ANAEROBIC BIOLOGICAL TREATABILITY OF CHLOROFORM CONTAMINATED SOIL

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NOMENCLATURE

Acronyms:

ALR	acetate loading rate
CF	trichloromethane (chloroform)
$CHCl_3$	chloroform
CH_2Cl_2	dichloromethane
CH_3Cl	monochloromethane
CO_2	carbon dioxide
DCM	dichloromethane
GC	gas chromatograph
GPS	global positioning system
NADH	nicotinamide adenine dinucleotide
p-DCB	para-dichlorobenzene
POTW	publicly owned wastewater-treatment work
RCRA	Resource Conservation and Recovery Act
SBR	serum bottle reactor
TCA	1,1,1-trichloroethane
TSS	total suspended solids
USEPA	United States Environmental Protection Agency
VOC	volatile organic compound

1.0 INTRODUCTION

For many years businesses have knowingly and unknowingly polluted the environment. In the 1980s, environmental engineers were asked to find economically and environmentally sound solutions for some of these environmental mistakes. Many of those mistakes were in the handling and disposal of toxic organic chemicals, with the result that the public felt very threatened, and would probably even characterize the 1980s as the "Decade of Toxic Pollutants" (Grady, 1990). Politicians responded to public concerns by stating that the problems will be corrected and funds will be made available to do it. However, realistic responses from government can cause society to question whether the engineer can deliver what is expected, thereby damaging credibility and hindering cleanup efforts. It is the responsibility of environmental engineering professionals to take it upon themselves to scrutinize the approaches proposed for dealing with toxic organic chemicals to ensure that innovation is encouraged while protecting the public and their tax dollars (Grady, 1990). Part of this responsibility includes evaluation and testing of treatment technologies.

Biodegradation is the least expensive and most widely used method for removing organic compounds from wastewater and is the primary mechanism responsible for their destruction in nature (Naziruddin et al., 1995). Literature reviews reveal that conventional biological treatment systems, such as those used in publicly owned wastewater treatment works (POTWs), are remarkably robust and effective in removing such chemicals (Grady, 1986; Lewandowski, 1988). For example, anaerobic degradation of benzenes was long considered impossible but is now known to be common in methanogenic communities, and the pathway is well understood (Berry et al., 1987; Evans and Fuchs, 1988). Furthermore, the results from a study conducted in England on the anaerobic biodegradability of 77 organic compounds were in general agreement with studies done in the United States (Battersby and Wilson, 1989). This suggests that

biodegradability assessments made with one source of microorganisms can be extrapolated to another with a reasonable degree of confidence (Grady, 1990).

Information on biodegradation kinetics is essential during design of biological treatment systems and during the process of establishing limits on the discharge of toxic compounds to the environment. Consequently, there is a need for a database on kinetic parameters of biodegradation (Naziruddin et al., 1995). To date, most published biodegradation information is qualitative, or, if quantitative, the parameter values are not intrinsic, thereby limiting their application (Howard et al., 1991; Pitter and Chudoba, 1990). While biodegradability information is sufficient for making early feasibility decisions, information about rates of biodegradation is necessary for engineers to compare processes (Grady, 1990). Rate information from studies must be available as intrinsic coefficients to allow its use in treatment system models. A key factor in determining the economic attractiveness of biological processes for chlorinated solvent degradation is the rate of degradation (Speitel and Leonard, 1992).

Volatile organic chemicals (VOCs) are common ground water contaminants, and their presence in aquifers is being reported with increasing frequency. Chlorinated aliphatic compounds widely used as industrial degreasers, dry cleaning solvents, propellants, and insecticides are common groundwater contaminants (Barbash and Roberts, 1986). Chlorinated aliphatic compounds, including dichloromethane (DCM), trichloromethane or chloroform (CF), and 1,1,1–trichloroethane (TCA), are among the most commonly detected contaminants of groundwater in the United States (Gossett, 1985). They have become widely distributed in the environment as a result of discharges of industrial and municipal wastewaters, urban and agricultural runoff, leachates from landfills, and leaking underground tanks and pipes. Because they are denser than water, plumes of non-aqueous aliphatics may sink below the water table where the compounds may persist for decades (Hughes and Parkin, 1992). Despite the fact that a large portion of a plume of DCM, CF, or TCA may remain as a non-aqueous phase liquid, significant quantities of these compounds can become dissolved in the groundwater and transported by

advective and dispersive mechanisms (Hughes and Parkin, 1992). Many of these compounds are toxic at high concentrations and are suspected human carcinogens and/or mutagens (*Federal Register*, 1984; *Federal Register*, 1985). The discharge and subsequent fate of VOCs and semivolatile organic compounds (SVOCs) in wastewater streams is a topic of growing interest in wastewater treatment. POTWs are coming under increasing scrutiny as sources of air toxic emissions, and aggressive air toxic control programs are being enacted by state and local agencies all over the country (Narayanan et al., 1995). Furthermore, many VOCs and SVOCs, especially chlorinated compounds, are not degraded under aerobic conditions and thus cannot be removed by aerobic processes (Dobbs, 1990; Melcer et al., 1989).

This paper represents the results of studies that were conducted to address the feasibility of employing anaerobic treatment of a chloroform-contaminated aquifer sample under varying conditions. In these studies, five aspects of treating contaminated soil samples with mixed cultures of anaerobic microorganisms are investigated. The first objective is to evaluate the effect of chloroform alone with methanogenic, denitrifying, and sulfate-reducing microorganisms. Secondly, other parameters affecting chloroform degradation will be investigated, including the effects of metals, non-chlorinated aliphatics, and changing concentrations of chlorinated aliphatics with the three types of microorganisms mentioned above. These research objectives address a significant area of concern that must be investigated before any large-scale implementation of biological processes for the remediation of severely contaminated groundwaters. The potential for toxicity to the microorganisms exists when treating high concentrations of chloroform, and relatively little is known of the degradative rates of microorganisms when treating chloroform, especially under "real world" (i.e. complex solutions) conditions.

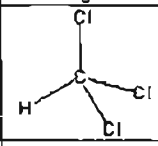
2.0 LITERATURE REVIEW

Laboratory studies have demonstrated that dichloromethane (DCM), chloroform (CF), and trichloroethane (TCA) are all transformed by anaerobic microorganisms (Vogel et al., 1987). The implementation of an anaerobic treatment process (above ground or in-situ) may provide significant advantages over more traditional treatment options such as activated carbon adsorption or air stripping (McCarty, 1988).

Chloroform is a suspected human carcinogen and a common groundwater contaminant (Davidson, 1982; Herzog et al., 1988). Chloroform appears as a priority pollutant on the Resource Conservation and Recovery Act (RCRA) report of priority pollutants. The National Priority Pollutants List database indicates that chloroform appears at 24% of all Superfund sites. The physical and chemical characteristics of chloroform are summarized in Table 1.1. Chloroform migrates relatively rapidly and may move from highly contaminated groundwaters beneath leaking hazardous waste landfills and other improper storage facilities to contaminate potable waters (Roberts et al., 1982). Chloroform-contaminated groundwaters should be remediated as near to the contamination source as possible (Bagley and Gossett, 1995). Since many chlorinated compounds, including chloroform, break through very quickly in activated carbon columns, a cost-effective technology such as bioremediation to treat this compound is required (Gupta et al., 1996b).

Table 2.1

Chemical and Physical Properties of Chloroform

Chemical Name	Chloroform
Synonyms	Trichloromethane, Methane Trichloride
CAS Number	67-66-3
Molecular Formula	$CHCl_3$
Chemical Structure	
Molecular Weight	119.3779
Physical State	Clear colorless liquid with a pleasant, sweet odor detectable at 133 to 276 ppm. Light sensitive.
Boiling Point	61.7°C
Melting Point	-63.7°C
Refractive Index	1.4459
Evaporation Rate	0.09
Relative Density (water=1)	1.49845
Vapor Pressure at 20°C	159
Relative Vapor Density (air=1)	4.1
Solubility in Water at 20°C	0.795 g/100 mL

Source: Chemfinder, www.chemfinder.com, 2000

Biodegradation of hazardous chemicals, particularly heavily chlorinated compounds, can be considered complete only when the carbon skeleton is converted to harmless metabolites, and the halogen, such as chlorine, is returned to the mineral state (Fathepure and Vogel, 1991) A crucial point in the complete destruction of chlorinated hydrocarbons is the removal of the chlorine substituent from the molecule (Fathepure and Vogel, 1991) The most widely reported transformation of halogenated compounds under anaerobic conditions is reductive dechlorination (Bhatnagar and Fathepure, 1991). Reductive dechlorination is relatively rapid for chemicals with a higher number of chlorine substituents, including chloroform, when compared with dechlorination of less-chlorinated compounds (Bhatnagar and Fathepure, 1991) The reductive dechlorination of chloroform in the anaerobic environment is consistent with recently observed dechlorinations under both methanogenic and sulfate-reducing environments (Bagley and Gossett, 1990). Bouwer (1981) and others suggest that chloroform cannot be degraded under aerobic conditions except under methanotrophic conditions. Chloroform has been shown to be

biodegradable under methanogenic conditions, but higher concentrations of chloroform have been shown to be inhibitory to methanogenesis (Gupta et al., 1996b).

Chloroform can be aerobically degraded by methanotrophic organisms (Alvarez-Cohen et al., 1992), ammonia-oxidizing organisms (Vannelli et al., 1990), and a recombinant pseudomonad expressing soluble methane monooxygenase (Jahng and Wood, 1994). However, in methanotrophic cultures, chloroform and methane compete for the reaction site decreasing the reaction rate of each (Speitel and Leonard, 1992). Furthermore, the requirement for dissolved oxygen and methane may impose practical and economical limitations on aerobic degradation (Bagley and Gossett, 1995).

Chloroform can be degraded anaerobically to CO_2 and dichloromethane by methanogenic enrichment cultures and pure methanogenic cultures and also by nonmethanogenic anaerobic cultures (Mikesell and Boyd, 1990; Fathepure and Tiedje, 1994). However, although chloroform degradation in methanogenic cultures could be stimulated by methanol addition, chloroform remains extremely inhibitory to methanogenesis (Yang and Speece, 1986; Fathepure and Tiedje, 1994). Cultures that received methanol degraded chloroform more rapidly than did those without methanol (Bagley and Gossett, 1995). The presence of methanol, not its concentration or consumption rate, is the most significant variable affecting the chloroform degradation rate (Bagley and Gossett, 1995). This is in contrast to aerobic chloroform degradation, in which the growth substrate competes with chloroform for the reaction site (Oldenhuis et al., 1991). These observations suggest that in an anaerobic treatment system designed to remove chloroform, very little methanol consumption would be required to stimulate chloroform degradation (Bagley and Gossett, 1995).

Recent data collected from a leachate-treatability study conducted at the U.S. Environmental Protection Agency (USEPA) Test and Evaluation Facility emphasized the importance of the type of anaerobic environment with respect to inhibition at higher concentrations of chloroform.

Parallel anaerobic reactors operating under sulfate-reducing and methanogenic conditions revealed that methanogenic activity was completely inhibited at a feed chloroform concentration ranging between 16.7 μM and 27.2 μM while the sulfate-reducing reactor showed no inhibition and promoted efficient chloroform degradation (Suidan et al., 1993). No other reports were identified regarding the degradation of chloroform by sulfate-reducing organisms (Suidan et al., 1993).

The biotransformation of chloroform under methanogenic conditions was discussed in detail by Gupta et al. (1996a). In this study, the rate of biotransformation of chloroform and the primary substrate (acetic acid) utilization rate were investigated as a function of the initial chloroform concentration using serum bottle reactor (SBR) tests. They varied the initial chloroform concentration to investigate its effect on the transformation of chloroform and the utilization of the primary substrate (acetic acid). The tests showed a single large step increase in the concentration of an inhibitory compound can lead to failure of a biological system while gradual increases can help a biological system function very efficiently.

The tests conducted by Gupta et al. (1996a) revealed a biotransformation rate of 0.80 μM/h at an initial concentration of 0.4 μM. The rate increased as the initial chloroform concentration was increased. The maximum rate was approximately 16.3 μM/h, corresponding to an initial chloroform concentration of 22.6 μM. At initial chloroform concentrations exceeding 22.6 μM, the rate decreased, indicating inhibition due to the presence of chloroform. The rate decreased to 12.2 μM/h for initial chloroform concentration of 25.1 μM and further to 8.4 μM/h for initial chloroform concentration of 29.3 μM. The experiment goes on to show that chloroform does not inhibit the utilization of the primary substrate in the sulfate-reducing culture.

Hughes and Parkin (1992) also studied biodegradation of chloroform. They suggest that a major concern regarding biological treatment of high concentrations of chlorinated aliphatics (chloroform) is the potential for toxicity to the organisms, resulting in the incomplete removal of

the contaminants. Chloroform degradation was not sustained in any system unless it was fed along with dichloromethane. This suggests that, in the bioremediation of a severely contaminated groundwater, the availability and utilization of a prime substrate are primary concerns. Chloroform is not believed to provide the necessary energy to support bacterial growth (Hughes and Parkin, 1992). Recent studies have demonstrated that dichloromethane may serve as a growth substrate for acetogenic bacteria (Freedman and Gossett, 1991). However, other studies by Hughes and Parkin have indicated that reduced acetate loading rate (ALR) significantly reduces the removal of dichloromethane, as well as chloroform (Hughes and Parkin, 1991). Presumably, an electron donor (primary substrate) will be required to support a microbial population large enough to reach the treatment objectives, particularly when the concentrations of the chlorinated aliphatics are in excess of 1 mg/L.

Studies have suggested that in-situ biorestoration with a selected native bacterial population stimulated by the addition of a primary substrate and possibly also nutrients is possible (Semprini et al., 1987). This process would be particularly useful if developed for aquifers containing organic contaminants that are difficult to degrade, significantly sorbed to aquifer solids, and/or present at low concentrations (Lanzarone and McCarty, 1990).

Previous work with mixed cultures of methanotrophs demonstrated relatively low rates of chloroform degradation (Speitel et al., 1989). At low concentrations of chlorinated solvents, degradation follows pseudo-first-order kinetics, as described by the following rate expression (Speitel and Leonard, 1992):

$$r = - k_1 X S$$

Where

r = degradation rate, mg/L·d;

k_1 = pseudo-first-order degradation rate constant, L/mg TSS·d;

X = cell concentration, mg TSS/L; and

S = the chlorinated solvent concentration, mg/L

Methane must be supplied to the organisms on some regular basis, since this is the growth substrate for the organisms, as well as the inducer for methane monooxygenase synthesis (Speitel and Leonard, 1992). Metabolism of methane to carbon dioxide requires considerable oxygen and concentrations of methane greater than a few milligrams per liter will cause complete depletion of the dissolved oxygen, even in waters saturated with oxygen (Speitel and Leonard, 1992). A decreased degradation rate even after the presence of formate as a source of nicotinamide adenine dinucleotide (NADH) probably is attributable to depletion of necessary metabolic chemicals within the cells that cannot be regenerated by formate addition alone (Speitel and Leonard, 1992). Speitel and Leonard continue to write that another possibility for the decrease in the chloroform degradation rate is some toxicity to the cells from a metabolic intermediate (1992). In work with other methanotrophic organisms, Alvarez-Cohen and McCarty observed a toxicity response from a metabolic intermediate (most probably phosgene) in batch tests using large chloroform concentrations of greater than 15 mg/L (1991). They observed that the cells had a finite capacity to degrade chloroform before inactivation from toxicity occurred.

Speitel and Leonard explain that an exponential decay model described the decrease in the pseudo-first-order rate constant over time (1992). The decay constants were 0.27 day^{-1} with formate (R^2=0.88) and 0.34 day^{-1} in the absence of formate (R^2=0.92). The decay constants correspond to a half-life of 2-2.5 days for the pseudo-first-order rate constant. Formate, however, did not affect reactor performance beyond the first several days of operation, which suggests that depletion of other chemicals within the cells, enzyme inactivation, toxicity from metabolic intermediates, or some combination of these are more important contributors to the decreased degradation rate at longer operating times (Speitel and Leonard, 1992). The pseudo-first-order rate constant in the sequencing reactor decayed exponentially over time with a decay constant of approximately 0.30 day^{-1}

Under anaerobic conditions, the reductive dechlorination of chloroform ($CHCl_3$) by *Acetobacterium woodii* has been reported to produce mostly carbon dioxide (CO_2), with dichloromethane (CH_2Cl_2) and traces of monochloromethane (CH_3Cl) identified as intermediates (Egli et al., 1988). Zitomer and Speece reported with 320 µg/L chloroform, gas production was 110±4% of the theoretical, and the specific first-order rate constant for chloroform was 4.55 $Lg^{-1}day^{-1}$. With 800 µg/L chloroform, gas production was reduced to 56±12% of theoretical, and the first-order rate constant was 1.21 $Lg^{-1}day^{-1}$ (1995). When relatively non-toxic $CHCl_3$ initial concentrations were employed, the transformation rate constant was higher than when relatively toxic doses were administered (Zitomer and Speece, 1995).

Narayanan and others (1995) conducted a study on the potential of the expanded bed granular activated carbon anaerobic reactor in treating a municipal wastewater containing RCRA volatile and semivolatile organic compounds. The only compound found to be somewhat resistant to biodegradation was chloroform, which persisted in the effluent at concentrations of 200 µg/L, even after its removal from the feed because of the presence of carbon tetrachloride in the influent. Based on the potential for chloroform production from carbon tetrachloride, this effluent concentration still represents a reasonable removal efficiency of 75% (Narayanan et al., 1995).

Alvarez-Cohen and McCarty described a mixed culture of bacteria enriched with methane and oxygen from aquifer material from Moffett Field Naval Air Station, Mountain View, California (1991). When grown in a bioreactor under methane and nitrogen limitation, this mixed culture rapidly oxidized chloroform (0.30 to 0.40 mg · mg of $cells^{-1}$ · day^{-1}). Alvarez-Cohen and others went on to demonstrate that a mixed culture of bacteria that was grown with methane as the sole source of carbon and energy was capable of rapid transformations of chloroform (1992).

Metals have been shown to inhibit growth of bacteria to degrade contaminates. In an experiment to determine the ability for degradation of nickel-citrate, Francis et al. found that the bacterium used to degrade nickel-citrate failed due to the toxicity of the nickel released in the culture

medium (1996). They found as nickel-citrate was being broke down, the nickel released from the process was toxic to the bacterium. Also, in a study to determine if metal toxicity could be reduced by a metal-complexing biosurfactant, rhamnolipid, Sandrin et al. (2000) found that, as cadmium concentration increased, cadmium toxicity increased, resulting in a delay or complete inhibition of growth. Malakul and others also had similar results (1998). They found as they increased the concentration of cadmium, it inhibited the growth of their bacteria until complete inhibition of the bacteria resulted.

Many of the aforementioned studies have investigated $CHCl_3$ without the presence of other compounds and other "real world" effects. This study investigates the degradation of $CHCl_3$ in complex mixtures. These results can help determine the best conditions for $CHCl_3$ degradation in municipal landfills.

3.0 METHODS AND MATERIALS

3.1 EXPERIMENTAL APPROACH

This study focused on evaluating the anaerobic reactions of chloroform under various conditions including various redox conditions, effects of metals, effects of additional organics, and effects of changing concentrations. A series of batch reactor experiments were employed in this investigation. The chemicals used, analytical methods, experimental procedures, and the methods of data analysis of rate constants are described below.

3.2 SOIL SAMPLES

The soil samples used in these experiments were collected from a municipal landfill located in Norman, Oklahoma. The following description of the landfill was obtained from the United States Geological Survey's website:

> The Norman Landfill is a closed municipal landfill located on alluvium associated with the Canadian River in central Oklahoma (see Figure 3.1). The U.S. Geological Survey began a multi-disciplinary investigation in 1994 at the Norman Landfill, as part of the Toxic Substances Hydrology Program, in collaboration with scientists at the University of Oklahoma, Oklahoma State University, and the Environmental Protection Agency. The contamination of the shallow alluvial aquifer at the Norman Landfill provides an excellent opportunity to study the spatial variability of biogeochemical processes and the resulting effects on the fate of degradable contaminants in the leachate plume. The emphasis of this multi-disciplinary research project is on developing a unified understanding of the processes controlling contaminant distribution and migration.

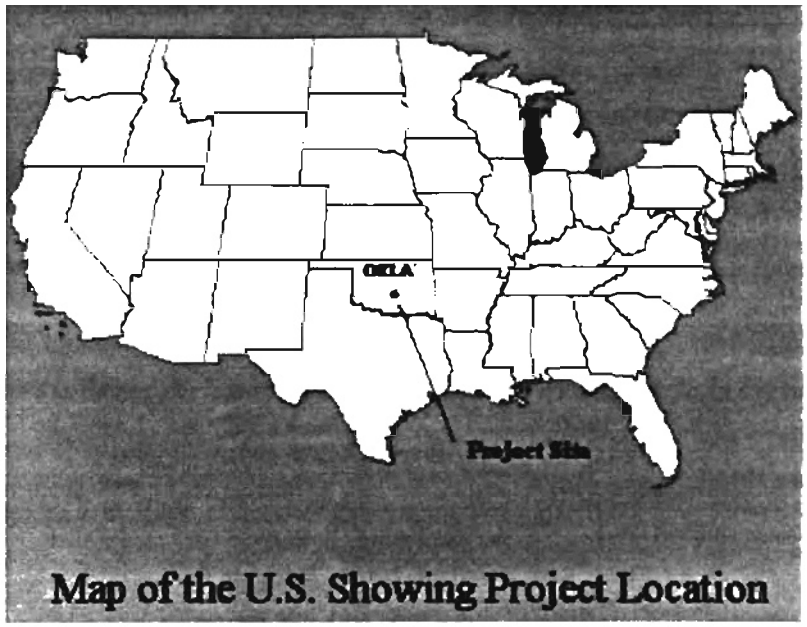


Figure 3.1. Norman Landfill Location Map
(Source: United States Geological Survey's website)

Considering the need for constructing new landfills and the increasing volumes of existing landfills, the results from this study can be utilized worldwide.

The landfill accepted solid waste from 1922 to 1985 and was covered with a clay cap and vegetated when it was closed. The landfill was estimated to have received about 1,128 tons of municipal waste per week in 1982. The landfill is excavated in alluvium adjacent to the Canadian River. The alluvium thickness ranges from 10 to 15 meters and consists of mostly clay, silt, sand, and gravel. The ground water is measured to about 4 meters with shale and sandstone beneath the alluvium (see Figure 3.2).

Depth to ground water was measured in the Canadian River alluvium in the winter of 1995-96 to construct a potentiometric-surface map (see Figure 3.3). The winter was chosen to minimize the effects of transpiration of water by plants at the site, many of which have root systems that extend to the water table. Numerous monitor wells were constructed to measure the ground water. The potentiometric surface in the Canadian River alluvium near the Norman Landfill was a relatively simple surface during the winter of 1995-96. The surface slopes toward the Canadian River, indicating that ground water is moving through the alluvium toward the River.

Geophysical electromagnetic induction surveys were performed to determine the vertical and horizontal extent of the leachate plume. Electromagnetic Induction Surveys measure the electrical conductivity of the aquifer materials, both soils and fluids. The surveys show higher conductivity south of the landfill, which is consistent with hydraulic and geochemical evidence indicating a leachate plume has developed and is flowing toward the Canadian River. Conductivity measurements and dissolved organic carbon analyses confirm that the plume has migrated beneath the slough and extends through the entire thickness of the alluvium.

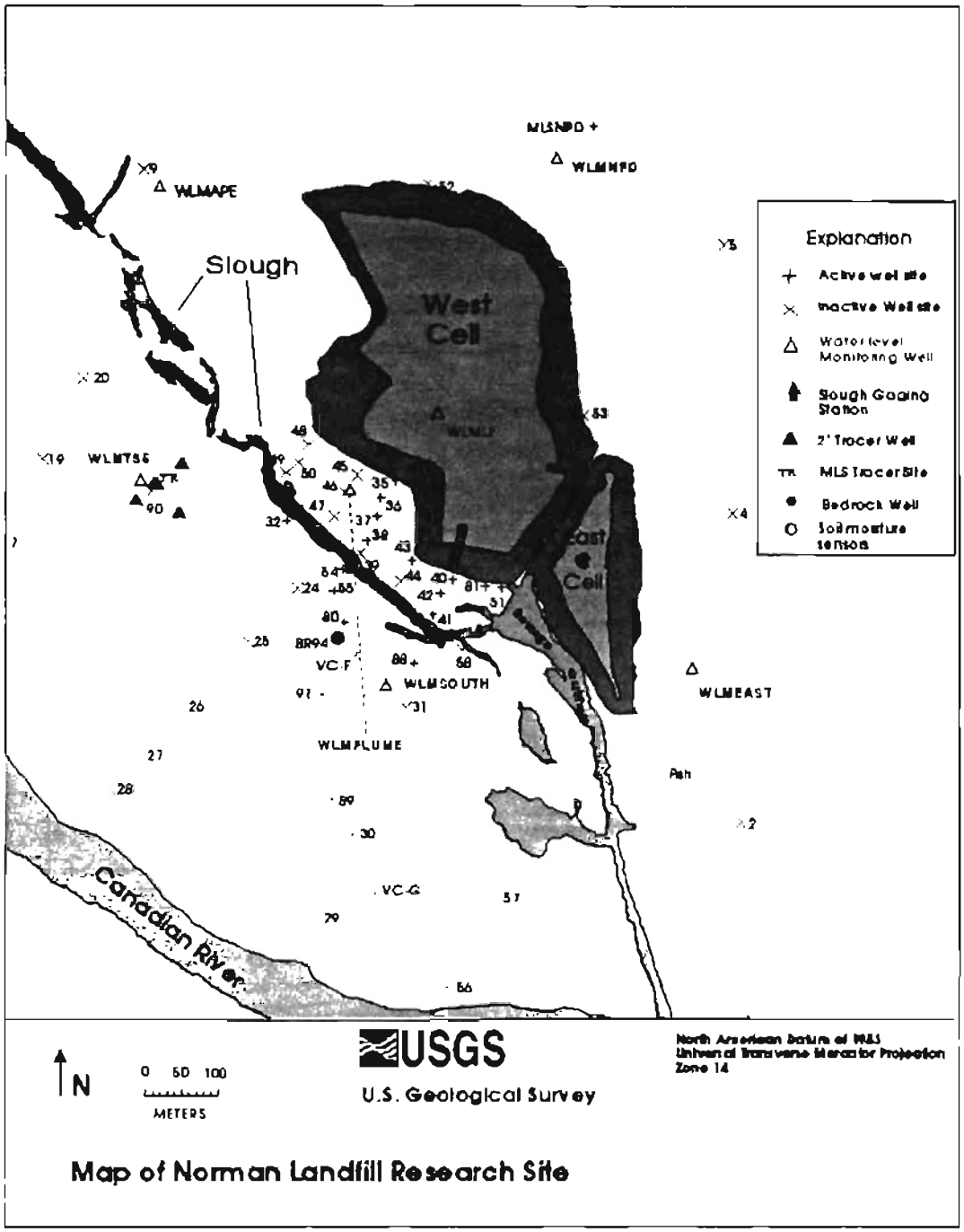


Figure 3.2. Norman Landfill Site Features Map
(Source: United States Geological Survey's website)

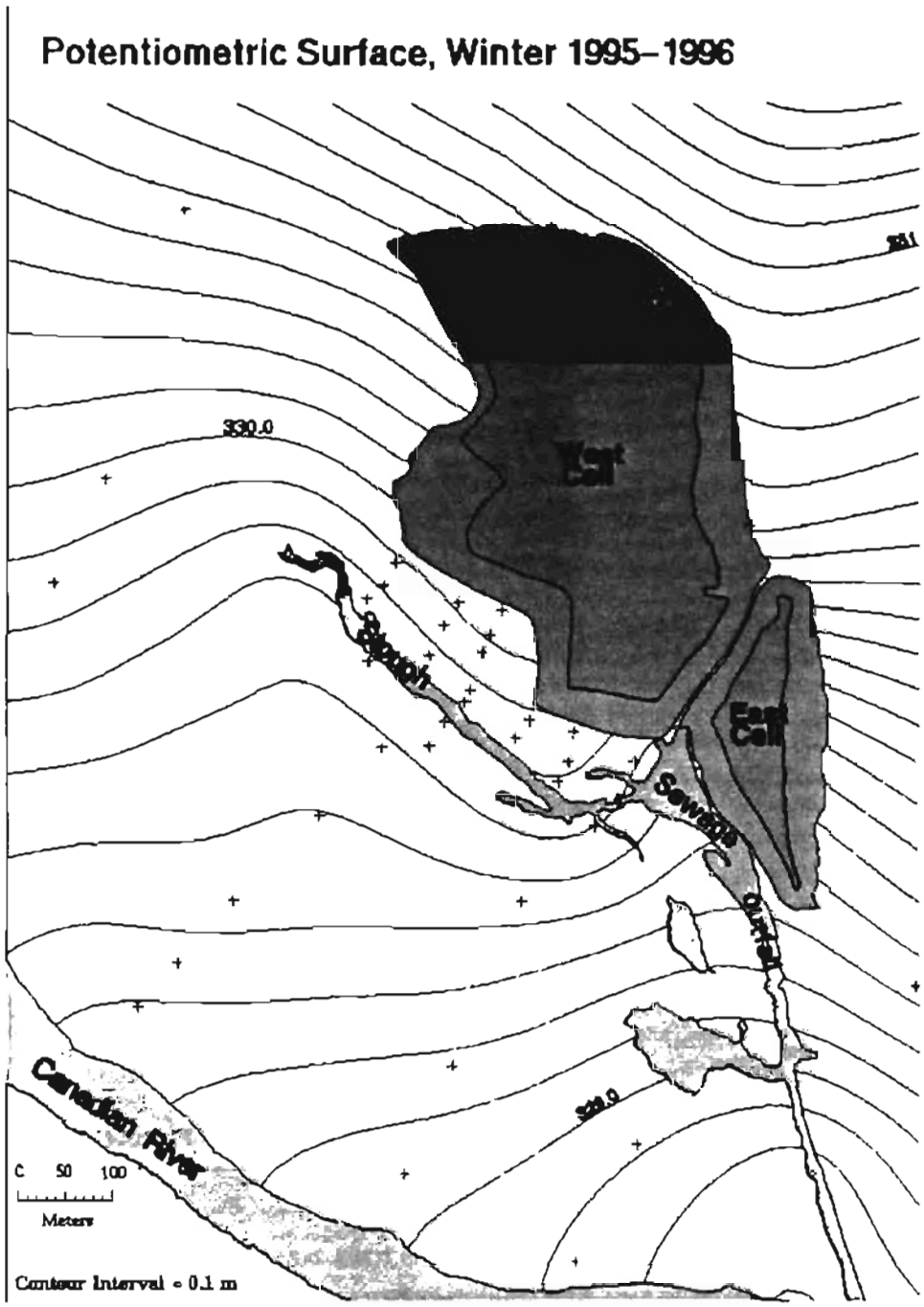


Figure 3.3 Norman Landfill Potentiometric-Surface Map
(Source: United States Geological Survey's website)

The aquifer materials used for the samples were collected from a methanogenic site located within the aquifer adjacent to the landfill. Landfill leachate was also collected at this site. The aquifer site is described above. The aquifer materials were very sandy and had been polluted by municipal landfill leachate, with volatile solids content of about 3 g/kg dry wt. (i.e. 0.3%). Samples of aquifer solids and leachate were collected in August 1994, by digging to the top of the ground water table (4 m depth) and collecting the solids and the leachate separately into glass or plastic vessels. Samples were then stored at 4°C until use.

3.3 REAGENT-GRADE MATERIALS AND LABORATORY PROTOCOLS

The water (≤18 MΩ·cm purity) used in all the experiments was produced by a Mill-Q purification system (Millipore Corp., CA) using deionization and reverse osmosis technology. Reagent-grade para-dichlorobenzene (p-DCB) and chloroform were obtained from Fisher Scientific, Inc. Other chemicals were of analytical grade and, unless stated otherwise, were obtained from Fisher Scientific, ChemService (West Chester, PA), Sigma Chemical Company (St. Louis, MO), or Supelco (Bellefonte, PA).

All glassware was washed with detergent, followed by triple-rinsing with tap water, Milli-Q water, and drying for 4 hours at room temperature (24 °C) before use.

3.4 BIOLOGICAL REACTORS

Three primary series of experiments were performed, each including three sets of reactors under different electron accepting conditions (denitrifying, methanogenic, and sulfate reducing). All the reactors were run in triplicate. Prior to running the experimental reactors, reactors were prepared and autoclaved for abiotic controls. The initial series of experiments was conducted using reactors containing only chloroform as a base line degradation study. The purpose of these experiments was to determine the rate at which each electron accepting condition degraded the

chemical, if at all. The second series of reactors contained chloroform combined with common metals found in landfill leachate. The third series of chloroform reactors was injected with ethylbenzene, decahydronapthalene, 2,2,4-trimethylpentane, and a mixture of all three. These organics were chosen because they are typically found in municipal landfills. Appendix A contains concentrations of chemicals found in the Norman Landfill leachate. As mentioned previously, *all* of the experiments were performed under different electron accepting conditions to determine the effect of the redox condition. The last series of reactors contained varying concentrations of chloroform and dichlorobenzene. This shows how small or large amounts of another common organic can affect the degradation of chloroform under different electron-accepting conditions. The following table shows all of the parameters tested.

Table 3.1

Summary of Experimental Parameters

Experiments	Conc. of $CHCl_3$ (μg/L), μM	Conc. of Added Contaminant (μg/L), μM
Baseline Chloroform Degradation	100, 0.84	
Effects of Metals		
Zinc	100, 0.84	150, 2.29
Nickel	100, 0.84	130, 2.22
Cadmium	100, 0.84	30, 0.27
Chromium	100, 0.84	460, 8.85
Combined Metals	100, 0.84	190, 0.66
Effects of Additional Organics		
Ethylbenzene	100, 0.84	50, 0 47
Decahydronapthalene	100, 0.84	50, 0.36
2,2,4-Trimethylpentane	100, 0.84	50, 0 44
Combined Non-Chlorinated Organics	100, 0.84	50, 0 14
100 $CHCl_3$ and 500 p-DCB	100, 0.84	500, 3 40
100 $CHCl_3$ and 60 p-DCB	100, 0 84	60, 0 41

Serum bottles of 160 mL were used as reactors for these experiments. Three types of electron accepting conditions (denitrifying, sulfate reducing, and methanogenic) were employed for these reactors, including abiotic controls. Reactors were prepared in triplicate for each series of experiments. The volume of liquid culture in each reactor was 150 mL. The formulas of the

media used for the reactors are presented in Table 3.2. The nutrient concentrations, which were the same for the three types of electron accepting conditions, are shown in Table 3.3. The trace metals solution used in the nutrient solution is shown in Table 3.4. These formulas were adopted by modifying the medium recipes reported by other researchers (Boopathy et al., 1993; Han, 1993; Shah, 1995).

Table 3.2

Enrichment Medium Formulas

Denitrifying Reactors		Methanogenic Reactors		Sulfate-Reducing Reactors	
Na Acetate	290 mg/L	Na Acetate	290 mg/L	Na Acetate	390 mg/L
KNO_3	200 mg/L	Na_2S	10 mg/L	Na_2SO_4	250 mg/L
Na_2SO_4	40 mg/L				
pH	7 3	pH	7.0	pH	6.9

NaAc: sodium acetate

Table 3.3

Nutrient Concentrations (mg/L)

$CaCl_2$	20
KH_2PO_4	340
$MgCl_2$	5
NaCl	25
$NaHCO_3$	100
Na_2HPO_4	355
NH_4Cl	150
1 mL/100 mL trace metal solution	

Table 3.4

Trace Metals Solution (mg/L)

$FeSO_4 \cdot 7H_2O$	200
$ZnSO_4 \cdot 7H_2O$	10
$MnCl_2 \cdot 4H_2O$	3
$CoCl_2 \cdot 6H_2O$	20
$CuCl_2 \cdot 2H_2O$	1
$NiCl_2 \cdot 6H_2O$	2
$Na_2MoO_4 \cdot 2H_2O$	3

The serum bottles were filled 1/3 full of the landfill soil sample (approximately 50 mL). Stock solutions of the electron acceptor and other additives and nutrients listed in Tables 3.2, 3.3, and 3.4 were added. Water was added to bring the reactor content to the 150 mL mark, and the pH was adjusted to 7.1 using either 0.1% HCl (hydrochloric acid) or 0.1 M NaOH (sodium hydroxide) solution. The bottles were then purged with nitrogen gas for 20 minutes to induce anaerobic conditions, then quickly capped with Teflon® septa and sealed with aluminum crimp seals. The capping was finished as quickly as possible to prevent large amounts of gas escaping. A known concentration of chloroform (and metals or organics, as appropriate) was injected into each bottle before initial extractions were performed. The reactors were shaken then incubated at room temperature (approximately 25°C) in the dark.

3.5 CONTAMINANT EXTRACTION PROCEDURE

A 6 mL sample was extracted from the reactor bottle and injected into a 10 mL test tube. A 1.5 mL volume of pentane was also injected into the test tube to extract the chloroform from the sample. The test tube was capped and set on a test tube shaker for 5 minutes. This procedure was performed for all of the batch reactors. The extracts were stored in the dark at 4°C until analysis by gas chromatograph (GC).

3.6 CONTAMINANT ANALYSIS

Extracted contaminants were analyzed on a HP 5890 Gas Chromatograph (GC) (Hewlett-Packard Company). Using a micro-syringe, 2 μL of pentane extracts were injected onto a DB-5 fused silica capillary column, with film thickness 0.25 μm, inner diameter 0.25 mm, length 30 m (J & W Scientific, Folsom, CA). Quantification was achieved by comparing relative areas under separated peaks for chloroform standards as well as samples from reactors as recorded by a model 3396 Hewlett-Packard Series II integrator. Injections were made in the split mode (ratio 8.9:1) at an injector temperature of 225°C and a column temperature of 40°C. Helium gas was employed as the carrier gas, with a flow rate of 2.8 mL/min and a column head pressure of 12

psi. The column temperature was held at 40°C for 4 minutes and then ramped at a rate of 15°C/min to a final temperature of 130°C. The gas chromatograph was calibrated with a minimum of three calibration standards for each experiment, and triplicate measurements were made for each sample or standard. The average of the three measures was used.

4.0 RESULTS AND DISCUSSION

4.1 TEST OF AQUIFER SOLIDS FOR BIOLOGICAL ACTIVITY

Preliminary, qualitative experiments were conducted to determine if the aquifer soils would need to be amended with an additional microbial culture. Several reactors were prepared with the landfill aquifer soil, nutrient solution, and trace metal solution. The reactors were visually studied and the tests yielded no significant change from one reactor to another. All reactors were determined to produce gas by inserting a syringe into the reactor and watching the head space of the reactor equalize with the syringe. It was determined to use only the landfill aquifer soil and appropriate nutrients to establish the degrading condition.

4.2 ABIOTIC CONTROLS

Prior to performing the baseline experiments, abiotic controls were tested. Two reactors were prepared, autoclaved, and measured every five days for twenty days. The test was to ensure that the only biological activity occurring in the reactors was due to the landfill leachate microbes. Figure 4.1 shows the concentration of chloroform versus time for the control data Linear plots were fit to the data to establish a reaction rate. The figure shows that there was no activity occurring after the samples had been autoclaved.

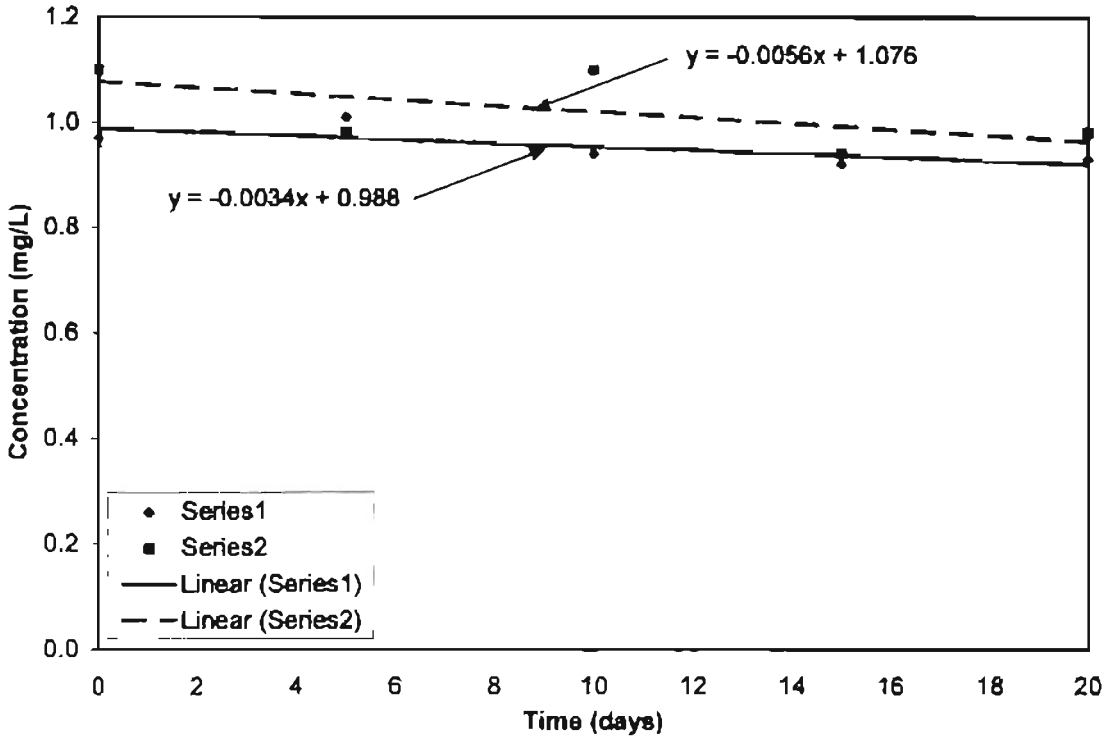


Figure 4.1. Abiotic Control Data for the Chloroform Reactors

4.3 MISCELLANEOUS PLOTS NOT USED FOR COMPARISON

The data generated from this study was plotted many different ways. Percent of chloroform removed versus time and zero-order degradation was examined. For simplicity of comparison, first-order degradation plots were used. Some of the data actually fit a zero-order curve better than a first-order curve, but for consistency first-order was used. First-order was expected from the data and the information in the literature review is given in first-order units.

4.4 BASELINE CHLOROFORM DEGRADATION

The degradation of chloroform was studied under three different conditions: baseline degradation, effects of metals, and effects of additional organics. The different chemicals used for each condition are discussed in the sections below, along with the decay rates calculated. Triplicate sets of soil-water reactors were set up and operated under three electron-accepting conditions: denitrifying, methanogenic, and sulfate reducing. Each reactor was dosed with

100 μg/L (0.84 μM) of chloroform. Initial activity in all such reactors was indicated by the production of gas. All reactors are assumed to have the same amount of bacteria in the sample. While all reactors do not fit "first-order decay" curves perfectly, most of the data were fit to a first-order decay model as well as possible for the sake of comparison.

Baseline degradation is an essential step for the comparison of decay rates. For baseline degradation studies, chloroform alone was subjected to the three conditions. The chloroform was calculated and measured for the desired concentration in each reactor. The reactors were maintained at ambient temperature (approximately 22°C) in the dark and checked periodically for visual signs of bacteria production. Original data and calculated data are presented in Appendix B. Representative data plots are presented below along with discussion. Only three points were presented on each plot for all experiments. A summary table of reaction rates is included at the end of this chapter.

Figure 4.2 shows the baseline degradation of chloroform for three reactors under methanogenic conditions. The data plotted were fit to represent first-order reactions. All three reaction rates were within 10% of each other so the three were averaged to give one representative rate. The averaged rate is 0.76 day^{-1}.

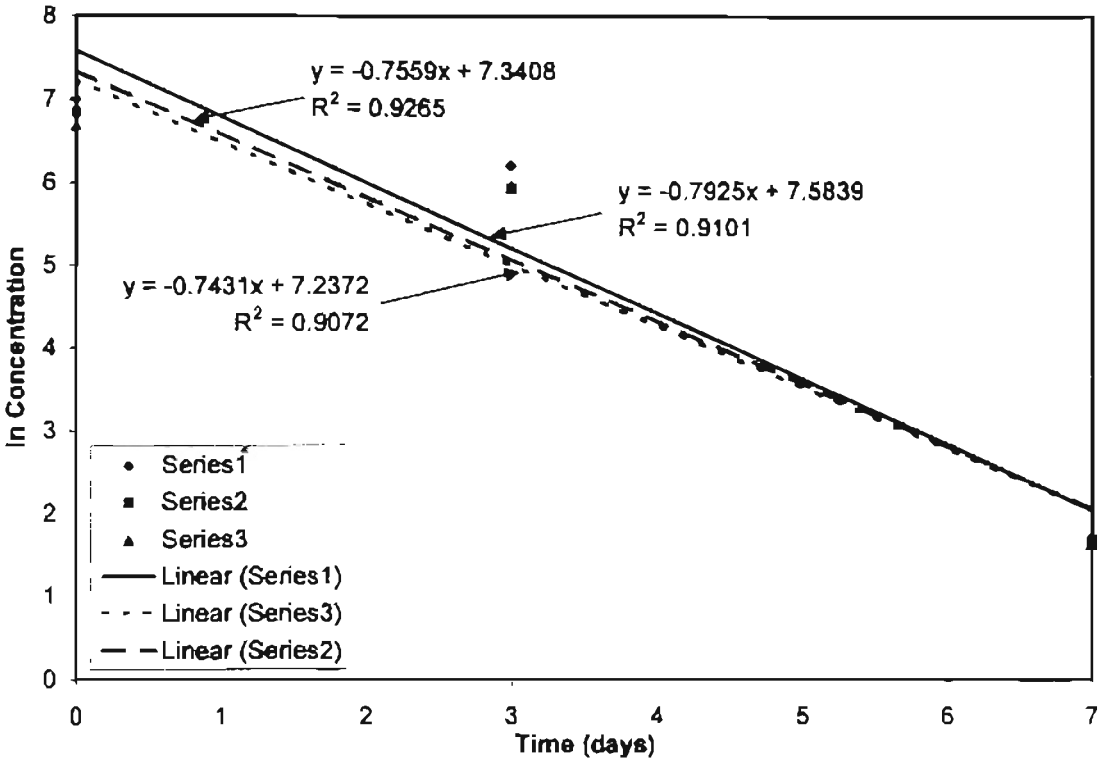


Figure 4.2. Baseline First-Order Methanogenic Degradation of Chloroform

Figure 4.3 represents the baseline degradation of chloroform under denitrifying conditions. The data was plotted to represent a first-order reaction. Series one data was excluded from the results because the reaction rate that it produced was more than 10% lower than the other two. The two reaction rates shown were averaged so a representative reaction rate could be used for the baseline conditions under denitrifying conditions. The averaged reaction rate is 0.65 day^{-1}.

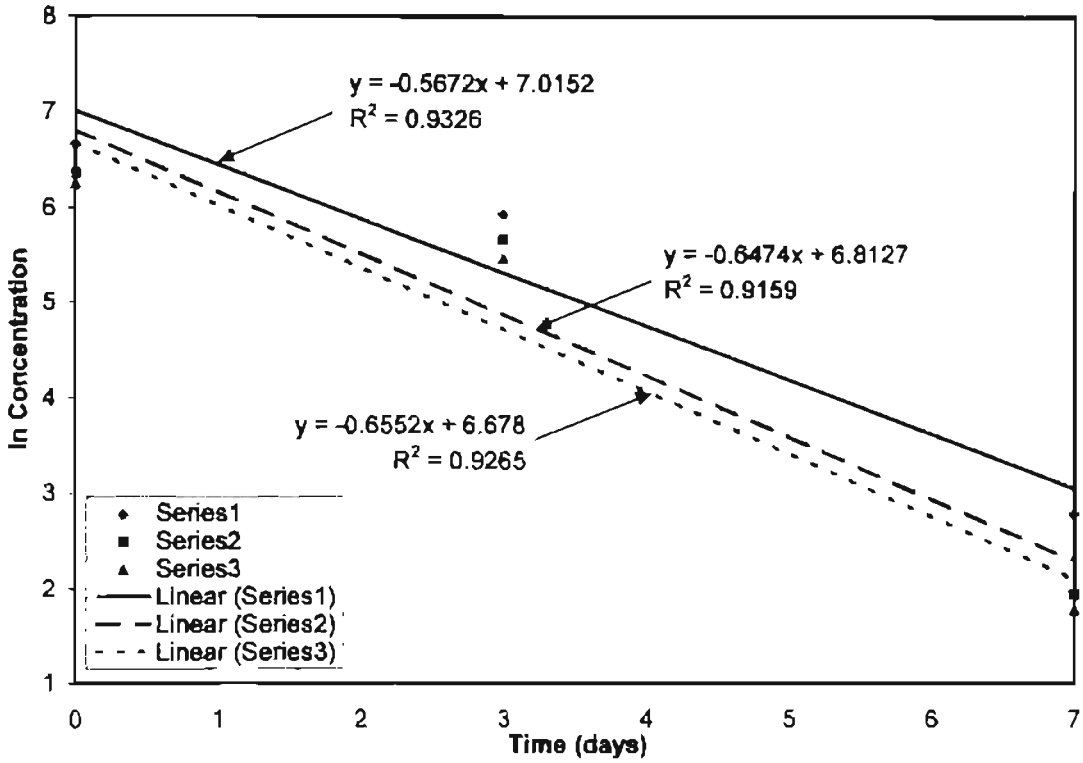


Figure 4.3. Baseline First-Order Denitrifying Degradation of Chloroform

Figure 4.4 represents the baseline degradation of chloroform under sulfate-reducing conditions. The data plotted are fit to represent a first-order reaction. Again, not all three were within 10% of each other, so series three data was excluded from the results. The averaged reaction rate was 1.04 day^{-1}. This corresponds to Gupta et al. (1996a) where he states that chloroform does not inhibit the utilization of the primary substrate in the sulfate-reducing culture. But in this case, the sulfate-reducing culture actually degraded the chloroform faster than the methanogenic and denitrifying cultures. This was not expected due to past experiments demonstrating that methanogenic cultures degrade faster than sulfate-reducing cultures.

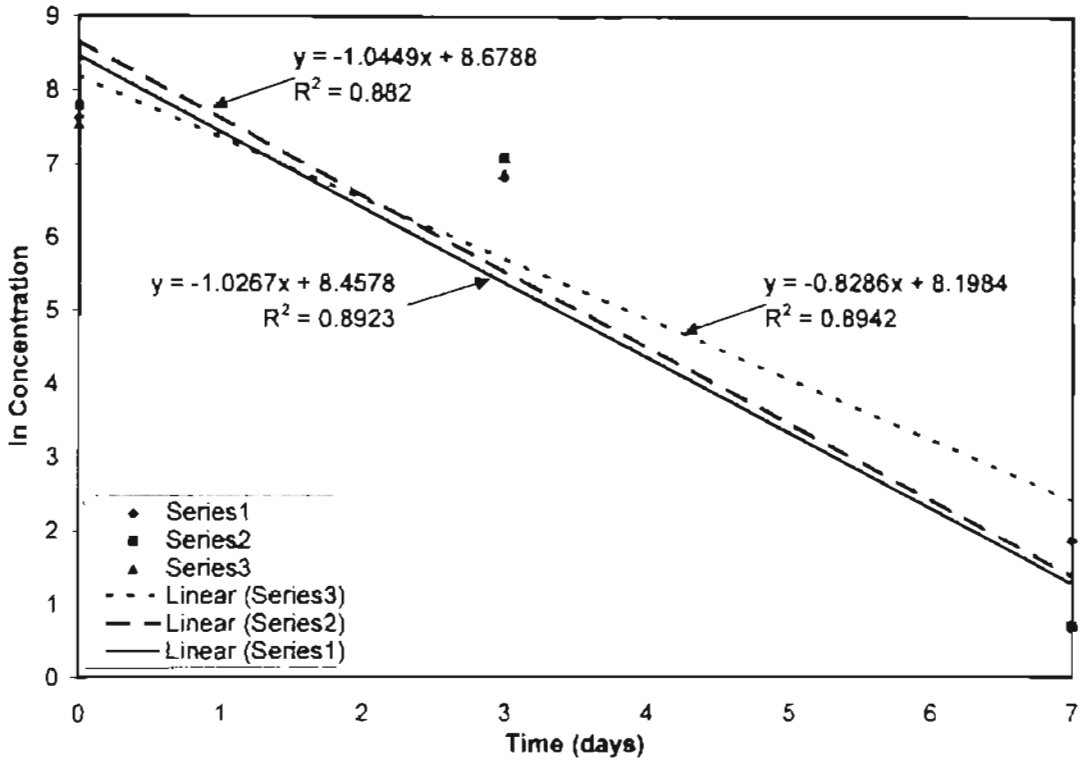


Figure 4.4. Baseline First-Order Sulfate-Reducing Degradation of Chloroform

4.4 EFFECTS OF METALS

Once the baseline studies were completed, experiments were performed with metals introduced with the chloroform. These experiments try to emulate the environment in which chloroform is encountered. Experiments that were performed to study the effects of metals on the chloroform degradation included mixing the chloroform reactors as previously stated and adding known concentrations of nickel, zinc, cadmium, and chromium, first separately and then with the four (4) metals combined in triplicate reactors. These particular metals were selected because they were present in analytical results compiled from the Norman Landfill (see Appendix A) Their concentrations are representative concentrations found in the analytical results of the monitor well samples. Results of experiments conducted to evaluate the effects of metals are presented in Appendix B. A summary table of reaction rates is presented at the end of the chapter

4.4.1 EFFECT OF ZINC

Figure 4.5 shows 100 µg/L (0.84 µM) of chloroform under methanogenic degrading microbes with 150 µg/L (2.29 µM) of zinc added to solution. Series one data was not used for the results since the r^2-value was less than 0.90. Since only two data sets remained for the plot, they were plotted and a first-order reaction curve was fit. Their reaction rates were averaged. The averaged reaction rate is 0.15 day^{-1}.

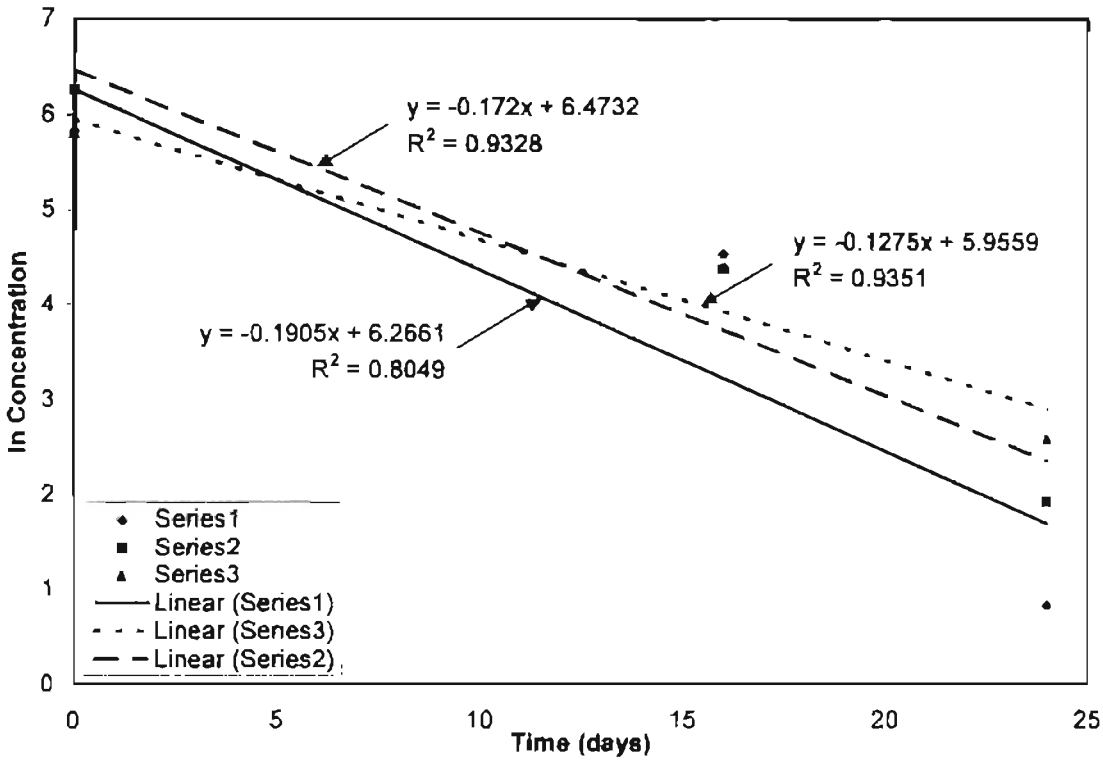


Figure 4.5. Zinc Added First-Order Methanogenic Degradation of Chloroform

Figure 4.6 illustrates the degradation of 100 µg/L (0.84 µM) of chloroform when 150 µg/L (2.29 µM) of zinc is present under denitrifying conditions. The data that are plotted are fit to a first-order reaction curve. Series three data was removed from the results due to the result of the r^2-value being less than 0.90. The reaction rates for the curves plotted were averaged and the averaged reaction is 0.11 day^{-1}.

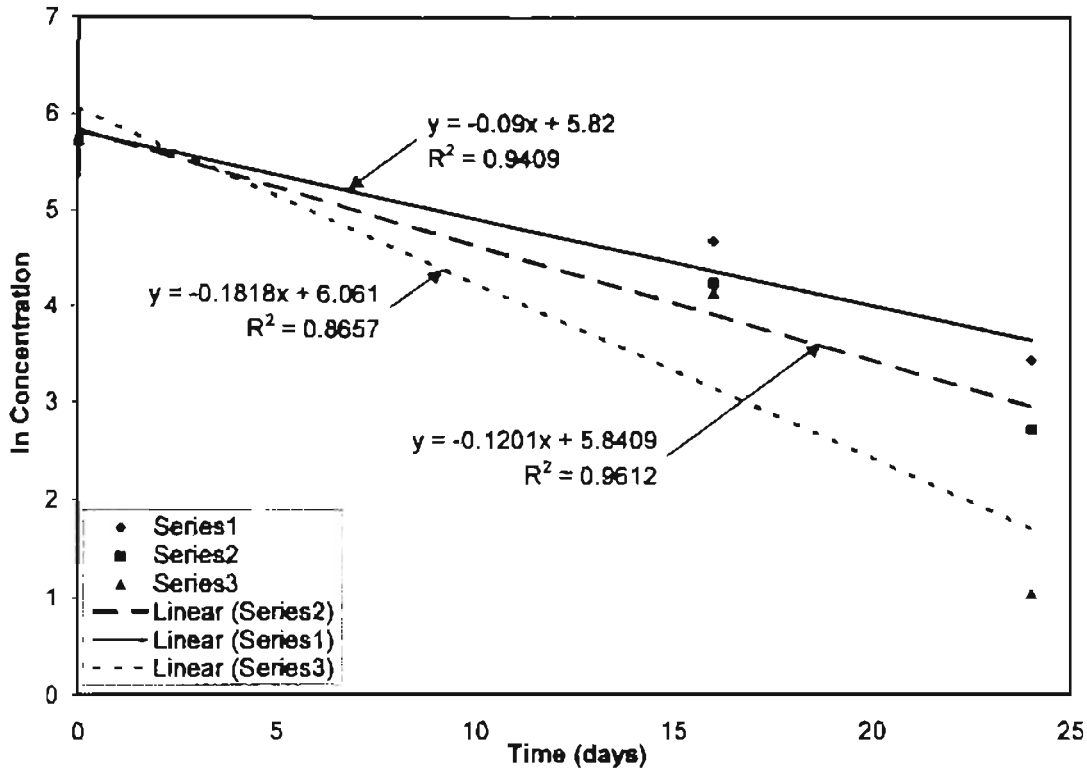


Figure 4.6. Zinc Added First-Order Denitrifying Degradation of Chloroform

Figure 4.7 demonstrates 100 µg/L (0.84 µM) of chloroform degradation under sulfate-reducing conditions with the addition of 150 µg/L (2.29 µM) of zinc. The data plotted on the chart were fit to a first-order reaction. Series two data was removed from the results because it clearly differed from the other data plots. Series one data was used for the results even though the r^2-value resulted in a value less than 0.90 because series one data and series data three data were very similar in plotted results. A possibility for this could have been a lack of sufficient amount of bacteria in the reactor. The two remaining reaction rates were averaged for a representative value. The averaged rate is 0.15 day^{-1}.

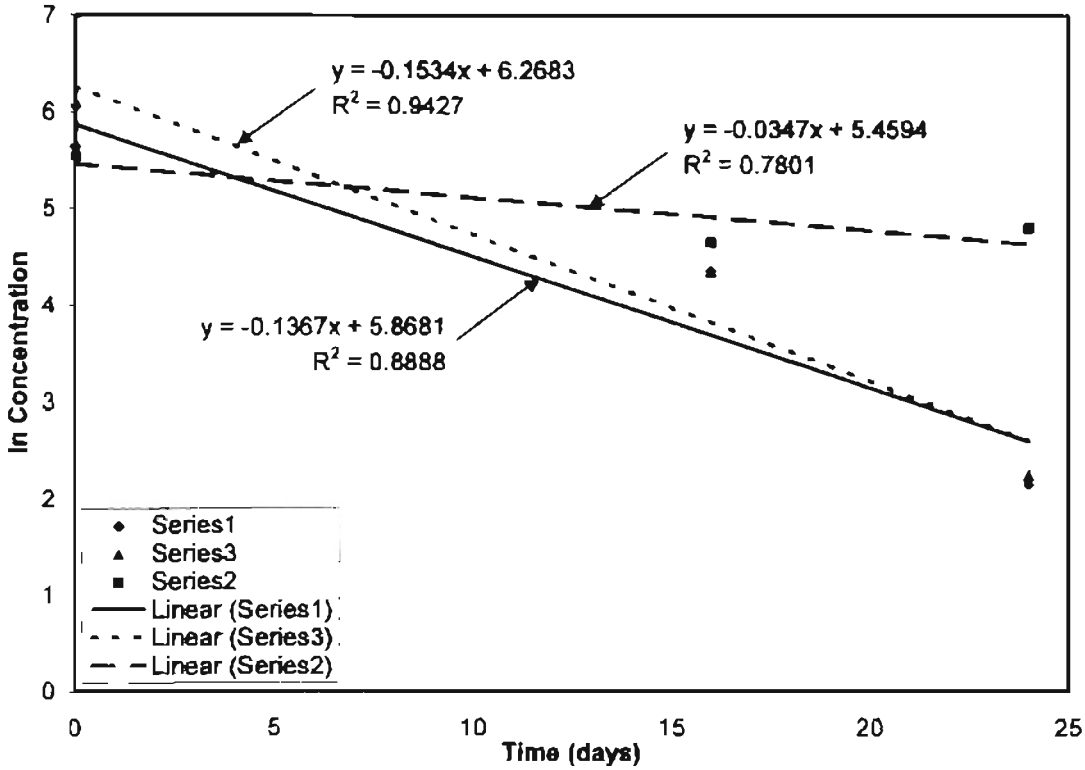


Figure 4.7. Zinc Added First-Order Sulfate-Reducing Degradation of Chloroform

The degradation rates for zinc added to the reactors were considerably lower than the baseline degradation rates. The rates did follow the order that was expected from highest to lowest degradation rates. Methanogenic was the fastest, sulfate-reducing second, and denitrifying third. Zinc was expected to slightly inhibit the degradation of the chloroform, but this is a significant reduction in degradation.

4.4.2 EFFECT OF NICKEL

Nickel is another metal found in typical landfills. Past research has found nickel to be toxic to degrading bacteria. Figures 4.8, 4.8, and 4.10 represent 130 µg/L (2.22 µM) of nickel added to reactors that 100 µg/L (0.84 µM) of chloroform is being degraded by methanogenic, denitrifying, and sulfate-reducing cultures, respectively. All data were plotted to fit first-order reactions for comparison. Figure 4.8 uses only one data set for the results because series one and two data

plotted increasing amounts of chloroform. This result is not expected to occur so the data is not used in the results. Figure 4.9 illustrates only one data set because series two and three data have r^2-values well below 0.90. The other data was used because it was considered more reproducible and reliable. Figure 4.10 utilizes two data sets for the results because series two data's r^2-value was below 0.90. The representative reaction rates are 0.05 day^{-1}, 0.15 day^{-1}, and 0.12 day^{-1} for methanogenic, denitrifying, and sulfate-reducing bacteria, respectively.

The reaction rates again were considerably lower than the baseline rates. Slight inhibition of degradation was expected with the presence of nickel. Francis et al. (1996) found that nickel released in the culture medium was toxic to the bacterium and did not allow the bacterium to completely degrade nickel-citrate. Their experiments showed that when nickel was not present, 70% of nickel-citrate was degraded. When 0.10 and 0.20 mM of nickel was present, only 46% and 29% of the citric acid was degraded. Anything over 0.20 mM of nickel was observed to have not degradation. With the reaction rates for this experiment, the nickel could be affecting what bacteria was in the reactors and causing the rate to decrease.

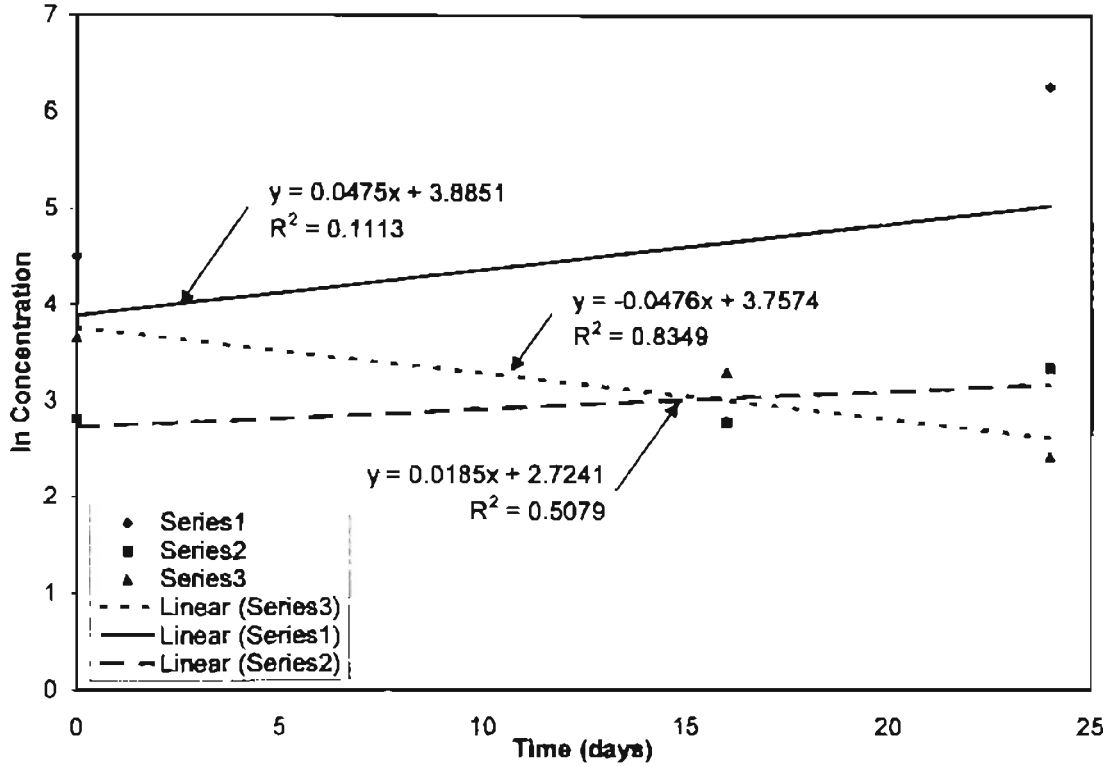


Figure 4.8. Nickel Added First-Order Methanogenic Degradation of Chloroform

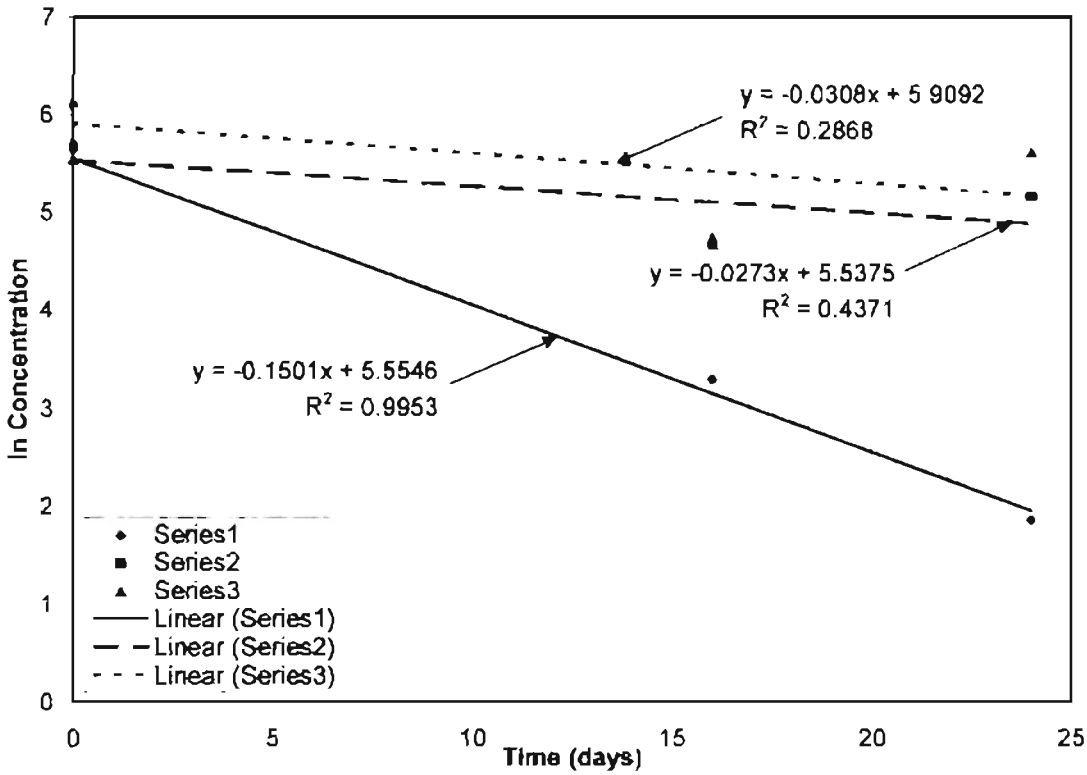


Figure 4.9. Nickel Added First-Order Denitrifying Degradation of Chloroform

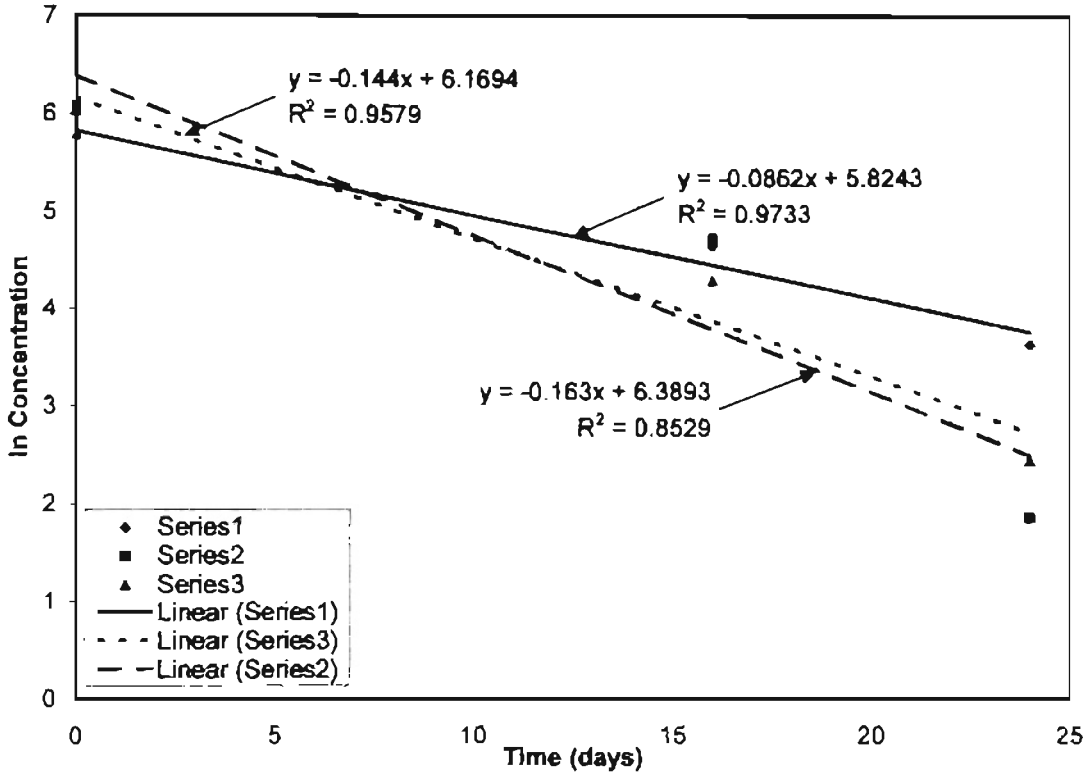


Figure 4.10. Nickel Added First-Order Sulfate-Reducing Degradation of Chloroform

4.4.3 EFFECT OF CADMIUM

Cadmium was used in this set of experiments to show how a typical metal from a landfill can affect the degradation of chloroform. Figures 4.11, 4.12, and 4.13 show the addition of 30 µg/L (0.27 µM) of cadmium in reactors where 100 µg/L (0.84 µM) of chloroform is being degraded by methanogenic, denitrifying, and sulfate-reducing bacteria, respectively. The data were plotted to fit a first-order reaction. Only one data set was used in Figure 4.11 because series two plotted a flat line that represents no biological activity and regardless of the fact that the other data sets r^2-values are less than 0.90, series one data has an r^2-value closer to 0.90. Figure 4.13 also has only one data set used in the results because series two data plots a flat line and series one data plots an increasing amount of chloroform over time. Figure 4.12 two data plots were used because the other data set more than 10% lower than the other two. The representative reaction

reactions rates for the methanogenic, denitrifying, and sulfate-reducing bacteria were 0.14 day^{-1}, 0.15 day^{-1}, and 0.13 day^{-1}, respectively.

Slight inhibition to the degradation was expected with the addition of cadmium. Sandrin et al. (2000) and Malakul et al. (1998) found as the cadmium concentration increased, it inhibited the growth of the bacterium until complete inhibition resulted. In the Sandrin et al. (2000) experiments, with the presence of 8.90 µM cadmium, delay of exponential growth was beginning to occur. At 45, 89, and 450 µM concentrations, the bacterium was completely inhibited. Malakul et al. (1998) found that cadmium has no affect on the growth of bacteria at concentrations less than 10 ppm. Inhibition of growth on the bacteria was first noticed at 10 ppm and complete inhibition was observed at a cadmium concentration of 170 ppm.

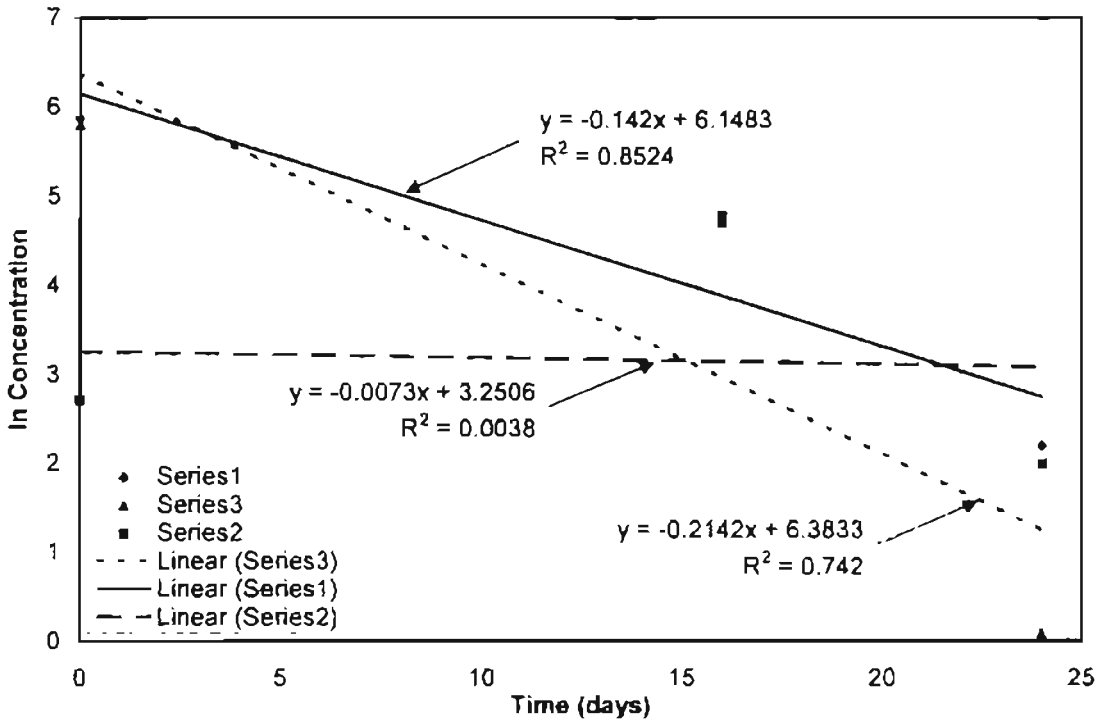


Figure 4.11. Cadmium Added First-Order Methanogenic Degradation of Chloroform

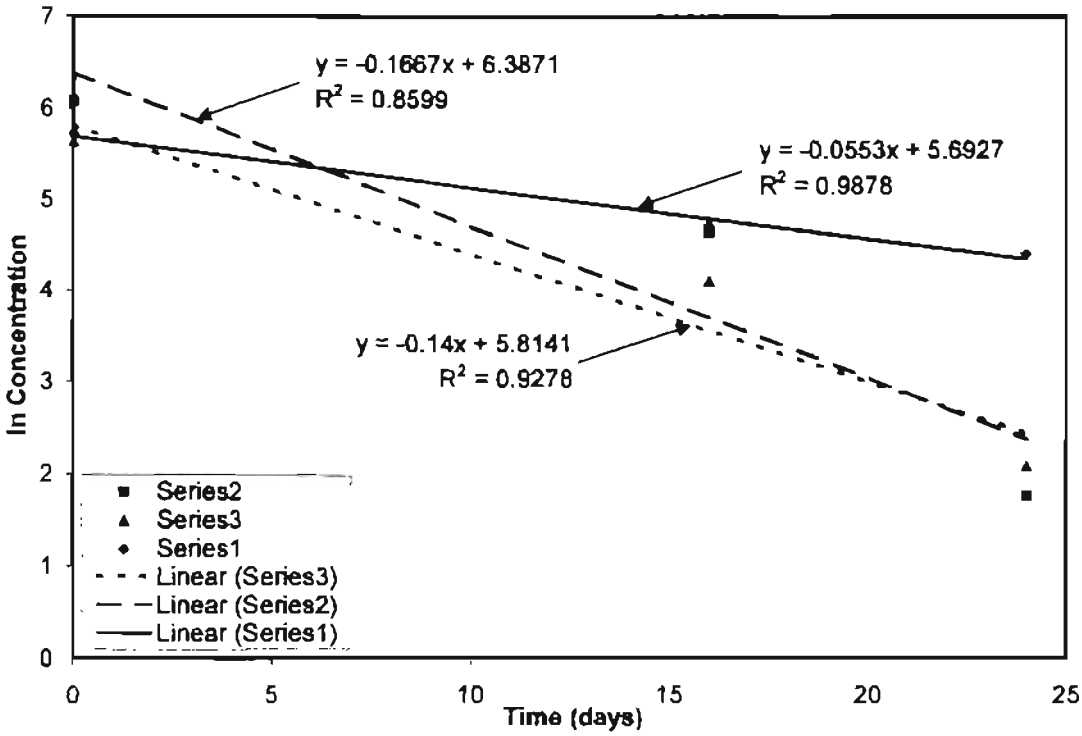


Figure 4.12. Cadmium Added First-Order Denitrifying Degradation of Chloroform

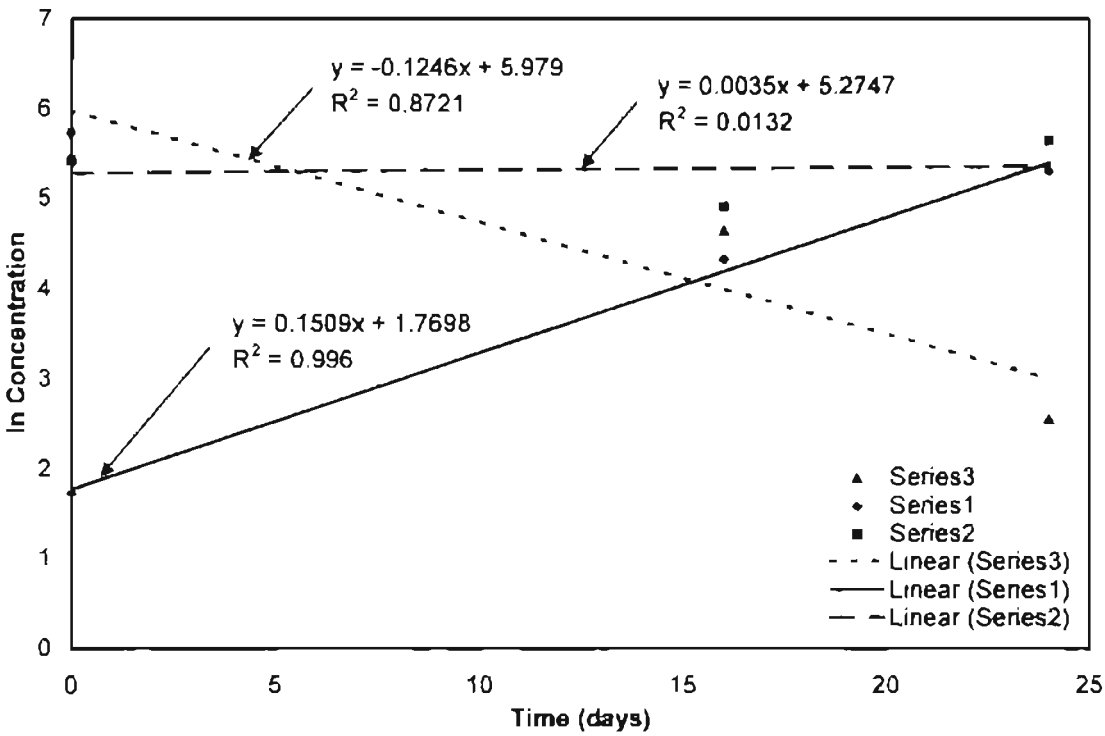


Figure 4.13. Cadmium Added First-Order Sulfate-Reducing Degradation of Chloroform

4.4.4 EFFECT OF CHROMIUM

Chromium is abundant in the Norman landfill. It is important to test the effects of chromium on the degradation of chloroform. 460 µg/L (8.85 µM) of chromium was added to the 100 µg/L (0.84 µM) of chloroform reactors with methanogenic, denitrifying, and sulfate-reducing bacteria. The data are plotted in figures 4.14, 4.15, and 4.16, respectively. The data was plotted to fit first-order reactions for comparison purposes. Only one data set was plotted for figure 4.14 because series two and three plotted a curve showing the chloroform increasing in the reactor. Figure 4.15 used two data sets because series two plotted an increase reaction rate. Figure 4.16 used only the series three data because the r^2-value was the closest to 0.90. This data was used because it was deemed more reproducible and reliable. The representative reaction rates for the methanogenic, denitrifying, and sulfate-reducing cultures are 0.14 day^{-1}, 0.13 day^{-1}, and 0.17 day^{-1}, respectively.

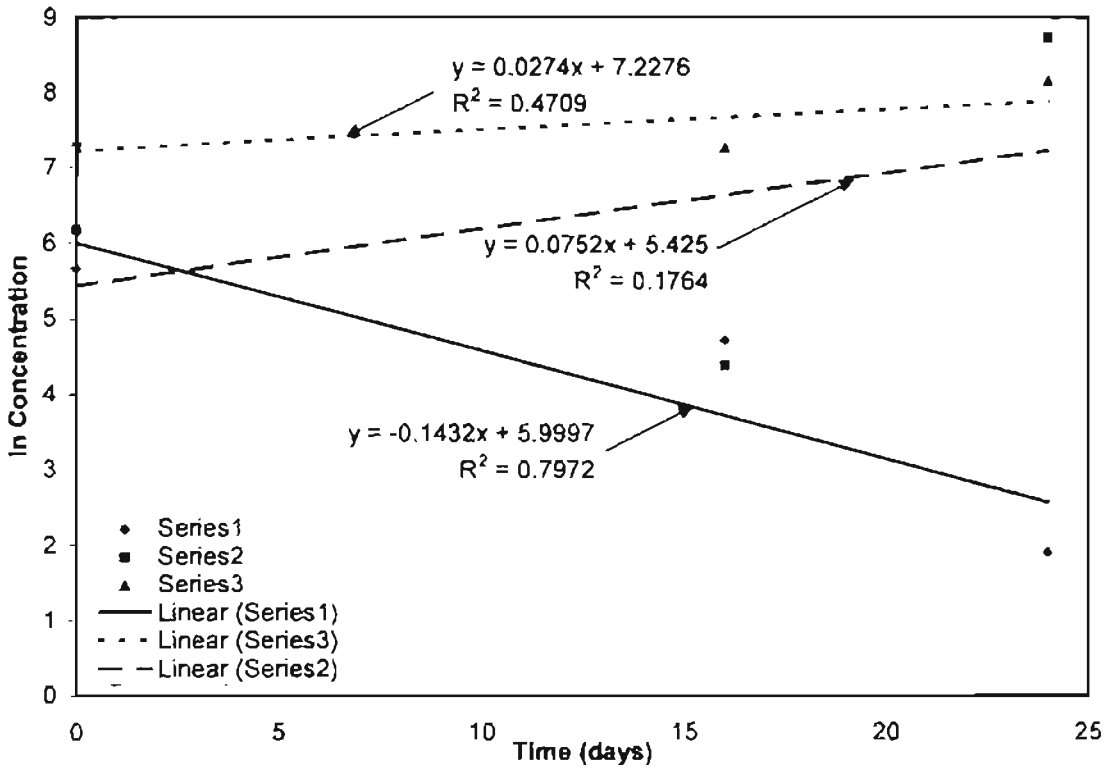


Figure 4.14. Chromium Added First-Order Methanogenic Degradation of Chloroform

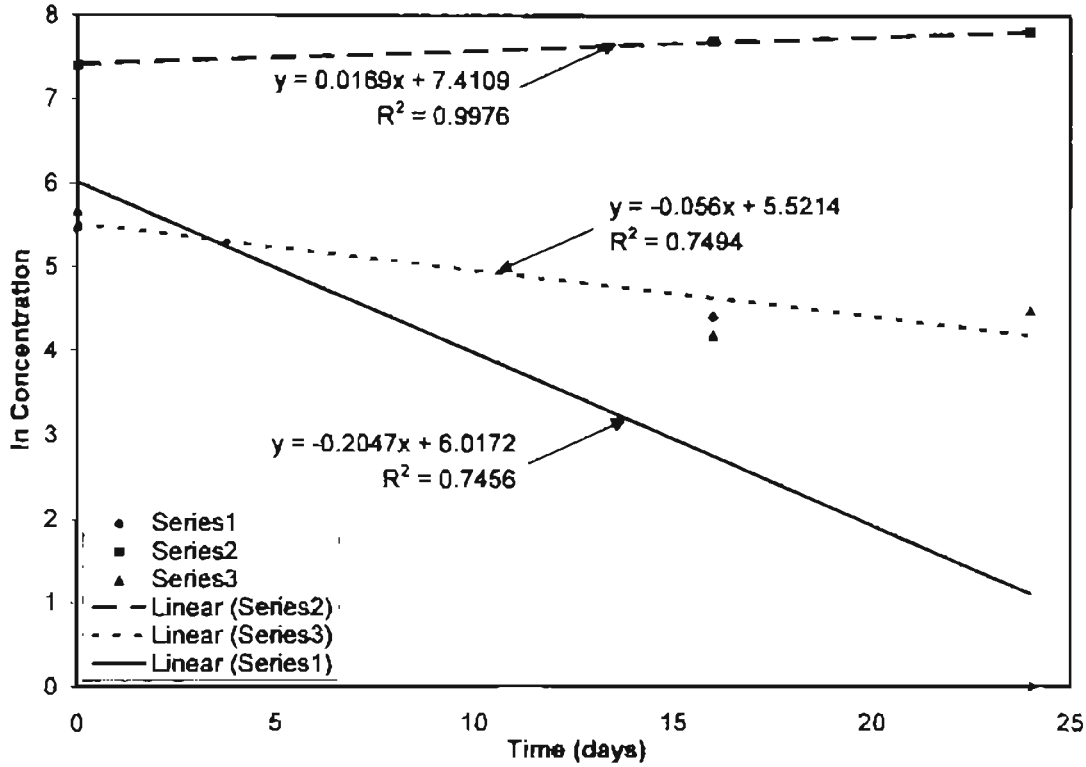


Figure 4.15. Chromium Added First-Order Denitrifying Degradation of Chloroform

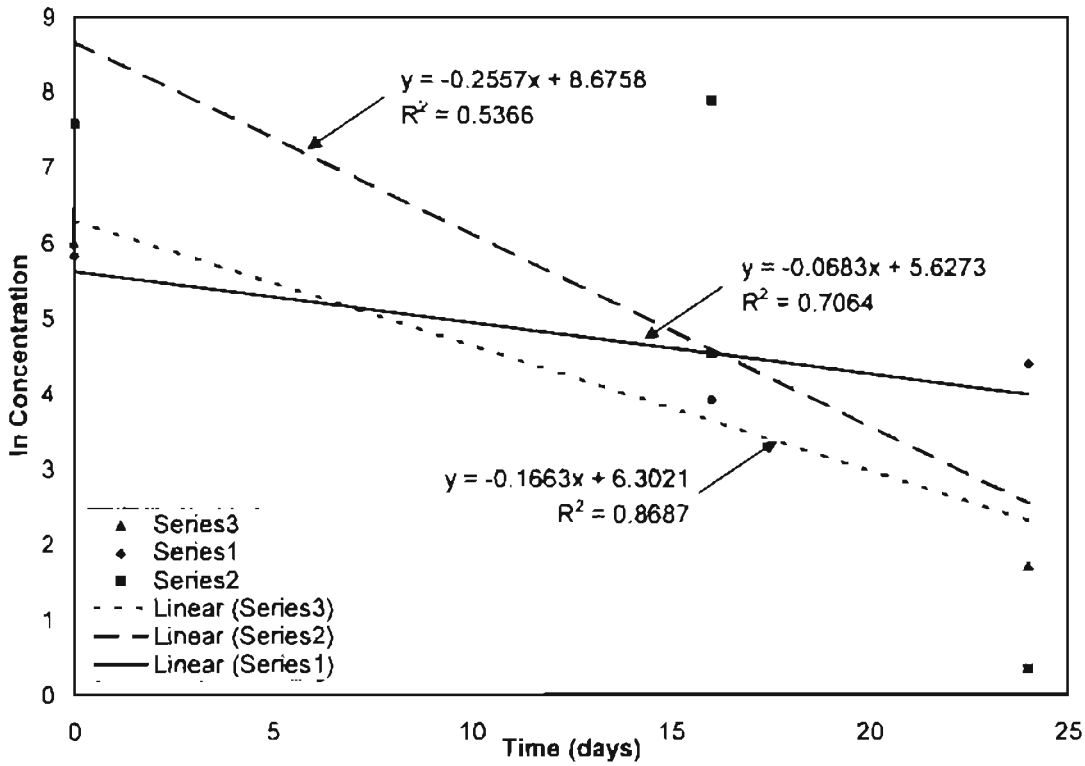


Figure 4.16. Chromium Added First-Order Sulfate-Reducing Degradation of Chloroform

4.4.5 EFFECT OF COMBINED METALS

The effect of all of the previously studied metals on the degradation of chloroform is important to demonstrate since the "real world" application of this study will incorporate many metals affecting the degradation of chloroform. This set of reactors mixed 190 μg/L (0.66 μM) of combined zinc, nickel, cadmium, and chromium with 100 μg/L (0.84 μM) of chloroform degrading under methanogenic, denitrifying, and sulfate-reducing bacteria. The data plotted from each set was fit to a first-order reaction curve. Figures 4.17, 4.18, and 4.19 represent the effect of the combined metals on the degradation of chloroform under methanogenic, denitrifying, and sulfate-reducing bacteria, respectively. Series one data was omitted from the results obtained from figure 4.17 because the data plotted the chloroform increasing over time. Only series two data was utilized for figure 4.18 results, the other two were removed because their r^2-values fell below 0.90. Figure 4.19 omitted series two data because it resulted in an increasing reaction rate. Figures 4.17 and 4.19 averaged the two reaction rates from the plots to obtain a representative reaction rate. The reaction rates are 0.12 day^{-1}, 0.14 day^{-1}, 0.11 day^{-1} for methanogenic, denitrifying, and sulfate-reducing cultures, respectively.

The toxicity of the combination of metals was expected to exceed those of the single metals. The toxicity for the sulfate-reducing bacteria seemed to be cumulative, which is what was expected. The reaction rate for the methanogenic case was lower than all of the reaction rates separately except for nickel. The reaction rate for the denitrifying case was lower than all of the reaction rates separately except for zinc and chromium. It was assumed that the amount of bacteria in all of the reactors did not vary. If the bacteria amount differed, this could be a reason why the reaction rates for a some of the reactors were less than the combined metals reaction rates.

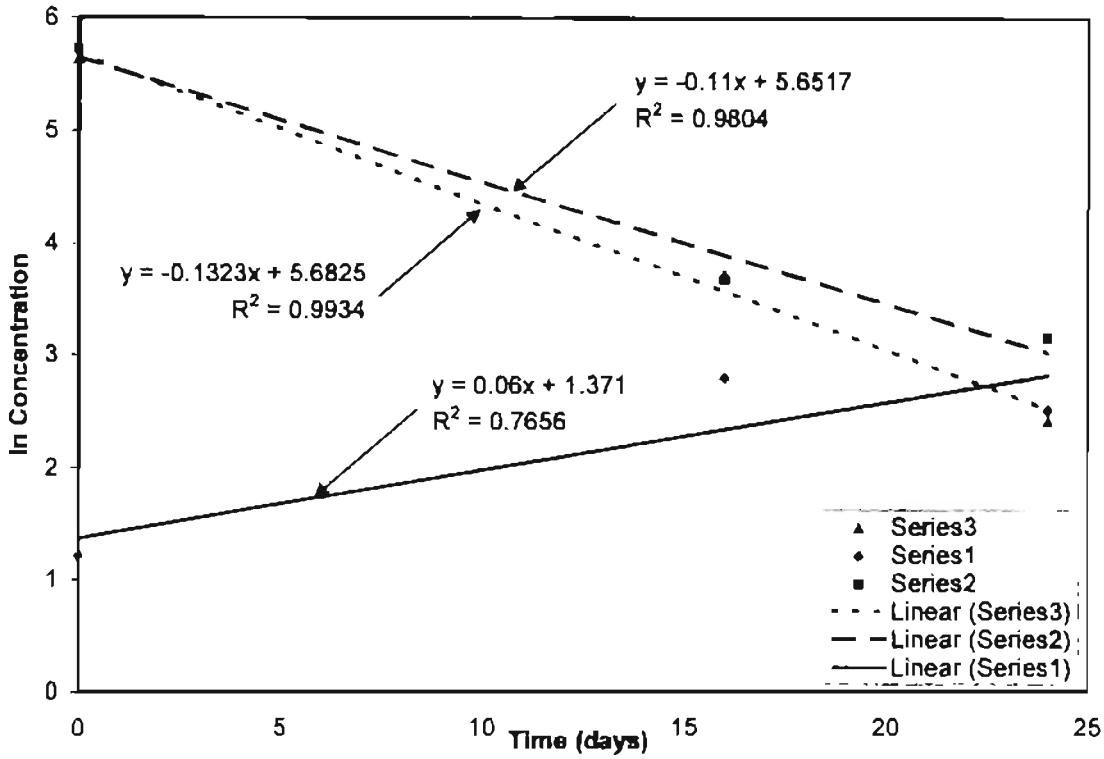


Figure 4.17. Combined Metals Added First-Order Methanogenic Degradation of Chloroform

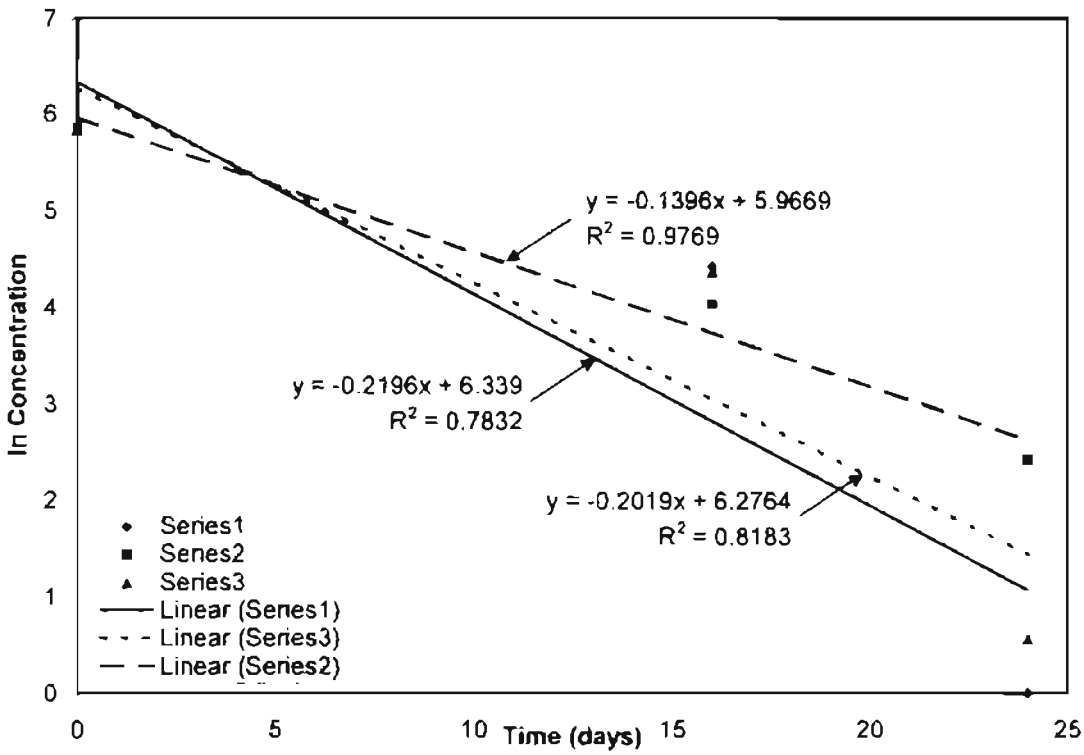


Figure 4.18. Combined Metals Added First-Order Denitrifying Degradation of Chloroform

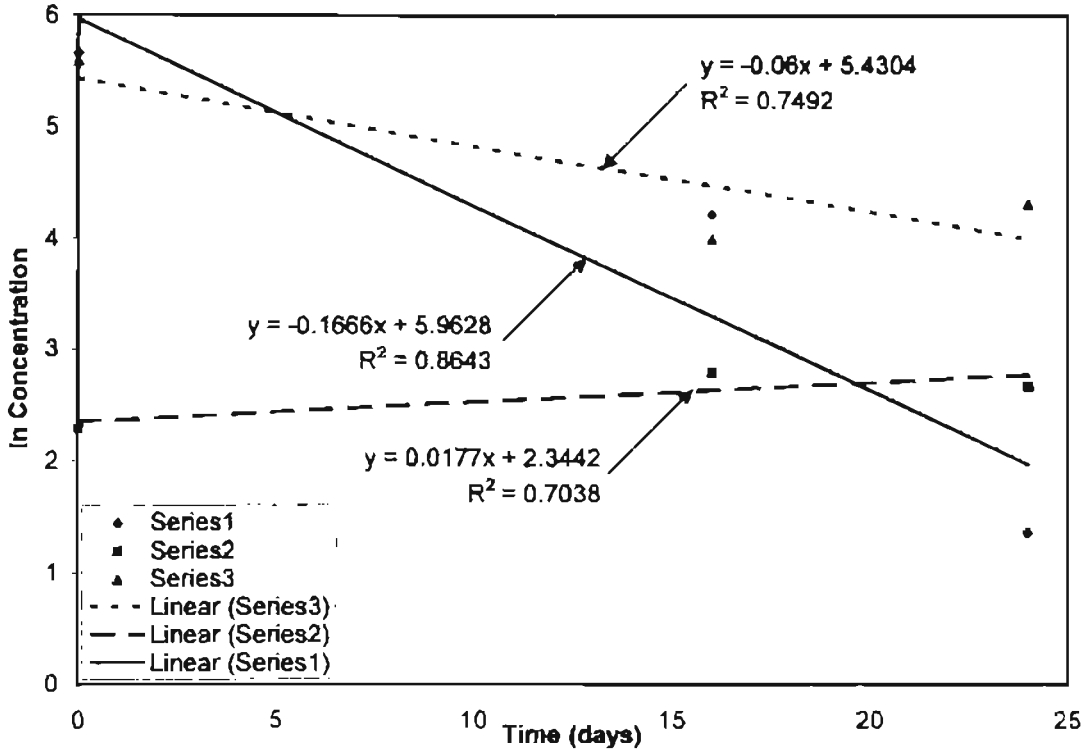


Figure 4.19. Combined Metals Added First-Order Sulfate-Reducing Degradation of Chloroform

4.5 EFFECTS OF ADDITIONAL ORGANICS

To understand how other organics affect the degradation of chloroform, this study incorporated organics taken from typical landfills. These experiments mixed ethylbenzene, decahydronapthalene, 2,2,4-trimethylpentane separately and then with all three (3) chemicals combined in triplicate reactors. Also, to see how another chlorinated organic would affect the degradation of chloroform, para-dichlorobenzene and chloroform were analyzed together. The concentration of para-dichlorobenzene was varied from 60 µg/L (0.41 µM) to 500 µg/L (3.40 µM), in two different experiments, while maintaining chloroform at 100 µg/L (0.84 µM). These particular organics were selected because they were present on the analytical results compiled from the Norman Landfill (see Appendix A). Their concentrations are representative concentrations found in the analytical results of the monitor well samples. Raw data for

experiments conducted to evaluate effects of additional organics are presented in Appendix B. A summary table of reaction rates is presented at the end of this chapter.

4.5.1 EFFECT OF ETHYLBENZENE

Ethylbenzene was chosen for this study because it is a common organic found in typical landfills. Figure 4.20 illustrates 100 µg/L (0.84 µM) of chloroform under methanogenic degrading conditions with 50 µg/L (0.47 µM) of ethylbenzene added to the reactor. Only series two data was utilized for the results because the other two data sets' r^2-values were below 0.90. The representative reaction rate is 0.15 day^{-1}.

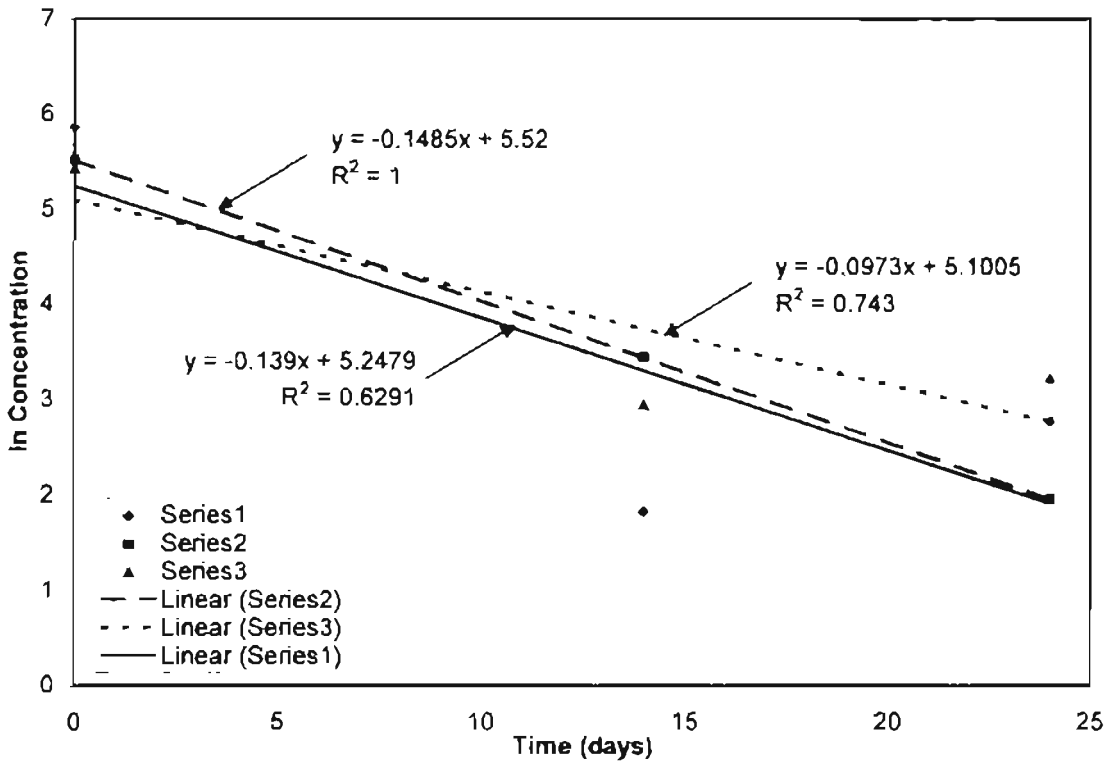


Figure 4.20. Ethylbenzene Added First-Order Methanogenic Degradation of Chloroform

Figure 4.21 demonstrates the effect of ethylbenzene on the degradation of chloroform under denitrifying conditions. The data curves were fit to a first-order reaction. Series one data was omitted from the results because the other two two data sets were deemed more reliable and reproducible. The two reaction rates were averaged for a representative reaction rate. The average reaction rate is 0.12 day^{-1}.

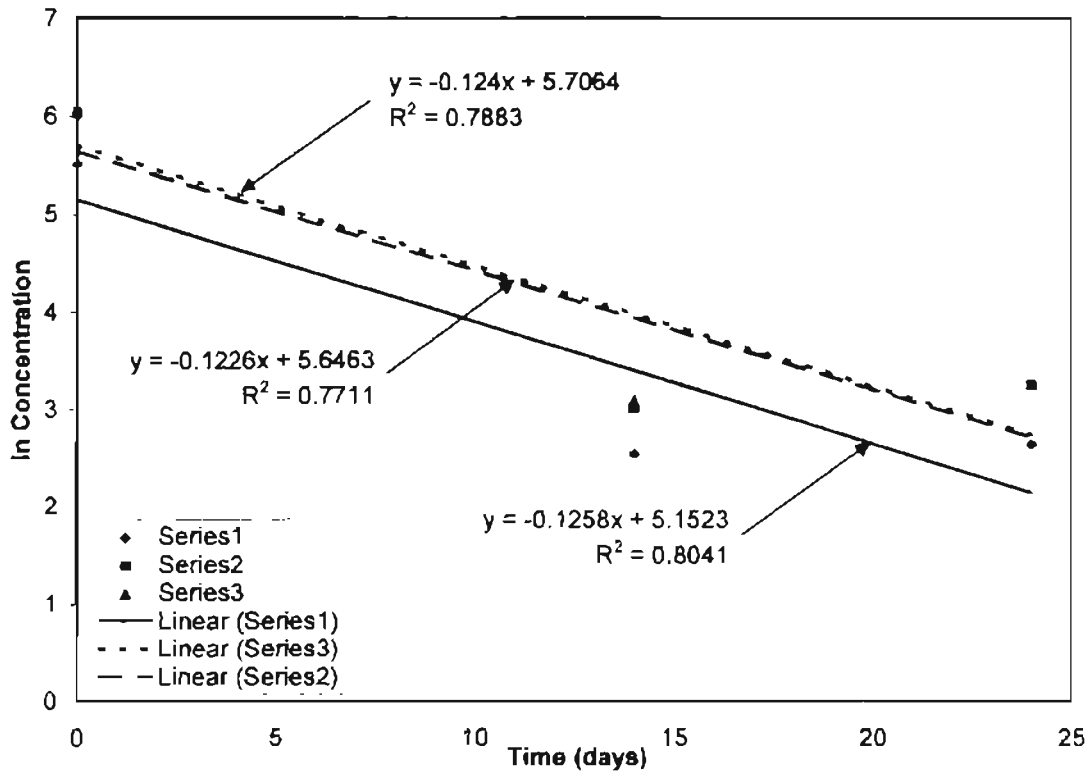


Figure 4.21. Ethylbenzene Added First-Order Denitrifying Degradation of Chloroform

Figure 4.22 is a plot of the degradation of chloroform by sulfate-reducing bacteria with ethylbenzene added to the reactor. The data were fit to first-order reaction rates. The three reaction rates were averaged to obtain a representative value The representative value is 0.13 day^{-1}.

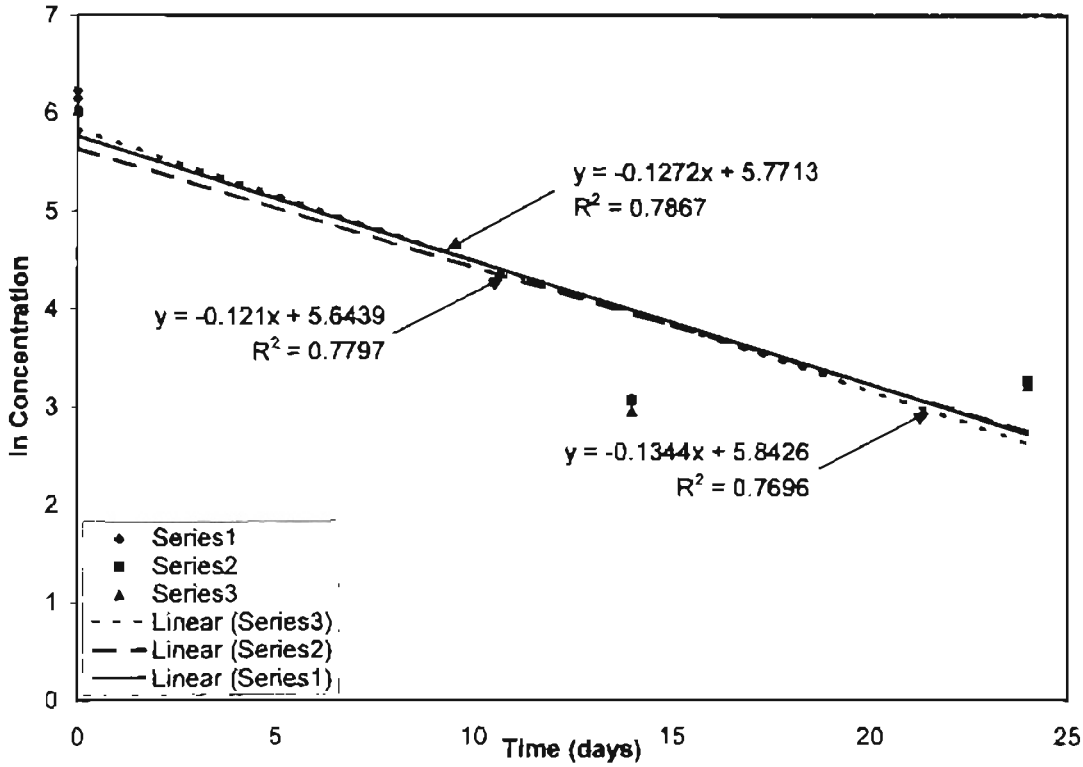


Figure 4.22. Ethylbenzene Added First-Order Sulfate-Reducing Degradation of Chloroform

4.5.2 EFFECT OF DECAHYDRONAPTHALENE

Decahydronapthalene is another organic contained in the list of contaminants found in typical landfills (Appendix A). Figures 4.23, 4.24, and 4.25 contain data that show the degradation of 100 μg/L (0.84 μM) of chloroform with the addition of 50 μg/L (0.36 μM) of decahydronapthalene in the reactors under methanogenic, denitrifying, and sulfate-reducing cultures, respectively. The data plotted were fit to a first-order reaction so comparisons between experiments could be performed. Both figures 4.23 and 4.24 omitted series one data because the other two data sets were deemed more reproducible and reliable. Figure 4.25 used only series two data because the other r^2-values from the other data sets fell below 0.90. Figures 4.23 and 4.24 averaged the reaction rates to establish a representative reaction rate for the plots. The representative reaction rates are 0.10 day^{-1}, 0.09 day^{-1}, and 0.16 day^{-1} for methanogenic, denitrifying, and sulfate-reducing cultures, respectively.

The methanogenic and denitrifying culture reaction rates were the lowest rates out of all of the organics tested, while the sulfate-reducing bacteria was the fastest of the non-chlorinated organics. The reaction rates for the methanogenic and denitrifying cultures are an order of magnitude lower than the other reaction rates. A likely explanation for this is that the reactors may have been contaminated during the testing process.

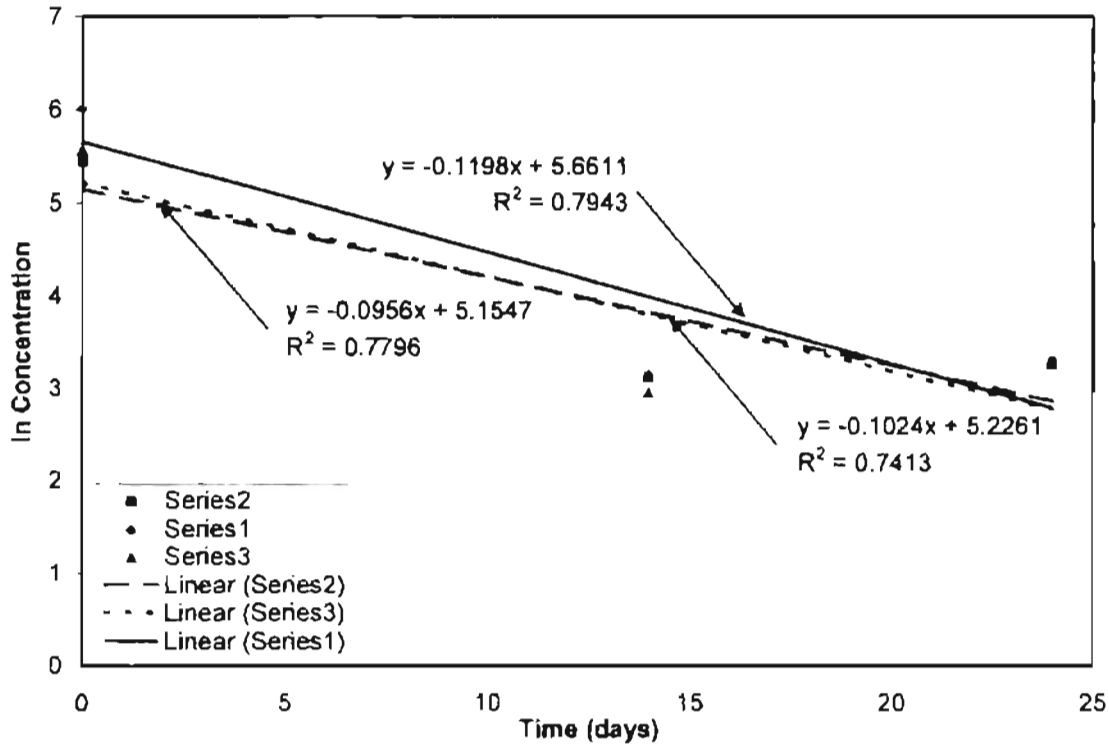


Figure 4.23. Decahydronapthalene Added First-Order Methanogenic Degradation of Chloroform

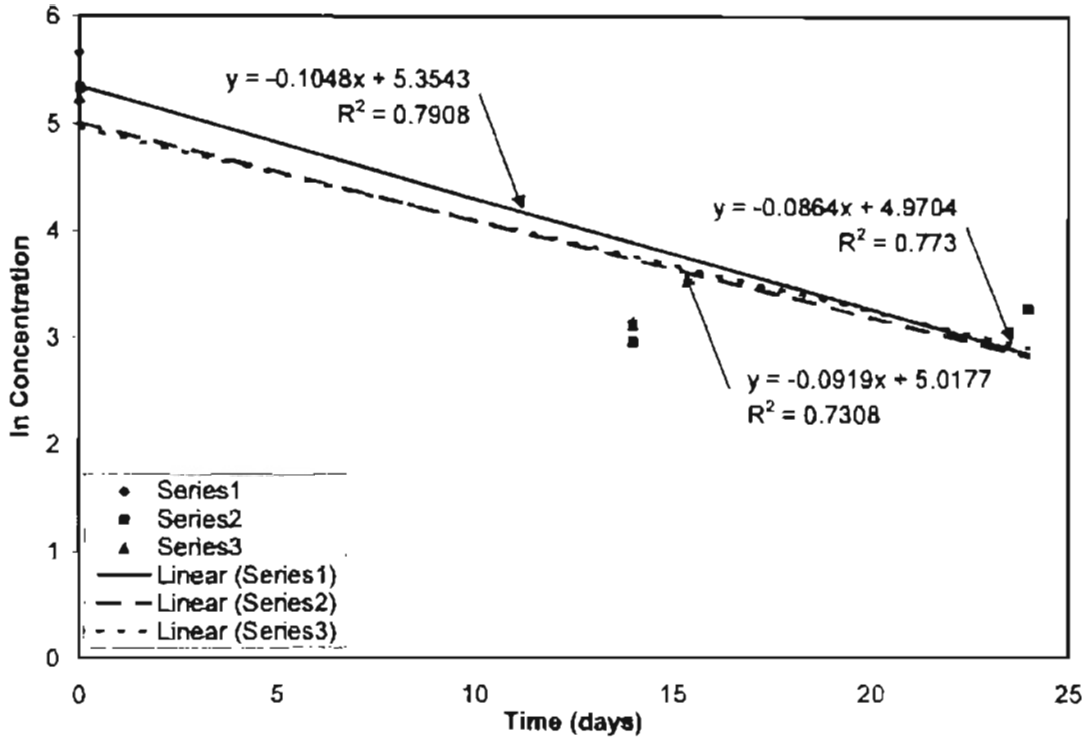


Figure 4.24. Decahydronapthalene Added First-Order Denitrifying Degradation of Chloroform

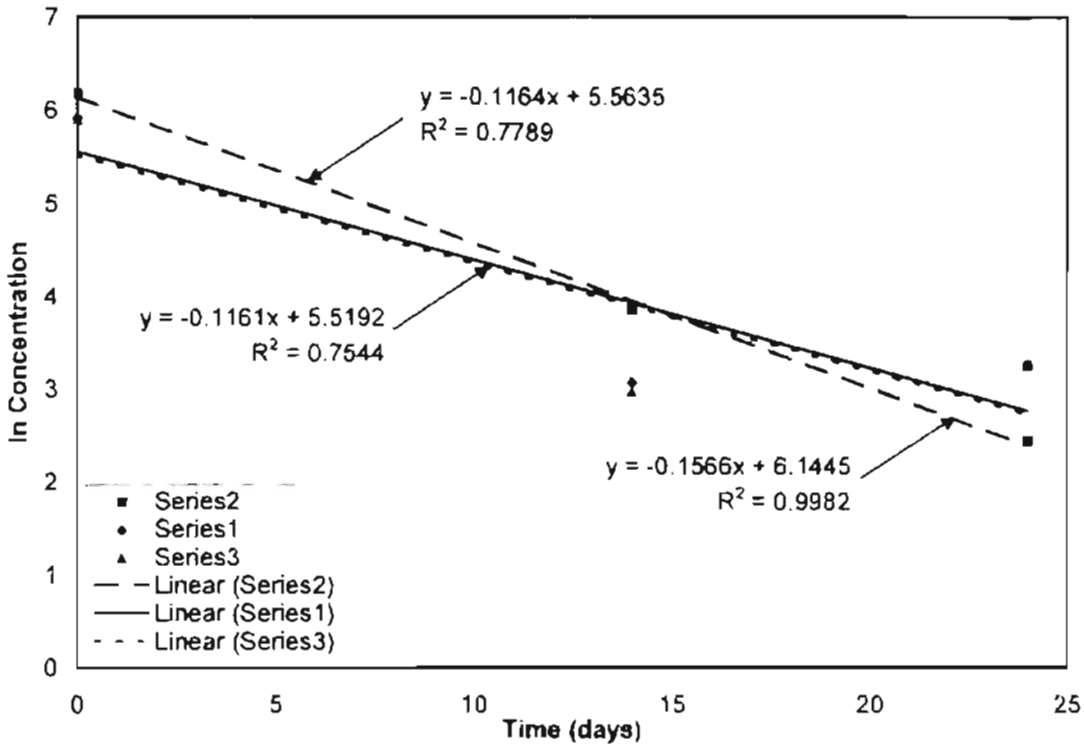


Figure 4.25. Decahydronapthalene Added First-Order Sulfate-Reducing Degradation of Chloroform

4.5.3 EFFECT OF 2,2,4-TRIMETHYLPENTANE

Degradation of 100 μg/L (0.84 μM) of chloroform under methanogenic, denitrifying, and sulfate-reducing conditions with the addition of 50 μg/L (0.44 μM) of 2,2,4-trimethylpentane is presented in figures 4.26, 4.27, and 4.28, respectively. The data were fit to a first-order reaction for comparison purposes. Figures 4.26 omitted series one data because it's r^2-value fell below 0.90. Figure 4.27 omitted series one and two data because their r^2-values were below 0.90. Figure 4.28 omitted series two data because the other two data sets were deemed more reliable and reproducible. The reaction rates were averaged on figure 4.26 and 4.28 to obtain one representative reaction rate. The reaction rates are 0.19 day^{-1}, 0.19 day^{-1}, and 0.12 day^{-1} for methanogenic, denitrifying, and sulfate-reducing cultures, respectively.

The reaction rates for the methanogenic and denitrifying were nearly identical, while the sulfate-reducing reaction rate was somewhat lower. The reaction rates for the methanogenic and denitrifying bacteria were the highest of the organics that were tested.

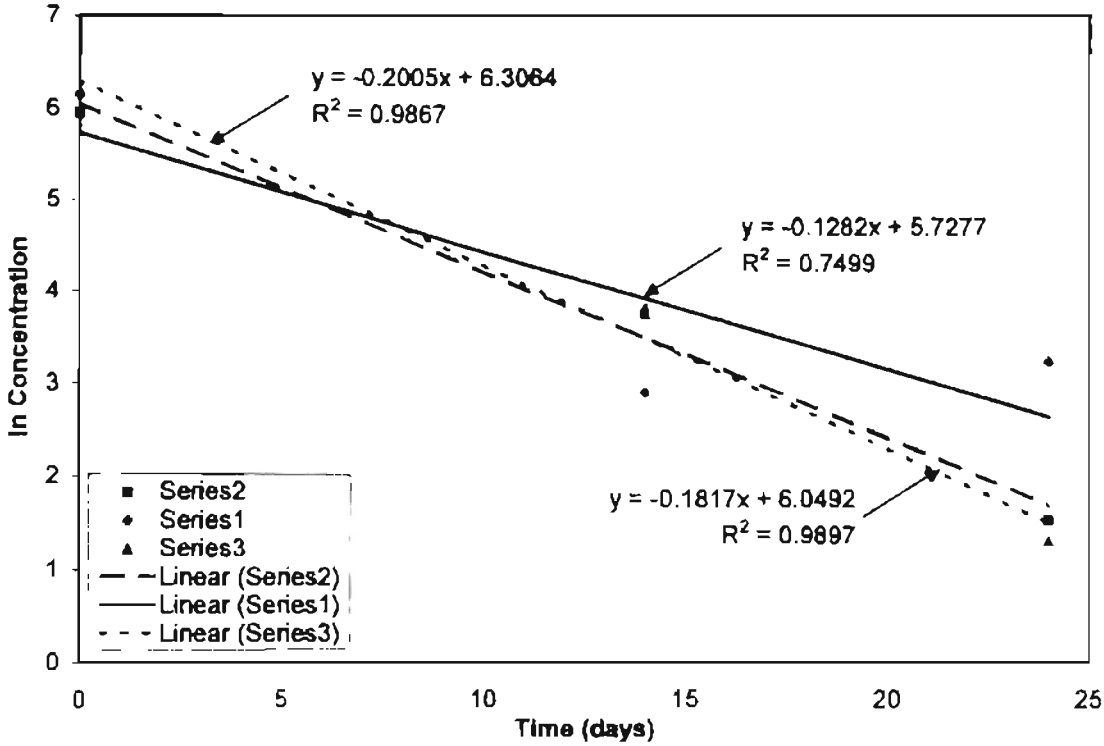


Figure 4.26. 2,2,4-Trimethylpentane Added First-Order Methanogenic Degradation of Chloroform

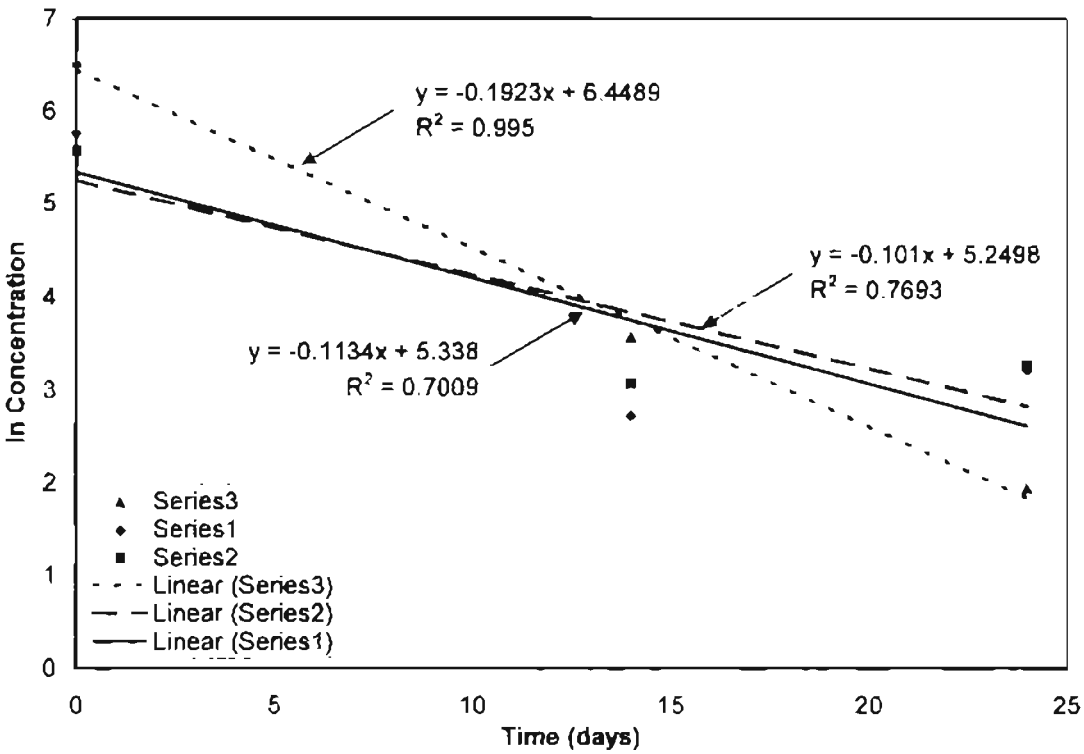


Figure 4.27. 2,2,4-Trimethylpentane Added First-Order Denitrifying Degradation of Chloroform

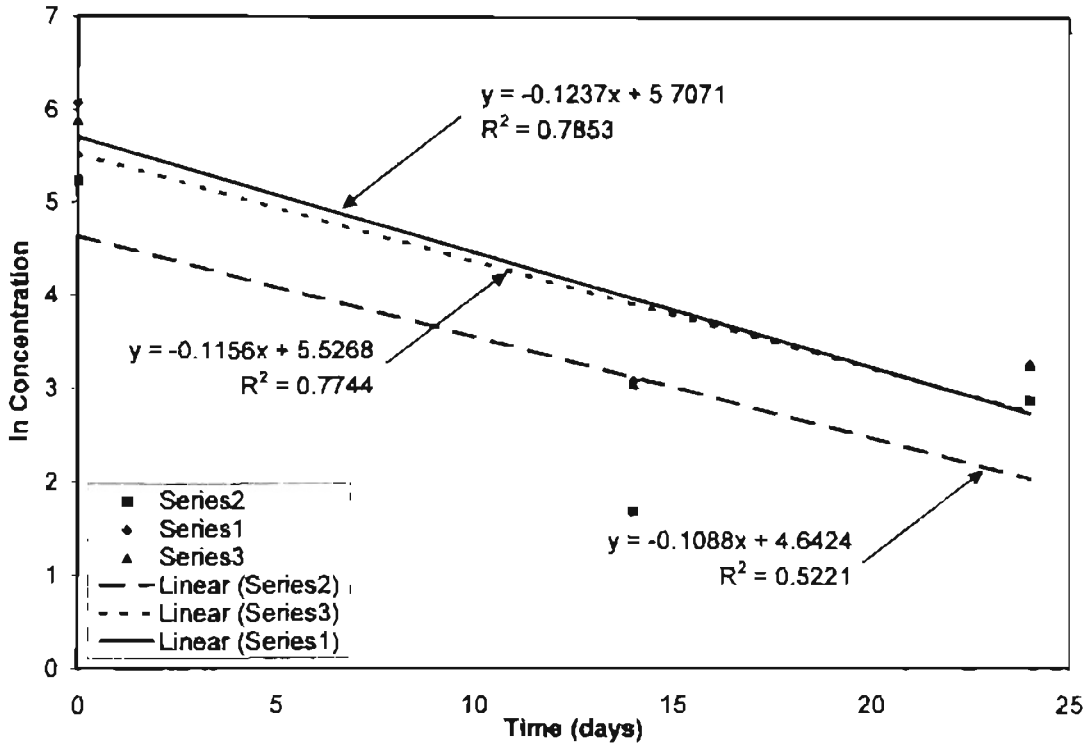


Figure 4.28. 2,2,4-Trimethylpentane Added First-Order Sulfate-Reducing Degradation of Chloroform

4.5.4 EFFECT OF COMBINED NON-CHLORINATED ORGANICS

Again, the real world application of this study in important. The organics studied previously were combined at a concentration of 50 µg/L (0.14 µM) with 100 µg/L (0.84 µM) of chloroform to determine how the mixture affects the degradation of chloroform. Figures 4.29, 4.30, and 4.31 combined ethylbenzene, decahydronapthalene, and 2,2,4-trimethylpentane with chloroform. The compounds were treated with methanogenic, denitrifying, and sulfate-reducing bactena, respectively. The data plotted from each set were fit to a first-order reaction curve. All of the reaction rates were averaged from each figure to give a representative reaction rate for each electron-accepting condition. The reaction rates are 0 12 day^{-1} 0 13 day^{-1}, and 0.12 day^{-1} for the methanogenic, denitrifying, and sulfate-reducing cultures, respectively.

The reaction rates for the methanogenic and sulfate-reducing bacteria decreased as expected compared to the individual organic reaction rates, with the exception of decahydronapthalene in the methanogenic culture. It was lower, but it was within 10% of the reaction rate for the combined organics. This could likely be the same number and decahydronapthalene might have possibly not had an effect on the combined organics reaction rate. The reaction rate for the combined organics is higher than the decahydronapthalene and ethylbenzene for the same bacteria culture. This was not expected as a cumulative inhibition should likely have occurred.

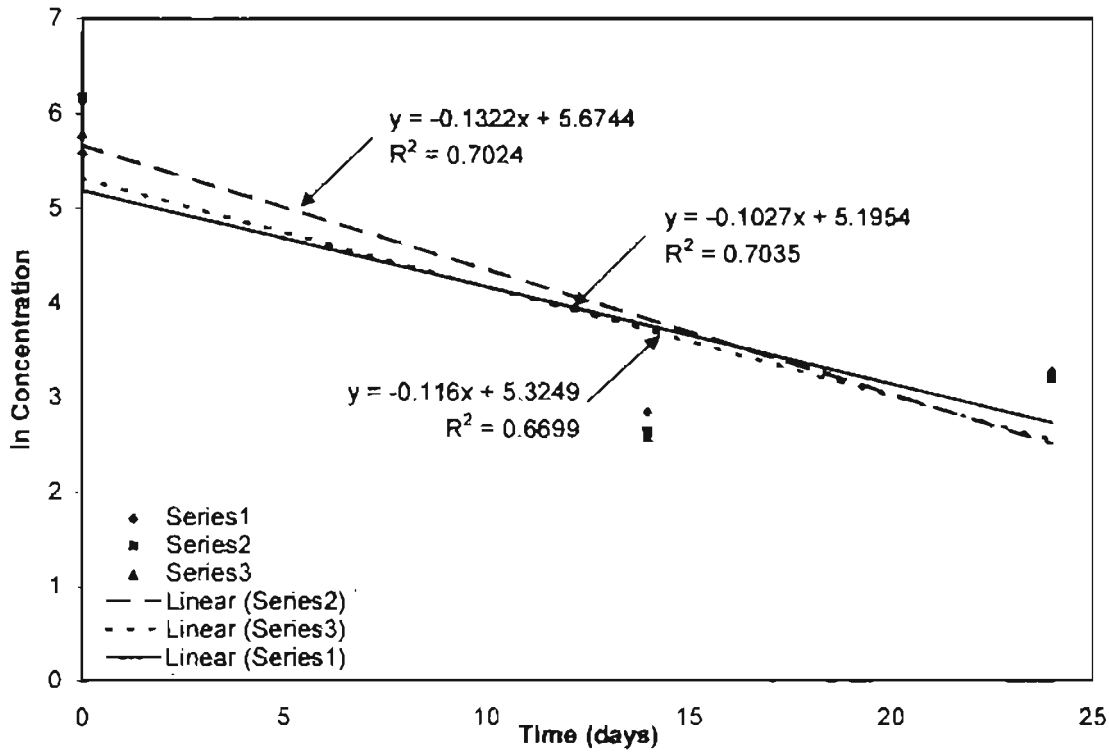


Figure 4.29. Combination of Non-Chlorinated Organics First-Order Methanogenic Degradation of Chloroform

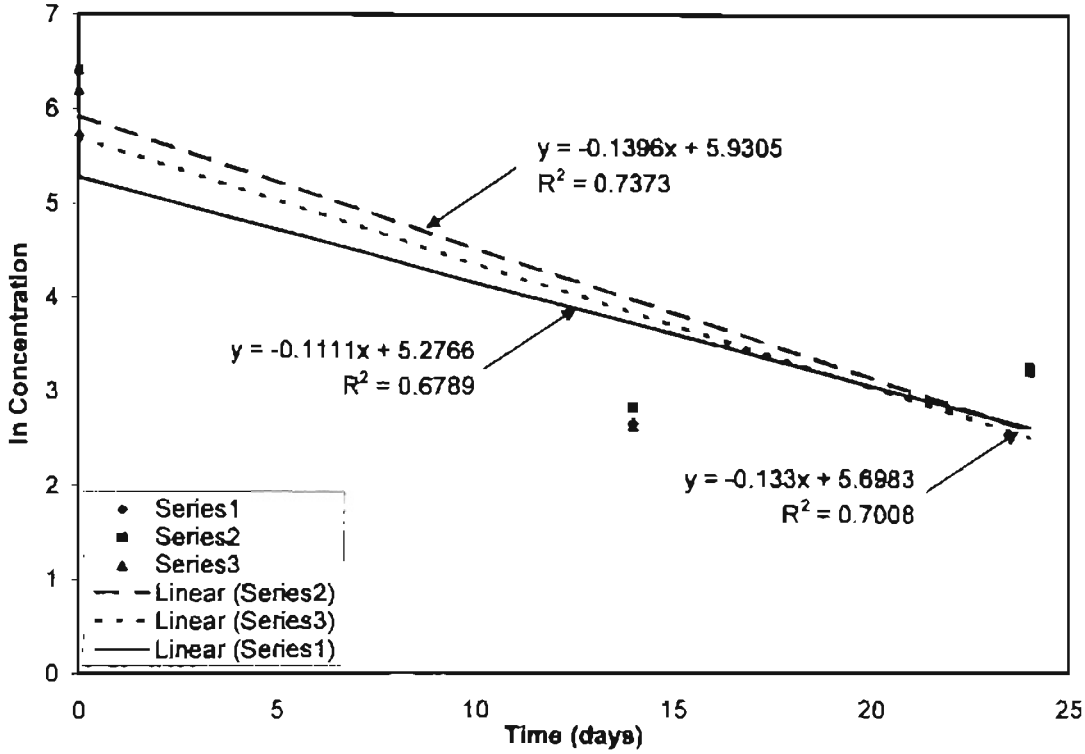


Figure 4.30. Combination of Non-Chlorinated Organics First-Order Denitrifying Degradation of Chloroform

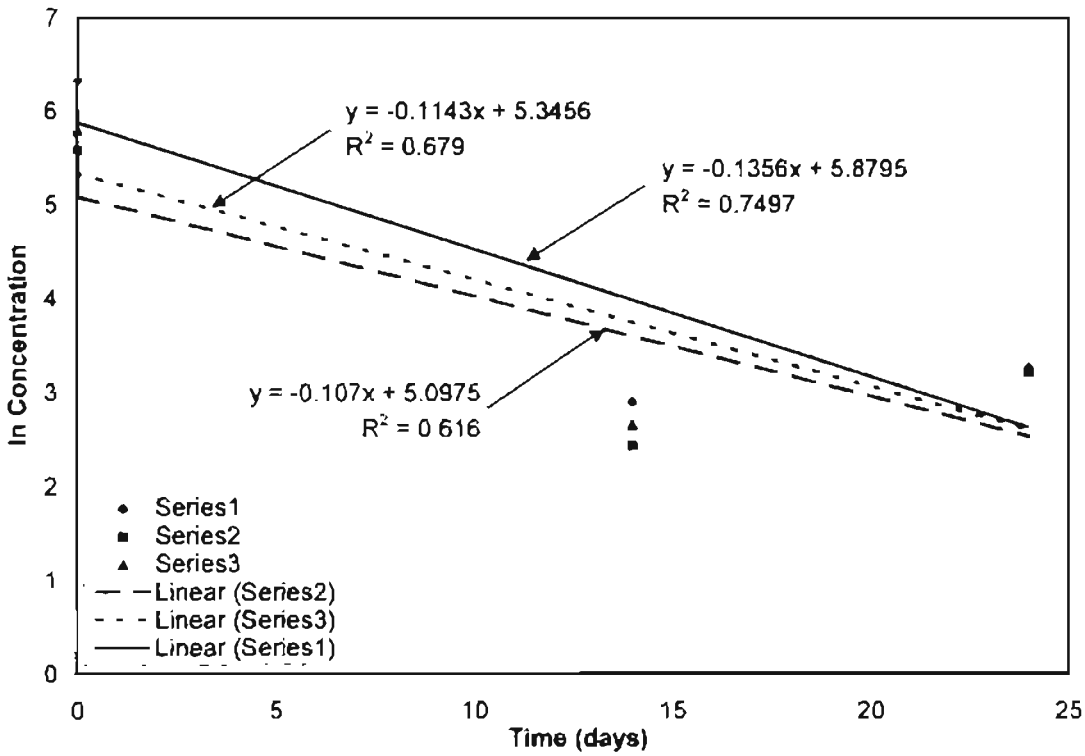


Figure 4.31. Combination of Non-Chlorinated Organics First-Order Sulfate-Reducing Degradation of Chloroform

4.5.5 COMBINATION OF 100 µg/L $CHCl_3$ with 500 µg/L p-DCB

Para-dichlorobenzene was analyzed with chloroform to see if greater or lesser concentrations of a similar chlorinated organic would affect the degradation of chloroform under different electron-accepting conditions. Figures 4.32, 4.33, and 4.34 combined 100 µg/L (0.84 µM) of chloroform with 500 µg/L (3.40 µM) of para-dichlorobenzene using methanogenic, denitrifying, and sulfate-reducing cultures, respectively. The data plotted were fit to a first-order reaction curve. The reaction rates for each electron-accepting condition were averaged for a representative value. The reaction rates are 0.16 day^{-1}, 0.18 day^{-1}, and 0.18 day^{-1} for methanogenic, denitrifying, and sulfate-reducing, respectively.

The reaction rate for the methanogenic bacteria seemed to fall in between the rates for the other organics tested. The denitrifying and sulfate-reducing bacteria reaction rates were observed to be slightly higher than the other reaction rates for the organics tested.

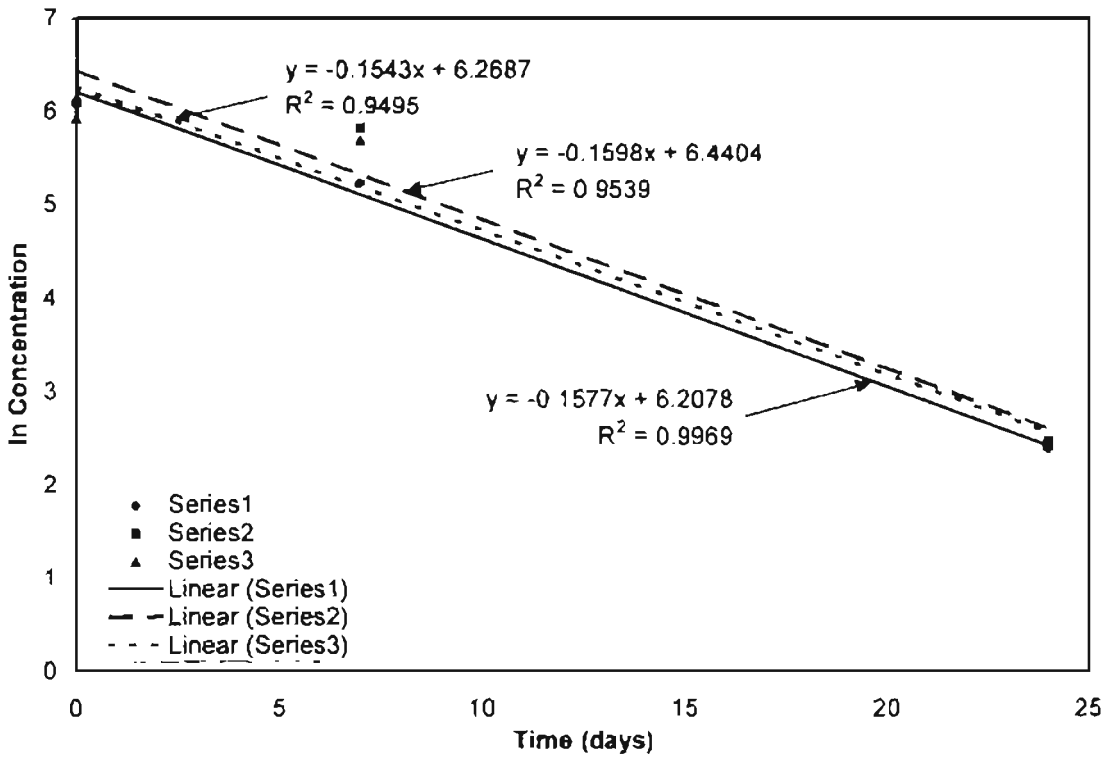


Figure 4.32. 100 µg/L of Chloroform and 500 µg/L of para-Dichlorobenzene Solution First-Order Methanogenic Degradation of Chloroform

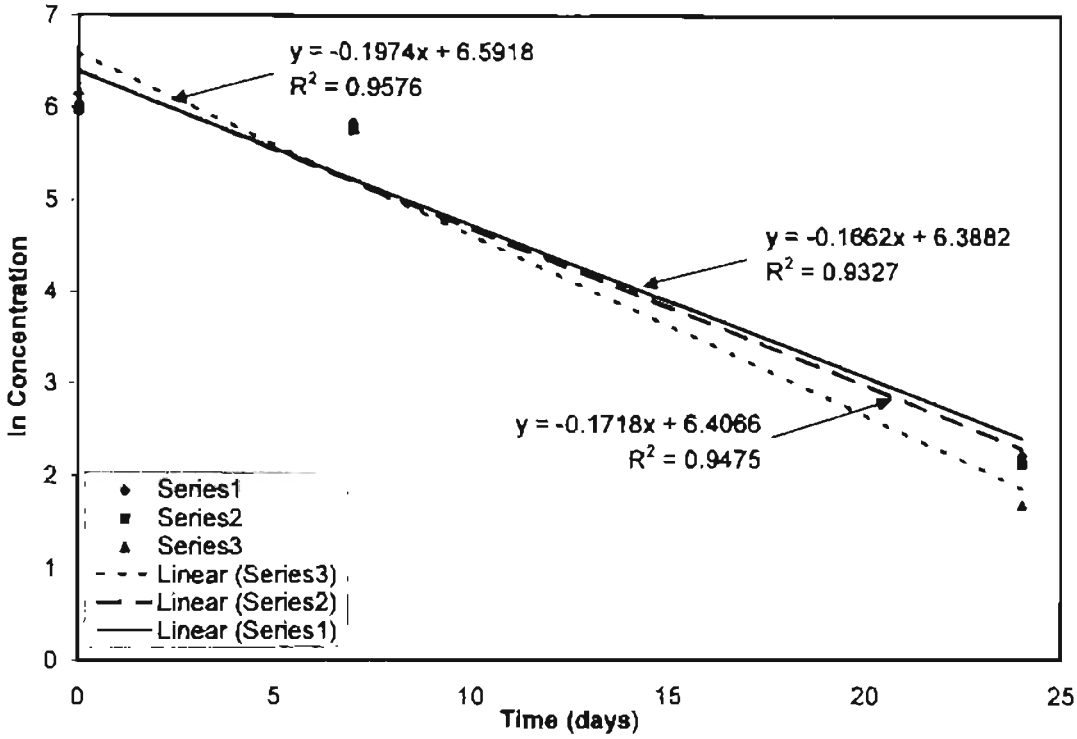


Figure 4.33. 100 µg/L of Chloroform and 500 µg/L of para-Dichlorobenzene Solution First-Order Denitrifying Degradation of Chloroform

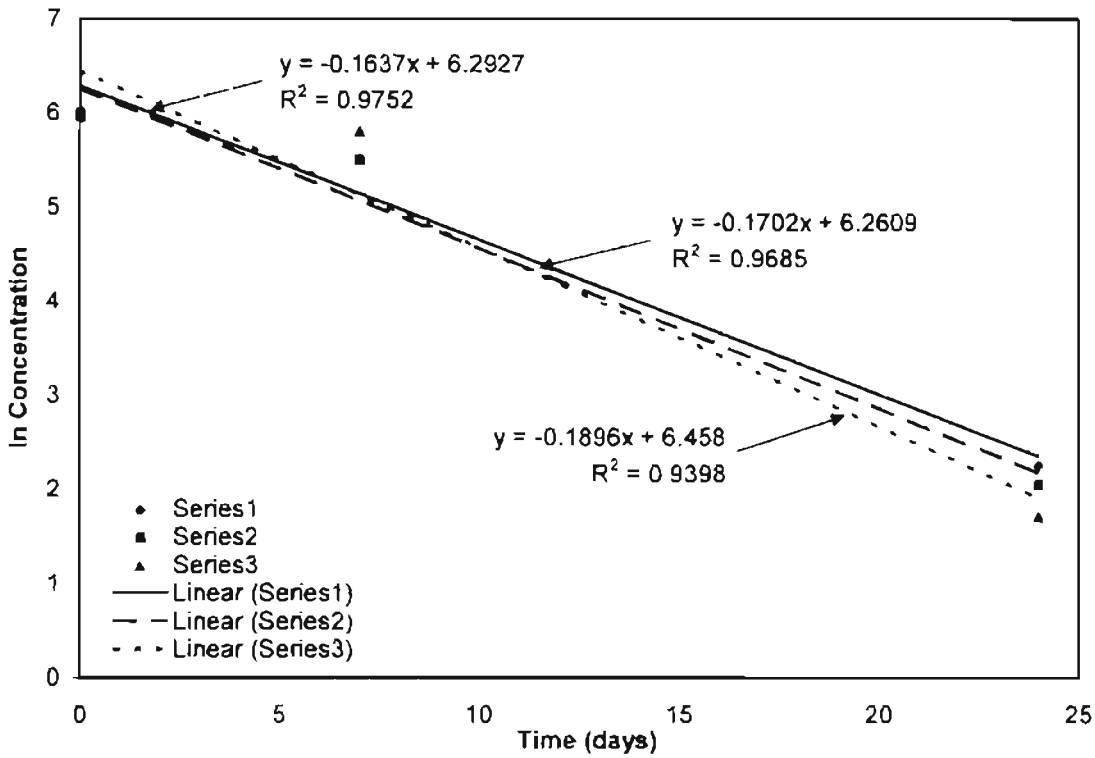


Figure 4.34. 100 µg/L of Chloroform and 500 µg/L of para-Dichlorobenzene Solution First-Order Sulfate-Reducing Degradation of Chloroform

4.5.6 COMBINATION OF 100 µg/L $CHCl_3$ with 60 µg/L p-DCB

Figures 4.35, 4.36, and 4.37 represent the data plotted for the degradation of 100 µg/L (0.84 µM) of chloroform with 60 µg/L (0.41 µM) of para-dichlorobenzene under methanogenic, denitrifying, and sulfate-reducing conditions, respectively. The data plotted were fit to a first-order reaction. Series one data was removed from the results of figure 4.37 because data was deemed unreliable and irreproducible. The reaction rates for all cases were averaged to present a representative reaction rate. The reaction rates are 0.15 day^{-1}, 0.14 day^{-1}, and 0.17 day^{-1} for methanogenic, denitrifying, and sulfate-reducing conditions, respectively.

The reaction rates observed from the addition of the 60 µg/L of p-DCB were smaller than those observed with the addition of 500 µg/L of p-DCB. The exact opposite resulted than what was anticipated. This would conclude that the lesser concentration of additional contaminate inhibits the degradation of chloroform.

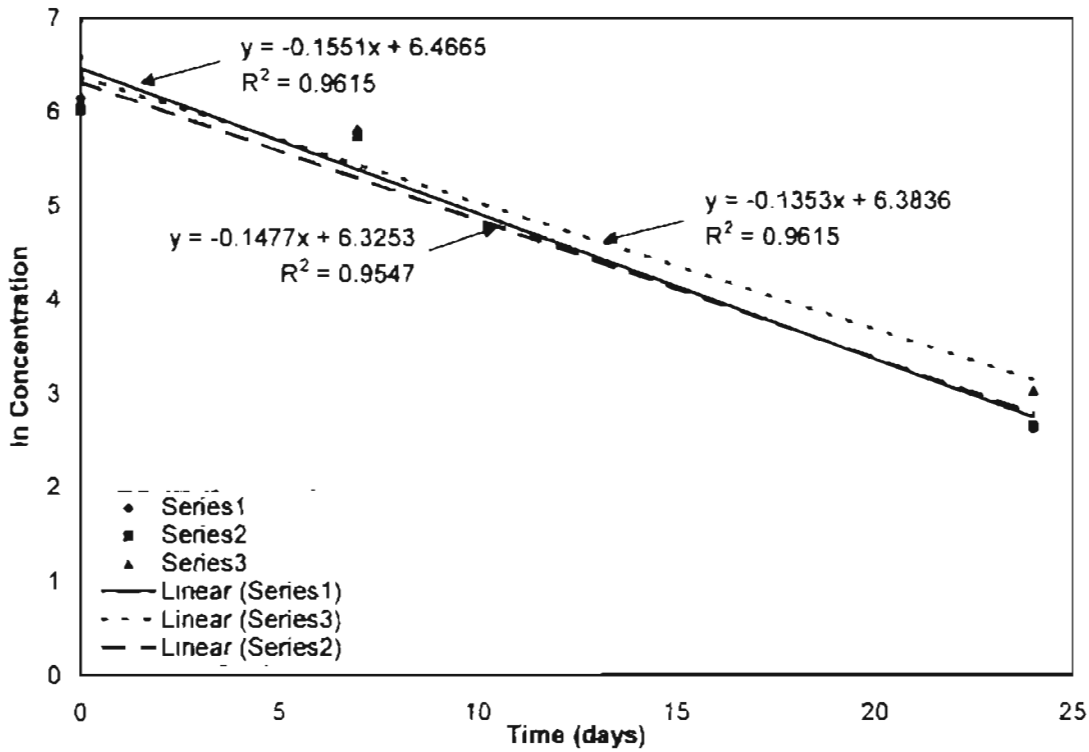


Figure 4.35. 100 µg/L of Chloroform and 60 µg/L of para-Dichlorobenzene Solution First-Order Methanogenic Degradation of Chloroform

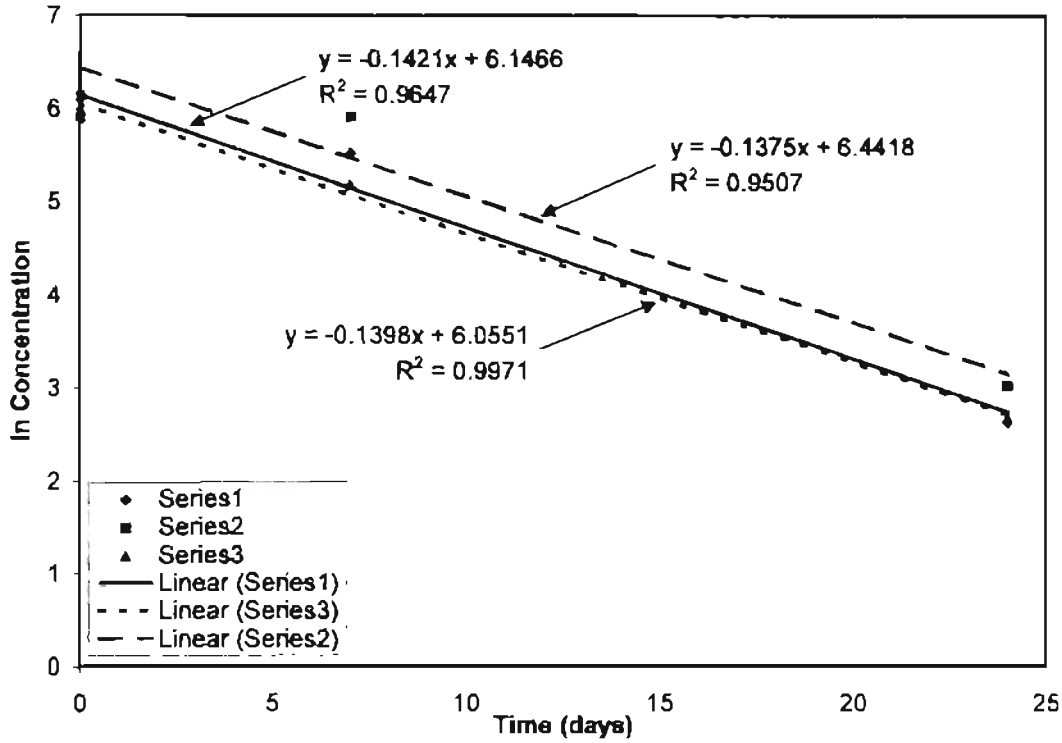


Figure 4.36. 100 µg/L of Chloroform and 60 µg/L of para-Dichlorobenzene Solution First-Order Denitrifying Degradation of Chloroform

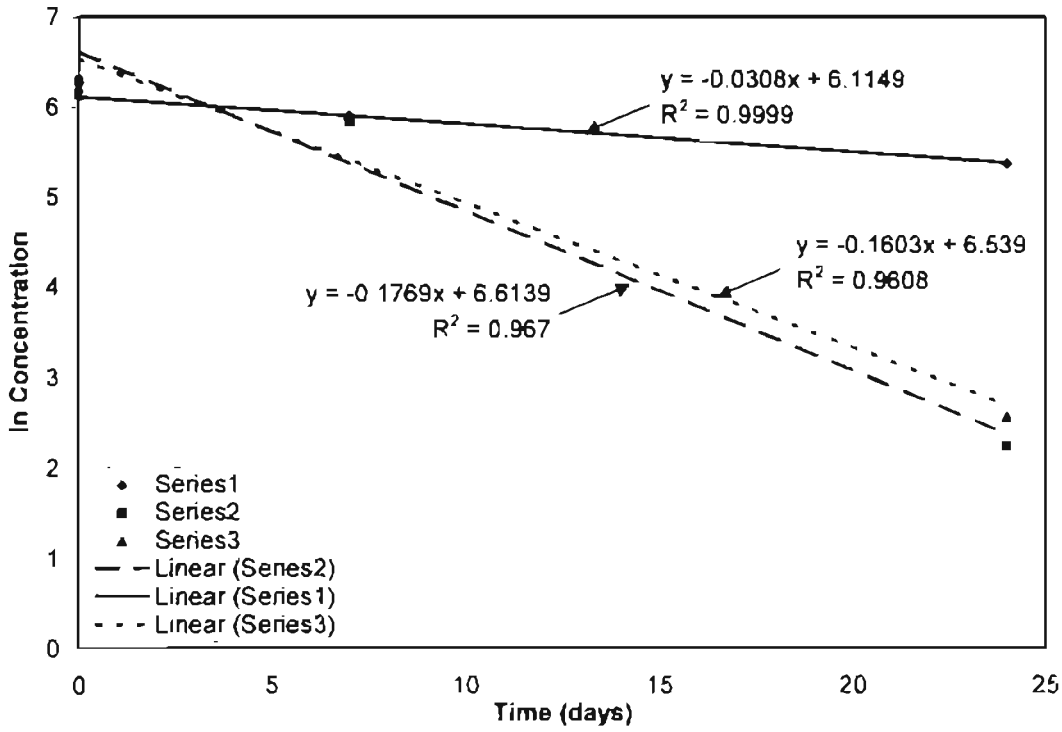


Figure 4.37. 100 µg/L of Chloroform and 60 µg/L of para-Dichlorobenzene Solution First-Order Sulfate-Reducing Degradation of Chloroform

Table 4.1 summarizes the results of the first-order reaction rates for all cases evaluated during these experiments. All values are given in unit of day^{-1}. The most noticeable difference is the rates in the baseline study with all of the other rates. The different electron-accepting conditions did not seem to have noticeable differences on the degradation rates.

The lower degradation rates with the added metals could be the result of the metal toxicity to the bacteria for each case. The metals did not completely inhibit the degradation but decreased the rate significantly. That would be consistent with the conclusions of Malakul et al. (1998) that as they increased the concentrations of cadmium, the growth of the bacteria was inhibited until complete inhibition resulted. This might be possible with all of the metals in this study that the concentration of metal affected the amount of bacteria in the reactor that caused inhibition on degradation.

The degradation of chloroform was also lower with the additional organics compared to the baseline degradation. One explanation could be that the chloroform degradation is secondary to the degradation of the organic added. Another explanation is that the bacteria are degrading both contaminants equally and slowing the overall degradation.

Table 4.1

Summary of First-Order Reaction Rates (day^{-1})

Experiment	Methanogenic	Denitrifying	Sulfate-Reducing
Baseline Degradation	0.76	0.65	1.04
Effects of Metals			
Zinc	0.15	0.11	0.15
Nickel	0.05	0.15	0.12
Cadmium	0.14	0.15	0.13
Chromium	0.14	0.13	0.17
Combined Metals	0.12	0.14	0.11
Effects of Additional Organics			
Ethylbenzene	0.15	0.12	0.13
Decahydronapthalene	0 10	0.09	0.16
2,2,4-Trimethylpentane	0.19	0.19	0.12
Combined Non-Chlorinated Organics	0.12	0 13	0 12
100 $CHCl_3$ with 500 p-DCB	0.16	0.18	0.18
100 $CHCl_3$ with 60 p-DCB	0 15	0.14	0 17

5.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The major aim of this study was to investigate the anaerobic treatability of chloroform contaminated soils from the aquifer below the Norman Landfill in Norman, Oklahoma. Three sets of soil-slurry reactors were operated under one of three conditions (sulfate-reducing, methanogenic, or denitrifying) with three varying parameters (baseline, effects of metals, and effects of additional organics).

The main objectives of this study were the following:

1. To study the ability of native soil bacteria to degrade chloroform under methanogenic, denitrifying, and sulfate-reducing conditions.
2. To study the affects of additional metals and organics on the base case chloroform degradation.
3. To study the ability of bacteria to degrade chloroform under different electron accepting conditions with varying substrates added.

Based on the results of this study, the following conclusions can be drawn:

- When chloroform consumption was studied without any additional substrates, the sulfate-reducing bacteria were observed to consume the chloroform at a faster degradation rate than methanogenic or denitrifying bacteria.
- Although chloroform was successfully consumed in all soil-water reactors where metals or additional organics were introduced, the overall rate of degradation compared to the base rate degradation fell dramatically.
- The effects of the metals on the degradation of chloroform were most likely due to the toxicity of the metal with the bacteria which was inhibiting growth of the bacteria
- The effects of the additional organics on the degradation of chloroform were likely due to the bacteria consuming the added contaminant before chloroform. This could be due to the added contaminate being a better candidate for consumption.
- From the results, nickel is the most toxic to the methanogenic cultures compare to other metals.
- With the increased concentration of p-DCB, the degradation rate of chloroform increases.

Results from this study indicate that any one of the conditions used for the soil-slurry reactor is a viable treatment alternative for treating chloroform contaminated soil at the Norman Landfill. However, further studies are recommended. Recommendations include:

- Monitor both solid-phase and aqueous-phase chloroform in bench-scale slurry reactors operated under denitrifying, methanogenic, and sulfate-reducing conditions. These data would be useful in predicting required treatment times in a pilot scale system as well expound the relationship between desorption and biodegradation.

- Conduct further experiments of more metals and organics that are found to be in typical landfills to isolate substrates that limit degradation under separate conditions.

- Conduct further experiments to decide how temperature affects the rate of degradation under the various conditions with various substrates.

- Conduct further experiments varying the pH that is more applicable to landfill conditions with varying compounds.

- All of the experiments were conducted under anaerobic conditions, typical landfills might contain both conditions during different environmental conditions. Conduct further research to investigate the degradability of chloroform under aerobic conditions.

- Isolate and identify bacteria involved in the biotransformation of chloroform under various conditions.

- The compounds that these experiments produced after degradation are unclear. Therefore, it is recommended that the reactions that these compounds produce be further investigated to find whether their transformation products are of similar or even greater environmental concern than their parent compounds. If so, more research is necessary to focus on their transformations, both abiotic and biological, to ultimately find the pathways which render these chemicals harmless.

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APPENDICES

APPENDIX A –

Norman Landfill Analytical Results

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
SUBSURFACE PROTECTION AND REMEDIATION DIVISION
P.O. BOX 1198 • ADA, OK 74820

March 9, 1996

OFFICE OF
RESEARCH AND DEVELOPMENT

Dr. Robert Knox
202 W. Boyd Room 334
University of Oklahoma
Norman, OK 73019

Dear Dr. Knox,

Enclosed are the analytical results of samples obtained from the Norman landfill by the U.S. Geological Survey. Please feel free to call me at (405) 436-8556 if you have any questions regarding this data.

Sincerely,

Cynthia J. Paul

Prepared by Cindy Paul 3/5/96

Filtered	mg/L									
Well	Na-1	K	Ca	Mg	Fe	Mn	Co	Mo	Al	As
Slough	322	12.5	103	97.9	<0.018	0.019	<0.0061	0.008	<0.11	<0.030
PS10	27.4	<2.3	124	36.1	2.29	1.03	<0.0061	0.0147	<0.11	<0.030
PS12	10.6	3	149	29.4	3.77	2.12	<0.0061	0.0173	<0.11	<0.030
PS16D	75.6	2.9	98.2	32.2	3.45	1.38	<0.0060	0.006	<0.11	<0.030
PS17	17.6	3.7	135	35.6	2.48	1.5	<0.0061	0.0053	<0.11	<0.030
PS18	70.8	3.7	93.5	30.7	3.26	1.3	<0.0061	0.0053	<0.11	<0.030
PS22	4.1	<2.3	66.5	14.9	2.09	1.14	<0.0061	0.0061	0.16	<0.030
PS35	508	199	140	82.8	6.79	0.274	0.0091	0.0067	<0.11	0.032
PS36	581	214	113	80.2	6.66	0.462	0.0154	0.0068	<0.11	<0.030
PS37	312	43	292	37.9	2.42	0.788	0.0094	0.0144	<0.11	<0.030
PS38	191	61.7	235	71.4	8.17	1.17	<0.0061	0.0124	<0.11	<0.030
PS39	172	44.8	234	34.7	2.59	0.835	0.0085	0.0122	0.11	<0.030
AB01	<1.0	<2.8	<0.23	<0.14	<0.011	<0.0036	<0.0033	<0.021	<0.046	0.0138
CR01	105	<2.8	178	56.6	<0.011	0.0204	<0.0033	<0.021	<0.046	0.01
FB01	<1.0	<2.8	<0.23	<0.14	<0.011	<0.0036	<0.0033	<0.021	0.08	0.0101
PS38B	516	<2.8	467	177	12.8	1.27	0.0181	<0.021	<0.046	<0.014
PS38BD	515	<2.8	464	176	12.6	1.25	0.0175	<0.021	0.048	<0.013
PS38C	573	14.3	444	176	23.8	0.811	0.0208	<0.021	<0.046	<0.012
PS38D	622	<2.8	489	182	16.5	1.09	0.0211	<0.021	0.057	<0.015
PS40	652	394	168	116	21.9	0.398	0.0226	<0.021	<0.046	<0.012
PS43B	531	175	298	90.2	11.3	0.607	0.017	<0.021	<0.046	<0.012
PS54	224	9.5	108	53	1.4	0.597	<0.0033	<0.021	<0.046	<0.0099
PS54B	405	<2.8	398	141	13.9	0.976	0.0149	<0.021	0.059	<0.011
PS54C	439	<2.8	474	165	20.1	0.988	0.0163	<0.021	<0.046	<0.013
PS54D	541	<2.8	484	183	15.2	1.12	0.0196	<0.021	<0.046	<0.016
WSI	184	1.37	88.8	33.2	1.58	0.314	0.0004	<0.015	0.104	<0.011
PS04	11.8	1.54	117	22.8	1.11	0.346	0.004	<0.015	0.071	0.025
PS06	260	0.35	117	24.1	<0.0026	0.019	0.0023	<0.015	<0.069	0.018
PS07	92	46.9	163	35.6	2.11	0.554	<0.0033	0.013	<0.069	<0.0095
PS08	49.2	24.2	118	30.4	3.13	0.35	0.003	<0.015	<0.069	<0.011

Prepared by Cindy Paul 3/5/96

Filtered	mg/L									
Well	Se	Cd	Be	Cu	Sb	Cr	Ni	Zn	Ag	Tl
Slough	<0.038	<0.0021	<0.0013	<0.076	<0.079	0.002	0.0103	<0.012	<0.017	<0.018
PS10	<0.038	<0.0021	<0.0014	<0.076	<0.079	0.0041	0.0644	<0.012	<0.017	<0.018
PS12	<0.038	0.0027	<0.0018	<0.076	<0.079	<0.0019	0.0218	<0.012	<0.017	<0.018
PS16D	<0.037	<0.0021	<0.0013	<0.075	<0.077	<0.0019	<0.0069	<0.012	<0.017	<0.017
PS17	<0.038	0.0024	<0.0015	<0.076	<0.079	0.0022	0.0152	<0.012	<0.017	0.024
PS18	<0.038	<0.0021	<0.0012	<0.076	<0.079	<0.0019	<0.0070	<0.012	<0.017	<0.018
PS22	<0.038	0.0025	<0.0011	<0.076	<0.079	<0.0019	<0.0070	<0.012	<0.017	<0.018
PS35	<0.038	0.004	<0.0015	<0.076	<0.079	0.0077	0.0343	0.015	0.019	<0.018
PS36	<0.038	0.0048	<0.0013	<0.076	<0.079	0.0058	0.027	0.019	<0.017	<0.018
PS37	<0.038	0.0059	<0.0025	<0.076	<0.079	0.0047	0.0215	<0.012	0.027	0.03
PS38	<0.038	0.0038	<0.0021	<0.076	<0.079	0.0029	0.0255	<0.012	0.018	0.023
PS39	<0.038	0.0058	<0.0021	<0.076	<0.079	0.0031	0.0216	<0.012	0.029	0.025
AB01	<0.019	<0.0020	<0.0081	<0.010	<0.029	<0.0084	<0.0087	<0.0027	<0.0075	<0.014
CR01	<0.019	0.0048	<0.0063	0.023	<0.029	<0.0084	0.0146	<0.0028	0.0205	0.028
FB01	0.021	<0.0020	<0.0081	<0.010	0.055	<0.0084	<0.0087	<0.0027	0.0149	<0.014
PS38B	<0.021	0.0117	<0.0072	0.072	<0.029	<0.0084	0.0437	<0.0030	0.0535	0.044
PS38BD	<0.021	0.0108	<0.0071	0.07	<0.029	<0.0084	0.0423	<0.0030	0.0549	0.046
PS38C	<0.026	0.0115	<0.0071	0.063	<0.029	0.009	0.0414	0.003	0.0474	0.033
PS38D	0.025	0.0129	<0.0073	0.062	<0.029	<0.0084	0.0491	<0.0029	0.0556	0.038
PS40	<0.025	0.0048	<0.0063	0.023	<0.029	<0.0084	0.0272	<0.0028	0.0258	<0.014
PS43B	<0.021	0.0092	<0.0066	0.04	<0.029	<0.0084	0.0297	<0.0028	0.031	0.015
PS54	<0.019	0.0022	<0.0062	<0.010	<0.029	<0.0084	0.0139	<0.0027	<0.0076	<0.014
PS54B	<0.022	0.0101	<0.0069	0.063	0.034	<0.0084	0.0355	<0.0029	0.051	0.031
PS54C	0.037	0.0119	<0.0072	0.068	<0.029	<0.0084	0.0415	0.0036	0.0552	0.039
PS54D	<0.022	0.0105	<0.0072	0.067	<0.029	<0.0084	0.0416	0.0057	0.0454	0.032
WSI	<0.017	0.0005	<0.0019	<0.043	<0.020	0.0002	0.0093	<0.0009	0.0124	0.0021
PS04	<0.017	0.0038	<0.0020	<0.043	<0.020	0.0016	0.0249	0.0377	0.016	0.0176
PS06	<0.017	0.0034	<0.0020	<0.043	<0.020	<0.0012	0.0161	0.0763	0.0126	0.0178
PS07	<0.017	0.0038	<0.0022	<0.047	<0.037	<0.0017	0.0168	<0.011	0.0128	<0.013
PS08	<0.017	0.0039	<0.0020	<0.043	<0.020	0.0014	0.037	0.035	0.0131	0.0107

Prepared by Cindy Paul 3/5/98

Filtered	mg/L									
Well	Pb	Hg	Li	Te	Sr	Ge	V	Ba	B	Tl
Slough	<0.033	<0.051	<0.59	<0.073	2.31	0.13	<0.027	0.805	1.23	<0.014
PS10	<0.033	<0.052	0.81	<0.073	0.791	<0.10	<0.027	0.501	0.151	<0.014
PS12	<0.033	<0.054	0.92	<0.074	1.28	<0.10	<0.027	0.438	0.093	<0.014
PS16D	<0.032	<0.052	<0.58	<0.072	1.26	<0.10	<0.026	0.828	0.238	<0.014
PS17	<0.033	<0.052	0.96	0.076	1.51	0.11	<0.027	0.317	0.115	<0.014
PS18	<0.033	<0.053	0.66	<0.073	1.18	<0.10	<0.027	0.589	0.212	<0.014
PS22	<0.033	<0.052	<0.59	<0.073	0.657	<0.10	<0.027	0.342	0.074	<0.014
PS35	<0.033	<0.059	0.69	<0.073	2.34	<0.10	<0.027	3.42	5.07	<0.014
PS36	<0.033	<0.059	0.65	<0.073	2.69	<0.10	<0.027	5.84	7.3	<0.014
PS37	<0.033	<0.052	1.42	0.075	2.1	<0.10	<0.027	0.15	3.05	<0.014
PS38	<0.033	<0.058	1.19	<0.074	2.79	<0.10	<0.027	0.204	1.9	<0.014
PS39	<0.033	<0.052	1.14	0.091	1.88	<0.10	<0.027	0.184	2.6	<0.014
AB01	<0.010	<0.058	<0.70	<0.028	<0.0025	<0.063	<0.011	<0.0024	<0.11	<0.013
CR01	<0.010	<0.058	0.85	0.066	1.86	<0.063	0.016	0.15	0.28	<0.013
FB01	0.021	<0.058	<0.70	0.037	<0.0025	<0.063	0.019	<0.0024	<0.11	<0.013
PS38B	<0.011	<0.081	<0.70	0.129	7.29	0.128	<0.011	8.04	7.09	<0.013
PS38BD	<0.011	<0.081	<0.70	0.133	7.08	0.126	<0.011	7.83	6.92	<0.013
PS38C	<0.011	<0.13	0.78	0.12	7.73	0.133	<0.011	7.78	9.58	<0.013
PS38D	<0.011	<0.094	<0.70	0.144	6.27	0.119	<0.011	3.17	3.85	<0.013
PS40	<0.010	<0.13	<0.70	0.053	3.24	0.088	0.013	12.8	6.54	<0.013
PS43B	<0.011	<0.077	<0.70	0.064	3.71	<0.064	<0.011	5.66	3.66	<0.013
PS54	<0.010	<0.058	<0.70	<0.028	1.56	0.077	<0.011	0.549	1.07	<0.013
PS54B	<0.011	<0.085	<0.70	0.135	5.07	0.148	0.012	1.54	4.76	<0.013
PS54C	<0.011	<0.12	<0.70	0.153	6.56	0.177	<0.011	3.18	8.01	<0.013
PS54D	<0.011	<0.089	<0.70	0.114	6.23	0.16	<0.011	2.75	5.19	<0.013
WSI	<0.012	<0.023	0.203	0.037	1.21	<0.081	<0.010	0.105	0.457	<0.0018
PS04	<0.012	<0.023	0.43	0.053	0.983	<0.081	<0.010	0.427	0.11	<0.0018
PS06	<0.012	<0.022	0.335	0.033	2.37	<0.081	<0.010	0.484	0.246	<0.0018
PS07	<0.015	<0.042	<0.28	<0.051	1.13	0.147	<0.011	0.239	0.714	<0.0081
PS08	<0.012	<0.028	0.47	0.038	0.956	<0.081	<0.010	0.343	0.847	<0.0018

Prepared by Cindy Paul 3/5/96

Unfiltered	mg/L									
Well	Na-1	K	Ca	Mg	Fe	Mn	Co	Mo	Al	As
Slough	329	18.1	209	108	16.9	0.828	0.0101	0.0097	17.8	<0.031
PS10	25.5	3.5	126	38.2	5.64	1.05	<0.0061	0.0227	4.97	<0.030
PS12	10.7	2.8	152	28.9	3.96	2.13	<0.0061	0.0135	<0.11	<0.030
PS16D	73.6	3.3	96.6	30.9	3.35	1.33	<0.0061	0.005	<0.11	<0.030
PS17	16.3	4.1	133	34.3	2.37	1.46	<0.0061	0.0075	<0.11	<0.030
PS18	79.2	2.4	96.4	31.9	3.42	1.36	<0.0035	0.0101	<0.20	<0.025
PS22	4.32	1.8	65.6	14.8	2.03	1.11	<0.0035	0.0057	<0.20	<0.025
PS35	539	230	142	84.4	7.17	0.278	0.0114	0.0116	0.66	<0.025
PS36	590	235	117	82.6	7.87	0.475	0.0143	0.007	1.45	<0.025
PS37	328	47.1	287	38.5	2.94	0.844	0.0118	0.0148	0.69	0.03
PS38	192	87.8	236	72.5	6.45	1.16	0.012	0.0142	<0.20	<0.026
PS39	185	51.5	241	35.8	2.74	0.858	0.0119	0.0184	<0.20	<0.026
AB01	<0.082	<0.57	<0.0082	<0.048	<0.0059	<0.083	<0.0087	<0.0044	<0.084	<0.014
CR01	110	2.57	181	57.5	0.99	<0.083	<0.0087	0.01	1.9	<0.014
FB01	0.24	<0.57	0.108	<0.048	<0.0059	<0.083	<0.0087	<0.0044	<0.084	<0.014
PS38B	511	5.07	442	173	13.1	1.18	0.0218	0.0277	0.397	0.044
PS38BD	526	3.25	426	168	13.1	1.27	0.0178	0.024	0.259	0.048
PS38C	636	14.6	406	166	25.1	0.831	0.0198	0.0247	2.63	0.0479
PS38D	642	2.71	444	153	17	1.09	0.0206	0.0238	0.142	0.0358
PS40	690	352	153	108	21.7	0.363	0.018	<0.0095	2.81	<0.035
PS43B	558	166	288	89.5	11.6	0.53	0.019	0.014	0.144	<0.014
PS54	224	7.6	98.8	48.3	1.49	0.525	<0.0042	<0.0095	0.324	<0.035
PS54B	382	2.6	358	131	13.2	0.879	0.0086	0.0154	0.677	0.036
PS54C	483	4.6	415	150	18.8	0.868	0.0101	0.0219	1.2	0.045
PS54D	585	4.5	418	146	14.3	0.984	0.016	0.0205	1.13	0.041
JPESW	112	<1.0	94.4	35.7	1.34	0.41	<0.0042	<0.0095	<0.090	<0.035
JPWSW	163	1.4	142	49.3	2.54	0.362	<0.0042	<0.0095	<0.090	<0.035
WSI	187	1.39	88.4	33.3	1.56	0.393	<0.0017	<0.015	<0.069	<0.011
PS04	39.4	<0.12	334	61.6	21.9	1.13	0.0111	0.067	20.6	0.06
PS06	277	0.38	121	25.4	1.39	0.049	0.0026	<0.015	2.41	0.013
PS07	83.1	44.2	157	34.5	3.08	0.526	0.0031	<0.015	2.02	0.02
PS08	50.6	24.5	118	30.5	3.86	0.364	0.0041	<0.015	1.05	0.029

Prepared by Cindy Paul 3/5/98

Unfiltered	mg/L									
Well	Se	Cd	Be	Cu	Sb	Cr	Ni	Zn	Ag	Tl
Slough	<0.040	0.0056	<0.0020	<0.076	<0.079	0.019	0.0277	0.035	<0.017	0.033
PS10	<0.038	0.0035	<0.0014	<0.076	<0.079	0.0208	0.108	0.015	<0.017	0.021
PS12	<0.038	0.0041	<0.0016	<0.076	<0.079	0.0027	0.0269	<0.012	<0.017	<0.018
PS16D	<0.038	<0.0021	<0.0013	<0.076	<0.079	<0.0019	<0.0070	<0.012	<0.017	<0.018
PS17	<0.038	0.0039	<0.0015	<0.076	<0.079	0.0022	0.011	<0.012	<0.017	<0.018
PS18	<0.034	<0.0022	<0.0019	<0.058	<0.096	<0.0024	<0.0098	<0.18	<0.017	<0.017
PS22	<0.034	<0.0022	<0.0019	<0.058	<0.096	<0.0024	<0.0098	<0.18	<0.017	<0.017
PS35	<0.034	0.004	<0.0021	<0.058	<0.096	0.0154	0.0356	<0.18	<0.017	0.02
PS36	<0.034	0.0055	<0.0020	<0.058	<0.096	0.02	0.0308	<0.18	<0.017	<0.017
PS37	<0.034	0.0072	<0.0030	<0.058	<0.096	0.012	0.033	<0.18	0.031	0.02
PS38	<0.034	0.005	<0.0026	<0.058	<0.096	0.0036	0.0279	<0.18	0.022	0.022
PS39	<0.034	0.0049	<0.0026	<0.058	<0.096	0.0047	0.0288	<0.18	0.027	0.022
AB01	<0.023	<0.0009	<0.0018	<0.043	<0.038	<0.011	<0.0042	<0.0056	<0.0096	<0.021
CR01	<0.023	0.0046	<0.0023	<0.043	<0.038	<0.011	0.0136	0.0115	0.0128	<0.021
FB01	<0.023	<0.0009	<0.0018	<0.043	<0.038	<0.011	<0.0042	<0.0056	<0.0096	<0.021
PS36B	<0.025	0.0106	<0.0040	0.079	<0.039	<0.011	0.0454	<0.0057	0.049	0.061
PS36BD	<0.017	0.0112	<0.0034	0.108	<0.021	0.0111	0.0414	0.0064	0.0374	0.047
PS36C	<0.027	0.0088	<0.0033	0.093	<0.021	0.0225	0.0449	0.0207	0.0351	0.039
PS36D	<0.019	0.0116	<0.0036	0.097	<0.021	0.0117	0.0438	0.0068	0.0366	0.037
PS40	<0.038	0.0053	<0.0014	<0.11	<0.067	0.013	0.0248	0.0111	0.019	<0.049
PS43B	<0.025	0.0062	<0.0029	0.048	<0.038	<0.011	0.0268	<0.0057	0.0293	0.038
PS54	<0.032	<0.0017	<0.0011	<0.11	<0.067	<0.0013	0.0116	0.0037	<0.011	<0.049
PS54B	<0.033	0.0093	<0.0030	<0.11	<0.067	0.0068	0.032	0.0036	0.035	<0.049
PS54C	<0.035	0.0108	<0.0034	<0.11	<0.067	0.0163	0.047	0.0208	0.046	<0.049
PS54D	<0.034	0.01	<0.0034	<0.11	<0.067	0.0151	0.0469	0.0234	0.038	<0.049
JPESW	<0.032	0.0028	<0.0011	<0.11	<0.067	<0.0013	<0.0066	0.004	<0.011	<0.049
JPWSW	<0.032	0.0029	<0.0014	<0.11	<0.067	<0.0013	0.0126	0.0013	<0.011	<0.049
WSI	<0.017	0.0037	<0.0019	<0.043	<0.020	<0.0012	0.0117	<0.0009	0.0131	<0.0097
PS04	0.049	0.0113	<0.0032	0.233	0.066	0.23	1.52	3.38	0.1043	0.066
PS06	<0.017	0.0039	<0.0020	<0.043	<0.020	0.0075	0.0204	0.0317	0.0128	0.0112
PS07	<0.017	0.0038	<0.0021	<0.043	<0.020	0.0048	0.0242	0.0245	0.221	<0.0097
PS08	<0.017	0.0039	<0.0020	<0.043	<0.020	0.0044	0.0383	0.0352	0.0144	0.0116

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Unfiltered	mg/L									
Well	Pb	Hg	Li	Te	Sr	Ge	V	Ba	B	Tl
Slough	<0.034	<0.095	0.89	<0.074	2.73	0.16	<0.027	1.21	1.32	0.295
PS10	<0.033	<0.057	1.24	<0.073	0.769	0.18	<0.027	0.539	0.18	0.086
PS12	<0.033	<0.054	0.85	<0.074	1.29	<0.10	<0.027	0.438	0.114	<0.014
PS16D	<0.033	<0.053	0.65	<0.073	1.2	<0.10	<0.027	0.604	0.238	<0.014
PS17	<0.033	<0.052	1.13	<0.073	1.45	<0.10	<0.027	0.309	0.111	<0.014
PS18	<0.037	<0.045	<0.35	<0.090	1.23	0.025	<0.032	0.648	0.228	<0.018
PS22	<0.037	<0.043	<0.35	<0.090	0.845	0.031	<0.032	0.353	0.078	<0.018
PS35	<0.037	<0.053	0.46	<0.090	2.36	0.089	<0.032	3.62	5.37	<0.018
PS36	<0.037	<0.055	0.44	<0.090	2.72	0.044	<0.032	6.01	7.74	<0.018
PS37	<0.037	<0.044	1.22	0.092	2.09	0.124	<0.032	0.185	3.25	<0.018
PS38	<0.037	<0.051	0.95	<0.091	2.77	0.059	<0.032	0.219	1.97	<0.018
PS39	<0.037	<0.044	1.32	<0.091	1.69	0.084	<0.032	0.178	2.75	<0.018
AB01	<0.020	<0.098	<0.38	<0.040	<0.0007	<0.15	<0.014	<0.0016	<0.029	0.0037
CR01	<0.021	<0.098	0.64	<0.040	2	<0.15	<0.014	0.18	0.281	0.0315
FB01	<0.020	<0.098	<0.38	<0.040	0.0009	<0.15	<0.014	<0.0016	<0.029	<0.0027
PS38B	<0.021	<0.11	1.84	0.148	7.15	0.19	<0.014	7.46	6.85	0.0058
PS38BD	<0.015	<0.074	1.57	0.089	6.82	0.129	<0.010	7.28	6.7	<0.0055
PS38C	<0.015	<0.14	1.41	0.058	7.43	0.241	<0.010	7.15	8.95	0.0429
PS38D	<0.015	<0.098	1.19	0.077	5.97	0.14	<0.010	2.88	3.85	<0.0055
PS40	<0.022	<0.13	0.53	<0.029	3.09	<0.092	<0.015	11.5	5.89	0.048
PS43B	<0.021	<0.11	1.18	0.064	3.77	<0.15	<0.014	5.64	3.53	<0.0029
PS54	<0.022	<0.093	0.34	<0.029	1.49	<0.091	<0.015	0.492	0.955	<0.020
PS54B	<0.022	<0.11	1.36	0.074	4.88	0.123	<0.015	1.4	4.45	<0.020
PS54C	<0.022	<0.12	1.87	0.135	6.08	<0.092	<0.015	2.8	7.2	0.026
PS54D	<0.022	<0.11	1.78	0.083	5.65	<0.092	<0.015	2.39	4.57	<0.020
JPESW	<0.022	<0.093	0.43	<0.029	0.968	<0.091	<0.015	0.355	0.388	<0.020
JPWSW	<0.022	<0.094	0.82	<0.029	1.71	0.104	<0.015	1.19	0.309	<0.020
WSI	<0.012	<0.023	0.228	0.033	1.22	<0.081	<0.010	0.102	0.456	<0.0018
PS04	0.089	<0.11	<0.12	0.142	2.9	<0.081	0.042	1.74	0.366	0.243
PS06	<0.012	<0.023	0.213	0.037	2.45	0.084	<0.010	0.53	0.259	0.0329
PS07	<0.012	<0.026	0.52	0.046	1.02	<0.081	<0.010	0.236	0.689	0.0297
PS08	<0.012	<0.028	0.5	0.054	0.955	<0.081	<0.010	0.372	0.643	0.019

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USGS Samples collected from Norman Landfill site							
Samples collected October 25 and 26, 1995							
mg/L	Glass	Plastic					
	Silver filtered	Acidified					
Well #	DOC	DOC	TOC	F	Br	Cl	SO4
WS1	No sample	5.2	5.1	1.66	<.5	135	63
PSO4	1.5	2.2	2.7	1.1	3.07	4.81	33.9
PSO6	0.2	0.1	0.5	<2	<2	509	35.6
PSO7	4.4	4.6	4.5	2.23	3.81	32.9	153
PSO8	4.8	4.2	5.3	1	3.27	15.6	77.5
PS10	3.5	*	17.7	<5.5	<5.5	13.6	43.7
PS12	3.3	*	30.1	<5.5	<5.5	2.88	95.6
PS17	4.5	*	16	<5.5	<5.5	8.19	169
PS18	4.3	*	24.1	<5.5	<5.5	25.9	5.31
PS22	2.1	*	8.4	<5.5	<5.5	<5.5	3.02
PS35	101	*	302	<5.5	<5.5	603	4.82
PS36	101	*	249	<5.5	<5.5	723	<5.5
PS37	37.5	*	119	<5.5	<5.5	281	458
PS38	33.8	*	85.5	<5.5	<5.5	250	303
PS39	33.5	*	79.9	<5.5	<5.5	208	164
PS16D	4.5	*	11.3	<5.5	<5.5	26.6	5.66
Slough	26.1	*	75	<5.5	<5.5	300	133
PS43B	110	111.3	117	<3	<3	832	<3
PS40	182	191.6	197.4	<3	<3	970	<3
PS54	23.7	21.3	23.3	<.5	10	265	17.7
FB01	<0.1	0.1	0.1	<3	<3	<3	<3
PS54B	77.9	78.4	82.7	<3	<3	622	3.37
PS38B	142	*	147.5	<3	<3	821	<3
PS38BD	143	147.6	149.6	<3	<3	836	<3
PS54C	102	103	108	<3	<3	823	<3
PS38C	154	157.6	162.7	<3	<3	1000	<3
AB01	<0.1	0.1	0.1	<3	<3	<3	<3
PS38D	116	118.4	123	<3	<3	1081	<3
PS54D	109	110.5	114.6	<3	<3	948	<3
CR01	2.8	2.8	3.6	<3	<3	124	486
JPESW	no sample	2.3	3	<3	<3	91	81
JPWSW	no sample	3.2	3.9	<3	<3	166	75
* Sample not analyzed for DOC							

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mg/L							
Well #	NO2+NO3	NO2	NO3	NH3	O-PO4	Total PO4	
WS1		<.05	<.05	1.57	0.3		
PSO4		<.05	0.12	0.21	0.44		
PSO6		<.05	0.72	<.05	0.05		
PSO7		<.05	<.05	0.11	0.13		
PSO8		<.05	<.05	0.25	0.51		
PS10	0.31			0.51	<.02	0.27	
PS12	0.29			0.69	0.61	0.57	
PS17	0.23			1.83	1.02	1.1	
PS18	0.14			2.47	1.28	1.27	
PS22	0.09			1.72	0.84	0.95	
PS35	0.38			212	0.8	0.87	
PS36	0.49			233	0.58	0.61	
PS37	0.38			20.2	0.27	0.28	
PS38	0.34			54	0.48	0.48	
PS39	0.29			38.1	1.07	1.03	
PS18D	0.15			2.48	1.31	1.33	
Slough	6.3			4.75	0.75	0.91	
PS43B		<.05	<.05	184	<.05	0.07	
PS40		<.05	<.05	321	<.05	0.1	
PS54		<.05	<.05	0.87	<.05	0.31	
FB01		<.05	<.05	<.05	<.05	0.05	
PS54B		<.05	<.05	2.82	<.05	0.1	
PS38B		<.05	<.05	5.3	<.05	0.08	
PS38BD		<.05	<.05	5.3	<.05	0.09	
PS54C		<.05	<.05	5.41	<.05	0.1	
PS38C		<.05	<.05	45.4	<.05	0.08	
AB01		<.05	<.05	<.05	<.05	0.12	
PS38D		<.05	<.05	4.23	<.05	0.07	
PS54D		<.05	<.05	4.73	<.05	0.11	
CR01		<.05	1.71	<.05	<.05	0.09	
JPESW		<.05	<.05	1.22	<.05	0.08	
JPWSW		<.05	<.05	1.54	<.05	0.06	

Note: Some samples were analyzed for NO2+NO3 and some were for both NO2 and NO3.

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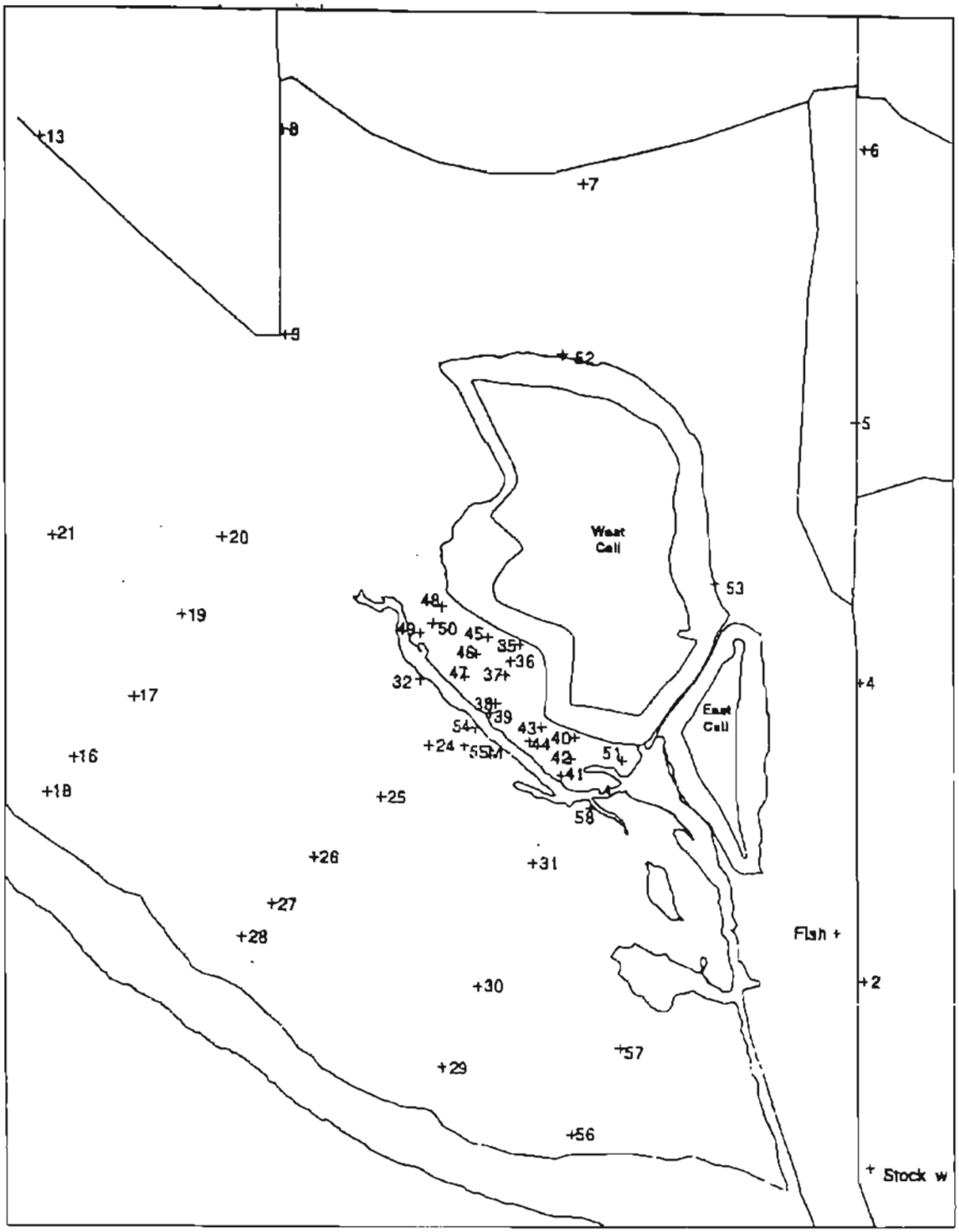
		ppb	ppm	ppm	ppm
		Hg	As	Se	Pb
Slough	gold fixed	<1.0	<1.0	<1.0	<1.0
PS10	gold fixed	<1.0	<1.0	<1.0	<1.0
PS12	gold fixed	<1.0	<1.0	<1.0	<1.0
PS16D	gold fixed	<1.0	<1.0	<1.0	<1.0
PS17	gold fixed	<1.0	<1.0	<1.0	<1.0
PS18	gold fixed	<1.0	<1.0	<1.0	<1.0
PS22	gold fixed	<1.0	<1.0	<1.0	<1.0
PS35	gold fixed	<1.0	<1.0	<1.0	<1.0
PS36	gold fixed	<1.0	<1.0	<1.0	<1.0
PS37	gold fixed	<1.0	<1.0	<1.0	<1.0
PS38	gold fixed	<1.0	<1.0	<1.0	<1.0
PS39	gold fixed	<1.0	<1.0	<1.0	<1.0
AB01	gold fixed	<1.0	<1.0	<1.0	<1.0
CR01	gold fixed	<1.0	<1.0	<1.0	<1.0
FB01	gold fixed	<1.0	<1.0	<1.0	<1.0
PS38B	gold fixed	<1.0	<1.0	<1.0	<1.0
PS38BD	gold fixed	<1.0	<1.0	<1.0	<1.0
PS38C	gold fixed	<1.0	<1.0	<1.0	<1.0
PS38D	gold fixed	<1.0	<1.0	<1.0	<1.0
PS40	gold fixed	<1.0	<1.0	<1.0	<1.0
PS43B	gold fixed	<1.0	<1.0	<1.0	<1.0
PS54	gold fixed	<1.0	<1.0	<1.0	<1.0
PS54B	gold fixed	<1.0	<1.0	<1.0	<1.0
PS54C	gold fixed	<1.0	<1.0	<1.0	<1.0
PS54D	gold fixed	<1.0	<1.0	<1.0	<1.0
JPESW	gold fixed	<1.0	<1.0	<1.0	<1.0
JPWSW	gold fixed	<1.0	<1.0	<1.0	<1.0
WSI	filtered	<1.0	<1.0	<1.0	<1.0
WSI	unfiltered	<1.0	<1.0	<1.0	<1.0
PS04	filtered	<1.0	<1.0	<1.0	<1.0
PS04	unfiltered	<1.0	<1.0	<1.0	<1.0
PS06	filtered	<1.0	<1.0	<1.0	<1.0
PS06	unfiltered	<1.0	<1.0	<1.0	<1.0
PS07	filtered	<1.0	<1.0	<1.0	<1.0
PS07	unfiltered	<1.0	<1.0	<1.0	<1.0
PS07	gold fixed	<1.0	<1.0	<1.0	<1.0
PS08	filtered	<1.0	<1.0	<1.0	<1.0
PS08	unfiltered	<1.0	<1.0	<1.0	<1.0
PS08	gold fixed	<1.0	<1.0	<1.0	<1.0
Ran on AA Graphite					
Detection limit for Hg = 1 ppb					
Detection limit for As, Se and Pb = 1 ppm					



North American Datum of 1983
Universal Transverse Mercator Projection
Zone 14

U.S. Geological Survey

The following is a list of organic compounds detected in water quality samples taken from the Norman landfill.

VOLATILE ORGANIC COMPOUNDS	CONCENTRATION ug/l
Benzene	5
Chlorobenzene	23

TARGETED PESTICIDE COMPOUNDS (All of these hits were later refuted on a second column)	CONCENTRATION ug/l
Diazinon	1.0
Ethylparathion	0.47
4,4- DDT	0.16
gamma-BHC(lindane)	0.28
delta-BHC	0.081

TENTATIVELY IDENTFIED SEMI-VOLATILE COMPOUNDS(TIC's)	Occurances	min.	max.	avg.	CONCENTRATION ug/l
1,3- Oxathiolane	1				6.4
Siloxane	12	5	40	12.3	
2-bromo-Hexane	1				8.3
nitro-Methane	1				13
Oxygenated Hydrocarbons	45	4.1	100	15	
3,3'-oxybis-2-Butanol	1				9.6
1-(2 methoxy-1-methylethoxy)-2-Propanol	6	4.6	17	8.6	
1-methyl-5-trideutero Methyltetrazole	1				6.8
Propaline Glycol	1				5.2
1-Amino-4-methylpiperazine	1				4.6
1,3,3-Trimethoxybutane	1				5.2
2,3,4,6-Tetramethyl-4-pyrone	1				6.7
2-ethoxy-1-Propanol	1				11
Diethyltoluamid	6	9.2	30	17	
6-chloro-1H- Purine	1				8.3
N-ethyl-4-methyl Benzenesulfonamid	5	6.6	21	12	
1,8-Diaza-2,9-diketocyclotetradecane	1				35
Octadecanoic acid,butyl ester	1				21
Nitrogen compound	5	10	81	33	
Cyanogen chloride	6	6.9	36	17	
3-Methylaniline	1				7.2
2-methyl-3-Buten--2-ol	1				6.8
5-Isopropyl-2,4-dioxo-1,2,3,4-tetrahydropyrimid	3	10	16	13	
N,N-4-trimethyl Benzenesulfonamid	2				20
2(3H)-Benzothiazolone	1				7.3
2,2-dimethylethenyl ester, Pentanoic acid	2				7.2
1,1'-oxybis(2-ethoxy) Ethane	1				4.6
2-(2-ethoxyethoxy)Ethanol	5	4.6	23	16	
4-acetyl-Morpholine	3	16	21	19	
Sterol	1				5.5
1-hydroxymethyl-5,5- di..... 2,4-Imidazolidinedione	1				6.3
6-methyl-2-(1-methylethyl)-4-(1H) Pyrimidinone	1				14
p-tert-butyl Benzoic acid	1				24
1,1'-oxybis-2-Propanol	1				16
Cyclic Hydrocarbons	3	5.7	8.9	7.6	
1-ethoxy-1-methoxy Ethane	1				9.3
4-propoxy-Phenol	1				5.4
Aromatic hydrocarbon	1				12
1,1'-(1-methyl-1,2-ethanediyl) bis..... 2-Propanol	2				26
2-(2-methoxy-1-methyl ethoxy) 1-Propanol	1				6.4

SITE ID	DATE	TIME	VOCS TARGETED COMPOUNDS ug/l	VOCS TIC ug/l	SEMIVOLATILES TARGETED COMPOUNDS ug/l	SEMIVOLATILES TIC ug/l	CHLORINATED PEST. AND PCB's ug/l	ORGANOPHOSPHATE PESTICIDES ug/l	CHLORINATED HERBICIDES ug/l	METALS mg/l	INORGANICS mg/l	METHOD BLANKS ug/l
5100009/250001 Heston Blank-1-M	01/08/95	1000	Methylene Cl 8100/250	ND	ND	2 TID's 6.0&7.0	ND	ND	ND	ND	ND	1,2-Dibromo-3Chloro-propane 1.7/10 Methylene Cl 1/5 Methyl methacrylate 1.2/20
5100009/250001 Heston Blank-2-M	03/08/95	1450	Methylene Cl 520/25	ND	ND	2 TID's 1767.6	ND	ND	ND	Pb .0077/.005	ND	Same as Above
5100309/264601 Field Blank SS01	04/13/95	1600	Methylene Cl 3200/100	ND	ND	1 TID@6.1	ND	ND	ND	FE .052/.04 ZN .024/.02	ND	a,a-dimethylphenethyl amine 1.1/10
5100309/264601 SS WEST INTERMEDIATE	04/14/95	1300	ND	ND	ND	20 TID's 4.6-35	ND	ND	ND	Ba 10.6/.01 Co .012/.01 Fe 16.9/.04	Cl 1030/10 NO3 1.3/1.0	a,a-dimethylphenethyl amine 1.1/10
5100309/264602 SS WEST SHALLOW	04/15/95	1000	Benzene 5.0/5.0 Chlorobenzene 23.0/5.0	ND	ND	20 TID's 4.6-100	ND	Diazinon 1/.25 EthylParathion, 0.47/0.25 ND's on second col. (prefored)	ND	As .0077/.005 Ba 3.5/.01 Co .012/.01 Fe 9.3/.04	Cl 642/5 NO3 1.1/1.0 SO4 90.4/1.0	2-Butanone 2.2/10 Methylene Cl 2.0/5.0 Fe .049/.04 Sn 0.16/.1
5100309/264603 SS WEST DEEP	04/15/95	1500	ND	ND	ND	17 TID's 4.1-81	ND	ND	ND	Ba 4.8/.01 Co .018/.01 Fe 7.5/0.04	Cl 689/5.0 NO3 0.96/.5 SO4 3.6/0.5	Same as Above
5095909/264301 SS EAST INTERMEDIATE	04/16/95	1200	ND	ND	ND	14 TID's 4.6-44	ND	ND	ND	As 0.017/.005 Ba 0.86/0.01 Fe 18.9/0.04	Cl 569/5.0 NO3 0.70/0.5 SO4 56.1/0.5	Same as Above
5095909/264302 SS EAST SHALLOW	04/16/95	1600	ND	ND	ND	20 TID's 8.4-40	4,4' DDT .16/.10 ND on second col. (preforced)	Diazinon 1.3/.25 ND on second col. (prefored) g-BHC (lindane) 0.28/0.05 (on second col.)	ND	Ba 5.6/0.01 Co 0.019/0.01 Fe 16.9/0.04	Cl 941/5.0 NO3 1.5/1.0 SO4 18.1/1.0	Same as Above
5095909/264302 Field Blank SS EAST B	04/17/95	1200	Methylene Cl 250/10	ND	ND	1 TID 8.5	ND	ND	ND	ND	ND	Same as Above
5095909/264401 SS EAST DEEP	04/18/95	1100	ND	ND	ND	20 TID's 5.0-75.0	d-BHC 0.081/0.05 ND on second col. (preforced)	ND	ND	Ba 3.8/0.01 Fe 9.9/0.04	Cl 498/5.0 NO3 0.87/0.5 SO4 11.3/0.5	Fe .043/.04
5100309/264501 SS CENTRAL INTERMEDIATE	04/19/95	1200	ND	ND	ND	20 TID's 8.5-76	ND	ND	ND	Ba 6.9/0.01 Fe 9.2/0.04	Cl 763/5.0 SO4 7.8/1.0	ND

APPENDIX B –

Experimental Data

Baseline Chloroform Degradation using 100 µg/L $CHCl_3$

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate-Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	912,781	781,587	668,655	0	652,495	487,327	439,751	0	1,687,391	1,980,231	1,538,084
3	423,896	325,687	336,452	3	324,543	253,726	210,681	3	759,056	987,543	793,254
7	17,596	17,278	17,520	7	34,600	27,218	26,347	7	23,154	23,233	16,195

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	7 01	6.85	6.69	0	6.66	6.36	6.25	0	7.63	7 80	7.54
3	6.21	5 93	5.97	3	5 93	5.66	5.46	3	6.82	7.09	6.86
7	1.60	1 68	1.62	7	2.78	1.94	1.77	7	0.65	0.70	1.90

Notes:

1. Use y=805 7x+21606 from calibration curve
2. Time is in days
3. Conc. is in µg/L

Chloroform Degradation With Added Zinc using 100 µg/L $CHCl_3$

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate-Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	296,600	443,222	287,930	0	266,230	269,601	269,788	0	249,502	227,720	378,559
16	95,388	84,729	85,981	16	109,528	78,273	72,422	16	84,114	105,778	83,290
24	19,765	16,111	10,923	24	47,025	34,018	19,336	24	14,744	119,193	14,054

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	5.83	6.26	5.80	0	5.72	5.73	5.73	0	5.64	5.54	6.09
16	4.52	4.36	4.38	16	4.69	4.25	4.14	16	4.35	4.65	4.34
24	0.83	1.92	2.58	24	3.45	2.73	1.04	24	2.14	4.80	2.24

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3. Conc. is in µg/L

Chloroform Degradation With Added Nickel using 100 µg/L $CHCl_3$

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate-Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	94,508	34,965	52,906	0	220,177	257,773	392,980	0	276,865	372,552	356,520
16	8,552	8,776	0	16	43,359	107,673	114,276	16	105,291	111,948	80,044
24	445,554	44,258	12,551	24	26,772	163,104	243,685	24	51,798	16,467	12,410

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	4.51	2.81	3.66	0	5.51	5.68	6.13	0	5.76	6.08	6.03
16	2.79	2.77	3.29	16	3.30	4.67	4.75	16	4.64	4.72	4.28
24	6.27	3.34	2.42	24	1.86	5.17	5.62	24	3.62	1.85	2.43

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3 Conc. is in µg/L

Chloroform Degradation With Added Cadmium using 100 µg/L $CHCl_3$

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	308,559	33,672	287,744	0	267,527	372,484	246,974	0	26,132	202,730	276,916
16	109,777	116,249	110,766	16	112,157	106,099	70,986	16	81,940	130,835	105,531
24	14,373	27,481	22,476	24	88,631	16,894	15,066	24	183,557	248,407	31,890

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	5.88	2.71	5.80	0	5.72	6.08	5.63	0	1.73	5.42	5.76
16	4.70	4.77	4.71	16	4.72	4.65	4.12	16	4.32	4.91	4.65
24	2.19	1.99	0.08	24	4.42	1.77	2.09	24	5.30	5.64	2.55

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3. Conc. is in µg/L

Chloroform Degradation With Added Chromium using 100 µg/L $CHCl_3$

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	254,404	408,935	1,290,206	0	211,961	1,349,120	255,530	0	296,044	1,597,282	347,778
16	111,038	85,747	1,171,571	16	87,147	1,789,531	74,044	16	62,373	2,145,952	96,879
24	16,235	5,006,720	2,820,701	24	21,236	2,007,782	92,395	24	86,875	20,468	17,136

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	5.67	6.18	7.36	0	5.46	7.41	5.67	0	5.83	7.58	6.00
16	4.71	4.38	7.26	16	4.40	7.69	4.18	16	3.92	7.88	4.54
24	1.90	8.73	8.15	24	0.00	7.81	4.48	24	4.39	0.35	1.71

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3. Conc. is in µg/L

Chloroform Degradation With a Combination of the Metals using 100 µg/L $CHCl_3$

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	18,883	268,134	246,715	0	289,131	306,416	297,776	0	252,492	29,572	237,471
16	8,488	53,401	54,707	16	88,960	66,968	84,961	16	75,992	8,541	65,139
24	11,755	40,487	12,654	24	21,474	12,555	23,007	24	18,482	10,058	81,654

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	1.22	5.72	5.63	0	5.81	5.87	5.84	0	5.66	2.29	5.59
16	2.79	3.68	3.72	16	4.43	4.03	4.36	16	4.21	2.79	3.99
24	2.50	3.15	2.41	24	0.00	2.42	0.55	24	1.36	2.66	4.31

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3. Conc. is in µg/L

Chloroform Degradation With Added Ethylbenzene using 100 µg/L $CHCl_3$

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	305,374	222,265	205,608	0	220,862	357,182	372,799	0	400,684	351,653	446,160
14	26,591	46,881	6,295	14	31,735	5,345	4,069	14	4,213	4,451	6,322
24	8,694	15,934	1,295	24	10,365	946	824	24	759	628	1,598

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	5.86	5.52	5.43	0	5.51	6.03	6.08	0	6.15	6.02	6.27
14	1.82	3.45	2.94	14	2.53	3.00	3.08	14	3.07	3.06	2.94
24	2.77	1.95	3.23	24	2.64	3.24	3.25	24	3.25	3.26	3.21

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3. Conc. is in µg/L

Chloroform Degradation With Added Decahydronapthalene using 100 µg/L $CHCl_3$

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	350,893	208,808	234,180	0	254,216	189,571	173,734	0	322,088	411,990	316,232
14	2,989	3,511	6,145	14	2,969	6,091	3,513	14	4,154	59,834	5,821
24	203	389	673	24	286	564	302	24	364	12,356	458

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	6.01	5.45	5.58	0	5.67	5.34	5.24	0	5.92	6.18	5.90
14	3.14	3.11	2.95	14	3.14	2.96	3.11	14	3.08	3.86	2.98
24	3.28	3.27	3.26	24	3.28	3.26	3.27	24	3.27	2.44	3.27

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3. Conc. is in µg/L

Chloroform Degradation With Added 2,2,4-Trimethylpentane using 100 µg/L $CHCl_3$

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	401,277	328,345	407,718	0	278,788	232,889	572,464	0	373,920	174,121	311,920
14	6,873	56,294	58,401	14	9,336	4,273	50,151	14	4,089	25,918	4,701
24	853	17,854	18,632	24	1,549	358	15,982	24	589	7,352	692

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	6.16	5.94	6.17	0	5.77	5.57	6.53	0	6.08	5.24	5.89
14	2.91	3.76	3.82	14	2.72	3.07	3.57	14	3.08	1.68	3.04
24	3.25	1.54	1.31	24	3.21	3.27	1.94	24	3.26	2.87	3.26

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3. Conc is in µg/L

Chloroform Degradation With a Combination of Non-Chlorinated Organics using 100 µg/L $CHCl_3$

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	235,284	407,354	286,400	0	266,683	512,186	418,677	0	474,598	236,286	287,495
14	7,916	10,416	11,050	14	10,048	8,071	10,416	14	7,031	12,465	10,116
24	436	1,896	1,854	24	1,267	753	1,687	24	649	1,598	1,064

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	5.58	6.17	5.79	0	5.72	6.41	6.20	0	6.33	5.59	5.80
14	2.83	2.63	2.57	14	2.66	2.82	2.63	14	2.90	2.43	2.66
24	3.27	3.20	3.20	24	3.23	3.25	3.21	24	3.26	3.21	3.24

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3. Conc. is in µg/L

Chloroform Degradation With 100 μg/L $CHCl_3$ and 500 μg/L p-DCB

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	388,546	379,262	321,504	0	330,819	349,888	412,320	0	358,654	333,846	342,359
7	171,485	290,118	257,933	7	299,576	278,367	283,990	7	220,439	217,702	286,618
24	12,840	12,136	12,539	24	14,188	14,891	17,253	24	13,906	15,334	17,139

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	6.12	6.10	5.92	0	5.95	6.01	6.18	0	6.04	5.96	5.99
7	5.23	5.81	5.68	7	5.84	5.76	5.79	7	5.51	5.49	5.80
24	2.39	2.46	2.42	24	2.22	2.12	1.69	24	2.26	2.05	1.71

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3. Conc. is in mg/L

Chloroform Degradation With 100 mg/L $CHCl_3$ and 60 mg/L p-DCB

Chromatogram Peaks

Methanogenic				Denitrifying				Sulfate Reducing			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	403,790	349,692	387,357	0	309,879	393,464	340,762	0	385,090	457,291	427,114
7	290,560	271,556	290,790	7	224,475	319,557	164,825	7	316,762	295,446	305,849
24	10,564	10,201	4,986	24	10,462	5,174	9,962	24	195,341	14,068	11,163

First-order Degradation

Methanogenic (Natural Log)				Denitrifying (Natural Log)				Sulfate-Reducing (Natural Log)			
Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.	Time	Conc.	Conc.	Conc.
0	6.16	6.01	6.12	0	5.88	6.13	5.98	0	6.11	6.29	6.22
7	5.81	5.74	5.81	7	5.53	5.91	5.18	7	5.90	5.83	5.87
24	2.62	2.65	3.03	24	2.63	3.02	2.67	24	5.37	2.24	2.56

Notes:

1. Use y=805.7x+21606 from calibration curve
2. Time is in days
3. Conc. is in mg/L

VITA

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