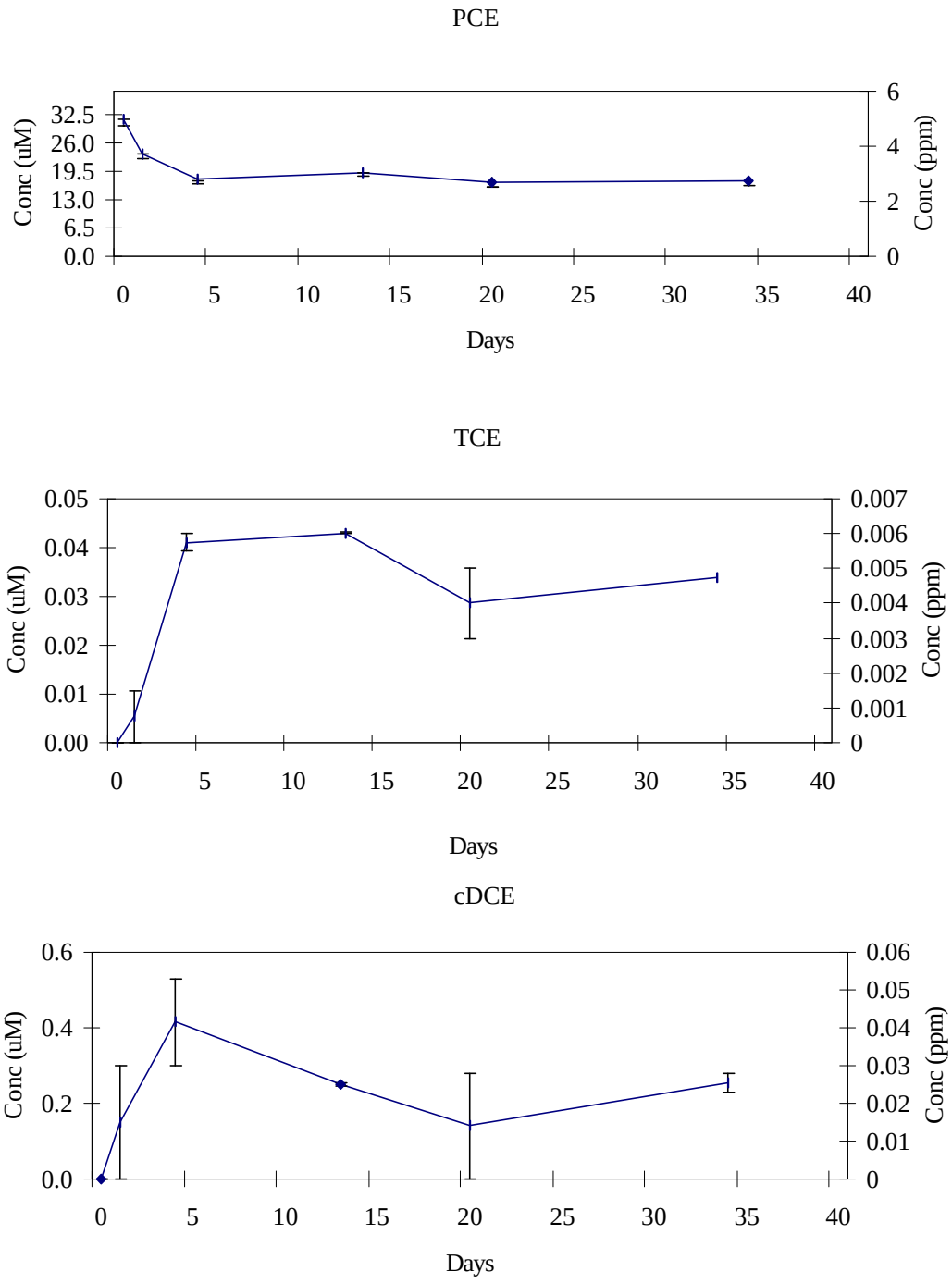
SB2 Deep Sediment (25-40 ft) Amended With 3 mM Na-Acetate and 3 % Yeast Extract Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



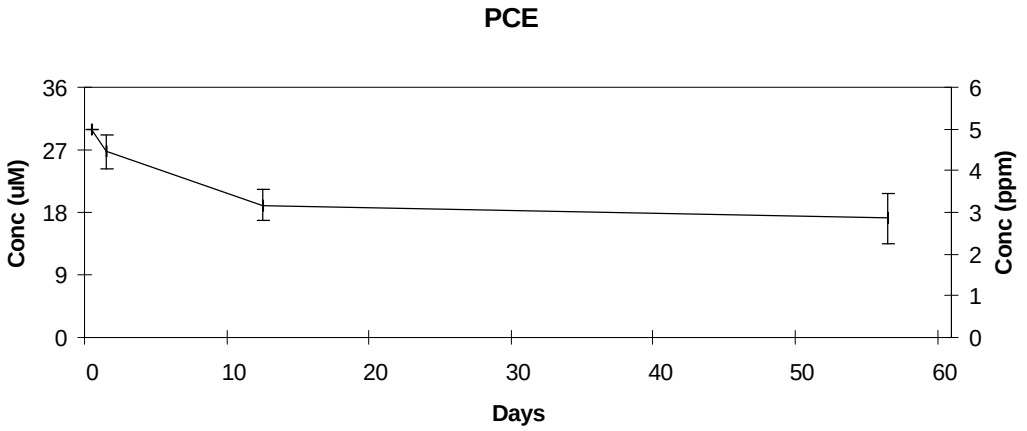


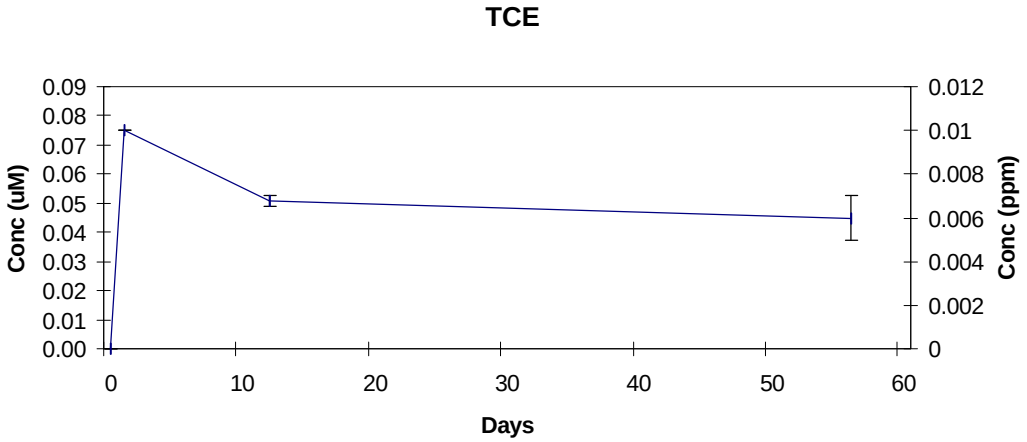


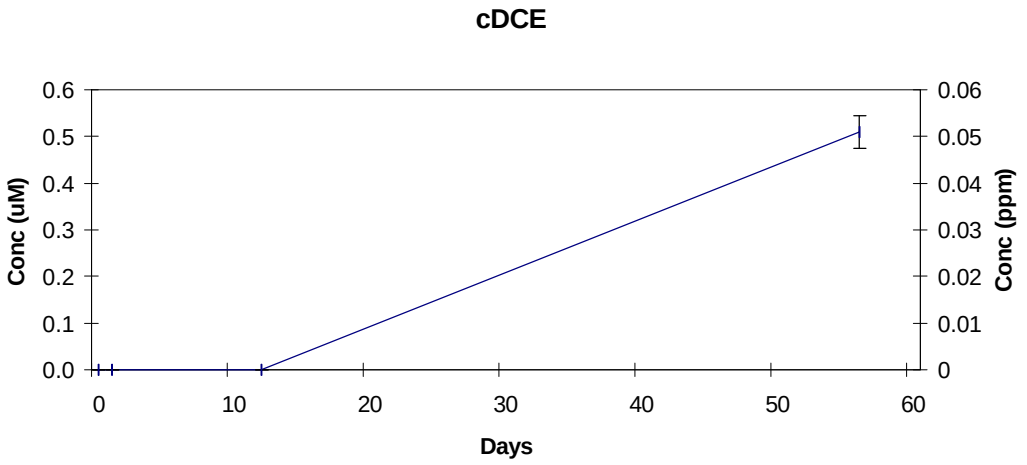
SB2 Deep Sediment (25-40 ft) Amended With 15 % HRC Compound
Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



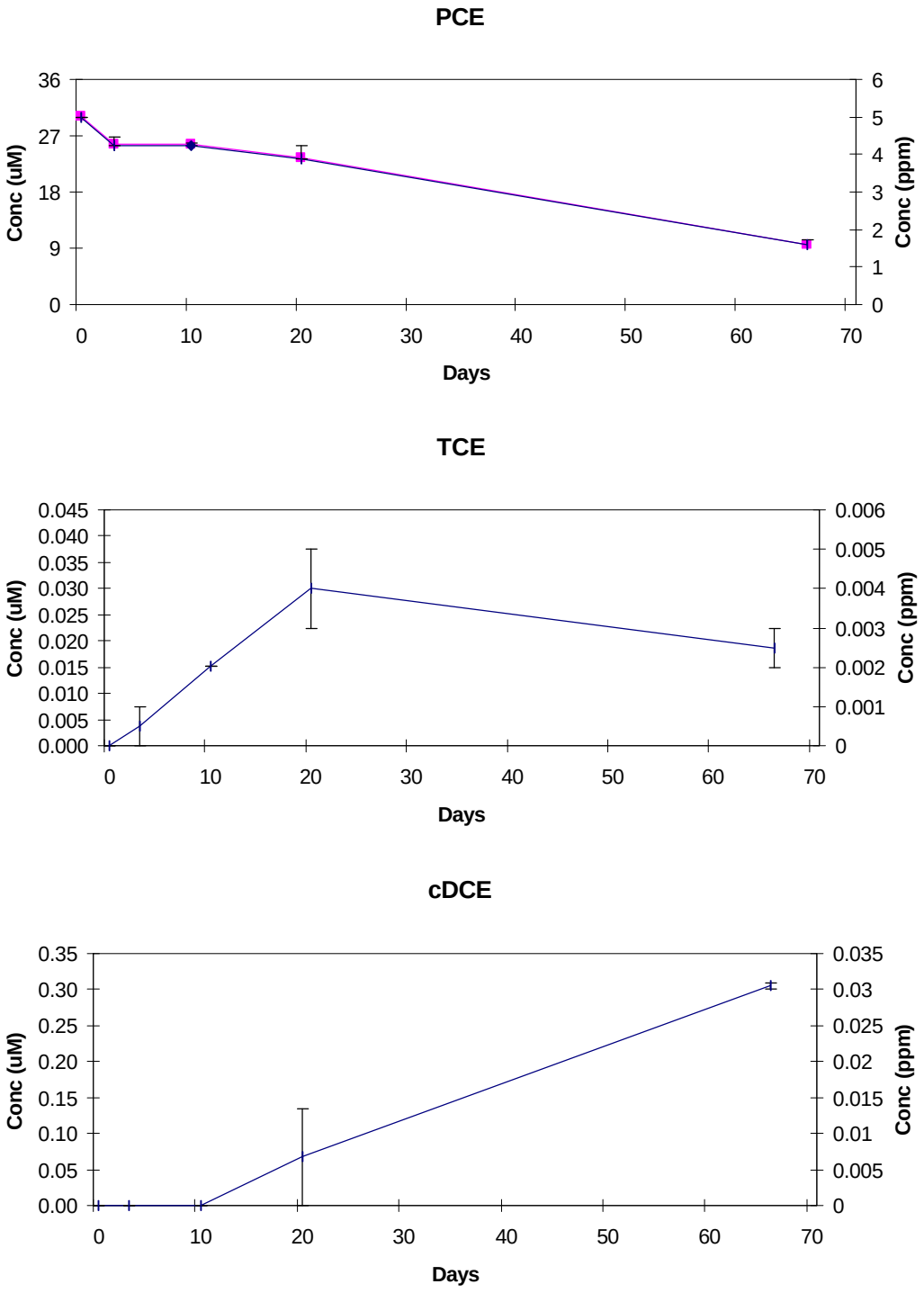
SB2 Deep Sediment (25-40 ft) Amended With 15 % Molasses
Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



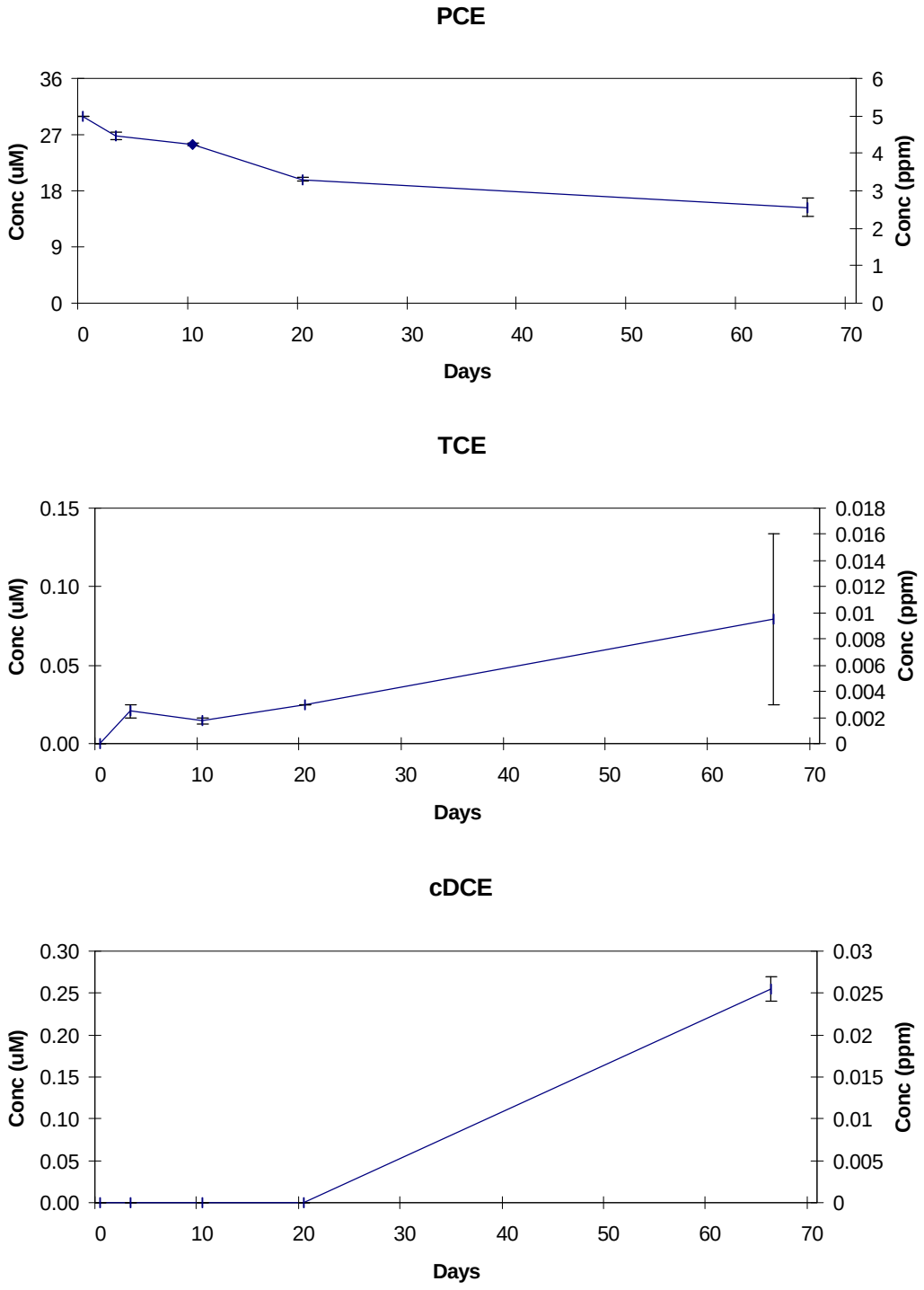




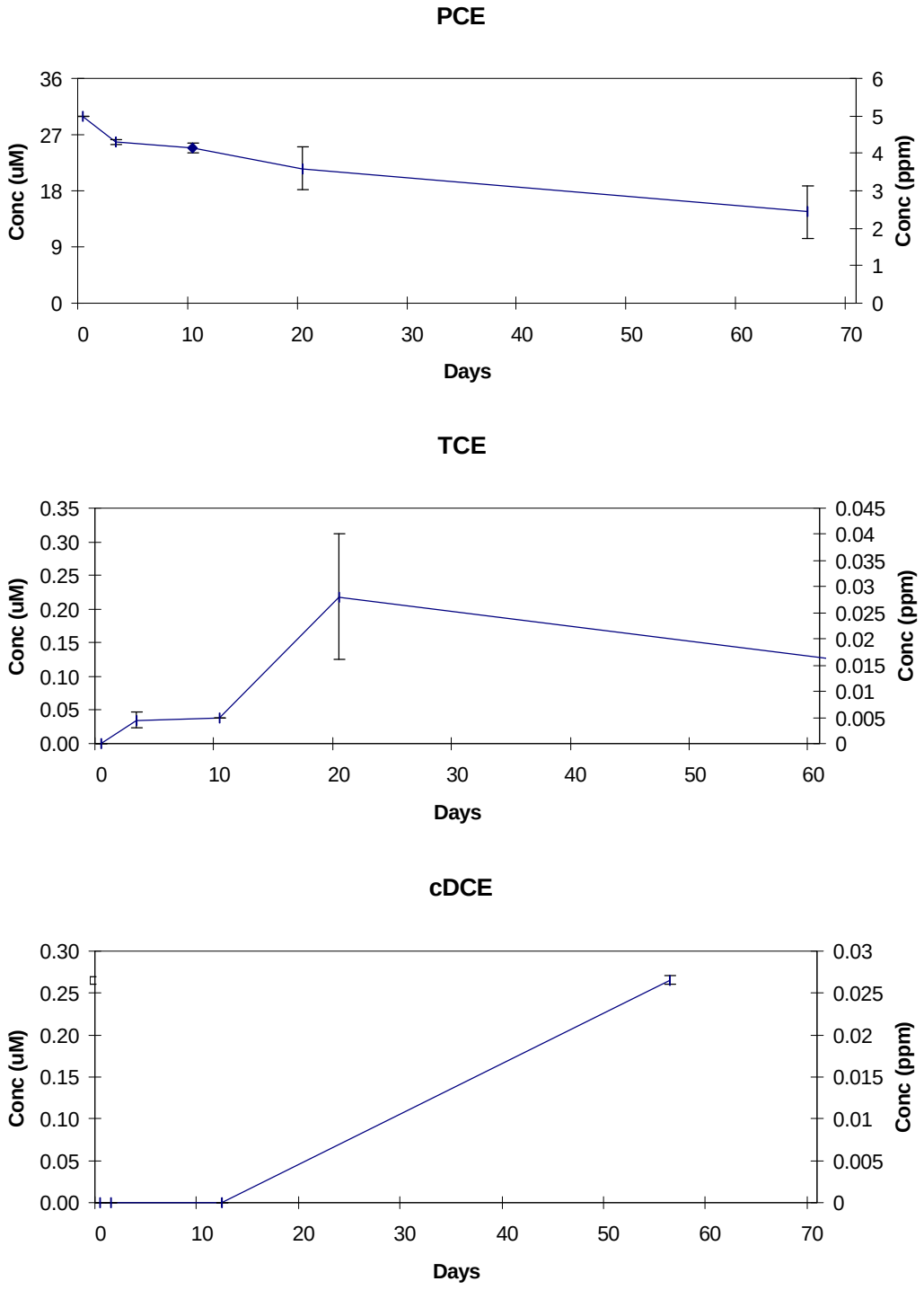
Unamended SB3 Deep Sediment (25-40 ft) Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



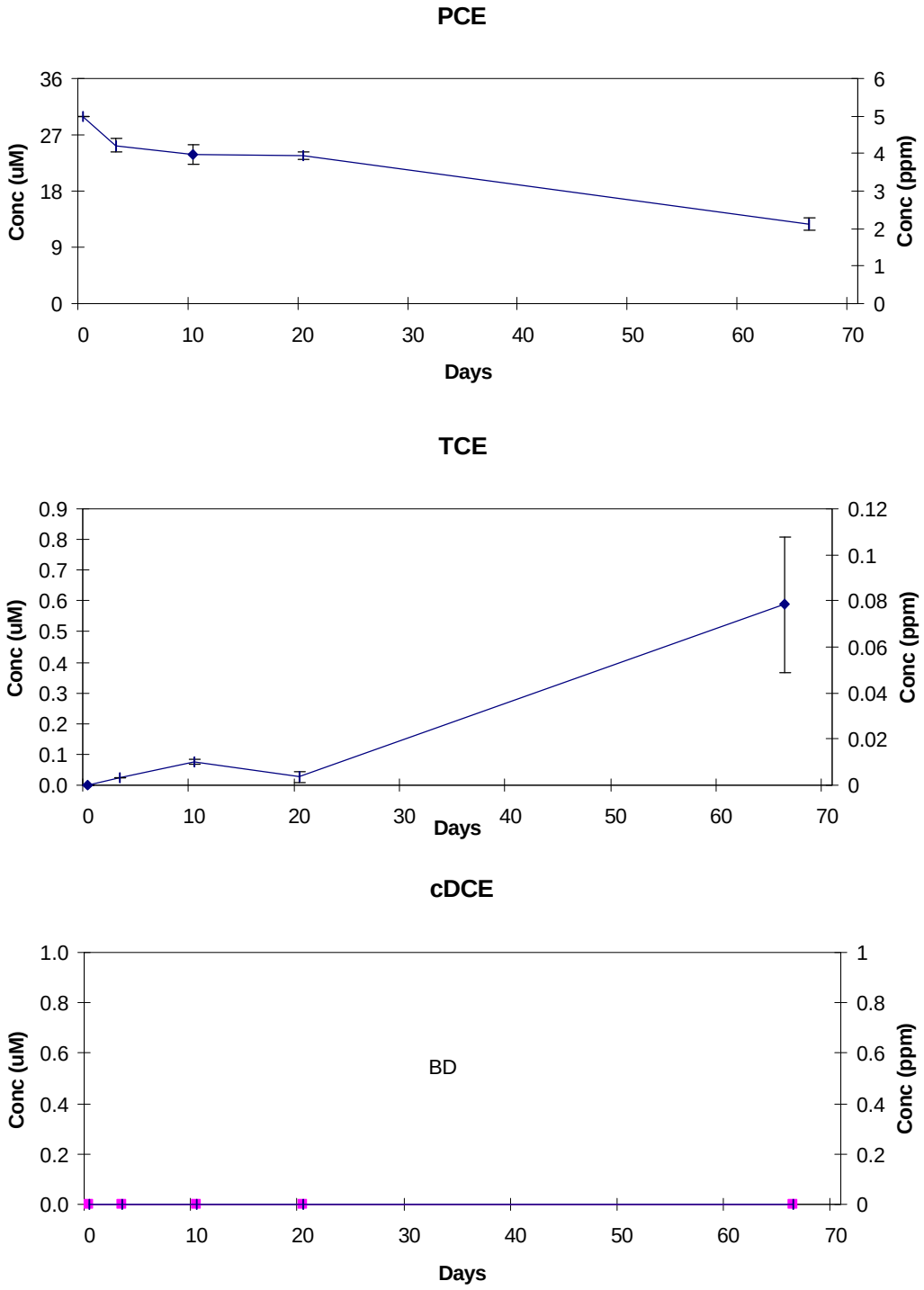
SB3 Deep Sediment (25-40 ft) Amended With 3 mM Na-Lactate and Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



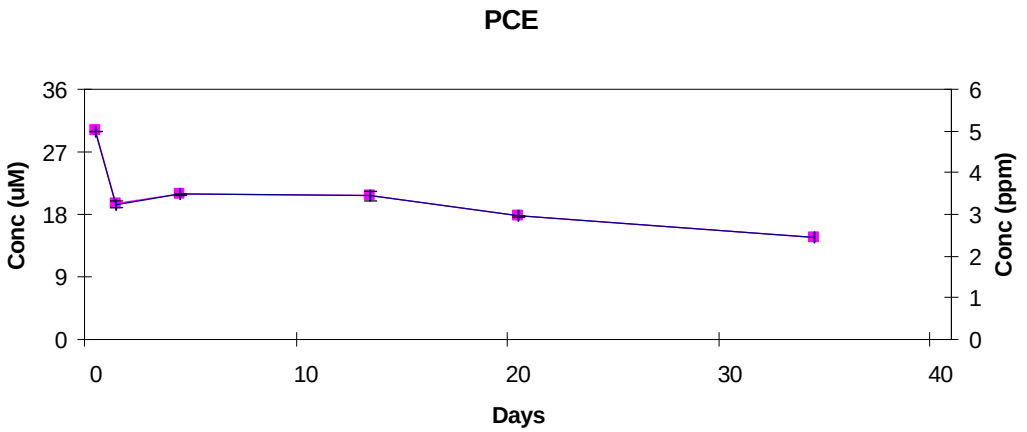
SB3 Deep Sediment (25-40 ft) Amended With 3 mM Na-Acetate and Dosed With 5 mg/L PCE After a 1 Week Acclimation Period

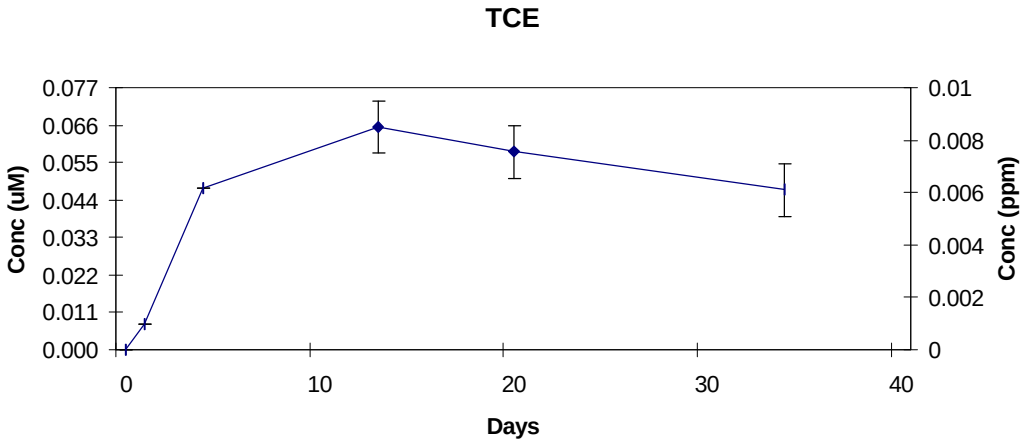


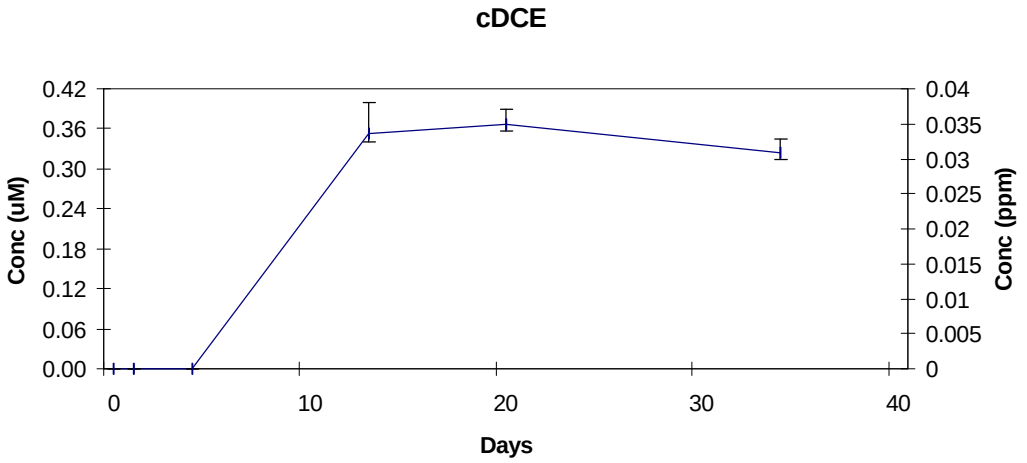
SB3 Deep Sediment (25-40 ft) Amended With 3 mM Na-Lactate and 3 % Yeast Extract Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



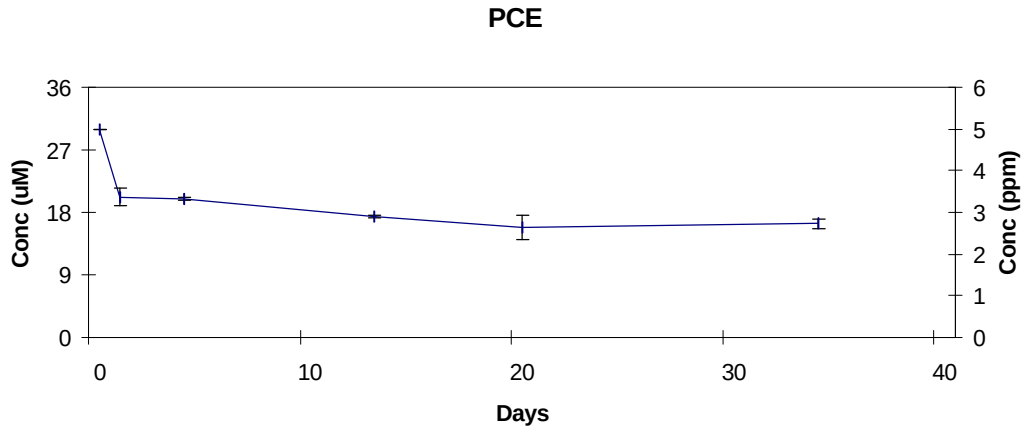
SB3 Deep Sediment (25-40 ft) Amended With 3 mM Na-Acetate and 3 % Yeast Extract Dosed With 5 mg/L PCE After a 1 Week Acclimation Period

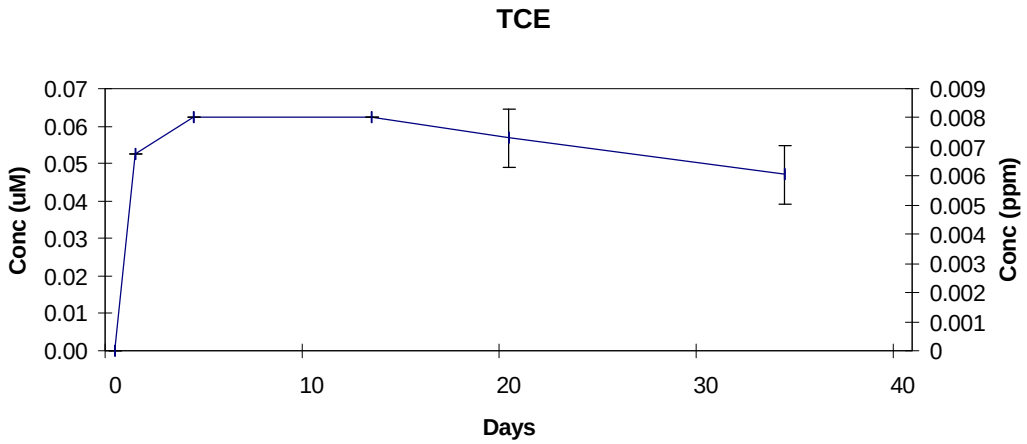


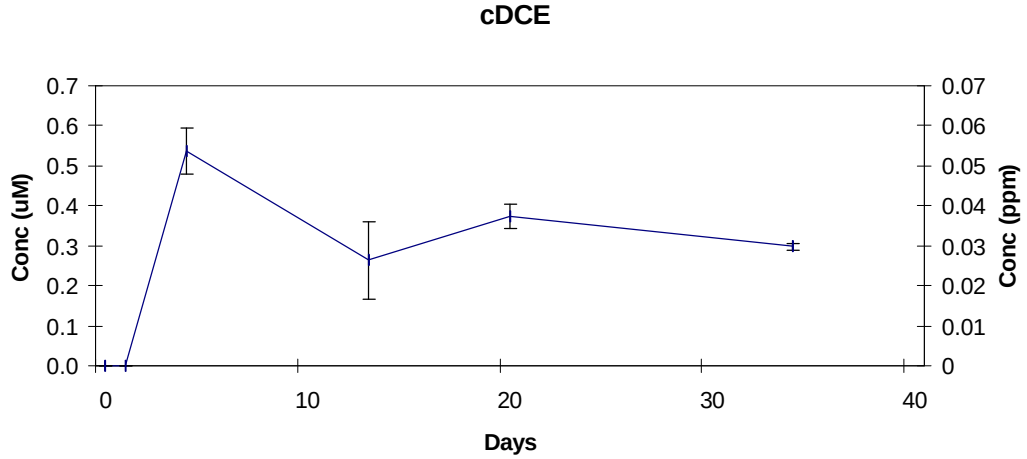




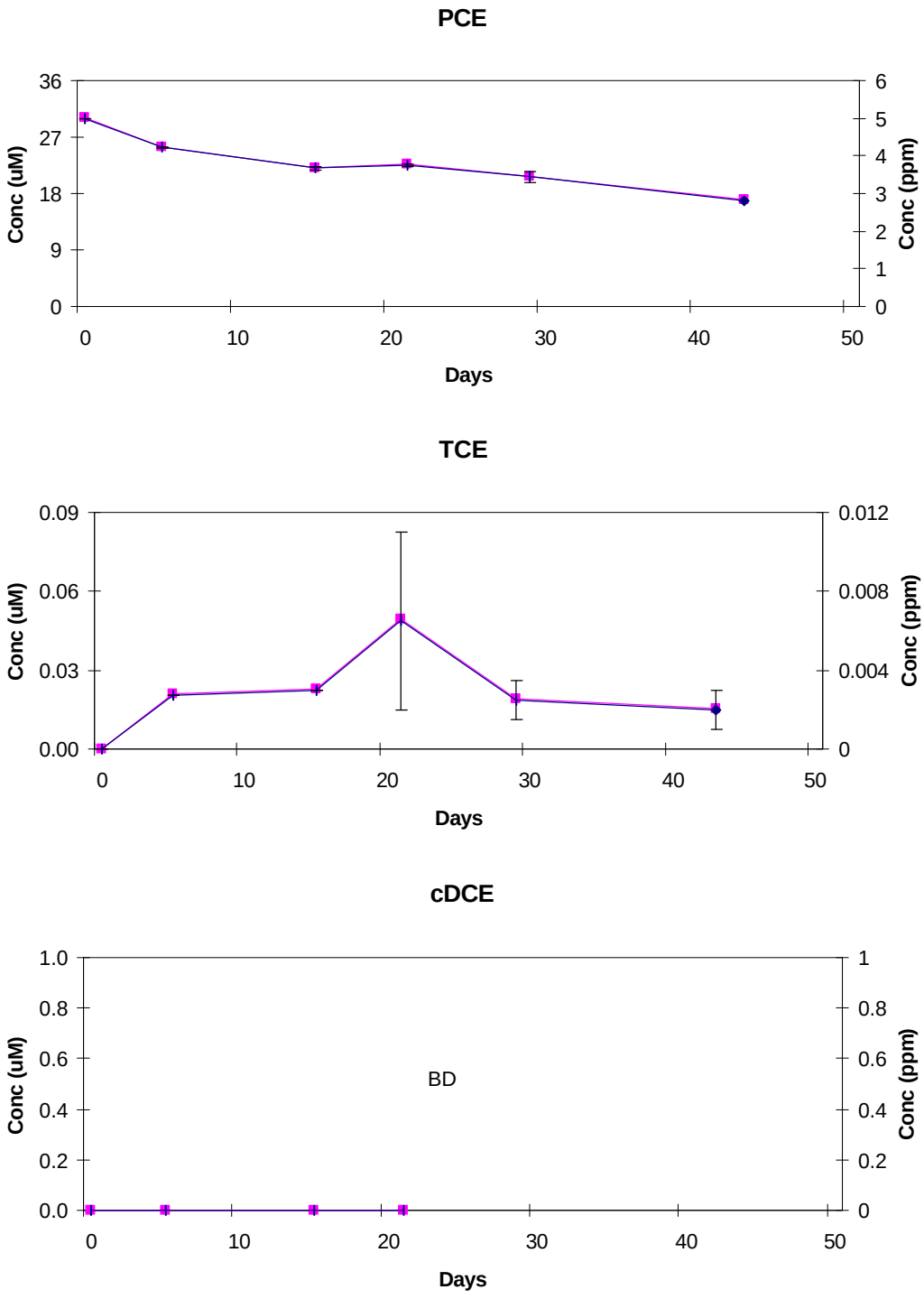
SB3 Deep Sediment (25-40 ft) Amended With 15 % HRC Compound
Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



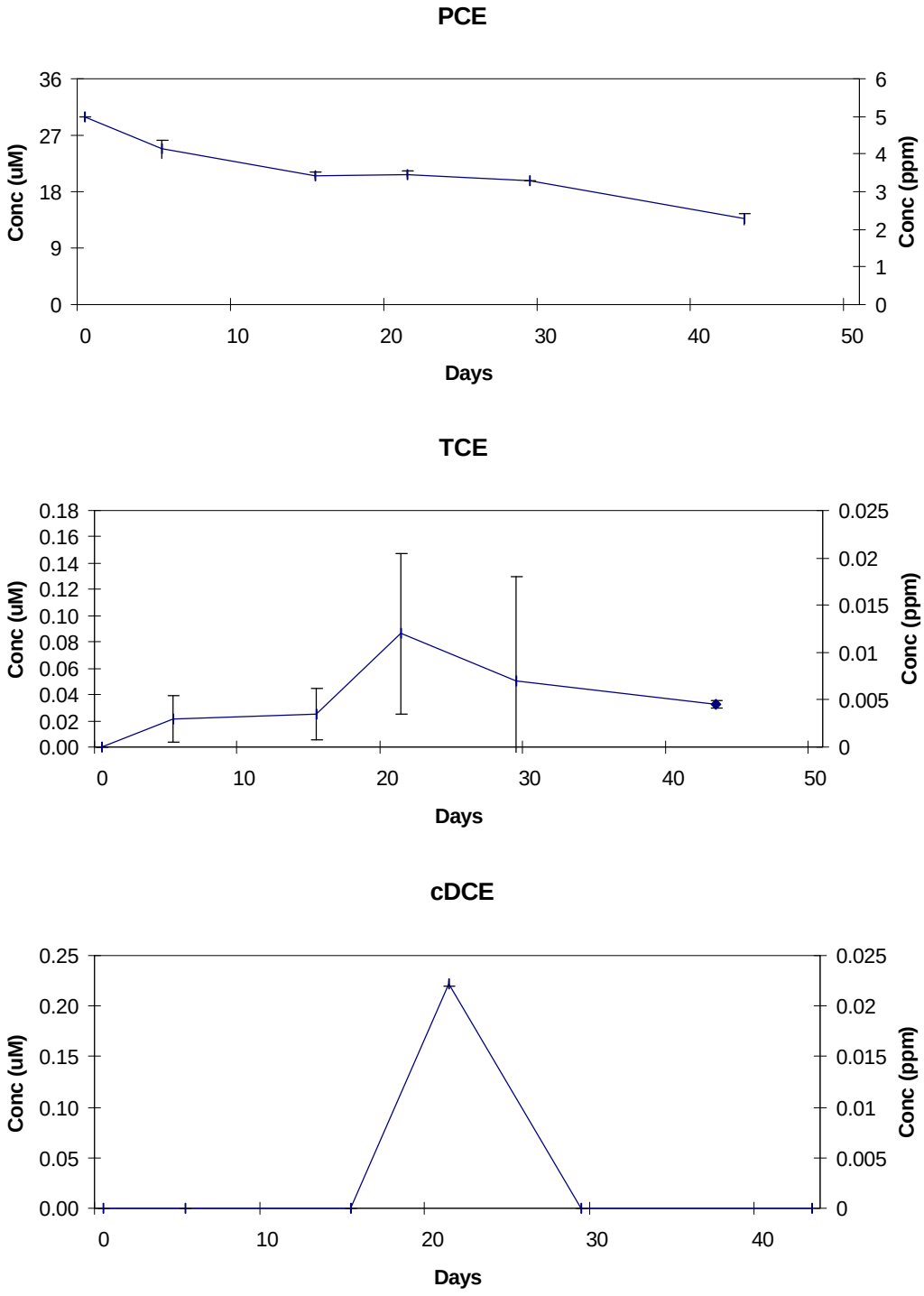




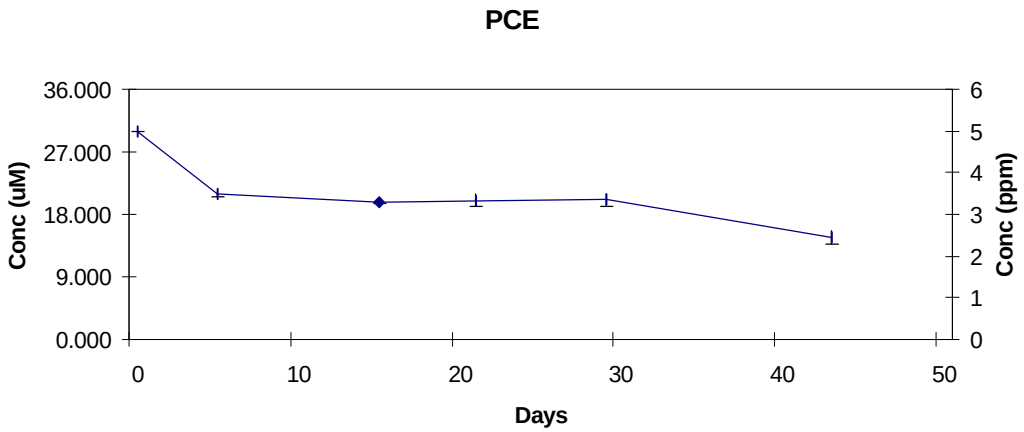
SB3 Deep Sediment (25-40 ft) Amended With 15 % Molasses
Dosed With 5 mg/L PCE After a 1 Week Acclimation Period

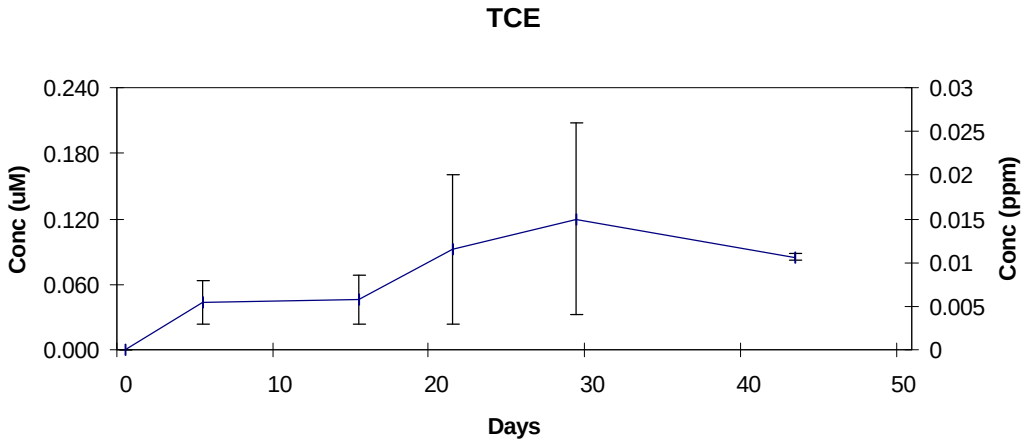


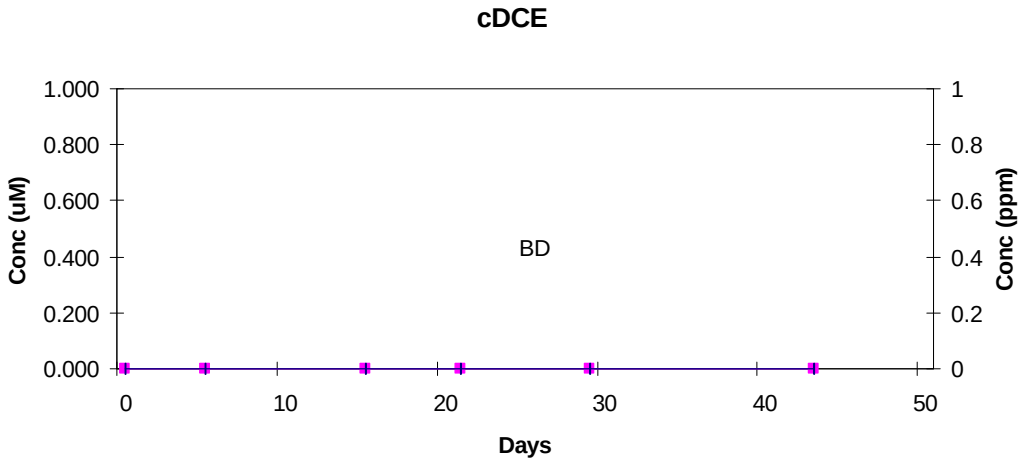
SB3 Deep Sediment (25-40 ft) Amended With 10 mM Na-Acetate and Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



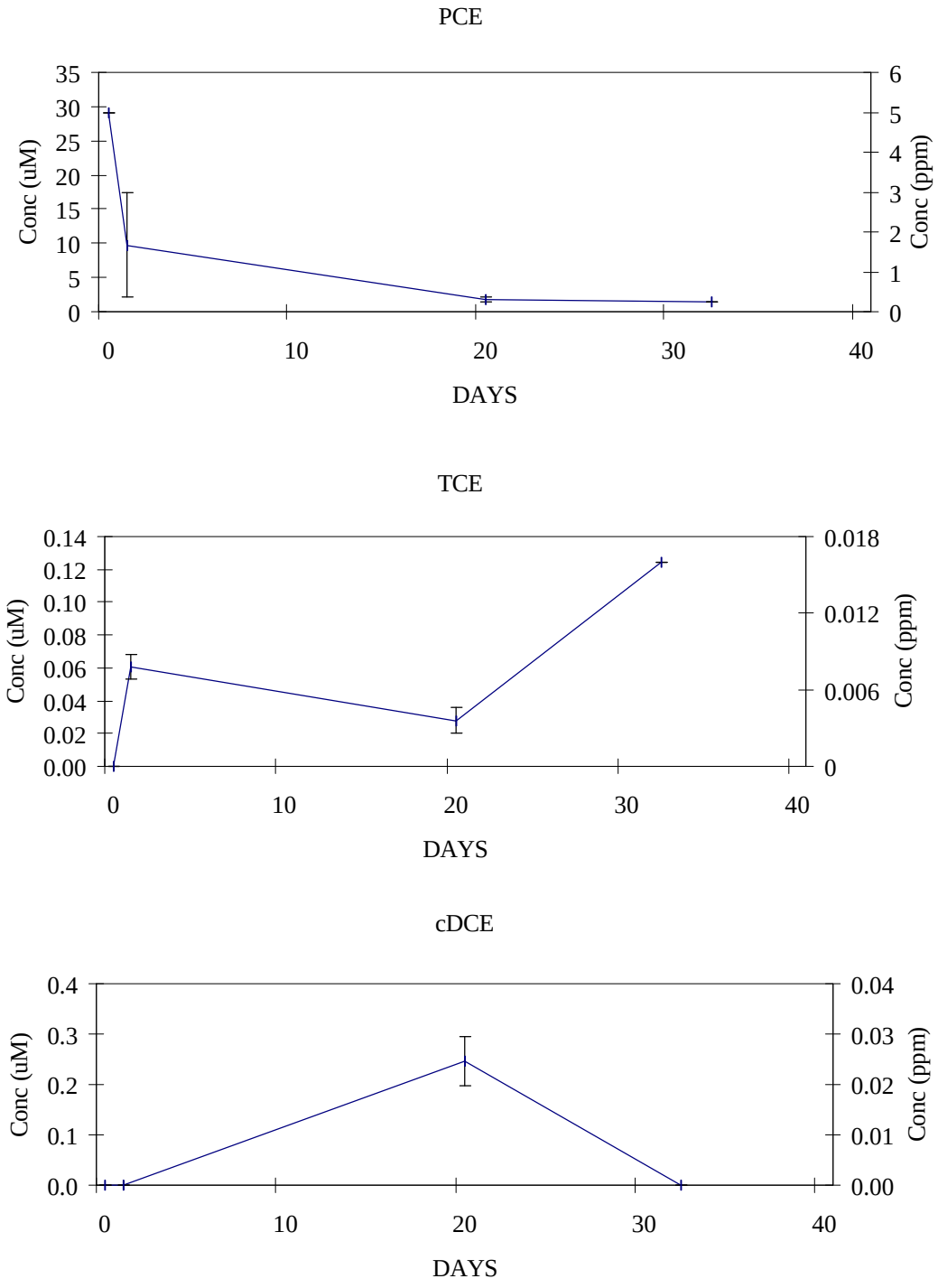
SB3 Deep Sediment (25-40 ft) Amended With 10 mM Na-Acetate and 10 % Yeast Extract Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



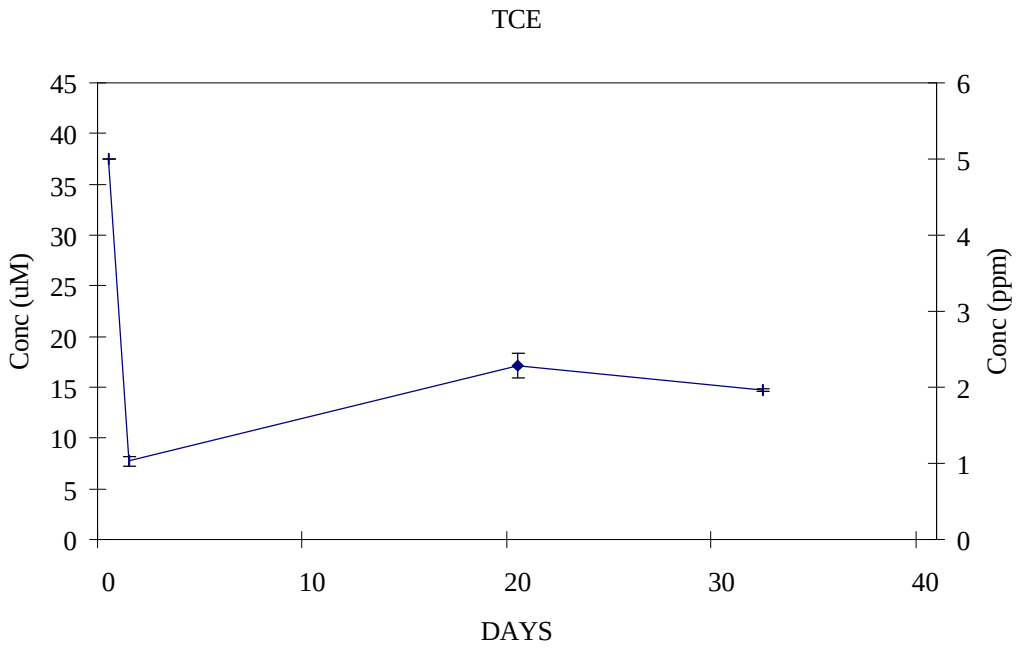


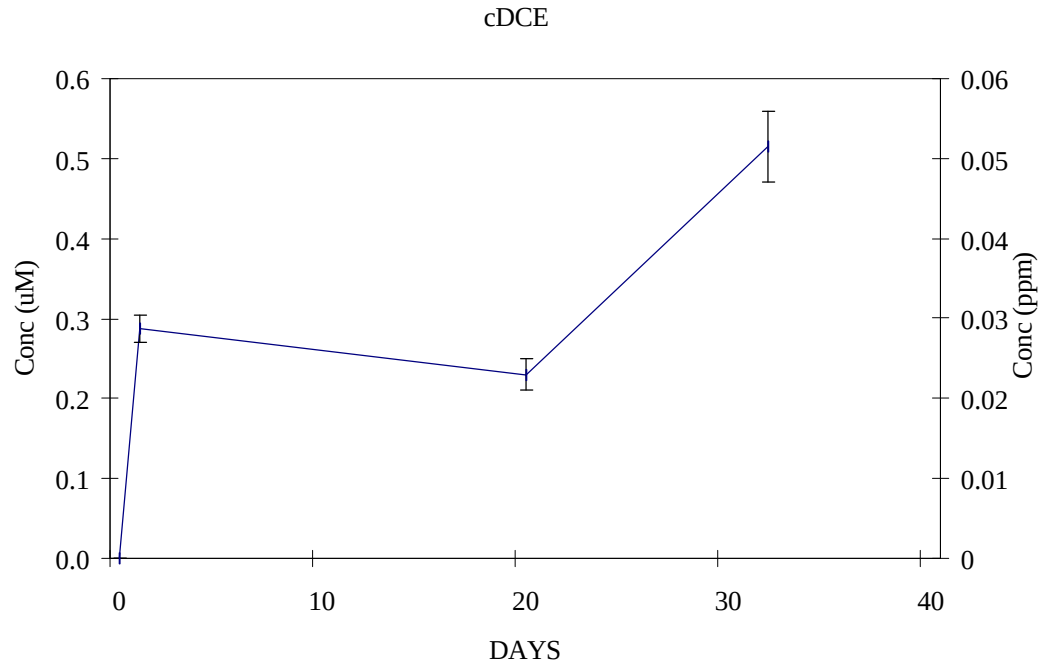


SB3 Deep Sediment (25-40 ft) Amended With 10 mM Na-Lactate and 10% Yeast Extract Dosed With 5 mg/L PCE After a 1 Week Acclimation Period



SB3 Deep Sediment (25-40 ft) Amended With 10 % Corn Oil
Dosed With 5 mg/L PCE After a 1 Week Acclimation Period

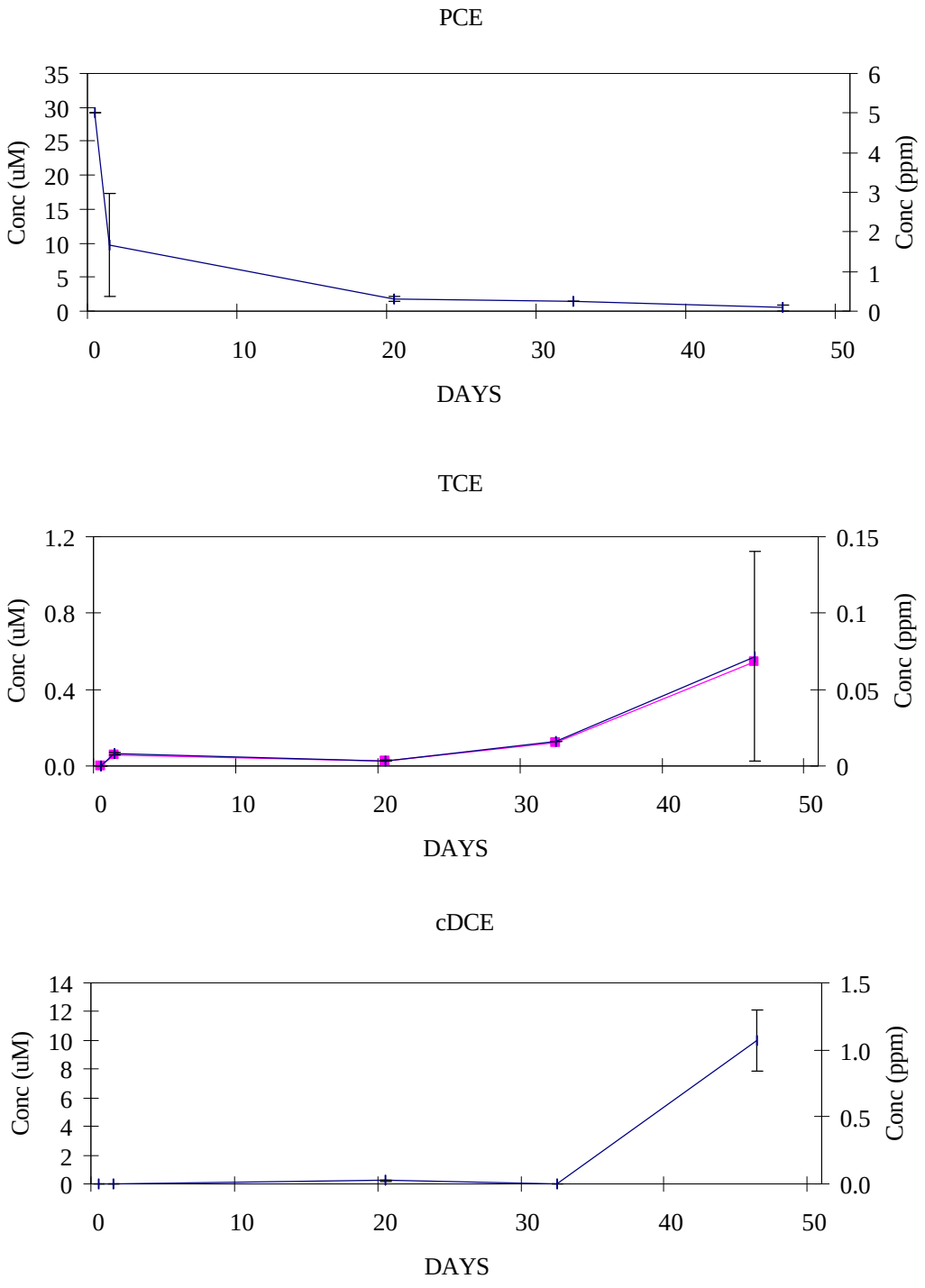




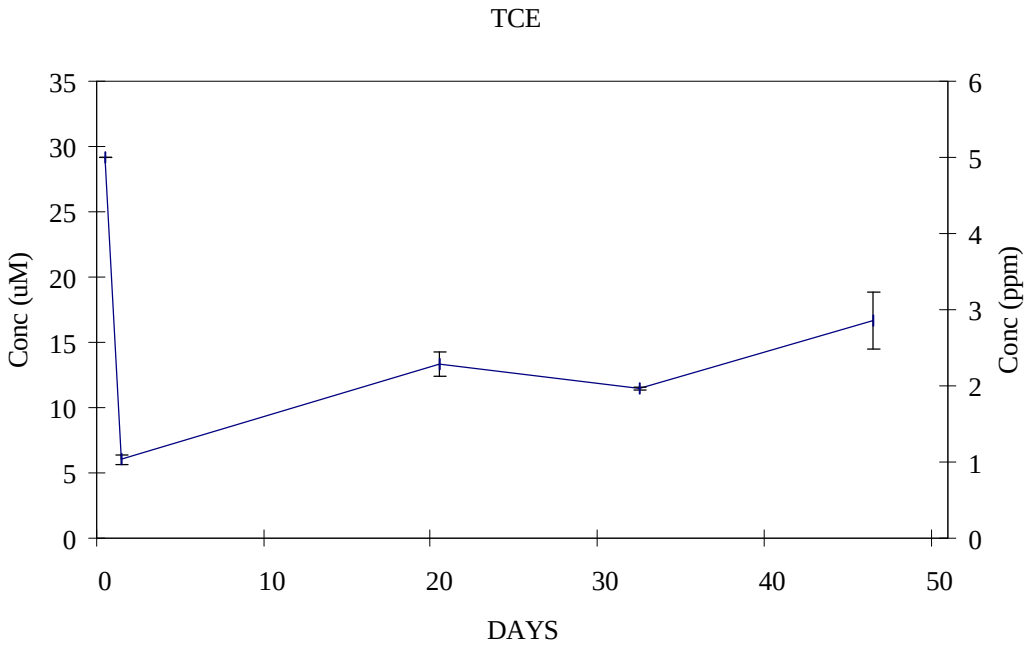
SB3 Deep Sediment (25-40 ft) Amended With 10 % Corn Oil
Dosed With 5 mg/L TCE After a 1 Week Acclimation Period

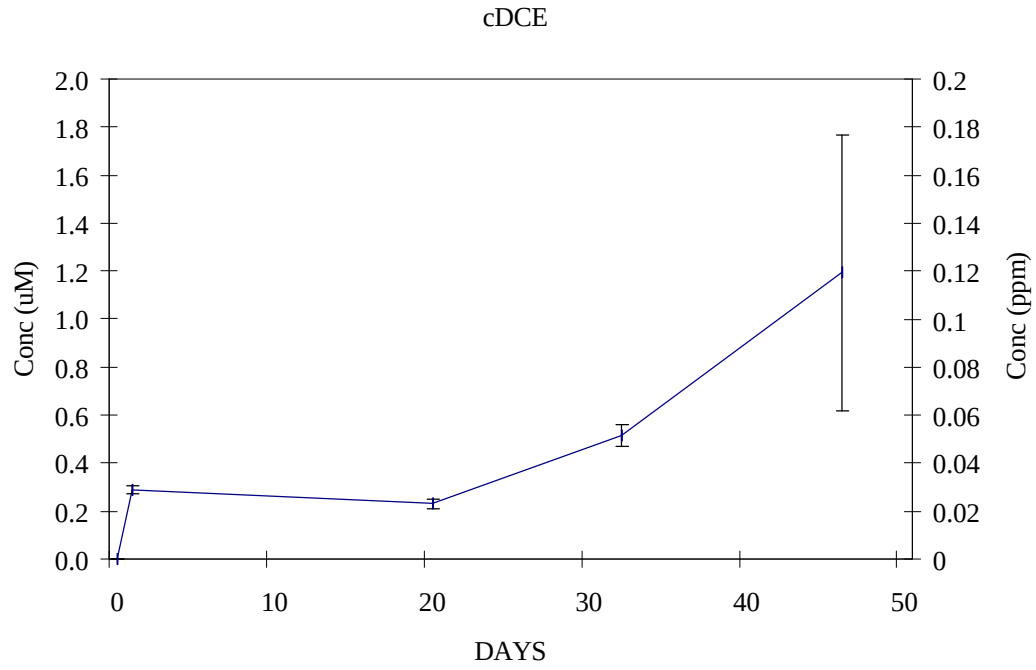
APPENDIX D

INVIDUAL RESULTS OF PCE DECHLORINATION IN LAKE SEDIMENT AND AMENDED SB1 SURFACE SEDIMENT (0-4 FT) MICROCOSM STUDIES

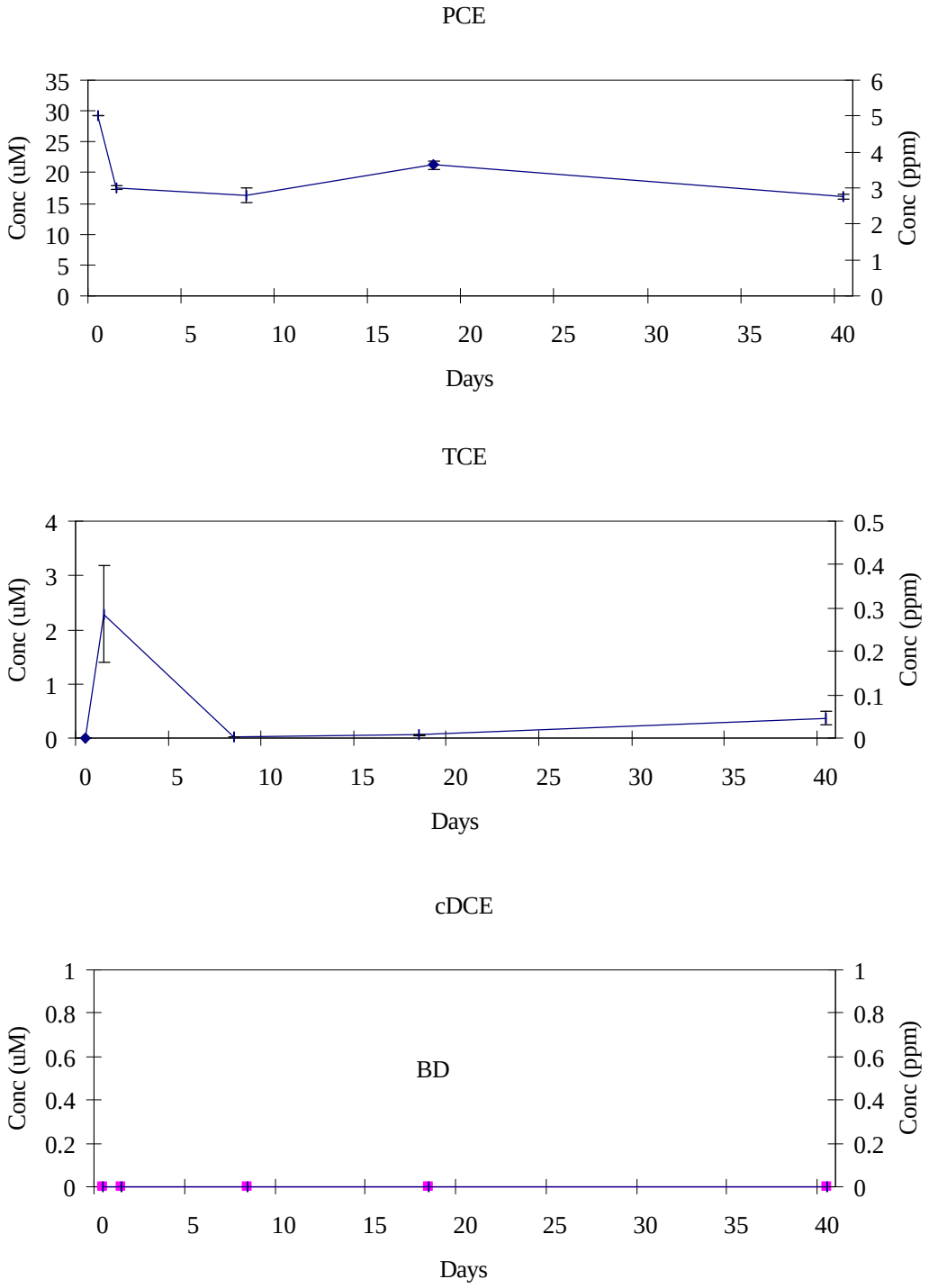


Unamended Lake Sediment Dosed With 5 mg/L PCE After a 1 Week Acclimation Period

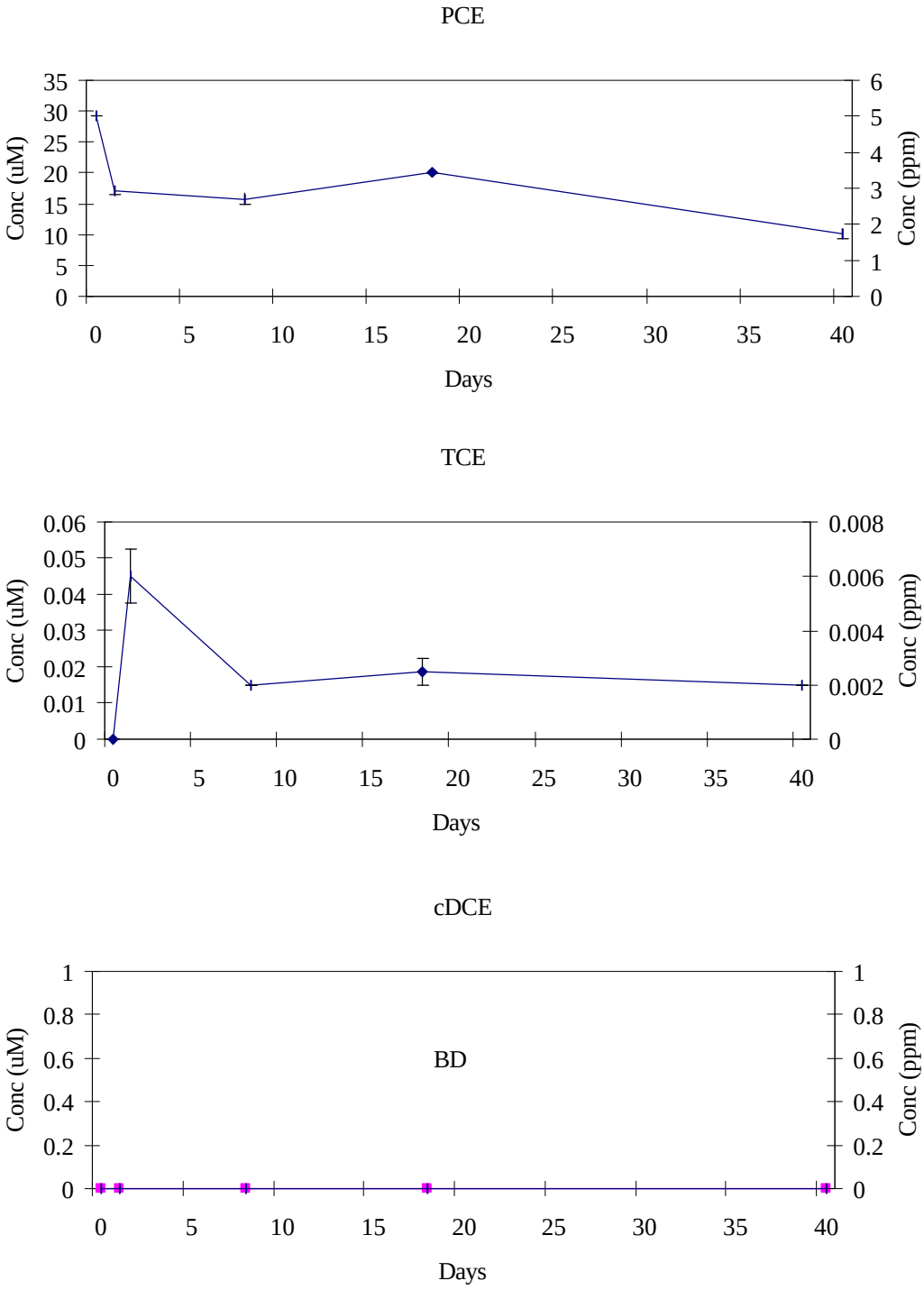




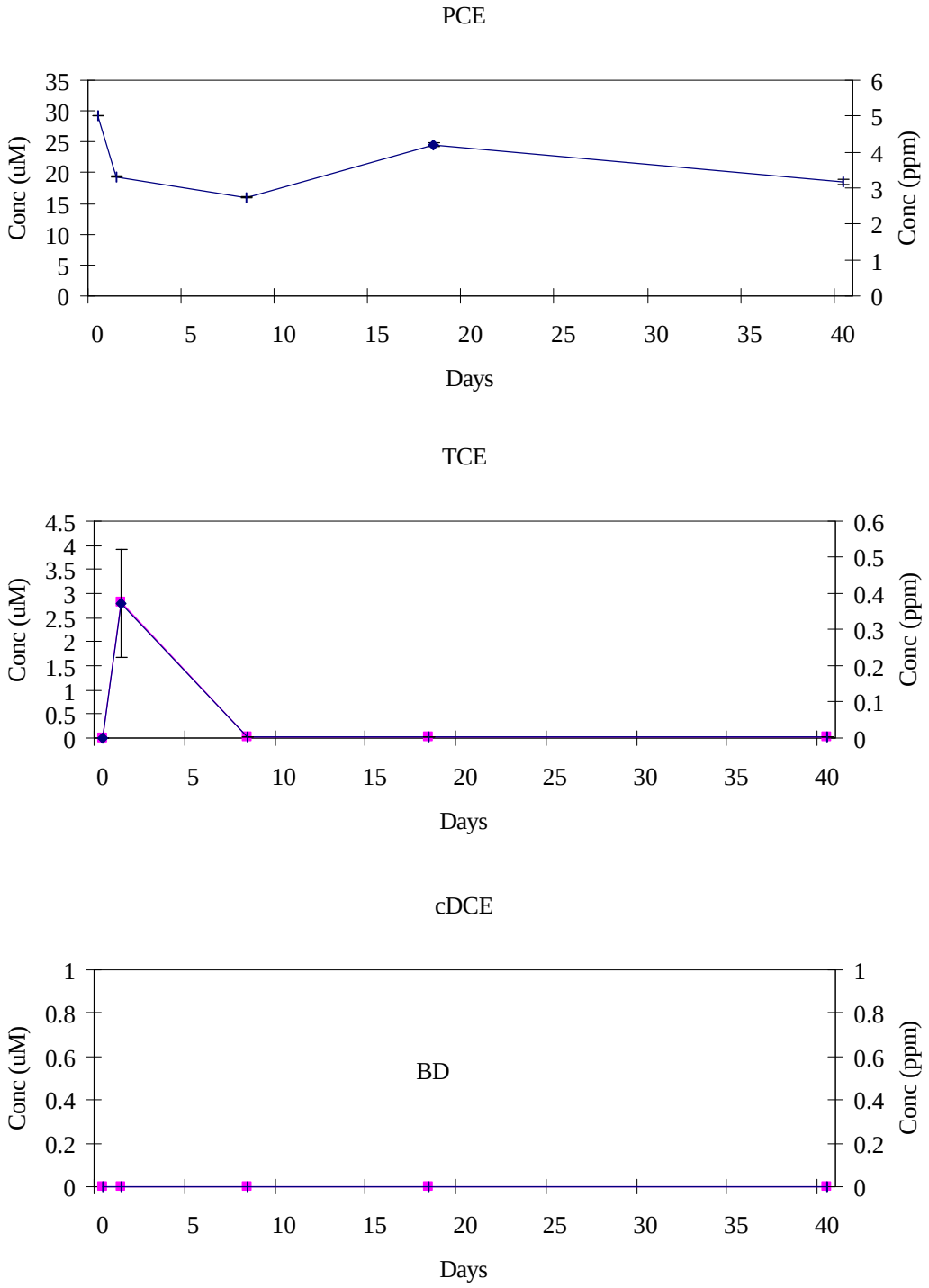
Unamended Lake Sediment Dosed With 5 mg/L TCE After a 1 Week Acclimation Period



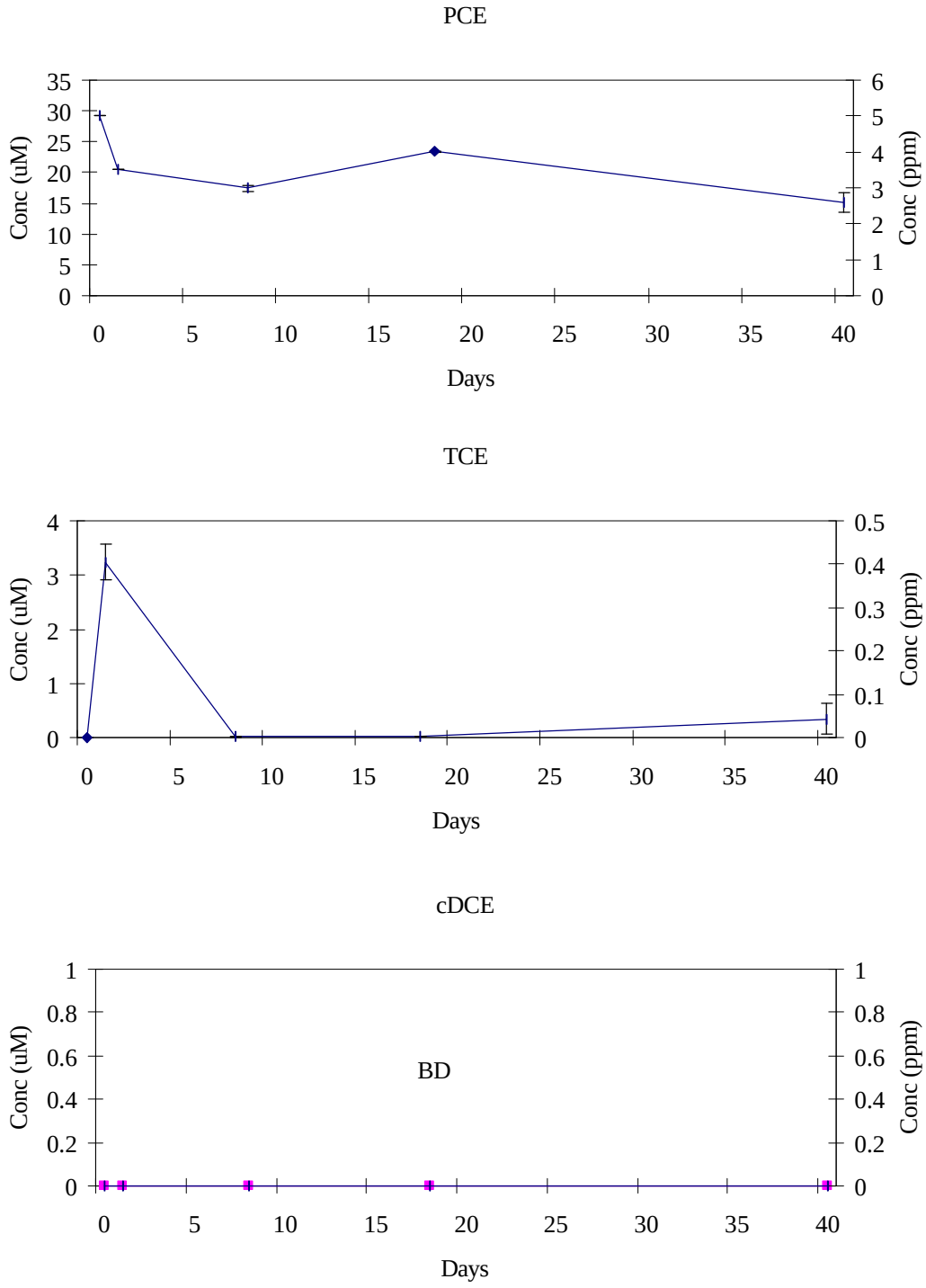
SB1 Surface Sediment (0-4ft) Amended with 3 % Yeast Extract and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



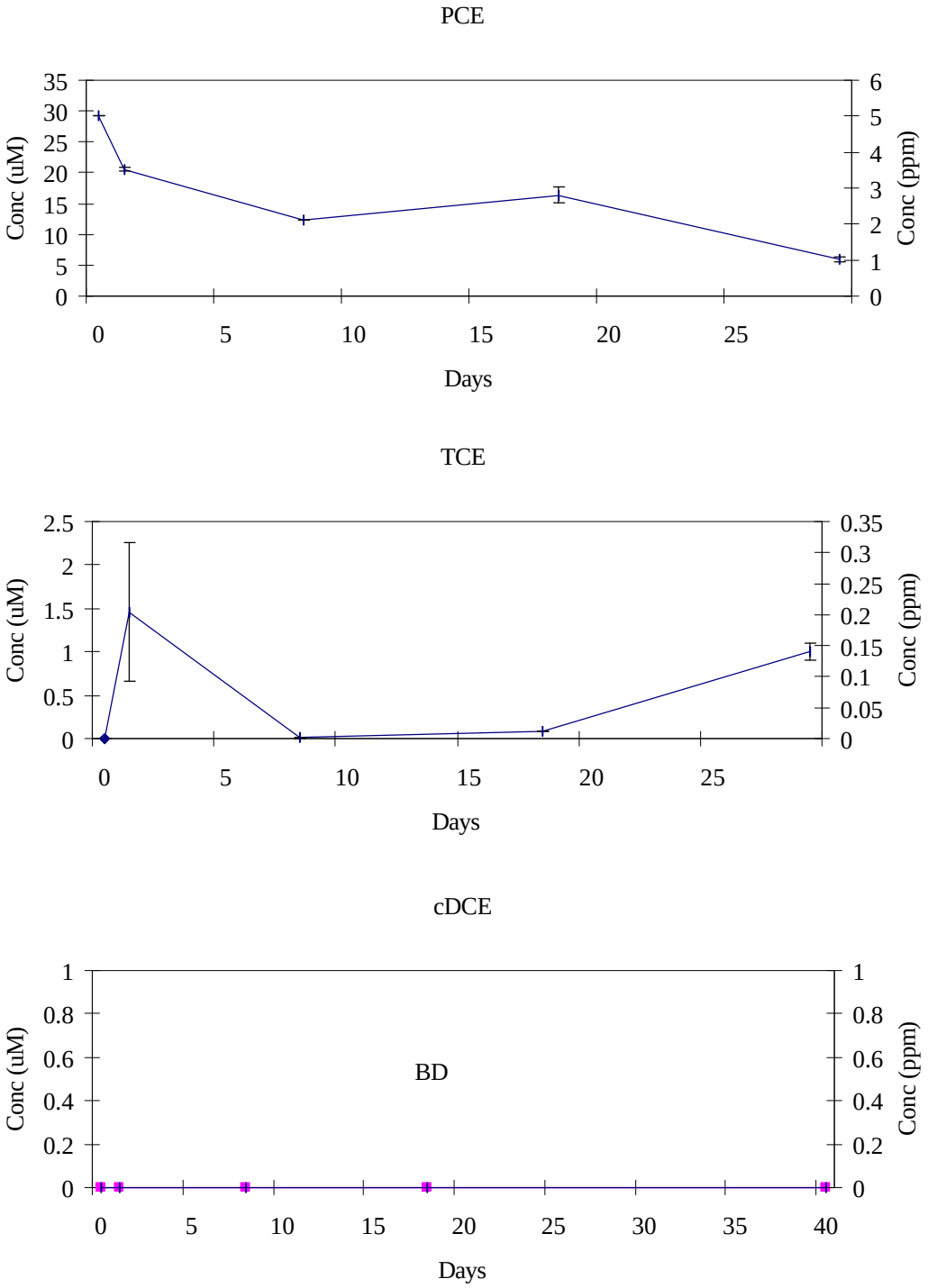
SB1 Surface Sediment (0-4ft) Amended with 3 % Molasses and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



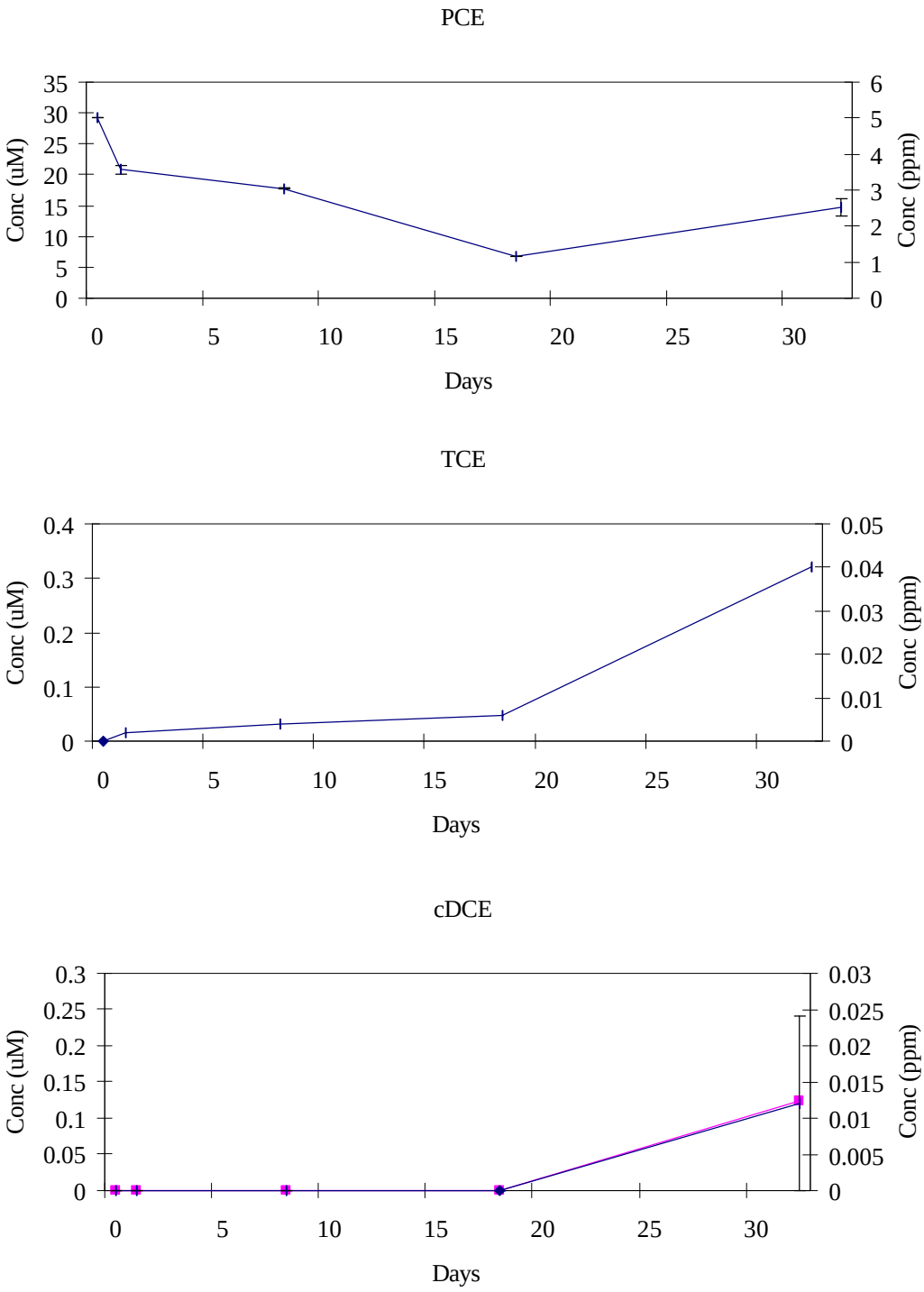
SB1 Surface Sediment (0-4ft) Amended with 3 mM Na-Lactate and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



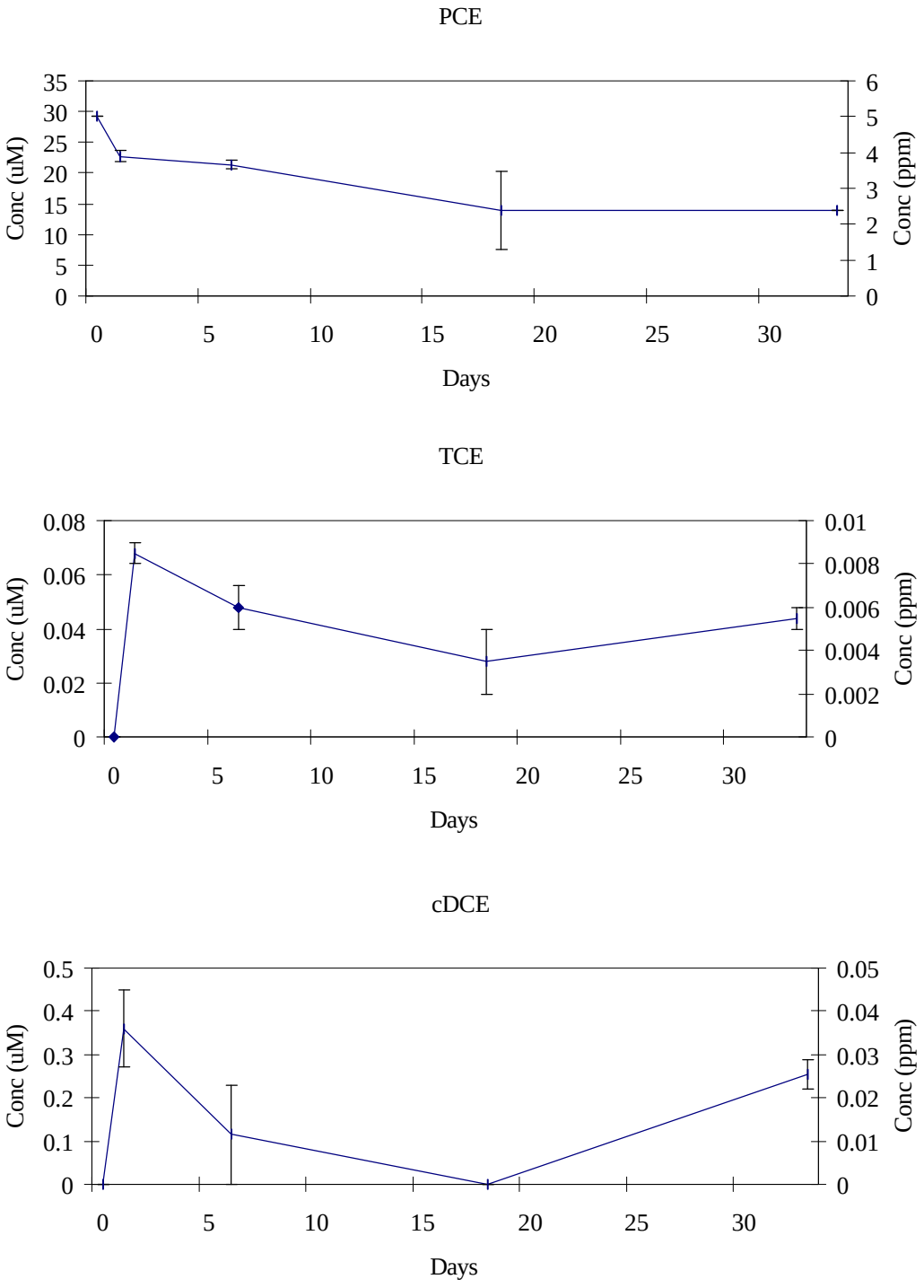
SB1 Surface Sediment (0-4ft) Amended with 3 mM Na-Acetate and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



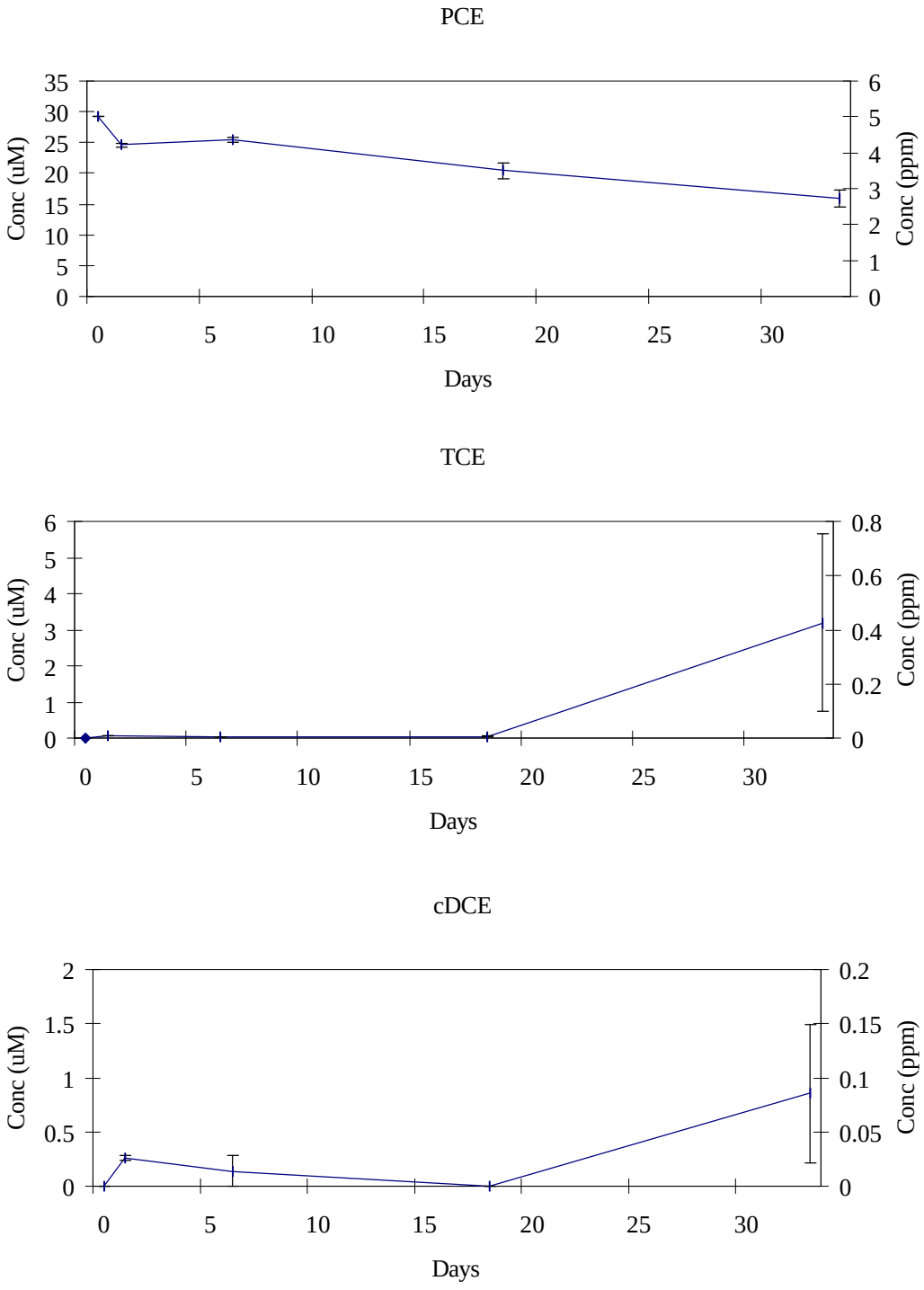
SB1 Surface Sediment (0-4ft) Amended with 3 mM Na-Lactate and 3 % Yeast Extract Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



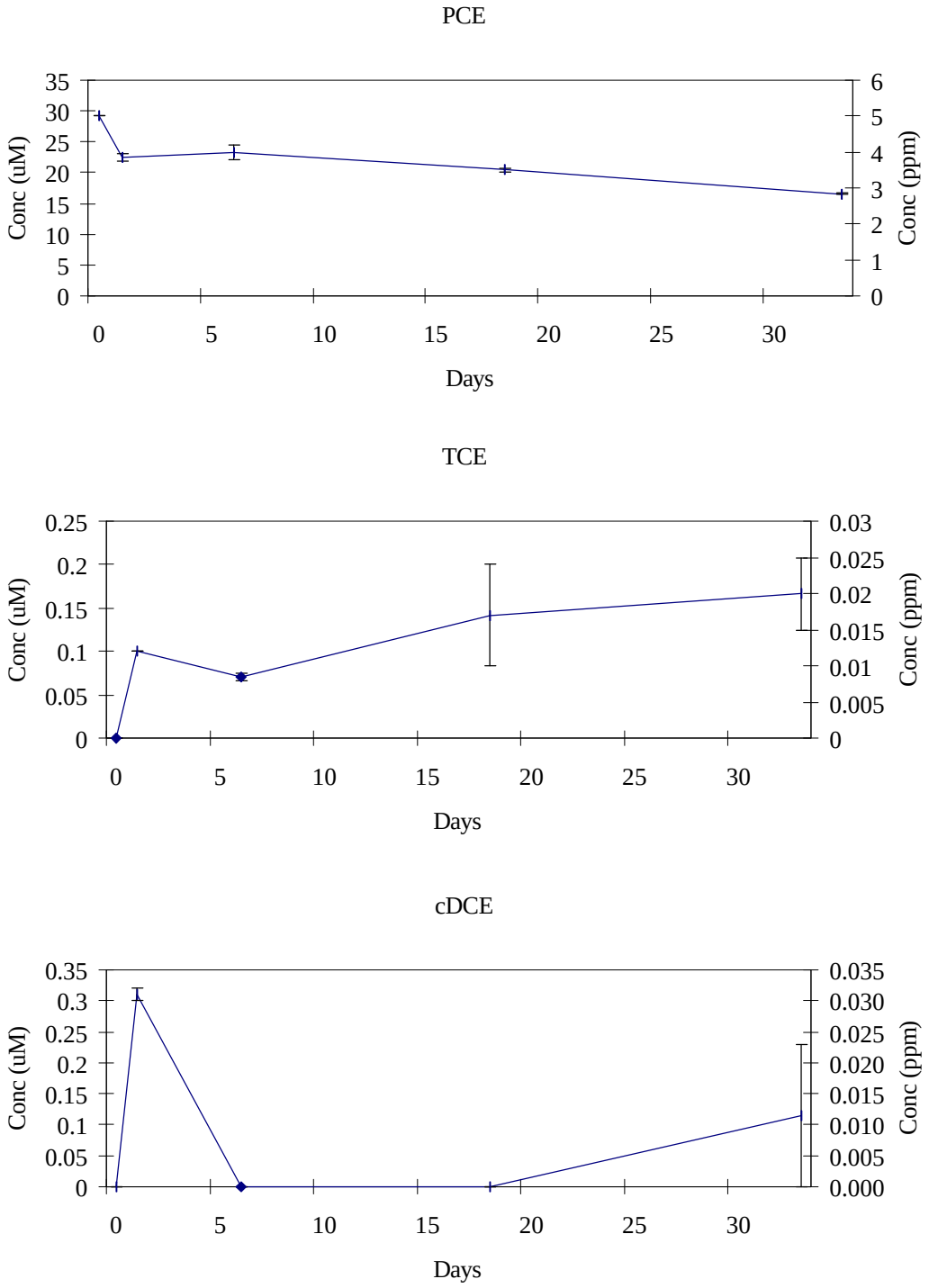
SB1 Surface Sediment (0-4ft) Amended with 3 mM Na-Acetate and 3 % Yeast Extract Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



SB1 Surface Sediment (0-4ft) Amended with 10 % Molasses and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



SB1 Surface Sediment (0-4ft) Amended with 10 mM Na-Acetate and Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period



SB1 Surface Sediment (0-4ft) Amended with 10 mM Na-Acetate and 10 % Yeast Extract Dosed With 5 mg/L of PCE After a 1 Week Acclimation Period