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**Anaerobic Biodegradation of Hazardous Organics in Groundwater
Down Gradient of a Sanitary Landfill**

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ABSTRACT

The primary objectives of this investigation were to evaluate the distribution and anaerobic biodegradability of selected organic contaminants leaching from the Wilder's Grove landfill in Raleigh, NC. This facility is typical of sanitary landfills located in the Piedmont region of North Carolina and was constructed without an engineered liner or leachate control system.

The aquifer studied was shallow and unconfined and consisted of a saprolite material. The major organic compounds identified were c-dichloroethylene (c-DCE) and toluene. A tracer test utilizing chloride and bromide was conducted to characterize the hydraulic properties of the aquifer. The groundwater velocity was determined to be 6.4 cm/day in the vicinity of the study area.

A series of monitoring wells was installed along a single streamline and monitored to determine if there was evidence of contaminant biodegradation. Large temporal and spatial variations were observed in groundwater chemistry. These large variations are typical of leachate impacted aquifers and made it impossible to determine if biodegradation was a significant process in limiting contaminant migration.

The biodegradative potential of anaerobic aquifer sediment was further explored in laboratory experiments. Anaerobic aquifer sediment was obtained down gradient of the landfill and used to construct microcosms in which the degradability of benzene, toluene, ethylbenzene, meta- and ortho-xylene (BTEX) and trichloroethylene (TCE) was examined under ambient and amended conditions. The ambient condition study consisted of live microcosms and killed controls constructed using groundwater and aquifer sediment from each of three boreholes. Aquifer sediment and groundwater from one borehole were used to construct microcosms in which the potentially stimulatory effects of buffering, nutrient addition and availability of readily degradable carbon sources were tested. Benzene, ethylbenzene and xylene isomers were recalcitrant in both ambient and amendment experiments. Variations in TCE and toluene degradation in the ambient condition study indicated varied affinity for these compounds within the aquifer. TCE exhibited an inhibitory effect on toluene degradation at one location. Stimulatory effects of the three amendments tested were minimal if not negligible with respect to BTEX. Biotransformation of TCE was stimulated by buffering with calcium carbonate. TCE was converted to ethylene, a harmless byproduct, in several tests.

key words: anaerobic biodegradation, biotransformation, benzene, toluene, ethylbenzene, meta- and ortho-xylene, trichloroethylene, landfills, groundwater

TABLE OF CONTENTS

	Page
Abstract	ii
Table of Contents	iii
List of Figures	v
List of Tables	vi
1.0 Summary and Conclusions	vii
2.0 Recommendations	x
3.0 Introduction	1
4.0 Anaerobic Degradation of Hazardous Organics	2
4.1 Anaerobic Microbiology of the Subsurface	2
4.2 Anaerobic Biodegradation of Alkylbenzenes	3
4.3 Anaerobic Biodegradation of Chlorinated Aliphatics	4
4.4 Anaerobic Biodegradation Summary	6
5.0 Study Site	8
5.1 Location and Characteristics	8
5.2 Hydrogeology	8
5.3 Tracer Test	10
5.4 Results of Previous Groundwater Monitoring	10
6.0 Chemical Characterization of the Aquifer	13
6.1 Groundwater Monitoring	13
6.2 Sampling and Analytical Procedures	13
6.3 Geochemical Conditions in the Aquifer	14
6.3.1 Temporal Variation in BTEX and CAHs	14
6.3.2 Spatial Distribution of BTEX and CAHs	14
7.0 Laboratory Studies of Anaerobic Biodegradation	23
7.1 Experimental Design and Methods	23
7.2 Experimental Methods	24
7.2.1 Soil and Water Collection and Preparation Collection	24
7.2.2 Preparation of Spike Solutions	25
7.2.3 Microcosm Construction	25
7.2.4 Sampling and Analysis of Microcosms	26

8.0 Results of Laboratory Studies	28
8.1 Ambient Microcosms	28
8.1.1 Biodegradation in LFN Microcosms	28
8.1.2 Biodegradation in LFM Microcosms	34
8.1.3 Biodegradation in LFF Microcosms	40
8.1.4 Biodegradation of BTEX and TCE in the Presence of Buffer, Nutrients and Readily Degradable carbon	44
9.0 Discussion	58
9.1 Field Monitoring	58
9.2 Biodegradation in Ambient and Amended Microcosms	58
9.2.1 TCE Biodegradation in Ambient Microcosms	59
9.2.2 TCE Biodegradation in Amended Microcosms	60
9.2.3 Methane Production in Microcosms	62
9.2.4 BTEX Biodegradation in Ambient Microcosms	62
9.2.5 BTEX Biodegradation in the Amended Microcosms	63
9.3 Effect of Biotransformation on Contaminant Fate and Transport	63
References	66

LIST OF FIGURES

	Page
1. Monitoring Well and Soil-Boring Locations	9
2. Monitoring Well Locations from Douglass and Borden (1992)	12
3. Variation in Toluene Concentration in Monitoring Wells with Time	18
4. Comparison of Toluene in Monitoring Wells M and N with First-Order Regression	19
5. Spatial Variation in Average Concentrations of Toluene, c-DCE, t-DCE and PCE	21
6. TCE Degradation in LFN Microcosms	31
7. Toluene Degradation in LFN Microcosms	33
8. TCE Degradation in LFM Microcosms	37
9. Benzene Degradation in LFM Microcosms	39
10. Best Fit Regression Lines for TCE Degradation in Amended Microcosms	45
11. Best Fit Regression Lines for Benzene Degradation in Amended Microcosms	55

LIST OF TABLES

Page

1.	Average Groundwater Quality Monitoring Results - 1989	11
2.	Average Concentrations of Electron Acceptors and Nutrients	15
3.	Average Values of Geochemical Indicators	16
4.	Average Concentrations of Dissolved Metals and Ions in Groundwater	17
5.	Average Concentrations of Organics Detected in Groundwater	20
6.	Experimental Design for Amended Microcosms	24
7.	Spikes Added to Each Set of Microcosms	26
8.	BTEX, TCE and Methane Concentrations in LFN Microcosms	29
9.	First-Order Degradation Rate Constants in Live and Abiotic LFN Microcosms	32
10.	BTEX, TCE and Methane Concentrations in LFM Microcosms	35
11.	First-Order Degradation Rate Constants in Live and Abiotic LFM Microcosms	38
12.	BTEX, TCE and Methane Concentrations in LFF Microcosms	41
13.	First-Order Degradation Rate Constants in Live and Abiotic LFF Microcosms	43
14.	TCE Concentrations in Amended Microcosms	46
15.	Ethylene Concentrations in Amended Microcosms	48
16.	Expected and Observed Ethylene Recovery	47
17.	Toluene Concentrations in Amended Microcosms	50
18.	Benzene Concentrations in Amended Microcosms	51
19.	Ethylbenzene Concentrations in Amended Microcosms	52
20.	m-Xylene Concentrations in Amended Microcosms	53
21.	o-Xylene Concentrations in Amended Microcosms	54
22.	Methane Concentrations in Amended Microcosms	57
23.	Summary of Biodegradation Rates	59
24.	Comparison of TCE Biodegradation Rates at Various Time Intervals	61
25.	Ethylbenzene Concentrations in Individual Amended Microcosms	64

1.0 SUMMARY AND CONCLUSIONS

The anaerobic biodegradability of alkylbenzenes (benzene, toluene, ethylbenzene and xylene isomers or BTEX) and chlorinated aliphatic hydrocarbons (CAHs) leaching from a sanitary landfill was studied to evaluate the potential for these contaminants to naturally attenuate during transport through the subsurface. The site selected for study was the Wilder's Grove Sanitary Landfill in Raleigh, NC. This facility is typical of sanitary landfills located in the Piedmont region of North Carolina and was constructed without an engineered liner or leachate control system.

Field Characterization

The hydrogeology and contaminant distribution immediately down gradient of the refuse disposal area was characterized by a tracer test and periodic groundwater sampling. A series of wells was installed and monitored over a 6-month period to determine the spatial and temporal variation in BTEX, CAHs and indicator parameters. A non-reactive tracer test using chloride and bromide was performed to estimate the groundwater velocity in the study area and allow comparison of the laboratory degradation rates with the field monitoring results. While the chloride pulse was masked by the high background chloride concentrations, the appearance of bromide at a monitoring well immediately down gradient was used to estimate the groundwater velocity. The groundwater velocity estimated from the tracer test (0.07 m/d) is very similar to preliminary estimates of groundwater velocity (0.11 m/d) based on measurements of hydraulic conductivity and water table gradient.

Groundwater within the study area is highly reduced as evidenced by the absence of dissolved oxygen and nitrate, negative redox potential, and high concentrations of dissolved iron and manganese. The chemical oxygen demand (COD) is highest near the edge of refuse and lowest near the adjoining drainage channel indicating some attenuation of organic contaminants during transport through the subsurface.

Groundwater throughout the study area is contaminated with a variety of hazardous organic contaminants including benzene, toluene, ethylbenzene, xylene isomers, tetrachloroethylene (PCE), and cis- and trans-dichloroethylene (c-DCE and t-DCE). Benzene, toluene, PCE, and both c-DCE and t-DCE all exceed groundwater standards at one or more wells although the maximum benzene concentration is 5 µg/l. There was no evidence during the study of an increase or decrease in overall contaminant concentrations in the study area, although concentrations in individual wells did occasionally show trends.

A series of wells was installed and monitored along a single streamline to evaluate potential for contaminant attenuation during transport through the subsurface. Based on 6 months of monitoring over a 12-m distance, there is no evidence of significant contaminant attenuation. Over a larger scale, contaminant attenuation may or may not be evident.

Laboratory Studies

A laboratory microcosm study was conducted to evaluate the potential for natural attenuation of alkylbenzenes and chlorinated aliphatics under anaerobic conditions in the aquifer immediately down gradient of the landfill. Attenuation of compounds under ambient aquifer conditions was monitored in three sets of microcosms constructed using aquifer sediment and groundwater collected three meters apart along a groundwater flow path. In a second experiment, attempts were made to enhance biotransformation of compounds through the following amendments: buffering with calcium carbonate to pH 7.5, addition of nutrients

(ammonia chloride and potassium phosphate) and addition of easily degradable carbon (acetate, formate, benzoate, glucose and yeast extract).

Benzene, ethylbenzene and xylene isomers (BEX) appeared recalcitrant in microcosms in both sets of experiments. There may have been limited and localized biological activity towards BEX; however, any such activity was minimal (statistically insignificant in all but one case). Given the low total organic carbon (TOC) content of the soil (0.028%), sorption to the aquifer material in microcosms was negligible in comparison to sorption/diffusion into the stoppers. Buffering, nutrient addition and carbon supplements did not significantly stimulate biodegradation of BEX.

There was a varying affinity for toluene in the three sets of ambient microcosms. Pockets of toluene degraders apparently exist within the aquifer. However, complete biodegradation of toluene was rarely observed. Toluene-degrading microcosms rapidly degraded toluene to the 30 µg/l range after which degradation ceased. Toluene is one of the predominant hydrocarbons in the groundwater at the research site and the toluene degrading ability in the aquifer is highly variable.

TCE was completely removed from microcosms with complete or near complete conversion to ethylene through the process of reductive dechlorination. TCE removal was not observed in microcosms containing bromoethanesulfonic acid, a methanogen inhibitor, indicating that methanogens were involved in TCE removal. The groundwater contains sufficient carbon sources (electron donors) to support methanogenesis without external carbon addition. Buffering the groundwater to approximately pH 7.5 significantly enhanced the TCE biotransformation rate but was not necessary to achieve complete removal of TCE. Nutrient addition and supplemental carbon addition did not stimulate TCE biotransformation beyond buffering alone, although the rate of complete conversion to ethylene was increased.

CONCLUSIONS

1. The aquifer down gradient of the refuse disposal area at the Wilder's Grove Sanitary Landfill is contaminated with a variety of hazardous organic contaminants including benzene, toluene, ethylbenzene, xylene isomers, tetrachloroethylene (PCE), and cis- and trans-dichloroethylene (c-DCE and t-DCE). Benzene, toluene, PCE, and both c-DCE and t-DCE all exceed groundwater standards at one or more wells although benzene is present at very low concentrations (maximum concentration = 5 µg/l).
2. Conventional field monitoring techniques were not adequate to determine if anaerobic biotransformation processes are significant in limiting the migration of hazardous organics in the subsurface. Large variations in contaminant concentration were observed in groundwater down gradient from waste deposits. Because of these large variations, it would not be possible to detect a slow, but environmentally significant, decline in contaminant concentration without extensive repeated sampling over a large area. This level of monitoring is not practical in most cases.
3. General conditions are appropriate in the aquifer down gradient of the Wilder's Grove landfill to allow the anaerobic biodegradation of TCE and toluene in the contaminated groundwater. Microorganisms are present that can carry out these reactions, and there is no indication that environmental conditions (pH, nutrients, etc.) would inhibit the biodegradation of these compounds.
4. If laboratory biodegradation rates under ambient conditions can be extrapolated to the field, naturally occurring anaerobic biotransformation reactions should prevent the off-site migration of TCE and toluene at this site. It is not yet known whether laboratory-derived biodegradation rates can be reliably used to estimate contaminant transport in the field.
5. Laboratory microcosm results indicate that the rate of TCE biotransformation can be enhanced by buffering the groundwater to approximately pH 7.5. Complete conversion of chlorinated compounds to ethylene may be further enhanced through the addition of inorganic nutrients and an easily degradable carbon source.
6. Benzene, ethylbenzene, meta- and ortho-xylene (BEX) were recalcitrant in the first destructive microcosm study under ambient conditions. While one set of microcosms (LFM) exhibited statistically greater benzene degradation rates in live replicates than in abiotic replicates, this phenomenon was likely the result of greater scatter in the live data. Accelerated BEX loss was observed in a few microcosms in the amendment study. Biodegradation of BEX may have occurred in these isolated cases, but further research will be required to confirm this result.

2.0 RECOMMENDATIONS

1. The North Carolina groundwater quality standards have recently been modified to allow consideration of natural bioremediation in the management of contaminated groundwater. Our results clearly show that anaerobic biotransformation processes have the potential to significantly reduce the migration of alkylbenzenes and chlorinated aliphatic hydrocarbons in the subsurface. Conventional monitoring techniques are not sufficiently sensitive to estimate anaerobic degradation rates in the field at a reasonable cost. If natural attenuation processes are to be considered in the management of contaminated groundwater, better methods will be needed to evaluate the rate and extent of biotransformation under in-situ conditions. Additional research should be performed to understand the factors which influence biodegradation in the field and to develop more accurate and precise methods for estimating degradation rates under in-situ conditions.
2. Our laboratory studies indicate that benzene, ethylbenzene and xylenes were anaerobically biodegraded in a few isolated microcosms. There are very few well-documented cases of anaerobic benzene biodegradation. Additional studies should be performed to determine if this observation can be repeated and to identify the factors that control this process.

3.0 INTRODUCTION

Sanitary landfills constructed without engineered liners release leachate into the subsurface, resulting in groundwater contamination (Hughes et al., 1971; Reinhard et al., 1984; Baedecker and Apgar, 1984; Douglass and Borden, 1992). Leachate composition is highly variable and can contain high concentrations of dissolved ions, ammonia-nitrogen, phosphorus, dissolved solids, heavy metals and hazardous organics. The focus of this study is on the movement and biotransformation of two groups of hazardous organic compounds in groundwater down gradient of the Wilder's Grove sanitary landfill near Raleigh, NC. This landfill is typical of many landfills constructed in the Piedmont of North Carolina prior to 1980. The two groups of compounds to be examined are chlorinated aliphatic hydrocarbons and alkylbenzenes.

Over the past 50 years, chlorinated aliphatic hydrocarbons (CAH) have been widely used as solvents and degreasers and as intermediates in chemical synthesis. Poor disposal practices have led to widespread contamination of groundwater supplies. CAHs are persistent in the environment due in part to their resistance to aerobic biotic and abiotic degradation (Sewell et al., 1990; Sufliita and Sewell, 1991; Semprini et al., 1992). The low retardation factors of CAHs increase their environmental impact relative to other hydrocarbons (Sufliita and Sewell, 1991).

Another class of compounds of concern are the alkylbenzenes including benzene, toluene, ethylbenzene and xylene isomers (BTEX). Poor disposal practices have made alkylbenzenes a leading contaminant of groundwater supplies. Alkylbenzenes have low solubilities and are relatively resistant to anaerobic degradation (Sufliita and Sewell, 1991). Alkylbenzenes sorb easily to organic aquifer material, making it particularly difficult to remove them to acceptable levels by traditional pump-and-treat technologies.

Some CAHs and BTEX components such as vinyl chloride and benzene are known carcinogens (Merck and Co., Inc., 1989). Due to the risk to public health, concentrations of BTEX and a variety of CAHs [tetrachloroethylene (PCE), trichloroethylene (TCE), cis-1,2-dichloroethylene (c-DCE), trans-1,2-dichloroethylene (t-DCE), and vinyl chloride (VC)] in groundwater are regulated under subchapter 2L of the North Carolina Administrative Code (Classifications and Water Quality Standards Applicable to the Groundwaters of North Carolina, sections .0100, .0200 and .0300).

Effective techniques for remediation of groundwater contaminated by CAHs and BTEX are needed. Pump-and-treat technology is often expensive to implement and maintain over the period of time necessary to restore a contaminated site. In addition, pump and treat may not reduce contamination to an acceptable level. In-situ biological treatment is an attractive alternative for aquifer restoration because complete mineralization to non-toxic end products or less toxic intermediates may be achieved without the removal of large volumes of groundwater. However, it is necessary to understand and possibly control the process because harmful intermediates such as dichloroethylenes or vinyl chloride may be produced from PCE and TCE biodegradation.

Aerobic biological treatment of organic compounds is widely documented and practiced. Aerobic metabolism is energetically more favorable to organisms and generally proceeds faster than anaerobic processes (Brock and Madigan, 1991). However, contaminated aquifers are typically anaerobic due to the biological oxygen demand (BOD) placed on them by the contaminant load. Leachate contains numerous organic contaminants including products of refuse decomposition, BTEX, CAHs and a variety of other hazardous compounds. Groundwater contaminated with leachate will quickly become anaerobic as aerobic respiration by

microorganisms depletes the available dissolved oxygen. Bioremediation processes based on external addition of oxygen have been demonstrated. However, oxygen addition is expensive. Thus, to the extent that natural bioremediation is to be successful, contaminants must be primarily degraded under anaerobic conditions.

The objective of this study was to measure the biodegradability of BTEX and TCE in a landfill leachate contaminated aquifer. A series of monitoring wells was installed along a single flow line immediately down gradient from the edge of the landfill to determine the spatial variation in these contaminants and, if possible, estimate ambient degradation rates. Laboratory-scale tests were conducted to measure biodegradability under conditions which simulated ambient conditions in the aquifer. Additional laboratory tests were conducted to evaluate the potential to enhance biodegradation by alteration of environmental conditions. Buffer, nutrients and addition of easily degradable carbon were evaluated for their potential to stimulate BTEX and TCE biodegradation.

4.0 ANAEROBIC DEGRADATION OF HAZARDOUS ORGANICS

4.1 Anaerobic Microbiology of the Subsurface

Most of the subsurface microorganisms identified to date are aerobes, but obligate anaerobes have been identified from a few sites (Ghiorse and Wilson, 1988). Microbially mediated denitrification was observed in a sand and gravel aquifer contaminated with treated sewage (Smith and Duff, 1988). Anaerobic bacteria were recovered by Van Beelen and Fleuren-Kemila (1989) from two sandy aquifers, a saturated peat soil and a river sediment.

Several recent studies have shown that obligate anaerobes are present in deep sediments. Chapelle et al. (1987) identified methanogenic and sulfate-reducing bacteria from sediments collected 20 to 180 m below grade in the Maryland coastal plain. More recent work by Jones et al. (1989) has shown that methanogens are present at over 300 m below grade in sediments at the Savannah River Plant near Aiken, SC. Although the microbial community was dominated by aerobic microorganisms, sulfate-reducing and methanogenic organisms could be identified from most sediments throughout the depth profile. In most cases, the total number of methanogens was very low, but the anaerobic organisms present were capable of degrading a wide variety of organic (benzoate, phenol, lactate, formate, acetate).

Additional evidence for the presence of methanogens in the subsurface comes from research on contaminated aquifers. Microbiologists from the U.S. Geological Survey have studied two different creosote contaminated aquifers where methanogenic degradation of organic compounds has been observed. Field studies at a contaminated aquifer in St. Louis Park, MN showed that methane production was occurring in zones within the aquifer that had been contaminated with creosote (Godsey et al., 1983). Later studies demonstrated that the presence of anaerobes (denitrifiers, iron reducers, sulfate reducers and methanogens) was highly correlated with the presence of creosote. More recent work at an abandoned creosote plant in Pensacola, FL has shown a wide variety of organic compounds present in the aquifer were undergoing methanogenic biodegradation and that transport distances in the aquifer could be correlated with biodegradation rates observed in laboratory microcosms (Goerlitz et al., 1985; Troutman et al., 1984).

Monitoring at petroleum-contaminated sites also provides evidence of methanogenic biotransformation of petroleum-related compounds. Ehrlich et al. (1985) observed elevated numbers of sulfate-reducing and methanogenic bacteria in a jet-fuel-contaminated aquifer. Evans and Thompson (1986) and Marrin (1987) monitored methane concentrations in soil gas to map subsurface hydrocarbon contamination. In a study of soil gas concentrations near

underground storage tanks, Payne and Durgin (1988) found elevated methane concentrations at over 20% of the 36 sites surveyed. Methane gas production can be so rapid that safety problems occur at some sites. Hayman et al. (1988) had to develop a special apparatus to remove the large quantities of methane generated from a fuel spill at the Miami, FL, airport.

Hult (1987) observed the production of large volumes of methane in the unsaturated zone immediately below a crude oil spill at the U.S. Geological Survey research site in Bemiji, Minnesota. At this same site, Eganhouse et al. (1987) observed a two-order-of-magnitude decrease in alkylbenzene concentration over 150 m. This decrease was accompanied by elevated concentrations of aliphatic and aromatic acids in the groundwater (Baedecker et al., 1987). The acids identified in the groundwater included benzoic, methylbenzoic, trimethylbenzoic, toluic, cyclohexanoic, and dimethylcyclohexanoic. These are the same acids identified by Grbic-Galic and Vogel (1987) as intermediates in the anaerobic degradation of alkylbenzenes. Groundwater and sediment analyses demonstrated that methanogenic biodegradation was resulting in a pH decrease and a rise in bicarbonate concentrations in the groundwater. The actual drop in groundwater pH appears to have been limited by dissolution of carbonate minerals (and possibly aluminosilicates) (Siegel, 1987). Most recently, dissolved methane has been detected in alkylbenzene contaminated aquifers at Sleeping Bear Dunes in Michigan. This was accompanied by a concurrent decline in dissolved alkylbenzenes (Wilson et al., 1994).

Adaptation is defined as the ability of microorganisms to degrade a chemical at an increasing rate with exposure to the chemical (Aelion et al., 1987). Such adaptation has been reported for groundwater microorganisms. Wilson et al. (1985) compared the polynuclear aromatic hydrocarbon (PAH) degrading capability of microorganisms in pristine aquifer material to microorganisms at the margin of a creosote contaminated plume. In a demonstration of adaptation, microorganisms with prior exposure were able to degrade the PAHs in laboratory microcosms while those from the pristine area exhibited no such activity. However, adaptation does not occur for every chemical in every ecosystem. Of nine chemicals tested by Aelion et al. (1987), only one exhibited a typical adaptation response and the time of the response varied from a few days to 6 weeks in different samples. An additional six of the nine chemicals were biotransformed by pristine aquifer sediment. These data on adaptation suggest that the prior exposure of aquifer microorganisms increases the potential for biodegradation of the target compounds in aquifer sediment.

4.2 Anaerobic Biodegradation of Alkylbenzenes

Early studies of hydrocarbon biotransformation indicated that aromatic hydrocarbons were refractory under anaerobic conditions (Atlas, 1988). More recent research has shown that a wide variety of organics may be biodegraded by methanogenic consortia. These compounds include substituted monoaromatic compounds including creosol isomers (Healy and Young, 1979; Smoleski and Suflita, 1987), homocyclic and heterocyclic aromatics (Berry et al., 1987), nitrogen containing compounds (Godsy et al., 1983), benzothiophene (Godsy and Grbic-Galic, 1989), phthalates and ketones (Shelton and Tiedje, 1984), and phenols (Boyd et al., 1983). While earlier work had indicated that alkylbenzenes are recalcitrant under methanogenic conditions, recently there have been a few reports of the successful anaerobic biodegradation of alkylbenzenes.

Wilson et al. (1986) observed 99% removal of benzene, toluene, ethylbenzene and o-xylene as well as TCE, DCE isomers and 1,2-dibromoethane in microcosms constructed with methanogenic aquifer material from a landfill site. Long lag periods were required for significant removal of all compounds except toluene. Toluene removal occurred within the first six weeks of incubation. Significant removal of benzene, ethylbenzene and o-xylene did

not occur through 20 weeks of incubation; however, after 40 weeks, approximately 25% of the original material remained. After 120 weeks, less than 1% of the initial BTEX remained.

Wilson et al. (1990) performed microcosm studies using aquifer material from the Traverse City, MI, field site. In these studies, microcosms containing aquifer material from an anaerobic portion of the aquifer were amended with an alkylbenzene dosing solution and incubated anaerobically at 12°C for 2 months. At the end of the incubation, the concentrations of benzene, toluene, m,p-xylene and o-xylene (BTX) had dropped from 450, 420, 440, and 410 µg/l to 6, 40, 17, and 6 µg/l, respectively. The disappearance of BTX in the anaerobic microcosms was accompanied by the production of methane, indicating that anaerobic conditions were maintained. The alkylbenzenes were removed even more rapidly in microcosms prepared using material from an aerobic portion of the aquifer (stations B and C) and incubated under aerobic conditions. In a sterile control, there was a 40 to 50% drop in each of the alkylbenzenes, presumably due to irreversible adsorption. These results clearly demonstrate that anaerobic biotransformation of alkylbenzenes is occurring in the subsurface at the Traverse City site.

Barker et al. (1986) observed decreases in o-xylene concentrations relative to ethylbenzene in a leachate-contaminated aquifer. Their data were suggestive of anaerobic transformation. In anaerobic groundwater down gradient from a Raleigh, NC, landfill, Douglass and Borden (1992) reported a decrease in toluene from 813 to 10 µg/l and in xylenes from 125 to <5 µg/l, while chloride decreased from 90 to 59 mg/l. Again, these data are suggestive of anaerobic transformation.

Grbic-Galic and Vogel (1987) observed benzene and toluene degradation under methanogenic conditions in an enrichment culture fed ferulic acid for 5 years. Unlabeled and ¹⁴C-labeled substrates (ring-labeled toluene and benzene and methyl-labeled toluene) were used. More than 50% of the substrates were converted to CO₂ and methane, with methane accounting for over 60% of the mineralized carbon. A high percentage of CO₂ was recovered from the methyl-labeled toluene, suggesting nearly complete conversion of the methyl group to CO₂ and not methane. Low percentages of CO₂ were produced from ring labeled substrates, indicating incomplete conversion of ring carbon to CO₂. Phenol, cresols and aromatic alcohols were observed as intermediates (Vogel and Grbic-Galic, 1986). Most recently, Sewell and Gibson (1991) showed toluene to be degraded under methanogenic conditions.

Edwards and Grbic-Galic (1992) observed anaerobic benzene degradation in microcosms constructed with material from an anaerobic gasoline contaminated aquifer. Benzene was degraded in all microcosms after a minimum 30-day lag. Radio-labeled carbon was used to verify mineralization of benzene. Approximately 90% of the ¹⁴C was recovered as ¹⁴CO₂. The electron acceptor was not established, although the data suggest that sulfate reduction was involved. Methane was produced, but not enough to account for the benzene disappearance, thus ruling out methanogenesis as the dominant electron sink.

4.3 Anaerobic Biodegradation of Chlorinated Aliphatics

Many highly chlorinated hydrocarbons, including most CAHs, are resistant to aerobic biodegradation (Sufflita and Sewell, 1991). TCE, which is both a widespread contaminant and an anaerobic biotransformation product of PCE degradation, can be degraded aerobically by co-metabolism with toluene or an alkane (Neilson, 1990) but is also degradable under anaerobic conditions (Sewell et al., 1990). Given the recalcitrance of CAHs to aerobic metabolism, anaerobic processes are particularly important. Since chlorinated compounds are relatively oxidized by the presence of chlorine substituents, they are susceptible to reduction (Vogel et

al., 1987). Anaerobic degradation of CAHs may occur through a process termed reductive dechlorination. During reductive dechlorination, the CAH serves as the electron acceptor when the chloride moiety is removed and replaced by a hydrogen, forming a less chlorinated and more reduced intermediate (Sufliata and Sewell, 1991).

Reductive dechlorination requires the presence of an organic electron donor. In the presence of an organic electron donor, PCE can be reductively dechlorinated to TCE. TCE can be sequentially dechlorinated to DCE isomers, then vinyl chloride, and possibly completely dechlorinated to ethylene or ethane (Freedman and Gossett, 1989; De Bruin et al., 1992). Acetate, benzoate, glucose, lactate, methanol, toluene and hydrogen have been shown to be suitable electron donors (Vogel and McCarty, 1985; Scholz-Muramatsu et al., 1989; De Bruin et al., 1992; Freedman and Gossett, 1989; Sewell and Gibson, 1991; DiStephano et al., 1992). In addition, the natural background organic carbon present in many ecosystems may serve as an electron donor for reductive dechlorination. Reductive dechlorination has been shown to occur primarily under methanogenic conditions. Although sulfate and nitrate may inhibit reductive dehalogenation (Mohn and Tiedje, 1992), reductive dechlorination under denitrifying and sulfate-reducing conditions has also been reported (Bouwer and McCarty, 1983; Semprini et al., 1992).

Obligate anaerobes, though not necessarily methanogens, appear to be the primary organisms responsible for reductive dechlorination and require varying acclimation periods. Reductive dechlorination has been reported to occur in several natural anaerobic environments including freshwater sediment (De Bruin et al., 1992; Gibson and Sufliata, 1986), marine sediment (King, 1988), anaerobic sewage sludge (Gibson and Sufliata, 1986) and aquifer sediment (Sewell et al., 1990). Reductive dechlorination has been demonstrated for a variety of compounds including chlorobenzenes (Fathepure and Boyd, 1988; Bosma et al., 1988), chloroanilines (Kuhn and Sufliata, 1989), trichlorophenoxyacetic acid (Gibson and Sufliata, 1989), polychlorinated biphenyls (Quensen et al., 1988), and chlorophenols (Woods et al., 1988).

The reductive dehalogenation of chlorinated aliphatics has also been widely reported. Bouwer and McCarty (1983) were among the first to note reductive dechlorination of halogenated compounds, under both methanogenic and denitrifying conditions. In batch experiments using a methanogenic mixed culture in a deoxygenated anaerobic medium, PCE and carbon tetrachloride (CT) were reductively dechlorinated within 16 days and 8 weeks, respectively. TCE was an intermediate in the reductive dechlorination of PCE. Of chloroform (CF), CT and 1,1,1-TCE tested in batch experiments under denitrifying conditions, only CT was removed. Final end products were not reported. In work with a pure *Methanosarcina* culture, Fathepure and Boyd (1988) showed a direct linkage between PCE dechlorination and methane production. In the absence of a growth substrate, the methanogen culture did not dechlorinate PCE, thereby demonstrating the need for a supplementary carbon source.

In batch experiments using anaerobic enrichment cultures from a sludge digester, Freedman and Gossett (1989) observed complete dechlorination of PCE to ethylene under methanogenic conditions. After an initial dose of PCE was completely removed, serum bottles were respiked with PCE or TCE. Samples from first-generation cultures that degraded PCE were used to seed second-generation cultures and so on until sixth-generation cultures were produced. Early cultures exhibited accumulations of DCE isomers. However, in successive cultures, PCE was rapidly degraded to vinyl chloride, which accumulated prior to conversion to ethylene. The dechlorinating step from vinyl chloride to ethylene was the rate-limiting step. Complete conversion of PCE to vinyl chloride and ethylene was not observed apparently due to leakage losses. Radio tracer studies with ^{14}C -PCE indicated ^{14}C -ethylene was the terminal product. Significant conversion to $^{14}\text{CO}_2$ or $^{14}\text{CH}_4$ was not observed. Although methanol was the most

effective electron donor, hydrogen, formate, acetate and glucose also supported reductive dechlorination.

Sewell and Gibson (1991) observed reductive dechlorination of PCE in batch experiments using aquifer solids exposed to both alkylbenzenes and chlorinated ethenes. TCE and DCE isomers were detected after 120 and 140 days, respectively. DCE isomers and PCE were never detected together at the same sampling time. PCE reduction was not observed in microcosms that did not also receive an inorganic nutrient spike of ammonium phosphate. Acetate was the only metabolic intermediate of toluene degradation observed, reaching a maximum concentration of 180 μM (11 ppm) by 184 days. PCE reduction lagged behind acetate production, which lagged behind toluene removal, which is consistent with the idea that an intermediate of toluene degradation serves as the immediate electron donor for PCE reduction (Scholz-Muramatsu et al., 1989). The reaction stalled at DCE, with DCE reaching a maximum concentration of 20 μM versus an initial PCE concentration of approximately 35.8 μM . The failure to complete a mass balance was attributed to losses during sampling.

De Bruin et al. (1992) observed complete reductive dechlorination of PCE to ethylene and ethane in column studies using anaerobic Rhine River sediment mixed with anaerobic granular sludge and lactate as the electron donor. TCE, DCE isomers and vinyl chloride were observed as dechlorination intermediates. However, after 105 days only ethylene and ethane were observed in the column effluent. The transformation did not occur in the presence of bromoethanesulfonic acid (BES), a methanogen inhibitor, indicating that methanogens play an important role in the transformation in this ecosystem. PCE was not reduced in columns containing Rhine River sediment or granular sludge individually.

Semprini et al. (1992) observed in-situ transformations of carbon tetrachloride (CT), 1,1,1-trichloroethane (TCA), trichlorofluoromethane (CFC-11) and 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) in the presence of acetate as a growth substrate and nitrate and sulfate as potential electron acceptors. CT disappearance began 2 weeks after active denitrification and gradually increased over the 10-week study. Chloroform appeared as an intermediate product, representing only 30-60% of the CT transformed. When nitrate was removed from the injection fluid, CT transformation increased, indicating either that (a) microorganisms other than denitrifiers mediate the transformation of CAHs or (b) a secondary microbial population that grew slowly was responsible for the transformation and its growth was inhibited in the presence of nitrate. Isolated denitrifiers from the test zone failed to transform CT in subsequent studies. Sulfate reducers may have been responsible for the observed removal, but there were insufficient data to confirm this. Methanogens were ruled out since methane production was not observed.

DiStefano et al. (1992) examined hydrogen as a potential electron donor to the reductive dechlorination of PCE in batch experiments using a PCE/MeOH enrichment culture. In culture suspensions fed hydrogen, PCE was completely reduced to vinyl chloride and ethylene in 14 to 40 days. However, this culture could not sustain reductive dechlorination for extended periods. In identically prepared methanol-fed suspensions, reductive dechlorination of PCE was sustainable over time. Further work showed that hydrogen was the direct electron donor for reductive dechlorination but both acetogenic and methanogenic activity were required for the process to proceed.

4.4 ANAEROBIC BIODEGRADATION SUMMARY

The presence of anaerobic bacteria in aquifers has been documented for both pristine and contaminated sites. Preliminary evidence indicates that alkylbenzenes (benzene, toluene, ethylbenzene and xylene isomers) are biodegradable under highly reducing anaerobic

conditions typical of leachate-contaminated aquifers. Toluene appears to be the most degradable of the alkylbenzenes while benzene appears to be the most recalcitrant. Acclimation periods for biodegradation range from several days to several months and are highly variable. It is not yet known under what conditions alkylbenzenes will degrade anaerobically or at what rate biodegradation may occur in leachate-contaminated aquifers.

Highly chlorinated ethenes are often degraded in anaerobic settings via reductive dechlorination, given sufficient electron donors. The ease of dechlorination appears to decrease as the number of chlorine atoms decreases. Recent work has shown that under certain circumstances, chlorinated ethenes may be completely dechlorinated to ethylene and ethane. Most previous research on anaerobic degradation of chlorinated ethenes has used readily degradable carbon sources (e.g., acetate or lactate). The rate and extent of reductive dechlorination in a leachate-contaminated aquifer, where the most readily degradable electron donors have been depleted, is unknown.

5.0 STUDY SITE

5.1 Location and Characteristics

The Wilder's Grove Sanitary Landfill was chosen for study and is located in the Piedmont physiographic province of North Carolina in eastern Wake County. The facility has been in operation since 1972 and receives approximately 1000 tons of municipal refuse per day including domestic, commercial and industrial solid wastes. Disposal of hazardous waste within the landfill is not permitted, although prior to 1989 an active program was not in place to exclude hazardous materials.

This landfill has no design features intended to prevent movement of leachate into the groundwater. The landfill does not have an engineered cover system. In operating the landfill, general nonsegregated solid waste is placed in lifts with 6 to 12 inches of daily cover. After the site is filled to the approved elevation, an additional 24-inch final cover of compacted soil is applied. The refuse disposal area is divided into two regions by a small stream channel passing through the center of the landfill. The portion of the landfill to the west of the channel was deposited between about 1972 and about 1982. Refuse on the eastern side is younger, having been buried from about 1982 to present. Our research has been conducted in a small area on the eastern side of the site immediately adjoining the drainage channel. A site plan showing the monitoring well and soil boring locations is shown in Figure 1.

5.2 Hydrogeology

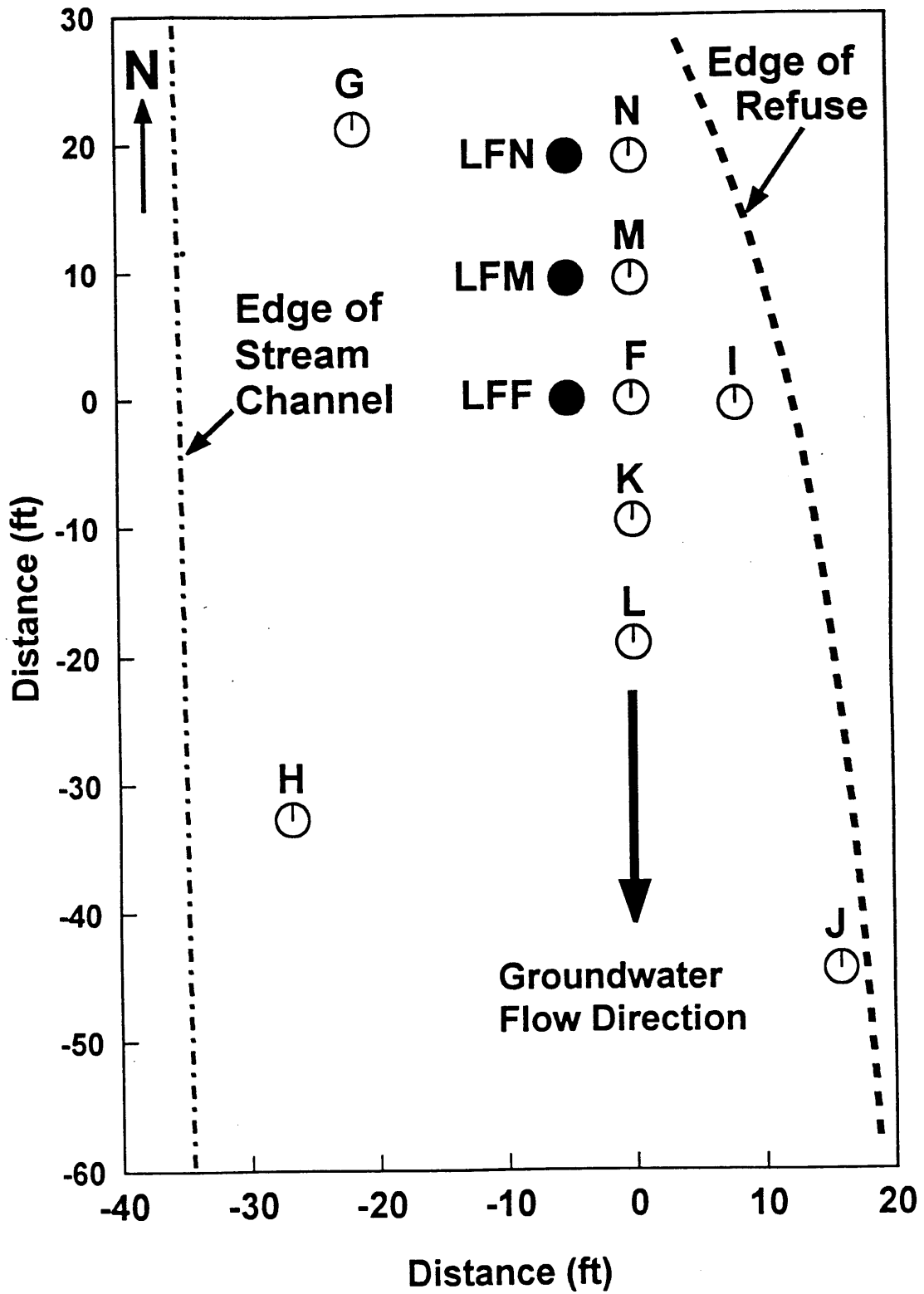
The landfill is located over a granite intrusion known as the Rolesville Batholith which was probably formed during the Middle Paleozoic Era and is described as being an intrusion of Adamellite (Parker, 1979). Adamellite is a massive, gray, granite rock that is composed of subequal parts of sodic plagioclase and potassium feldspars with quartz, biotite, muscovite and other accessory minerals. To the immediate west of the landfill are injected gneiss and schist that may underlie a portion of the site. The gneiss and schist are described as being layered and having numerous dikes and sills of granite, pegmatite and aplite.

Core samples taken from the study area during drilling have revealed 6 to 9 m of colluvial sedimentary deposits. These deposits vary widely in composition from silty sand to sandy clay, and are often similar in appearance to surrounding granitic saprolite. Part of the upper colluvium was noted to have a high organic fraction. The hydraulic conductivity of this area was determined to be approximately 0.8 m/d from short term specific capacity tests. This is similar to hydraulic conductivity measurements in other wells around the site (Britt and Van Tassel, 1988; Marshall, 1989; Roudebush and Whitman, 1989).

Typically, groundwater flows from higher elevations, converging toward the lower lying drainages. Monitoring wells in the immediate vicinity of the study area indicate that groundwater flow is almost due south, parallel to the natural stream channel and toward a small pond-wetland. The water table in the study area has a constant slope of 4% which is approximately equal to the stream channel slope. Using the measured water table gradient and hydraulic conductivity, the average groundwater velocity was estimated to be 0.11 m/day.

Measurement of the piezometric surface in nearby wells screened in the fractured bedrock and transition zone indicates a very weak downward hydraulic gradient. This finding indicates that the study area is not in a groundwater discharge area.

Figure 1 - Monitoring Well and Soil-Boring Locations



5.3 Tracer Test

As part of the site characterization, a non-reactive tracer test was performed to estimate the groundwater velocity in the study area. This velocity was needed to allow comparison of the laboratory degradation rates with the field monitoring results. The tracers selected for the test were chloride and bromide. Chloride and bromide are non-toxic in low concentrations, are inexpensive, move with the water, can be detected at low concentrations, are chemically stable, and are generally not filtered or absorbed by the porous media.

The up gradient Well N was used as the point of injection. A 1040-liter capacity pillow tank was filled with water from Well N at a pumping rate of between 85 and 100 l/hr over a period of 12 hrs. The pillow tank was constructed of a polyester fabric based membrane with a PVC coating. Prior to the injection, the pillow tank was soaked for 48 hrs with well water to allow equilibration of the tank lining with any contaminants present. The tank was placed flat on a mat on the ground surface's up gradient side to create a positive head for the injection. The tank was filled and flushed with argon to remove oxygen in the tank. Argon gas was continuously injected into the well void space to displace oxygen during the pump-out and injection.

After the tank was filled with well water, a concentrated 2-liter stock solution of chloride and bromide was pumped into the tank and thoroughly mixed. This stock solution consisted of 95 gm/l CaCl_2 , 100 gm/l NaCl, 10 gm/l NaBr and 11.9 gm/l KBr mixed in anaerobic D.I. water. The solution in the tank was sampled at several intervals during the injection period and was found to have average concentrations of chloride and bromide of approximately 590 mg/l (s.d.=54) and 102 mg/l (s.d.=7.1), respectively. The injection concentrations were selected to ensure that the NC groundwater quality standards would not be violated due to the introduction of foreign compounds (chloride and bromide). Wells down gradient of the injection point were then monitored for chloride and bromide 5 times over the next 43 days to determine the rate of tracer migration.

In reviewing the monitoring data, there were no significant trends in the chloride concentrations over the 43-day test period. Monitoring could not be continued beyond this time because the study area was covered by refuse. It appears that the injected chloride solution was masked by the high background concentration of 100 to 200 mg chloride/l. A measurable increase in the bromide concentration was observed at well M, 43 days after the injection. The bromide concentration increased from 2.5 mg/l to 11.0 mg/l over a 7-day period. This would indicate a groundwater velocity of 0.07 m/day, very near the predicted velocity of 0.11 m/day.

5.4 Results of Previous Groundwater Monitoring

Previous monitoring at the landfill by Douglass and Borden (1992) has shown the groundwater to be contaminated with a wide variety of pollutants. Average concentrations of selected organic and inorganic pollutants at wells in 1989 are shown in Table 1. Monitoring well locations are shown in Figure 2. Elevated concentrations of chemical oxygen demand (COD), total organic carbon (TOC), iron, manganese and synthetic organic chemicals (SOCs) were observed in groundwater at the study site immediately down gradient from the refuse. In 1989, groundwater in the study area (monitoring well F) contained elevated concentrations of phenol, diethyl phthalate, 4-methylphenol, vinyl chloride, methylene chloride, 1,1-dichloroethane, 1,2-dichloroethene, benzene, toluene, ethylbenzene, xylenes, acetone, 2-butanone, 2-hexanone, MIBK, caprolactam and a variety of organic acids. At the down gradient edge of the working area (wells A, B and D), approximately 1,000 ft up gradient from the

Table 1. Average Ground Water Quality Monitoring Results - 1989*

	MONITORING LOCATION							
	A	B	D	E	F	F-2	RW-1	RW-2
pH ¹	6.23	5.60	6.10	5.67	4.62	ND	ND	ND
SPECIFIC COND. ²	619	213	229	294	1351	754	451	685
CHLORIDE	32.9	39.0	10.4	58.5	90.0	59	16	59
NITRATE-N (mg/l)	0.1	ND	0.1	0.15	0.2	0.06	0.11	0.1
AMMONIA-N (mg/l)	7.5	1.3	0.72	0.95	0.64	ND	ND	ND
SULFATES (mg/l)	<3.0	ND	<3.0	<3.0	<3.0	<3.0	<3.0	3.0
COD (mg/l)	126.5	23	49	35	893	84	13	23
TOC (mg/l)	86	ND	21	63	385.5	60	25	60
TDS (mg/l)	268	ND	236	172	1080	484	280	448
IRON (mg/l)	96.2	31.3	2.2	13.9	109.8	3.5	2.5	3.8
MANGANESE (mg/l)	7.98	<0.1	6.1	1.9	64.11	19.7	8	8.3
ZINC (mg/l)	0.07	ND	<0.05	<0.05	0.05	0.16	<0.05	<0.05
LEAD (mg/l)	<0.03	ND	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Phenol (ug/l)	<5.0	<5.0	<5.0	<5.0	32	<5.0	<5.0	<5.0
Diethyl Pthalate (ug/l)	<5.0	<5.0	<5.0	<5.0	20	<5.0	<5.0	<5.0
4-Methylphenol (ug/l)	<5.0	<5.0	<5.0	20	253	<5.0	<5.0	<5.0
Vinyl Chloride (ug/l)	<5.0	<5.0	<5.0	69	37	26	3 ^E	8
Methylene Chloride (ug/l)	<5.0	<5.0	<5.0	18	13	<5.0	2 ^E	<5.0
1,1-dichloroethane (ug/l)	<5.0	<5.0	<5.0	39	92	60	3 ^E	26
1,2-dichloroethene (ug/l)	<5.0	<5.0	<5.0	109	83	12	68	<5.0
Trichloroethylene (ug/l)	<5.0	<5.0	<5.0	10	<5.0	<5.0	<5.0	<5.0
Benzene (ug/l)	<5.0	<5.0	<5.0	6	13	8	<5.0	2 ^E
Toluene (ug/l)	<5.0	<5.0	<5.0	61	813	126	<5.0	10
Xylenes (total) (ug/l)	<5.0	<5.0	<5.0	12	125	12	<5.0	<5.0
Tetrachloroethene (ug/l)	<5.0	<5.0	<5.0	14	<5.0	<5.0	<5.0	<5.0
Ethylbenzene (ug/l)	<5.0	<5.0	<5.0	7	38	3 ^E	<5.0	<5.0
Acetone (ug/l)	<5.0	<5.0	<5.0	<5.0	1524	181	<5.0	<5.0
2-Butanone (MEK) (ug/l)	<5.0	<5.0	<5.0	111	1575	102	<5.0	<5.0
2-Hexanone (ug/l)	<5.0	<5.0	<5.0	<5.0	70	<5.0	<5.0	<5.0
MIBK (ug/l)	<5.0	<5.0	<5.0	6	84	<5.0	<5.0	<5.0
Caprolactam (ug/l)	995	95	133	78	88	<5.0	<5.0	<5.0
Hexanoic Acid ³	-	-	-	+	+	ND	ND	ND
Heptanoic Acid ³	-	-	-	+	+	ND	ND	ND
Octanoic Acid ³	-	-	-	+	+	ND	ND	ND

* From Douglass and Borden, 1992

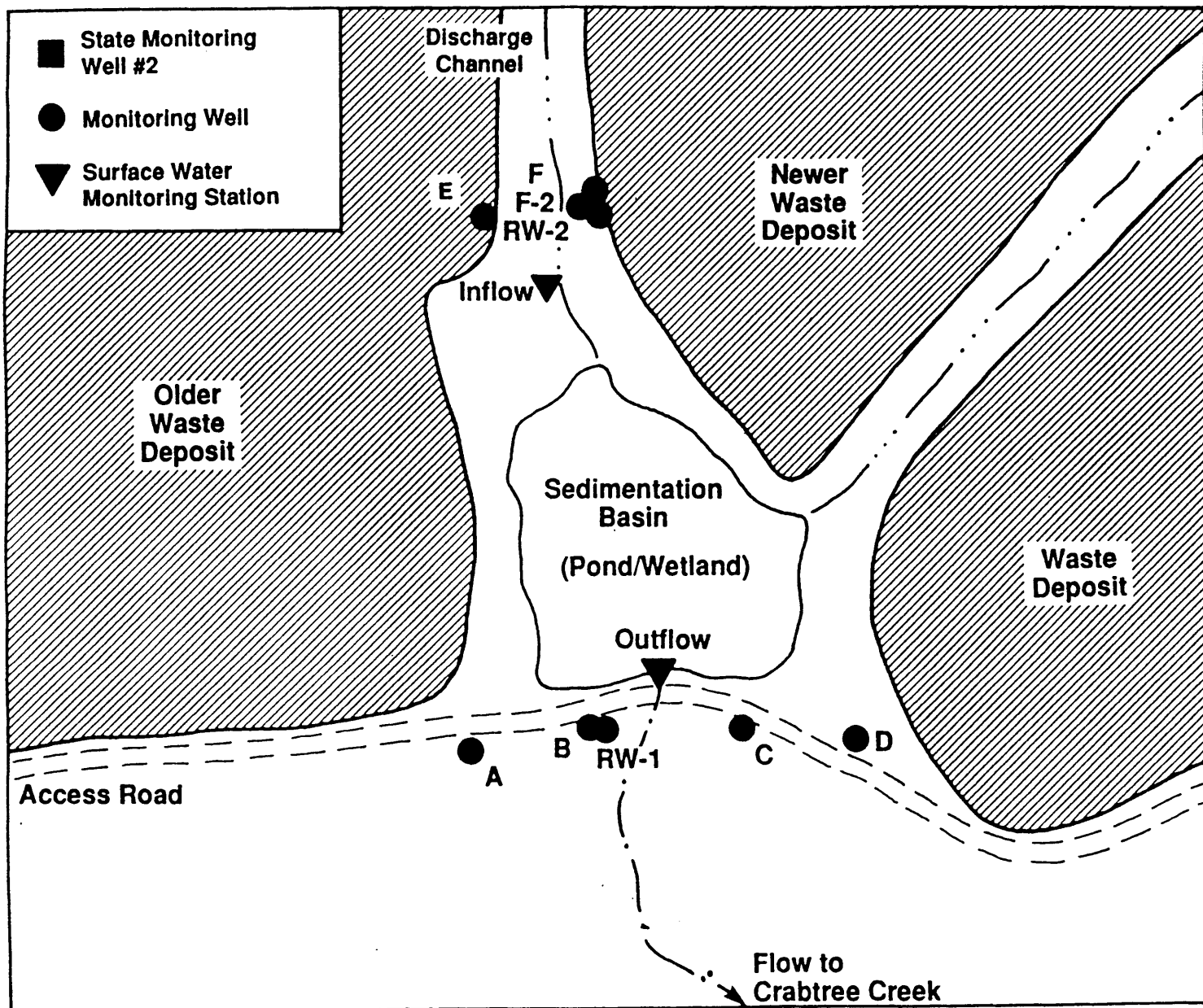
1 Standard pH units

2 umho/cm

3 + means detected, - means not detected

E estimated concentration

Figure 2 - Monitoring Well Locations from Douglass and Borden (1992)



property boundary, concentrations of most pollutants were much lower. Concentrations of many of the organic contaminants decreased with travel distance much more rapidly than chloride suggesting that some attenuation mechanism other than dilution was occurring. The relative order and rates of disappearance of the different compounds suggest that biotransformation may result in significant removal of some compounds.

6.0 CHEMICAL CHARACTERIZATION OF THE AQUIFER

6.1 Groundwater Monitoring

A total of nine monitoring wells were installed at the site. Initially, five wells (F, G, H, I, and J) were located to determine the groundwater flow direction and hydraulic gradient. Upon determining the direction of flow, four additional wells were located on a streamline passing through well F. These wells were designed to allow the estimation of contaminant attenuation during transport along this streamline. Two wells, M and N, were located up gradient of well F; and the two wells, K and L, were located down gradient of well F. The five wells (F, K, L, M, and N) were located approximately 3 m (9 ft) apart.

All the wells with exception of K and L were constructed using a 5-cm (2-inch) diameter PVC well casing with a 1.5-m (5-foot) long, number-10-slot well screen. Wells K and L were constructed of 2.5-cm (1-inch) diameter PVC well casing utilizing a 15-cm (6-inch) long well screen (10 slot). All wells were installed in the saturated shallow saprolite-colluvium soil zone. The wells were drilled using a 7-cm (2.75-inch) diameter hollow-stem auger and a soil sampling hydraulic probe. The screens were packed with native material that formed as the borehole collapsed after drilling. Bentonite seals were placed above the water table. Steel protective covers were set in concrete above the bentonite seals and fitted with locking caps. The monitoring wells were developed by repeated surging and bailing to remove fine-grained sediments.

Water table elevation and flow direction were remarkably constant over the study period. Groundwater flow direction was consistently due south down the line of monitoring wells N to L. Depth to the water table in well M varied from 2.08 to 2.30 m (6.8 to 7.5 ft) below ground surface.

6.2 Sampling and Analytical Procedures

Dissolved BTEX, CAHs and related parameters were monitored in groundwater six times from March to July 1992. The original intent was to continue monitoring into the late fall of 1992. Unfortunately, the study area was covered with refuse in August 1992. Prior to sampling, all wells were filled with pre-purified argon gas to minimize oxygen exchange with the sample and then purged of at least five well volumes using a dedicated inertial pump (Waterra). Groundwater samples were then collected in 40-ml vials with Teflon-lined septa and no headspace. Samples for metals and ions were pumped through a 0.45- μm filter prior to collection. Temperature, pH, oxidation-reduction (redox) potential, and dissolved oxygen were measured in the field with standard probes. Carbon dioxide was measured in the field by titrating with NaOH to pH 8.3 and is reported as total CO₂ (carbonate, bicarbonate and free CO₂). When dissolved iron exceeded 1 mg/l, CO₂ results were corrected for NaOH consumed during the reaction with iron. BTEX and CAH concentrations were analyzed as described in section 7.2.4.1. Inorganic nutrients and ions (NO₃, NH₄, PO₄, SO₄) and metals (Ca, Cd, Zn, Ni, Fe, Mn, Mg, Na, K, Cu, S) were analyzed by ion chromatography and inductively coupled plasma emission spectroscopy following Standard Methods (American Public Health Association, 1992).

6.3 Geochemical Conditions in the Aquifer

Results of the geochemical monitoring are summarized in Tables 2 through 4. Overall geochemical conditions in the aquifer were fairly uniform. The aquifer was strongly reducing (Eh < -100 mV) except in those wells directly adjoining the stream channel. Dissolved oxygen was consistently below 1 mg/l in all wells. The small amount of oxygen that was present is believed to be due to oxygen exchange at the water table interface. Alkalinity and dissolved carbon dioxide were high and pH ranged from 6.2 to 6.8. The parameter that showed the greatest variability was chemical oxygen demand (COD), which varied from over 300 mg/l directly adjoining the refuse (well I) to less than 30 mg/l near the drainage channel. High concentrations of iron and manganese were present due to the strongly reducing conditions.

6.3.1 Temporal Variation in BTEX and CAHs. As the first step in evaluating the monitoring data for the hazardous organics, an analysis was conducted to determine if there had been any systematic variation in the BTEX and CAH concentrations with time. Correlation coefficients were calculated between the concentration of individual compounds and time. Whenever the correlation coefficient exceeded 0.5, the data were plotted and examined to evaluate the significance of any trends. In general, only toluene showed a systematic variation with time. Toluene concentrations in four representative wells (F, G, I, and N) are shown in Figure 3. Wells nearest the stream (G and H) had consistently low toluene concentrations with little variability. In contrast, the wells nearest the refuse (I and J) had the highest toluene concentrations and these concentrations increased over the monitoring period. Along the intensively monitored streamline, toluene concentrations in wells N and M decreased, whereas toluene concentrations in wells F, K and L were highly variable with no apparent trend. The decline in toluene in N and M appeared to follow an exponential decay curve. To evaluate this, toluene concentration in each well was fit to the equation $C_t = C_0 e^{-Kt}$ where C_t is the toluene concentration at time t and K is the effective first-order decay coefficient. The effective first-order decay coefficients for toluene were 0.022 (\pm 0.003) per day for well N and 0.025 (\pm 0.006) per day for well M (value in parentheses is the standard error). Figure 4 shows the comparison between the field monitoring results and the regression lines.

In summary, most wells did not show any systematic trends for BTEX or CAHs with time. A few wells did show a systematic trend of decreasing toluene while others showed a consistent trend of increasing toluene. There was no overall trend of increasing or decreasing contaminant concentrations throughout the study area. On the basis of these results, we have chosen to use the arithmetic average of all concentration measurements in all further analyses. Average concentrations of BTEX and CAHs are presented in Table 5.

6.3.2 Spatial Distribution of BTEX and CAHs. The highest contaminant concentrations are present in wells I and J, immediately adjoining the refuse. The lowest concentrations are in wells G and H, closest to the drainage channel. There were no consistent trends in the average concentrations of toluene, cis-DCE or PCE along the intensively monitored streamline between wells N and K (Figure 5). At well L, there was a significant increase in the trans-DCE concentration and a decrease in the toluene concentration. The reason for this shift is unclear. The decline in toluene and increase in trans-DCE could be due to biological activity or could be due to minor shifts in the groundwater flow path. The aquifer has a higher clay content in the area of well L that could cause the flow line to bypass well L. Also, wells K and L have shorter 15-cm (6-inch) screens, which could affect the measured contaminant concentration.

The monitoring data were evaluated to identify any evidence of biodegradation during transport along the groundwater flow path. If biodegradation were occurring, the contaminant concentrations should decrease as groundwater migrates from well N to M to F to K. The absence of a measurable decrease indicates that either biodegradation is not occurring or is

Table 2.

Average Concentrations of Electron Acceptors and Nutrients

Well ID	O ₂ (mg/l)	Nitrate NO ₃ -N (mg/l)	Total Phosphorus (mg/l)	Ammonia NH ₄ -N (mg/l)	Total Kjeldahl Nitrogen (mg/l)
F	.3	<0.2	<0.2	4.1	NA
G	.4	<0.2	<0.2	5.8	4.1
H	.7	<0.2	<0.2	.2	NA
I	.6	<0.2	<0.2	1.7	5.1
J	.7	<0.2	<0.2	.5	NA
K	NA	<0.2	<0.2	.7	4.9
L	NA	<0.2	<0.2	<0.2	1.4
M	.4	<0.2	<0.2	4.8	NA
N	.6	<0.2	<0.2	3.2	NA

BDL - Below Detectable Limit

NA - Not Available

Table 4.

Average Concentrations of Dissolved Metals and Ions in Groundwater

WELL ID	Fe (mg/l)	Mn (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	Cl (mg/l)	Al (mg/l)	Zn (mg/l)	Cu (mg/l)	K (mg/l)	Si (mg/l)	Br (mg/l)
F	31.2	49.4	246.3	43.7	87.8	162.	0.10	0.04	0.00	5.9	3.0	1.2
G	27.6	24.0	82.0	24.2	54.2	64.	0.10	0.02	0.00	8.1	1.9	0.0
H	0.5	12.4	85.3	37.4	54.2	56.	0.10	0.04	0.02	2.2	2.7	0.3
I	40.7	48.5	242.4	42.9	103.0	118.	0.02	0.03	0.01	5.3	3.9	0.7
J	12.9	44.1	168.0	37.3	79.7	132.	0.06	0.10	0.00	1.7	7.7	0.7
K	33.2	33.4	76.4	23.4	57.2	106.	0.10	0.17	0.00	2.0	0.8	0.4
L	34.5	19.8	38.2	9.7	57.6	72.	0.00	0.23	0.00	2.0	0.3	0.0
M	34.1	36.3	235.5	55.4	111.8	186.	0.10	0.10	0.00	6.4	4.3	0.9
N	30.5	43.0	186.5	48.5	101.5	151.	0.10	0.00	0.00	7.8	8.8	1.2

Figure 3 - Variation in Toluene Concentration in Monitoring Wells with Time

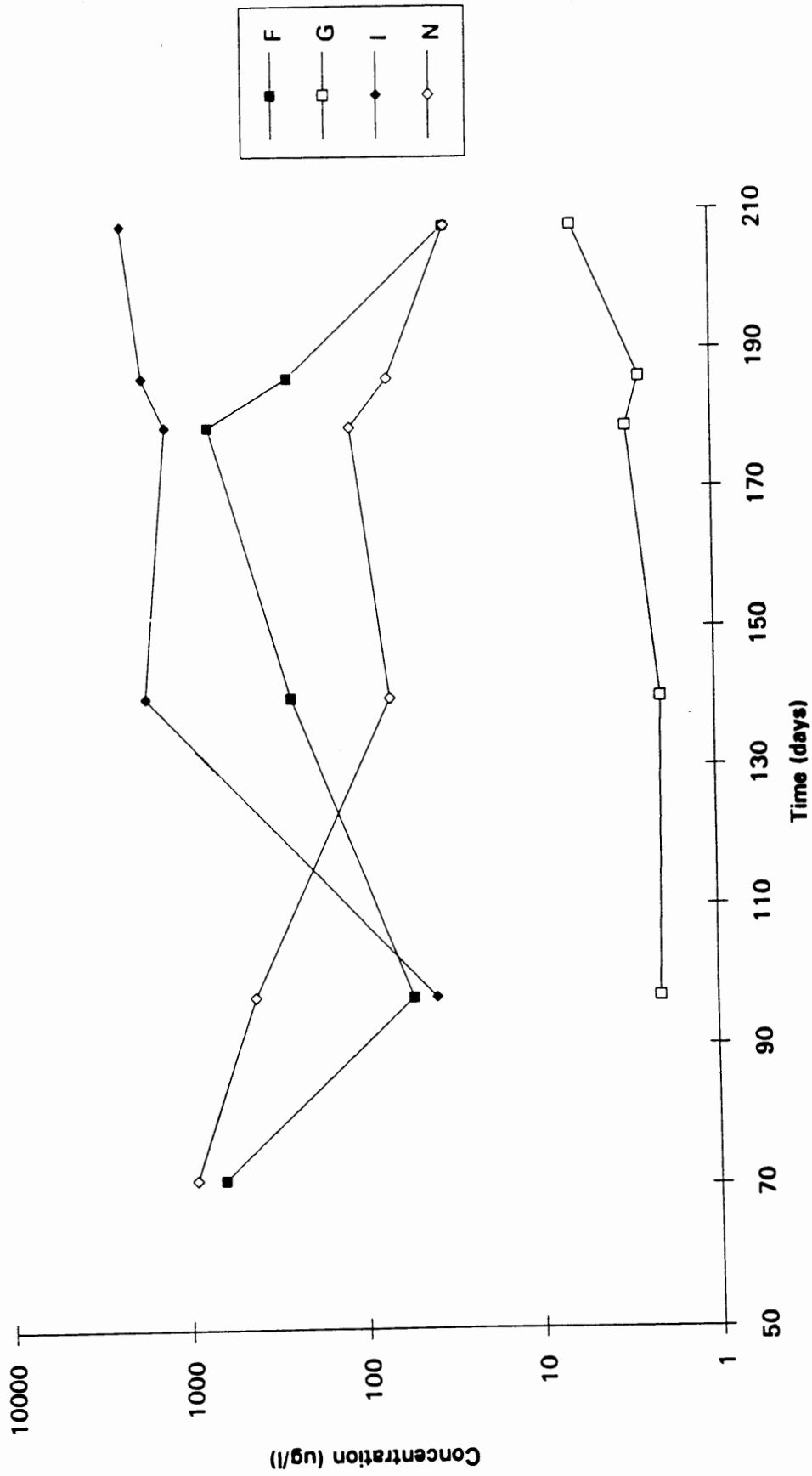


Figure 4 - Comparison of Toluene in Monitoring Wells M and N with First-Order Regression

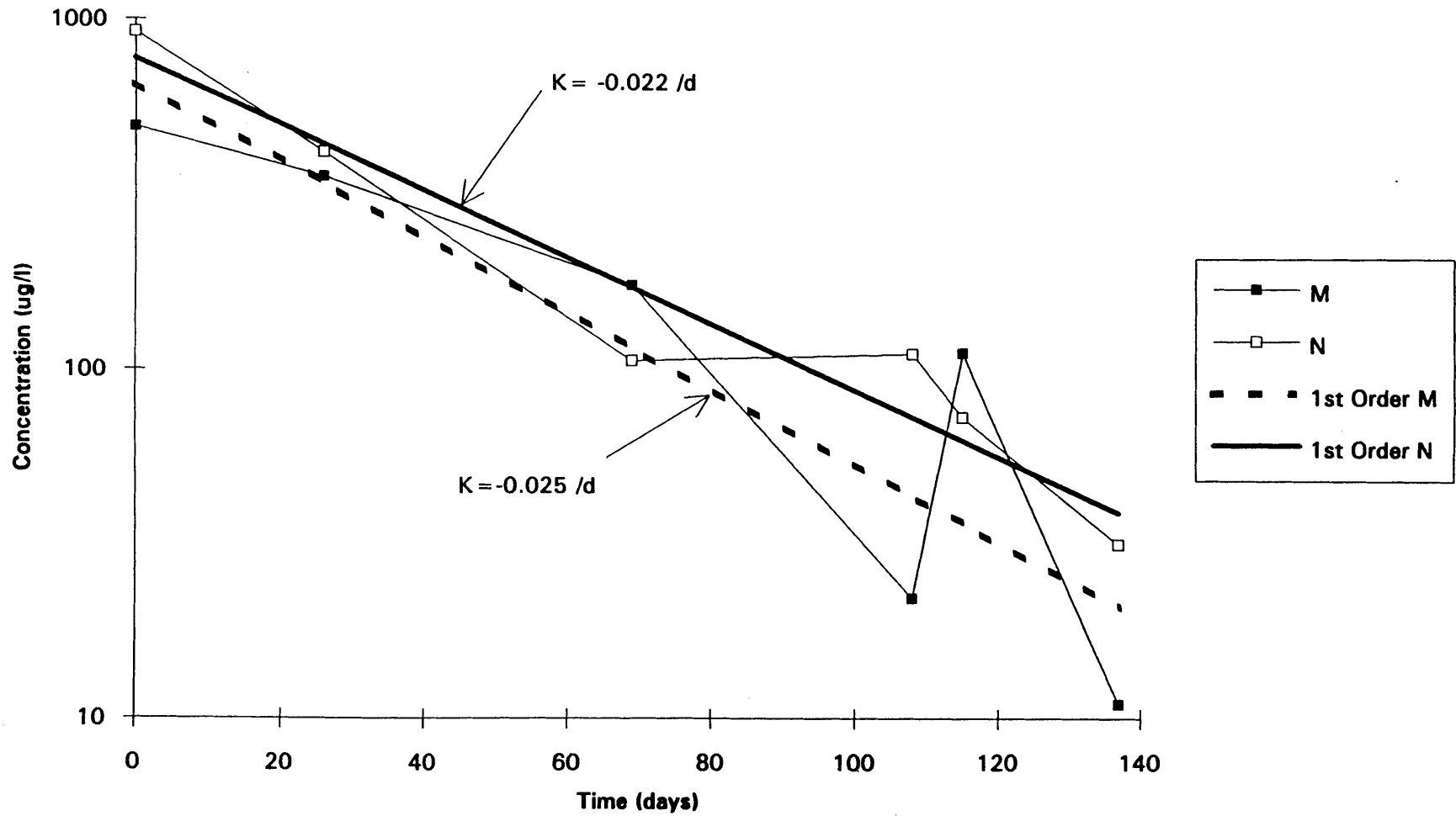


Table 5.

Average Concentration of Organics Detected in Groundwater (all concentrations in µg/l)

	-----F-----		-----G-----		-----H-----		-----I-----		-----J-----	
	AVG.	STD.	AVG.	STD.	AVG.	STD.	AVG.	STD.	AVG.	STD.
Benzene	2.	1.	2.	0.	1.	1.	1.	1.	2.	1.
Toluene	326.	286.	3.	2.	1.	1.	1358.	807.	772.	482.
Ethylbenzene	4.	3.	2.	1.	0.	0.	2.	3.	5.	4.
m,p-Xylene	6.	3.	2.	1.	1.	1.	6.	5.	6.	3.
o-Xylene	5.	2.	1.	1.	1.	0.	4.	3.	3.	2.
trans-Dichloroethylene	6.	5.	9.	9.	6.	NA	10.	NA	14.	NA
cis-Dichloroethylene	67.	104.	5.	4.	3.	NA	340.	NA	241.	NA
Trichloroethylene	0.	0.	2.	2.	2.	NA	0.	NA	0.	NA
Tetrachloroethylene	68.	119.	7.	7.	57.	NA	23.	NA	24.	NA
	-----K-----		-----L-----		-----M-----		-----N-----			
	AVG.	STD.	AVG.	STD.	AVG.	STD.	AVG.	STD.		
Benzene	3.	1.	4.	3.	3.	2.	4.	4.		
Toluene	211.	201.	24.	21.	184.	196.	270.	348.		
Ethylbenzene	5.	3.	5.	4.	7.	4.	12.	11.		
m,p-Xylene	12.	4.	7.	6.	15.	3.	24.	9.		
o-Xylene	6.	1.	6.	2.	8.	1.	13.	5.		
trans-Dichloroethylene	11.	8.	76.	120.	12.	8.	0.	0.		
cis-Dichloroethylene	82.	93.	64.	105.	3.	2.	59.	111.		
Trichloroethylene	0.	0.	0.	0.	0.	0.	2.	2.		
Tetrachloroethylene	77.	111.	73.	112.	92.	103.	76.	117.		

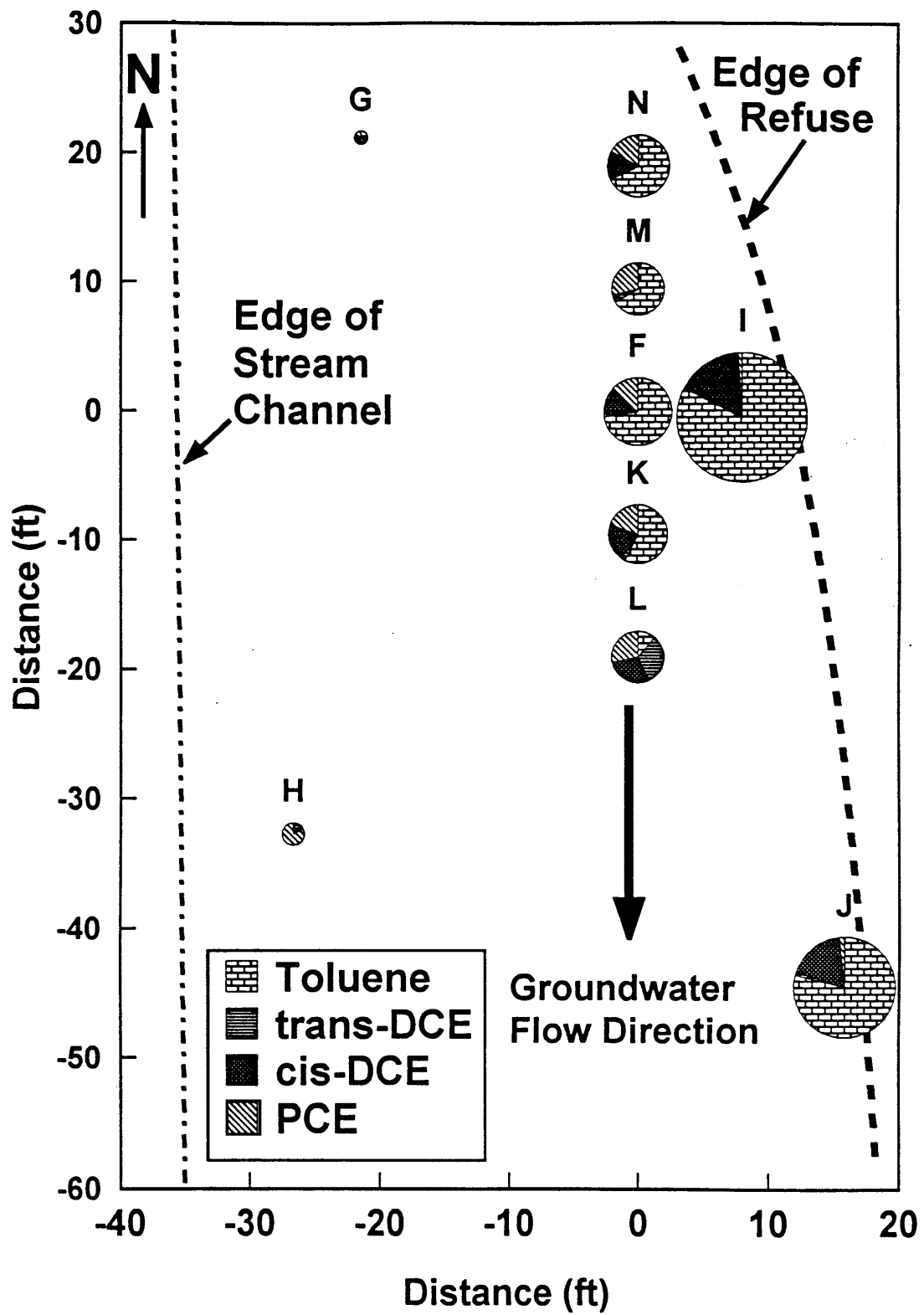
BDL - below detection limit of 1 µg/l

AVG. - average concentration

STD. - standard deviation

NA - not available

Figure 5 - Spatial Variation in Average Concentrations of Toluene, c-DCE, t-DCE and PCE



occurring too slowly to be detected given the high variability in contaminant concentrations. The coefficient of variation typically exceeded 100% for the chlorinated solvents and ranged from 60 to 130% for toluene. Coefficients of variation for benzene, ethylbenzene and the xylenes were lower because the averages were close to the analytical detection limit. Because of this high variation in contaminant concentrations, the rate of biodegradation would have to be very high to be detectable. Field monitoring results indicate that there is no evidence of significant biodegradation over the 4- to 5-month travel time from well N to K. Previous laboratory studies had suggested that significant biodegradation would occur during this transport period. The lack of measurable biodegradation in this test suggests that it may not be feasible to accurately estimate in situ biodegradation rates using conventional monitoring well networks when the biodegradation rate is low. While monitoring wells could be spaced further apart to increase the travel time, this would increase the uncertainty about whether the wells are on the same streamline and could further increase the temporal variability in contaminant concentrations.

