University of Alberta

Comparison of Sampling Technologies in a Monitored Natural Attenuation Application

By ©

Dean Maurice Morin

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of Master of Science

In

Geoenvironmental Engineering

Department of Civil and Environmental Engineering

Edmonton, Alberta

Fall 2008

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 978-0-494-47370-2
Our file Notre référence
ISBN: 978-0-494-47370-2

NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

For my family, and most importantly my wife Stephanie, whose continual patience and support throughout the duration of completing this thesis made it possible.

Thanks to my good friend Kelsey for his tireless efforts and assistance in professionally editing my thesis. Your support throughout the editing process was crucial in creating this final thesis version.

Thank you all with my deepest gratitude, you are all the reason that gave me the motivation to succeed in this endeavor.

ABSTRACT

Laboratory and field results are used to assess how the selected sampling methodologies, well types and well construction affect the findings of a monitored natural attenuation assessment. Concentrations from two discrete interval well types and two discrete interval sampling methods with sampling intervals of approximately 0.5 to 1.0 metres are compared to bulk samples from three metre screened wells at two research sites.

A diffusion sampler design is developed; however it did not demonstrate discrete interval sampling due to well homogenization and partial equilibration issues. The BarCad System is unable to collect discrete interval samples, as the water appears to move through the sand annulus during sampling. The diffusion samplers and BarCad System do collect samples representative of the well they are installed in. The drive point wells demonstrate the ability to collect discrete interval samples. The multilevel wells collect discrete interval samples; however bentonite seal materials impact ion concentrations, with elevated sulfate being the greatest concern.

ACKNOWLEDGEMENTS

I acknowledge the financial and in-kind support of the following agencies, without which the research and this thesis would not have been possible:

CORONA Program and all its partners
ConocoPhillips Canada
Devon Canada
Maxxam Analytics
Faculty of Graduate Studies and Research, University of Alberta
Geotechnical and Geoenvironmental Engineering Group, Department of Civil and Environmental Engineering, University of Alberta

I also acknowledge the significant contributions of the following individuals:

My supervisor Dr. Kevin Biggar for his guidance throughout the research and his review that was instrumental in forming this thesis.

Mr. James Armstrong for his continual guidance and brilliant insight throughout the research program and for always being there to answer all of my questions. I would like to thank him for teaching me all the ropes of environmental monitoring and the ability to smile and laugh through all the hardships that come with a field research program, even when temperatures reach over 35°C and drop to -42°C.

Ms. Kim McLeish for her assistance in the field sampling programs; special thanks for her assistance in hand sewing filter socks with me in the sweltering heat of southern Alberta.

Mr. Steve Gamble for his assistance in obtaining the materials required for the laboratory experiments and set up of the various studies.

TABLE OF CONTENTS

Chapter 1 – Introduction 1

1.1 Statement of Problem 1

1.2 Thesis Research Objective 2

1.3 Research Framework 3

1.4 Monitored Natural Attenuation 4
  1.4.1 Introduction 4
  1.4.2 Basic Processes of Natural Attenuation 6
  1.4.3 Application 8
    1.2.3.1 General 8
    1.2.3.2 Thesis Research Considerations 12

1.5 Geochemical Trends of Interest for Monitored Natural Attenuation 13

1.6 References 16

Chapter 2 – Diffusion Sampler Development and Application for Monitored Natural Attenuation at Upstream Oil and Gas Sites 22

2.1 Introduction 22

2.2 Background 23
  2.2.1 Diffusion Sampler Historical Research 23
  2.2.2 Selection of Diffusion Sampler Material 26
  2.2.3 Research Considerations for Diffusion Sampler Application 27

2.3 Methods 28
  2.3.1 Field Diffusion Sampler Development 28
  2.3.2 Field Diffusion Sampler Installation 29
  2.3.3 Site Descriptions 30
  2.3.4 Laboratory Experiments 31
    2.3.3.1 Dissolved Hydrocarbon Equilibration Study 31
    2.3.3.2 Effect of Monovalent and Divalent Salts Study 32
    2.3.3.3 Hydraulic Gradient and Evaporation Study 32

2.4 Results 33
  2.4.1 Laboratory Experiments 33
    2.4.1.1 Dissolved Hydrocarbon Equilibration Study 33
    2.4.1.2 Effect of Monovalent and Divalent Salts Study 33
    2.4.1.3 Hydraulic Gradient and Evaporation Study 34
  2.4.2 Field Testing Program 35
    2.4.2.1 Field Installation Considerations 35
    2.4.2.2 Assessing Variability of Sample Results 36
    2.4.2.3 Field Data Comparison 37

2.5 Discussion 40
  2.5.1 Laboratory 40
    2.5.1.1 Dissolved Hydrocarbon Equilibration Study 40
    2.5.1.2 Effect of Monovalent and Divalent Salts Study 41
    2.5.1.3 Hydraulic Gradient and Evaporation Study 42
  2.5.2 Field Performance 44
    2.5.2.1 Considerations of Sampling Method Differences 44
    2.5.2.2 Findings from Sample Results Comparison 45

2.6 Conclusions 56
  2.6.1 Laboratory Research 56
  2.6.2 Field Research 56

2.7 References 59

Chapter 3 – Comparison of Sampling Well Types and Methodologies for Monitored Natural Attenuation at Upstream Oil and Gas Sites 69

3.1 Introduction 69

3.2 Background 70
  3.2.1 Sampling Technologies 70
    3.2.1.1 Well Types Investigated 71
    3.2.1.2 Sampling Methods Investigated 71
  3.2.2 Site Descriptions 71
  3.2.3 Previous Research on Alternative Sampling Technologies 71
  3.2.4 Basis for Sampling Technology Comparison 72
  3.2.5 Sources of Variability 73

3.3 Methods 75
  3.3.1 Comparison Method for Sample Variability 75
  3.3.2 Acceptable Variability for Sample Results 76
  3.3.3 Parameters Compared 78
  3.3.4 Sampling Technologies Comparison at the Research Sites 79
    3.3.4.1 Well Types Comparison 79
      3.3.4.1.1 Site 1 80
      3.3.4.1.2 Site 2 82
    3.3.4.2 Sampling Methodologies Comparison 83
      3.3.4.2.1 Site 1 84
      3.3.4.2.2 Site 2 85
  3.3.5 Sample Collection 86
  3.3.6 Method of Comparison of Sample Results 88
  3.3.7 Material Impacts of Bentonite Seals on Water Chemistry 88

3.4 Results 89
  3.4.1 Laboratory Research 89
    3.4.1.1 Impact of Bentonite Seal Materials on Water Chemistry 89
  3.4.2 Field Research 90
    3.4.2.1 Comparison of Sampling Technologies Results 90
      3.4.2.1.1 Inherent Variability of Groundwater Geochemistry 91
      3.4.2.1.2 PrePak Drive Point Wells 92
      3.4.2.1.3 CMT Multilevel Wells 95
      3.4.2.1.4 Conventional Well Types & Common Sample Collection Methods 100
      3.4.2.1.5 Dialysis Membrane Diffusion Sampler 105
      3.4.2.1.6 BarCad System 110

3.5 Discussion 113
  3.5.1 Interpretation of Well Construction Impacts 113
  3.5.2 Summary of General Findings from Sampling 118
  3.5.3 Comparison of Sampling Technologies Results 120
    3.5.3.1 Inherent Variability of Groundwater Geochemistry 120
    3.5.3.2 PrePak Drive Point Wells 121
    3.5.3.3 CMT Multilevel Wells 122
    3.5.3.4 Conventional Well Types & Common Sample Collection Methods 124
    3.5.3.5 Dialysis Membrane Diffusion Sampler 125
    3.5.3.6 BarCad System 128

3.6 Conclusions 130
  3.6.1 General 130
  3.6.2 Conventional Well Types & Common Sample Collection Methods 130
  3.6.3 CMT Multilevel Wells 131
  3.6.4 PrePak Drive Point Wells 131
  3.6.5 BarCad System 131
  3.6.6 Dialysis Membrane Diffusion Sampler 131

3.7 References 133

Chapter 4 – Summary of Conclusions for Various Sampling Technologies Research and Recommendations for Future Research 138

4.1 Summary of Conclusions 138
  4.1.1 Laboratory Research 138
    4.1.1.1 Dissolved Hydrocarbon Equilibration Study 138
    4.1.1.2 Effect of Monovalent and Divalent Salts 139
    4.1.1.3 Hydraulic Gradient and Evaporation Study 140
    4.1.1.4 Bentonite Seal Material Impacts on Water Chemistry Study 140

- 4.1.2 Field Research 141
  - 4.1.2.1 Conventional Well Types and Common Sample Collection Methods 142
  - 4.1.2.2 CMT Multilevel Wells 142
  - 4.1.2.3 PrePak Drive Point Wells 143
  - 4.1.2.4 BarCad System 144
  - 4.1.2.5 Dialysis Membrane Diffusion Sampler 145

4.2 Author's Opinion on Sampling Technologies Application 147
- 4.2.1 Conventional Well Types and Common Sample Collection Methods 147
- 4.2.2 CMT Multilevel Wells 148
- 4.2.3 PrePak Drive Point Wells 149
- 4.2.4 BarCad System 150
- 4.2.5 Dialysis Membrane Diffusion Sampler 151

4.3 Recommendations for Future Research 152
- 4.3.1 Diffusion Sampler Research 152
- 4.3.2 Other Research Areas 153

Appendices

Appendix A – Researched Sampling Technologies Detailed Description 154

Appendix B – Research Site Descriptions 173

Appendix C – Laboratory Experiment Descriptions 182

Appendix D – Dialysis Membrane Diffusion Sampler and Waterra Sampler Detailed Field Data Comparison 192

Appendix E – Laboratory Study Result Tables and Experimental Calculations 209

Appendix F – Sampling Technology Summary Result Tables for Selected Parameters of Interest in a MNA Program 218

Appendix G – Sampling Technology Figures for Selected Parameters of Interest in a MNA Program 236

LIST OF TABLES

Chapter 1 – Introduction

No tables listed.

Chapter 2 – Diffusion Sampler Development and Application for Monitored Natural Attenuation at Upstream Oil and Gas Sites

Table 2.1 Purgeable concentrations inside dialysis membrane and mesocosm over time. 62
Table 2.2 Mass water loss from initial membrane mass with time due to salt gradient. 62
Table 2.3 Electrical conductivity difference between dialysis membrane and vessel with time. 62

Chapter 3 – Comparison of Sampling Well Types and Methodologies for Monitored Natural Attenuation at Upstream Oil and Gas Sites

Table 3.1 Parameters of interest concentrations for seal material. 136

Chapter 4 – Summary of Conclusions for Various Sampling Technologies Research and Recommendations for Future Research

No tables listed.

LIST OF FIGURES

Chapter 1 – Introduction

Figure 1.1 Redox ladder indicating redox potentials and redox reaction sequences. 19
Figure 1.2 Recommended groundwater monitoring well network for demonstrating natural attenuation and geochemical data trends within and outside plume. 20
Figure 1.3 Redox reactions involved in degradation of organic matter in different redox environments. 21

Chapter 2 – Diffusion Sampler Development and Application for Monitored Natural Attenuation at Upstream Oil and Gas Sites

Figure 2.1 Diffusion sampling nozzle. 63
Figure 2.2 Diffusion sampler end seal. 64
Figure 2.3 Rigid diffusion sampler system. 65
Figure 2.4 Dissolved hydrocarbon equilibration with time. 66
Figure 2.5 Salt concentration effects on dialysis membrane sampler. 67
Figure 2.6 Electrical conductivity equilibration for various sodium chloride (NaCl) concentrations. 67
Figure 2.7 Electrical conductivity equilibration for various calcium sulfate ($CaSO_4$) concentrations. 68
Figure 2.8 Dialysis membrane sampler water loss over time. 68

Chapter 3 – Comparison of Sampling Well Types and Methodologies for Monitored Natural Attenuation at Upstream Oil and Gas Sites

Figure 3.1 Multilevel well borehole log (Site 2, Well Cluster 35). 137

Chapter 4 – Summary of Conclusions for Various Sampling Technologies Research and Recommendations for Future Research

No figures listed.

Chapter 1

Introduction

1.1 STATEMENT OF PROBLEM

At many Alberta oil wells, oil, gas and many of their by-products are extracted, processed, handled and stored on site. Many of the upstream oil and gas sites have some hydrocarbon impact to soil and groundwater due to the various activities that have occurred over the life of the site. The Alberta Energy and Utilities Board (AEUB) indicated that there were 37,000 active oil wells and almost 98,000 active natural gas in Alberta in 2005 (Alberta Energy and Utilities Board, 2006). It forecasted that 2000 crude oil wells and over 12,000 natural gas wells would be drilled per year. The Pembina Institute has estimated that there are over 34,000 inactive wells and 2,500 abandoned wells documented in Alberta (Pembina Institute, 2002). As this estimate is conservative, the degree of hydrocarbon impact on the province's soil and groundwater is likely underestimated as well.

Contamination at upstream oil and gas sites can occur in many forms, with differing effects. The most commonly encountered contaminants are salts and hydrocarbons. Salt contamination comes from the brine formation water that often accompanies the oil. This water accounts for up to 95% of the waste in most oilfields (Pacific Northwest Pollution Prevention Research Center, 1993). Hydrocarbon contamination often occurs during extraction and processing of the oil and gas at the well site (Schneider, 2001).

The most common sources of contamination at upstream oil and gas sites include (Canadian Association of Petroleum Producers, 1999):

- Sumps – drilling mud containing oil and other petroleum products is often stored and eventually disposed of in an on-site sump (not a current practice);
- Pits – flaring to a pit, often resulting in the discharge of hydrocarbons (not a current practice);
- Drilling – underground leakage during drilling due to faulty well casings;
- Operations – spills and continuous leaks due to system interruption or malfunction;
- Storage Structures – releases from faulty tanks, buildings and process equipment;
- Disposal – improper transport and disposal of oilfield wastes;
- Pipelines – leaking or failure of pipelines used to transport oil and gas.

There is broad consensus that natural attenuation is an effective remediation option in many cases where hydrocarbon contamination is present. However, conventional monitoring technologies and practices do not adequately characterize when natural attenuation is sufficient, and when a more active remedial approach is needed.

1.2 THESIS RESEARCH OBJECTIVE

The objective of this research is to identify monitoring technologies that are better able to distinguish between situations where natural attenuation can be used and where conventional remediation approaches are more appropriate. Such technology is necessary to maximize the appropriate use of natural attenuation in the province.

1.3 RESEARCH FRAMEWORK

The CORONA (Consortium for Research on Natural Attenuation) research program was created to investigate the use of natural attenuation as a remedial option for hydrocarbon contamination at upstream oil and gas sites. It consists of a variety of laboratory and field studies aimed at increasing the knowledge and application of natural attenuation. As part of the CORONA program, this thesis examines how selected sampling methodologies, well types and well construction details impact the monitoring of natural attenuation. Slow groundwater recharge and vertical heterogeneity in some typical Alberta soil profiles also affect the ability to monitor accurately.

The CORONA program highlighted several emerging technologies capable of discrete interval characterization of the groundwater system. These are:

Well Types - selected based on ability to provide discrete interval sampling at flexible installation depths.

1. Solinst Continuous Multichannel Tubing (CMT) Multilevel Well (www.solinst.com); and
2. GeoInsight Drive Point Wells (www.geoinsightonline.com).

Sampling Methods - selected based on ability to collect discrete interval samples from within three metre screened monitoring well.

1. Diffusion sampling using dialysis membrane (Membrane Filtration Products Inc., www.membrane-mfpi.com); and
2. BESST BarCad System (www.BESSTINC.com).

Field tests compared these technologies to conventional three metre screened wells for their ability to show the natural attenuation trends of a site.

At the time that the research was conducted, a dialysis membrane diffusion sampler was not commercially available to sample for hydrocarbon contamination encountered at upstream oil and gas sites. Background research was conducted to determine whether samplers built for previous research were appropriate for our purposes, and, insofar as they were not appropriate, what alterations needed to be made (Chapter 2). This was necessary in order to include the sampler in the comparison of new technologies to the conventional three metre screened wells (Chapter 3).

1.4 MONITORED NATURAL ATTENUATION

1.4.1 Introduction

The term "natural attenuation" refers to the ability of a groundwater system to control the spread of a petroleum plume by means of physical, chemical and biological processes that exist naturally within soil and groundwater systems (USEPA, 1999). Naturally occurring microorganisms and bacteria may be responsible for degrading contamination, but their ability to treat hydrocarbon contamination has only been thoroughly investigated in the last 25 years.

Microbial breakdown has been used for many years in wastewater treatment. Treatment plants discharge a permitted amount of organic waste to surface bodies of water, allowing naturally existing microorganisms to degrade the waste while ensuring oxygen concentrations in the water are not depleted (Minnesota Pollution Control Agency, 2007). The use of drainfields in rural septic systems is a common example of using microorganisms in the soil to treat wastewater, and is similar to the processes observed in natural attenuation of hydrocarbons within the subsurface.

Monitored natural attenuation (MNA) typically involves assessment of dissolved hydrocarbon concentrations and geochemical indicators (i.e., sulfate, manganese, iron, etc.) through groundwater sampling. This indirectly indicates on-site microbial degradation of hydrocarbons (Wiedemeier et al., 1999). MNA has several advantages and disadvantages (USEPA, 1999) that must be carefully considered when evaluating its effectiveness as a remedial option in a given situation.

Advantages

- No subsurface disturbance (e.g., excavation changing local hydrogeology);
- No waste requiring disposal (at landfills, through deep well injection, etc.);
- Reduced risk of human exposure;
- Reduced risk of disturbances to ecological receptors;
- Reduced risk of cross-media transfer of contaminants (common in ex-situ treatment);
- Potential for application to part or all of a site (depending on site conditions and remediation objectives);
- Use in conjunction with, or as follow-up to, other active remedial measures (e.g., removal of source of contamination prior to MNA implementation); and
- Potentially lower overall remediation costs compared to other active remediation options.

Disadvantages

- Performance monitoring generally more extensive and possibly longer than under active remedial measures;
- May be more complex and costly to clearly demonstrate that natural attenuation is occurring;
- Toxicity and/or mobility of contaminant degradation products may be of greater concern than the initial contaminant;
- Institutional controls may be required for long-term protection of site (e.g., groundwater drinking ban);
- Potential for continued migration and cross-media transfer of contaminant;
- Hydrogeological and geochemical conditions amenable to natural attenuation may change over time, resulting in remobilization of stabilized contaminants or metals (e.g., arsenic); and
- Extensive education required to gain public acceptance of MNA as an effective remedial option.

1.4.2 Basic Processes of Natural Attenuation

As this research program focuses on the effects of sampling technologies in a MNA context, natural attenuation will be explained only briefly to assist in framing the research. As defined earlier, natural attenuation involves physical, chemical and biological processes (USEPA, 1999). The physical processes involve:

Dispersion - wherein pollutant decreases in concentration as it travels through the aquifer, mixing with clean water infiltrating from surface or groundwater that flows into the impacted area (Bear, 1979).

Sorption - wherein contaminant partitions between aqueous phase and soil matrix. This process is controlled by the organic carbon content of soil (Karickhoff, 1981). Sorption retards contaminant migration, but desorption can later counteract this (Patrick et al., 1985).

Volatilization - wherein contaminant compounds are transported from soluble groundwater plume into vadose zone soil gas through the capillary fringe (McAllister and Chiang, 1994). However, volatilization results in minor reduction of contaminant mass, resulting, for example, in total mass loss of no more than 5% for benzene (Chiang et al., 1989).

Physical processes reduce contaminant concentration in groundwater, but do not degrade contaminant mass. Chemical processes are often limited, involving stabilization of certain biological process products through reaction with inorganic materials in the groundwater system (Wiedemeier et al., 1999). Research by Kemblowski et al. (1987) and Salanitro (1992) indicates no evidence of the chemical transformation of aqueous benzene, toluene, ethylbenzene and xylenes (BTEX) in groundwater. Therefore, reduction of the contaminant mass occurs predominantly through biological processes.

Biological processes involve microorganisms and bacteria that naturally inhabit the subsurface environment and use the hydrocarbon as an organic substrate. These microorganisms and bacteria actively degrade the contamination into less harmful end products (USEPA, 1996). For example, the aerobic and anaerobic biodegradation of BTEX in groundwater (Mikesell et al., 1993), leaves only carbon dioxide and water (McAllister and Chiang, 1994). During microbial degradation, the breakdown of organic substrate (e.g., contaminant, natural organic matter) results in energy (i.e., electrons) being transferred to subsurface system elements to maintain the energy balance (Langmuir, 1997). The elements accepting the energy are known as Terminal Electron Acceptors (TEAs).

During microbial degradation of organic contaminants, TEA utilization reactions occur in sequence, from those providing the most energy to those providing the least (Langmuir, 1997), causing the groundwater system to progress from aerobic (oxygen rich) to anaerobic conditions (Azadpour-Keeley, 1999). These sequences are known as the redox ladder, and the general half reaction sequences are indicated in Figure 1.1.

As quantifying microbial populations is expensive and often inaccurate, MNA programs must rely on indirect methods to demonstrate that microbial biodegradation of the contamination is occurring. This involves measuring the dissolved TEA concentrations (oxygen, nitrate, iron, manganese, sulfate and methane) at all on-site monitoring wells (Wiedemeier et al., 1995). If natural attenuation is occurring, the following trends are expected for the various geochemical parameters and these are demonstrated in Figure 1.2 (Wiedemeier et al., 1999):

As aerobic biodegradation occurs:

- Dissolved oxygen concentrations decrease below background concentrations.

As anaerobic biodegradation occurs:

- Nitrate and sulfate concentrations decrease below background concentrations;
- Soluble manganese and iron increase within the plume above background concentrations; and
- Sulfide and methane concentrations increase within the plume above background concentrations.

A groundwater monitoring program demonstrating these geochemical trends, in conjunction with decreasing hydrocarbon constituent concentrations, indicates that MNA would likely be an effective remedial option. To better demonstrate the by-products of the various redox reaction sequences, the expected degradation sequence for a generic organic compound (CH_2O) to the basic end-product carbon dioxide (CO_2) is outlined in Figure 1.3 (Christensen et al., 1994).

1.4.3 Application

1.4.3.1 General

To properly assess if MNA is appropriate for a given situation, it is necessary to determine the concentrations and distribution of the contaminants, as well as how they have moved and will move in the subsurface environment. Contaminants move through the subsurface in two ways: as free product (light non-aqueous phase liquid (LNAPL) contaminant) floating along the water table, or as dissolved constituents in a groundwater plume, which are more mobile and of greater concern (USEPA, 1999).

Natural attenuation efficiency is measured by comparing contaminant transport rates to biodegradation rates (Landmeyer et al., 1998). If the former are slower, then the contaminants are likely to degrade to safe concentrations before reaching points of contact, and natural attenuation is a viable option. This comparison also involves assessing the hydrogeological (e.g. groundwater flow rates), geochemical (e.g. TEA properties of the aquifer material), physical (e.g. adsorption), microbial (e.g. biodegradation rates) and receptor (e.g. points of contact) constraints of the system (Chapelle et al., 1996, Wiedemeier et al., 2006).

To clearly demonstrate that MNA can achieve remedial objectives for a site, certain actions must be taken (Wiedemeier et al., 2006).

1. Characterize contaminant impacts and demonstrate that the plume is stable or shrinking.
2. Demonstrate that microbial activity indicative of natural attenuation is occurring on site and by-products of degradation are not harmful.
3. Continually monitor to ensure natural attenuation is achieving site cleanup objectives over time.

The first activity of any remedial program is to investigate and characterize the contamination source by determining the form, distribution and concentrations of contaminants throughout the subsurface environment (USEPA, 1988). If MNA is to be utilized, it is imperative to demonstrate that a contaminant plume is stable or shrinking over time, with no unacceptable impact on environmental receptors (Azadpour-Keeley, 1999).

Natural attenuation is most effective at remediating dissolved contaminants and not free product (USEPA, 1999), so it is important to remove, as much as possible, the free product sources that may be contributing dissolved hydrocarbons to the subsurface environment. Following characterization, most MNA programs or remedial cleanup operations remove the contamination source, (e.g., leaking underground storage tank, contaminated flare pit), as it continually replenishes dissolved contaminants that may cause plume growth (USEPA, 1999).

To demonstrate that a plume is stable or shrinking, a monitoring well sampling program must completely delineate contaminant impacts and define the extent of the plume. The monitoring well network (Figure 1.2) required to demonstrate the feasibility of MNA as a remedial option is made up of performance monitoring wells (which monitor hydrocarbon concentrations and geochemical data trends in and adjacent to the plume) and contingency wells (which monitor plume growth) (Wiedemeier and Haas, 2002). Figure 1.2 shows an example layout and expected data trends of a monitoring well network used for MNA of a LNAPL plume. Any MNA monitoring well program should consist of at least (Wiedemeier et al., 1999):

- One well near the release source;
- Several performance monitoring wells along the longitudinal axis of the contaminant plume;
- One upgradient well (background); and
- Several wells along the outer boundary of the contaminant plume (sentinel or contingency wells) that monitor plume growth.

Monitoring well screens must intersect the stratigraphic interval within which the contaminants are known to be migrating. As contaminant concentrations can vary vertically throughout the subsurface, monitoring wells should be screened at different depth intervals throughout the plume to allow vertical characterization. This also allows both lateral and vertical plume geometry to be determined within the subsurface at the site.

Microbial reduction of the relevant contaminant must also be demonstrated for MNA. It has been thoroughly documented that microbes can degrade organic matter such as hydrocarbon contaminants to less harmful end-products (Azadpour-Keeley, 1999). Microbiological laboratories directly measure microbial populations of iron-reducing and sulfate-reducing bacteria, but these processes are not widely accepted as a means to demonstrate natural attenuation. Instead, microbial degradation is monitored indirectly by measuring contaminant daughter products, electron acceptors, metabolic byproducts and general water quality parameters (Wiedemeier and Haas, 2002). This typically involves measuring concentrations of dissolved oxygen, nitrate, iron (III), sulfate and carbon dioxide within and outside the contaminant plume. These represent naturally occurring electron acceptors commonly used in microbial metabolism. The water quality parameters of alkalinity, oxidation-reduction potential (ORP), pH, temperature and conductivity should be measured (Wiedemeier et al., 1995).

It must be shown, through continual monitoring, that MNA continues to achieve clean up objectives for a site. Concentrations of contaminants and associated daughter products should be monitored over time to determine plume stability and distribution of any toxic by-products (Wiedemeier et al., 2006). Other factors to consider in long-term monitoring programs include (Wiedemeier at al., 1995):

- seasonal fluctuations in groundwater levels, causing more of the contaminants to be in contact with the groundwater and higher dissolved concentrations to exist;
- changes in groundwater geochemistry, causing mobilization of undesirable inorganic substances or creation of harmful intermediate degradation by-products; and
- complete TEA utilization, leading to decreased microbial degradation rates.

Quarterly sampling during the first year may confirm plume direction and better establish baseline contaminant flow conditions and potential seasonal variability (Wiedemeier and Haas, 2002). Monitoring plans should have flexibility to decrease monitoring frequency once natural attenuation is progressing as expected and increase under unexpected conditions (e.g. plume migration) (USEPA, 1999).

Natural attenuation is not always the most effective treatment for groundwater contamination. For example, where contamination is expanding faster than biodegradation can occur, where potential drinking water sources can be impacted by the contamination plume, or where biodegradation end-products of contamination are toxic or cannot be biodegraded, contaminants must be treated or removed by engineered systems to eliminate exposure to them (McAllister and Chiang, 2002).

1.4.3.2 Thesis Research Considerations

The glacial tills common in most of Alberta have slow groundwater movement and high concentrations of sulfate and organic material. As such, most of the groundwater systems at these sites are anaerobic. Under these conditions, aerobic respiration (dissolved oxygen utilization) and anaerobic denitrification (nitrogen reduction) may occur naturally without being measured. These reductive reaction sequences often do not play a part in the natural attenuation of hydrocarbon contaminants. As a result, biodegradation relies heavily on the anaerobic, reductive reactions of manganese, iron and sulfate. These geochemical parameters are focused on in this thesis research program, as both sites have glacial till soils with anaerobic conditions due to slow groundwater flow rates.

Most monitoring programs involve collecting groundwater samples from 0.05 m diameter PVC wells, often with 3 m screened sections intersecting the water table. This is where LNAPL contamination is expected. Three metre screens are common because that is a standard length for PVC pipe. Well screens are created simply by cutting this pipe with a specific slot size to allow water to enter and prevent soil material ingress. Many wells are sampled using dedicated sampling methods, including bailers or inertial Waterra pumps (foot valve and tubing). Within the environmental monitoring industry in Alberta it is common practice to purge up to three well volumes before sampling, based on the three to five volumes recommended by United States federal regulatory programs (USEPA, 1988). Originally intended as a guideline, three to five well volumes has become a rule in the industry (Barcelona et al., 2005), as values of water quality parameters were often found to stabilize after less than six well volumes were purged (Gibb et al., 1981).

Low-flow purging methods are increasingly used to collect samples to reduce the volume of purge water requiring disposal. These techniques may more accurately measure representative geochemical parameters (Parker, 1994). Puls and Paul (1995) demonstrated that contaminant concentrations and water quality parameters equilibrate with less than 7.5 L and 10 L of purge volume, respectively. Parker (1994) found that purging techniques and collection methods used at the time could negatively impact results, through, for example, oxidation/ precipitation of inorganics (e.g., iron, sulfide, etc.) and volatilization of organics.

Through multi-layer sampling in conventional wells, Puls and Paul (1997) demonstrated that contaminant distribution and mass varied vertically throughout the subsurface. This research indicates that "traditional" sampling methods provide misleading information on distribution and mass and can miss the presence of contamination altogether. As contaminant concentrations and geochemical parameters relevant to MNA can vary over small depth intervals, effective discrete interval sampling is needed. This was an underlying focus in the development of this thesis research program.

1.5 GEOCHEMICAL TRENDS OF INTEREST FOR MONITORED NATURAL ATTENAUTION (MNA)

To assess the various sampling technologies' ability to accurately measure parameters of interest to a MNA program, there are a couple of key processes of interest that must be first understood prior to critically assessing the data collected. Of particular interest are the iron, manganese and sulfate concentrations, in correspondence with the hydrocarbon concentrations, that are being measured across the site. The importance of these results and the expected trends are briefly described below (Langmuir, 1997) so that this information can be used in interpreting the results measured by the various technologies.

Metals

Iron, and to a lesser extent manganese, are common components of the mineralogy encountered in the subsurface throughout the world. Both manganese and iron are geochemical indicators of natural attenuation, as both of these metals act as electron acceptors to the microbes. The microbe utilizes these TEA metals to accept the electrons involved in the oxidation of a carbon substrate food source (organic matter), which in many instances is dissolved hydrocarbon contamination since it is readily available and the low-end hydrocarbon fractions (BTEX constituents) are easily broke down.

Elevated dissolved concentrations of these metals in groundwater above natural levels measured in non-impacted, background wells often indicate microbial degradation activity in the subsurface. Commonly encountered iron reduction in the subsurface environment involves highly amorphous iron oxyhydroxides in a solid phase (as coating on mineral grains) changing from Fe^{3+} (the form of iron measured in the laboratory metals analysis and presented in this study) to Fe^{2+} as it accepts an electron during hydrocarbon degradation. The manganese reduction follows a similar process, changing from Mn^{4+} (MnO_2) to Mn^{2+} as it accepts electrons during microbial biodegradation of the hydrocarbon constituents.

Sulfate

Sulfate reduction works on a similar principle as outlined for the metals, however it is typically utilized once most of the manganese and iron have been consumed by microbial degradation. It is common to observe both reductive processes occurring at the same time within an impacted area given the right conditions. The sulfate can accept eight electrons from the bacteria, typically of the genus *Desulfovibrio* or *Desulfotomaculum*, when it is being reduced to assist in the degradation of the carbon source, in this case the hydrocarbon contaminant. This reduction process converts the sulfate into an aqueous dihydrogen sulfide (H_2S) compound or if in the presence of iron can result in iron sulfides.

The presence of dissolved sulfate in the groundwater system comes from the dissolution of sulfate from mineral sources; a common source on the Prairies coming from the dissolution of gypsum (calcium sulfate) within the surficial soils by infiltration (Van Stempvoort et al., 1994). Sulfate concentration trends in natural attenuation are the opposite of those for the metals, where the sulfate concentrations will be considerably lower in an area that the sulfate is being utilized for microbial degradation of hydrocarbon impacts. As a result, higher sulfate concentrations will be measured in background wells and locations where there is no or very limited hydrocarbon degradation occurring.

Hydrocarbons

The benzene, toluene, ethylbenzene and xylenes (BTEX) and CCME petroleum hydrocarbon Fraction 1 minus BTEX (PHC F1-BTEX), are the typical hydrocarbon constituents that are monitored as part of a MNA program. These hydrocarbon constituents are presented in this study, as they are the most readily available due to their mobility and are the most easily consumed by the microbes as a substrate during microbial degradation. The hydrocarbon constituent reduction is a key component in assessing the effectiveness of a MNA program, as these dissolved hydrocarbon concentrations must remain stable or decrease over time for MNA to be considered a feasible remedial option.

It is known for both research sites that the hydrocarbon contaminant source being investigated is a light non-aqueous phase liquid (LNAPL). The low-end hydrocarbon fractions (F1 fractions) slowly dissolve into groundwater when in direct contact with the LNAPL contaminant or due to infiltration through the source zone. The LNAPL contaminant floats on the water table causing higher dissolved concentrations within the sample intervals that intersect the water table. Since the subsurface stratigraphy is dominated by clayey silt and silt at the sites, the dissolved concentrations do not readily move downward through these formations and tend to migrate laterally near the water table. Therefore lower concentrations should be measured within deeper intervals where the groundwater is not in contact with free product and the small amount of groundwater that migrates downwards is likely diluted.

Knowing this, higher manganese and iron concentrations are expected at shallow depths where hydrocarbon impacts have been noted at the sites. It would be expected that the metals concentrations would decrease with depth or as the sample locations move further from the free product source, as the hydrocarbon concentrations would decrease in these situations. Contrarily, the sulfate concentrations would be expected to be lower near the source and increase in concentration as the sample locations move closer to non-impacted, background conditions.

1.6 REFERENCES

Alberta Energy and Utilities Board. 2006. Alberta's Energy Reserves 2005 and Supply/Demand Outlook 2006-2015. ST98-2006. 178 pages.

Azadpour-Keeley, A., Russell, H. and Sewell, G.W. 1999. Microbial processes affecting monitored natural attenuation of contaminants in the subsurface. USEPA Ground Water Issue. EPA/540/S-99/001. 18 pages.

Barcelona, M.J., Varljen, M.D., Puls, R.W. and Kaminski, D. 2005. Ground water purging and sampling methods: history vs. hysteria. Ground Water Monitoring & Remediation. 25(1): 52-62.

Bear, J. 1979. Hydraulics of groundwater. McGraw-Hill: New York. 567 pages.

Canadian Association of Petroleum Producers. 1999. Environmental operating practices for upstream petroleum operations: Alberta operations. Volume IV: Production. Canadian Association of Petroleum Producers, Calgary, Alberta.

Chapelle, F.H., Landmeyer, J.E. and Bradley, P.M. 1996. Assessment of intrinsic bioremediation of jet-fuel contamination in a shallow aquifer, Beaufort, South Carolina. US Geological Survey Water-Resources Investigations Report 95-4262. 30 pages.

Chiang, C.Y., Salanitro, J.P., Chai, E.Y., Colthart, J.D. and Klien, C.L. 1989. Aerobic biodegradation of benzene, toluene and xylene in a sandy aquifer: Data analysis and computer modeling. Ground Water. 27(6): 823-834.

Christensen, T.H., Kjeldsen, P., Albrechtsen, H.J., Heron, G., Nielsen, P.H., Bjerg, P.L. and Holm, P.E. 1994. Attenuation of landfill leachate pollutants in aquifers. CRC Press, Inc.: Boca Raton, FL. 138 pages.

Gibb, J.P., Schuller, R.M. and Griffin, R.A. 1981. Procedures for the collection of representative water quality data from monitoring wells. Cooperative Ground Water Report 7. Illinois State Water Survey and Illinois State Geological Survey.

Karickhoff, S.W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere. 10: 883-884.

Landmeyer, J.E., Chapelle, F.H., Petkewich, M.D. and Bradley, P.M. 1998. Assessment of natural attenuation of aromatic hydrocarbons in groundwater near a former manufactured-gas plant, South Carolina, USA. Environmental Geology. 34(4): 279-292.

Langmuir, D. 1997. Aqueous environmental geochemistry. Prentice-Hall. 600 pages.

McAllister, P.M. and Chiang, C.Y. 1994. A practical approach to evaluating natural attenuation of contaminants in ground water. Ground Water Monitoring Review. Spring: 161-173.

Mikesell, M.D., Kuko, J.J. and Olsen, R.H. 1993. Fundamentals of bacterial degradation of BTEX. In Proceedings of the CoBioRem conference on bioremediation of petroleum hydrocarbons in soils and groundwater. Lansing, Michigan. March 1-2, 1993.

Minnesota Pollution Control Agency. 2007. What is natural attenuation? www.pca.state.mn.us/water/groundwater/natural-attenuation.html. Accessed July 20, 2007. 5 pages.

Pacific Northwest Pollution Prevention Research Center. 1993. Pollution prevention opportunities in oil and gas production, drilling and exploration. A Northwest Industry Roundtable Report. 16 pages.

Parker, L.V. 1994. The effects of ground water sampling devices on water quality: a literature review. Ground Water Monitoring Review. Spring: 130-141.

Patrick, G.C., Ptacek, C.J., Gillham, R.W., Barker, J.F., Cherry, J.A., Major, D.W., Mayfield, C.I. and Dickhout, R.D. 1985. The behaviour of soluble petroleum product derived hydrocarbons in groundwater, phase I. Petroleum Association for Conservation of the Canadian Environment. PACE Report No. 85-3. 70 pages.

Pembina Institute. 2002. The Alberta GPI Accounts: Municipal and Hazardous Waste. Report # 27. 44 pages.

Puls, R.W. and Paul, C.J. 1995. Low-flow purging and sampling of ground water monitoring wells with dedicated systems. Ground Water Monitoring Review. Winter: 116-123.

Puls, R.W. and Paul, C.J. 1997. Multi-layer sampling in conventional monitoring wells for improved estimation of vertical contaminant distribution and mass. Journal of Contaminant Hydrology. 25: 85-111.

Schneider, R. 2001. The oil and gas industry in Alberta: Practices, Regulations and Environmental Impact. Alberta Centre for Boreal Research. 24 pages.

U.S. Environmental Protection Agency (USEPA). 1988. Guidance for conducting remedial investigations and feasibility studies under CERCLA. OSWER Directive 9355.3-01. Office of Emergency and Remedial Response, Washington, D.C. 186 pages.

U.S. Environmental Protection Agency (USEPA). 1996. A citizen's guide to natural attenuation. Technology Fact Sheet. EPA 542-F-96-015. 4 pages.

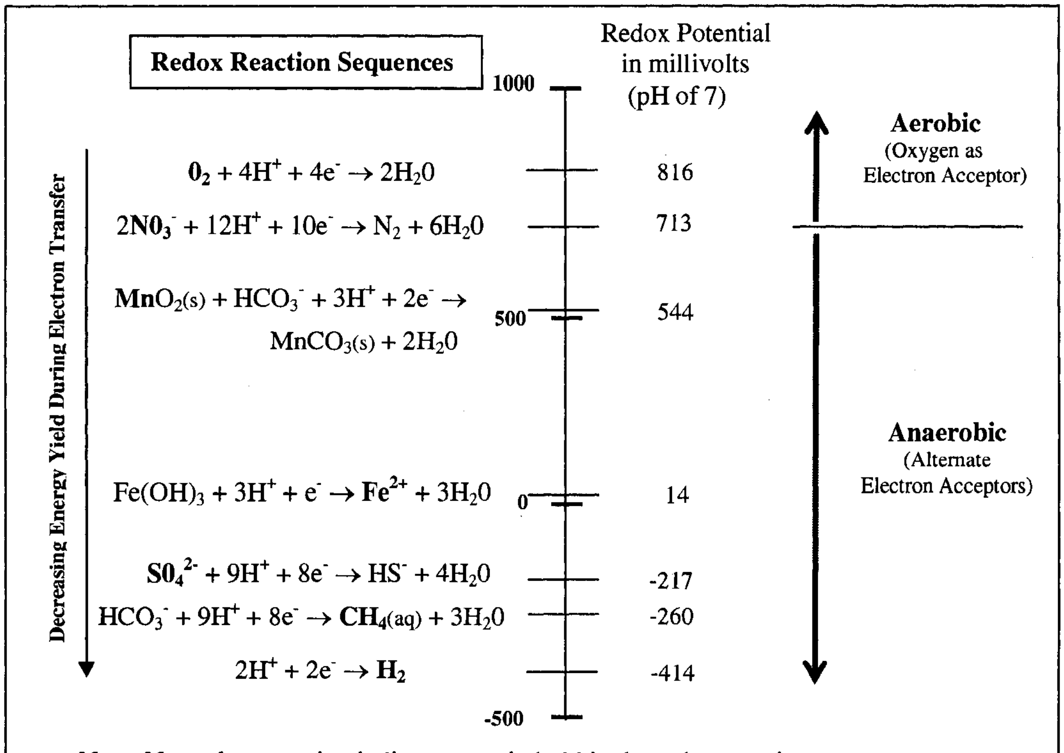
U.S. Environmental Protection Agency (USEPA). 1999. Use of monitored natural attenuation at Superfund, RCRA corrective action, and underground storage tank sites. Directive 9200.4-17P. 32 pages.

Wiedemeier, T.H., Wilson, J.T., Kampbell, D.H., Miller, R.N. and Hansen J.E. 1995. Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. U.S. Air Force Center for Environmental Excellence: San Antonio, Texas. 295 pages.

Wiedemeier, T.H., Rifai, H.W., Newell, C.J. and Wilson, J.T. 1999. Natural attenuation of fuels and chlorinated solvents in the subsurface. John Wiley & Sons: New York. 617 pages.

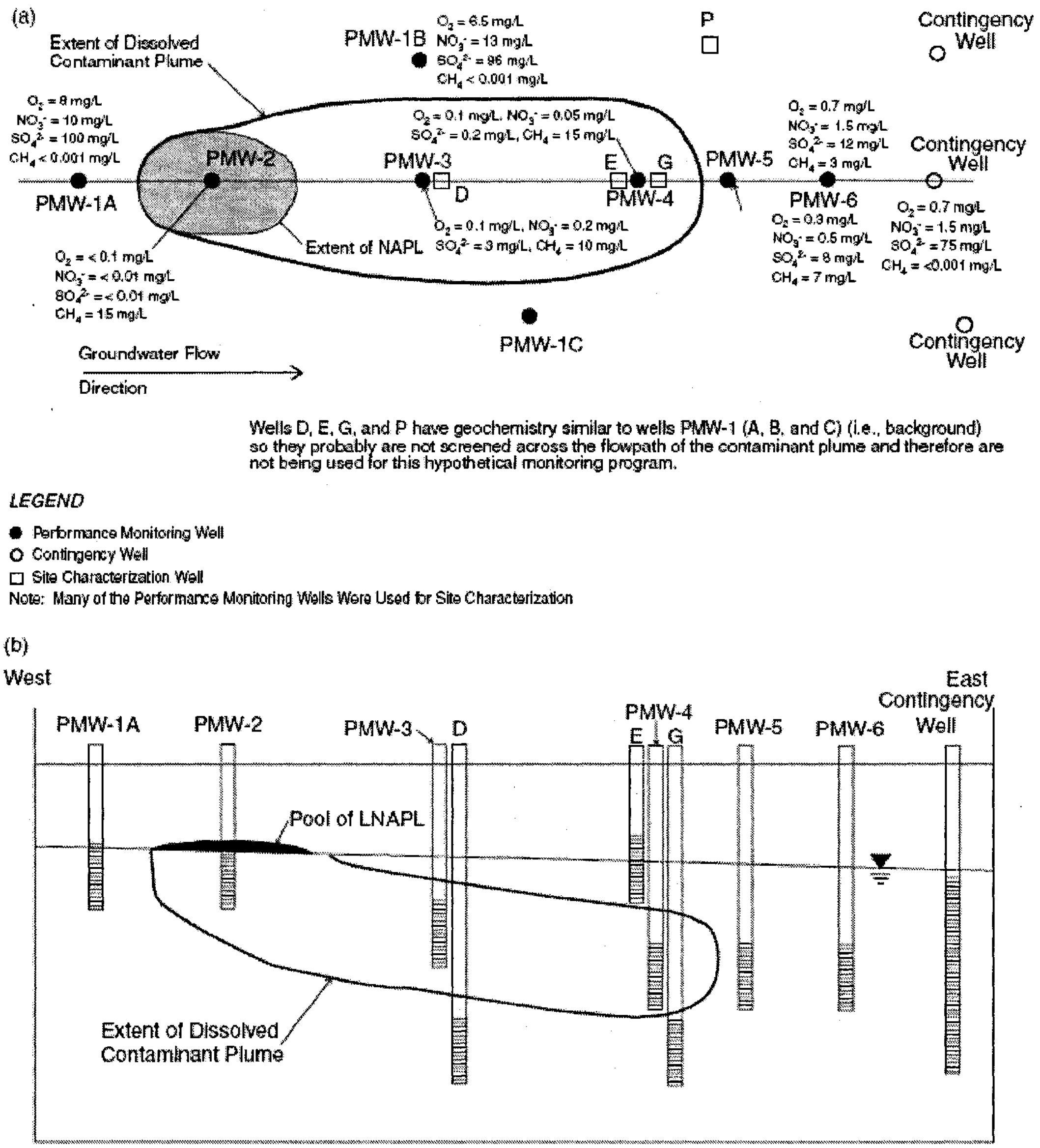
Wiedememier, T.H. and Haas, P.E. 2002. Designing monitoring programs to effectively evaluate the performance of natural attenuation. Ground Water Monitoring & Remediation. 22(3): 124-135.

Wiedemeier, T.H., Barden, M.J., Haas, P.E. and Dickson, W.Z. 2006. Chapter 9: Designing monitoring programs to effectively evaluate the performance of natural attenuation. Practical handbook of environmental site characterization and ground-water monitoring (Second edition). CRC Press, Taylor Francis Group: New York. Pages 573-637.



Note: Natural attenuation indicators are in bold in the redox reaction sequences.

Figure 1.1. Redox ladder indicating redox potentials and redox reaction sequences (Modified from Azadpour-Keeley et al., 1999 and Langmuir, 1997).



Wells D, E, G, and P have geochemistry similar to wells PMW-1 (A, B, and C) (i.e., background) so they probably are not screened across the flowpath of the contaminant plume and therefore are not being used for this hypothetical monitoring program.

LEGEND

- ● Performance Monitoring Well
- ○ Contingency Well
- ☐ Site Characterization Well

Note: Many of the Performance Monitoring Wells Were Used for Site Characterization

Figure 1.2. Recommended groundwater monitoring well network for demonstrating natural attenuation [(a) plan view (b) cross-sectional view] and geochemical data trends within and outside plume (Modified from Wiedemeier et al., 1999).

Stoichiometric reactions for different redox environments for a model compound (CH_2O) at pH of 7.

Oxygen Reduction, Aerobic Respiration	$CH_2O + \mathbf{O_2} \rightarrow CO_2 + H_2O$
Denitrification	$5CH_2O + 4\mathbf{NO_3^-} + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$
Manganese Reduction	$CH_2O + 2MnO_2 + 4H^+ \rightarrow CO_2 + 2\mathbf{Mn^{2+}} + 3H_2O$
Iron Reduction	$CH_2O + 4Fe(OH)_3 + 8H^+ \rightarrow CO_2 + 4\mathbf{Fe^{2+}} + 11H_2O$
Sulfate Reduction	$2CH_2O + \mathbf{SO_4^{2-}} + H^+ \rightarrow 2CO_2 + HS^- + 2H_2O$
Methanogenic, Fermentative	$CH_2O \rightarrow CH_3COOH \rightarrow \mathbf{CH_4} + CO_2$

Note: These processes are microbially mediated. Natural attenuation indicators are in bold in the redox reaction sequences.

Figure 1.3. Redox reactions involved in degradation of organic matter in different redox environments (Modified from Azadpour-Keeley et al., 1999).

Chapter 2

Diffusion Sampler Development and Application for Monitored Natural Attenuation at Upstream Oil and Gas Sites

2.1 INTRODUCTION

Diffusion is a molecular-scale process of spreading due to concentration gradient and random motion, with movement from areas of high concentration to areas of low concentration as all matter seeks a state of balance (Bedient et al., 1997). Diffusion is the dominant transport mechanism where groundwater velocities are very low, as in tight soils like clays (Bedient et al., 1997). Diffusion sampling works on the fundamental principle that all aqueous systems approach chemical equilibrium due to diffusive and osmotic flux gradients that exist in all groundwater systems.

Diffusion sampling has several key advantages compared to other sampling methods (Vroblesky, 2001):

- Diffusion samplers equilibrate with monitoring well groundwater throughout installation, so sample results are time averaged rather than point-in-time concentrations.
- Diffusion samplers can be installed within the well screen where groundwater continually flows, so purging and the associated disposal cost of this groundwater is eliminated.
- Diffusion sampler membrane is a filtration material so it eliminates the time and cost of filtering groundwater samples for analysis, such as dissolved metals.
- Because the sample is sealed inside the membrane during retrieval, oxidation and volatilization effects due to atmospheric exposure is limited.
- Diffusion samplers can be fabricated for installation in pre-existing wells and implemented in various ways depending on the requirements of the sampling program.

- Diffusion samplers can measure vertical concentration profiles in groundwater (Ronen et al., 1986; Kaplan et al., 1991; and Dasika and Atwater, 1995).

2.2 BACKGROUND

2.2.1 Diffusion Sampler Historical Research

Diffusion sampling relies on groundwater and the water in the sampler reaching geochemical equilibrium across a porous membrane (Imbrigiotta et al., 2002). Possible diffusion membrane materials include: cellulose acetate, polysulfone, polyethylene, polycarbonate, nylon and regenerated cellulose. The use of diffusion sampling technology to collect in-situ water samples for analysis of chemical concentrations was initially studied by Hesslein (1976) and Mayer (1976) using cellulose acetate dialysis membrane.

A variety of diffusion membrane materials and diffusion sampler designs have since been investigated for their ability to measure both inorganic and organic concentrations in groundwater. The historical research on the various diffusion materials investigated in this thesis are detailed below.

Cellulose Acetate Dialysis Membrane

Hesslein (1976) developed a diffusion sampler using cellulose acetate dialysis membrane to measure dissolved phosphate and methane concentrations in sediments. It was placed over the open end of an acrylic plastic container filled with deionized water and fastened in place with a thin acrylic sheet and nylon screws. Prior to installation, the dissolved gases were removed by placing the sampler in a closed bath of degassed distilled water. The diffusion samplers were allowed to equilibrate for a week in the sediment before being removed and sampled using a syringe. The results demonstrated variations in phosphate and methane concentration over the 5 cm depth intervals to a depth of 35 cm. Mayer (1976) conducted a similar study using this membrane to sample dissolved silica concentrations in lake water and sediments.

Vroblesky et al. (2002) used cellulose acetate dialysis membrane samplers to collect representative samples of inorganic constituents from groundwater in wells and a discharge zone beneath a stream. They were fabricated using pretreated high-grade tubular dialysis membrane with a molecular weight cutoff of 8,000 Daltons. The membranes were designed to collect 350 mL samples by filling 60 cm long membrane sections with deionized water and tying both ends in knots.

The membrane sampler had a PVC pipe inside the membrane for rigidity and a low density polyethylene (LDPE) mesh on the outside for abrasion protection. The diffusion samplers were deployed by attaching them to 6 mm diameter rigid polyethylene tubing. Similar inorganic concentrations were measured for samples from cellulose acetate dialysis membranes installed in the monitoring wells and those from low-flow sampling at similar depths.

Low Density Polyethylene Membrane

Vroblesky (2001) investigated the field application of polyethylene samplers to collect groundwater samples containing VOC concentrations (BTEX and several chlorinated compounds). The samplers were fabricated by heat sealing one end of the 10 cm flat width polyethylene tubing, filling it with deionized water, and heat sealing the other end with no headspace in the bag. The samplers could then be cut to any length to accommodate the desired amount of sample volume.

The diffusion samplers were placed inside LDPE mesh tubing for protection and positioned in the well using a weighted line or fixed pipe. The results indicated that polyethylene diffusion bag samplers may be a cost effective method to obtain representative VOC concentrations within a monitoring well; however, the research indicated that dissolved inorganic constituents cannot be accurately sampled by this membrane technology.

Nylon-Screen Samplers

Vroblesky et al. (2002) also used nylon-screen samplers to collect representative samples of inorganic constituents from groundwater in wells and a discharge zone beneath a stream. The nylon-screen samplers consisted of fastening a 125 or 250 micron mesh nylon screen over the mouth of a 30 mL polyethylene sampling jar while submerged in deionized, deoxygenated water. Three to four of these nylon-screen samplers were deployed in a monitoring well with the opening facing down at a half to one inch spacing inside a low density polyethylene mesh. The sample was collected for analysis by retrieving the nylon-screen samplers from the well, removing the caps and pouring the contents into sample bottles. The inorganic solute concentrations in these samples were similar to those collected by low-flow sampling from similar depths.

Regenerated Cellulose Dialysis Membrane

Regenerated cellulose dialysis membranes filled with deionized water were used in laboratory and field research to sample concentrations of various inorganic species. Numerous dialysis membranes installed at close intervals within a well screen demonstrated the membrane's ability to effectively sample inorganic concentration changes over small depth intervals (Ronen et al., 1986; Dasika and Atwater, 1995). Imbrigiotta et al. (2002) used regenerated cellulose membranes in bedrock wells to monitor several chlorinated VOCs, calcium, chloride and alkalinity and found no statistical difference when compared to low-flow sampling techniques from the same wells. Inconsistent variations among dialysis membrane iron concentrations called into question how representative these samples were. Ehlke et al. (2004) observed equilibration within seven days for inorganic constituents and three days for various VOCs in a laboratory study using regenerated cellulose dialysis membranes.

2.2.2 Selection of Diffusion Sampler Material

Vroblesky et al. (2002) field research using nylon-screen and dialysis membrane samplers was among the earliest to measure several key inorganic constituents in groundwater wells. Most previous inorganic research involved sampler installation directly in sediments (Hesslein, 1976; Mayer, 1976; Bottomly and Bayley, 1984). The inorganic constituents tested included arsenic, calcium, chloride, iron, manganese, sulfate and dissolved oxygen, all of which are important in MNA programs. For a MNA program at upstream oil and gas sites, the diffusion sampling technology must be able to collect representative samples of dissolved cations, anions, metals and all hydrocarbon constituents.

Previous research by Vroblesky (2001) indicated that polyethylene membrane diffusion samplers are incapable of collecting water samples containing dissolved inorganic species. As there are many inorganic parameter trends that must be demonstrated for MNA to be an accepted remedial option, these samplers were not considered for this research program. Commercial laboratories request several hundred millilitres of sample volume to analyze for the various parameters of interest in a MNA program, so the diffusion sampler must be capable of retrieving this volume. Although Vroblesky et al. (2002) demonstrated that the nylon screen samplers collected representative samples, too many samplers would be required to obtain the necessary volume. A sample depth interval containing enough 30 mL samplers to get the requested sample volume for commercial laboratory analysis would be too large to represent discrete interval sampling. Thus, the nylon-screen sampler is not efficient enough for this research program.

The dialysis membrane technology was judged to be most appropriate for this study since it can measure both inorganic and organic constituents and can be fabricated to supply the necessary sampling volume. Two types of dialysis membranes were available based on previous research efforts: cellulose acetate (Hesslein, 1976; Vroblesky et al., 2002) and regenerated cellulose (Ronen et al., 1986; Ehlke et al., 2004). The regenerated cellulose dialysis membrane is more durable than the cellulose acetate and more chemically compatible for most environmental applications (Ehlke et al., 2004).

2.2.3 Research Considerations for Diffusion Sampler Application

As mentioned in Chapter 1, there is no previous published research on the application of diffusion samplers to assess MNA in hydrocarbon-contaminated groundwater. Previous research had mostly studied volatile organic compounds (VOCs) in groundwater (Kaplan et al., 1991; Vroblesky, 2001; Imbrigiotta et al., 2002) or dissolved inorganic constituents in riverbed and lakebed sediments (Hesslein, 1976; Mayer, 1976). Vroblesky et al. (2002) indicated that in field installed monitoring well dialysis samplers, most contaminants should equilibrate within two week. However, little research was found on equilibration times for dissolved organic compounds common to upstream oil and gas sites, other than VOCs. These times are measured in this thesis.

Limited research had been done on diffusion sampling of inorganic constituents (Dasika and Atwater, 1995; Imbrigiotta et al., 2002; Vroblesky et al., 2002). However, further work was necessary to successfully apply the process to those constituents relevant to MNA.

Another concern was the membrane could serve as a carbon source to microbes in the groundwater environment, leading to membrane degradation (Vargo et al., 1975). This could limit the dialysis samplers' time in the well, possibly preventing constituent equilibrium. Additional research was necessary to determine if a representative sample of the formation water could be obtained before membrane integrity was compromised.

Vroblesky et al. (2002) hypothesized that if a dialysis membrane diffusion sampler was installed in a high concentration salt solution, osmotic forces could cause water loss from the sampler. However, further research was needed to determine if salt, at various concentrations, causes water loss from a regenerated cellulose dialysis membrane sampler. Vroblesky et al. (2002) suggested that a rigid pipe be installed inside the membrane to prevent it from collapsing as water is drawn from it in an attempt to achieve osmotic equilibrium.

2.3 METHODS

A detailed description of the components, fabrication, installation and sample retrieval of the regenerated cellulose dialysis sampler (with photos) can be found in Appendix A. Hence forth dialysis membrane diffusion sampler will be referred to simply as "diffusion sampler" and dialysis membrane diffusion sampling as "diffusion sampling".

2.3.1 Field Diffusion Sampler Development

A design similar to the dialysis membrane sampler used by Vroblesky et al. (2002) was selected for the diffusion sampler in this study. Membrane Filtration Products Inc. in Seguin, Texas provided 10 m of pretreated "CelluSep H1" regenerated cellulose membrane with a flat width of 77 mm and a molecular weight cutoff of 8000 Daltons (Part No. 0810-76, US$178 in June, 2003). Membrane pretreated to remove any impurities was more expensive than dry membranes, but easier to use. The membrane was stored in a solution of ethylenediaminetetra acetic acid (EDTA) and methanol, and must be kept at 4°C to minimize biological degradation during shipping and storage (Membrane Filtration Products Inc., 2003).

The 8,000 Daltons molecular weight cutoff was chosen because it worked well for determining inorganic concentrations for Vroblesky et al. (2002). The 77 mm flat width tubing was selected because it provided the maximum sample volume, which was necessary so all groundwater parameters of interest in the MNA program could be analyzed by the commercial laboratory. The membrane was cut into 75 cm lengths to ensure that the samplers were 60 cm long after the ends were sealed, providing a sufficient volume of water for analysis.

Our design omitted Vroblesky et al.'s (2002) LDPE protective mesh around the membrane during installation. This minimized new material entering the monitoring well and prevented chemical compounds sorbing from or leaching into the sampled groundwater, which could impact the sample results. To provide abrasion protection for the dialysis membrane, it was placed inside a 65 cm length of PVC pipe. As it was the same material as the existing well casing, the PVC should have minimal impact on the sample results. A 37 mm inner diameter (ID) pipe was the largest that could be installed in the 50 mm ID well screen. The pipe had 9.5 mm holes drilled throughout it to expedite dialysis membrane equilibration.

In this study, one end of the dialysis tubing was knotted and the other was sealed with a capped brass sampling nozzle (Figure 2.1) connected using O-rings for easy sampling. Initial designs relied on piercing or cutting the end of the dialysis membrane to collect the sample water inside, however this proved inefficient as flow was difficult to control, resulting in loss of the limited sample volume. The brass sampling nozzle design allowed the equilibrated water within the membrane to be easily poured into the laboratory sample bottles without wastage.

After sealing, the membrane was slid into the protective PVC pipe and filled with deoxygenated, deionized water through the nozzle. Deoxygenated water was used because Vroblesky et al. (2002) reported that samplers containing aerobic water underestimated dissolved iron concentrations due to oxidation and precipitation of iron. Iron is an important MNA geochemical indicator, so accurate measurement is necessary. The samplers in our research were then stored in PVC canisters filled with deionized, deoxygenated water for storage and transport to the site.

2.3.2 Field Diffusion Sampler Installation

To measure vertical heterogeneity in groundwater constituents, seals were developed between each sampler (Figure 2.2) to isolate them vertically within the well screen. The seals were fabricated from a rigid PVC disk and a flexible PVC geomembrane, so as not to introduce new materials into the well. The rigid PVC disk was slightly smaller in diameter than the monitoring well ID, and the flexible PVC membrane was cut to a diameter slightly larger than the monitoring well ID. The flexible PVC membrane was placed on the end of the dialysis sampler pipe, with the rigid PVC disk directly on top of the membrane, and this was fastened in place using cable ties.

A rigid system of PVC pipe (Figure 2.3) was created to push the samplers to the desired sampling depth. An initial design using rope and a weight was unable to overcome the seal friction on the well casing walls. The rigid system consisted of 19 mm ID PVC pipe cut into lengths that ensured the samplers were at the correct depth. The pipe was connected to the diffusion sampler end seals using cable ties. The samplers were installed with the nozzle end facing upward to eliminate sample leakage if the o-rings did not seal properly.

Just before field installation, a nylon rope was tied to the top of the rigid PVC riser pipe and pinched in the well cap to keep the rigid system at the desired sampling depth. To retrieve the samplers, the pipe was pulled out of the well with the rope, and the diffusion samplers were freed from the rigid riser and spacer pipe by cutting the cable ties. The groundwater sample was obtained by cutting the end seal cable ties, unscrewing the brass nozzle cap and pouring the water into the laboratory sample bottles.

The samples were compared to Waterra samples from the same well to check their representativeness. The Waterra sampler consisted of the inertial Waterra foot valve connected to the end of rigid, Teflon-lined PVC tubing. Waterra sampling was conducted by purging three well volumes before groundwater samples were collected. In most sampling instances, the Waterra sample was collected within two hours of retrieving the diffusion samplers from the well.

2.3.3 Site Descriptions

The research was conducted at two upstream oil and gas sites in Alberta. Site 1 was a decommissioned well site and flare pit located in the northwest of the province, while Site 2 was a natural gas processing facility located in the southeast. Detailed site descriptions including site plans and borehole logs are in Appendix B.

2.3.4 Laboratory Experiments

Field research conducted by Vroblesky et al. (2002) demonstrated that diffusion samplers and low-flow sampling from the same well yield groundwater samples with similar inorganic concentrations, but much of these data were obtained using nylon-screen samplers and not dialysis membrane samplers. Thus, further tests were required to determine appropriate equilibration time for organic and inorganic compounds, and to assess equilibration rates for inorganic compounds to determine how long the diffusion samplers need to be installed in the field. The laboratory research studied the effects of varying ionic charges on equilibration rates and the potential for water loss due to osmotic gradients (in saline groundwater environments) and hydraulic gradients (seasonal water table fluctuations).

Thus, this program studied the ability for diffusion samplers to sample the inorganic and organic constituents expected in the MNA field program. A detailed description of all the laboratory studies can be reviewed in Appendix C.

2.3.4.1 Dissolved Hydrocarbon Equilibration Study

The laboratory study involved suspending dialysis membranes in 1.5 L vessels of groundwater taken from a hydrocarbon-impacted well from one of the sites. The vessels had zero headspace. The 77 mm flat width regenerated cellulose dialysis membrane contained a 15 cm long, 19 mm ID PVC pipe filled with deionized, deoxygenated (as per ASTM# D854) water. Clamps sealing the ends of the dialysis membrane were removed to retrieve the sample water in the membrane.

To better simulate conditions expected in a monitoring well in the field, the vessels were kept in the dark and stored at approximately 4°C. The water in the vessel and the membrane was analyzed at two, four and six weeks for benzene, toluene, ethylbenzene, xylene (BTEX) and Canadian Council of Ministers for the Environment (CCME, 1996) petroleum hydrocarbon F1 fraction (C_6 to C_{10}) minus BTEX (PHC F1-BTEX). The dialysis membranes were visually inspected for degradation during each sampling event.

2.3.4.2 Effect of Monovalent and Divalent Salts Study

Research using monovalent and divalent dissolved salts investigated the effects of ionic charge on equilibration time and the impact of salinity concentration on dialysis sampler water loss. Monovalent sodium chloride and divalent calcium sulfate were used because they were prominent in the historical sampling data from the sites. Five sodium chloride solutions ranging from 50 to 5000 mg/L and five calcium sulfate solutions ranging from 100 to 2000 mg/L were created in airtight vessels to prevent evaporation.

Two 77 mm flat width membrane samplers filled with deionized water were suspended in each vessel. One was sealed by tying both ends and weighed periodically to examine dialysis sampler mass loss. A clamp on the second membrane was removed to measure electrical conductivity (EC); similar EC values in the vessel and the sampler indicated equilibration. Another vessel filled only with deionized water acted as a control for the mass water loss experiment.

2.3.4.3 Hydraulic Gradient and Evaporation Study

During some field events, the water table in the well dropped below the diffusion sampler due to seasonal fluctuations, and significant water loss was observed from the dialysis membranes. The author hypothesized that water loss occurred through two processes: hydraulic head difference and evaporation. The quantity of the loss was tested by studying diffusion samplers under three conditions described below. Three diffusion samplers were fabricated in the same manner as if to be installed in the field, except both ends of the dialysis membrane were tied to eliminate leakage since no sampling was to occur during this experiment. Each sampler was weighed and suspended in a 50 L water reservoir. Two were situated in the laboratory under ambient atmospheric conditions similar to the sampling well headspace, with one installed just below the water surface and the other half-submerged. A third membrane was half-submerged in a cold room at 4°C and 100% humidity where little to no evaporation was expected. This comparison assisted quantifying the evaporation rates for the ambient condition samplers.

Water was added throughout the experiment to keep the water's surface at the same height. This ensured equal membrane exposure in both environments. Each diffusion sampler was weighed periodically throughout the experiment.

2.4 RESULTS

2.4.1 Laboratory Experiments

2.4.1.1 Dissolved Hydrocarbon Equilibration Study

The results of the dissolved hydrocarbon equilibration study are contained in Table 2.1, and are plotted for comparison in Figure 2.4. The week four sample was analyzed for total purgeable hydrocarbons instead of the CCME F1 fraction (C_6 to C_{10}). Therefore, it cannot be compared directly with the PHC F1 – BTEX values for week two and week six.

The results demonstrate that BTEX equilibration occurs between weeks two and four. The BTEX and PHC F1-BTEX concentrations in the sampler are 35 to 45 percent lower than the vessel concentrations at two weeks and 15 to 20 percent higher than the vessel concentrations after four weeks. At six weeks, there is no consistent pattern of which concentration is higher, but they are within 20% of each other.

Hydrocarbon contaminated water had no visual degradation effects on the dialysis membrane. Inspection of the membrane after removal from the vessels revealed little change besides a slight orange discoloration.

2.4.1.2 Effect of Monovalent and Divalent Salts Study

The author investigated significant water loss from the samplers due to osmotic gradients (Table 2.2), and the time required for inorganic salts to equilibrate across the membrane (Table 2.3). Both the mass water loss from the initial membrane mass (Eq 1) and the EC variation between the membrane and vessel (Eq 2) are expressed in terms of percent difference:

$$\frac{M_{Wt} - M_{Wi}}{M_{Wi}} \times 100\% \qquad \text{[Eq 1]}$$

where: M_{Wt} = membrane mass for time t

M_{Wi} = initial membrane mass

$$\frac{EC_{St} - EC_{Vt}}{EC_{Vt}} \times 100\% \qquad \text{[Eq 2]}$$

where: EC_{St} = electrical conductivity in the sampler for time t

EC_{Vt} = electrical conductivity in the vessel for time t

Valency and concentration of the salt solution have no impact on mass water loss from the membranes, as mass loss only ranges from 5 to 10 percent of initial membrane mass after 70 days for all salt solutions (Figure 2.5). Salt concentrations have no impact on equilibration time, as the EC in the dialysis membranes equilibrate with the vessel within the first 24 to 48 hours (Figure 2.6, Figure 2.7).

2.4.1.3 Hydraulic Gradient and Evaporation Loss Study

Mass loss results for the dialysis samplers are plotted in Figure 2.8. Sampler mass measurements were discontinued once they stabilized. Mass water loss dramatically increased when a portion of the sampler was above the water surface. At ambient temperature and humidity, the sampler installed just below the water surface lost 19.2 grams (4.1% of the initial mass) over 28 days, while the half submerged sampler lost 401.3 grams (95% of the initial mass). As the 19.9 grams remaining at the end of the experiment in the half submerged sampler was the mass of the moist dialysis membrane, nearly all water was lost.

The half submerged sampler in the 100% humidity cold room lost 182.5 grams over 65 days, at which point the mass stabilized and the experiment was discontinued. The water level in the sampler stabilized after dropping to the level in the reservoir, so only the mass below the water surface remains in the sampler.

This is a mass loss of 42% of the original sampler mass, or half the mass loss observed for the half submerged sampler in ambient conditions. The rate of mass loss in this sampler is much slower than the half submerged sampler under ambient conditions, shown by the flatter slope of the line in Figure 2.8.

2.4.2 Field Testing Program

2.4.2.1 Field Installation Considerations

Diffusion sampler results were compared to inertial Waterra sampler results (the system historically used at this site) to ensure that the former were representative. The results from the two discrete interval diffusion samplers and the Waterra sampler are plotted for the October and February sampling events at both sites.

The discrete interval seals and the diffusion sampler installation method were modified to try to make the sampling as effective as possible. The October diffusion samplers at Site 1 used ropes between the samplers with a weight at the bottom to pull the samplers to the desired sampling depth. The rope threaded through the hole in the center of the seals, which were held in place by knots on each side of the seal. The rope was then fastened to the diffusion samplers.

The rope installation design may have allowed the seals to rotate from the intended horizontal position, allowing the water to flow vertically within the well during the sampler installation period. Consequently, the diffusion samplers may or may not have sampled a discrete interval. They were lowered until the mark on the rope was at the top of the well casing, indicating that the top sampler was at the correct depth. However, it was uncertain if the bottom sampler was immediately beneath the top sampler or at the intended sampling depth, because seal friction may have prevented the weight from pulling it to the correct depth.

To overcome these uncertainties, a rigid system was developed (Section 2.3.2). It ensured that the seals create a discrete interval within the well screen for the diffusion sampler, and that the lower sampler was at the intended depth. The rigid system was used for October at Site 2 and for all February sampling events, so these samples may be more representative of discrete intervals.

The data used to compare the dialysis membrane diffusion samplers and Waterra sampler include selected dissolved cations, anions, metals and hydrocarbon constituents in groundwater. The selected cations (sodium, calcium and magnesium) are common in soil, providing an indirect indication of the soil mineralogy (Langmuir, 1997). The anions selected are bicarbonate, sulfate and chloride. Bicarbonate provides an indication of the buffering capacity (Bedient et al., 1997), and sulfate is a geochemical indicator of natural attenuation (Thorstenson et al., 1979; Chapelle and Lovley, 1990). Chloride is a non-reactive, stable anion providing insight into groundwater flow and mixing (Wiedemeier et al., 1995). The selected metals (iron and manganese) are both geochemical indicators of natural attenuation (Vroblesky and Chapelle, 1994; Azadpour-Keeley et al., 1999; Wiedemeier et al., 2006). The selected hydrocarbon constituents are benzene, ethylbenzene, total xylenes and CCME F1 fraction. The toluene values are not presented because the concentrations measured are all below the reliable detection limit at the sites studied.

2.4.2.2 Assessing Variability of Sample Results

When comparing field research data to assess the ability to collect representative samples, an amount of acceptable variability must be established. Houghton and Berger (1984) indicated the order of analytical bias ranged from +/-10 to 50%, however, improvements in analytical equipment and procedures has improved accuracy. Barcelona and Helfrich (1986) documented analytical errors for volatile organic compounds of up to 20%. The Quality Assurance Program of approved commercial laboratories often allows variability within the Quality Control Limits of up to +/-20% for many of the parameters analyzed. Where duplicate analyses are conducted on certain parameters as part of a laboratory's Quality Assurance program, the acceptable relative percent difference (RPD) variability allowed in the results is 20% for many constituents (Maxxam Analytics, 2003). This is based on the sensitivity of current laboratory equipment and techniques, which can measure very low concentrations for many parameters (especially for hydrocarbon constituents). As a result, remnants of previous analysis at the laboratory or any small variation in sample collection or preparation can cause substantial variability in sample results. This must be considered when comparing low hydrocarbon concentration sample results.

Variability is also common among parameters measured in the field (pH, EC, temp, etc.), even when samples are collected at the same time. Barcelona et al. (1984) indicated systematic errors related to sampling mechanisms can reduce accuracy by two to three times that of analytical procedures, and can result in sampling bias from +/-5 to 20%. Barcelona et al. (1985) suggested sampling mechanisms for collecting groundwater samples were among the most error-prone elements of monitoring programs. Parker (1994) stated that sampling methods and devices can greatly impact sample integrity.

This suggests that up to 40% of variability in sample results may be due to factors independent of the sampling method.

2.4.2.3 Field Data Comparison

A detailed comparison of the diffusion sampler and Waterra sampler results and the supporting figures are provided in Appendix D. Depth intervals varied between sampling events due to fluctuations in the water table. These discrete depth intervals are indicated on the y-axis of the sample result figures in Appendix D for the October and February sampling events. Notable results are summarized below for each site.

Site 1

Diffusion samplers were installed in well 03-MW1. Unfortunately no Waterra sample was obtained in October. While diffusion sampler results cannot be compared to Waterra sample for October, the two diffusion samplers can be compared to examine discrete interval sampling.

The results of the diffusion samplers are almost identical for all sampling events, with concentrations varying by less than 20% between the two sample depth intervals. The only notable variation is in the February iron concentrations (Figure

D3), which varies by 35%. However this is insignificant as the concentration difference is less than a 2 mg/L. The February Waterra results closely match those for the diffusion samplers for most parameters. The only parameters that vary notably for the Waterra sampler are (Figure D3 and D4):

- the iron concentration is over twice that for the diffusion samplers;
- the ethylbenzene and xylenes concentrations are three times larger than those for the diffusion samplers; and
- the F1-BTEX concentration is six times larger than that for the diffusion samplers.

Site 2

Sampling was conducted at two locations: near well 34 (closest to the source) and near well 35 (farthest from the source). Regarding the October sampling period, the diffusion samplers were installed after the Waterra sample was collected and were sampled 21 days later. The October diffusion samplers were fabricated in the field using deoxygenated water that was transported in airtight, zero headspace bottles to limit atmospheric interaction, and were only stored for several hours before installation. The February diffusion samplers were fabricated in the laboratory at the University of Alberta and stored in the transport containers two days prior to installation.

Well Cluster 34

Samples were collected from well 34-MW1. The diffusion samplers demonstrate increasing cation and anion concentrations with depth for both the October and February, however the largest variation is 39% for the February calcium concentrations. The Waterra cation and anion concentrations closely match those for the deep diffusion sampler in both October and February, however the Waterra sulfate concentrations (Figure D6) are four times those for the diffusion samplers for both sampling events.

The diffusion sampler metal results are similar for both depth intervals during both sampling events. The Waterra metal results are always higher than those for the diffusion samplers, the most notable being the October iron concentrations, which are twice as large (Figure D7). The diffusion samplers demonstrate an unexpected increasing concentration with depth for all hydrocarbon constituents in both October and February. The Waterra hydrocarbon results closely match those for the deeper diffusion sampler, however the October F1-BTEX concentration is over 2.5 times larger than the closest diffusion sampler result (Figure D8).

Well Cluster 35

Samples were collected from well 35-MW1. The diffusion samplers measure almost identical cation and anion concentrations for both October and February. The Waterra cation and anion results closely match those for the diffusion samplers, with the largest variation (40%) for the October calcium and bicarbonate results. The diffusion sampler metal results closely match for October and February. The Waterra sampler has the highest metal results for all sampling events. The October manganese and February iron concentrations for the Waterra sampler are over twice and over two and half orders of magnitude larger than those for the diffusion samplers respectively (Figure D11). These are the most notable differences.

For both sampling events, the diffusion samplers demonstrate expected decreasing concentrations with depth for all hydrocarbon constituents. The Waterra hydrocarbon results are similar to those for the diffusion samplers, with the October results being lower then both diffusion samplers and the February results matching closely with the deeper diffusion sampler. The exception is the Waterra F1-BTEX concentration in October, which is three times larger than that for the diffusion samplers (Figure D12).

2.5 DISCUSSION

2.5.1 Laboratory

2.5.1.1 Dissolved Hydrocarbon Equilibration Study

Previous research by Vroblesky et al. (2002) indicated that most contaminants should equilibrate in dialysis samplers within two weeks. In this laboratory study, equilibration occurs within the dialysis membranes after two to four weeks (Table 2.1). The 15 to 20% variation in the week four concentrations is within the generally accepted (+/-20%) analytical variance on duplicates. However, it must be noted that week four concentration values are higher for the dialysis sampler than for the vessel. This indicated that equilibrium likely occurred before the week four sample was collected.

Visual inspection of the membrane over the duration of the experiment showed no observable degradation over six weeks. The Vargo et al. (1975) study of microbial growth on regenerated dialysis membrane placed in surface waters demonstrated that the dialysis tubing collapses due to microbial degradation after nine days in 20°C water. An identical study in 1°C to 4°C surficial waters found significant microbial growth on the membrane after 17 days, equivalent to Day 5 or 7 of the 20°C study, However, the membranes had not collapsed by the end of the experiment.

The lack of membrane degradation or bacterial growth over the six week experiment in this study may be due to the colder groundwater (approximately 4°C) having limited nutrients compared to the surficial water used by Vargo et al. (1975). Also, sunlight may have caused increased microbial growth on the membrane in the surficial waters. The combination of colder groundwater temperature, decreased nutrient availability and no sunlight likely limits microbial activity in the groundwater system that is responsible for membrane degradation.

The interesting slight orange discoloration on the dialysis membrane is believed to be an iron precipitate, most likely a reaction of dissolved iron (Fe^{2+}) with oxygen. The deoxygenation process used in the experiment only decreased the dissolved oxygen (DO) to about 4 mg/L, or 2 mg/L higher than the formation water. The slight negative surface charge on the dialysis membrane (Ehlke et al., 2004) may develop a weak bond with the positive charge of the dissolved iron. The DO concentration gradient likely causes DO to pass outward through the membrane, and the DO reacts with the weakly bonded dissolved iron. This orange material easily sloughed off the outside of the membrane and collected at the bottom of the vessel, even when the vessel was carefully handled. The amount of precipitate was similar in most of the vessels.

The hydrocarbon equilibration observed over approximately three weeks led to the installation of diffusion samplers for three weeks at the field sites. The lack of membrane degradation over the six week laboratory study portends no adverse impacts for the field research program. The laboratory experiment provided confidence that the field dialysis samplers could collect representative groundwater samples.

2.5.1.2 Study on Effects of Monovalent and Divalent Salts

The small water loss from the dialysis membranes when installed in the various salt concentrations demonstrates that salt has a minor effect on mass loss. The 1000 mg/L sodium chloride solution had the largest mass loss (9.3%), which was minimal volume loss considering these samplers were installed for more than three times the duration of the field application (68 days vs 21 days). As the dialysis membrane can be fabricated to collect sufficient volume for the suite of sample analyses, the water loss due to salt does not impede representative sampling. The fact that the control's mass loss (4%) was only slightly lower than all membranes' mass loss (5 to 10%) likely indicates other causes of mass loss.

Water loss ranges from just 5 to 10% for the various salt concentrations and valence states. The amount of water initially in the dialysis membrane does not impact water loss. The largest sampler (67.7 g), in 1000 mg/L sodium chloride solution, has the highest mass loss (9.3%), whereas the smallest sampler (40.5 g), in the 10 mg/L calcium sulphate solution, has the second highest mass loss (7.9%). The two duplicate dialysis membranes in the 2000 mg/L calcium sulfate solution have similar mass losses, demonstrating consistency and reliability in the results. The experiment demonstrates that water loss is not dependent on the size of the dialysis membrane or the concentration or valence of the salt being sampled.

The results demonstrate that equilibration occurs quickly for simple salt ions, with most membranes equilibrating within 24 hours (Figures 2.6 and 2.7). Valence and salt concentration has no apparent effect on equilibration time. To more accurately determine equilibration times, more frequent measurements are required in the first 24 hours. It is concluded that simple ionic species in formation water do not dictate sampler installation time, as the water in the samplers equilibrates within 48 hours.

The small water loss in the high concentration salt solutions, even without internal rigidity in the dialysis membrane, is likely due to rapid equilibration. Small ions of dissolved inorganic salts easily pass through the membrane, rapidly equilibrating. This decreases or eliminates the concentration gradient, possibly causing membrane water loss.

2.5.1.3 Hydraulic Gradient and Evaporation Study

This laboratory study found that a half submerged diffusion sampler in ambient conditions lost all water within 23 days, and in two phases. First, the membrane water level dropped to the reservoir water surface. This is likely a combination of hydraulic gradient and evaporation effects. Then, water loss continued, possibly due to suction and evaporation effects. Both phases are described below.

Hydraulic gradient water loss occurs when the water in the sampler is above the surface of the water source being tested, forcing water out through the membrane pores due to head gradients. Evaporation water loss is caused by a moisture gradient across the portion of the membrane exposed to the atmosphere. Complete water loss from the portion of the membrane below the water surface is likely due to wicking water from inside the sampler via the membrane, causing the sampler to shrivel. An initial lack of membrane headspace may cause suction, drawing water from below the surface and keeping the membrane moist. This likely continues until the water inside the membrane runs out, drying out the membrane, at which point the membrane ends becomes brittle.

As per Figure 2.8, phase one (hydraulic gradient and evaporation) occurred in 10 days for the half submerged sampler under ambient conditions, resulting in 197 g of water loss (19.7 g/day). Phase two (evaporation) occurred from Day 10 to Day 23, resulting in 204.3 g of water loss (15.7 g/day). In comparison, the fully submerged sampler lost 19.2 g of water (0.7 g/day) over 28 days under ambient conditions.

To verify the postulated explanation for these findings and to quantify the water loss during the two phases, another sampler was half submerged in a 100% humidity moisture room at 4°C. With limited evaporation, the author hypothesizes that water loss occurs only though hydraulic head effects in phase one and does not occur in phase two.

The author hypothesizes that more hydraulic head water loss occurs when there is larger head acting downward in the porous membrane (i.e., increased initial water loss and less as the head decreases). The data supported this, with the highest loss (6 g/day) during the first seven days, decreasing to 1.2 g/day for Day 44 to Day 65, when the experiment was terminated due to limited water loss. As evaporation was limited, the hydraulic head effect on water loss was slow. In comparison, the half submerged sampler in ambient air conditions lost all water in 23 days.

For the first seven days, under ambient conditions water loss was 19.7 g/day and 6 g/day in the cool, 100% humidity atmosphere. This demonstrates that evaporation effects were responsible for two thirds of the mass loss in phase one and all mass loss in phase two under ambient conditions. These findings illuminate the amount of water loss that may occur if the water table drops below the top of the sampler, and demonstrate that evaporation is the dominant reason for water loss.

2.5.2 Field Performance

2.5.2.1 Considerations of Sampling Method Differences

Results from Waterra and diffusion samplers were compared from three wells for the October and February sampling events. Several sampling method differences must be addressed. Firstly, the Waterra sampler obtains a point in time sample, which is representative of groundwater for that particular date, while diffusion samplers collect a time averaged sample.

At the research study sites the groundwater flow velocities ranged from <1 to 5 m/yr. At these flow velocities, the groundwater would migrate <6 to 29 cm through the well screen over the 21 day installation. The variability of the groundwater constituent concentrations over this distance was expected to be small because diffusion was the dominant migration mechanism at these velocities. Therefore, concentration gradients are small and presumably would not cause variation in sample results.

Another difference is the sampler position in the well. For the diffusion samplers, effective end seals restricted vertical water movement in the well screen, allowing discrete interval sampling. However, for the slow groundwater velocities at the research sites, collection of discrete interval samples may be hampered by diffusion through the sand annulus around the well screen. A Waterra sample is typically representative of the most conductive layer(s) that the sand annulus intersects. However, if it is collected more quickly than the formation can produce the groundwater, then the sample is a mixture of formation water and water from the sand annulus and well casing (Puls and Paul, 1995), which may not be representative.

The Waterra sample was collected with as little drawdown as possible. Thus, it was likely representative of the most conductive layer(s) intersecting the well screen, since recharge was dominated by these intervals. As the discrete interval where the diffusion samplers were installed may not include the depth of the most conductive layer(s), diffusion sampler results and Waterra results may differ.

The last difference is the effect of well purging. Since the diffusion samplers equilibrate with formation water for 21 days as it passes through the well screen, no purging was required. Standard practice before collecting a Waterra sample is to purge three well volumes or purge the well dry. Improper purging in low flow formations like the sites may drop the water level in the well and induce flow from many hydraulically conductive geological formations that the 3 m screen intersected.

Drawdown caused by purging may expose the well screen to the atmosphere, causing oxidation and volatilization. Thus, concentrations of sulfides, metals, and VOCs could be lower in Waterra and bailers samples than in diffusion samples. As it was impractical to operate the Waterra sampler while a water level indicator was in the well, the water level was not monitored. Thus, drawdown impacts on Waterra results were uncertain.

2.5.2.2 Findings from Sample Results Comparison

Despite the rigid installation system with seals above and below the discrete intervals being sampled, concentrations of relevant parameters varied insignificantly, probably due to the similarly low hydraulic conductivities of the formations (At Site 1, the shallower sampler was in silty clay and the deeper sampler was in silt. At Site 2, both samplers were in silt). The results collected from the two diffusion sampler depth intervals closely match the Waterra cation and anion results during most sampling events.

This explanation appears incorrect for drive point wells installed within a metre of diffusion sampler wells. At both sites, concentrations varied with depth over similar discrete intervals. As the samplers were pushed to depth, the well water was likely mixed and homogenized by moving around the seals and through the sand pack throughout the sample intervals. Powell and Puls (1997) noted similar mixing throughout the well during pump insertion, resulting in unpredictable geochemical data. The 15.2 cm sand annulus and low groundwater flow rate at the sites (6 to 17 cm over the 21 day installation period) caused 1/3 to 1 well volume of displacement over the installation period. This limited displacement of homogenized well water by representative formation water, combined with the potential vertical diffusive flux discussed previously, may be responsible for the similar concentrations.

Concentrations of relevant MNA parameters were similar in both diffusion sample intervals, but differed from Waterra sample from the same well. During some of the sampling events differences were most notable in iron and F1-BTEX concentrations, and to a lesser extent sulfates. The differing results between the diffusion and Waterra samplers are developed below.

Iron

Iron concentrations measured by the diffusion samplers during all sampling events at both sites ranged from 35% (October, Well Cluster 35) to 2.5 orders of magnitude (February, Well Cluster 35) lower than the Waterra iron results from the same well (Figure D11, Appendix D). This may have been due to incomplete equilibration, iron oxidation due to higher DO concentrations in the diffusion samplers or a combination of these two factors.

To assess incomplete equilibration by the diffusion samplers, Fick's Law was used to develop a sampler equilibration time calculation for any dissolved constituent in formation water adjacent to the diffusion sampler (Sanford et al, 1996). Details and assumptions made in these calculations are listed in Appendix E. A range of diffusion coefficients for typical commercial passive diffusion samplers (Divine and McCray, 2004) were used because this information was not available for this study's dialysis membrane.

When the Waterra iron concentration is applied as the formation concentration variable (Cr), the calculation demonstrates that iron may not fully equilibrate in the samplers, depending on which effective diffusion coefficient is used. Only values from the higher end of the range for typical commercial passive diffusion samplers ($5\text{x}10^{-7}$ cm^2/s) yield calculations close the Waterra sampler concentrations.

If incomplete equilibration is fully responsible for the difference in iron concentrations measured by the diffusion sampler and the Waterra sampler, this indicates a diffusion coefficient for the dialysis membrane near the low end of the range ($0.5\text{x}10^{-7}$ cm^2/s). This is based on the iron concentrations calculated for this coefficient being closest to the concentrations measured by the diffusion samplers in the field. For example, for the diffusion coefficient $0.5\text{x}10^{-7}$ cm^2/s, the calculation yields 3.93 mg/L for February at Site 1, and the diffusion samplers measured 3.4 mg/L and 5.2 mg/L.

The effective diffusion coefficient for the membrane was not specified by the manufacturer, so the expected equilibration rate cannot be calculated with any certainty. The partial equilibration of iron indicated by this calculation is not observed for the other ions in this study. As the diffusion samplers measure cation and anion concentrations similar to the Waterra sampler, indicating complete equilibration, it appears that partial equilibration of iron through the membrane is not likely responsible for the lower iron concentrations.

The lower concentrations were likely due to iron oxidation by dissolved oxygen (DO). Although every effort was made to prevent DO from entering the diffusion samplers during preparation and storage, the transport containers were unable to seal out atmospheric gases completely. The transport container DO concentration was 1.5 to 3 mg/L prior to sampler installation in February at Site 1, which was elevated from <1 mg/L at the laboratory. Since DO concentration in the formation water was less than in the membrane, iron may have precipitated out as iron oxide.

The orange precipitate that formed on the dialysis membrane during the laboratory hydrocarbon equilibration study suggests oxidation of dissolved iron. Any orange on the field sampler membranes confirming iron oxidation was occurring may have sloughed off during sampler retrieval. Iron oxidation would continue until all excess DO in the membrane is consumed and then iron comes into equilibrium. Groundwater flow rates at the research sites (2 to 5 m/yr) only corresponded to 1/3 to 2 well volumes of formation water moving through the well screen during the 21-day installation. This may not provide sufficient dissolved iron to completely consume the DO in the membrane and cause equilibration. Because of oxidation, diffusion sampler iron concentrations may only partially equilibrate over the installation period, making them significantly lower than the Waterra sampler concentrations from the same well.

Waterra iron concentrations more than two orders of magnitude greater at Well Cluster 35 (Site 2) in February are likely due to higher initial DO concentrations in the samplers because of different sampler preparation. This is supported by the diffusion samplers measuring identically low iron concentrations for both depths, indicating similarly high initial DO concentrations in both samplers.

In October, diffusion samplers were fabricated in the field several hours prior to installation, whereas in February, they were fabricated in the laboratory two days prior to installation. Thus, it was expected that the October sampler DO remains at the concentrations similar to those in the laboratory (<1 mg/L). The deionized water used to fabricate the diffusion samplers in October was transported to the field in airtight, zero headspace bottles. DO concentrations were less than 1 mg/L in the airtight bottles during fabrication. The DO of the sampler storage container water could not be tested, as the water was inaccessible before installation and was lost during field installation.

As diffusion sampler DO concentrations should be similar to the formation concentrations in October, minimal iron was expected to oxidize, as it equilibrated within the membrane. Even if DO concentrations slightly increased during several hours of on-site storage, the higher iron concentrations at Well

Cluster 35 would consume the DO quickly and allow equilibration. This is supported by the diffusion samplers measuring the highest iron concentrations of any location in the research study, varying by less than 30% from the Waterra sample from the same well.

In contrast, the February diffusion samplers were in transport containers two days before installation. Their results were three orders of magnitude lower than the Waterra iron result. As the February Waterra sampler measured an iron concentration similar to October, the February iron concentration was likely representative and the diffusion iron results were likely impacted by elevated DO concentrations in the samplers.

The DO could not be measured for the February Site 2 installation event. However, at Site 1 the DO after one day of storage was between 1.5 and 3 mg/L, so the DO concentration in the February samplers may be up to twice this amount (3 to 6 mg/L). The groundwater flow at Site 2 moved insufficient volume to consume the elevated DO in the diffusion samplers over the 21-day installation.

As the diffusion samplers were installed over similar depth intervals for both the October and February sampling events, the higher initial DO concentrations likely explain the significantly lower iron concentrations compared to the February Waterra result. The iron results clearly demonstrate the need to completely deoxygenate the water in the diffusion samplers and maintain this DO concentration until installation, otherwise the diffusion samplers will not collect representative metals samples. This is imperative when sampling low flow formations with installation periods of three to four weeks, as is the case at these sites.

To prevent microbial degradation, the membrane was stored in ethylene diaminetetra acetic acid (EDTA), a complexing agent for a variety of metal compounds (van den Berg, 1995; Sillanpaa and Oikari, 1996; Inoue et al., 1999). The research membrane was designed for sensitive dialysis applications where low amounts of heavy metals may be encountered (Membrane Filtration Products Inc., 2003). Thus, it should have no adverse effect on constituent sampling.

Despite following the manufacturer's directions for rinsing the membranes, it was impossible to determine if all EDTA was removed from the membrane prior to fabricating the diffusion samplers. Thus, it was possible that some EDTA reacted with the dissolved iron and decreased the iron concentrations being sampled. At Well Cluster 35 in October, the sampler was fabricated in the field the day before, leaving minimal time for remnant EDTA to leach away. Despite that, this location shows the highest iron concentrations in the study, suggesting EDTA has insignificant impact on a diffusion sampler's ability to sample iron.

F1-BTEX

The diffusion samplers measured lower F1-BTEX concentrations than the Waterra sampler from the same well and had similar concentrations for both diffusion sample intervals. The difference was most notable for the February event at Site 1, where the diffusion F1-BTEX concentrations were almost an order of magnitude lower (Figure D4, Appendix D). It was also notable during the October event at both Well Cluster 34 and 35 (Site 2). As the Waterra F1-BTEX concentration for Site 1 in February seemed elevated, the other wells in the cluster were reviewed. The next highest concentration was the bailer sample (5.6 mg/L), typically between 1 to 2 mg/L. This suggested that the elevated F1-BTEX Waterra result may be anomalous.

Comparing the Waterra F1-BTEX results for August (23.8 mg/L) and February (13.9 mg/L), a decreasing concentration trend over time was established for all hydrocarbon constituents. This suggested that a source of free phase hydrocarbon was slowly being removed over time. The exact source responsible for the elevated hydrocarbon concentrations was not known, however the borehole log for this well (Figure B2, Appendix B) noted dark staining from 1.96 to 2.43 metres below ground surface. This indicates a LNAPL smear zone created by seasonal fluctuations in groundwater elevation. Groundwater in contact with free phase residuals from this interval may have provided the elevated F1-BTEX results.

As the LNAPL likely migrated through the most conductive layer, the Waterra sampler would likely draw groundwater from this conductive interval during purging and sampling that is in contact with the free phase residual. Powell and Puls (1997) indicated that long well screens intersecting variable stratigraphy draw water preferentially into the well during purging and sampling from the higher permeability flow zones. Preferential recharge of groundwater from the interval containing LNAPL could be responsible for the higher hydrocarbon concentrations detected by the Waterra than by the diffusion samplers.

As the Site 1 groundwater surface dropped from 1.2 m to 3.4 m below ground surface from August to February, the degree of contact between groundwater and the LNAPL smear zone was expected to decrease. The free phase residuals in the smear zone may be the source of the elevated hydrocarbon concentrations, and exposure to the smear zone due to groundwater level fluctuations may be the reason for the observed decrease in F1-BTEX concentrations from August to February. The February Waterra sample had a noteworthy hydrocarbon odour and a slight sheen, indications of contact with free phase contaminant.

Similar decreasing trends from October to February were observed for F1-BTEX Waterra results at both Site 2 well clusters. The borehole logs indicated black staining and hydrocarbon odour from 1.5 to 3.8 metres at Well Cluster 34 and from 2.1 to 3.7 metres at Well Cluster 35 (Figure B4 and B5, Appendix B). As the groundwater surface at Site 2 dropped to near three metres below ground surface in February, the most conductive layer that provides the Waterra sample may come from a smaller portion of the smear zone compared to October, resulting in the lower F1-BTEX concentration.

The diffusion samplers were installed for both sampling events at discrete sample intervals below (Site 1) or near the bottom (Site 2) of the darkly stained interval noted in the borehole logs. This may be partly responsible for the lower F1-BTEX concentrations compared to the Waterra sampler. Because the diffusion sampler discrete intervals do not intersect groundwater from this stained interval, or only do so at the bottom portion (which may be in direct contact with the residual free phase hydrocarbon in the smear zone), the diffusion samplers may show lower hydrocarbon concentrations.

No diffusion samplers at any studied location measured a F1-BTEX concentration higher than 2 mg/L (Site 1, February), even though bailer and Waterra samples from similar three metre screened wells typically showed concentrations ranging from 5 to 10 mg/L. This may be attributed to partial equilibration due to the longer, complex chains of the F1 hydrocarbon fraction. Product information provided by Membrane Filtration Products Inc. (2003) indicated that the size and three-dimensional shape of a molecule (molecular weight cutoff) determine if it will pass through a membrane.

As some of the larger F1 hydrocarbon chains may not easily enter the small pores of the dialysis membrane, only a portion of the dissolved F1 fraction may pass through the membrane over the duration of installation. This would lead to partial equilibration of these hydrocarbon constituents, resulting in lower F1-BTEX concentrations for the diffusion samplers. This may explain why the diffusion samplers can collect representative concentrations for benzene, ethylbenzene and xylenes, as these are smaller compounds, but only partially equilibrate with the F1 hydrocarbon fraction, leading to lower concentrations. Unfortunately, the formation water used in the dissolved hydrocarbon equilibration study had low F1 fraction concentrations (<1 mg/L), so the results could not address this hypothesis.

When the diffusion samplers' F1-BTEX results are compared with the results from the discrete interval wells installed over similar intervals at both sites, the F1-BTEX concentrations are similar for all three well cluster locations. This tends to indicate that the diffusion samplers may be collecting representative discrete interval hydrocarbon results, and that the Waterra F1-BTEX results are dictated by an interval not intersected by the discrete interval samplers.

Sulfate

The sulfate concentrations measured by the diffusion samplers for both sampling events at both research sites were similar for both depth intervals. Well Cluster 34 (Site 2) was the only sample location with significant observed differences in results, with Waterra sulfate results over three times larger than the diffusion results (Figure D6, Appendix D). Differences in the sulfate results are likely caused by differences between the two sampling methods.

Gypsum dissolution (calcium sulfate) from surficial minerals (Van Stempvoort, 1994) resulting from snowmelt infiltration is likely largely responsible for calcium and sulfate concentrations in the groundwater. The gypsum dissolution is expected to move downward through the soil as a slug input since snowmelt infiltration is rapid. As Site 2 sees limited precipitation, there is not continual gypsum dissolution by infiltration, and the dissolved calcium and sulfate concentrations may vary significantly over time. This trend was measured in the adjacent discrete interval well types installed in the study of alternative sampling technologies (Chapter 3).

Slug input is expected to have higher concentrations at the leading edge of the migration and decreasing concentrations at the tail end due to dispersion and dilution. The sulfate data from Well Cluster 34 supported this because the Waterra and diffusion concentrations in February were both 3.5 times lower than in October; this indicated that October was sampling from somewhere in the centre of the slug input and February from the tail end.

The diffusion samplers most likely measured lower sulfate concentrations due to sulfate reducing bacteria activity in the subsurface. The MW1 borehole log (Figure B4, Appendix B) noted a hydrocarbon sheen, odour and dark grey staining from 1.5 to 3.8 metres. The staining likely indicated a reductive state. It may be sulfides produced from sulfate reduction, formed by bacteria degrading the hydrocarbon contamination over this depth interval. The installation of both diffusion samplers in this highly reduced interval may explain the lower sulfate concentrations in the diffusion results.

The discrete interval wells measuring very low sulfate concentrations over similar depth intervals supports the hypothesis of sulfate reduction at the shallower depth interval. The remaining well type intervals demonstrated increasing sulfate concentration with depth. As the Waterra sample was collected from a three metre screen installed to 4.6 metres below ground surface, it may have been collected from (a) hydraulically conductive layer(s) deeper than the reductive layer. This may explain the higher concentrations measured by the Waterra, as purging and sampling may draw in groundwater from conductive layer(s) intersecting the bottom portion of the well screen where sulfate reduction was minimal.

The diffusion samplers' sulfate concentrations were elevated compared to those from the discrete interval wells at similar depths. This was likely due to well volume homogenization during diffusion sampler installation, developed in detail for the iron results. As groundwater flow was likely insufficient to completely displace the higher sulfate inputs (resulting from well homogenization) with the lower concentrations expected for the discrete interval, the diffusion samplers likely only partially equilibrated. This is supported by similar sulfate concentration measurements from the diffusion samplers for both depth intervals in October and February, when the discrete interval wells demonstrated a clear increase in concentration over similar depth intervals.

Based on the available data, it appears that variability between Waterra and diffusion sampler sulfate concentrations may be due to a combination of infiltration effects, sulfate reduction and the inability to completely overcome well homogenization impacts.

<u>General Trends</u>

Diffusion sampler concentrations at Well Cluster 34 (Site 2) all increase by 20 to 275% over the two depth intervals for both sampling events. The exceptions are sulfate and metal concentrations. The Waterra and deeper diffusion sampler results are similar in both October and February (less than 20% variation), except for the sulfate (75%) and iron (40%) concentrations for both events and the calcium (35%), manganese (30%) and F1-BTEX (65%) in October. Result variance between sampling methods for these parameters is greater in October than in February. This could be due to the length of time between Waterra and diffusion sampling in October (21 days). In contrast, February samples were collected on the same day. This hypothesized time effect more likely explains the calcium and manganese differences.

The more significant differences for sulfate, iron and F1-BTEX appear dependent on depth. In this study, the 15 to 18% concentration increases in chloride support this, as this stable ion does not usually vary in concentration over different depths in uniform formations. The concentration increases are also evidence of diffusion samplers' ability to collect discrete interval samples.

However, this is brought into question by hydrocarbon constituent concentrations that increase with depth at this site (Figure D8, Appendix D). Concentrations of LNAPL contaminants like this are expected to decrease with depth.

The Waterra sample more closely matches the deeper diffusion sample for both events (except regarding sulfate and metals). This indicates that the most conductive Waterra-sampled layer(s) likely exist(s) within the depth interval at which the deeper diffusion sampler was installed (2.7 to 3.4 metres below ground surface). This also demonstrates the seal's ability to create discrete sample intervals, as the shallow diffusion sampler has a lower concentration, leading to the unexpected trend of increasing hydrocarbon concentration with depth.

All hydrocarbon constituent concentrations in diffusion samples at Well Cluster 35 (Site 2) decrease with depth. This is true in both sampling periods, but more apparent in February. As the contaminant plume is a LNAPL that floats atop the groundwater surface, this decreasing trend is also expected.

2.6 CONCLUSIONS

2.6.1 Laboratory Research

The results from the laboratory experiments demonstrate:

- Salt equilibrates within the first 24 to 48 hours.
- Water loss due to various salt concentration gradients ranging from 5 to 10 percent after 70 days. However, this has no effect on collecting a representative sample.
- Ionic charge, salt concentration and sampler size have no apparent impact on the equilibration time or water loss from the diffusion sampler.
- Equilibration for BTEX and F1-BTEX occurs between two and four weeks; approximately three weeks.
- Visual inspection of membrane indicates no degradation over the six week study.
- Partial membrane exposure above the groundwater surface during sampling causes significant water loss in samplers, with evaporation having the greatest impact.
- Wicking action in a partially exposed membrane draws water above the water surface to evaporate and can result in limited or no sample volume after a 21 day installation. This illustrates the importance of diffusion samplers remaining below the water surface for the duration of sampling.

2.6.2 Field Research

The field research at two upstream oil and gas sites investigated the diffusion sampler's ability to collect representative samples for parameters of interest in a MNA program. It also examined the diffusion sampler's ability to measure how vertical concentrations change with depth in a three metre well screen. Waterra and diffusion sampler results from the same well at three locations (two sites) and over two periods demonstrated similar concentrations for most parameters analyzed. Significant differences were observed between the metals and F1 – BTEX concentrations in certain instances at both sites.

The variability in the metals' concentrations, most notable for iron, demonstrate the importance of deoxygenating the diffusion sampler water to concentrations similar to the well. Elevated diffusion sampler DO concentrations show low metal concentrations. This is likely the result of incomplete equilibration due to oxidation, causing precipitation of dissolved metals from solution.

F1 – BTEX concentration variability may be due to partial equilibration, as some of the longer F1 hydrocarbon structures are too large to enter the pores of the dialysis membrane. However, discrete interval well hydrocarbon results closely match those from the diffusion samplers over similar depth intervals, suggesting that the latter collected representative discrete interval samples. Results indicate that these discrete intervals may not have incorporated the conductive layers that provide the higher F1-BTEX concentrations measured by the Waterra sampler.

The ability to measure and demonstrate discrete vertical variations in groundwater concentrations at the research sites is controlled by two factors:

1. Nature of Stratigraphy:

   The screen intervals of the wells were installed into uniform stratigraphy, Site 1 being silt and silty clay and Site 2 being silt. Uniform stratigraphy should have similar geochemistry throughout that interval, making vertical concentration differences difficult to demonstrate for many parameters. However, vertical differences for dissolved hydrocarbon concentrations are not dictated by stratigraphy, but are controlled by the physical characteristics of the contaminant (i.e., LNAPL contamination is expected to have higher dissolved hydrocarbon concentrations near the groundwater surface and decrease with depth).

   As a result, dissolved hydrocarbon is an effective measure of a diffusion sampler's ability to detect vertical concentration differences. The concentrations are found to vary with depth at two of the three well locations for both sampling events, most notably at Well Cluster 35. This suggests that the diffusion sampler is capable of measuring vertical concentration differences in the groundwater.

2. Groundwater Flow Rates:

   Low flow formations do not displace well contents homogenized during sampler installation, thus impeding characterization of discrete intervals samples. This demonstrates the importance of groundwater movement sufficient to displace at least one well volume with groundwater from the formation. Faster groundwater flow rates (and replacement of mixed well water with representative groundwater) were likely responsible for concentration differences between the diffusion sampler intervals for most parameters at Site 2, especially at monitoring well 34-MW1.

   Chloride concentrations (a non-reactive, stable ion) differ by 9 to 18% between diffusion sampler depth intervals at Site 2 (except for October at 35-MW1) compared to a 2.5% difference at Site 1 where groundwater movement was slower. This demonstrates the diffusion sampler's ability to collect discrete interval samples and to measure vertical concentration differences for most cation and anion parameters (where variations in groundwater conditions exist and groundwater flow rates can overcome well volume homogenization).

The research demonstrates that diffusion samplers effectively collect representative groundwater samples to assess MNA feasibility at upstream oil and gas sites. They can be fabricated for installation in existing monitoring wells and can measure vertical concentration profiles if properly installed under favourable site conditions. No obvious membrane degradation was observed after 21 days in the field, indicating that diffusion samplers made from regenerated cellulose dialysis membrane are sufficiently robust to collect groundwater samples within a hydrocarbon plume. A significant potential application for diffusion samplers is in low flow environments, where conventional sampling methods involving purging may compromise sample integrity due to mixing with atmospheric gas during recharge. The diffusion sampler's quick installation, quick retrieval and ease of sampling make it cost effective for collecting representative groundwater samples.

2.7 REFERENCES

Azadpour-Keeley, A., Russell, H. and Sewell, G.W. 1999. Microbial processes affecting monitored natural attenuation of contaminants in the subsurface. USEPA Ground Water Issue. EPA/540/S-99/001. 18 pages.

Barcelona, M.J., Helfrich, J.A., Garske, E.E. and Gibb, J.P. 1984. A laboratory evaluation of ground water sampling mechanisms. Ground Water Monitoring Review 4(2):32-41.

Barcelona, M.J., Helfrich, J.A. and Garske, E.E. 1985. Sampling tubing effects on ground water samples. Analytical Chemistry 57: 460-464.

Barcelona, M.J. and Helfrich, J.A. 1986. Well construction and purging effects on ground-water samples. Environmental Science and Technology 20(11):1179-1184.

Bedient, P.B., Rifai, H.S. and Newell, C.J. 1997. Ground water contamination transport and remediation. Prentice Hall, Inc. 604 pages.

Bottomly, E.Z. and Bayley, I.L. 1984. A sediment porewater sampler used in root zones studies of the submerged macrophyte. Limnology and Oceanography. 29: 671-673.

Canadian Council of Ministers of the Environment (CCME). 1996. A Protocol for the Derivation of Environmental and Human Health Quality Guidelines. CCME-EPC-101E.

Chapelle, F.H. and Lovley, D.R. 1990. Hydrogen concentrations in ground water as an indicator of bacterial processes in deep aquifer systems. First International Symposium on the Microbiology of the Deep Subsurface. USEPA: Orlando, Florida.

Dasika, R. and Atwater, J. 1995. Groundwater nitrate profiling by passive sampling over extended depth beneath the water table: A demonstration. Water Resources 29(11): 2609-2612.

Divine, C.E. and McCray, J.E. 2004. Estimation of membrane diffusion coefficients and equilibration times for low-density polyethylene passive diffusion samplers. Environmental Science and Technology 38(6): 1849-1857.

Ehlke, T.A., Imbrigiotta, T.E. and Dale, J.M. 2004. Laboratory comparison of polyethylene and dialysis membrane diffusion samplers. Ground Water Monitoring & Remediation. 24(1): 53-59.

Hesslein, R.H. 1976. An in situ sampler for close interval pore water studies. Limnology and Oceanography 21: 912-914.

Houghton, R.L. and Berger, M.E. 1984. Effects of well casing composition and sampling method on apparent quality of ground water. Proceedings of Fourth National Symposium on Aquifer Restoration and Ground Water Monitoring, Columbus, Ohio. May 23-25, 1984. pp 487-490.

Inoue, K., Yoshizuka, K. and Ohto, K. 1999. Adsorptive separation of some metal ions by complexing agent types of chemically modified chitosan. Analytica Chimica Acta 388(1-2): 209-218.

Imbrigiotta, T.E., Ehlke, T.A., Lacombe, P.J. and Dale, J.M. 2002. Comparison of dialysis membrane diffusion samplers and two purging methods in bedrock wells. Remediation of chlorinated and recalcitrant compounds, Third International Battelle Conference, Monterey, California. May 20-23, 2002. 11 pages.

Kaplan, E., Banerjee, S., Ronen, D., Magaritz, M., Machlin, A., Sosnow, M. and Koglin, E. 1991. Multilayer sampling in the water table region of a sandy aquifer. Ground Water 29(2): 191-198.

Langmuir, D. 1997. Aqueous environmental geochemistry. Prentice-Hall. 600 pages.

Maxxam Analytics. 2003. Quality assurance report. Attachment to analytical data report. 2 pages.

Mayer, L.M. 1976. Chemical water sampling in lakes and sediments with dialysis bags. Limnology and Oceanography 21: 909-912.

Membrane Filtration Products Inc. 2003. CelluSep T-Serires Instructions. www.membrane-mfpi.com.com. Accessed June 3, 2003.

Parker, L.V. 1994. The effects of ground water sampling devices on water quality: a literature review. Ground Water Monitoring Review, Spring: 130-141.

Powell, R.M. and Puls, R.W. 1997. Hitting the bull's-eye in groundwater sampling. Pollution Engineering, Winter International. December, 1997. 7 pages.

Puls, R.W. and Paul, C.J. 1995. Low-flow purging and sampling of ground water monitoring wells with dedicated systems. Ground Water Monitoring Review, Winter: 116-123.

Ronen, D., Magaritz, M. and Levy, I. 1986. A multi-layer sampler for the study of detailed hydrochemical profiles in ground water. Water Resources Research 20(3): 311-315.

Sanford, W.E., Shropshire, R.G. and Solomon, D.K. 1996. Dissolved gas tracers in groundwater: Simplified injection, sampling, and analysis. Water Resources Research 32(6): 1635-1642.

Sillanpaa, M. and Oikari, A. 1996. Assessing the impact of complexation by EDTA and DTPA on heavy metal toxicity using microtox bioassay. Chemosphere 32(8): 1485-1497.

Thorstenson, D.C., Fisher, D.W. and Croft, M.G. 1979. The geochemistry of the Foxs Hills-Basal Hell Creek aquifer in southwestern North Dakota. Water Resources Research 15: 1479-1498.

Van den Berg, C.M.G. 1995. Evidence for organic complexation of iron in seawater. Marine Chemistry 50(1-4): 139-157.

Van Stempvoort, D.R., Hendry, M.J., Schoenau, J.J. and Krouse, H.R. 1994. Sources and dynamics of sulfur in weathered till, Western Glaciated Plains of North America. Chemical Geology 111: 35-56.

Vargo, G.A., Hargreves, P.E. and Johnson, P. 1975. Scanning electron microscopy of dialysis tubes incubated in sea water. Marine Biology 31: 113-120.

Vroblesky, D.A. and Chapelle, F.H. 1994. Temporal and spatial changes of terminal electron-accepting processes in petroleum hydrocarbon-contaminated aquifer and the significance for contaminant biodegradation. Water Resources Research 30(5): 1561-1570.

Vroblesky, D.A. 2001. User's Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells: Part 2. Field Tests. U.S. Geological Survey, Water Resources Investigations Report 01-4061. 39 pages.

Vroblesky, D.A., Petkewich, M.D. and Campbell, T.R. 2002. Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water Discharge Zone. U.S. Geological Survey, Water Resources Investigations Report 02-4031. 24 pages.

Wiedemeier, T.H., Wilson, J.T., Kampbell, D.H., Miller, R.N. and Hansen J.E. 1995. Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. U.S. Air Force Center for Environmental Excellence: San Antonio, Texas. 617 pages.

Wiedemeier, T.H., Barden, M.J., Haas, P.E. and Dickson, W.Z. 2006. Chapter 9: Designing monitoring programs to effectively evaluate the performance of natural attenuation. Practical handbook of environmental site characterization and ground-water monitoring (Second edition). CRC Press, Taylor Francis Group: New York. Pages 573-637.

Table 2.1. Purgeable concentrations inside the dialysis membrane and mesocosm over time.

Parameter	**Sample Type**	**Concentration (mg/L)**		
		Week 2	**Week 4**	**Week 6**
Benzene	Sampler	0.034	0.096	0.0506
	Vessel	0.057	0.08	0.056
Toluene	Sampler	<0.003	<0.002	<0.0009
	Vessel	<0.004	<0.002	<0.0007
Ethylbenzene	Sampler	0.096	0.287	0.0481
	Vessel	0.173	0.23	0.0584
Xylene - Total	Sampler	0.47	1.35	0.21
	Vessel	0.85	1.10	0.25
PHC F1 - BTEX (C_6-C_{10})	Sampler	0.6	5.9*	<0.1
	Vessel	0.9	4.9*	<0.1

* Analyzed for total purgeable hydrocarbons, but not PHC F1 - BTEX, so Week 2 and 6 results cannot be compared directly to these values.

Table 2.2. Mass water loss from initial membrane mass (%) with time due to salt gradient. [Eq 1]

Salt Type	Conc. (mg/L)	Day 1 (%)	Day 2 (%)	Day 5 (%)	Day 7 (%)	Day 15 (%)	Day 42 (%)	Day 68 (%)
NaCl	50	-3.2	-4.4	-5.2	-5.4	-6.0	-7.9	-7.9
NaCl	500	-1.7	-1.8	-2.0	-2.2	-3.1	-3.8	-5.1
NaCl	1000	-4.3	-4.9	-6.4	-6.7	-7.5	-8.7	-9.3
NaCl	5000	-1.6	-1.6	-2.4	-2.7	-3.3	-4.6	-5.4
$CaSO_4$	100	-3.0	-3.3	-4.1	-4.6	-5.4	-6.7	-7.3
$CaSO_4$	500	-2.9	-2.9	-4.0	-4.5	-5.3	-6.0	-7.4
$CaSO_4$	1000	-2.6	-2.9	-3.8	-4.3	-5.2	-6.7	-7.6
$CaSO_4$	2000	-2.3	-2.5	-3.0	-3.8	-4.3	-5.4	-5.5
		-2.8	-3.4	-3.9	-4.7	-5.4	-6.6	-6.9
Control	-	-0.9	-1.3	-1.4	-1.9	-2.4	-3.6	-4.0

Table 2.3. Electrical conductivity difference (%) between dialysis membrane and vessel with time. [Eq 2]

Salt Type	Concentration (mg/L)	Day 1 (%)	Day 2 (%)	Day 5 (%)	Day 7 (%)
NaCl	50	1.2	2.3	0.2	3.9
NaCl	500	-5.6	-1.5	-3.0	-0.2
NaCl	1000	-3.3	-2.3	-1.1	-1.7
NaCl	5000	-9.3	-3.4	-4.7	-1.6
$CaSO_4$	100	-5.5	-2.5	0.0	-0.6
$CaSO_4$	500	-8.2	-2.1	-2.5	-0.4
$CaSO_4$	1000	-8.4	-3.4	-3.9	-0.7
$CaSO_4$	2000	-5.6	-2.0	-2.5	-1.3

Figure 2.1. Diffusion Sampling Nozzle

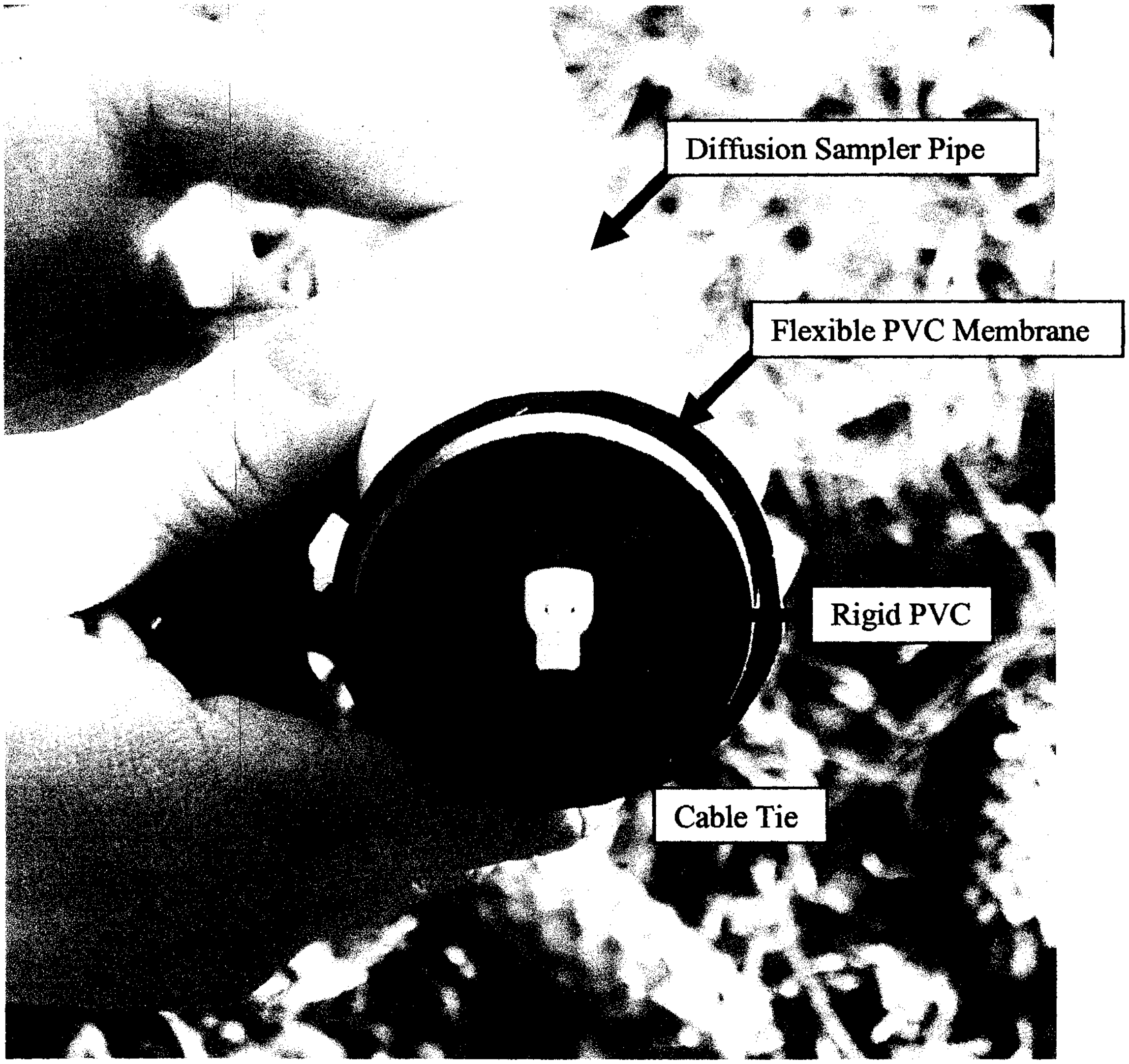


Figure 2.2. Diffusion Sampler End Seal

How End Seal Creates Discrete Intervals Within Monitoring Wells:
Flexible PVC membrane is cut slightly larger than the inner diameter of the monitoring well. The PVC membrane is placed between the diffusion sampler pipe and a rigid PVC disk and is held tightly on the end of the diffusion sampler pipe using the cable tie. As the end seal is pushed to depth, the flexible membrane flexes slightly to allow it to enter the well, however if the sampler is lifted slightly when at the desired depth the flexible PVC membrane seals against the walls of the monitoring well casing. This creates a seal that prevents water from moving vertically within the well and allows a discrete interval sample to be collected from within the well screen.

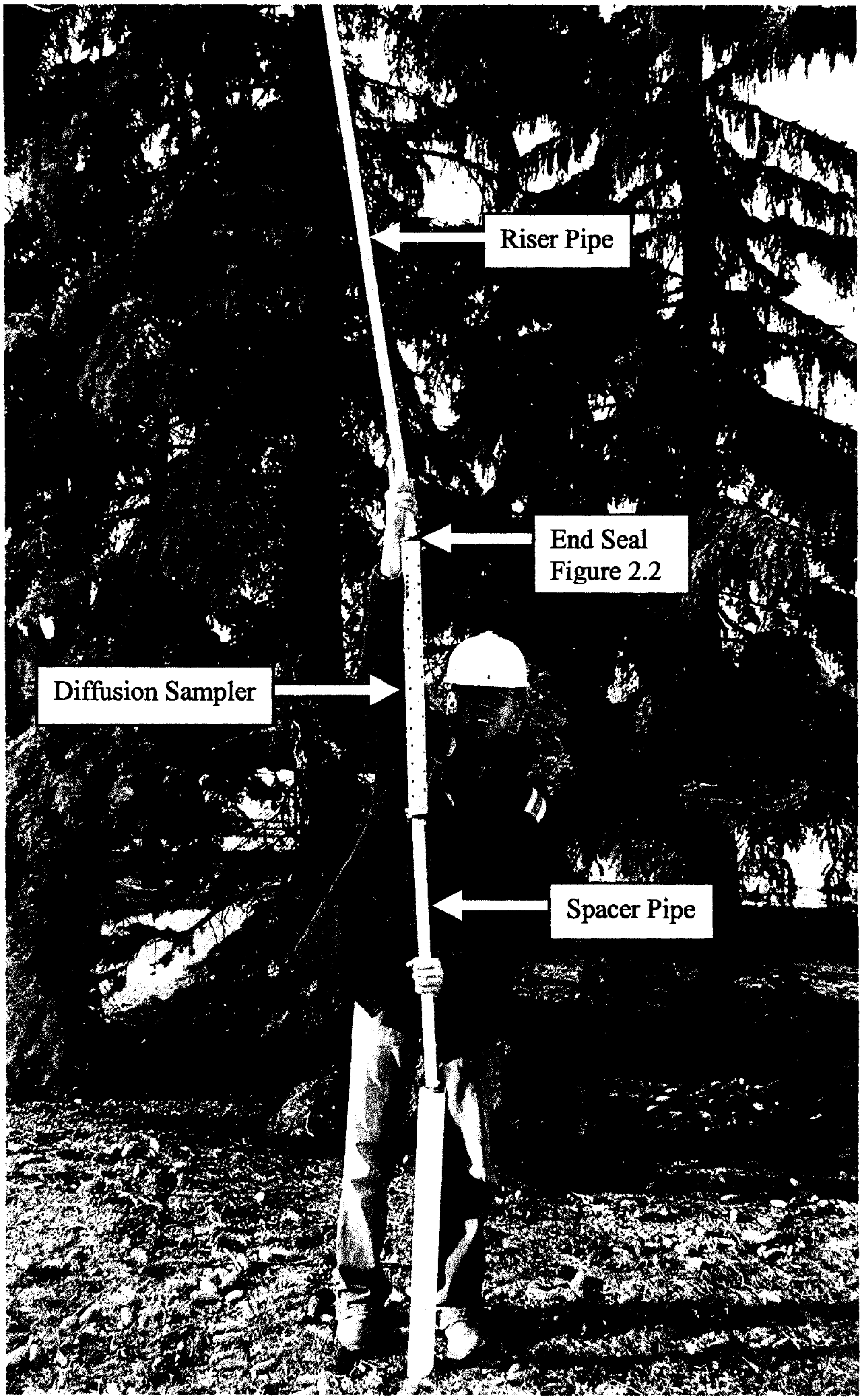


Figure 2.3. Rigid Diffusion Sampler System.

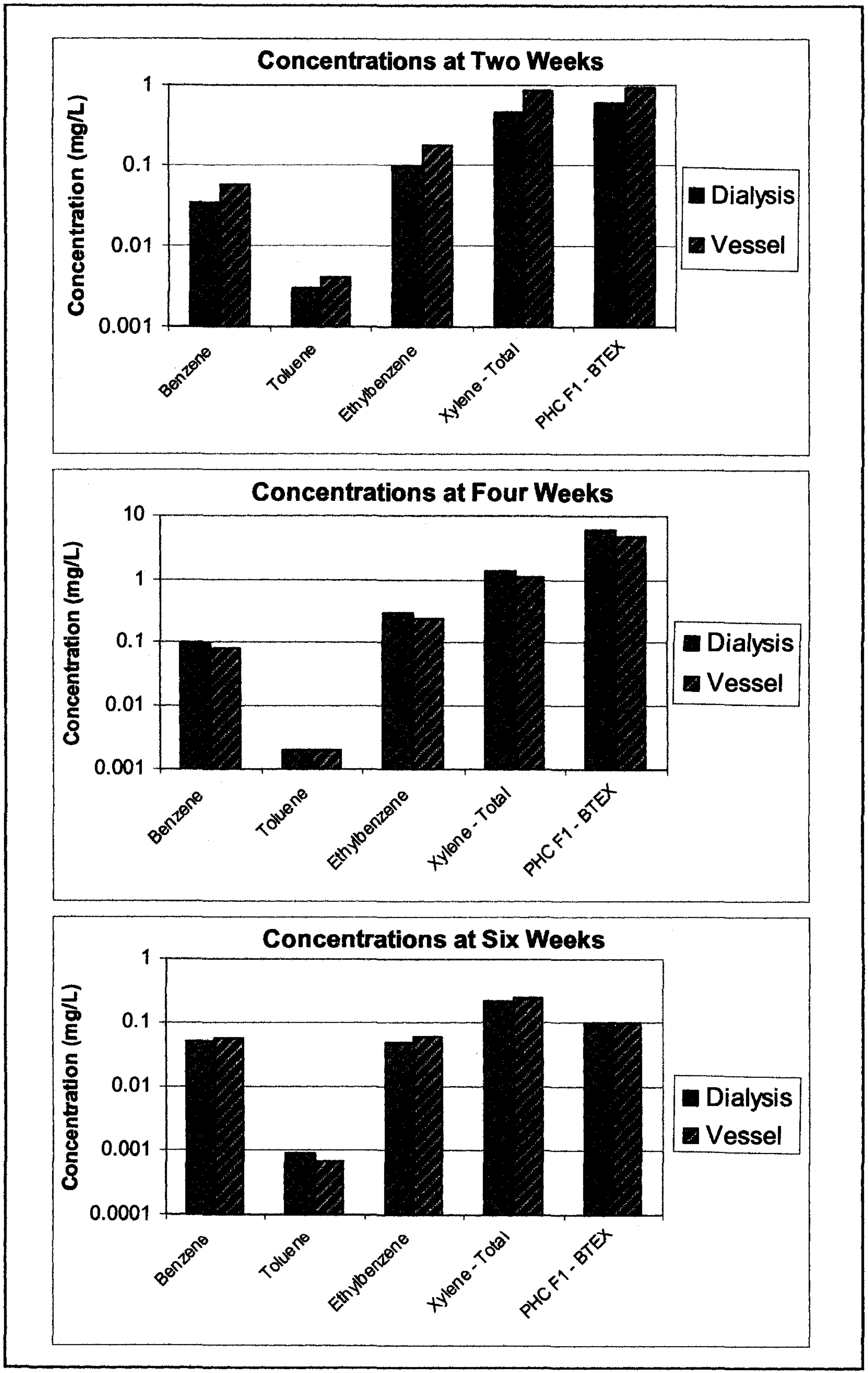


Figure 2.4. Dissolved Hydrocarbon Equilibration with Time.

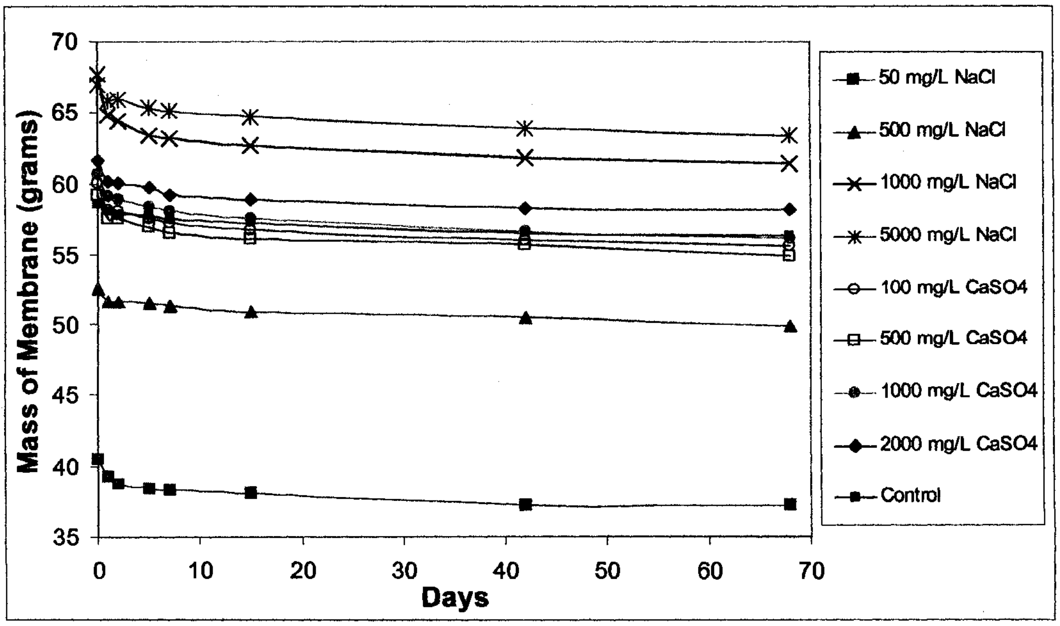


Figure 2.5. Salt Concentration Effects on Dialysis Membrane Sampler Water Loss.

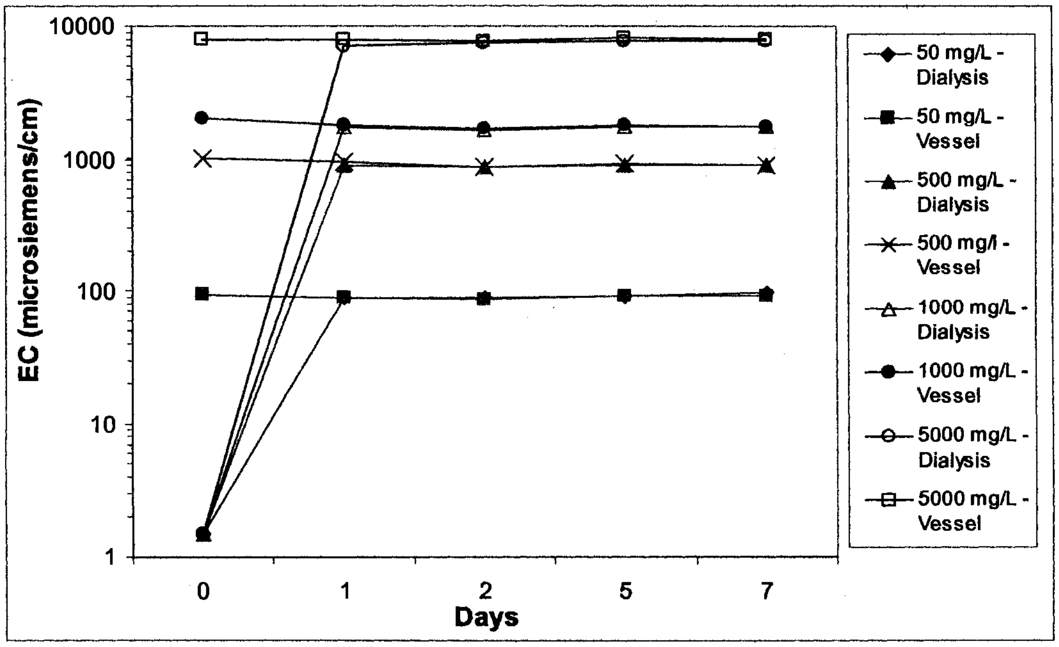


Figure 2.6. Electrical Conductivity Equilibration for Various Sodium Chloride (NaCl) Concentrations.

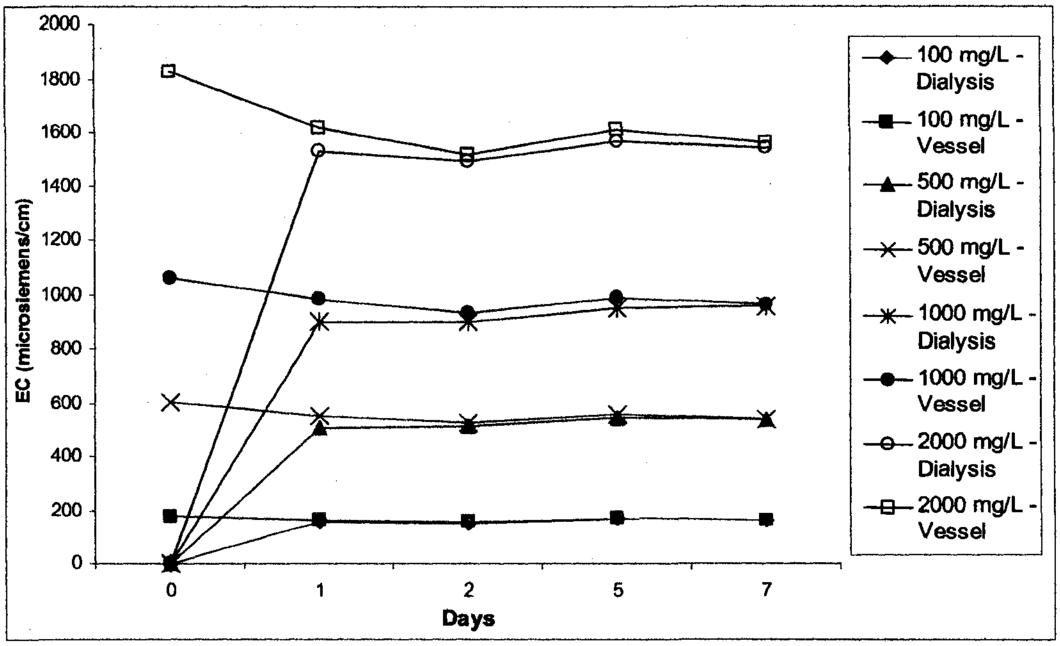


Figure 2.7. Electrical Conductivity Equilibration for Various Calcium Sulfate ($CaSO_4$) Concentrations.

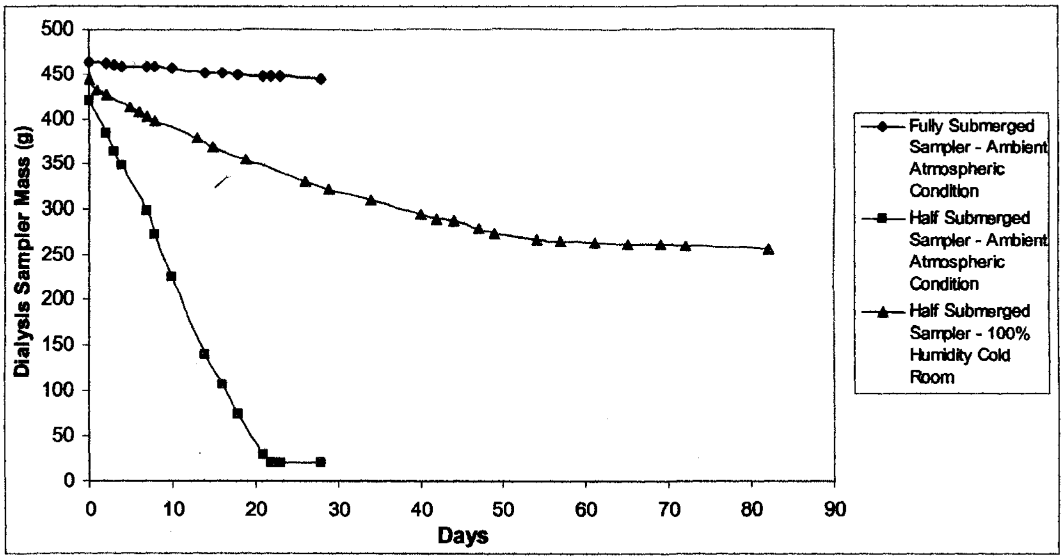


Figure 2.8. Dialysis Membrane Sampler Water Mass Loss Over Time.

Chapter 3

Comparison of Sampling Well Types and Sampling Methodologies for Application of Monitored Natural Attenuation at Upstream Oil and Gas Sites

3.1 INTRODUCTION

Polyvinyl chloride (PVC) monitoring wells are commonly used to assess groundwater contamination from various activities in the upstream oil and gas industry. These wells are cost effective, easy to install, and the equipment required for installation is readily available. However, this well type has known limitations. Slotted well screens are typically installed in three metre lengths, thus possibly intersecting several groundwater formations with varying geochemical characteristics and degrees of contaminant impact. This can lead to cross connection of aquifers by the well screen and contamination dilution within the well screen.

In cross connection, harmful contaminants can impact a clean groundwater aquifer, leading to a larger problem. Contamination dilution can occur when a highly contaminated formation and a clean formation are both intersected by the well screen. In some instances, a clean formation can input much more water into the well screen than a highly contaminated one, diluting concentrations of harmful constituents to below regulatory limits. This may obscure the risk of contaminant exposure, which may still be present if one is exposed to only the highly contaminated formation.

Many recent innovations overcome the limitations of traditional three metre screen monitoring wells. Such technologies include wells with discrete sampling intervals and sampling systems that can collect discrete interval samples from traditional three-metre well screens. Accurate vertical characterization is necessary to understand and better predict the movement and potential impact of contamination in the subsurface.

After investigating available options, several promising discrete interval sampling technologies were selected for this study. From the discrete interval sampling wells commercially available, the Continuous Multichannel Tubing (CMT) Multilevel Well (Solinst) and Drive Point Well (GeoInsight) were selected. From the sampling systems capable of discrete interval sampling in a three-metre well screen, the BarCad System (BESST, Inc.) and diffusion sampling using dialysis membranes were selected. This research compares these alternative sampling technologies to the bailer and Waterra sampling methods used on conventional three-metre screen monitoring wells.

Monitoring is the essential component of monitored natural attenuation (MNA), since the field data has to be able to accurately establish MNA as effective. The ability to detect and characterize discrete zones of oxidative and reductive natural attenuation indicators is important, as is the ability to effectively demonstrate contaminant reduction over time. The alternative discrete interval sampling technologies studied were selected because they were most likely to accurately characterize natural attenuation indicators vertically and better demonstrate contaminant reduction in the groundwater system. The focus of this research was to assess the alternative technologies' accuracy in measuring relevant MNA parameters, by comparing them to common sample collection methods at two field research sites.

3.2 BACKGROUND

3.2.1 Sampling Technologies

At each well nest location, two types of discrete interval monitoring wells and two conventional monitoring wells were installed around an existing conventional monitoring well. This enabled comparisons of different sampling methods and well types.

3.2.1.1 Well Types Investigated

Both the Solinst Continuous Multichannel Tubing (CMT) Multilevel Well system and the GeoInsight Drive Point Well system provided discrete interval sampling and flexible installation depths. Both were installed at depths similar to the nearby conventional three metre screen wells.

Detailed descriptions of all investigated well types, including advantages and disadvantages are included in Appendix A.

3.2.1.2 Sampling Methods Investigated

Peristaltic pump sampling was applied to discrete interval wells. The BarCad System and dialysis membrane diffusion samplers were applied to three-metre screen wells. Results of these alternative methods were compared to those for the conventional bailer and the Waterra inertial pump on three-metre screened wells. This was done to assess the feasibility of discrete interval sampling, a necessary tool of MNA.

Bailer, Waterra and peristaltic pump sampling will be described briefly, as their use is common and well researched (Parker, 1994; Puls and Barcelona, 1995; Puls and Paul, 1997). Detailed descriptions, including advantages and disadvantages, of all sampling methods investigated in this field research program are in Appendix A.

3.2.2 Site Descriptions

The research was conducted at two upstream oil and gas sites in Alberta. Site 1 was a decommissioned well site and flare pit located in northwestern Alberta. Site 2 was a natural gas processing facility located in southeastern Alberta. Detailed site descriptions including site plans and borehole logs are in Appendix B.

3.2.3 Previous Research on Alternative Sampling Technologies

As many of the investigated sampling technologies were new, there was limited published research or background information on them. Since this research focused on the abilities of the selected alternative sampling technologies, the more plentiful background on the common sampling methods and three-metre screen well will not be presented.

The background for diffusion sampling is thoroughly developed in Section 2.2. A case study involving the CMT Multilevel Well demonstrated its ability to characterize a MTBE plume in young alluvial sediments containing clayey sand and gravel intervals (Solinst, 2003). A leak from an underground storage tank was detected by measuring low concentrations in a private industrial well located down gradient from the tank. Thirteen CMT wells were installed to an average depth of 15 m midway between the tank and the impacted well to transect the dissolved plume. Measured groundwater elevations confirmed the hydraulic gradient, and groundwater sampling identified a thin, narrow plume. Non-detect MTBE values in adjacent wells ensured complete plume delineation. The case study demonstrated the ability to accurately characterize a thin contaminant plume both horizontally and vertically using a CMT Multilevel Well, which would not be possible using a conventional three metre screen monitoring well.

No background case study information was discovered for the BarCad System or Drive Point Wells.

3.2.4 Basis for Sampling Technology Comparison

As sampling and analysis for MNA is expensive, little money was spent on the extensive replicate sampling required for statistical comparisons. Thus, the research strictly compared the technologies. Historically, the well type applied in many upstream oil and gas groundwater monitoring programs has been the three-metre screen PVC monitoring well. The most frequently installed are two inch (5 cm) inner diameter PVC with either a 10 or 20-slot screen and a filter pack thickness between 2 to 4.5 inches (Aller and Gardner, 1993; Puls and Paul, 1997). The U.S. EPA's standard operating procedure for groundwater sample collection from low flow monitoring wells was developed for sampling a screen length of 10 feet (3 metres), as this is most common (U.S. EPA, 1996).

The bailer or Waterra inertial pump are the common samplers for three-metre screen PVC wells (Parker, 1994). Research by Connelly (1993) of Wisconsin landfills found 89% of monitoring wells used bailers. A handbook for subsurface assessment of contaminated sites prepared by the Canadian Council of Minister of the Environment (CCME) also indicated that bailer and Waterra were common sampling methods for these wells (CCME, 1994).

3.2.5 Sources of Variability

Potential sources of variability must be investigated to properly evaluate the sample results.

Laboratory Analysis

Houghton and Berger (1984) indicated that the order of analytical bias ranged from +/-10 to 50%. However since that time, improvements in analytical equipment and procedures have improved the accuracy of analysis. In a certified laboratory's Quality Assurance Program, it is common to accept control sample variability of up to +/-20% from the calibration curve value for many analyzed parameters. Barcelona and Helfrich (1986) documented analytical errors for volatile organic compounds of up to 20%. Where duplicate analysis is conducted as a part of the laboratory's Quality Assurance program, the acceptable relative percent difference (RPD) variability allowed for most analytes and media is typically 20% (can be higher for certain constituents and certain circumstances) (Maxxam Analytics, 2003).

Most commercial laboratories in the industry accept this degree of variability as they use similar methods and equipment to conduct the analysis and provide almost identical analytical results (part of the CAEAL certification is to be able to achieve this replication). The acceptable variability for a particular analyte and media is based on a database of historical variability observed for duplicate and calibration standard analysis of that analyte or media, so there is no governing literature to reference for this information.

This level of variability is accepted based on the sensitivity of current laboratory analytical equipment and techniques, which are capable of measuring very low concentrations for many parameters (especially hydrocarbon constituents). In such cases, any small variation in sample preparation or remnants of previous analysis in the analyzer can result in unacceptable variability in sample results.

Sample Collection

The sampling process can impact variability in results. Considerable effort was made to ensure samples were representative and limited in variability. A single person collected samples for all well types and methods during each sampling event to ensure consistency. Dedicated tubing and sampling devices prevented cross contamination, and where the same device was used to collect two different samples (BarCad System), it was thoroughly cleaned between collections. The samples were collected at similar rates and water levels were monitored where possible to ensure drawdown did not expose the well screen to the atmosphere.

Even with the best sampling protocols, there is always some inherent variability in samples. Even when samples are collected at the same time, variability in results for parameters measured in the field is not uncommon (e.g., pH, EC, temp). Barcelona et al. (1984) indicated that systematic errors related to sampling mechanism can reduce accuracy by two to three times more than analytical procedures, and can result in sampling bias of +/-5 to 20%. Barcelona et al. (1985) suggested that groundwater sampling mechanisms were among the most error-prone elements of monitoring programs. Parker (1994) stated that sampling method and device can greatly impact sample integrity.

3.3 METHODS

3.3.1 Comparison Method for Sample Variability

The sample results are presented in terms of relative percent difference (RPD). The milligram per liter (mg/L) concentration difference over which the sample values vary is also presented to facilitate comparison. The RPD is a United States Department of Energy approved measure of sample analysis precision and helps assess whether sample measurements are within acceptable limits (U.S. Department of Energy, 2002). The equation for determining RPD is:

$$\text{RPD}(\%) = \frac{|X_1 - X_2|}{X_{ave}} \times 100\%$$

where: X_1 and X_2 = analytical sample values being compared

X_{ave} = mean value of X_1 and X_2

Due to their close proximity, the different well types and sampling methods were believed to be collecting from the same groundwater. Barcelona et al. (1984) indicated that systematic errors related to sampling mechanisms can reduce monitoring data accuracy two to three times more than errors in analytical procedures. Therefore, most of the variability observed in parameter concentrations may be attributed to the sampling technologies inability to collect representative samples.

Assuming that the technologies were collecting duplicate samples, an RPD value was calculated to assess if the variability between two sample results was acceptable. An alternative technology RPD value was calculated by comparing the parameter concentration for each alternative technology to that measured by the common sample collection method (three metre screened PVC well sampled by bailer or inertial Waterra foot valve and tubing).

Where there was more than one result, the average RPD for the alternative technology results was compared to the average RPD for the common sample collection results.

Where only one common sample collection result exists (i.e., October event at Site 1 had only bailer results), the average RPD result from another sampling event (e.g., February event at Site 1 had three common sample collection results) is used. An example RPD calculation using sample results from the field research is demonstrated in detail in Appendix E.

The ability of alternative sampling technologies to accurately measure groundwater relevant MNA parameters is assessed by comparing RPD values calculated for the alternative technologies to industry-allowed RPD limits. Also, comparing average RPD values for the various common collection methods to those for each alternative technology helps determine the variability of the results.

A high average RPD value for the results of the common technology suggests considerable variability between the common sample collection methods (e.g., between bailer and Waterra, etc.). This likely indicates high variability and will likely result in higher RPD values for the alternative technology results. In these circumstances, average RPD values higher than the allowable limits described below may be acceptable, due to inherent variability in measuring this parameter.

3.3.2 Acceptable Variability for Sample Results

No clear legislation or reputable documents were uncovered dictating the degree of acceptable variability allowed between samples for any given parameter. Therefore, for the purposes of this research program, the degree of acceptable variability will be assessed using the relative percent difference (RPD) between the analytical results. Since there is no way to justify a specific cutoff value for acceptable variability, a scale of variability ranges was adopted.

The two previously described sources of variability common in a sampling program (laboratory analysis and sample collection) are typically responsible for the majority of variability observed in duplicate analysis results. Thus, the variability of sample analytical results with less than 30% RPD is often deemed acceptable. As +/- 20% variability is acceptable for laboratory analysis for most parameters, and sample collection may affect the results +/- 10%, the acceptable RPD between sample results could be as high as 60%. Therefore, variability from 30% to 60% may be acceptable depending on the circumstances. Determining this requires careful interpretation of the results.

For this research, the following scale will be utilized to assess variability between the analytical results:

Less than 30% RPD - Acceptable variability.
30% to 60% RPD - Variability may be acceptable.
Greater than 60% RPD - Unacceptable variability.

It must be considered that certain parameters are more unstable and thus may have more inherent variability than others. For example, concentrations of metals and hydrocarbons are more likely affected by poor sampling practices than are ionic parameters (i.e., the cations and anions in this program). Ionic parameters like magnesium, sodium or chloride are stable in groundwater and not easily affected during collection. Oxidizing the sample during collection can result in lower concentrations of metals. Excessive agitation during collection can cause volatilization of the dissolved hydrocarbon constituents and lower hydrocarbon concentrations. Therefore, for the hydrocarbon and metals parameters, the degree of acceptable variability is higher due to many factors other than the sampling technology itself.

Acceptable variability in the industry is based on the sensitivity of parameters to analytical and sampling procedures. For inorganic parameters like metals and sulfides, RPD variability of less than 50% between duplicate samples is deemed acceptable in most groundwater monitoring due to the difficulties of effectively sampling these parameters in the field. Organic constituents (i.e., benzene, ethylbenzene, xylenes, etc.) collected in a field sampling program are more susceptible to adverse microbial activities and volatilization and can be measured at very low concentrations where minor concentration differences can cause large variability. As a result, variability of less than 80% between duplicate samples is often accepted. This must be considered when comparing the variability of the results of different sampling techniques used in this field research program.

Where available, the relative percent difference (RPD) between the bailer and Waterra sample collection methods is used as a gauge of the degree of variation in the analytical results. The average RPD results from these common sample collection methods assists in assessing the acceptability of the variability in the alternative sampling technology's results. If the variability between the common results is high for a particular parameter, then the same is likely true for the alternative technology, and the range of acceptable variability is likely higher for this parameter.

3.3.3 Parameters Compared

Many parameters are analyzed in a thorough MNA program. For conciseness and ease of comparison, several relevant parameters are presented that assist in assessing MNA at the sites. These include:

Cations: sodium, calcium and magnesium

- Common cations encountered in soil, providing an indirect indication of the soil mineralogy (Langmuir, 1997).

Anions: bicarbonate, sulfate and chloride

- Bicarbonate provides an indication of the buffering capacity (Bedient et al., 1997).
- Sulfate is a geochemical indicator of natural attenuation prevalent in Alberta (Thorstenson et al., 1979; Chapelle and Lovley, 1990).
- Chloride is a non-reactive, stable anion providing insight into groundwater flow and mixing (Wiedemeier et al., 1995).

Metals: iron and manganese

- Both metals are geochemical indicators of natural attenuation (Vroblesky and Chapelle, 1994; Azadpour-Keeley et al., 1999; Wiedemeier et al., 2006).

Hydrocarbons: benzene, ethylbenzene, total xylenes and CCME F1-BTEX

- These hydrocarbon constituents dissolve into the groundwater and become mobile, which can be monitored to characterize the contaminant plume dimensions (Wiedemeier et al., 1999).
- Toluene values are not presented in this research because the concentrations measured were all below the reliable detection limit at the sites studied.

3.3.4 Sampling Technologies Comparison at the Research Sites

3.3.4.1 Comparison of Well Types

In this section, the discrete interval wells (Solinst Multilevel Well and GeoInsight Drive Point Wells) are compared to the conventional wells (5 cm diameter, 3 m screened PVC monitoring wells). When comparing the conventional wells, note that although the screened portion of the well is often three metres in length, the screen was situated to straddle the seasonal groundwater table. Therefore, the interval over which groundwater can be drawn and sampled exists from the water table at the time of sampling to the base of the well, which is less than three metres.

Both discrete interval wells had small diameters, with the drive point well having a 2.06 centimetre inner diameter (ID) and the multilevel well having a 1.05 centimetre ID. These wells were sampled with a peristaltic pump using 0.635 cm OD Teflon lined tubing. The conventional monitoring wells were sampled using bailers and Waterra samplers.

To allow for easier comparison between the various sampling technologies, the following notations are adopted for all three well cluster study locations. The multilevel and drive point well results are consecutively numbered with increasing depth interval (i.e. ML1 and DP1 being the shallowest sample interval and ML4 and DP4 being the deepest). As there was only one bailer sample collected from an existing well at Site 1 and Site 2, this is referred to as the "bailer sampled well". As there were Waterra samples collected from two conventional well types during certain sample events, for clarity the Waterra sampled wells are referenced by the well name during sample result comparison (i.e., MW1, MW2).

3.3.4.1.1 Site 1

At this site there were a total of eleven sampling wells in the research well nest (Figure B1): four DP wells, one ML well with four sampling intervals and three conventional monitoring wells with three-metre screens. The bailer sample was collected from an existing well (BH01) installed in 1997 with a screened depth from 0.6 to 3.5 m. The Waterra samples were collected from two newly installed prepak three-metre screen monitoring wells (MW1 and MW2), where MW1 had a screened interval from 1.5 to 4.8 m and MW2 from 1.3 to 4.3 m. The sample depth intervals for these three-metre screened wells depend on where the groundwater surface intersected the well screen at the time of sampling.

October

No Waterra samples were collected during the October sampling event. The only common sample collection method was the bailer sampled three-metre screen PVC well (BH01). Therefore, the alternative sampling technologies results can be compared against the bailer sample result obtained, and no RPD value can be calculated for the common sample collection results for comparison against the alternative sampling RPD results.

It must also be considered when comparing the alternative well type results to the common sample collection result, that the multilevel wells ML3 (3.7 to 4.4 m) and ML4 (5.0 to 5.4 m) and the drive point well DP3 (3.8 to 4.7 m) have deeper sample intervals than the bailer sampled well (2.0 to 3.5 m). These deeper sample intervals may have different geochemical characteristics and this can be responsible for differences observed in the analytical results.

This consideration becomes very important in light of immediate drawdown being detected in well DP4 when pumping a deeper well (02BH02) ten metres to the east of the nested wells. When pumping ceased the two wells recharged similarly. As the screened intervals for 02BH02 (5.28 to 7.00 m) and DP4 (5.24 to 6.15 m) had deeper sample intervals and drawdown was not noted in any of the other DP well sample intervals, it is believed that well DP4 was sampling from a deeper, confined aquifer. This is supported by the stratigraphy noted in borehole log MW1 (Figure B2) having a wet silty sand layer (5.03 to 5.49 m) between a silt layer above and a silty clay layer below. The geochemical sample results collected for DP4 also indicate that this well is likely sampling from a separate aquifer, as the groundwater geochemistry data varies significantly compared to the other well types measuring shallower intervals. Therefore the sample results of well DP4 cannot be compared fairly with the other well types and will not be included in the comparison of the various well types.

As the screened interval of well ML4 (4.98 to 5.38 m) also partially falls into the upper portion of the silty sand layer, it too may be sampling from the confined aquifer to some extent. Unfortunately the drawdown for ML4 was not measured during pumping, which could have confirmed this fact. Therefore it is uncertain to what extent ML4 may be impacted, if at all, by the deeper confined aquifer.

February

During this sampling event there were two Waterra samples (MW1 and MW2) collected in addition to the bailer sampled well, so the common sample collection average RPD value can be calculated for the two inch, three-metre screen PVC monitoring wells using the results collected by these two sampling methods. This assumes that the spatial variability between these three wells within a one-metre radius has no effect on the concentrations measured. It is noteworthy that the

Waterra wells sample deeper intervals (MW1 from 3.2 to 4.3 m and MW2 from 3.2 to 4.8 m) in comparison to the bailer sampled well (3.0 to 3.5 m), so the geochemistry may be different at these deeper depth intervals.

The deeper sample intervals of the Waterra sampled wells allowed for better comparison of common sample collection results with all sample depths for the alternative well types versus having only the shallower sample interval of the bailer sampled well in the October event. Multilevel well ML4 (5.0 to 5.4 m) was the only alternative well type that existed at a depth interval deeper than that intersected by the Waterra sampled well MW2 and this fact must be considered when comparing the results.

Because groundwater levels dropped to approximately three metres below ground from near two metres in the October sampling event, no samples could be collected for ML1 and DP1 and therefore no results are presented for these wells. Due to a laboratory error and insufficient volume to conduct another analysis, the routine analysis could not be conducted for ML3 so there are no cation or anion results to present. However, the metals and hydrocarbon constituent concentrations were sampled and are compared.

3.3.4.1.2 Site 2

At this site only the October sampling event results are presented, as samples were collected using all the various technologies. The sampling technologies being studied were installed in clusters at two different locations (Figure B3) and are compared in terms of Well Cluster 34 and Well Cluster 35. Each well cluster had a total of seven sampling wells: three DP wells, one ML well with four sampling intervals and three conventional wells sampled by bailer and Waterra.

The bailer and Waterra sampled wells had screened intervals that intersected all depth intervals investigated by the discrete well types (drive point and multilevel wells), therefore the sample results can be representative of one depth interval or a combination of intervals and this must be considered when comparing the data.

The results collected by the conventional well types are used to determine an average common sample collection concentration, which is then used in the RPD comparison of all well types.

Well Cluster 34

The bailer sample was collected from an existing three-metre screen well (93-P-34) with a screened interval from 2.2 to 5.2 m. The Waterra samples were collected from two newly installed prepak three metre screened monitoring wells (MW1 and MW2), where MW1 had a sample interval from 2.1 to 4.6 m and MW2 from 2.2 to 4.6 m. For the October sampling event the water table dropped below the depth of wells ML1 (1.5 to 2.1 m) and DP1 (1.2 to 2.0 m) so no samples could be collected for comparison.

Well Cluster 35

The bailer sample as collected from an existing three metre screen well (93-P-35) with a screened interval from 2.2 to 5.3 m. Two Waterra samples were collected from this well cluster during the October sampling event. The Waterra samples were taken from the newly installed prepak three-metre screen monitoring wells MW1 (2.7 to 5.3 m) and MW2 (2.6 to 5.3 m).

3.3.4.2 Comparison of Sampling Methods

The alternative sampling methods that were examined in this field study were the BarCad system and dialysis membrane diffusion samplers. The BarCad system and diffusion samplers were selected because of their potential to collect discrete interval samples from within a conventional three-metre screen well. These two methods sampled from the conventional three-metre screen monitoring wells. To assess the ability of these alternative samplers to collect representative groundwater samples, the sample results are compared to the common sample collection methods (bailer and Waterra samplers).

To allow for easier comparison between the various sampling technologies, the following notations have been adopted for all three study locations. As there was only one bailer sample collected from the existing conventional well, this is referred to as the "bailer sample". As both the BarCad system and diffusion samplers collected samples from only two depths within the same designated wells, the sample results are referenced by either shallow or deep and the technology name (i.e., shallow BarCad sample, deep diffusion sample). As there were two Waterra samples collected during certain sample events, for clarity the Waterra samples are referenced by the well name during sample result comparison (i.e., MW1, MW2, etc.).

Due to freezing temperatures making the operation of the BarCad system difficult, the BarCad was only sampled in October at both research sites.

3.3.4.2.1 Site 1

The dialysis membrane diffusion samplers were installed in well MW1 and the BarCad system sampled from well MW2.

October

During this sampling event no Waterra data was collected. Therefore, the bailer was the only sampling method available for comparison to the two BarCad and two diffusion samplers for October.

The diffusion samplers were installed from 3.1 to 3.7 m (shallow interval) and 4.1 to 4.7 m (deeper interval) and the BarCad system sampled from 2.7 to 3.7 m (shallow interval) and 3.3 to 4.3 m (deeper interval) during this event.

February

No BarCad samples were collected for this sampling event. Therefore, the diffusion samples were the only alternative sampling method to be compared to the common sample collection methods for this sampling event. The diffusion samplers were installed from 3.1 to 3.7 m (shallow interval) and 3.8 to 4.4 m (deeper interval) in February.

Waterra samples were collected in February, which in combination with the bailer sample allowed the establishment of a common sample collection average RPD value.

3.3.4.2.2 Site 2

The sampling methods were implemented in two clustered locations (Figure B3) and are compared in terms of Well Cluster 34 and Well Cluster 35. At each well cluster the dialysis membrane diffusion samplers were installed in well MW1 and the BarCad system sampled from well MW2.

Although samples were collected using the BarCad system for two depth intervals at each well cluster in July at this site and in October at Site 1, the shallow sample does not represent a discrete interval. The BarCad System had only a packer above the ceramic filter, and no packer beneath, so the shallow BarCad sample can come from any conductive interval along the depth of the three-metre well screen in which it is installed. Therefore, the shallow BarCad sample was no different than collecting a sample using a common sample collection method (i.e., bailer or Waterra) for this well.

The BarCad System may have created a discrete interval within a three-metre screen only when the ceramic filter was lowered to the lower portion of the well screen and the packer was inflated; assuming that there is no water movement around the packer through the sand pack. This isolated the bottom metre of the well screen, causing sample water to be drawn from this depth interval. As a result, only the deeper BarCad sample was collected in October at both well clusters, as this method of installation may collect a discrete interval sample.

The bailer sample was collected from an already existing conventional well and the Waterra samples were collected from newly installed prepak conventional wells at each well cluster. The bailer and Waterra samples came from conventional wells having screened intervals that intersected all the sample depth intervals investigated by the discrete interval sampling methods, therefore the sample results may represent one depth interval or a combination of intervals and this must be considered when comparing the data. The results collected by the bailer and Waterra are used to determine the average RPD result for the common sample collection methods, which is then used in the RPD comparison of all sampling methods investigated.

Well Cluster 34

The bailer sample was collected from well 93-P-34 (2.2 to 5.2 m) and two Waterra samples were collected from wells MW1 and MW2. The diffusion samplers were installed from 2.0 to 2.7 m (shallow interval) and 2.7 to 3.3 m (deeper interval) and the BarCad system sampled from 3.6 to 4.6 m at Cluster 34.

Well Cluster 35

The bailer sample was collected from well 93-P-35 (2.8 to 5.3 m) and two Waterra samples were collected from wells MW1 and MW2. The diffusion samplers were installed from 2.7 to 3.4 m (shallow interval) and 3.4 to 4.0 m (deeper interval) and the BarCad system sampled from 4.3 to 5.3 m at Cluster 35.

3.3.5 Sample Collection

For the three metre screen wells, dedicated bailer and Waterra samplers were used. For the CMT multilevel wells and GeoInsight Prepak Drive Point wells, dedicated 6.4 mm tubing and a peristaltic pump were used for each channel of the multilevel well and for each drive point well.

The first volume of water collected by the bailer was discarded to rinse the bailer of anything that may have come into contact with it since the last sampling event. During sampling, the water was removed from the bottom of the bailer using a flow-controlling device to minimize spray and aeration. The estimated rate of bailing was 2 to 3 L/minute.

The Waterra sampler was installed to the bottom of the well and oscillated until all silty material from the well bottom exited the top of the tubing. The groundwater sample was then collected by decanting out approximately the top one-metre of water in the tubing. The tubing was then oscillated again until the water reached the top, where it was again similarly decanted. This process was repeated until sufficient volume was retrieved for the suite of analysis. The pumping rates ranged from 0.2 L/minute in slow producing wells to 0.5 L/minute in faster producing wells. Between sampling events the Waterra sampler was stored with the foot valve at the top of the monitoring well.

The multilevel wells were purged at approximately 0.15 to 0.2 L/minute to remove any stagnant water within the well, ensuring the tube bottom was placed 10 to 15 cm above the sample port to prevent the inlet from being exposed to the atmosphere if the water level in the well was drawn down. In faster producing formations where drawdown to the tube bottom could not be achieved, the water was purged until approximately three well volumes were removed.

The multilevel wells were allowed 0.5 to 1 hour to recharge before sampling. During sampling the sample tubing was lowered to the middle of the well screen. The water level was monitored with a water level indicator to prevent drawdown into the screen interval during sampling. The groundwater sample was collected at a rate of 0.075 to 0.15 L/minute, depending on the rate of well recharge.

For the drive point wells the stagnant water above the screen interval was purged in a similar fashion as the multilevel wells, ensuring that the base of the sampling tube was above the well screen. The wells were purged at a rate of 0.1 to 0.15 L/minute. The wells were allowed 0.5 to 1 hour to recharge before sampling. The wells were also sampled from the middle of the well screen while the drawdown was monitored to ensure the screen was not exposed to the atmosphere. Sample collection was conducted at a rate of 0.1 to 0.15 L/minute.

The BarCad sample port was installed at approximately 0.3 to 1 m below the static water table for the shallow sample and near the well bottom during the deep sample collection. This was accomplished by inflating the packer so that the ceramic filter containing the sample port (located beneath the packer) was at the desired depth. The drawdown was monitored for the deeper installation to ensure that the water sample was coming from the formation and not from above the packer through the sand annulus. The drawdown for the shallow installation could not be monitored because the water level was below the packer. The sampling rate was dependent upon the well's ability to recharge, and sampling was intermittent, so it was difficult to measure the flow rate. It was estimated that samples were retrieved at approximately 2 L/minute.

For all water samples collected for metals analysis, except the diffusion samplers, the water passed through a dedicated 0.45 micron cartridge filter to remove any colloidal iron. The sample was then preserved using a 0.1 Molar nitric acid solution to ensure the iron remained in solution until laboratory analysis. The BTEX/F1 vials were filled to zero headspace and contained sodium thiosulphate to prevent any microbial degradation during transport and storage.

3.3.6 Method of Comparison of Sample Results

As the research focuses on comparing alternative sampling technologies for MNA assessment, the sample results obtained by each sampling technology are plotted against each other to allow comparison (Appendix G). To evaluate whether the differences in the sampling results are caused by the different sampling technologies, the confounding effects must be minimized. Individual sampling technologies were sampled by the same person during each sampling event. The lateral variability between wells was minimized by situating the wells in a cluster so the wells were no more than one and half metres apart horizontally. To eliminate any potential time dependent effects on the results, the results from each technology are plotted for each separate sample event.

To develop and address any depth trends for the discrete interval sampling technologies, the results are split according to the selected geochemical groundwater parameters (cations, anions, metals and hydrocarbons). To examine the effectiveness of the sampling technologies to collect representative samples, the discrete interval results are also compared with the three-metre screen well results (concentrations may be representative of a preferential discrete interval or a combination of intervals that the three-metre screen intersected).

3.3.7 Material Impacts of Bentonite Seals on Water Chemistry

In response to measuring elevated sulfate ion concentrations in the multilevel wells, the impact of bentonite seal material on water chemistry was investigated. The materials investigated were bentonite grout, chips and pellets used during the field installations.

In sterile, 0.5 L soil sampling jars, 50 g of bentonite chips and pellets were separately placed into 350 g of deionized water. In the same manner, 250 g of bentonite grout was placed into 250 g of deionized water. The jars were capped and the bentonite was allowed to hydrate at room temperature for 40 days. Over the 40 days the deionized water in each jar was allowed to equilibrate with the ions that dissolved from the different bentonite materials. At day 40, the supernatant liquid was collected using disposable pipets. The sample volumes collected were 270 mL, 100 mL and 70 mL for the bentonite grout, chips and pellets, respectively. These volumes were analyzed at Maxxam Analytical Laboratories for cations, anions and metals.

3.4 RESULTS

3.4.1 Laboratory Research

3.4.1.1 Impact of Bentonite Seal Materials on Water Chemistry

Table 3.1 summarizes the analytical results for the parameters selected for comparison in this research program. The bentonite pellet impacts are of most interest to this research program since the pellets were used to seal above and below the sand annulus surrounding the screen portion of the multilevel wells. This screened interval was very short (approximately 35 mm) so the ratio of the volume of bentonite seal to the sand annulus was much larger for the multilevel wells. Also the bentonite seal was closer to the well intake compared to the other well installations. The only well type that was not sealed using this bentonite material was the drive point wells because these wells came with a prefabricated powdered bentonite sleeve above a foam packer, which sealed the annulus above the screened interval.

The bentonite pellets analytical results indicate concentrations of cations, anions and iron that may impact the ability to accurately measure these parameters in the groundwater formation at the sites. The largest concentrations measured are sulfate (1720 mg/L), sodium (783 mg/L) and bicarbonate (107 mg/L). However, the magnesium (5.0 mg/L), calcium (16.8 mg/L), chloride (14.5 mg/L), and even the iron (1.26 mg/L), may have sufficiently elevated concentrations to impact the ability to accurately sample groundwater with low concentrations of these parameters, as is the case at Site 1. The only parameter that is not likely to impact sample results is manganese (0.090 mg/L). Barcelona and Helfrich (1986) similarly determined that contamination from cement grout seals significantly affected dissolved inorganic constituent from background concentrations.

Of greatest concern, from an MNA perspective, is the high sulfate concentration. The elevated sulfate concentration measured for the CMT multilevel well samples obscures the amount of sulfate reduction, making it difficult to demonstrate that this fundamental redox reaction is occurring in the MNA sampling program.

3.4.2 Field Research

3.4.2.1 Comparison of Sampling Technologies Results

The results from the various alternative sampling technologies and common sample collection methods (5 cm diameter, 3 m screened PVC monitoring wells sampled by bailer or Waterra) are compared in both tables and figures. The tables (Appendix F) and figures (Appendix G) include the data for October and February at Site 1 and October for Well Cluster 34 and 35 at Site 2.

Although the Site 1 data are temporally different, February data are presented because there was no Waterra sample collected for the October sampling event and it was desirable to ensure that all sampling technologies were compared. The February data can not be solely used for comparison because the BarCad System was not used in February due to difficulties in operating this equipment in freezing temperatures, so it is necessary to use both data sets.

The following sections outline the general trends and findings observed in the field results for the various sampling technologies investigated at both sites.

3.4.2.1.1 Inherent Variability of Groundwater Geochemistry

Although the affects of lateral heterogeneity were thought to be minimized by placing the various well types in a 1.5 m radius cluster, there is field result evidence indicating there was inherent variability occurring over these small lateral distances. The data that most clearly demonstrates this includes:

1. As the Waterra sampled wells at both research sites were sampled using the same sample method over similar sample depths it is expected that the sample results would match closely, however this is not the case for the following parameters, and demonstrates the inherent variability that exists.
    - The Site 1 ethylbenzene, total xylenes and PHC F1-BTEX concentrations in February have RPD values of 53%, 57% and 129% respectively for Waterra sample MW1 and MW2 (Table F4), with the PHC F1-BTEX having unacceptable variability (>60% RPD) since the concentrations are over four times different from each other (Figure G24).
    - At Site 2, the Well Cluster 34 iron and benzene have unacceptable RPD variability of 90% and 80% respectively (Table F11 and F12), with the iron (Figure G32) and benzene (Figure G33) concentrations varying by nearly 2.5 times for both parameters.
    - The sulfate, iron and PHC F1-BTEX concentrations at Well Cluster 35 (Site 2) have unacceptable variability of 182%, 128% and 104% respectively (Table F14, F15 and F16), with the sulfate (Figure G41), iron (Figure G44) and PHC F1-BTEX (Figure G48) varying over one order of magnitude, almost 5 times and over 3 times respectively.

2. Chloride is a stable anion that is not expected to vary much over small distances in the subsurface, however considerable variability was measured by the various technologies at Site 2.
    - At Well Cluster 34 the chloride concentrations (Figure G30) range from 20 mg/L (DP2) to 113 mg/L (ML2), with both these samples coming from a similar sample depth interval. The RPD value of 139% (Table F10) for these two wells demonstrates the significance of this range in concentrations.
    - At Well Cluster 35 the chloride concentrations (Figure G42) range from 27 mg/L (DP3) to 78 mg/L (bailer sampled well), which is significant since the RPD value is 97% (Table F14). Even the common sample collection from the 3 m screened wells over similar depth intervals (2.6 to 5.3 m) varies from 47 mg/L to 78 mg/L and has RPD values up to 52% (significant variability).

3.4.2.1.2 PrePak Drive Point Wells (GeoInsight)

For almost every parameter and location investigated the drive point wells measure concentration differences over the different sample depth intervals, however for many parameters it is difficult to conclude if the differences are representative of depth dependent trends or inherent variability in sampling. There are several parameter results where the variability appears to indicate that concentration variation trends are being measured with depth.

1. Although the following cation results demonstrate significant variability for the different sample depth intervals, the trends with depth are not obvious.
    - The Site 1 October and February sodium concentrations have RPD values that vary up to 144% (Table F1) and 92% (Table F5) respectively, however in both instances there is no clear trend with depth developed (Figure G3 and G15).

- At Well Cluster 34 at Site 2, the calcium RPD values vary by 132% (Table F10), however with only two sample depths it is difficult to definitively conclude if the increasing trend with depth is representative (Figure G26).

2. Although similar trends with depth are noted for most anions sampled at both research sites, the sulfate and chloride results are the only parameters demonstrating significant variability over the different sample depth intervals.

    - The Site 1 October and February sulfate concentrations have RPD values that vary from 125% to 184% (Table F2) and by 187% (Table F6) respectively, with the largest concentration being measured in the deepest sample interval in both sample events (Figure G5 and G17).
    - At Site 2, the Well Cluster 34 and Well Cluster 35 sulfate RPD values vary by 199% (Table F10) and from 81% to 196% (Table F14) respectively, with a significant increase in concentration with depth in both cases (Figure G29 and G41 respectively).
    - At Site 2, the chloride concentrations for Well Cluster 34 and Well Cluster 35 have RPD values varying by 96% (Table F10) and up to 66% (Table F14) respectively, with Well Cluster 34 having an increasing concentration (Figure G30) and Well Cluster 35 having a decreasing concentration with depth (Figure G42).

3. The following metals variability is noted at the research sites.

    - In October, the Site 1 iron RPD values vary up to 193% (Table F3), however it is uncertain if the shallow interval (DP1) being almost two orders of magnitude higher than the other intervals represents a trend with depth or erroneous data (Figure G8).

- At Well Cluster 34 (Site 2) the manganese RPD values vary by 168% (Table F11), however the shallow interval (DP2) iron concentration being over an order of magnitude lower may be erroneous since it is significantly less than the next lowest value for the bailer sampled well (Figure G31).

- The iron RPD values for Well Cluster 35 (Site 2) vary from 108% to 180% (Table F15), having a strong decreasing concentration with depth trend by decreasing over an order in magnitude (Figure G44).

4. The hydrocarbon constituents demonstrate a decreasing concentration with depth trend for almost every sampling event, however the following hydrocarbon results have variability that indicates this trend with depth is significant at the research sites.

    - In October, the Site 1 benzene, ethylbenzene, total xylenes and PHC F1-BTEX RPD values vary up to 133%, 180%, 178% and 172% (Table F4) respectively, with the ethylbenzene (Figure G10), total xylenes (Figure G11) and PHC F1-BTEX (Figure G12) concentrations decreasing almost 1.5 orders of magnitude with depth.

    - At Well Cluster 34 (Site 2) the benzene, ethylbenzene, total xylenes and PHC F1-BTEX RPD values vary by 192%, 102%, 176% and 120% (Table F12) respectively, with the benzene (Figure G33), ethylbenzene (Figure G34), total xylenes (Figure G35) and PHC F1-BTEX (Figure G36) concentrations decreasing from over 4 times to 1.5 orders of magnitude with depth.

    - The benzene, ethylbenzene, total xylenes and PHC F1-BTEX RPD values for Well Cluster 35 (Site 2) vary up to 197%, 197%, 199% and 169% (Table F16) respectively, with the benzene

(Figure G45), ethylbenzene (Figure G46), total xylenes (Figure G47) and PHC F1-BTEX (Figure G48) concentrations decreasing from 1 to over 2 orders of magnitude with depth.

5. During most sampling events the highest metals and hydrocarbon concentrations were sampled by the drive point wells where the water table intersects the well screen.
    - In October at Site 1, the shallow drive point well (DP1 from 2.1 to 3.0 m) fell near the water table (near 2 m) and measured iron (Figure G8) almost two orders of magnitude and ethylbenzene (Figure G10) and total xylenes (Figure G11) concentrations over an order of magnitude larger than the DP2 interval (2.8 to 3.7 m).
    - At Well Cluster 34 (Site 2) the shallow well DP2 (2.2 to 3.0 m) intersected the water table (2.2 m) and measured benzene (Figure G33), ethylbenzene (Figure G34), total xylenes (Figure G35) and PHC F1-BTEX (Figure G36) concentrations three times to 1.5 orders of magnitude larger than the deepest interval DP3 (3.2 to 4.0 m).
    - At Well Cluster 35 (Site 2) the shallow well DP1 (2.2 to 2.9 m) intersected the water table (2.7 m) and measured iron (Figure G44), benzene (Figure G45) and total xylenes (FigureG47) concentrations two to three times larger than the next deepest interval DP2 (3.3 to 4.0 m).

3.4.2.1.3 CMT Multilevel Wells (Solinst)

Similar to the drive point wells, the multilevel wells often measure concentration differences over the different sample depth intervals investigated. As the bentonite seal material used to seal the small multilevel sample intervals elevated ion concentrations, this makes it difficult to assess if the differences measured for these parameters are representative of depth dependent trends. The parameter results demonstrating significant variability and any notable trends are developed below.

1. The multilevel well cation and anion results are often higher compared to the other sampling technologies results over similar sample intervals. This effect is more apparent at Site 1 due to lower background ion concentrations, however sodium and sulfate are notably elevated for all sample events at both research sites.

    - At Site 1 in October all ML2 cation and anion concentrations (except bicarbonate) are elevated by almost double the other multilevel wells and even higher than the other sample technology results (Table F1 and F2). However, the difference is most notable for the sodium (Figure G3) and sulfate (Figure G5) concentrations, as these parameters are 3 times higher than the next highest result (RPD over 80% and 107% respectively).

    - Again in February (Site 1) most ML2 cation and anion concentrations (except bicarbonate) are twice as large compared to the other multilevel wells and even higher than the other sample technology results (Table F5 and F6). However, the difference is most notable for the sodium (Figure G15) and sulfate (Figure G17) that are three times and almost 3 orders of magnitude larger than the next highest result for the other sampling technologies (RPD over 105% and 194% respectively).

    - At Site 2, the Well Cluster 34 calcium (Figure G26) and sulfate (Figure G29) concentrations are higher than the other sampling technologies over similar sample depth intervals. Also the ML2 chloride (Figure G30) concentration is almost double all other results (RPD of >50%, Table F10).

- At Well Cluster 35 (Site 2) the sodium (Figure G39) and sulfate (Figure G41) concentrations are higher than the other sampling technologies over similar sample depth intervals, with ML3 having significantly elevated concentrations as indicated by sodium RPD values over 113% (Table F13) and sulfate RPD values over 164% (Table F14).

2. Similar to the cations and anions, the metals variability is more notable at Site 1, however there are trends noted at both research sites.

   - During both sampling events at Site 1 the manganese concentrations are elevated compared to the other well types and the iron concentrations demonstrate a decreasing concentration with depth. The elevated manganese concentrations are most notable for ML2 in October (RPD values >50%, Table F2) and for ML2 and ML3 in February (RPD values >88% and 57% respectively, Table F6). Although the multilevel iron concentrations are higher than the drive point wells over similar depth intervals, the iron decreases an order of magnitude (Figure G8) and four times (Figure G20) with depth in October and February respectively, similar to the trends with depth for the drive point wells. Although the February ML2 iron concentrations seem elevated compared to the drive point results (as indicated by RPD values >80%, Table F6), it appears to be representative as it matches closely with the common sample collection results (RPD values <25%).

   - The Well Cluster 34 (Site 2) multilevel manganese and iron concentrations are elevated compared to the drive point results (RPD values >70% and >50% respectively, Table F10), however they are in the same order as the common sample collection results so they are likely representative. The multilevel iron results demonstrate a decreasing concentration with depth trend, with almost an order of magnitude decrease occurring from ML3 to ML4 (Figure G32).

- Although the Well Cluster 35 multilevel manganese and iron results are quite variable (higher for manganese and lower for iron) compared to the drive point wells over similar depth intervals (RPD values >30% for both parameters, Table F15), the multilevel wells have the same trends with depth as the drive point wells for both metals (Figure G43 and G44). The only difference is ML4 (from a depth interval not intersected by any other well types) has concentrations that are unexpectedly high for that depth interval and match poorly with the trends established by the other multilevel and drive point wells, as supported by the manganese and iron RPD values for ML4 being >91% and >73% respectively.

4. The hydrocarbon constituents demonstrate an expected decreasing concentration with depth trend for almost every sampling event, however the following hydrocarbon results have variability that indicates this trend with depth is significant at the research sites.

    - With the exception of benzene having an unexpected increasing concentrations with depth trend during both sample events, the hydrocarbon results for all multilevel wells demonstrate a significant decreasing concentration with depth trend, as indicated by the RPD values ranging from 54% (benzene) to 189% (total xylenes) in October (Table F4) and 50% (PHC F1-BTEX) to 156% (ethylbenzene) in February (Table F8). The significance of this decreasing trend can be seen by the concentrations varying from 3 times for PHC F1-BTEX in February (Figure G24) to almost 2 orders of magnitude for ethylbenzene (Figure G10) and total xylenes (Figure G11) in October.

- All hydrocarbon parameters at Well Cluster 34 (Site 2) demonstrate the expected decreasing concentrations with depth trend, although it is not as apparent due to similar concentrations being measured over adjacent depth intervals (indicated by RPD values (Table F12) of 5% for benzene, and 11% for total xylenes and PHC F1-BTEX). The decreasing concentration with depth trend is most apparent for ethylbenzene (Figure G34), which gradually decreases over one order of magnitude with depth.

- With the exception of an unexpectedly elevated ML4 results, Well Cluster 35 (Site 2) benzene (Figure G45), ethylbenzene (Figure G46) and total xylenes (Figure G47) concentrations have the expected decreasing concentration with depth. The decrease is most apparent between the ML1 and ML2 sample intervals, differing by over an order of magnitude and the RPD values (>170% for these three parameters, Table F16) demonstrate the significance of this trend. Although not as apparent due to an anomalously high ML2 result (RPD >126% so significant), the PHC F1-BTEX concentrations decrease with depth as expected (Figure G48).

5. During most sampling events the highest metals and hydrocarbon concentrations were sampled by the multilevel wells where the water table intersected the well screen, as is the case for the drive point wells.

   - In October at Site 1, the shallow multilevel well (ML1 from 1.7 to 2.3 m) intersected the water table (near 2 m) and measured iron (Figure G8) almost one order of magnitude and ethylbenzene (Figure G10), total xylenes (Figure G11) and PHC F1-BTEX (Figure G12) concentrations 2 to 4 times larger than the ML2 interval (2.5 to 3.2 m) that is below the water table.

   - In February (Site 1), due to the water table dropping to near 3 metres, the trend is not as apparent as in October. Multilevel well

ML2 (2.5 to 3.2 m) intersected the water table and has iron (Figure G20), ethylbenzene (Figure G22), total xylenes (Figure G23) and PHC F1-BTEX (Figure G24) concentrations approximately 2 to 3 times larger than the next interval ML3.

- The metals and PHC F1-BTEX results at Well Cluster 34 (Site 2) do not support this trend, however the shallow well ML2 (2.6 to 3.1 m) did not intersect the water table (2.2 m) during this event and may be responsible for this. The benzene (Figure G33), ethylbenzene (Figure G34) and total xylenes (Figure G35) concentrations do follow the trend, being over 3 times to over an order of magnitude larger than the next deepest interval ML3 (3.5 to 4.1 m).

- With the exception of an anomalously high ML2 PHC F1-BTEX concentration, at Well Cluster 35 (Site 2) the shallow multilevel well ML1 (2.6 to 3.3 m) intersected the water table (2.7 m) and measured manganese (Figure G43), benzene (Figure G45), ethylbenzene (Figure G46) and total xylenes (Figure G47) concentrations over an order of magnitude larger than the next deepest interval ML2 (3.7 to 4.3 m).

3.4.2.1.4 Conventional Well Types & Common Sample Collection Methods

This section demonstrates the findings and trends that occur when a conventional 3 m screened well was sampled using the common sample collection methods bailer and Waterra inertial foot valve. The following notes the substantive trends that exist based on the data collected using these technologies.

1. Although the bailer and Waterra samples were collected from 3 m screened wells over similar sample depth intervals, the results of these common sample collection methods vary significantly for particular parameters. This variability often reflects that the sample is representative of a small interval of that 3 m screened well or mixing of the intervals over which the well screen exists (averaging effect).
    - In October the bailer sampled well results at Site 1 closely match the average of the wells DP1 and DP2 for several parameters.
        - ➢ An average of the DP1 and DP2 magnesium and calcium concentrations is 5.9 and 29 mg/L respectively (Table F1), which closely compares with the concentrations measured by the bailer (5.5 and 27 mg/L).
        - ➢ DP1 and DP2 bicarbonate and chloride average concentrations are 131 and 4.9 mg/L respectively (Table F2) and closely compares with the bailer concentrations (120 and 4.7 mg/L).
        - ➢ The average manganese and iron concentrations for DP1 and DP2 are 0.75 and 2.1 mg/L respectively (Table F3), which closely compares to the bailer results (0.72 and 3.1 mg/L).
        - ➢ Average DP1 and DP2 ethylbenzene and PHC F1-BTEX concentrations of 0.08 and 2.2 mg/L respectively (Table F4), closely match the bailer results (0.05 and 2.1 mg/L).
    - At Well Cluster 34 (Site 2) the bailer sampled well appears to be representative of a shallow depth interval, as the results closely match with many DP2 (2.2 to 3.0 m) results.
        - ➢ This is most apparent for similarly low magnesium (Figure G25), calcium (Figure G26) and sulfate (Figure G29) concentrations, as the bailer and DP2 results are nearly 25%, 50% and more than two orders of magnitude lower than the other results respectively.

  - This is supported by the bailer and DP2 RPD values being below 32% for these parameters (Table F9 and F10), indicating the sample results match well, whereas most of the other sampling technology RPD values are >60%.

- At Well Cluster 34 (Site 2) the Waterra sampled well MW1 appears be representative of deeper depth intervals, as the cation and anion results match closest with DP3.
  - The RPD results for Waterra sampled well MW1 and DP3 (Table F9 and F10) are below 22%, indicating the cation and anion results closely match for these wells.
  - Waterra sampled well MW1 has the highest concentration for every cation and anion compared to the other 3 m screened wells and DP3 also has the highest concentrations for the drive point wells, with these highest concentrations notably matching for calcium (Figure G26) and sulfate (Figure G29).

- At Well Cluster 34 (Site 2) the Waterra sampled well MW2 results suggest mixing of the intervals over which the well screen exists because the cation and anion results closely match the average of the DP2 and DP3 results.
  - Cations: The average DP2 and DP3 magnesium, calcium and sodium concentrations are 187 mg/L, 83 mg/L and 248 mg/L respectively (Table F9), which closely match (less than 6% variability) the Waterra MW2 concentrations (193 mg/L, 88 mg/L and 254 mg/L).
  - Anions: The average DP2 and DP3 bicarbonate and sulfate concentrations are 1580 mg/L and 215 mg/L respectively (Table F10), which closely match (less than 6% variability) the Waterra MW2 concentrations (1670 mg/L and 224 mg/L).

- At Well Cluster 35 (Site 2) the Waterra sampled well MW2 appears to be representative of a mid-screen depth interval, as the cation, anion and metals results closely match ML2 and DP2 results.
  - ➢ The RPD results for Waterra MW2 and ML2/DP2 (Table F13, F14 and F15) are below 28%, indicating the cation, anion and metals results closely match. The exceptions are DP2 sulfate (78%) and manganese for ML2 and DP2 (95% and 125%), which are likely different due to the reduction processes observed when natural attenuation is occurring.
  - ➢ Waterra sampled well MW1 and ML2/DP2 similarities are most prevalent for the magnesium (Figure G37), calcium (Figure G38), sulfate (Figure G41) and iron (Figure G44) results.

- At Well Cluster 35 (Site 2) the bailer sampled well and Waterra sampled well MW1 closely match (RPD <30%) for the cation, anion and metals results (except chlorides, RPD 52%) and appear to be representative of shallower sample depth intervals, as their concentrations more closely match the ML1 and DP1 results.
  - ➢ The chloride concentration (Figure G42) for the bailer sampled well (78.3 mg/L) appears to be elevated, as the value is almost twice the other 3 m screened well type results and discrete well type results (supported by bailer RPD values >36%, Table F14).
  - ➢ The remaining bailer and Waterra sampled well MW1 cation and anion results reasonably match ML1 and DP1 results (most RPD values <50%, Table F13 and F14). The similarity between these well results is most prevalent for the sulfate results (<3 mg/L difference, Figure G41), even though the RPD values are higher (20 to 126%) due to the large range of variability seen for this parameter (3 orders of magnitude).

    - ➢ Although the metal RPD values for the bailer, Waterra sampled well MW1, ML1 and DP1 results do not indicate that these results reasonably match (RPD from 27% to 118%, Table F15), when all manganese (Figure G43) and iron (Figure G44) concentrations are compared, the bailer and Waterra sampled well MW1 results match most closely with the shallow interval ML1 and DP1 results due to the large range in variability (1.5 orders of magnitude).

2. During most sampling events, conventional 3 m screened wells sampled by bailer or Waterra show the highest metals and hydrocarbon concentrations of all sampling technologies, representing the shallow groundwater MNA trends expected for a LNAPL contaminant.
    - At Site 1 in October and February, metal and hydrocarbon concentrations sampled by bailer and Waterra samplers are among the highest measured, and are closest to those for the shallow discrete interval wells (ML1 and DP1 in October and ML2 and DP2 in February). This is most notable for the iron (Figure G8) and PHC F1-BTEX (Figure G12) results in October and for the iron (Figure G20), ethylbenzene (Figure G22), total xylenes (Figure G23) and PHC F1-BTEX (Figure G24) results in February.
    - At Well Cluster 34 (Site 2), metal and hydrocarbon concentrations sampled by bailer and Waterra samplers are more variable, most notably for manganese (RPD from 83% to 166%), iron (RPD from 71% to 139%) and benzene (RPD from 80% to 145%) results (Table F11 and F12). It is noteworthy that the bailer iron result (Figure G32) appears elevated, as it is over twice as large as the next highest result (Waterra sampled well MW1) and over three times larger than all other results.

However, even with this variability the bailer and Waterra samplers are among the highest measured, and are closest to those for the shallow discrete interval wells (ML2 and DP2). This is most notable for the benzene (Figure G33), ethylbenzene (Figure G34), total xylenes (Figure G35) and PHC F1-BTEX (Figure G36) results.

- At Well Cluster 35 (Site 2), metal and hydrocarbon concentrations sampled by bailer and Waterra samplers are more variable, most notably for iron (RPD from 28% to 143%), total xylenes (RPD from 18% to 116%) and PHC F1-BTEX (RPD from 104% to 191%) results (Table F15 and F16). It is noteworthy that the bailer appears elevated for these results, with the PHC F1-BTEX concentration (Figure G48) over 25 times all other results being most notable.

  However, even with this variability the bailer and Waterra samplers are among the highest measured, and are closest to those for the shallow discrete interval wells (ML1 and DP1). This is most notable for the iron (Figure G44), benzene (Figure G45), and PHC F1-BTEX (Figure G48) results.

3.4.2.1.5 Dialysis Membrane Diffusion Sampler

The diffusion samplers investigated the ability to sample discrete intervals within a 3 m screened well. A Waterra sample MW1 was collected from the same well for comparison at both sites. Although the samplers measured similar concentrations for both depth intervals in many instances, there is some data that appears to demonstrate discrete interval sampling. The following develops these data trends.

1. The diffusion samplers have similar concentrations for both depth intervals for many of the parameters sampled at both sites and often closely match the Waterra sample MW1 collected from the same well. In most cases the diffusion samplers fail to demonstrate concentration differences measured by the discrete interval well types installed over similar depth intervals.

    - In October at Site 1, all concentrations are nearly identical for both diffusion sampler depth intervals, the RPD values varying by less than 18% (Tables F1 to F4) support this. The diffusion samplers match poorly for most of the parameters compared to the discrete well results over similar sample intervals (DP2, DP3, ML3 and ML4), especially for the iron and hydrocarbon results. This is most notable for iron (Figure G8), ethylbenzene (Figure G10) and total xylenes (Figure G11), where both diffusion sampler results are one to two orders of magnitude higher, and fail to represent the lower iron and hydrocarbon concentrations expected for this depth.

    - At Site 1 in February, all concentrations are similar for both diffusion sampler depth intervals, the RPD values varying by less than 41% (Tables F5 to F8) support this. The diffusion samplers match poorly for most of the parameters compared to the discrete well results over similar sample intervals (DP2, DP3, ML3 and ML4), especially for the iron (Figure G20) and hydrocarbon results where the diffusion samplers measure an opposite increasing concentration trend with depth. This is most notable for ethylbenzene (Figure G10) and total xylenes (Figure G11) where both diffusion sampler results are two to ten times higher, and fail to represent the lower iron and hydrocarbon concentrations expected for this depth.

The diffusion samplers cation and anion results closely match Waterra sample MW1 results from the same well, the RPD values (Table F5 and F6) less than 18% supports this (except for sulfate - RPD of 63% and 90%, however concentrations only vary over 2 mg/L so this is likely insignificant variability too). The diffusion sampler metal and hydrocarbon results are significantly lower than the Waterra sample MW1, as RPD values (Table F7 and F8) ranging from 35% to 159% indicates. The severity of the hydrocarbon differences may be due to elevated Waterra MW1 concentrations, which is most notable for PHC F1-BTEX results (Figure G24). This makes it difficult to state if the diffusion samplers fail to collect samples representative of the well in which they were installed.

- At Well Cluster 34 (Site 2), all cation, anion and metal concentrations are similar for both diffusion sampler depth intervals, the RPD values varying by less than 24% (Tables F9 to F11) support this. However, the diffusion samplers reasonably match (RPD <60%) for many of the parameters compared to the discrete well results over similar sample intervals (DP2, DP3 and ML2), except for diffusion calcium, sulfate and manganese results that fall in the middle of the other results. The sodium results (Figure G27) most clearly demonstrate how well both diffusion samplers match the discrete interval results over similar sample depths.

  The diffusion samplers cation, anion and metals results reasonably match Waterra sample MW1 results from the same well, with RPD values (Table F9 and F11) of less than 60% (except sulfate is significantly lower [Figure G29], RPD of 119% and 121%). This indicates that at Well Cluster 34 the diffusion samplers are collecting groundwater samples representative of the well in which they were installed.

- At Well Cluster 35 (Site 2), all cation, anion and metal concentrations are similar for both diffusion sampler depth intervals, the RPD values varying by less than 20% (Tables F13 to F15) support this. However, the diffusion samplers reasonably match (RPD <60%) for many of the parameters compared to the discrete well results over similar sample intervals (DP1, DP2, ML1 and ML2), except for the diffusion sulfate, manganese and iron results. The most notable of these is the diffusion iron results (Figure G44) are significantly higher (RPD ranging from 11% to 128%) than the discrete well results over similar depths intervals. This is surprising based on the difficulties the diffusion samplers have sampling iron (developed in Chapter 2).

  The diffusion samplers' cation, anion and metals concentrations poorly match the Waterra sample MW1 from the same well for most parameters, with the diffusion samplers measuring lower results for all parameters. The opposite trend was observed for the hydrocarbons, with the diffusion sampler results being larger than the Waterra sample MW1. This indicates that the diffusion samplers do not appear to be collecting groundwater samples representative of the well in which they were installed.

2. There are occasions where the diffusion samplers measure more significant differences in concentration between the two depth intervals sampled. These results may demonstrate the ability to collect discrete interval samples and are developed below.

   - At Well Cluster 34 (Site 2), the diffusion sampler hydrocarbon results demonstrate a significant increasing concentration with depth trend, with the benzene (Figure G33) and PHC F1-BTEX (Figure G36) almost doubling and the ethylbenzene and total xylenes (Figure G34 and G35) almost tripling in concentration with depth. The significance of these differences is seen in the RPD values ranging from 53% for benzene to 96% for ethylbenzene (Table F12).

The increasing hydrocarbon with depth trend is contrary to the decreasing concentration with depth trend demonstrated by the discrete interval well types for all hydrocarbon parameters and the expected decreasing hydrocarbon concentration with depth for a LNAPL contaminant. This suggests that the diffusion samplers are not collecting samples representative of the discrete depth intervals over which they have been installed.

- At Well Cluster 35 (Site 2), the diffusion sampler hydrocarbon results demonstrate a decreasing concentration with depth trend, which is expected for the LNAPL contaminant at this site. Although the difference in hydrocarbon concentrations is not clearly significant (RPD >60%) based on RPD values ranging from 20% to 46% (Table F16), these results reasonably match the differences measured by the drive point wells (DP1 and DP2) over similar depth intervals (RPD ranging from 18% to 53%). This is most apparent for the benzene (Figure G45) and PHC F1-BTEX (Figure G48) results. Considering the cation and anion results also closely match (RPD <26%, except sulfate), this suggests that the diffusion samplers may be collecting representative discrete interval samples.

  It must also be considered that wells ML1 and ML2 have considerable hydrocarbon concentration differences over similar sample depth intervals that are not observed for the diffusion sampler results, with the RPD values for the diffusion samplers and ML1/ML2 indicating this significant variability (RPD ranging from 12% to 187%). Also the diffusion samplers measure increasing metal concentrations with depth, contrary to the expected decreasing trend for a LNAPL contaminant and the trend that the discrete interval wells indicate. This information, and the fact that the differences of the diffusion sampler concentrations over both depth intervals is not clearly significant (RPD <60%) for all parameters, brings into question if the diffusion samplers are able to collect representative discrete interval samples.

3.4.2.1.5 BarCad System (BESST, Inc.)

The BarCad System's ability to collect discrete interval samples was assessed in this field study by situating it at two different depth intervals within a 3 m screened well. After determining that the shallow installation could collect samples from any depth throughout the 3 metre screen interval and was not collecting a discrete interval sample (two sample depth intervals only conducted in October at Site 1), only the deeper sample interval was sampled during the other sampling events. Due to freezing temperatures making sampling difficult, no samples were collected in February. A Waterra sample MW2 was collected from the same well for comparison at both sites. The trends in the data are as follows.

1. When the BarCad System was installed over two depth intervals in the same 3 m screened well (October, Site 1), it failed to demonstrate the ability to collect representative discrete interval samples.
    - The BarCad cation and anion concentrations are similar for both depth intervals, as the RPD values vary by less than 24% (Table F1 and F2). This is most apparent for sodium (Figure G3) and sulfate (Figure G5), where discrete interval well results vary significantly over similar depths in comparison to almost identical BarCad results.
    - Although the BarCad metal and hydrocarbon results (RPD ranges up to 168%, Table F3 and F4) appear to have significant

variability (RPD >60%), both measure an increasing concentration with trend that contradicts the discrete interval wells decreasing trend, which is expected for the LNAPL contaminant at site. The elevated deeper BarCad sample always appears representative of the shallowest discrete interval well type that intersected the water table. This inability to collect representative discrete interval samples is most apparent for ethylbenzene (Figure G10), total xylenes (Figure G11) and PHC F1-BTEX (Figure G12) results.

- Unfortunately a Waterra sample was not available for comparison from the same well that the BarCad System was installed in to determine if the BarCad samples are representative of the well from which they were collected.

2. When the BarCad System was only installed at the lower depth interval (Site 2), it failed to collect a sample representative of the depth interval over which it was installed. However, the BarCad results closely match with the Waterra sample from the same well, indicating that the BarCad collects a sample representative of the well it was installed in.

   - At Well Cluster 34 (Site 2), although the BarCad cation and anion results reasonably matches (RPD <15%, Table F9 and F10) the discrete interval wells for most parameters (except calcium and sulfate), the metals and hydrocarbon results are elevated for the depth interval at which it was installed and vary significantly (RPD ranges 45% to 195%, Table F11 and F12) from the discrete interval well results over similar depths (ML3, ML4 and DP3). This inability to collect a representative discrete interval sample is most apparent for ethylbenzene (Figure G34), total xylenes (Figure G35) and PHC F1-BTEX (Figure G36), as the BarCad concentrations are two times to over one order of magnitude higher than the ML3, ML4 and DP3 results.

The BarCad cation, anion and metal results closely match the Waterra sample MW2 from the same well (RPD <38%, Table F9, F10 and F11), which indicates that the BarCad is collecting a sample representative of the well it was installed in. Although the hydrocarbon results are more variable (RPD ranges from 12% to 88%, Table F12), the BarCad measures higher concentrations representative of a shallow interval near the water table and reasonably matches the higher concentrations measured by the conventional 3 m screened wells. The benzene (Figure G33) and PHC F1-BTEX (Figure G36) results for the BarCad and Waterra sample MW2 most clearly demonstrate for the hydrocarbon results that the BarCad is collecting a sample representative of the well, especially since these sampling methods from the same well measure the two largest PHC F1-BTEX concentrations.

- At Well Cluster 35 (Site 2), the BarCad results match poorly with the discrete interval well results over similar depth intervals (ML3 and DP3) for almost all parameters measured, with the RPD values ranging from 11% to 196% (Table F13, F14, F15 and F16). This is most apparent in the elevated BarCad metal and hydrocarbon results for the depth interval at which it was installed, where BarCad results are one and half times (PHC F1-BTEX, Figure G48) to over two order of magnitude (benzene, Figure G45) higher than the discrete well type ML3 and DP3 results. This appears to indicate that the BarCad is collecting groundwater from near the water table, as the higher BarCad metals and hydrocarbon concentrations are representative of trends expected for groundwater in close contact with the LNAPL contaminant.

Other than iron results that reasonably match (RPD of 52%), the BarCad cation, anion and metal results closely match the Waterra sample MW2 from the same well (RPD <20%, Table F13, F14 and F15), which indicates that the BarCad is collecting a sample representative of the well in which it was installed in. This match is most prominent for the sulfate (Figure G41) and iron (Figure G44) results because these results match closely considering the wide range of concentration variability measured by all technologies (two to four orders of magnitude). With the exception of a lower BarCad PHC F1-BTEX result, the BarCad and Waterra sample MW2 reasonably match (RPD <39%) and provide further support that the BarCad is collecting a representative sample from the well. Although the BarCad PHC F1-BTEX result is a third of the Waterra sample MW2 from the same well, this difference is likely insignificant considering that the concentrations measured for this parameter ranges over two orders of magnitude.

3.5 DISCUSSION

3.5.1 Interpretation of Well Construction Impacts

A typical monitoring program often involves the use of conventional three-metre screen monitoring wells for collecting groundwater samples. The well construction in this application was similar for each well, and the well screen existed over a deep groundwater interval, therefore the bentonite seal impacts in this application would likely be minimal and undetected. In this research, different well types were installed, therefore the method of well construction may have a more notable impact on the sample results obtained. Bentonite pellets were used to create a seal to the surface above the sand annulus that surrounds the well screen for all wells, except the drive point wells, so this material was of greatest interest since it was in direct contact with the groundwater that was sampled.

The impact of bentonite seal material on water geochemistry was investigated because the multilevel wells measured unexplainably elevated concentrations for several MNA parameters. As many of the factors known to cause variability were minimized (i.e., spatial, temporal, etc.), the observed impacts were likely associated with the well construction details for the different well types. As a result, the bentonite seal materials used to create the discrete sample intervals were tested to assess the extent that these materials may have influenced the geochemistry of pore water in direct contact with the bentonite.

The laboratory experiment found that sodium and sulfate dissolution from the bentonite pellets results in very high concentrations in the water adjacent to the bentonite. Bicarbonate, calcium, chloride and iron were also measured at concentrations that may notably impact sample results. Molar ratio calculations of the cation and anion concentrations collected during the bentonite laboratory experiment indicated the strongest speciation was sodium sulfate (molar ratio of 0.95).

The multilevel well's unique well construction allows multiple depths to be sampled within a single borehole by means of careful placement of sand intervals and bentonite seals. In this research program, typically the bentonite seal between the sand pack sample intervals was 0.4 metres (Figure 3.1). The typical sand pack height around a port was 0.6 metres, however in some instances the sand pack was as small as 0.15 metres high (Site 2, Cluster 34, ML4). Thus the volume of water within the sand interval around each multilevel port was small, therefore this volume may not adequately dilute the elevated ion concentrations from the bentonite pellets.

The volume of groundwater in the typical 0.6 m sand pack around the multilevel well was approximately 4.02 liters (see Sand Pack and Well Volume Calculation in Appendix E for details), whereas the largest well volume for a multilevel well was 0.45 Liters (ML4, Site 2 Well Cluster 35) and the smallest was 0.050 Liters (ML1, Site 2 Well Cluster 35). The act of purging three well volumes from the small multilevel well channel's volume (0.45 L x 3 = 1.35 L for largest well volume) would only draw in sample water from the sand pack around the port, which may contain elevated ionic concentrations from being in contact with the bentonite seal material. In the case of the largest well volume (0.45 L), a total of 9 well volumes (4.02 L in sand pack ÷ 0.45 L in well = 8.93 ≈ 9 well volumes) would need to be purged in order to completely remove the volume of impacted water (4.02 L typically) within the sand pack and draw in representative groundwater from the adjacent formation. As this is for the largest well volume, the other multilevel wells would require even greater well volumes be purged to remove the bentonite impacts (4.02 L in sand pack ÷ 0.050 L in well = 80.4 ≈ 81 well volumes for the smallest well volume).

The multilevel wells at most locations measured elevated ion concentrations compared to the other well types, especially for sodium and sulfate. This was most apparent at Site 1, where the background concentrations for these parameters were relatively low in the groundwater. Molar ratio calculations of the elevated ion concentrations measured at many multilevel well locations demonstrate strong speciation between the sodium and sulfate, likely indicating that the elevated concentrations are the result of bentonite seal impacts.

It is believed that as the bentonite hydrated, the ions in the bentonite are released into the groundwater that fills the pore spaces. The dissolution creates a concentration gradient between the elevated concentrations within the pore spaces and the low concentrations in the adjacent groundwater within the sand pack around the sampling port. This diffusive gradient causes ions to move into the sand pack annulus and elevate the groundwater concentrations being measured for that sample interval. This is believed to be responsible for the elevated inorganic concentrations measured by the multilevel wells in this research program.

At the research sites in this study the groundwater flow was very slow, < 1 to 5 m/year, which exacerbates the elevated concentration problem because the dissolved ions released from the bentonite were not readily flushed from the sand annulus around the well screen. It is expected that over time the inorganic results for the multilevel wells will drop to the levels measured by the other well types, as the finite mass of ions in the bentonite will be depleted by the groundwater that passes through the sand pack. This trend was most evident at Site 1, with the sodium and sulfate impacts at the most elevated multilevel well (ML2) measured a decline in concentrations since the well's installation. The sodium most clearly demonstrated the dissipating inputs over time, as the concentrations decreased by a half at each sample event from 167 mg/L in August, to 83 mg/L in October to 46 mg/L in February. The decreasing trend was also noted for ML4 at this site.

Also for most ports, except the bottom port, the sample volume within the sand interval was impacted by the bentonite seal both above and below it, thus increasing the likelihood that the sample being collected was impacted by the elevated concentrations coming from the bentonite. Comparatively the three-metre screen well had 3.3 metres of sand with 30 centimetres of bentonite pellets above it, so dissolved ions from the bentonite would be diluted by the large volume of water in the sand pack around the screened interval.

The multilevel well dissolved ion concentrations from the field tests were not elevated to the extent measured in the laboratory experiment. Ion dissolution from the bentonite is a slow process, so the rate of groundwater flow through the discrete interval sand pack controls the bentonite impacts on the ion results. In the laboratory study the deionized water was in continual contact with the bentonite pellets, which allowed more complete ionic equilibrium to be reached between the two materials.

This would suggest that a multilevel well sample interval that has slower groundwater movement through the sand pack should measure higher dissolved concentrations compared to an interval with a faster groundwater flow rate. This was observed at Site 1, where ML2 sodium and sulfate concentrations were over three times larger than the other multilevel wells. During purging and sampling of the multilevel wells, ML2 recharged at a much slower rate. Two days was often required to collect the minimum sample volume necessary for the suite of laboratory analysis, whereas the other wells could be sampled the same day as purging.

In some instances, ionic concentrations sampled by the multilevel wells were higher than the concentrations in the laboratory study. This was observed in October for ML2 at Site 1, where the calcium concentration was close to double the other multilevel wells. The laboratory experiment indicated a 16.8 mg/L increase in calcium, whereas the field data appeared to be elevated by approximately 35 mg/L compared to the other concentrations measured. As ML2 had bentonite above and below the sample interval, the groundwater sample collected from the sand annulus may be impacted by both seals and result in higher ionic concentrations being measured. It is also possible that the calcium increase could be the result of the higher calcium concentrations that exist within this depth interval. The sulfate concentration is also elevated at ML2, so a possible source may be gypsum dissolution from snowmelt or introduction into this interval during well construction.

Molar ratio calculations using the ion concentrations do not indicate strong speciation between calcium and sulfate, however since high concentrations of sulfate are introduced by the seal material, this likely puts the molar ratio out of balance. The exact reason for the higher ionic concentrations, in this case calcium, cannot definitively be determined. It is likely that one of these possibilities, or a combination of them, is responsible for the unexpectedly elevated ion results.

The findings of this study demonstrate how well construction can have an unanticipated impact on the sample results obtained. The different size sand packs where samples were collected is the likely explanation for the multilevel wells sample results being noticeably impacted, while the three-metre screen wells are not. As the multilevel well inorganic results are elevated in many cases, likely due to bentonite impacts, the variability in the multilevel inorganic sample results (especially cation and anion) will not be discussed further during the comparison of the discrete interval well types. As it is expected that the bentonite would not have any direct influences on organic concentrations, the multilevel wells hydrocarbon results are discussed. However, it must be considered that the elevated sulfate concentrations provided by the bentonite seal material may act as additional terminal electron acceptors for sulfate reducing microbes that breakdown the dissolved hydrocarbon constituents in the immediate vicinity of the well.

3.5.2 Summary of General Findings from Sampling Results Comparison

The key findings observed for the various sampling technologies studied in this field research program are:

i. In most instances the multilevel and drive point wells measure changing concentration profiles with depth, with the metals and hydrocarbon results typically decreasing with depth.

ii. The multilevel wells measure higher concentrations of inorganic constituents compared to the other well types, most notably for sodium and sulfate concentrations.

iii. There is considerable variability between the conventional well type results for the sulfate, metals and hydrocarbon results (key parameters of interest in a MNA program); this is most notable at Site 2 where the conventional well types appears to represent different sample depth intervals.

iv. The cation and anion results for the three-metre screened conventional wells appear to be representative of mixing of the entire sample interval over which the well screen is installed, however the metals and hydrocarbon results are typically representative of the upper portion of the well screen.

v. The highest hydrocarbon concentrations, and in most instances the metals, are measured in the wells where the water table intersected the well screen. Typically the conventional well types measure the highest concentrations compared to the alternative well type technologies.

vi. At Site 1, the diffusion samplers measure concentrations similar to the common sample collection results from the same or adjacent wells and do not demonstrate discrete interval sampling, as the diffusion samplers have almost identical concentrations for the different depth intervals over which the samplers were installed when the discrete interval well types demonstrated differences.

vii. At Site 2, the diffusion samplers measure concentration differences for the sample depth intervals investigated; having similar concentrations to the discrete interval well types installed over similar depth intervals. Many parameters have depth dependent trends based on differences in the diffusion samplers results for the two depth intervals over which the samplers were installed, which appears to indicate the diffusion sampler's ability to collect depth discrete samples.

However, the depth trends in the diffusion sample results are contrary to the trends expected within a LNAPL plume (iron and hydrocarbon results for Well Cluster 34) and the variability observed in the diffusion sampler results over the two depth intervals are within the acceptable range for duplicate sample results for most parameters. This provides contradictory evidence that the differences in concentration over the two sample depth intervals is the result of variability in sampling these parameters and may not be the result of the diffusion samplers ability to collect depth discrete samples.

viii. The Site 2 diffusion sampler's results reasonably match the common sample collection results for the same or adjacent wells for most parameters; indicating the diffusion samplers collected samples representative of the well in which the samplers were installed.

ix. In the only sampling event where the BarCad System collected samples from different depth intervals (October at Site 1), the BarCad System was unable to demonstrate the ability to collect discrete interval samples. This is also supported by the BarCad

System results varying considerably from the results of the discrete interval well types collected over similar sample depth intervals in the other sampling events.

x. The BarCad System results closely match the common sample collection results from the same well for most parameters measured in this study; this is most notable for Site 2.

3.5.3 Comparison of Sampling Technologies Results

This section provides generalized comments on the material presented in Section 3.4.2.1. The subsections discussed below mirror that used in Section 3.4.2.1, such that the results material used to develop the following discussion material can be referenced in Section 3.4.2.1 and is not presented again here.

3.5.3.1 Inherent Variability of Groundwater Geochemistry

Characterizing and understanding the trends of the geochemical parameters of interest in a natural attenuation program is complex and challenging. Even though wells were installed in a one-metre radius cluster, there is still notable variability in some of the field data. This is underscored by the variability of chloride concentrations measured at each well cluster, as chloride is a stable ion with low reactivity that is not expected to vary significantly laterally or with depth. In most cases, this variability was likely due to vertical concentration differences. In a few other cases, it was likely due to horizontal heterogeneity inherent in the stratigraphy.

Existing borehole logs indicate that the wells were installed in uniform formations (silty clay at Site 1 and silt at Site 2). However, the geochemistry measured in each well indicates narrow, discontinuous, and highly conductive layers that intersect the well screens. The layers also vary in depth within the well clusters. Thus, some sample results may be influenced by several layers. It is difficult to conclude if data variation is due to inherent variability in the subsurface or to limitations in sampling technology.

Although both sites indicate expected natural attenuation trends, Site 2 better demonstrates expected plume trends. Wells at Cluster 35 measured the highest hydrocarbon concentrations, indicating that they were near the leading edge of the LNAPL contaminant plume. The corresponding increase in metals and decrease in sulfate, which are terminal electron acceptors during microbial degradation, are both observed at this location. Well Cluster 34 measures lower hydrocarbon concentrations because it is further downstream in the plume. As expected, metals concentrations are correspondingly lower and sulfate concentrations higher than in Well Cluster 35. The accurate characterization of such trends is vital to demonstrating that natural attenuation is effectively remediating the plume.

3.5.3.2 PrePak Drive Point Wells (GeoInsight)

The drive point wells best demonstrate decreasing hydrocarbon concentrations with depth at both sites, and thus the ability to collect representative discrete interval samples. The trend is most evident at Well Cluster 35 (Site 2) where hydrocarbon concentrations decrease by one to two orders of magnitude over the different sample intervals. The corresponding decrease in iron concentrations with depth is also clearly demonstrated. The drive point well's most obvious demonstration of discrete interval sampling was at Site 1, where the deepest drive point well (DP4) was found to be sampling from a different aquifer than the other well types in the cluster. The ability to isolate the different aquifer was determined when water levels dropped in the drive point well, and in no other wells in the cluster, during a pump down test on another deep well located approximately five metres away. This well's geochemical trends were also very different, further supporting this finding.

Unlike the multilevel wells, the drive point wells were not impacted by bentonite seal construction because they have prefabricated bentonite seals that were separated from the sample interval by a foam bridge. This yields representative results for the cation and anion parameters and the development of accurate trends over depth.

The drive point wells intersecting the water table measured lower PHC F1-BTEX concentrations than the three-metre screened wells. A probable explanation is the drive point screened intervals do not intersect the entire depth that the three-metre screened wells do. It is therefore possible that the drive point wells do not intersect all the same conductive layers, resulting in lower hydrocarbon concentrations. However, the exact reasons are difficult to determine based on the lack of historical field data for comparison.

3.5.3.3 CMT Multilevel Wells (Solinst)

The multilevel well data illustrates the extent to which bentonite placement during well construction can impact results. A laboratory study of the bentonite seal material used in the field research indicated that significant concentrations of some ions were dissolving from the bentonite into the adjacent water. Most elevated were sodium and sulfate, with calcium, iron, bicarbonate and chloride dissolving at notable concentrations too. Although accurately measuring all the above-mentioned parameters is important, the sulfate is of greatest concern as it is a geochemical indicator of natural attenuation.

Elevated sulfate concentrations can obscure the extent of the microbial activity, and can also act as a terminal electron acceptor in the microbial degradation of hydrocarbons. This may result in non-representative, lower hydrocarbon concentrations due to enhanced hydrocarbon degradation.

The most likely reason for the multilevel well cation and anion results being notably impacted, while the other well types are not, is the small discrete sampling intervals that can be created using this well type. This small sample volume within these discrete intervals, combined with low on-site groundwater flow, does not displace the dissolved ions that diffuse into the sample volume from the bentonite seal material. This results in elevated cation and anion concentrations compared to most of the other wells. The bentonite seal impacts on sample results were most apparent at Site 1, where groundwater flow rates were slower and background sulfate concentrations were lower.

In some circumstances, where background ion concentrations are high enough not to be obviously skewed by bentonite seal impacts (Site 2), the multilevel wells collect representative data and sample discrete interval concentration changes. At both sites, these wells demonstrate obvious decreasing trends in iron and hydrocarbon concentrations with depth. They sampled isolated discrete intervals at Well Cluster 35 (Site 2), where ML4's geochemical parameters did not follow the trends established by the other discrete interval well types, indicating installation at a depth interval with different geochemistry (similar to that of DP4 known to be in a separate confined aquifer).

The multilevel well sample intervals intersecting the water table measure benzene, ethylbenzene and total xylenes concentrations similar to those from the conventional 3 m screened wells, however PHC F1-BTEX concentrations are considerably lower at most well clusters. This is most apparent at Site 2, where PHC F1-BTEX concentrations are five times lower than the conventional wells. When the multilevel well is compared to the drive point wells over similar depth intervals, the PHC F1-BTEX concentrations are almost identical at both sites. This is probably due to the small multilevel well sample intervals not intersecting the most conductive layers that carry the higher hydrocarbon concentrations. As the conventional well screen was continuous over three metres, it likely does so and thus provides higher values.

Although the multilevel and drive point wells often measure comparable concentrations over similar depth intervals, the former has one additional limitation with respect to discrete interval sampling. Because it was installed in a single borehole, enough bentonite had to be placed to create a proper seal that will prevent discrete sample intervals from being interconnected. Thus, some depth intervals were not sampled, possibly missing the most conductive layer.

In comparison, the drive point wells were installed in separate boreholes. Thus, the direct push well screens can be installed in a cluster to overlap and capture any conductive layers in the subsurface. Being able to sample the entire depth improves the ability to determine concentration profiles, which are key requirements for detailed understanding of a site's natural attenuation processes.

3.5.3.4 Conventional Well Types & Common Sample Collection Methods

The data from conventional well types and common sample collection methods indicate an averaging effect of the input of several conductive layers intersecting the well screen or represent only a particular portion of the formation that the 3 m screen intersects. The conductive intervals with the highest concentrations dictates what depth interval the well appears to be sampling for the various parameters measured and it may appear that the well is representative of different depth intervals depending which parameter is being reviewed. This is apparent in the Waterra samples from Well Cluster 34 (Site 2), which indicate the 3 m screened wells (MW1 and MW2) are collecting samples representative of deeper formations. However, these wells still measure high iron and hydrocarbon concentrations, representative of shallow intervals.

At both sites, the 3 m screened wells have the highest metals and hydrocarbon constituent concentrations. In most cases, this demonstrates the inability to assess the concentration gradient across the entire depth of the well screen. Discrete interval sampling technologies indicate that iron and hydrocarbon concentrations decrease with depth and that the metals and hydrocarbon concentrations measured by the 3 m screened wells are representative of a small upper portion of the well screen. Therefore, unless alternative discrete interval sampling technologies are implemented, it is difficult to determine whether inherent variability in the sampling methods is responsible for the differences in results or if the samples are from different depths within the subsurface where concentration gradients may exist. The 3 m screened wells fail to determine the depths to which hydrocarbon impacts are occurring, whereas this can be determined by the discrete interval well types.

This demonstrates the necessity of effective discrete sampling technologies to clarify trends in data and the variability that is occurring between the common sample collection methods. Without them, data variability makes detailed understanding of contaminant distribution and the geochemical processes very difficult. A more general understanding of natural attenuation over site-scale distances can however still be developed using these conventional well types.

3.5.3.5 Dialysis Membrane Diffusion Sampler

The dialysis membrane diffusion sampler's ability to accurately characterize cation and anion concentrations at depth is dependent on the stratigraphy and groundwater flow rates of a site. As the samplers were generally installed in 3 m screened wells in uniform stratigraphy (Silt and silty clay at Site 1 and silt at Site 2), the cation and anion geochemistry is often similar throughout the interval.

However, the field research demonstrates that groundwater flow rates have the greatest effect on accurate sampling of cation and anion concentrations. The seals used to create the discrete sample intervals homogenized the well volume during installation. As flow rates (less than 1 to 5 metres/year) were insufficient to displace the homogenized well volume over the period that the diffusion samplers were installed, the samples were taken from the same homogenized ground water and show similar concentrations for the different depth intervals. This is most evident at Site 1, since groundwater flow rates were slowest. The cation and anion concentrations measured in October and February are nearly identical for both depth intervals, even though the discrete interval well types indicate differences over similar depth intervals.

However, if the diffusion samplers are carefully installed and the discrete intervals intersect layers with higher conductivity, they can collect representative samples and demonstrate discrete interval sampling. This was the case for Well Cluster 34 at Site 2, where the diffusion samplers demonstrated increasing cation and anion concentrations with depth. This was also measured by the discrete interval drive point wells. The diffusion sampler results are representative of their depth interval, as the diffusion cation and anion results (except those for sulfate) match closely with the drive point well (DP2) and multilevel well (ML2) installed over a similar depth interval.

The ability to collect representative metals concentrations in the groundwater, and demonstrate discrete interval sampling, is controlled by the amount of dissolved oxygen in the diffusion sampler at installation, and the installation duration. The dissolved oxygen in the diffusion samplers reacts with dissolved metals as the groundwater enters the dialysis membrane. This causes the metals to oxidize and precipitate out of solution, resulting in the measurement of non-representative, low metals concentrations. Eventually the iron will entirely consume the finite oxygen in the membrane, and the dialysis membrane will equilibrate, allowing collection of a representative dissolved metals sample.

However, this did not occur at the sites because slow flow rates provided insufficient groundwater for equilibration over the installation period. Thus, the dissolved oxygen concentrations in the membrane were not overcome. Depending on the initial concentration of dissolved oxygen in the membrane and the groundwater flow rate, various degrees of equilibration were observed for the diffusion sampler's metals results. Partial equilibration is evident in the February results at Site 1 and for Well Cluster 34 at Site 2, as metals concentrations measured by the diffusion samplers are approximately half those measured by the Waterra sampler from the same well and the other common sample collection methods at those well clusters.

Groundwater metals concentrations also affect accurate metals sampling using the diffusion samplers, as higher concentrations more quickly consume the dissolved oxygen in the dialysis membrane. This was the case for Well Cluster 35 (Site 2) at the leading edge of the condensate plume where metals concentrations were the highest of all locations studied. The iron concentrations measured there by the diffusion samplers demonstrated the most iron equilibration of all the metals samples collected by the diffusion samplers at both sites.

The metals results measured by the diffusion samplers at all locations illustrate the importance of maintaining low dissolved oxygen levels in the dialysis membrane prior to installation if equilibration times are a limiting factor. Lower dissolved oxygen means that fewer metals must be consumed before equilibrium is achieved and a representative sample is collected. This is most critical in low flow situations because consumed metals are not replenished quickly enough to consume the dissolved oxygen, yielding lower metals concentrations.

The ability of the diffusion samplers to characterize hydrocarbon concentrations over depth is similarly dependent on the groundwater flow rate. Because the well volume is homogenized by the mixing of seals during installation, the groundwater flow rate within the created discrete depth interval must be sufficient to displace the homogenized well volume. As the groundwater flow rate was slowest at Site 1, the hydrocarbon results measured by the diffusion samplers were nearly identical for both sampling depths even though the discrete interval wells clearly demonstrated decreasing hydrocarbon concentrations over this depth. The ability to collect discrete interval hydrocarbon concentrations was more apparent for Well Cluster 35 at Site 2, where the diffusion samplers demonstrated decreasing hydrocarbon concentrations with depth and had concentrations closely matching the drive point wells that were installed over similar depth intervals.

The diffusion samplers appear to not effectively measure PHC F1-BTEX concentrations, as they always measured concentrations less than 2 mg/L when the results for the 3 m screened wells are several times larger. The exception is the October sampling event at Site 1, because PHC F1-BTEX concentrations measured by the bailer are lower during this sampling event (2.1 mg/L). In this situation, the diffusion samplers and other shallow discrete interval well types have similar PHC F1-BTEX concentrations. A possible explanation for low PHC F1-BTEX concentrations for the diffusion samplers during most sampling events may be that the pore size of the dialysis membrane is too small to allow the larger F1 hydrocarbon molecules to fully equilibrate within the short installation times.

3.5.3.6 BarCad System (BESST, Inc.)

Due to the complexity of collecting samples using the BarCad system, limited on-site data was collected to assess its ability for discrete interval sampling within 3 m screened conventional wells. It should be noted that the BarCad System is primarily intended to remain at a dedicated discrete depth interval by placing a sand annulus around the ceramic filter at the desired depth and using bentonite or cement to seal it there. It is not usually intended to create a discrete sample interval within an existing 3 m well screen.

Cold weather prevented collection of February BarCad data at Site 1. Only a deep BarCad sample was collected at Well Cluster 34 and Well Cluster 35 in October (Site 2). It was determined that the BarCad system cannot create a shallow discrete sample interval unless a packer is installed beneath the ceramic filter, as the shallow sample could come from any interval along the three-metre screen below. As a result, only a deep discrete interval was sampled by placing the filter at the bottom of the well and using the packer above to attempt to create a discrete interval within the three-metre screen. However, as the packer can only create a seal within the well itself and not within the adjacent sand annulus, the groundwater from above the packer can migrate through the sand pack. This can prevent the creation of a discrete interval within the screened portion of the well unless the sampling rate is equal to or less than the recharge rate.

The field research clearly demonstrates that groundwater flow rates control the ability to sample discretely within the three-metre screened portion of the conventional well. The BarCad system sampled by applying compressed gas, but low flow formations like those at both sites do not have sufficient recharge volume to allow this. Applying compressed gas to the sealed head space forces readily available groundwater above the packer to be drawn down through the sand annulus, hindering discrete interval sample collection. As groundwater moves through the sand annulus, samples are collected from the same conductive layer(s) that would be sampled by common sample collection methods, and are independent of the depth interval established by the packer. As a result, concentrations are similar for any sampled depth interval and are similar to Waterra samples collected from the same well.

The field data at both well clusters demonstrate similar concentrations for the different depth intervals investigated. A comparison of the BarCad results for the various parameters to those from the discrete interval wells indicates that the BarCad results are clearly representative of a deep conductive layer at Site 1 and an intermediate layer for Well Cluster 35 at Site 2. Groundwater within the well moving through the sand annulus during sampling is most evident in the BarCad hydrocarbon results at Site 1 when two depth intervals were attempted within the 3 m screen. The higher BarCad concentrations being measured by the deeper interval, representative of a sample collection from groundwater near the water table, is likely from the sample being drawn down within the sand annulus from near the water table. This occurs because the low groundwater flow rates at this site cannot provide water at a sufficient rate to prevent draw down within the well and sand annulus.

The well recharges before the shallow sample is collected, as the BarCad equipment must be cleaned between sample collections to prevent cross contamination. During this time, the well is likely recharged by groundwater from the more conductive layer in the deeper portion of the well screen where hydrocarbon concentrations are lower, diluting the well's hydrocarbon concentration. This results in lower hydrocarbon concentrations being sampled by the shallow BarCad sample and an increasing hydrocarbon concentration with depth trend, contrary to that expected for a LNAPL contaminant.

Based on this data and these site conditions, the BarCad system does not conclusively demonstrate effective discrete interval sampling from within the three-metre screened portion of a conventional well. However, at Site 2 the BarCad System does collect samples representative of the 3 m screened well in which it is installed.

3.6 CONCLUSIONS

The following outlines the conclusions of the field sampling program.

3.6.1 General

i. Subsurface geochemical conditions at hydrocarbon impacted sites were complex, making natural attenuation difficult to detect and characterize.

ii. Even when lateral distances between wells were small, inherent heterogeneity over these small distances can lead to variability in sample results.

iii. Although formation geochemistry was expected to be similar over its depth, narrow, discontinuous, highly conductive layers control the results obtained.

iv. The expected natural attenuation trends for LNAPL contaminants were noted at both research sites.

3.6.2 Conventional Well Types and Common Sample Collection Methods

i. The conventional well types sampled by the common sample collection methods were often representative of a small interval or an average of several conductive layers that the 3 m screen intersected.

ii. For the 3 m screened wells the metal and hydrocarbon results were controlled by the fact that the water table (where LNAPL contaminant concentrations are highest) intersected the 3 m screen.

iii. Although 3 m screened wells did not vertically characterize the groundwater in which they were installed, they could determine when natural attenuation was occurring at a particular sample location.

3.6.3 CMT Multilevel Wells (Solinst)

i. The multilevel wells demonstrated how bentonite seal material used to create discrete intervals can impact sample geochemistry, especially where background concentrations are low and groundwater flow rates are slow.

ii. Although ionic concentrations were impacted in this research, the multilevel well appeared to be able to characterize discrete vertical variations. This was most notable for hydrocarbons, where concentrations decreased with depth at most sites studied.

3.6.4 PrePak Drive Point Wells (GeoInsight)

i. The drive point wells characterized vertical concentration variations for most studied parameters and effectively characterized natural attenuation trends at both research sites.

3.6.5 BarCad System (BESST, Inc.)

i. System complexity made sample collection difficult. The system freezes in cold weather due to intermittent sample retrieval in low flow groundwater systems.

ii. The BarCad system failed to collect discrete interval samples from within a 3 m screen due to the movement of well water through the sand annulus. It did not accurately characterize natural attenuation trends any better than conventional bailer and Waterra samplers from a 3 m screened well.

3.6.6 Dialysis Membrane Diffusion Sampler

i. Because low flow formations did not displace well water homogenized during installation, the diffusion samplers did not demonstrate the ability to collect discrete interval samples in most cases.

ii. During installation, dissolved oxygen concentrations in the diffusion samplers were higher than those in the groundwater formation. This caused unrepresentatively low iron concentration measurements.

iii. Lower PHC F1-BTEX concentrations were measured because these compounds may be too large to pass through the membrane.

iv. Further research is required on these two outstanding issues before this technology can be widely adopted.

v. With faster groundwater flow rates, the diffusion samplers yielded more representative discrete interval samples and better characterized natural attenuation trends.

Dialysis membrane diffusion samplers and GeoInsight drive point wells show promise for distinguishing between situations where natural attenuation can be used and where conventional remedial approaches are more appropriate. Such technologies are necessary to maximize the appropriate use of natural attenuation in the province of Alberta.

3.7 REFERENCES

Aller, L. and Gardner, S. 1993. Well design, construction and development. U.S. Environmental Protection Agency Ground Water Sampling – A Workshop Summary. Dallas, Texas. EPA/600/R-94/205. pp 72-81.

Azadpour-Keeley, A., Russell, H. and Sewell, G.W. 1999. Microbial processes affecting monitored natural attenuation of contaminants in the subsurface. USEPA Ground Water Issue. EPA/540/S-99/001. 18 pages.

Barcelona, M.J., Helfrich, J.A., Garske, E.E. and Gibb, J.P. 1984. A laboratory evaluation of ground water sampling mechanisms. Ground Water Monitoring Review, Spring: 32-41.

Barcelona, M.J., Helfrich, J.A. and Garske, E.E. 1985. Sampling tubing effects on ground water samples. Analytical Chemistry 57: 460-464.

Barcelona, M.J. and Helfrich, J.A. 1986. Well construction and purging effects on ground-water samples. Environmental Science and Technology 20: 1179-1184.

Bedient, P.B., Rifai, H.S. and Newell, C.J. 1997. Ground water contamination transport and remediation. Prentice Hall, Inc. 604 pgs.

Canadian Council of Ministers of the Environment. 1994. Subsurface assessment handbook for contaminated sites. Report CCME-EPC-NCSRP-48E. Canada. 293 pages.

Chapelle, F.H. and Lovley, D.R. 1990. Hydrogen concentrations in ground water as an indicator of bacterial processes in deep aquifer systems. First International Symposium on the Microbiology of the Deep Subsurface. USEPA: Orlando, Florida.

Connelly, J. 1993. Monitoring well sampling – you can't always get what you want but can you get what you need? U.S. Environmental Protection Agency Ground Water Sampling – A Workshop Summary. Dallas, Texas. EPA/600/R-94/205. pp 43-46.

Houghton, R.L. and Berger, M.E. 1984. Effects of well casing composition and sampling method on apparent quality of ground water. Proceedings of Fourth National Symposium on Aquifer Restoration and Ground Water Monitoring, Columbus, Ohio. May 23-25, 1984. pp 487-490.

Langmuir, D. 1997. Aqueous environmental geochemistry. Prentice-Hall. 600 pages.

Maxxam Analytics. 2003. Quality assurance report. Attachment to analytical data report. 2 pages.

Parker, L.V. 1994. The effects of ground water sampling devices on water quality: a literature review. Ground Water Monitoring Review, Spring: 130-141.

Puls, R.W. and Paul, C.J. 1997. Multi-layer sampling in conventional monitoring wells for improved estimation of vertical contaminant distributions and mass. Journal of Contaminant Hydrogeology 25:85-111.

Puls, R.W. and Barcelona, M.J. 1995. Low-flow (minimal drawdown) ground-water sampling procedures. EPA Ground Water Issue, Office of Research and Development, United States Environmental Protection Agency. EPA/540/S-95/504. 17 pages.

Solinst Canada Ltd. 2000. Case study: expedited assessment of an MTBE release. www.solinst.com. Accessed May 10, 2003.

Thorstenson, D.C., Fisher, D.W. and Croft, M.G. 1979. The geochemistry of the Foxs Hills-Basal Hell Creek aquifer in southwestern North Dakota. Water Resources Research 15: 1479-1498.

U.S. Department of Energy. 2002. SRTC spreadsheet to determine relative percent difference (RPD) for duplicate waste assay results and to perform the RPD acceptance test. Office of Scientific and Technical Information Report WSRC-TR-2002-00055. 6 pages.

U.S. Environmental Protection Agency. 1996. Low stress (low flow) purging and sampling procedure for the collection of ground water samples from monitoring wells. U.S. Environmental Protection Agency Region I – SOP # GW 0001. 13 pages.

Van Stempvoort, D.R., Hendry, M.J., Schoenau, J.J. and Krouse, H.R. 1994. Sources and dynamics of sulfur in weathered till, Western Glaciated Plains of North America. Chemical Geology 111: 35-56.

Vroblesky, D.A. and Chapelle, F.H. 1994. Temporal and spatial changes of terminal electron-accepting processes in petroleum hydrocarbon-contaminated aquifer and the significance for contaminant biodegradation. Water Resources Research 30(5): 1561-1570.

Wiedemeier, T.H., Wilson, J.T., Kampbell, D.H., Miller, R.N. and Hansen J.E. 1995. Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. U.S. Air Force Center for Environmental Excellence: San Antonio, Texas. 295 pages.

Wiedemeier, T.H., Rifai, H.W., Newell, C.J. and Wilson, J.T. 1999. Natural attenuation of fuels and chlorinated solvents in the subsurface. John Wiley & Sons: New York. 617 pages.

Wiedemeier, T.H., Barden, M.J., Haas, P.E. and Dickson, W.Z. 2006. Chapter 9: Designing monitoring programs to effectively evaluate the performance of natural attenuation. Practical handbook of environmental site characterization and ground-water monitoring (Second edition). CRC Press, Taylor Francis Group: New York. Pages 573-637.

Table 3.1 Parameter of Interest Concentrations for Seal Material

	Grout Cement	Chipped Bentonite	Bentonite Pellets
Magnesium (mg/L)	<0.2	5.5	5.0
Calcium (mg/L)	39.5	1.1	16.8
Sodium (mg/L)	2740	191	783
Bicarbonate (mg/L)	4760	<0.5	107
Sulfate (mg/L)	97.2	143	1720
Chloride (mg/L)	8.4	0.3	14.5
Manganese (mg/L)	<0.004	0.037	0.090
Iron (mg/L)	<0.01	13.2	1.26

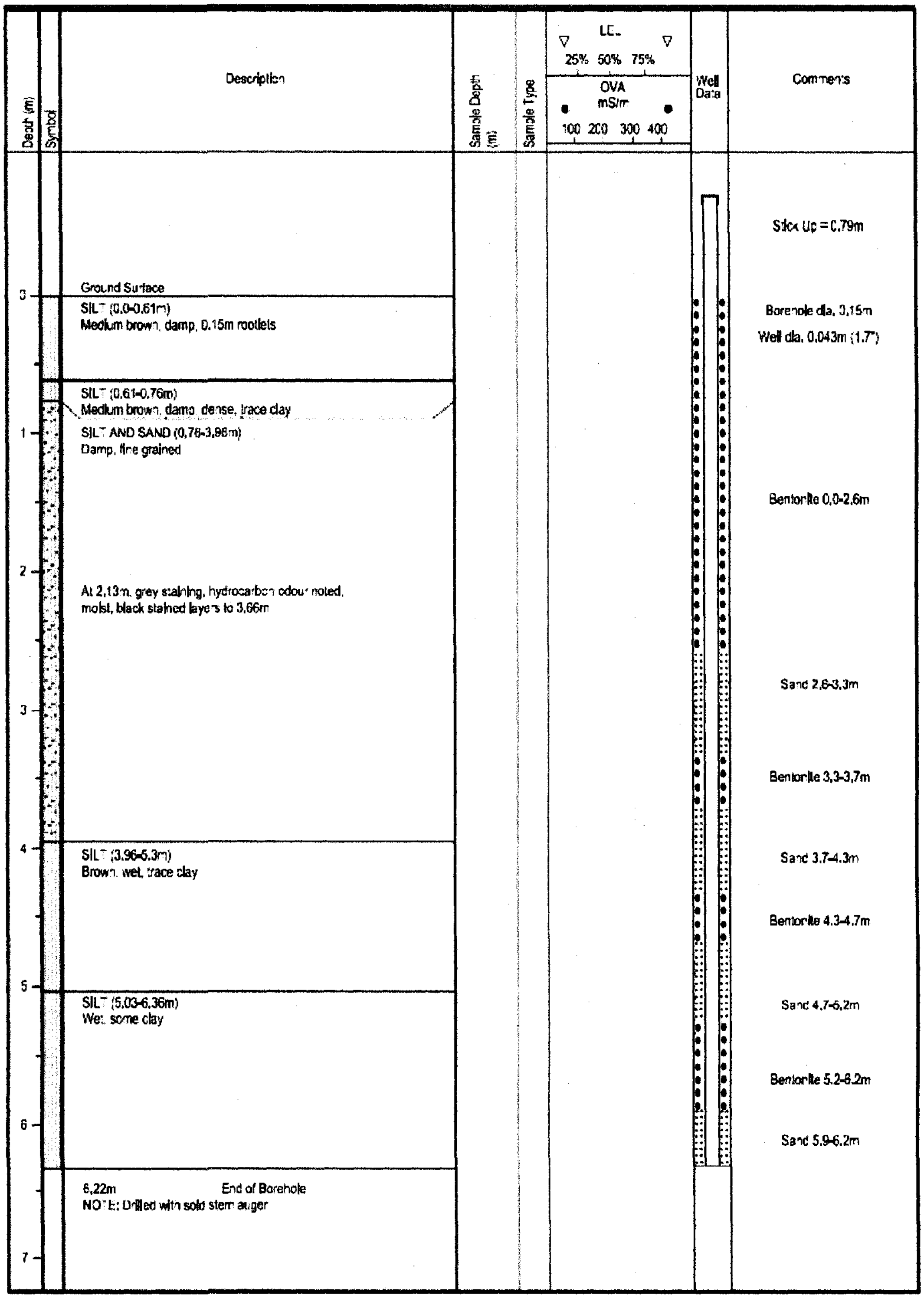


Figure 3.1. Multilevel Well Borehole Log (Site 2, Well Cluster 35)

Chapter 4

Summary of Conclusions for Various Sampling Technologies Research and Recommendations for Future Research

4.1 SUMMARY OF CONCLUSIONS

4.1.1 Laboratory Research

A number of laboratory studies undertaken during this research program increased understanding of the sampling technologies prior to field application. They determined potential causes of variation in analyte concentrations observed in the field data. A summary of the conclusions of each of these studies is as follows. (Note: In this chapter the term "diffusion sampler" refers specifically to the dialysis membrane diffusion sampler and the term "diffusion sampling" to dialysis membrane diffusion sampling.)

4.1.1.1 Dissolved Hydrocarbon Equilibration Study

Most of the previous diffusion sampling research involved sampling inorganic constituents within surface water and sediments, with limited research on organics. Previous organic studies focused on the ability to sample simple hydrocarbon constituents (i.e., volatile organic compounds) within water, however no research had been conducted on larger organic molecules (i.e., petroleum hydrocarbons). Thus, a laboratory study was undertaken to assess the dialysis membrane's ability to sample dissolved hydrocarbon constituents from formation water from one of the field research sites. The integrity of the dialysis membrane was assessed throughout the laboratory study, to ensure that it withstood the possible microbial degradation during installation.

The findings of this laboratory study is outlined in Chapter 2, however a summary of the conclusions is as follows:

- Equilibration for BTEX and F1-BTEX occurred between two and four weeks; at approximately three weeks.
- Visual inspection of membrane integrity indicated no degradation over the six week study.

4.1.1.2 Effect of Monovalent and Divalent Salts

In response to mass water loss from the diffusion samplers during several field applications at the research sites, a laboratory study was conducted to assess ionic charge effects on equilibration time and the impact of salinity concentration on dialysis sampler water loss. It was hypothesized that osmotic gradients caused by higher salt concentrations outside the membrane were drawing water out of the membrane in an effort to reach equilibrium. The detailed findings of this laboratory study are outlined in Chapter 2, however a summary of the conclusions is as follows:

- Both sodium chloride (NaCl) and calcium sulfate ($CaSO_4$) salts equilibrated within the first 24 to 48 hours.
- Water loss due to various NaCl and $CaSO_4$ salt concentration gradients ranged from 5 to 10 percent after 70 days, however this has an insignificant effect on obtaining a representative sample.
- Ionic charge, salt concentration (NaCl and $CaSO_4$) and sampler size had no apparent impact on equilibration time or water loss from the sampler.
- Salt concentrations (NaCl and $CaSO_4$) were not responsible for the water loss observed during the field application.

4.1.1.3 Hydraulic Gradient and Evaporation Study

The diffusion samplers experienced significant water loss when it was partially exposed above the groundwater surface during sampling (due to dropping groundwater levels). It is hypothesized that water loss under these conditions is due to hydraulic head difference and evaporation, so the extent of water loss caused by these two processes was investigated. The findings of this laboratory study is outlined in Chapter 2, however a summary of the conclusions is as follows:

- Partial membrane exposure above the groundwater surface during sampling caused significant water loss in samplers, with evaporation having the greatest impact.
- When a membrane is partially exposed above the water table, wicking action draws the water within the membrane above the water table. The resulting evaporation can cause limited or no sample volume after a 21 day installation. This illustrates the importance of diffusion samplers remaining below the water table for the duration of sampling.

4.1.1.4 Bentonite Seal Material Impacts on Water Chemistry Study

The impact of bentonite seal material on water chemistry was investigated following detection of elevated sulfate concentrations in the multilevel wells at the field research sites. The materials investigated were bentonite grout, chips and pellets, as all were used during field installations of the research site monitoring wells. The bentonite materials were allowed to hydrate with deionized water and then the water was collected and analyzed for numerous inorganic parameters to assess the materials' impact on the results obtained during the field research program.

The findings of this laboratory study is outlined in Chapter 3, however a summary of the conclusions is as follows:

- Each bentonite material was found to have elevated concentrations of a number of the analytes of interest.
- Bentonite pellets (used to seal most of the monitoring wells) had elevated concentrations of cations, anions and iron, adversely impacting their accurate measurement.
  - Concentrations of sulfate, sodium and bicarbonate were most elevated.
  - When background concentrations of magnesium, calcium, chloride, and iron are low, bentonite pellets may impede accurate measurement.
- Elevated sulfate concentrations prohibit accurate measurement of sulfate reduction, which is vital to monitored natural attenuation (MNA).

4.1.2 Field Research

The field research compared two discrete interval well types and two discrete interval sampling methods to conventional monitoring technologies for their ability to collect representative groundwater samples. These comparisons focused on analytes relevant to MNA.

The sampling well types were:

- Solinst Continuous Multi-channel Tubing (CMT) multilevel well
- GeoInsight Prepak drive point well

The sampling methods (collected from a 3 m screened monitoring well) were:

- BESST BarCad System
- dialysis membrane diffusion sampler

To limit sample variability caused by heterogeneity in the subsurface, all sampling technologies were installed in well clusters within one and half metres of each other. What follows is a summary of conclusions reached based on the field data collected from the two research sites, covering all investigated sample technologies.

4.1.2.1 Conventional Well Types and Common Sample Collection Methods

The conventional well type investigated in this field research program was a three-metre screened monitoring well. The well was sampled using two common methods: bailer, and inertial sampling using a Waterra foot valve. Details of the research carried out on the conventional well type and common sample collection methods are described in Chapter 3, however a summary of the conclusions is as follows:

- The conventional well types and sampling methods appeared to indicate an averaging effect of the input of several conductive layers that intersected the well screen at various depths.
- The conventional wells had higher metals and hydrocarbon constituent concentrations compared to all of the alternative sampling technologies, and were representative of the upper reaches of the well screen. This demonstrates an inability to assess the concentration gradient across the depth interval of the three-metre screen well.
- Unless alternative discrete interval sampling technologies are implemented, it is difficult to determine whether variability in results is due to the inherent variability of the sampling methods or if it is because the samples are from different depths within the subsurface where concentration gradients may exist.

4.1.2.2 CMT Multilevel Wells (Solinst)

The CMT multilevel well was selected for its ability to separate up to seven sand pack sample intervals within one borehole using bentonite seals. Details of the research carried out using the CMT multilevel well type are described in Chapter 3, however a summary of the conclusions is as follows:

- The multilevel well field data illustrated the extent to which bentonite placement during well construction impacts the concentrations measured. The most notable impacts were observed for sodium and sulfate.
- The elevated concentrations of sulfate were of greatest concern because these can obscure the sulfate reduction that is one indicator of MNA. If the additional sulfate acts as a terminal electron acceptor, results may show non-representative, lower hydrocarbon concentrations due to potentially enhanced hydrocarbon degradation.
- The small sample volume within the discrete interval, combined with slow groundwater flow at the research sites, did not displace the dissolved ions that diffused into the sample volume from the bentonite seal material, resulting in elevated cation and anion concentrations compared to most of the other wells.
- At locations where background cation and anion concentrations were high enough not to be skewed by the impact of the bentonite seal, the multilevel well demonstrated the ability to collect representative data and can sample discrete interval concentration changes.
- The multilevel wells at both sites demonstrated decreasing concentrations of iron and hydrocarbon as depth increased, thus demonstrating discrete interval sampling.
- Measured concentrations of benzene, ethylbenzene and total xylenes in multilevel wells intersecting the water table were similar to the conventional well type results.

4.1.2.3 PrePak Drive Point Wells (GeoInsight)

The drive point wells were selected because they come pre-packaged with all the materials required to easily create discrete interval sampling wells using readily available direct push drill equipment (i.e., bentonite sleeve, sand pack within a stainless steel mesh, foam bridge, etc.). Details of the research carried out using these well types is described in Chapter 3, however a summary of the conclusions is as follows:

- The drive point wells demonstrated the ability to collect accurate discrete interval samples, definitively measuring the decreasing hydrocarbon concentrations with depth at both research sites.
- The drive point wells were not impacted by bentonite seal construction because they had prefabricated bentonite seals that were separated from the sample interval by a foam bridge. Thus, they measure representative cation and anion concentration trends with depth.
- The drive point wells that intersected the water table had lower PHC F1-BTEX concentrations than the conventional well types.

4.1.2.4 BarCad System (BESST, Inc.)

The BarCad System was selected for its ability to collect discrete interval samples from within a three-metre screened monitoring well while preventing them from coming into contact with the atmosphere. The sample was collected by applying an inert gas to the well headspace. Minimizing atmospheric contact is particularly important for monitoring wells in low recharge environments like both research sites. Sample collection using an inert gas should minimize volatilization of dissolved hydrocarbon constituents during sampling and limit the introduction of oxygen caused by sample retrieval. This should yield more representative hydrocarbon and metals sample results. Details of the research carried out using the BarCad System is described in Chapter 3, however a summary of the conclusions is as follows:

- As the system freezes at ambient temperatures below 0°C, the BarCad System was not used and is not recommended for cold weather sampling.
- A shallow discrete sample interval could not be created by the BarCad system in a 3 m long screen unless a packer was installed beneath the ceramic filter, as the shallow sample could come from any depth

interval along the well screen. Consequently, only deep discrete intervals were sampled by placing the ceramic filter at the bottom of the well with the packer above.

- Where two depth intervals were sampled (Site 1), similar concentrations were observed for the different depth intervals investigated.
- Because the packer can only create a seal within the well itself and not within the sand annulus adjacent to the well screen, the groundwater from above the packer can migrate through the sand pack in such a way that the BarCad System fails to sample discrete intervals within the screened portion of the well.
- Groundwater flow rates controlled the ability to sample discretely within the three-metre screened portion of a conventional well, as low flow formations provided insufficient recharge to allow sampling with this system.
- The BarCad System results were similar to the conventional results from the same well, as the samples were collected from the same conductive intervals.
- Collecting representative volatile hydrocarbon samples was difficult using the BarCad System because they were compromised by an aerosol effect that occurred when the last of the groundwater within the well was delivered with a pulse of the compressed gas.

4.1.2.5 Dialysis Membrane Diffusion Sampler

The diffusion samplers were the only selected technology able to collect time averaged discrete interval samples rather than point-in-time samples. Regenerated cellulose dialysis membrane material was used to fabricate the diffusion samplers because this material had demonstrated the ability to measure dissolved volatile hydrocarbon and dissolved inorganic concentrations in previous research studies.

Details of the research carried out using the diffusion samplers is described in Chapter 2 and 3, however a summary of the conclusions is as follows:

- Accurate measurement of cation and anion concentrations at different depth intervals depends on stratigraphy and groundwater flow rates.
- The seals used to create the discrete sample intervals in the well screens homogenized the well volume during installation, yielding similar results for both depth intervals for most sampled parameters. The low groundwater flow rates at the research sites did not displace the homogenized groundwater during the 21 day installation period.
- The ability to accurately sample metals concentrations in the groundwater appeared to have been controlled by the amount of dissolved oxygen (DO) in the diffusion sampler at the time of initial installation. High DO concentrations within the diffusion samplers may have precipitated out metals through oxidation. This can result in non-representative, low metals concentrations for the diffusion samplers.
- Low groundwater flow rates provided insufficient quantities of metals to consume the initial DO inside the dialysis membrane. Thus, various degrees of equilibration were observed for the diffusion sampler's metals results.
- Results for metals illustrate that:
    - ➢ if metals concentrations are naturally low, or
    - ➢ if groundwater flow rates are too slow to consume initial DO concentrations inside the diffusion samplers,

  it is important to maintain low dissolved oxygen concentrations in the dialysis membrane prior to installation when equilibration times are short.
- The diffusion samplers were able to accurately measure concentrations of dissolved benzene, toluene, ethylbenzene and xylenes (BTEX), however diffusion samplers poorly characterized PHC F1-BTEX where concentrations were higher (greater than 2 mg/L). The pore size

of the dialysis membrane may be too small to allow the larger F1 hydrocarbon molecules to completely equilibrate.

- If the diffusion samplers are carefully installed and the discrete intervals intersect higher conductivity layers, the samplers can collect representative samples and demonstrate discrete interval sampling.
- During the field installation of the diffusion samplers, no degradation was observed in the dialysis membrane of any samplers.

4.2 AUTHOR'S OPINION ON THE APPLICATION OF SAMPLING TECHNOLOGIES

Based on the installation and use of the various sampling technologies, the author provides the following comments for consideration by those considering applying the technologies within a groundwater monitoring program.

4.2.1 Conventional Well Types and Common Sample Collection Methods

The following comments apply to sampling with a bailer or Waterra foot valve from a three-metre screened conventional well.

- Both the bailer and Waterra sampling methods can significantly agitate the groundwater sample if care is not taken during collection. Agitation can cause low metals concentrations due to oxidation and low hydrocarbon concentrations due to volatilization. The way that field personnel collect the sample critically influences the results, which are in turn vital in demonstrating that natural attenuation is effectively remediating the site.
- Dedicated bailer and Waterra samplers should be stored with great care between sampling events. It is not clear what impact leaving bailers or Waterra tubing in the well water between events has on groundwater geochemistry. Bailers should be stored upside down within the well between sampling events. This way, if they fall in, they do not change the water level when retrieved, allowing accurate measurement of groundwater surface elevations.

4.2.2 CMT Multilevel Wells (Solinst)

The following comments apply to the use of the CMT well at both sites.

- The CMT Multilevel well is a continuous tube along which seven sampling intervals can be developed at the desired depths (can be hundreds of feet long). As a result, the tubing is coiled during shipping and storage and is difficult to straighten prior to installation, even after following the manufacturer's direction to lay it flat in the sun. Consequently, in this field research program, the multilevel wells were installed with varying degrees of bend.
- A special tool kit is required to create the sampling ports, and plugs are placed in the continuous tubing to create the discrete sample intervals. This kit must be purchased, as it cannot be rented. Thus, several well installations must be carried out to make the purchase worthwhile.
- Short sample intervals (< 60 cm) require particular attention during sand and bentonite placement, as it is not easy to fix a sample port that has been mistakenly sealed off with improper bentonite placement. For this research program, nylon mesh socks were fabricated and attached to the multilevel well. This ensured that these intervals were properly achieved at the desired depths, since the soil was sloughing in when the well was being placed into the borehole. However, this procedure was very slow and tedious.
- Due to the narrow channels in the well, field personnel must have a narrow diameter water level tape to measure the depth to groundwater. Many of these tapes lack clear sub-centimetre markings (usually half metre intervals), potentially causing inaccurate measurement of groundwater elevations. These measurements are needed to determine groundwater flow direction. The narrow channels also make it impossible to have the water tape and peristaltic tubing in the well at the same time, so drawdown within the well during sampling cannot be monitored.

- The limited diameter of the channels within the multilevel well makes peristaltic pump sampling the only reasonable sampling method for this well type (Waterra foot valves and tubing can be purchased to fit the channels, but such narrow tubing would likely make sample collection difficult). As the peristaltic pump works by putting a vacuum on the groundwater to draw it up the tubing, suction lift limits its use to sampling groundwater shallower than ten metres. This limits the field capabilities of this sampling method and possibly the application of the multilevel well, since this well type does not have many other sampling methods.
- The limited well volume in low flow formations makes it very difficult to conduct sample analysis for the large suite of parameters in a MNA program. This limited volume would also make it very difficult to sample the well using a Waterra foot valve (if this method was selected) because there would be insufficient groundwater to fill the tubing and the water would likely have to be decanted to collect the sample.

4.2.3 PrePak Drive Point Wells (GeoInsight)

The following comments apply to the use of drive point wells at both sites.

- The expanding foam bridge prevents the well from remaining at the intended depth during rod retraction. The rod must be uncoupled, and the well pushed to the intended depth until the foam bridge exits the bottom of the drive rod. This cannot be done in sloughing soils.
- The above noted process of installation makes it difficult to achieve the desired sample depth intervals if the soil is susceptible to sloughing (i.e., coarse grain sands, etc), as the annulus created by the push rods would be filled in by the soil during retraction, and the drive point well could not be pushed to the desired depth.
- Prepak bentonite powder was provided with the drive point wells in a paper sleeve wrapped around the riser pipe. Care was taken when

handling and placing the drive point well into the drive rods during installation, as the paper was prone to tearing.

- The diameter of the drive point wells allowed both the water tape and peristaltic tubing in the well at the same time. Thus, drawdown within the well could be monitored during sampling to ensure that the low flow sampling was drawing water from the formation and not from the well itself.
- Limited well volume (relative to five centimetre diameter, three-metre screened conventional wells) in low flow formations may hinder sample analysis for the large suite of parameters in a MNA program. This was encountered in one of ten drive point wells installed at both research sites. Thus, with carefully monitored low flow sampling, sufficient volume should be available under most groundwater flow conditions.

4.2.4 BarCad System (BESST, Inc.)

The following comments apply to the operation of the BarCad System at both sites.

- As the BarCad System utilizes a compressed inert gas for sample collection (in this case, nitrogen was used), the field personnel must have Transportation of Dangerous Goods (TDG) certification and understand the requirements for storage and transportation of a compressed gas cylinder (i.e., the cylinder must be upright).
- As one BarCad System was used to sample all locations, it had to be carefully cleaned and rinsed between sample collections. The large number of components (ceramic filter, stainless steel sample port, number of tubing connections, etc.) made this difficult and time consuming in the field. Cost permitting, the author suggests dedicating a BarCad System to a single well.
- The sealed headspace of the three-metre screened monitoring well allows sampling using compressed gas, but does not allow monitoring

of drawdown using a water level tape. This results in an aerosol effect during sampling with the BarCad System, possibly causing oxidation of metals and volatilization of dissolved hydrocarbons. The aerosol effect occurs when the compressed gas applied to the headspace reaches the sample port, violently ejecting the groundwater sample as a mist from the end of the sample tubing.

- Two field personnel were often required due to the complexity of the system (several valves that require careful monitoring to prevent the aerosol effect).

4.2.5 Dialysis Membrane Diffusion Sampler

The following comments apply to diffusion samplers created and applied at both sites.

- As diffusion sampling using dialysis membrane was not commercially available, the diffusion samplers had to be fabricated by the author, requiring considerable time prior to field installation. Particular care was taken to ensure the delicate membrane did not tear during fabrication, installation or sample retrieval.
- Despite best efforts to minimize them, DO concentrations can impede accurate metals sampling. This may have to be overcome for diffusion samplers to be effective in future MNA programs.
- Despite design advances during this research, a simpler and more effective method must be developed to extract the groundwater sample from the dialysis membrane to make this technology viable. Protection required around the membrane during installation limits the volume of groundwater that can be collected. A method eliminating waste and spillage is needed.
- The final diffusion sampler design could collect discrete interval samples, but creating discrete installation takes a great deal of time and effort. A simpler design is needed for industry adoption.

- As future research resolves outstanding issues, the author believes that diffusion sampling technology will be effective. Its greatest potential would be in quarterly groundwater monitoring programs, where diffusion samplers are simply replaced every four months and submitted for analysis. This takes advantage of the technology's unique time-averaged sampling. This application also eliminates purging and issues of the proper disposal of contaminated groundwater created by this practice.

4.3 RECOMMENDATIONS FOR FUTURE RESEARCH

The following items are recommended for future research.

4.3.1 Diffusion Sampler Research

Although it appears that diffusion samplers are capable of sampling most MNA indicators and hydrocarbon constituents, unresolved issues still require further study.

1) It is difficult to ensure that the water in the diffusion sampler has DO conditions similar to the surrounding formation water. Low iron concentrations in some diffusion results compared to Waterra results suggested insufficient equilibration time and the need to deoxygenate the diffusion sampler water. However, if the sampler could be installed for longer so that the DO is consumed and the metals subsequently equilibrate, perhaps deoxygenation could be eliminated, making the sampler cheaper and more efficient. Its ability to effectively measure metals and the effect of different dissolved metals and DO concentrations on the time required for complete equilibration should also be assessed.

2) Currently, the dialysis membrane can obtain representative samples within three to four weeks without signs of deterioration. It would be beneficial to understand if deterioration may be an issue after three months (quarterly monitoring) typical of most MNA programs.

3) Before this application could take place, research would have to show that dialysis membrane could equilibrate with groundwater having high concentrations of dissolved F1 hydrocarbon constituents, as the field diffusion samplers measured low F1-BTEX concentrations at both study sites.

4) Investigate the ability to use the diffusion sampler as a dedicated sampler, which could be labeled for its well location, taken back to the laboratory to be refilled and cycled back into the well at the next sampling event. This would be dependent upon the durability of the dialysis membrane.

4.3.2 Other Research Areas

In response to the bentonite seal material impacts noted in the research program, the following should be investigated.

1) The multilevel wells at the two research sites should continue to be monitored to:
    a) Measure how long it takes for the inorganic constituents to reach natural, background concentrations, and;
    b) if the multilevel well yields representative discrete interval samples at that time.

2) More detailed investigation into the potential impacts of bentonite seal materials on the samples collected from other well types, and how best to minimize those effects.

3) The extent that the elevated sulfate concentrations (additional TEAs) in bentonite seal material causes hydrocarbon degradation (enhanced reduction potential).

APPENDIX A:

Researched Sampling Technologies Detailed Descriptions

Diffusion Samplers

Why Particular Technology Selected

Advantages:

- versatile, can be fabricated to fit inside traditional monitoring wells;
- provides a time-averaged water sample because diffusion gradients cause the sampler to approach equilibrium as formation water flows through the screen;
- require no purging because samplers are placed within the screened portion of the well where formation water flows, so collects sample in low flow formations where minimal well recovery prevents purging and sampling;
- multiple samplers can be installed and separated by seals to determine varying concentrations with depth in a well; and,
- groundwater does not mix with atmospheric gas, even in low flow wells.

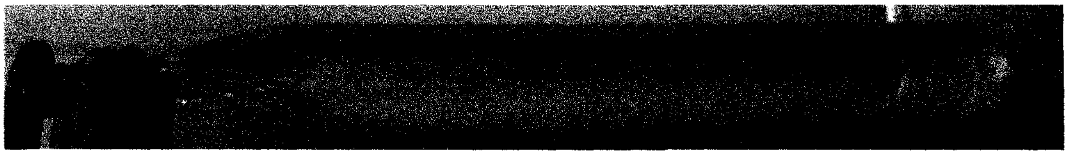
Disadvantages:

- dialysis membranes are delicate and require careful sampler construction;
- if redox reactions occur in the well or the sand annulus around the well that are not occurring in the adjacent formation, the diffusion sampler will collect groundwater that is not representative of the formation
- extra effort is required to prepare deoxygenated water and store samplers in low oxygen environment; and,
- limited state of current knowledge regarding the use of dialysis membranes to sample groundwater contaminants.

Sampler Materials

Dialysis Membrane

The regenerated cellulose dialysis membrane (below) was purchased ($178 U.S. for 10 m roll) from Membrane Filtration Products Inc (MPFI) in Seguin, Texas, U.S.A.. The CelluSep H1 77 mm flat width membrane with a molecular weight cutoff of 8000 daltons was selected because it eliminated any pretreatment requirements and would provide sufficient tubular sample volume for the suite of analysis to be conducted. The CelluSep H1 pretreated membrane guarantees the removal of all metals, which is important when iron and manganese are key parameters to be measured. The membrane was prepared as per the directions of the manufacturer; the membrane was soaked in distilled water for twenty minutes and then rinsed with clean distilled water before the membrane was used.



Dialysis Membrane Filled With Water

End Seals

To ensure discrete interval sampling, seals were created to prevent vertical flow in the monitoring well so only formation water at the depth of interest would equilibrate with the dialysis membrane as it passed through the well screen. The seals consist of a rigid PVC sheet cut to a diameter slightly smaller than the monitoring well diameter and a flexible PVC membrane material that has a diameter slightly larger than the monitoring well diameter. A hole, smaller than the head of a cable tie, is drilled in the center of both PVC materials and a cable tie is threaded through the holes. The rigid PVC disc should be nearest the head of the cable tie and the PVC membrane should be threaded on last.

The seals work by allowing water to flow by the flexible PVC membrane as it is pushed to the desired sampling depth. When the desired depth is reached the connector pipe is pulled up slightly and the flexible PVC membrane falls against the walls of the monitoring well, sealing the sampler in an interval of the screen.

Sample Water

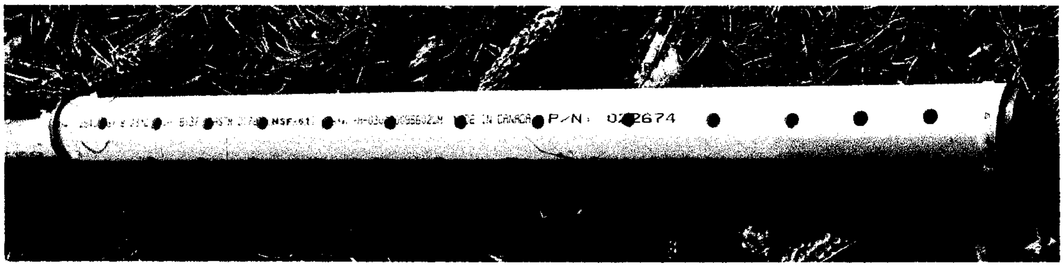
The sample water was deionized water, which was selected because the sampler will be sampling various ionic species in the groundwater environment and must be free of any levels initially so a representative sample can be obtained. To prevent the oxidation of contaminants as they enter the diffusion sampler from the anaerobic groundwater system, deoxygenated water was used in the membrane.

Deionized water was deoxygenated by placing it into a watertight cylindrical cell that had a nitrogen gas bottle attached to the bottom of the cell. The nitrogen gas (N_2) was applied at a pressure that created bubbles that gently rose to the water surface in the cell in approximately one second. The gas was able to escape the cell through a tube connected to an opening situated near the top of the cell so the rate of nitrogen application could not be to fast as large bubbles would displace water out the tube. A stirrer in the bottom of the cell helped to disperse the nitrogen gas bubbles to maximize the amount of oxygen being stripped. The deoxygenation process was carried out for twenty minutes, at which point the dissolved oxygen was less than 1 mg/L (measured using Chemets Dissolved Oxygen Ampoules).

The deoxygenation process works by nitrogen stripping the oxygen from the deionized water. The nitrogen gas is applied at a high rate that forces the dissolved oxygen out of the water, thereby deoxygenating it. To ensure the water was completely deoxygenated, it was created at the University of Alberta in the laboratory and stored in zero headspace amber jars until the dialysis sampler was fabricated in the field.

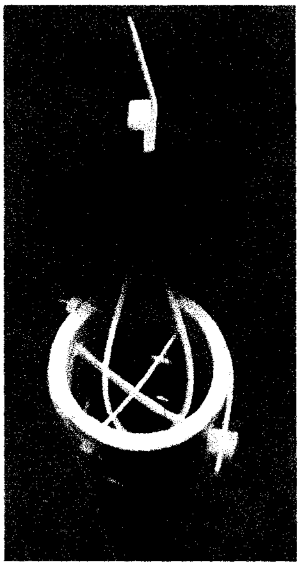
Sampler Description

The diffusion sampler is a simple fabrication, consisting of dialysis membrane and PVC pipe sized to fit inside the monitoring well to be sampled. Monitoring wells with an inner diameter of 50 mm were installed at the field sites, so a 38 mm inner diameter PVC pipe was purchased to provide maximum sample volume while still being able to fit inside the well. The PVC pipe was cut to the length of the desired sampling interval (for this research it was 65 cm long) and cleaned with soapy water before being rinsed. To allow equilibration of the membrane with the formation water, 9.5 mm holes were drilled every 38 mm throughout the entire length of the pipe at 90° intervals around the circumference of the pipe. The dialysis membrane was cut into 75 cm lengths, the extra length is to tie a knot on one end and to connect a capped brass sampling nozzle using o-rings on the other end to seal the membrane. The membrane is pulled into the PVC pipe using a string lightly tied to the nozzle, where it is filled with sample water through the nozzle.

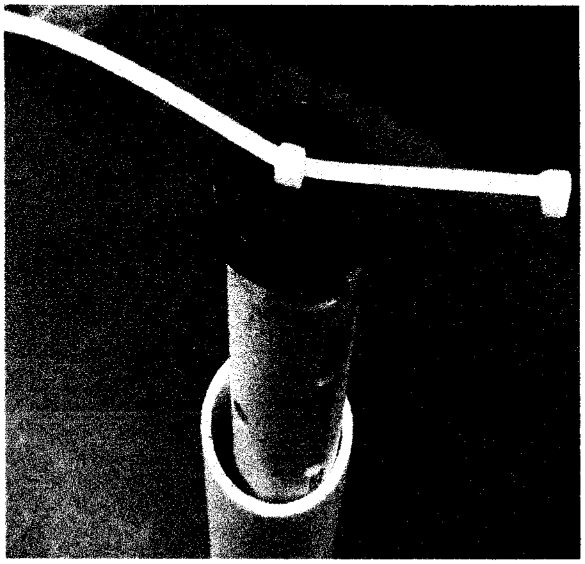


Diffusion Sampler Ready For Installation

Two cable ties are fastened through holes in the end of the 65 cm long PVC pipe to act as an anchor for the seal. The cable tie through the PVC materials is then looped around the anchor cable ties on the end of the PVC pipe and than threaded back through the hole in the middle of the PVC materials (below left). The cable tie is then threaded through the head of the cable tie and another cable tie is placed inside this loop to allow quick attachment of the connector pipe just before installation. The cable tie is than pulled tight, connecting the PVC materials tightly against the PVC pipe and holding the connector pipe cable tie in place until installation (below right).



Anchor Cable Ties with
PVC Materials Cable Tie

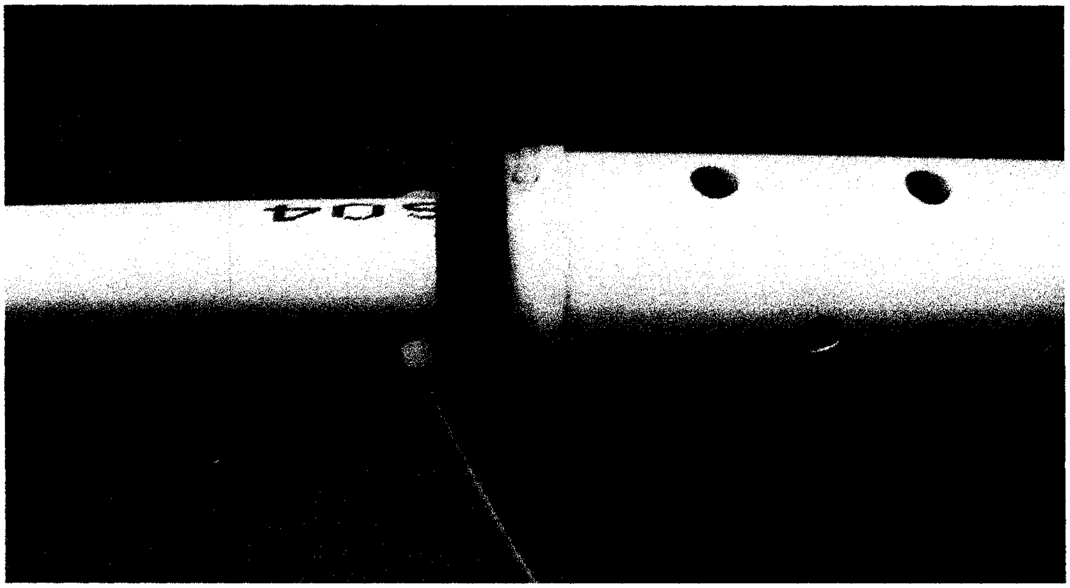


Fastened End Seal with Connector Pipe

The diffusion samplers are gently placed into airtight PVC canisters filled with deionized, deoxygenated water so to have minimal headspace. These canisters allow transportation to the site if the sampler can not be fabricated in the field or storage of the field fabricated sampler until it can be quickly installed in the desired monitoring well.

Sampler Installation

The diffusion samplers are pushed to the desired sampling depth in a conventional 50 mm inner diameter, 3 m screened pre-pack monitoring wells using a rigid system of PVC connector pipe. The rigid connector pipe system consisted of cutting a 19 mm inner diameter PVC pipe to reach from the top of the monitoring well to the first desired sampling depth and to a length that would place the second sampler at the desired sampling interval below the top sampler. The connector pipe was fastened to the samplers by threading the connector cable ties on the end seals through two holes on the end of the connector pipe and pulling the cable tie tight (below). Any excess cable tie was cut to prevent it from hooking on the well during installation.

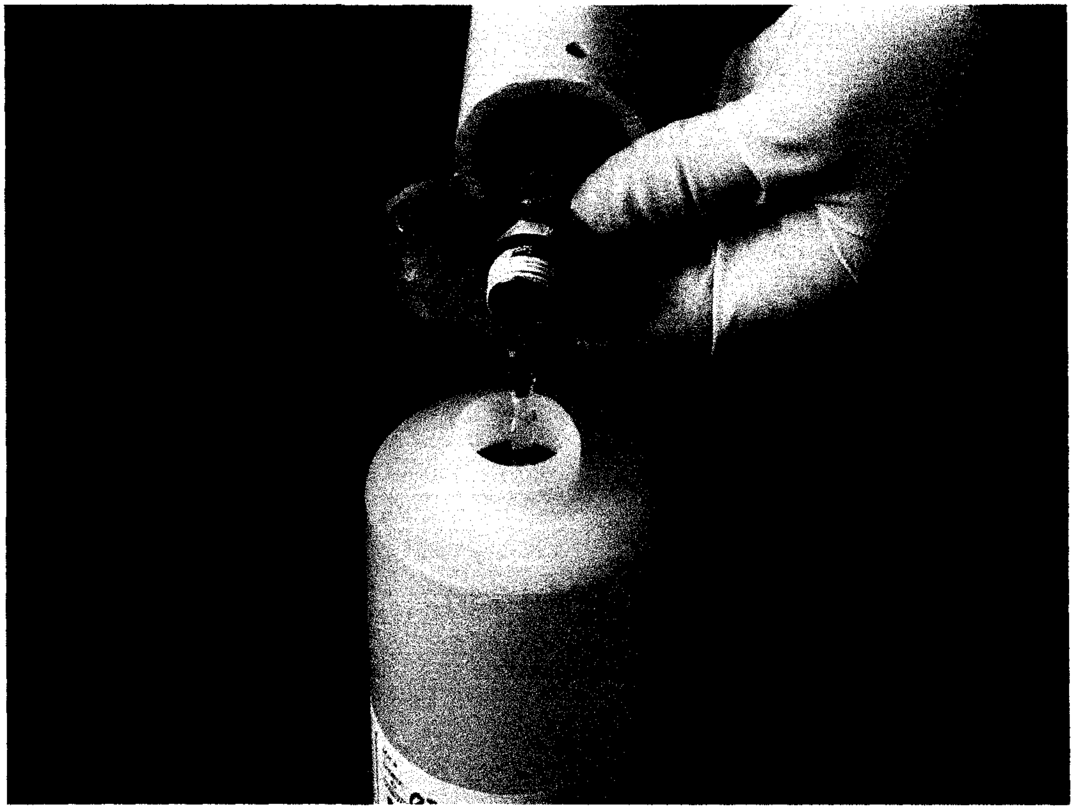


Connector Cable Tie Fastening Connector Pipe to Diffusion Sampler

The diffusion samplers can be installed by two methods. The first method is to remove all the diffusion samplers to be installed at the same time and fasten them to the connector pipe using the cable ties on the end seals before installing the entire rigid system. The second method is to construct the rigid system as it is being placed into the well, where each diffusion sampler would be removed from the storage canister as its sampling depth interval is encountered.

The dialysis samplers were installed with the nozzle end upward to eliminate the possibility of the sample volume leaking out if the o-rings did not seal the dialysis membrane properly. Once the rigid sampler system is at the desired depth, at which point the connector pipe should be even with the top of the well, a rope should be tied through the top of the connector pipe. The rope should be pinched in the well cap to ensure the diffusion samplers remain at the desired depth in case the seals do not maintain this position.

When the samplers are to be retrieved for sample collection, the rope should be held as the well cap is taken off. The PVC connector pipe is then pulled from the well and the cable ties fastening the connector pipe should be cut to free the diffusion samplers for sampling. The end caps are removed by cutting the cable tie holding the seal in place. The diffusion sample is then collected by removing the brass nozzle cap and pouring the water from the dialysis membrane into the various sample bottles as required.



Diffusion Water Sample Being Poured Through Brass Nozzle During Sample Collection

PrePak Drive Point Well (GeoInsight)

Why Particular Technology Selected

Advantages:

- Small sample interval allows better characterization of changes in groundwater geochemistry with depth;
- quick and easily installed monitoring well that provides discrete interval sampling (0.7 m);
- system contains prefabricated sand filter and primary annular seal, thereby reducing time, material and transport costs for bentonite and sand placement;
- small annular space during well installation and quick expansion of annular seal allow rapid grouting to surface (minimize cross connection of aquifers); and,
- use of hydraulic drive point installation involves minimal waste and cuttings generation and the equipment is readily available.

Disadvantages:

- small volume of water available for sampling in slow recharge sediments;
- many wells may be required to characterize large depth intervals;
- soil is not logged or sampled, therefore the installation depth has to be selected based on nearby borehole data; and,
- limited to 19 mm diameter monitoring well because equipment required to push larger diameter drive points is not cost effectively available.

Sampler Description

The GeoInsight PrePak Well Screen consists of a 0.76 m long 0.25 mm slotted Schedule 40, 20.5 mm ID, PVC pipe that has a 20 by 40 silica sand pack surrounding the pipe and the sand is contained by means of a 65 mesh stainless steel screen. Above the prepak well screen is an expandable foam bridge that expands to fill the annular space when the push rods are retracted and prevents any grout intrusion into the screen interval when the well is grouted to surface, thereby allowing the well to be grouted immediately. Above the expandable foam is another 0.76 m long Quick Seal Sleeve (Schedule 40, 20.5 mm inner diameter PVC pipe surrounded by a paper sleeve filled with a mixture of silica sand, granular bentonite and accelerator) that is threaded onto the Prepak Well Screen and foam bridge. The paper contains the mixture until it is placed inside the push rod at the desired depth and when the push rod is retracted the Quick Seal Sleeve comes into contact with water causing the bentonite to swell up to 2.8 inches, tearing the paper and sealing the annular space. This eliminates the potential for vertical flow in the annular space from water producing formations above the prepak screen. These pipe sections are then connected to riser pipe that brings the sampling system to the surface with a two foot stick up. The above mentioned components can be seen below in the schematic diagram (Figure A1).

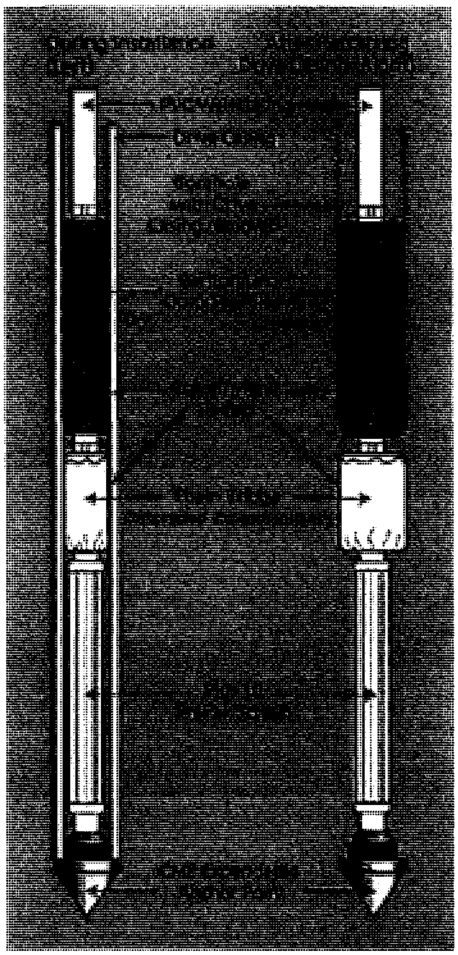


Figure A1. Well Component Diagram

Source: www.geoinsightonline.com/about_small_diam_wells/advantages.html

Sampler Installation

A typical drill truck outfitted with the accessories required to hydraulically drive 5 cm outside diameter hollow steel drive rod was used for this well installation. Expendable drive points are placed beneath the push rods, allowing the rods to be driven into the ground to the desired sampling depth. Once the rods have been driven to the desired depth, the prepak well screen is prepared to be slid down the inside of the push rods. A Push-In Screen Plug is placed into the bottom of the PrePak Well Screen to prevent any sediment from entering into the well when the push rod is retracted. The PrePak Well Screen, expandable foam bridge and Quick Seal Sleeve are connected together and then placed inside the push rods. Riser pipes of five or ten feet are then connected to sampler as it is lowered to the bottom of the push rods and then is cut off with a two foot stick up. The push rods are then retracted and for the initial retraction the riser pipe is checked to ensure it is not being pulled up with the retracting push rod. Once it known that the riser pipe is not moving, the push rod is completely removed. After allowing several hours for the bentonite sleeve to expand, the borehole annulus was filled with bentonite chips at Site 1 and bentonite grout at Site 2.

CMT (Continuous Multichannel Tubing) Multilevel Well (Solinst)

Why Particular Technology Selected

Advantages:

- cost effective because bundle type installation enables up to seven discrete sampling intervals in one borehole;
- short sampling intervals and small sand pack (as small as 10 cm);
- sampling ports can be cut at any depth along the tube;
- assuming a good annular seal, discrete depth sampling requires only one hole, thus spatial heterogeneity is not an issue;
- small diameter sampling channels mean low purge volumes;
- hollow stem drill equipment is readily available, enabling geologic characterization and port depth selection; and,
- system can be fabricated in the field using sampling depths chosen based on geologic data obtained during drilling.

Disadvantages:

- for each additional port in a borehole, installation time and care increases as more precise sand and bentonite intervals are required;
- shorter sand intervals give less room for error in bentonite placement;
- obtaining sufficient sample volume in low flow formations is difficult with small diameter sampling channels and sample intervals; and,
- small diameter sampling channels require small diameter level indicators and sampling equipment.

Sampler Description

The CMT Multilevel System is a seven channel continuous extruded pipe that is shipped in a large coil for fabrication on site. The seven channels consist of six polygonal shaped channels surrounding a central circular channel that is 3/8 (9.5 mm) of an inch in diameter. The tubing has a total diameter of 1.7 inches (43 mm) and the polygonal channels are about 7/16 inch (11 mm). An illustration of the CMT Multilevel tubing is provided in Figure A2.

The CMT Multilevel System (Figure A3) consists of:

- a seven channel continuous extruded pipe (six polygonal shaped and a central circular);
- a port cutting guide;
- port seal plugs and torque screwdriver (used to fix plugs);
- stainless steel mesh and clamps (prevents the ingress of sediment into the sampling ports);
- Guide Point Port Assembly and clamps (prevents sediment from entering bottom of tube and is tapered to prevent snagging during placement); and,
- centralizers and clamps (ensures tubing is centered during well construction).

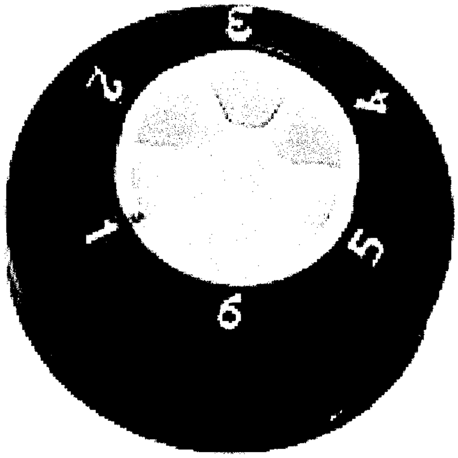


Figure A2. CMT Multilevel Tubing
Source: www.solinst.com/Prod.html

The CMT tubing is sent in a coil and must be straightened out in order to mark the depths at which the sampling ports will be situated. Once the port depths and the total depth of the well have been marked, the tubing is cut. A port cutting guide is then slid onto the tubing and positioned over the shallowest marked sample port, where it is looked into position by anchoring bolts. Three 3/8 inch diameter holes are cut into channel one of the tubing using the port cutting guide. A pair of tin snips is used to cut out the plastic between the top two 3/8 inch holes, thereby creating a sampling port for channel one (care must be taken in this process not to cut into an adjacent channel).

A plug is then slid into the channel through the cut port and positioned between the sampling port and bottom hole, as demonstrated in Figure A4. The plug is then torqued with a torque screwdriver in order to plug off the remainder of the channel that exists below in the tubing. The bottom hole acts as a vent to reduce the bouyancy on the well during installation by allowing air to escape from beneath the plug as the system is lowered into place. Finally a 8 by 6 inch stainless steel mesh is wrapped around the tubing over the port and vent hole in order to prevent the ingress of sediment into the sampling well. The mesh is fastened in place using Oetiker pliers to lock three clamps into position.

The above process is then repeated in the other channels in a clockwise direction at the other sampling port depths. Once all the sample ports have been cut, plugs are placed in the bottom of the well where the tubing was cut to total well depth. The plugs are only placed in the bottom on channels that have had a port and plug inserted at the desired sampling depth, the remainder are open to allow water to flow through them as the tubing is lowered into the borehole. A Guide Point Port Assembly is than attached to the end of the tubing, allowing sampling through a stainless steel mesh covered port that prevents any sediment from entering the bottom of the tubing.

The Point Port Assembly helps guide the tubing down the borehole as it is tapered to prevent snagging. The assembly is then fastened to the end of the tubing using two clamps and the Oetiker pliers. A base plate can be attached to the Guide Point Port Assembly to anchor the bottom of the CMT during well construction. Centralizers are then wrapped around the tubing at ten foot (3 m) intervals and fastened using two clamps. The centralizers ensure that the tubing is centered during well construction and have low profile fins to prevent any obstruction of sand or bentonite pellets as they are poured from the surface. The CMT Multilevel Well is now ready for placement in the borehole. The various components discussed can be observed in Figure A3.

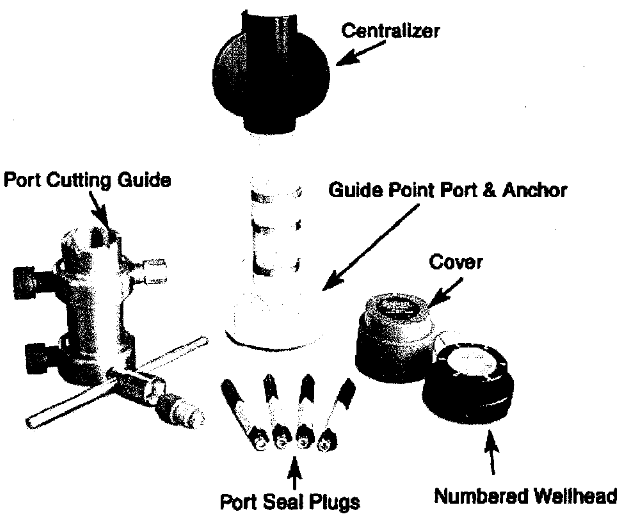


Figure A3. CMT System Components
Source: www.solinst.com/Prod.html

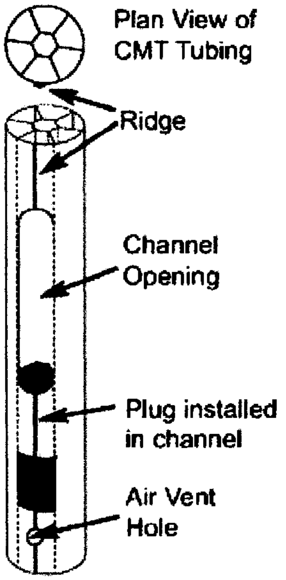


Figure A4. Port Configuration
Source: www.solinst.com/Prod.html

Sampler Installation

A 135 mm ID hollow stem auger was used at the sites as the boreholes refused to stay open as a result of the geology when a solid stem auger system was attempted. At Site 1 the CMT Multilevel Well discrete sampling intervals (0.6 m) were established by carefully pouring sand and bentonite from surface and measuring depths to get the desired sampling intervals, similar to traditional sampling well construction.

At Site 2, sloughing of native soil during auger retrieval threatened to compromise the isolation of discrete sampling intervals. As a result nylon mesh socks were sewn and then slid onto the tubing where they were filled with the appropriate sand and bentonite chips as to create the desired sampling intervals (see Figure A5). The nylon socks were held in place by cable tying them at each end of the socks at the desired depths. The tubing and nylon mesh socks were then lowered through the hollow stem auger to the desired depth and once the bentonite hydrated the sampling intervals were established and then the borehole was chipped to surface.

Figure A5. CMT Multilevel Well Installation with Nylon Mesh Socks

BarCad System (BESST, Inc.)

Why Particular Technology Selected

Advantages:

- system operation precludes mixing of groundwater and atmospheric gas (especially oxygen) during purging and sampling;
- system may be used as dedicated well sampler or moved between wells;
- system can provide discrete interval samples at various depths in one well;
- uses an inert gas drive system to retrieve samples (no suction depth limitation);
- inert gas limits oxidation of samples and minimizes volatile organic carbon (VOC) loss in the closed system; and,
- small internal storage minimizes purge volume.

Disadvantages:

- requires compressed gas, as well as transport certification;
- complicated system with a series of valves to control gas flow requires careful operation;
- requires careful gas pressure control by a skilled operator;
- poor gas pressure control may lead to aerosol effect on sample and result in VOC loss and metals oxidation;
- packer system does not prevent vertical mixing, if the sample is collected at a rate greater than aquifer recharge, via preferential movement through the sand-filled annulus outside the well screen; and,
- sampling time requirement is lengthy when used for multiple depth sampling due to additional system cleaning and assembly between depths.

Sampler Description (Figure A6)

The BarCad System consists of an inner stainless steel screen that is surrounded by a porous ceramic to filter the formation water as it is drawn into the screen during sampling. The porous ceramic section is 2.5 feet (0.76 m) long and uses standard pipe threading to connect to the reminder of the system. Above the porous ceramic sampler is a two foot (0.6 m) long expandable packer on the outside of a ¾ inch (19 mm) metal pipe. The packer is connected to a tank of compressed gas at the surface by tubing that run along the outside of the riser pipe. The ¾ inch metal pipe fastens to the ceramic on the bottom and ¾ inch (19 mm) riser pipe above it via a threaded connection. Riser pipe is connected until sufficient pipe has been added to get the ceramic sampler to the desired depth. A thin two foot (0.6 m) long stainless steel tube is attached to Teflon-lined tubing and lowered inside the riser pipe until it is inserted into the inner screen chamber inside the porous ceramic. The Teflon-lined tubing is cut to the length of the top riser pipe and is then connected to the bottom of well head adapter using a SwageLok fitting. The well head adapter is then threaded onto the top riser pipe, creating an airtight seal. The inert gas tank is then fastened to the gas input connection, the gas is then turned on and the BarCad System is ready to sample.

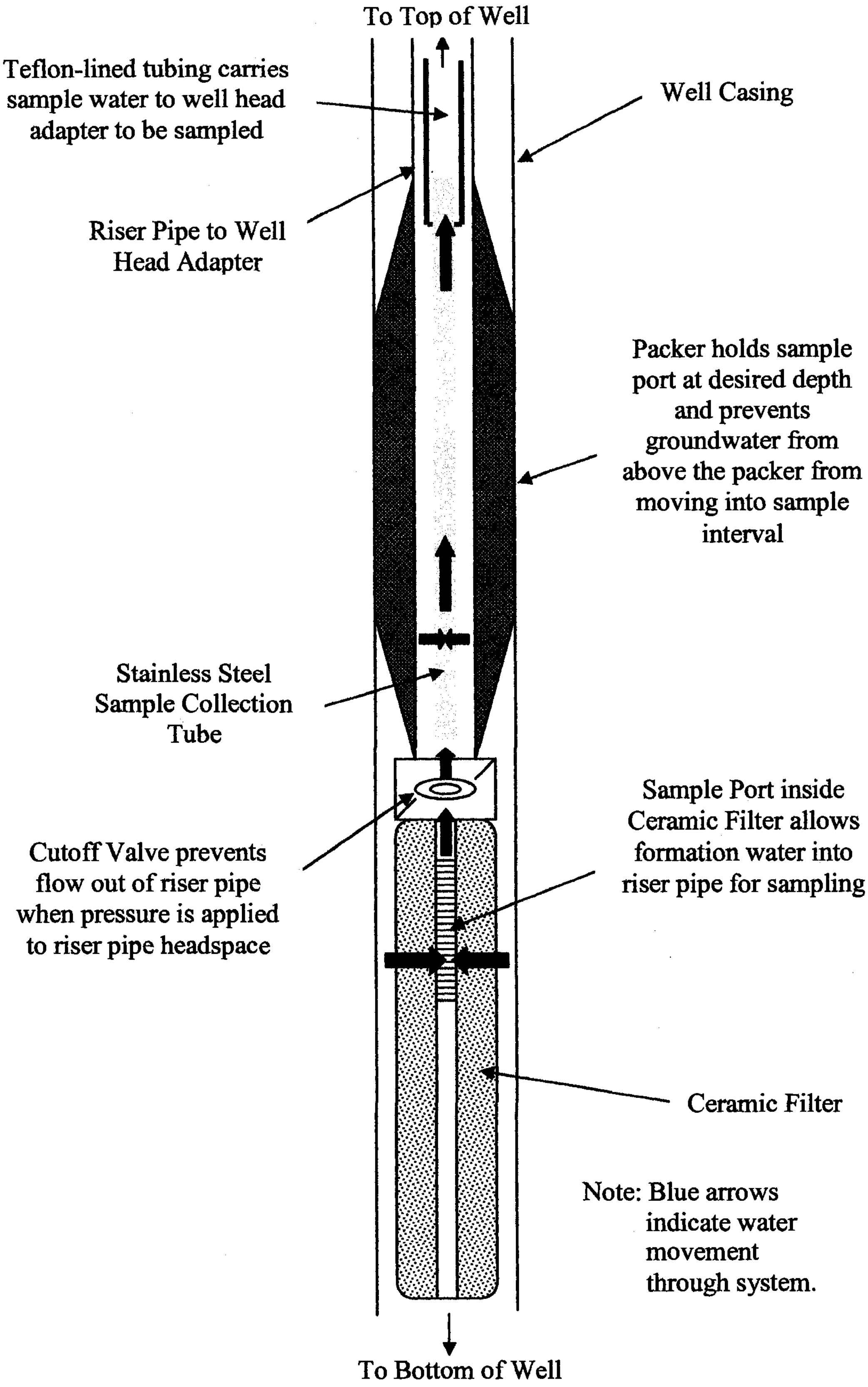
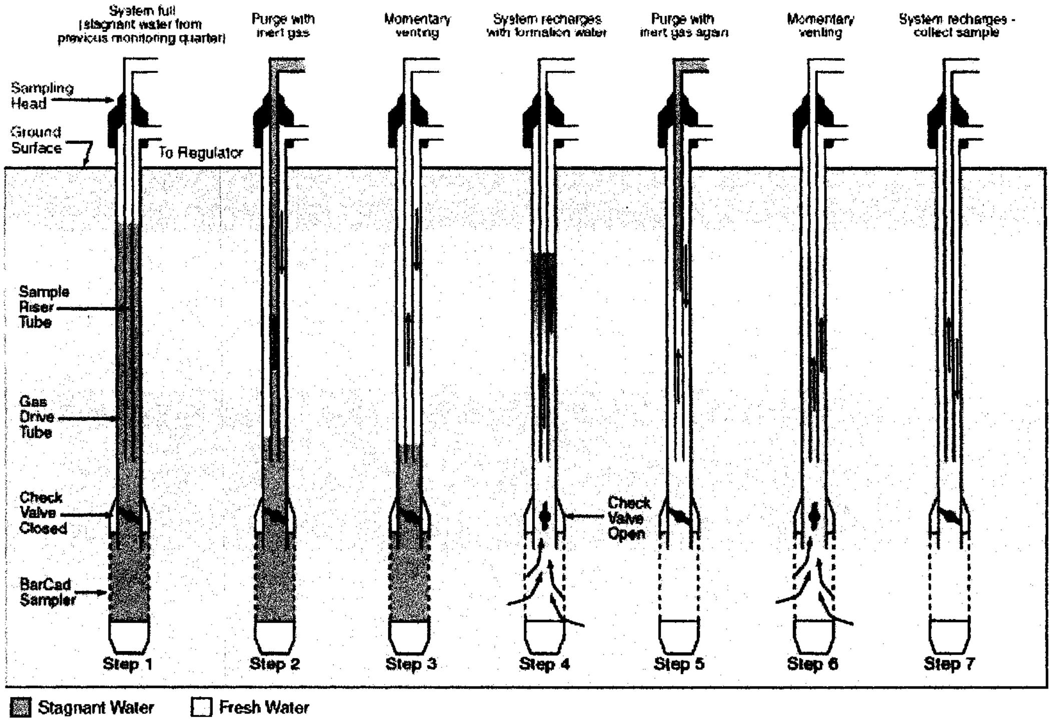


Figure A6. BarCad System Schematic Diagram.

Sampler Installation

The BarCad System was implemented in the newly installed two inch (5 cm) monitoring well monitoring well with a ten foot (3 m) pre-packed screen installed at the desired sampling depth by means of solid stem augering. The porous ceramic and gas line are connected to the packer and then lowered into the two inch (5 cm) well. Five or ten foot (1.5 or 3 m) long riser pipe are connected as the system is lowered until the ceramic sampler is at the desired depth. The gas line is then connected to the tank and pressurized gas is forced into the packer to seal the monitoring well off at the discrete sampling depth. This allows formation water to be sampled from that particular depth by applying inert gas inside the ¾ inch (19 mm) pipe headspace below the well head adapter, thereby pushing the formation water in the well below the packer and the adjacent formation to the surface to be sampled. The gas being applied to the headspace inside the ¾ inch (19 mm) pipe is controlled by a valve on the well head adapter so that when the water in the well is being drawn down to near the bottom of the stainless steel sampling tube the valve can be opened. The pressure in the head space is released so that the well can recharge and more sample can be taken again once the groundwater level reaches static conditions. A schematic diagram of the basic sampling process can be viewed in Figure A7 to assist in understanding the BarCad System.



BESST INC., 16 Diane Lane, Suite 100, Larkspur, CA 94939 1.800.553.1755 / 1.415.389.1657 / 1.415.389.1688 (fax) / SimulProbe@aol.com / www.BESSTINC.com

Figure A7. BarCad Systematic Process Diagram (BESST Inc., 2003)

Conventional Three Metre Screen Monitoring Well

Why Particular Technology Selected

Advantages:

- simple, quick and easily installed monitoring well;
- well known and accepted throughout the environmental industry;
- allows soil classification and ideal placement of sample interval based on this classification; and,
- equipment is economically and readily available to install wells.

Disadvantages:

- three metre screen interval can dilute contaminant concentrations and make vertical characterization of contamination difficult;
- three metre screen interval has potential to interconnect separate aquifers if improperly installed; and,
- for deeper installations, requires large amounts of bentonite seal material to fill annulus created by drilling.

Sampler Description

This well type is typically sampled using either a bailer or a Waterra inertial foot valve attached to tubing; both are commonly accepted methods used to collect samples in groundwater monitoring programs. These sampling methods will be discussed in more detail in the Sampling Methodologies section. The conventional monitoring wells were constructed using 3 m long, 5 cm inner diameter (ID) slotted PVC pipe and solid PVC riser pipe. These wells had pre-packed well screens, which consisted of 5 cm ID slotted PVC pipe inside a 10 cm ID with Sil 30 sand in the space between. The annulus around the pre-pack well screen was backfilled with sand to 0.3 m above the well screen, then a seal was created using 0.3 m of bentonite pellets above the sand. The remainder of the annulus was backfilled to surface with bentonite chips to prevent surface infiltration. The pre-existing three metre screen monitoring wells were constructed in the traditional manner; using 5 cm ID slotted pipe for the screen interval and solid pipe to the surface, with sand over the screen interval and a chipped bentonite seal to surface.

A solid stem auger was used where the borehole remained open (Site 1), whereas a hollow stem auger was used for sloughing soils (Site 2). These drilling methods provided soil samples that were then used to classify the geology with depth and to select the installation depths for the discrete interval sampling wells. The monitoring well depths were generally selected to have the groundwater surface elevation within the three metre screen interval.

Peristaltic Pump

Why Particular Technology Selected

Advantages:

- samples can be collected at controlled rates because the pump maintains continual suction pressure on the water and can be operated at different speeds. This is valuable in low flow formations because the water can be retrieved at a rate similar to the ability of the well to recharge; and,
- discrete interval samples can be obtained because the rigid tubing can be positioned at any depth within the well screen and the sample can be drawn at a slow rate.

Disadvantages:

- compared to bailers and Waterra pumps, there is a substantial initial capital cost;
- applying a suction to the water causes negative pressure that may draw dissolved gases out of solution, resulting in the volatilization of VOC's to some extent; and,
- during well recharge in long screen wells, water may flow in via the highest conductivity layer causing mixing in the well.

Sampler Description

The peristaltic pump works by placing semi-rigid tubing into the sample well to the desired depth and connecting this tubing to flexible surgical tubing, that is threaded around the drive gear on the pump (Figure A8). When the pump rotates the gear it compresses the flexible surgical tubing, pinching the tubing between the gear and a plastic device that holds the tubing. As the pump rotates along the surgical tubing it creates suction behind it, which draws the water up the semi-rigid tubing. As the pump rotates, continually compressing the tubing, it maintains suction on the water in the tubing so that it can be brought to the surface to be sampled.

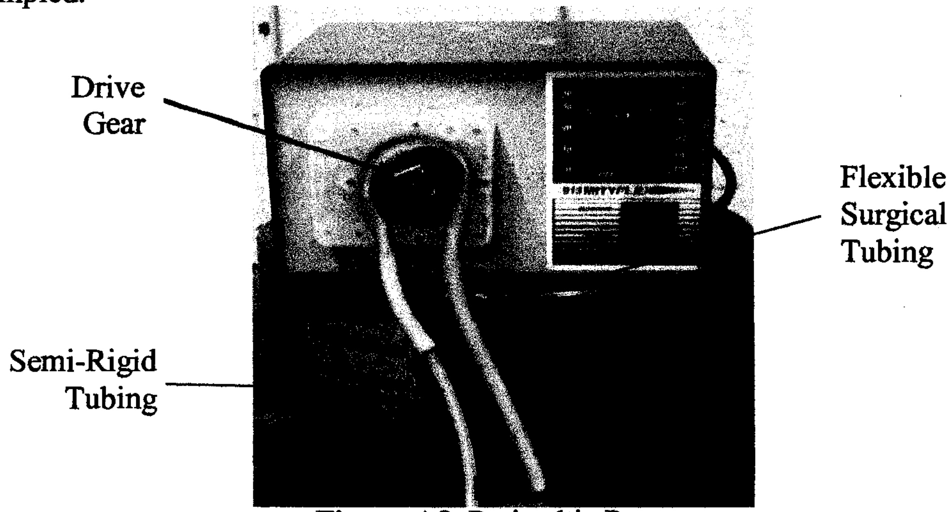


Figure A8. Peristaltic Pump.

Bailer

Why Particular Technology Selected

Advantages:

- very simple; and,
- fairly inexpensive and can be disposable, however it is often dedicated to one well.

Disadvantages:

- standard practice for bailer samples is to purge three well volumes before a sample is collected and this purging can expose the well screen to the atmosphere, resulting in oxidation of metals and volatilization of VOC's; and,
- a sample obtained using a bailer is a mixture of water from the conductive layers that intersect the well over the entire screened interval.

Sampler Description

The bailer consists of a thin, rigid PVC tube with a ball that covers a narrow opening in the bottom during sample retrieval. The sampling process is as follows:

- the bailer is attached to a rope with sufficient length to reach below the groundwater level in the monitoring well;
- the bailer is slowly lowered into the groundwater and as it sinks the plastic ball lifts off the opening allowing water to flow in the bottom;
- the bailer is allowed to sink until the desired depth is reached and sufficient sample volume enters the bailer tube;
- the rope is retrieved causing downward pressure on the plastic ball over the opening so the sample can be brought to the surface.

Waterra Inertial Foot Valve and Teflon-lined Tubing

Why Particular Technology Selected

Advantages

- very simple;
- fairly inexpensive and can be disposable, however it is often dedicated to one well; and,
- skillful operation of a inertial waterra pump can retrieve a water sample from a discrete interval within the well screen.

Disadvantages:

- The up and down action of an inertial Waterra sampler can agitate the water sample if not operated carefully, possibly resulting in oxidation of metals, volatilization of VOC's and generating turbid samples; and,
- during well recharge in long screen wells, water may flow in via the highest conductivity layer causing mixing in the well.

Sampler Description

The Waterra inertial sampler consists of a foot valve connected to Teflon lined tubing that brings the water sample to the surface. The sampling process is as follows:

- the foot valve is attached on the end of semi-rigid, Teflon lined PVC tubing, which has been cut to a length approximately 1 to 2 m longer than the total well depth;
- the tubing is lowered into the well until it reaches the bottom;
- water enters the PVC tubing because lowering the foot valve forces a plastic ball to come off a narrow opening at the bottom of the foot valve, allowing the water to enter the tube;
- when the tube is lifted, the water inside the tube forces the plastic ball onto the opening, containing the water within the tubing;
- the tubing is then repeatedly lifted and lowered approximately six inches until the water is pumped to the surface to be sampled.

APPENDIX B:

Research Site Descriptions

TWO UPSTREAM OIL AND GAS RESEARCH SITES

Site 1 – Decommissioned Well Site and Flare Pit

Site 1 is located in the wetter conditions of the northern boreal forest of northwestern Alberta and is a decommissioned well site and flare pit. Figure B1 shows a plan view of the site. The brush has been cleared from most of the site and only small shrubs and tall grasses remain, except for a small cluster of trees located south of the base of the hill. The flare pit was situated on the crest of the hill and has been excavated and backfilled with clean soil to remove the source of contamination.

The monitoring wells are located to the south of the old flare pit on the side and at the base of the hill, which is approximately 7.5 m below the crest of the hill. The cluster of wells being investigated in this research is highlighted in the detailed enlargement in Figure B1 to more clearly display the well positions. The diffusion samplers were installed in well 03-MW1.

The stratigraphy for well 03-MW1 is shown in Figure B2. Clayey silt was observed to a depth of 0.91 metres (m) with iron oxide staining (mottling) beginning at 0.15 m, indicating moist (but not saturated) conditions throughout the year. Below 0.91 m is silty clay to a depth of 3.98 m which is alternately mottled (iron oxide staining) and gleyed (grey, reduced soil), with the latter indicating saturated conditions for the majority of the year. The soil was saturated below a depth of 1.52 m at the time of drilling. As the monitoring well was screened to straddle the groundwater table, the well screen was installed from 1.83 to 4.83 m below ground surface because the alternating iron mottling and gleying at approximately 3 m indicated this to be the seasonal groundwater surface.

Beneath the silty clay is silt containing some fine grained sand lenses to a depth of 5.03 m. These lenses may be preferential flow paths for both water and contaminants. There is silty sand below the silt from 5.03 to 5.49 m. This silty sand has coarse grained sand and gravel lenses through which the greatest amount of water may move as it is likely the preferred flow path for the entire stratigraphy. This is underlain by silty clay to a depth of 6.25 m. The silty clay at this depth is very stiff and likely acts as a limited permeability layer to water flow. The reddish brown colour of the soil and the iron oxide staining indicates that this layer is not continuously saturated due to the tight nature of the clay. As the groundwater level has been historically measured between 0.55 to 2.95 m below ground surface and the silty clay layer has evidence of not being continuously saturated (mottling), this indicates the likely existence of a perched water table above the silty clay layer.

A thin layer of grey silt containing brown sandy lenses was observed below this clay layer before bedrock was encountered at a depth of 6.40 m. The brown sandy lenses likely move water through this silt layer, indicating the likely presence of a lower aquifer beneath the low permeability silty clay layer. Typical of silt and clay soils, the groundwater at Site 1 moves at a very slow rate of 1 to 3 m/yr (J. Armstrong, personal communication, June 10, 2003) and generally flows in a southwest direction across the site. The contaminant encountered on site is flare pit residue, which floats atop the water table and is dark brown to black in color. Laboratory analysis of a free product sample from the site indicated a wide variety of compounds that range from approximately C_4 to C_{40}.

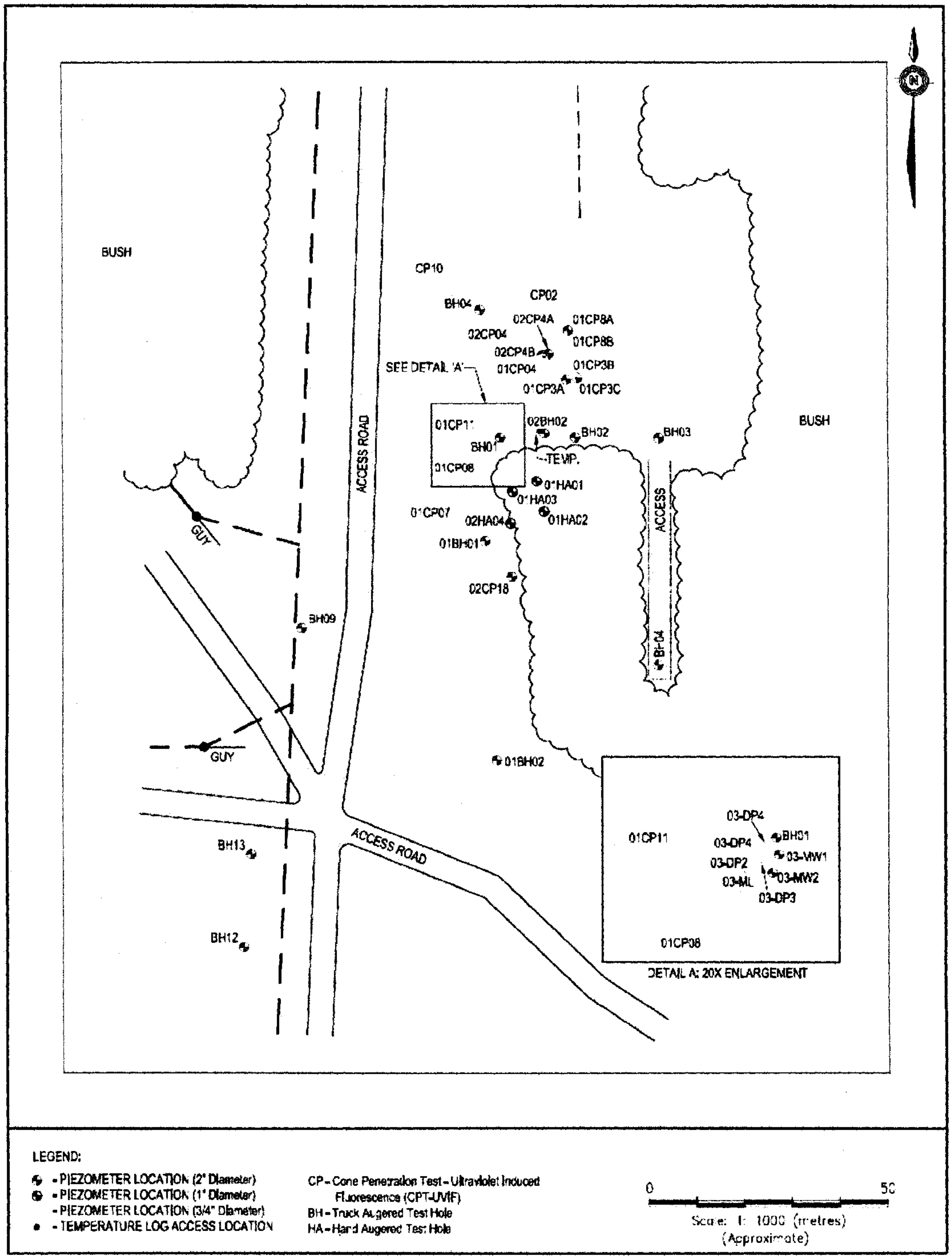


Figure B1. Plan view of Site 1

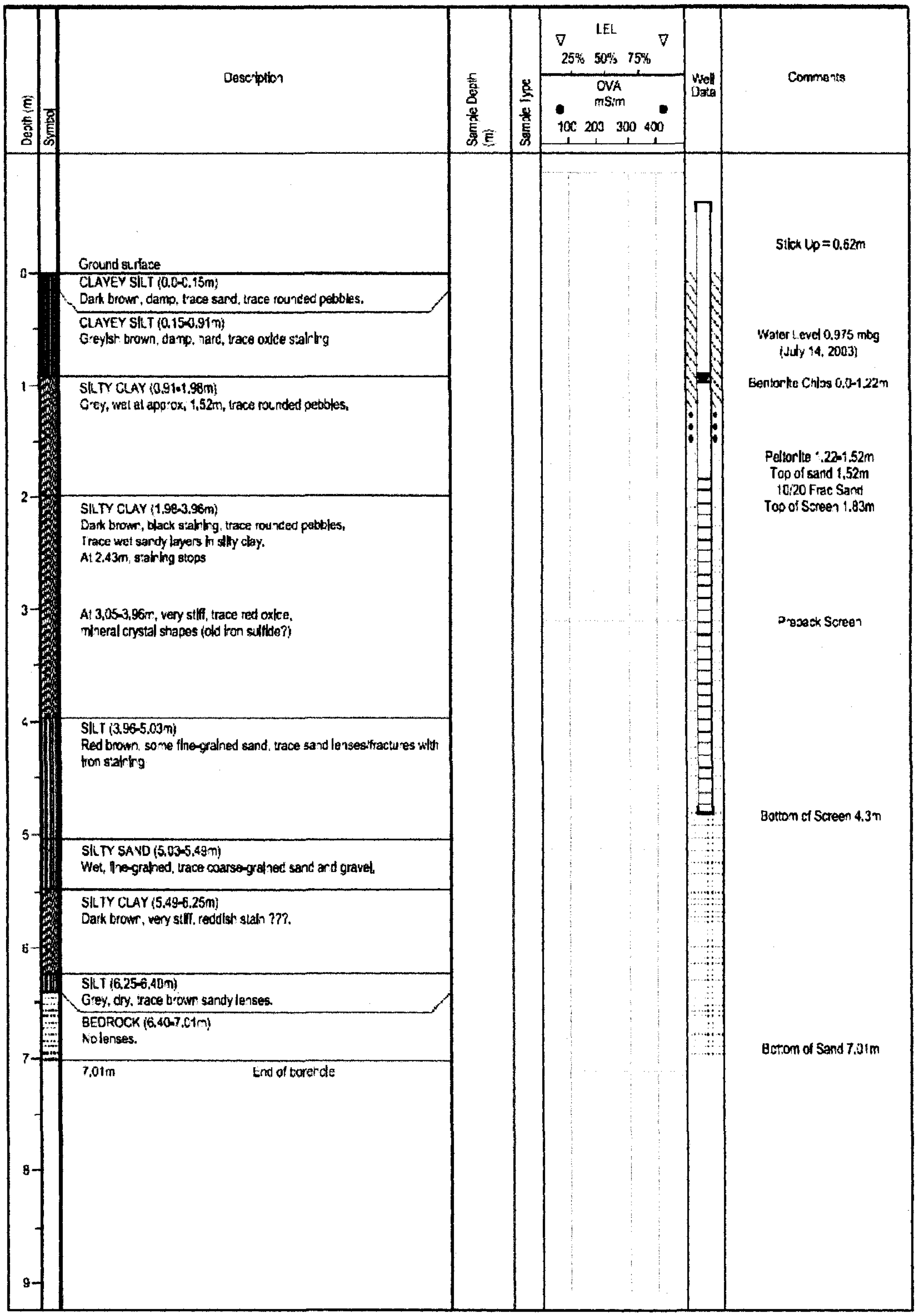


Figure B2. Well 03-MW1 Borehole Log.

Site 2 – Natural Gas Processing Facility

Site 2 is located in southeastern Alberta in the drier short-grass prairie zone and is at a natural gas processing facility. The site is nearly level and the vegetation is primarily prairie grass. At this site there are two well nest locations (Well Cluster 34 and Well Cluster 35) within the condensate-contaminated groundwater plume, shown in Figure B3. The wells used in the diffusion sampler study are 34-MW1 and 35-MW1. The stratigraphy at well 34-MW1 is documented in Figure B4.

Silt was observed for the entire depth of 4.64 m. From 1.53 to 3.81 m the soil is wet, stained dark grey and has a distinct hydrocarbon odour, indicating the range of the top of the water table and the location of the main zone of contamination. The monitoring well was screened from approximately 1.6 to 4.6 m below ground surface to intersect the groundwater surface that was present in the silt layer. The stratigraphy at well 35-MW1 is shown in Figure B5. There is silt to a depth of 0.76 m overlying silt and sand to a depth of 3.96 m. From 2.13 to 3.96 m the soil is wet, stained dark grey and has a distinct hydrocarbon odour, indicating the range of the top of the water table and the location of the main zone of contamination. The monitoring well was screened from approximately 2.2 to 5.2 m below ground surface to intersect the groundwater in the silt and sand layer. Beneath 3.96 m was silt to the bottom of the borehole at 6.22 m.

Groundwater at this site moves slowly (2 to 5 m/yr) to the west (J. Armstrong, personal communication, June 10, 2003). Condensate comprises low molecular weight hydrocarbon compounds (C_4 to C_{21}) removed from natural gas after production. Condensate contaminant encountered at this site floats atop the water table and ranges from a light amber color to clear.

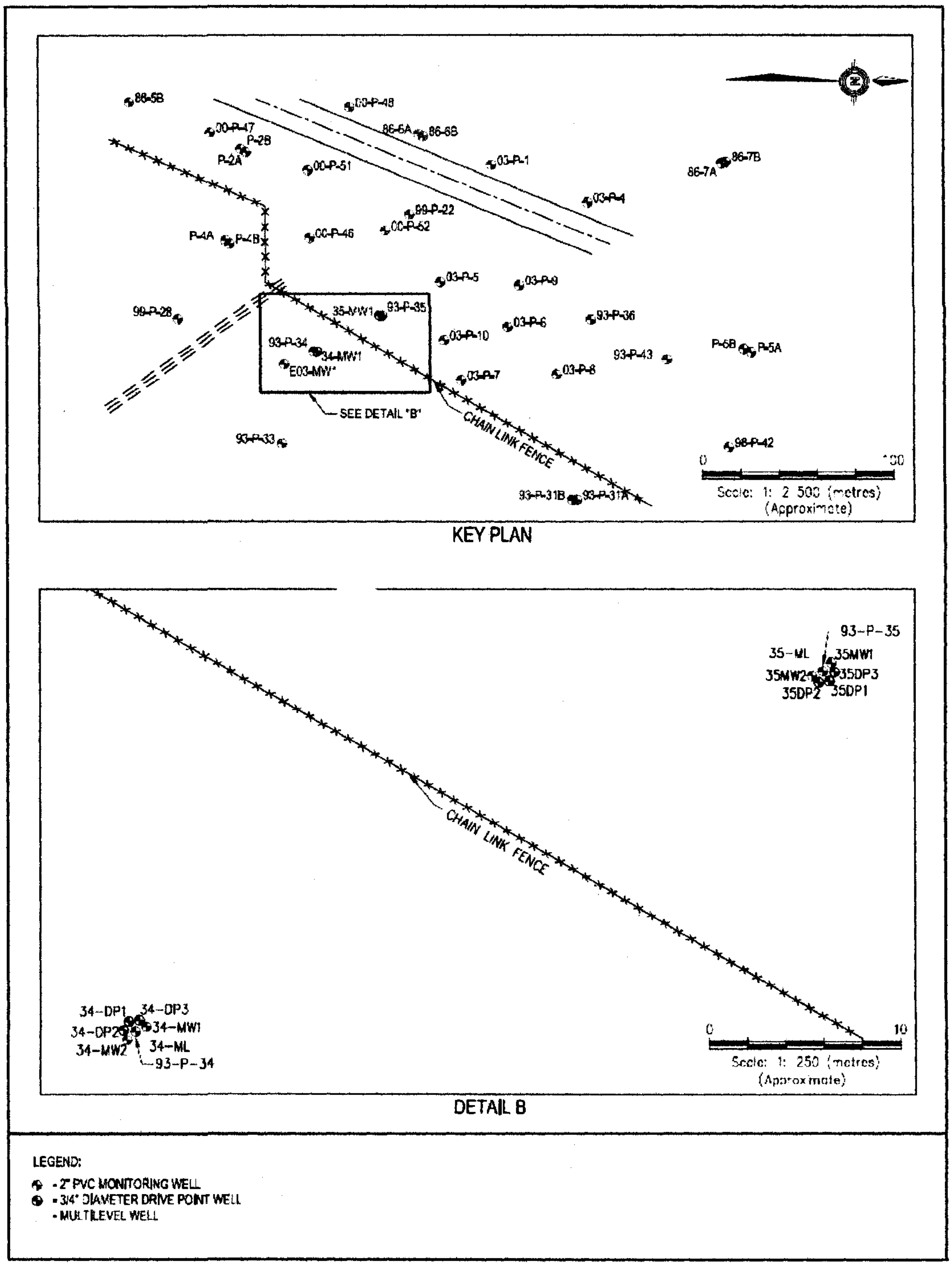
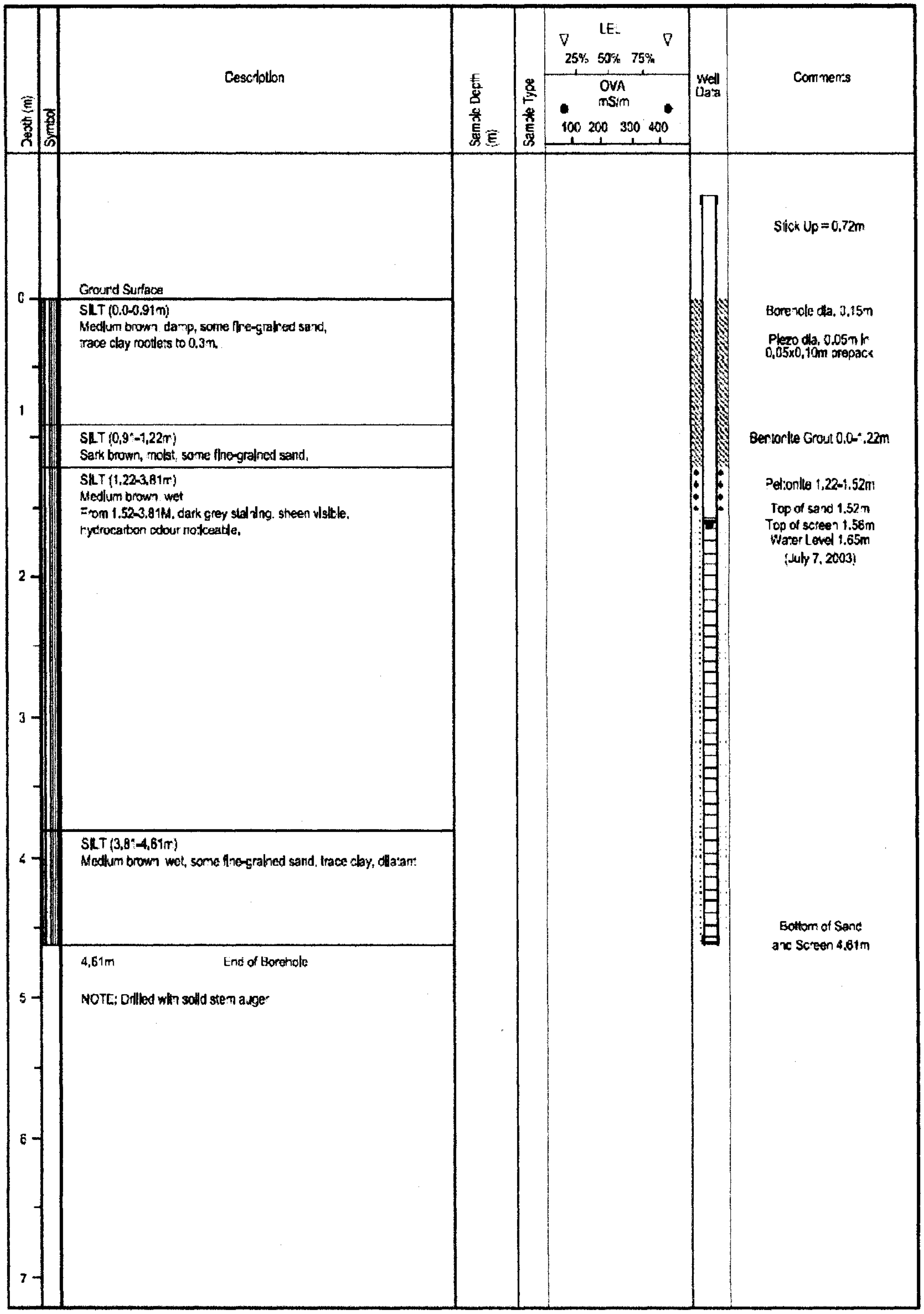


Figure B3. Plan view of Site 2.



Ground Surface

SILT (0.0-0.91m)
Medium brown, damp, some fine-grained sand,
trace clay rootlets to 0.3m.

SILT (0,91-1,22m)
Dark brown, moist, some fine-grained sand.

SILT (1,22-3,81m)
Medium brown, wet
From 1.52-3.81M, dark grey staining, sheen visible,
hydrocarbon odour noticeable.

SILT (3,81-4,61m)
Medium brown, wet, some fine-grained sand, trace clay, dilatant

4,61m End of Borehole

NOTE; Drilled with solid stem auger

Stick Up = 0.72m

Borehole dia. 0.15m

Piezo dia. 0.05m in
0,05x0,10m prepack

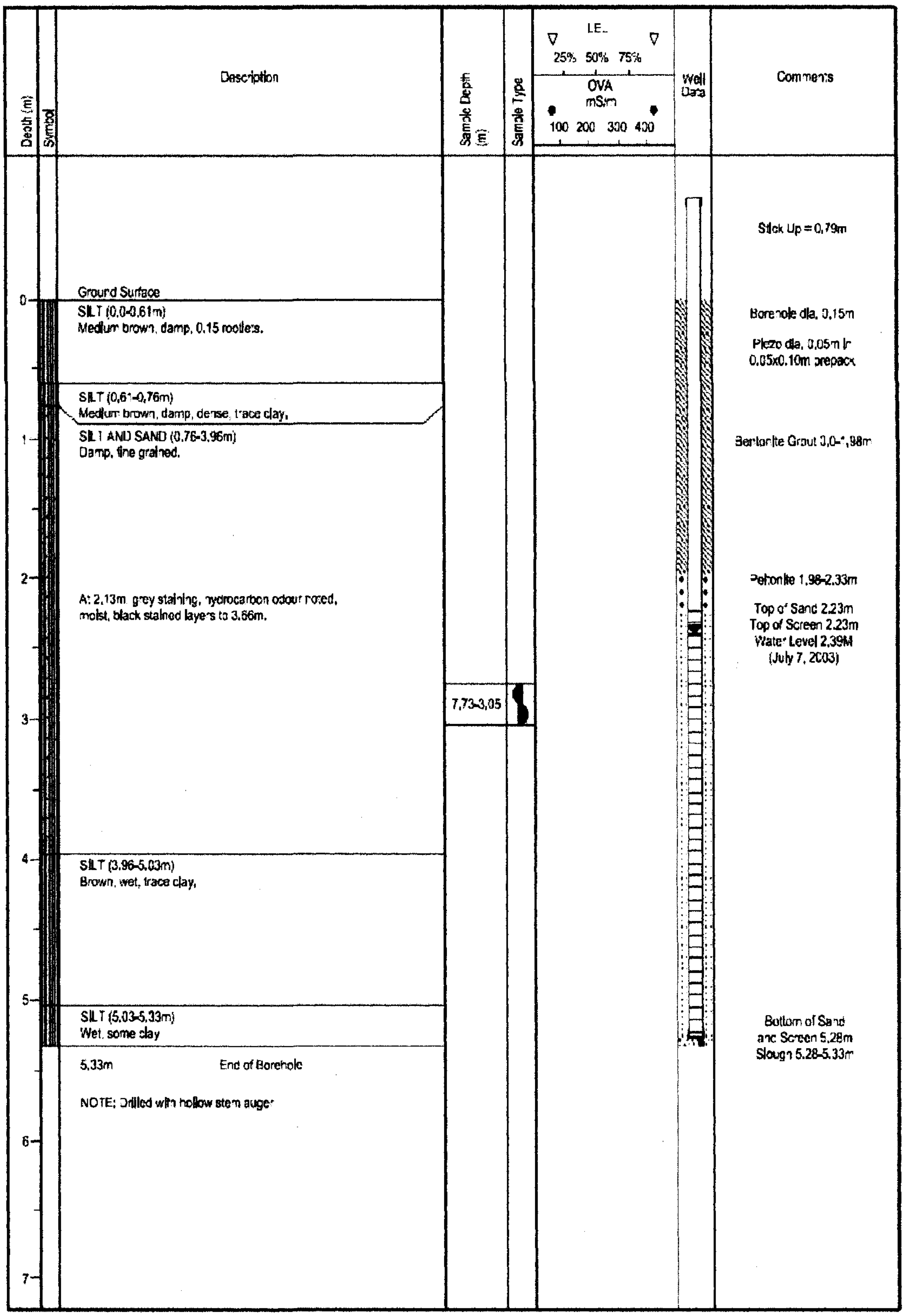
Bentonite Grout 0.0-1.22m

Peltonite 1,22-1.52m

Top of sand 1.52m
Top of screen 1.56m
Water Level 1.65m
(July 7, 2003)

Bottom of Sand
and Screen 4.61m

Figure B4. Well 34-MW1 Borehole Log.



Ground Surface

SILT (0,0-0.61m)
Medium brown, damp, 0.15 rootlets.

SILT (0,61-0,76m)
Medium brown, damp, dense, trace clay,

SILT AND SAND (0.76-3,96m)
Damp, fine grained.

At 2.13m grey staining, hydrocarbon odour noted, moist, black stained layers to 3.66m.

SILT (3.96-5.03m)
Brown, wet, trace clay,

SILT (5.03-5.33m)
Wet, some clay

5,33m End of Borehole

NOTE; Drilled with hollow stem auger

Stick Up = 0,79m

Borehole dia. 0,15m

Piezo dia. 0,05m in
0.05x0.10m prepack

Bentonite Grout 0,0-1,98m

Peltonite 1,98-2,33m

Top of Sand 2.23m
Top of Screen 2.23m
Water Level 2,39M
(July 7, 2003)

Bottom of Sand
and Screen 5,28m
Slough 5.28-5.33m

Figure B5. Well 35-MW1 Borehole Log.

APPENDIX C:

Laboratory Experiment Descriptions

LABORATORY STUDY – Ability of Dialysis Membrane to Sample Hydrocarbon Contaminated Groundwater

Objective

To investigate the potential for dialysis membrane degradation by formation water containing a variety of contaminants. The contaminants of concern are the hydrocarbon fraction, so a sample with elevated hydrocarbon levels was used. The timeframe of potential dialysis membrane degradation was also of interest, as this would dictate the length of time the samplers could remain in the wells. The sampler must remain in the well for a sufficient period of time to collect a representative sample of the formation water before membrane integrity is compromised in order to be an effective sampling device.

Sampler Material Preparation

A 1.9 centimetre (¾ inch) inner diameter (I.D.) solid PVC pipe was cut into 14 centimetre lengths and than sanded to smooth each end. The PVC pipe was cleaned using soapy water and then soaked in distilled water to remove any potential contaminants. All PVC pipe pieces were created from the same three metre length of pipe to ensure similar characteristics (ie., sorption, leaching, etc.) for each macrocosm.

A 6.35 millimetre (¼ inch) drill bit was used to drill holes into the PVC pipe at one 2.5 centimetre increments (5 holes were drilled straight through the pipe and another 4 holes straight through the pipe at 90° to the first holes – a total of 18 holes were drilled in each PVC pipe). The holes were then sanded to ensure a smooth surface so the dialysis membrane would not be punctured during sampler preparation. The holes were drilled to facilitate equilibration between the water in the macrocosm and water inside the dialysis sampler.

The dialysis membrane, a 50 millimetre flat width regenerated cellulose dialysis tubing, was selected as it was the largest available at the time and would provide the largest sample volume for analysis. The dialysis membrane was purchased from Membrane Filtration Products Inc. (MFPI). The dialysis membranes were cut into 25 centimetre lengths; the excess length was to seal the ends of the membrane with a stainless steel U-clamp. The membranes were soaked in distilled water for 20 minutes to remove any remnants of the preservative solution that the dialysis membrane was stored in. The dialysis membranes were then rinsed using fresh distilled water and were then ready to create the sampler. The soaking and rinsing of the membrane was done in accordance with the directions provided by MFPI. The U-clamps used to seal the ends of the sampler were also cleaned with soapy water and then left to soak in distilled water until the sampler was created to limit any contamination by the clamps.

Canning jars were selected for the macrocosm because they provided an airtight seal, limiting oxidation of the formation water during the experiment. The canning jars consisted of the fastener, the sealer lid and 1.5 liter glass jars. All the jars were cleaned with soapy water, then rinsed thoroughly and dried. The jars were then placed in an oven at 300°C for 30 minutes to ensure complete sterilization before being used in this experiment.

Experiment Water Preparation

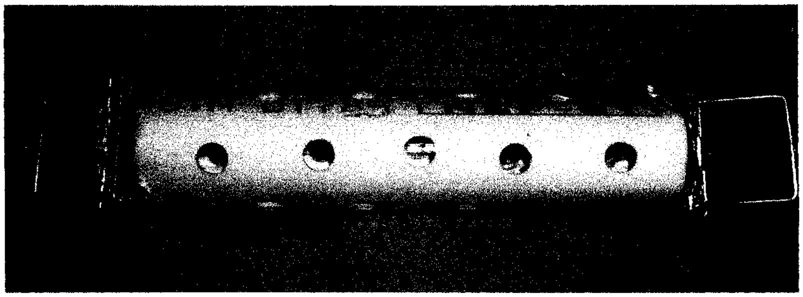
The formation water used in the macrocosms was obtained from a well (Site 1) where high levels of hydrocarbon contamination were known to exist from historical sampling data. The water was collected using a dedicated bailer and stored in a two liter zero headspace amber jar to minimize any volatilization, oxidation or any other degradation processes. The jars were kept in a cooler with ice to ensure the groundwater sample remained near 4°C during transported to the University of Alberta, where the sample was stored in a 4°C cold room until the experiment was conducted. The formation water collected was selected because it contained the highest hydrocarbon levels expected in the field so if dialysis membrane degradation did not occur under these conditions than it was believed that membrane degradation would not be a concern during the sampling program.

The formation water was in an anaerobic state as a result of hydrocarbon degradation. Therefore, the dialysis sampler water needed to be anaerobic and deionized to ensure that no reactions occur during equilibration through the membrane, which would give non-representative results. For this reason, deionized water was deoxygenated in accordance to ASTM# D854. The deoxygenation involved placing the deionized water into an airtight cell that had a vacuum pump attached to the headspace. The applied backpressure vacuum of 10 to 15 inches of mercury would draw the dissolved oxygen out of the deionized water. To assist dissolved oxygen removal, a stirring device at the bottom of the cell circulated the water and forced any bubbles to the headspace for removal. The deionized water was subjected to this process for 30 minutes, as specified by the standard.

Sampler Fabrication

The 14 centimetre length of 1.9 centimetre (¾ inch) I.D. PVC pipe was positioned inside the dialysis membrane as close to the central location as possible (equal amounts of unsupported dialysis membrane remained on both sides of the pipe, approximately 5.5 centimetres). The PVC was positioned by gently rolling the cylindrical dialysis membrane onto the pipe because the skin friction was to great if the pipe was slid into the membrane (this led to tearing of the membrane and the use of the rolling method).

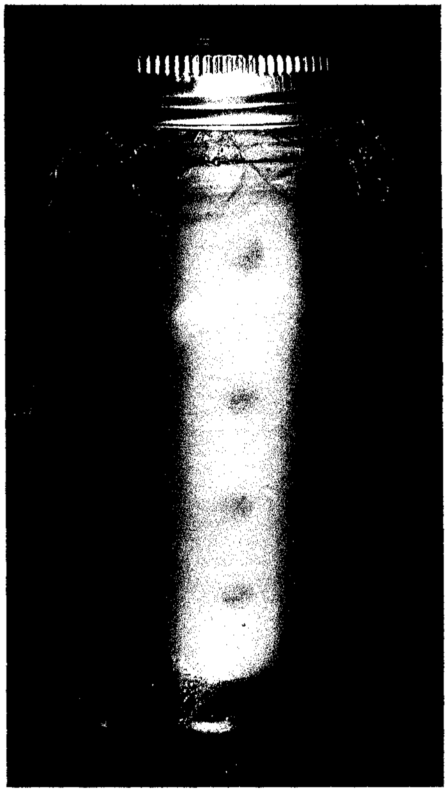
Once the PVC pipe was in position, one end of membrane was folded in a manner to create a leak-proof seal and was then clamped with a U-clamp. The dialysis sampler was then carefully filled with the deoxygenated water through the unsealed end until the sampler was full and free of air bubbles. The membrane was then sealed using a twisting method (pinch the open end and spin the sampler several times) before being U-clamped to prevent unraveling. The folding method was not employed on this end as it would trap air in the dialysis sampler, introducing unwanted air into the system. As all the deoxygenated water was used to construct the dialysis samplers, the dissolved oxygen concentrations were unable to be measured.



Fabricated Sampler with U-clamps

Experiment Procedure

The formation water was poured into the macrocosm until a meniscus formed; this ensured that no headspace was available for potential volatilization or oxidation. The prepared dialysis samplers were then lowered into the formation water using a string tied to one of the U-clamps. Two samplers were placed in each macrocosm to provide enough sample volume to analyze hydrocarbon concentrations. The samplers were lowered to the point where it remained suspended in the formation water, making sure not to touch the bottom or sides of the macrocosm. This was done to simulate the conditions expected to be encountered when the sampler is installed in a well. The string was then draped over the edge and the sealer lid was placed on the macrocosm, thereby keeping the sampler suspended in its final position. Plastic saran wrap was placed over the top of the macrocosm as an addition barrier and then the fastener was screwed tightly onto the macrocosm to secure the sealer lid and saran wrap in place for the experiment duration.



Macrocosm with Sampler Installed

This process was repeated until three macrocosms were created. All the macrocosms were then placed into a cardboard box and then sealed with tape to simulate the dark conditions of a well; limiting light exposure that may cause or inhibit membrane degradation. The box was then placed into the cold room at around 4°C to simulate the groundwater temperatures at the research sites.

The macrocosms were left undisturbed for a period of two, four and six weeks, at which time the macrocosms were opened for sampling. The upper clamp that was used to suspend the sampler was removed and then the membrane contents were carefully decanted into 40 mL BTEX/PHC F1 (BTEX = benzene, toluene, ethylbenzene, xylene and PHC F1 = petroleum hydrocarbon fraction 1) zero headspace sample vials. Formation water from the same macrocosm was also poured into another set of 40 mL BTEX/PHC F1 zero headspace sample vials for analysis. The analysis was conducted by Maxxam Analytical, as per the remainder of the sampling for the CORONA project. Limited sample volume was available from the dialysis sampler so only one BTEX/ATF1 vial could be obtained (Maxxam usually requires the submittal of two vials for analysis).This sampling was conducted at the designated time intervals to determine whether hydrocarbon equilibration had occurred between the macrocosm and the dialysis sampler, as indicated by similar hydrocarbon concentrations in the membrane and the macrocosm.

LABORATORY STUDY – Effects of Monovalent and Divalent Salts on Diffusion Samplers

Background

A water loss phenomenon was encountered during field installation of the diffudion samplers. The dialysis membrane was filled in the laboratory with deionized, deoxygenated water before being transported to the site for a 21 day installation. When certain samplers were retrieved it was discovered they had lost water, in some cases there was only approximately 30 millilitres of water. The water loss was most dramatic in the shallowest dialysis sampler and decreased with depth.

Further literature review revealed that if dialysis membrane were installed in a high concentration salt solution, water loss could result. The high concentration salt solution will attempt to reach equilibrium by drawing water from the membrane into the salt solution. If a rigid structure is not placed inside the dialysis membrane to prevent the membrane from shrinking as water is drawn out, then the membrane could lose all of its water in an attempt to equilibrate with the salt solution.

Objective

The study was conducted to:

- To determine if a salt concentration gradient effect could be responsible for the water loss observed in the field diffusion samplers.
- Examine if valency has an impact on water loss from the diffusion samplers.
- Determine the equilibration time for simple inorganic salt ions into dialysis membrane samplers.

Method

Two salt types were selected to investigate the possible valency effects on water loss and to determine the time required for equilibration to occur. The monovalent salt chosen was sodium chloride, commonly known as table salt. The divalent salt used was calcium sulphate, better known as gypsum. In each salt solution two dialysis samplers were suspended in the jar, ensuring not to touch the sides or bottom of the jar where non dissolved salt could impact the membrane. The first dialysis membrane was tied shut on both ends and was used to measure mass loss over the experiment duration. The second membrane was tied on the one end and clamped on the other end so it could be retrieved, unclamped and an electrical conductivity (EC) measurement taken inside the membrane.

EC was used to determine when equilibration occured because EC measures the solutions ability to conduct an electrical charge, which depends on the concentration of ions in solution that help carry the charge. When the EC is the same inside the membrane and the jar, equilibration has been achieved. The sample vessels were opened periodically and the mass loss dialysis membrane was removed, patted dry and weighed to determine the mass. At the same time the equilibration membrane was opened to measure EC to determine the extent of equilibration.

Sampler Material Preparation

Dialysis membranes were cut into two different lengths depending upon the parameter that was being measured. The membranes examining water loss were cut into 20 centimetre lengths. The membranes measuring EC were cut to 15 centimetre lengths. The reason for the different dialysis length was more dialysis membrane is needed to tie a knot than to seal the membrane with a stainless steel U-clamp. The membranes were soaked in distilled water for 20 minutes to remove any remnants of the preservative solution that the membrane was stored in. The membranes were than rinsed using fresh distilled water. The soaking and rinsing of the membrane was done in accordance with the directions provided by Membrane Filtration Products Inc. (MFPI). The U-clamps used to seal the ends of the sampler were cleaned using soapy water and left to soak in distilled water to limit any contamination by the clamps.

One litre canning jars were selected as the vessel to install the dialysis membranes in the salt solution since the seal would limit evaporation. The canning jars consisted of the fastener, the sealer lid and one liter glass jars. All the jars were cleaned with soapy water, then rinsed thoroughly and dried.

Experiment Water Preparation

Five concentrations for both salt types were prepared to ensure that expected field concentrations would be bounded within the range of the concentrations studied. The sodium chloride concentrations selected were 10, 50, 500, 1000 and 5000 milligrams per liter. The calcium sulphate concentrations selected were 10, 100, 500, 1000 and 2000 milligram per liter. All the salt solution concentrations were created by weighing one liter of water (one kilogram = one liter) and weighing the mass of salt required. The water was deionized to ensure that there were no ions initially in the water which could change the EC and possibly impact the results of the study. The salt was then placed into the liter of water and stirred until all the crystals were dissolved. For the higher salt concentrations, heat was applied to the water to facilitate complete dissolution of the salt crystals. This was necessary for the higher concentration calcium sulphate solutions.

Sampler Fabrication

The mass loss dialysis samplers (20 centimetre long membrane) were simply tied on one end and then filled with deionized water. The other end was then tied by pinching the membrane below the water level in the membrane, spinning it without trapping any air and then tying the membrane. The equilibration dialysis sampler (15 centimetre long membrane) was tied on one end and filled with deionized water. In order to have the capability to measure EC, the sampler needed to be opened at periodic intervals to place the EC probe in the water inside the dialysis membrane. This was accomplished by spinning the membrane, as described for the mass loss samplers, but instead of tying the membrane it was U-clamped.

The test vessels were created by pouring the various one liter salt concentrations into the one liter canning jars. The dialysis samplers were suspended in the vessels by means of tying nylon fishing line to the clamp for the equilibration membranes and the one of the knots for the mass loss membranes. The membranes were suspended so not to touch the bottom or the sides of the jar and were held in place by pinching the fishing line in the sealer lids. When the membranes were placed in the vessels this displaced some salt solution, but a meniscus was formed so no headspace existed when the sealer lids were placed on the vessel. Saran wrap was placed over the sealer lids as an additional evaporation barrier and then the fastener was placed on the jar as tight as possible to hold the sealer lids and saran wrap. An additional vessel was created in the same manner, except deionized water was used instead of a salt solution to act as a control for the experiment. A duplicate mass loss sampler was installed in the 2000 mg/L calcium sulphate solution to examine the variability between samplers in the same solution.

LABORATORY STUDY – Effects of Hydraulic Head and Evaporation on Diffusion Samplers

Background

After determining that salt gradients were not responsible for the water loss phenomenon occurring in the field diffusion samplers, a new hypothesis was devised. It was discovered that the field samplers installed at intervals partially above the water table had a severe water loss compared to samplers below the water table. It was postulated that evaporation could be occurring in the well headspace and hydraulic head of the water in membrane above the water table may be responsible for the sample volume loss.

Objective

The study was conducted to:

- To examine the potential for sample volume loss due to hydraulic head and evaporation effects.
- To determine if the water loss due to these processes was responsible for the water loss effects observed in the field.

Method

The initial masses of two diffusion samplers (created as described in Appendix A) were recorded and then hung from the ceiling into a 50 liter plastic barrel in a room under normal atmospheric conditions. One sampler was positioned so its top was just below the water surface and the other sampler had 25.5 centimetres submerged (18 centimetre was above water) so it was approximately half submerged. Hydraulic head is created by the 18 centimetre column of water acting downwards in the dialysis membrane, which may drive the water out of the membrane. The sampler remained in this position until the samplers were retrieved from the barrel, patted dry and weighed to the nearest tenth of a gram to determine the amount of water loss. The samplers were weighed daily for the first four days and then every two to three days afterwards. To ensure that the one dialysis sampler remained fully submerged and the hydraulic head pressure in the half submerged sampler was the same, water was added to maintain a marked initial water level. By recording the amount of water added to the barrel, the evaporation rate could be approximated. This process was continued until the mass of the sampler remained the same over a series of days, indicating no further water loss.

To examine evaporation effects on the sampler, another dialysis sampler was positioned so that it was submerged 25.5 centimetre below the same water surface in a 100% humidity cold room. Every effort was made to simulate the conditions of the half submerged sampler under normal atmospheric conditions: same plastic barrel, same water in barrel and inside dialysis membrane, same water level, and similar sampler design. In a 100% humidity room only minimal evaporation should occur so the effects of hydraulic head on water loss could be examined. The sampler was periodically removed, patted dry and its weight recorded to determine the amount of mass water loss.

Sampler Material Preparation

The sampler material preparation can be reviewed in Appendix A.

Experiment Water Preparation

As the samplers were field samplers, the detailed description for the sample water preparation can be reviewed in Appendix A. As the samplers were created for field installation, the samplers were transported back from the field before being used in this experiment. The diffusion samplers remained in storage containers for about 24 hours before the experiment was initiated. The dissolved oxygen was measured in the storage container water at approximately 2 mg/L, so the water inside the samplers should be similar due to equilibration. The water used to fill the plastic barrel was taken directly from the tap and was not treated in any manner. The plastic barrel was washed and rinsed thoroughly to eliminate any impact to the experiment results.

Sampler Fabrication

The diffusion sampler was fabricated as described in Appendix A, except no seals were fastened onto the end of the sampler. Instead a cable tie is connected through two holes in the end of the PVC pipe to tie a rope so the sampler can be suspended from the ceiling into the plastic barrel.

APPENDIX D:

Dialysis Membrane Diffusion Sampler and Waterra Sampler Detailed Field Data Comparison

Site 1

Cation Comparison

Figure D1 compares the cation results for the diffusion samplers and Waterra samples. For both the October and February sampling events the two diffusion sampler results were nearly identical. The Waterra sample obtained in February provided results that were nearly identical to the diffusion sampler results; the cation concentrations varied by less than 1 mg/L.

Anion Comparison

Anion data are plotted in Figure D2. The anion concentrations for the two diffusion samplers were nearly identical for the October sampling event. For the February sampling event the chloride and bicarbonate concentrations were nearly identical for both samplers, with the Waterra bicarbonate and chloride concentrations being approximately 10% (17 mg/L) and 2% (0.1 mg/L) higher than the diffusion samplers respectively. This difference is deemed insignificant. The sulfate concentrations for both sampler types were 2.7 mg/L +/-1 mg/L.

Metals Comparison

A comparison of the metal concentration is shown in Figure D3. The metals concentrations measured by the two diffusion samplers in October were nearly identical. The February iron results for the two diffusion samplers were slightly more variable than October, with a variation of 35% (1.8 mg/L). The Waterra manganese and iron concentrations were both higher than the diffusion samplers. The manganese was 40% (0.5 mg/L) higher and iron was nearly 2.5 times larger (10.5 mg/L) than the average diffusion sampler result (4.3 mg/L).

Hydrocarbon Comparison

The hydrocarbon comparison is shown in Figure D4. All the October hydrocarbon constituent concentrations in the two diffusion samplers varied by less than 0.005 mg/L. The diffusion sampler concentrations were also very similar in February. However, all the hydrocarbon results for the diffusion samplers were lower than the Waterra sampler results, except for benzene which was nearly identical.

Ethylbenzene and xylene concentrations were three times (0.05 mg/L) higher in the Waterra samples. The Waterra sampler's F1 – BTEX concentration was approximately seven times (12 mg/L) higher than the diffusion samplers.

Site 2

Well Cluster 34

At this well cluster, samples were collected from well 34-MW1.

Cation Comparison

Figure D5 compares the cation results for diffusion samplers and the Waterra samples. For both the October and February sampling events the diffusion samplers measured increasing concentration with depth. In October the deeper sampler was approximately 17 to 21% higher for the cations measured, with the magnesium, sodium and calcium concentrations being 39 mg/L, 48 mg/L and 13 mg/L higher than the shallow sampler. In February the deeper sampler was approximately 18% (56 mg/L), 24% (68 mg/L) and 39% (37 mg/L) higher than the shallow sampler for the magnesium, sodium and calcium concentrations, respectively.

The Waterra sample results were approximately 40 mg/L (13 to 36%) higher than the deepest diffusion sampler for all the cation concentrations in October. In February the Waterra magnesium and sodium concentrations fell between the diffusion sampler concentrations. The Waterra calcium concentration was slightly higher than the deeper diffusion sampler concentration. The cation concentrations for the Waterra and deeper diffusion sampler varied by less than 10% in February.

Anion Comparison

Anion data are plotted in Figure D6. For both sampling events the diffusion sampler's bicarbonate and chloride concentrations increased with depth, however the sulfate concentration was similar. The Waterra sampler again was within 10% or less of the deeper diffusion sampler for the bicarbonate and chloride concentrations for both sampling periods, however the sulfate concentration was approximately four times larger than the diffusion samplers.

Metals Comparison

A comparison of the metals concentrations is shown in Figure D7. The October manganese and iron concentrations were nearly identical for the diffusion samplers, and in February both metals varied by one mg/L or less. The Waterra manganese concentrations were less than 1.5 mg/L higher than the diffusion samplers for both October and February. The Waterra iron concentration for October and February was almost twice the average diffusion sampler results.

Hydrocarbon Comparison

The hydrocarbon comparison is shown in Figure D8. In October and February the diffusion samplers appeared to show a slight increase in concentration with depth for all hydrocarbon constituents, however the increase with depth was more apparent in the October sampling data. The Waterra results closely matched (less than 25% variance) the deeper diffusion sampler; the exceptions were the October F1 – BTEX varied by 65% (3 mg/L) and the February benzene was 50% (0.01 mg/L) different.

Well Cluster 35

At this well cluster, samples were collected from well 35-MW1.

Cation Comparison

Figure D9 compares the cation results for the diffusion samplers and the Waterra samples. The diffusion samplers were nearly identical (<8% variability) for both the October and February sampling periods except the calcium concentrations in the deeper sampler was 11% higher in October and 16% higher in February (9 and 15 mg/L). The October Waterra sample results were higher (18-43%) than the diffusion sampler for all cations, however the February results were nearly identical to the deeper diffusion sampler concentrations (<7% difference). There was no indication from the sample results of any vertical concentration differences within this well.

Anion Comparison

The anion results are plotted in Figure D10. The sulfate and chloride concentrations were nearly identical for the diffusion samplers for both October and February. The diffusion samplers bicarbonate concentrations demonstrated an increasing concentration with depth, with an increase of 7% in October and a 12% in February. The Waterra sampler matched closely for both sampling events, except in October the bicarbonate concentration was approximately 40% (400 mg/L) higher. The Waterra and deepest diffusion sampler were nearly identical again for the February sampling period.

Metals Comparison

A comparison of the metals concentration is shown in Figure D11. The October and February manganese concentration matches well (<0.7 mg/L difference) for both diffusion samplers considering the low concentrations measured. The Waterra manganese concentration is nearly identical to the deeper diffusion sampler in February, however the October manganese was 60% (2.7 mg/L) higher than the diffusion sampler average. The diffusion sampler iron concentrations for October and February matched closely. The October Waterra iron concentration was approximately 30% (15 mg/L) higher than the diffusion samplers' average concentration. The February Waterra iron concentration was over two and half orders of magnitude larger than the diffusion samplers (from 0.06 to 31 mg/L).

Hydrocarbon Comparison

The hydrocarbon comparison is shown in Figure D12. For both sampling events the diffusion samplers demonstrate a decreasing concentration with depth for all hydrocarbon constituents, with February (52 to 72%) having a more apparent difference than October (18 to 38%). In October the Waterra sampler measured lower hydrocarbon concentrations compared to both diffusion samplers (10 to 33%), with the exception of the Waterra F1-BTEX concentrations, which were three times higher (4 mg/L) than the diffusion samplers. The February Waterra and deepest diffusion sampler had nearly identical hydrocarbon concentrations (7 to 15% difference), however ethylbenzene varied by 38% (0.08 mg/L).

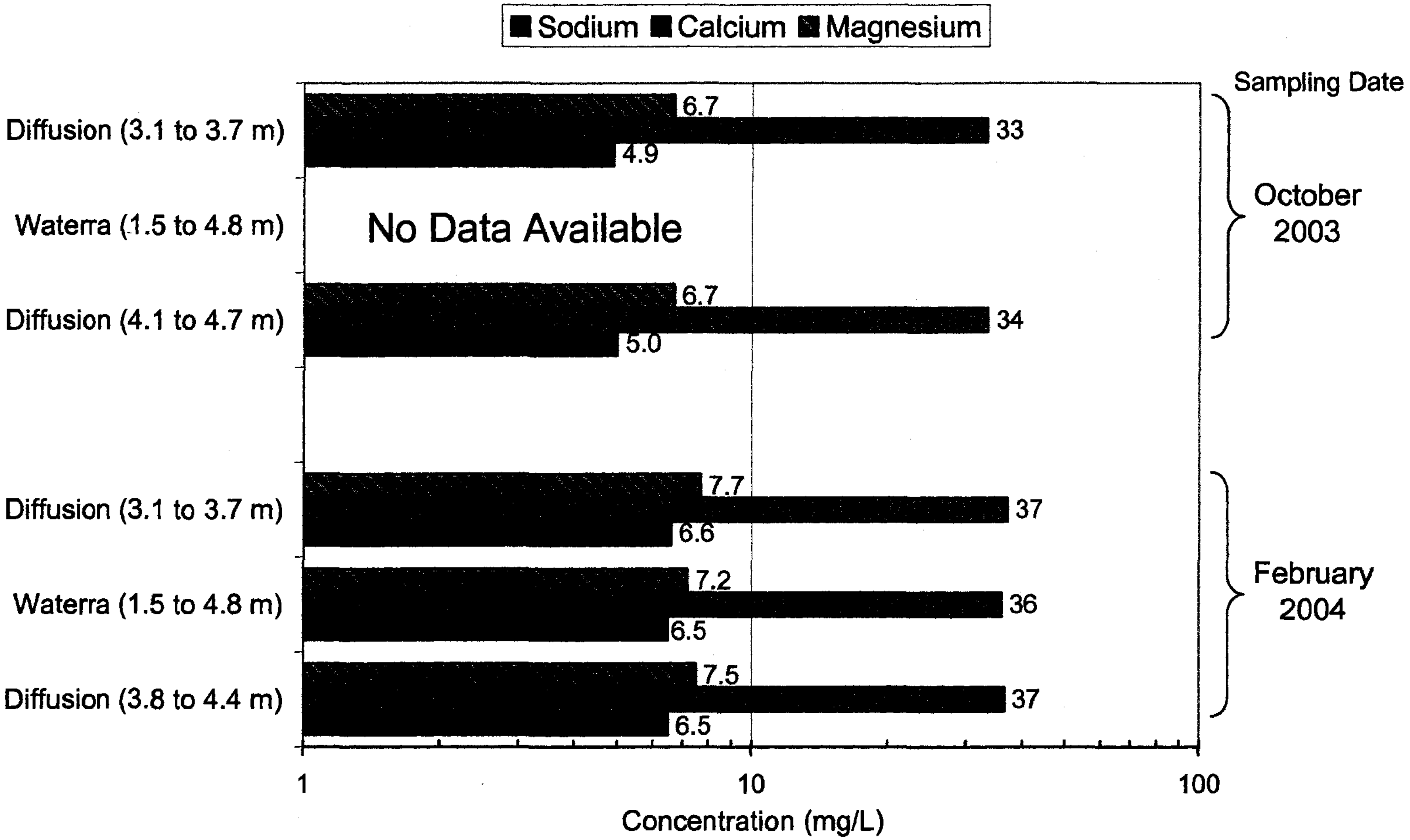


Figure D1. Waterra and Diffusion Sampler Cation Concentration Comparison (Site 1)

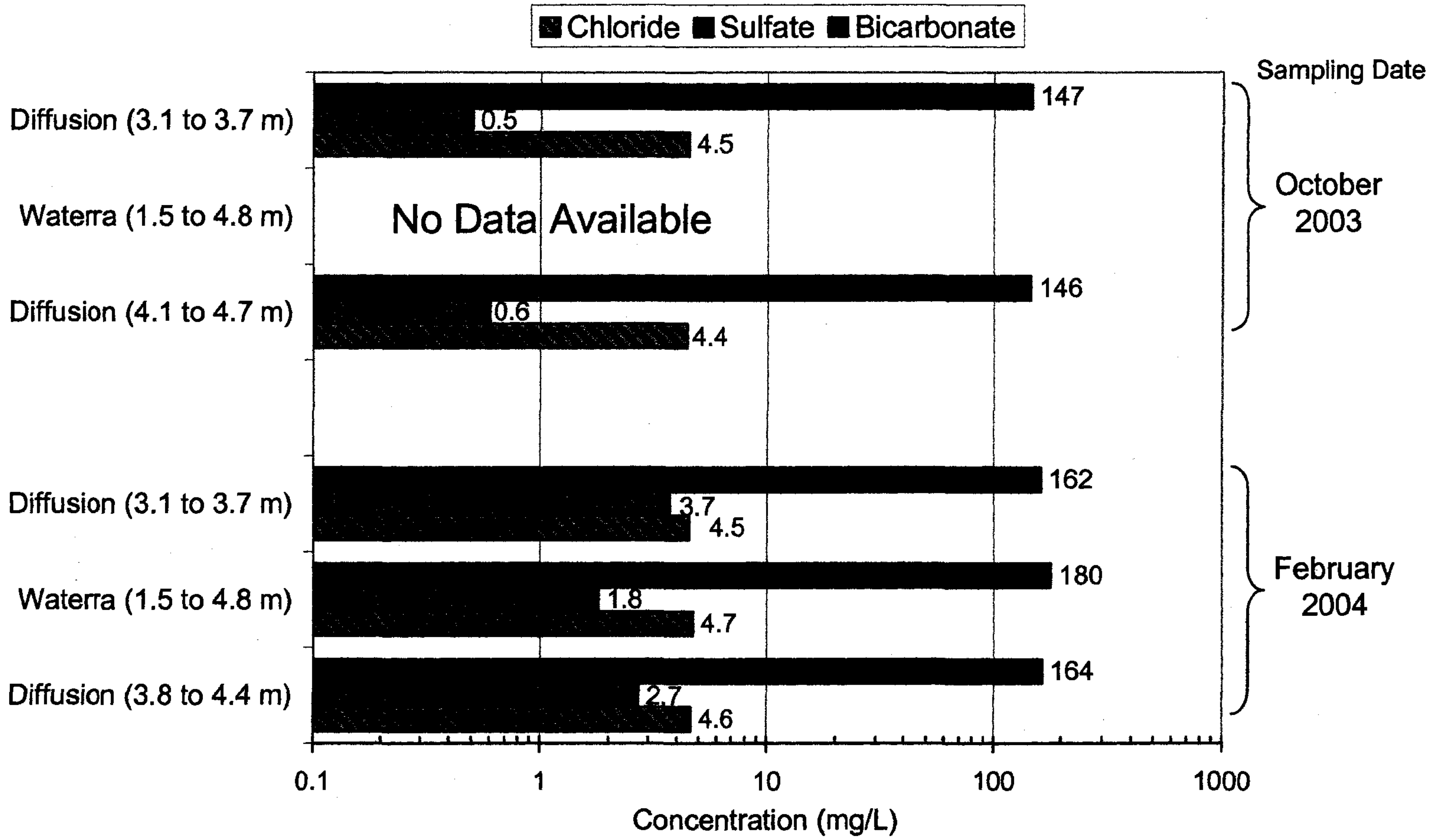


Figure D2. Waterra and Diffusion Sampler Anion Concentration Comparison (Site 1)

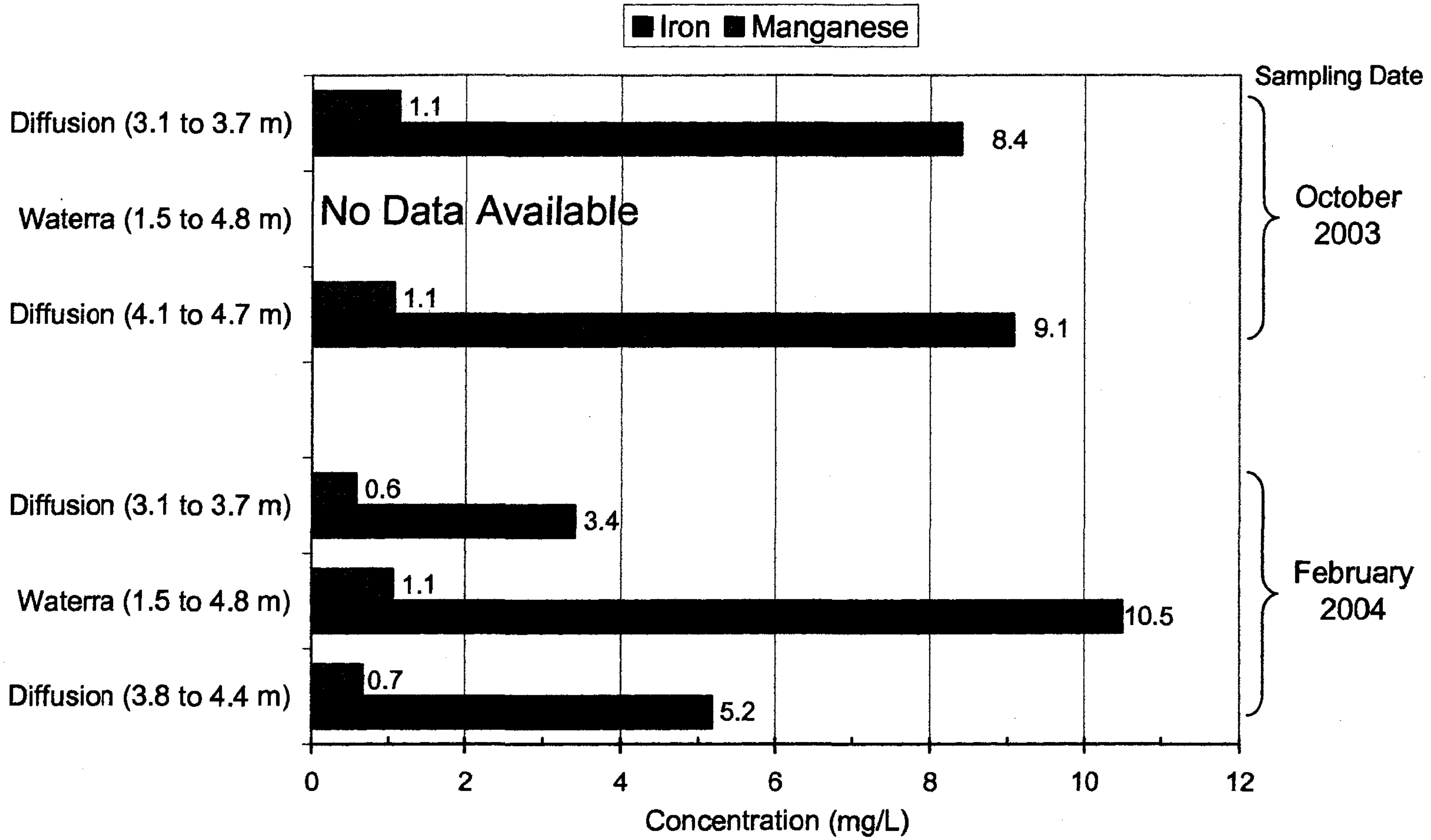


Figure D3. Waterra and Diffusion Sampler Metals Concentration Comparison (Site 1)

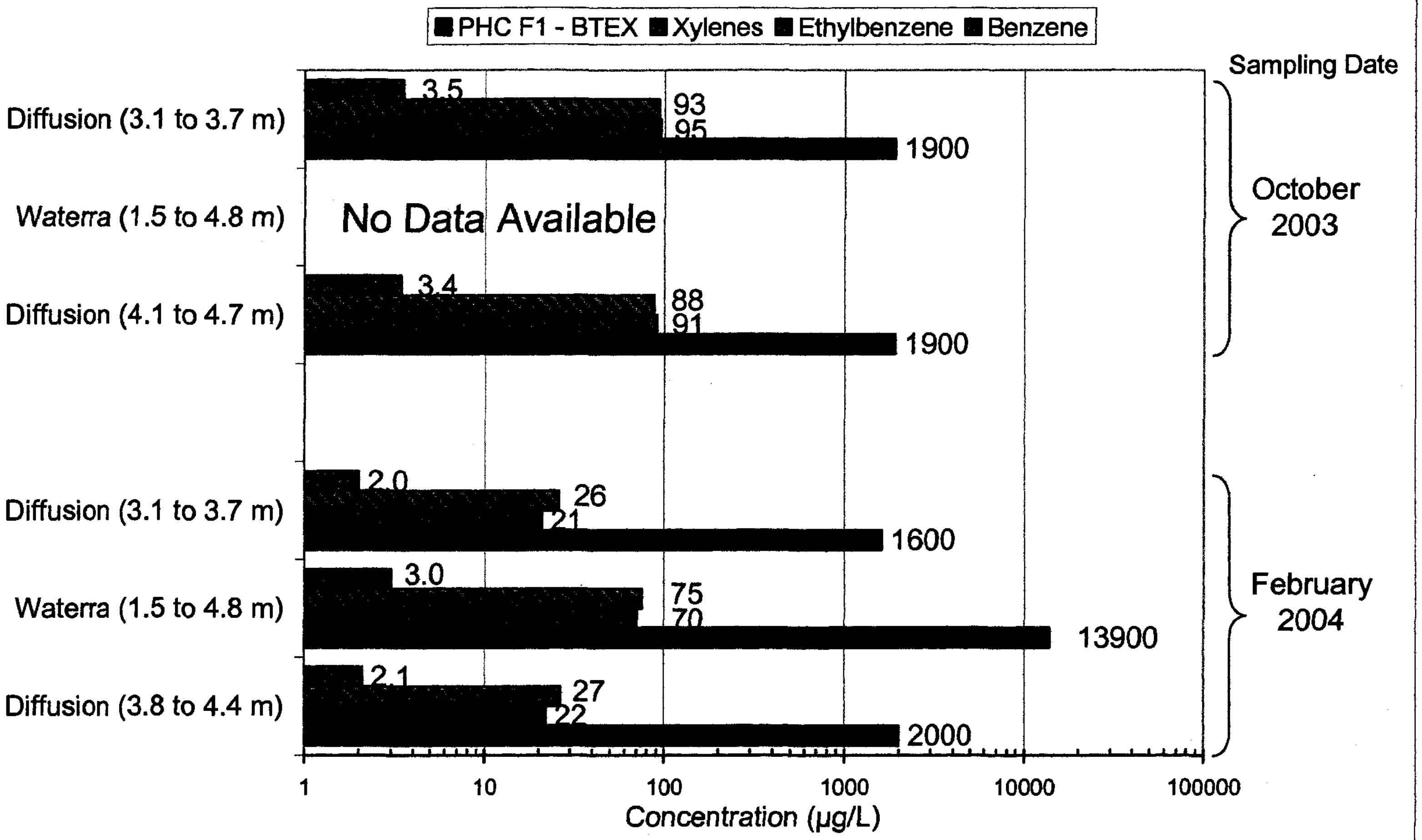


Figure D4. Waterra and Diffusion Sampler Hydrocarbon Concentration Comparison (Site 1)

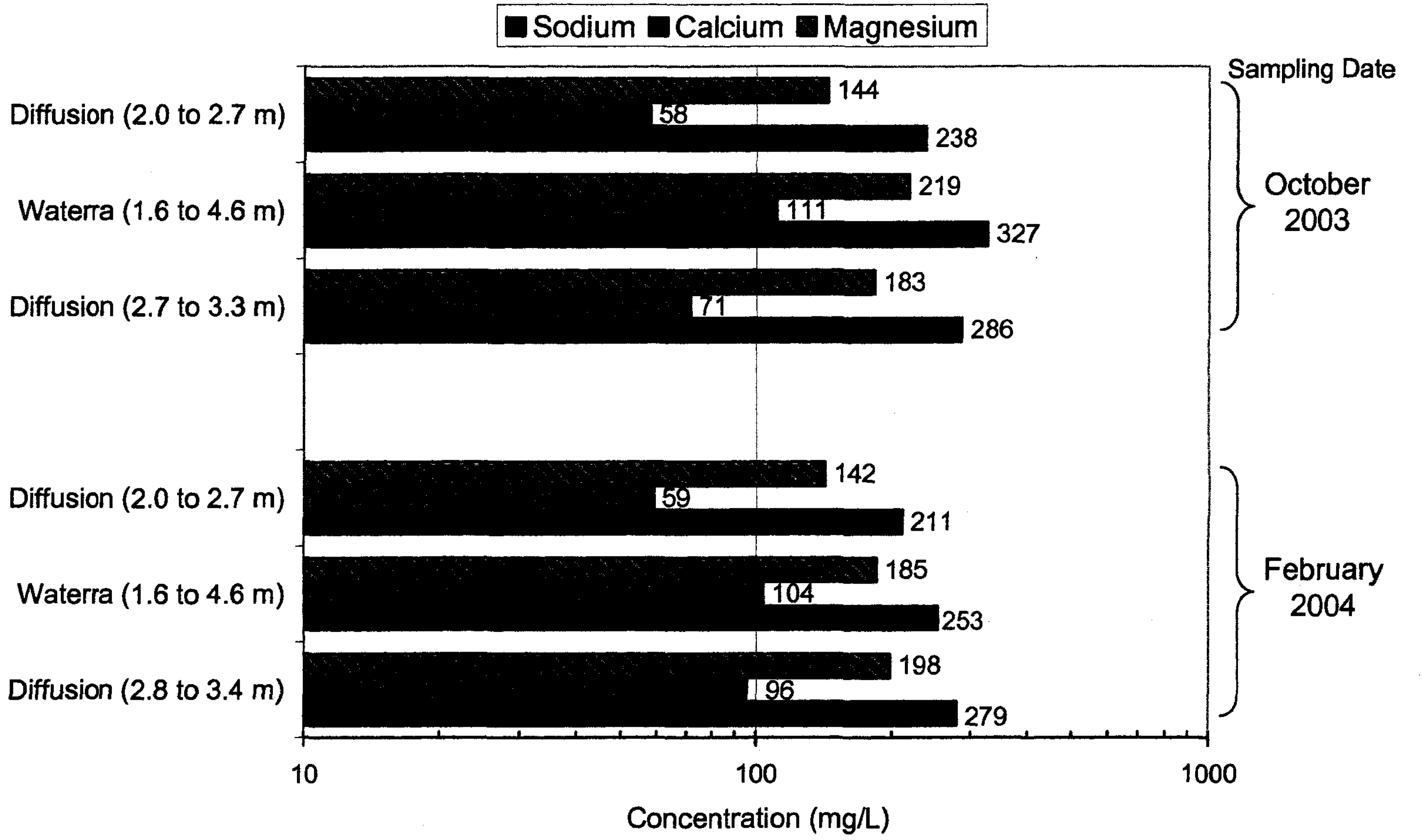


Figure D5. Waterra and Diffusion Sampler Cation Concentration Comparison (Site 2, Well Cluster 34)

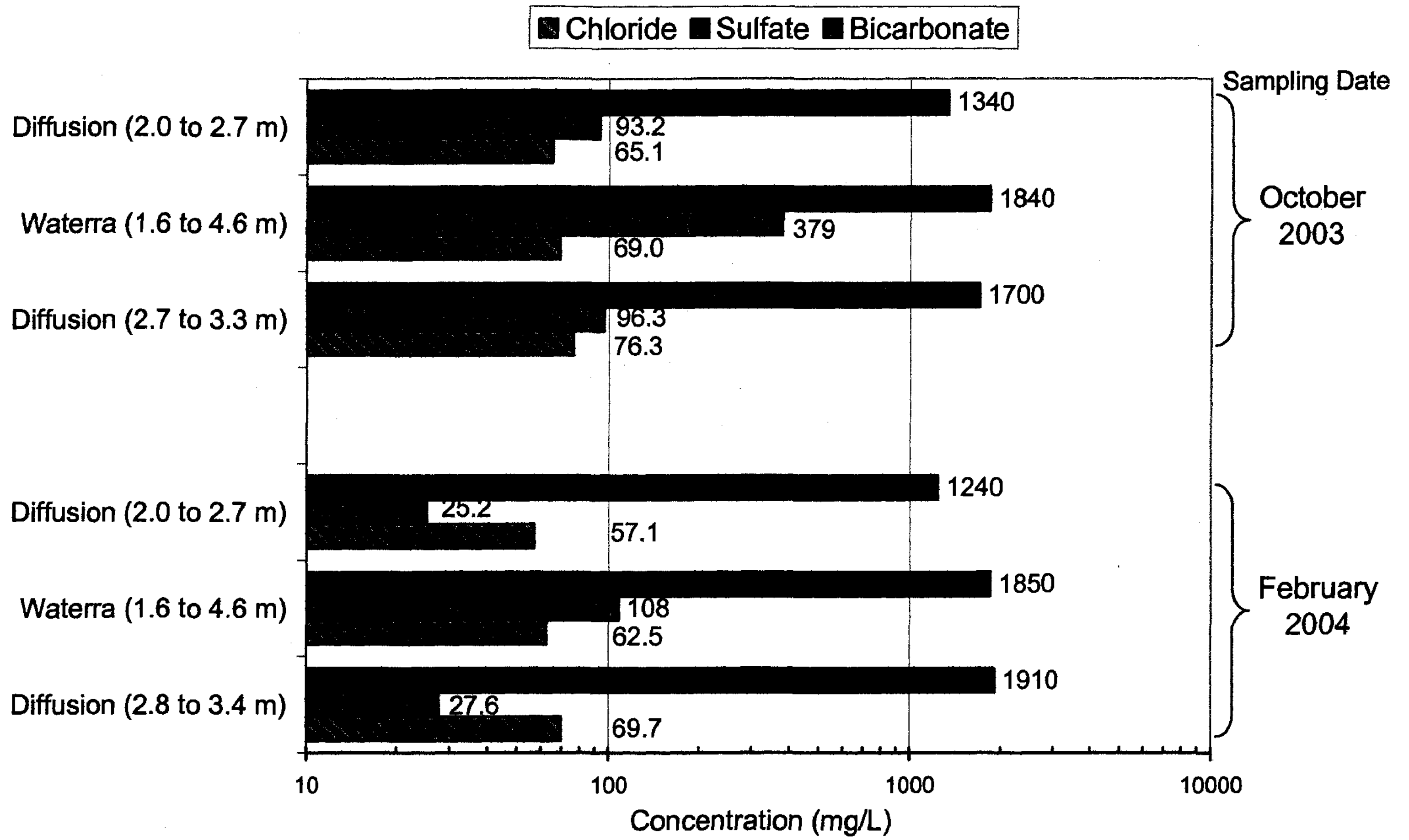


Figure D6. Waterra and Diffusion Sampler Anion Concentration Comparison (Site 2, Well Cluster 34)

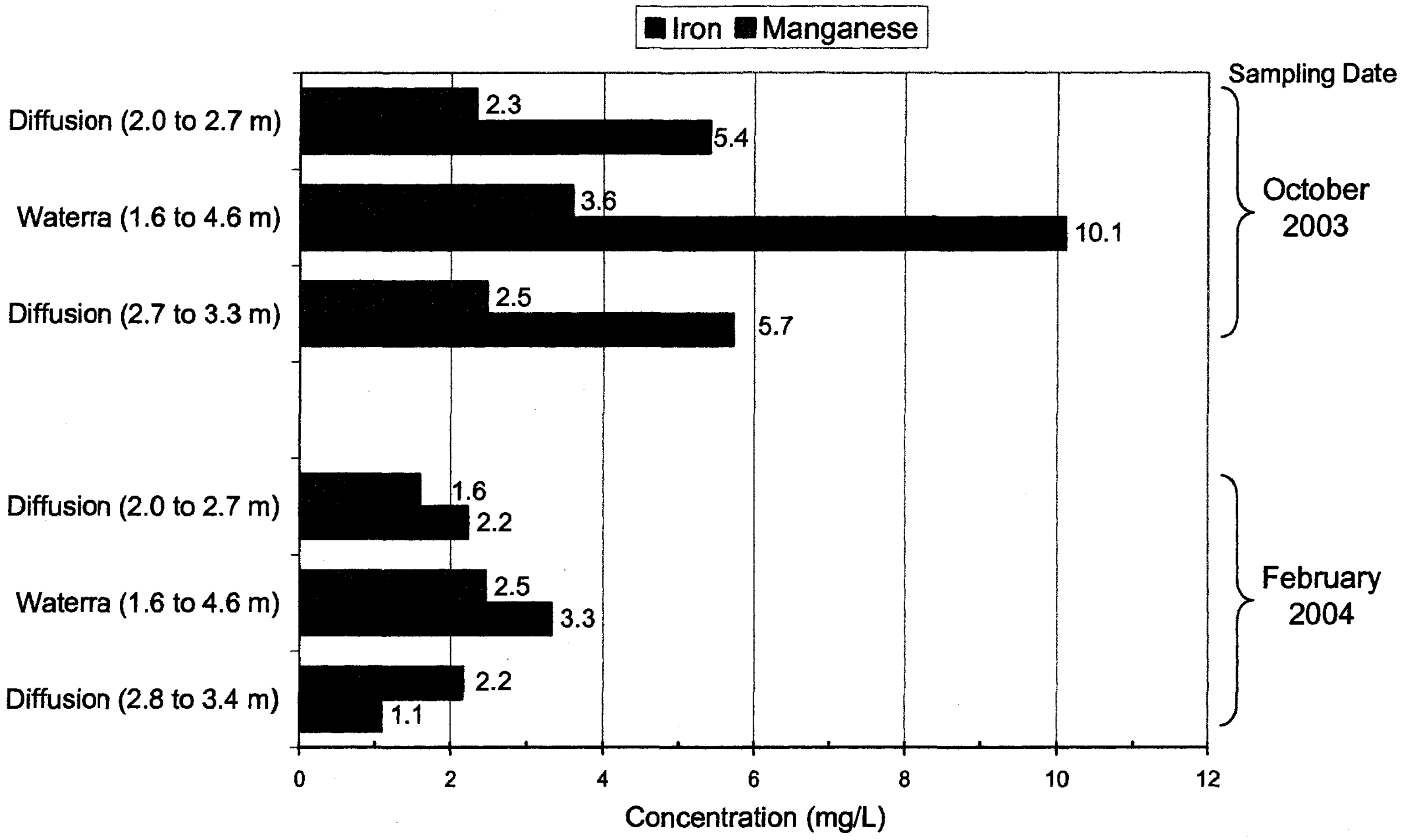


Figure D7. Waterra and Diffusion Sampler Metals Concentration Comparison (Site 2, Well Cluster 34)

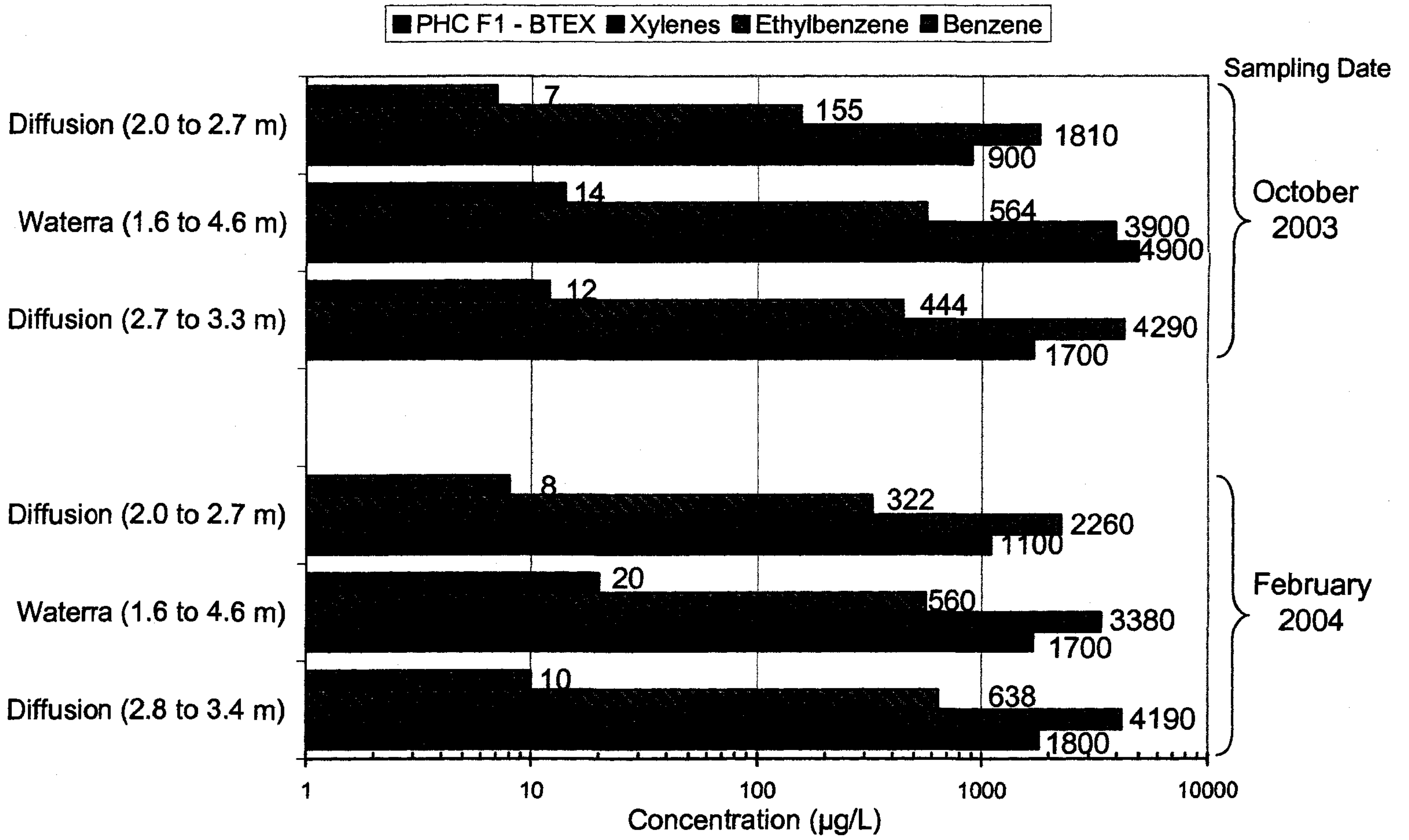


Figure D8. Waterra and Diffusion Sampler Hydrocarbon Concentration Comparison (Site 2, Well Cluster 34)

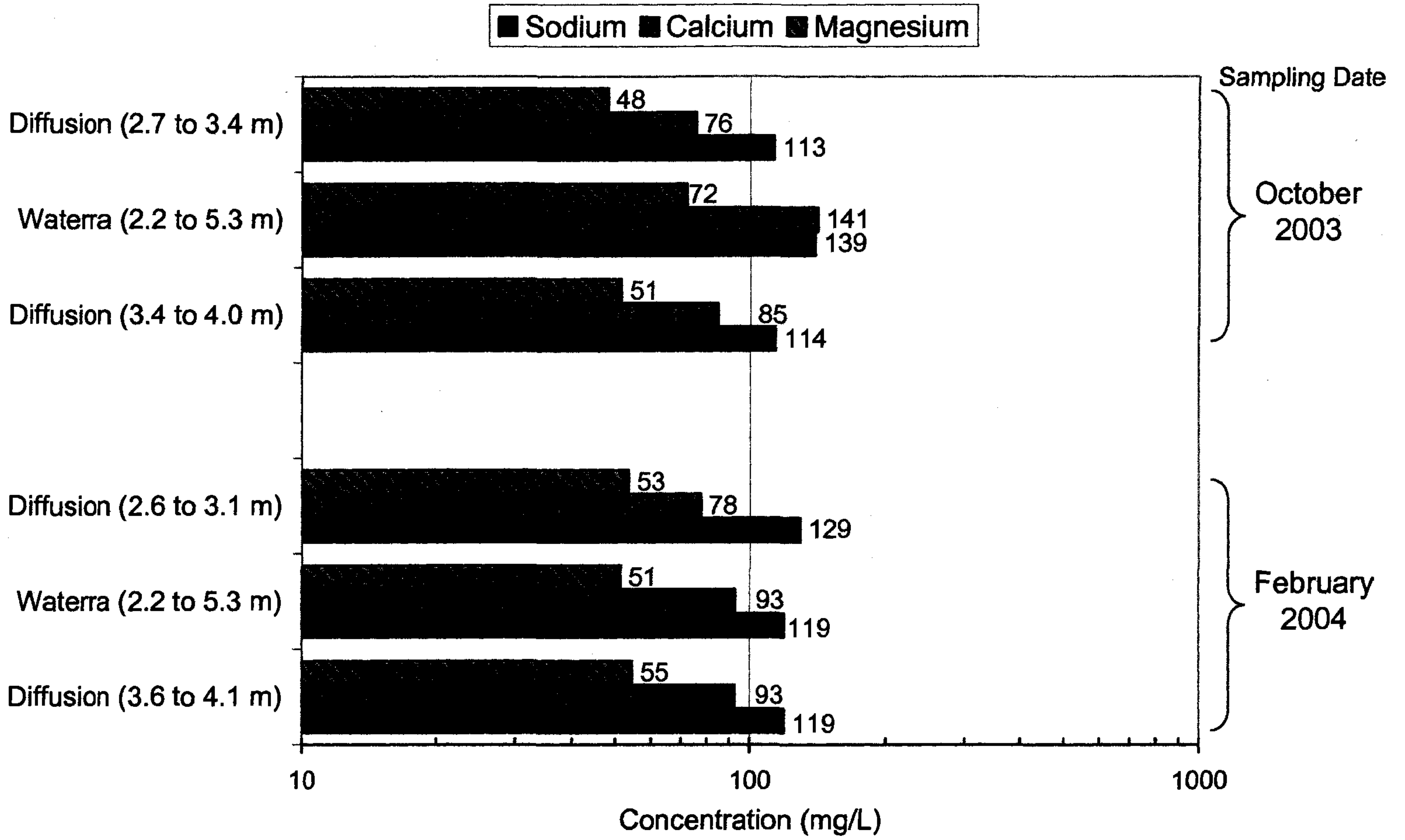


Figure D9. Waterra and Diffusion Sampler Cation Concentration Comparison (Site 2, Well Cluster 35)

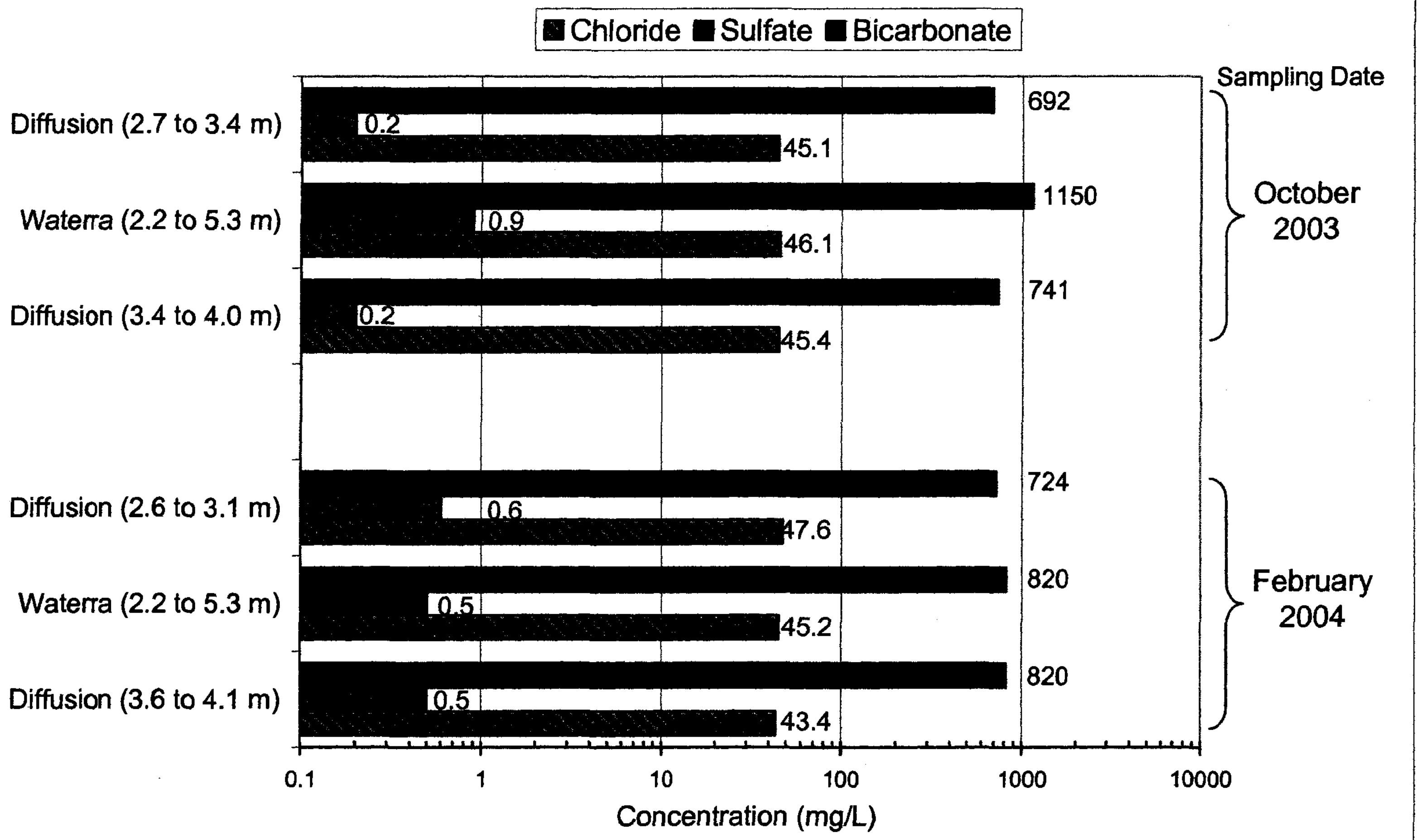


Figure D10. Waterra and Diffusion Sampler Anion Concentration Comparison (Site 2, Well Cluster 35)

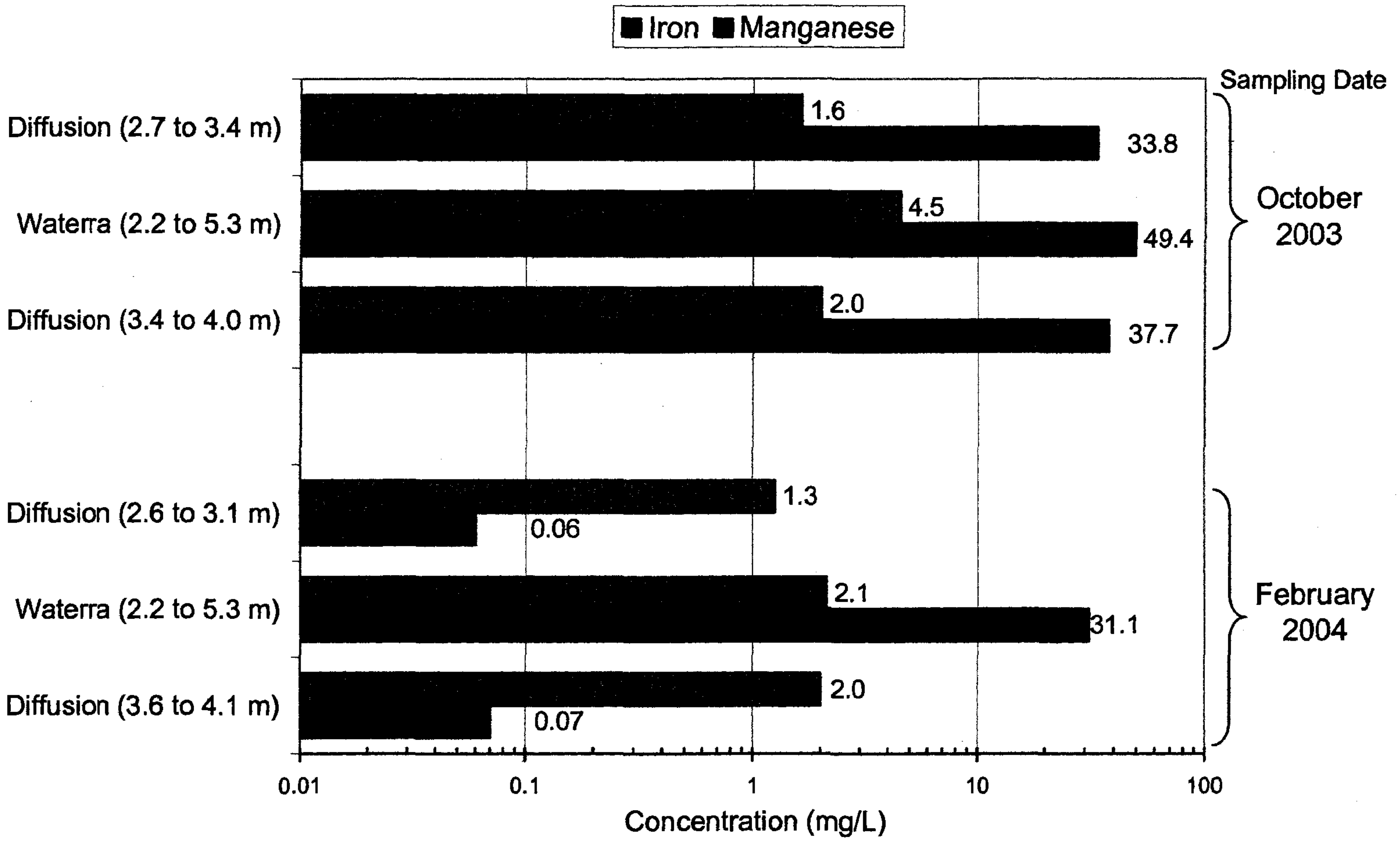


Figure D11. Waterra and Diffusion Sampler Metals Concentration Comparison (Site 2, Well Cluster 35)

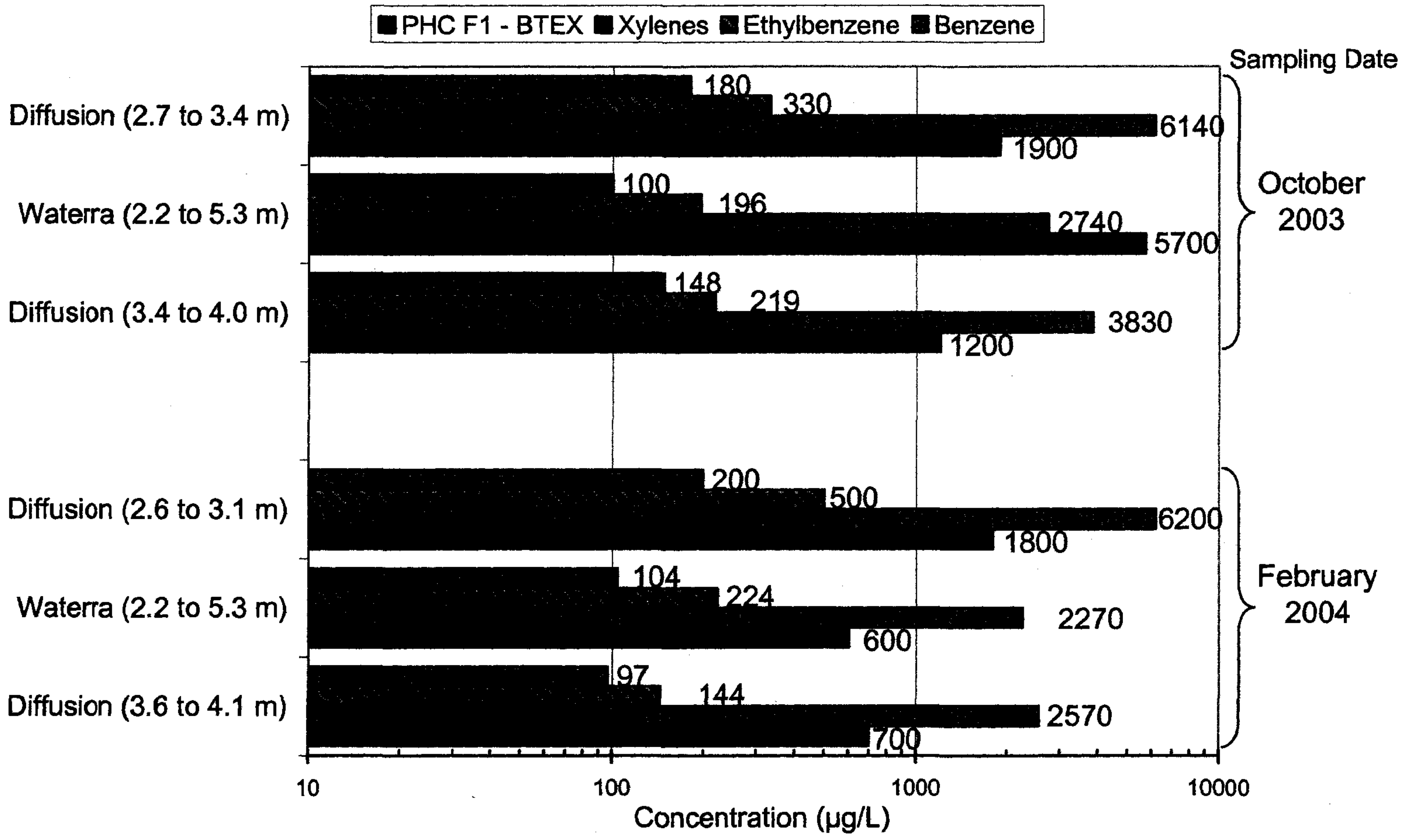


Figure D12. Waterra and Diffusion Sampler Hydrocarbon Concentration Comparison (Site 2, Well Cluster 35)

APPENDIX E:

Laboratory Study Result Tables And Experimental Calculations

Relative Percent Difference (RPD) Sample Calculations

The relative percent difference (RPD) was selected to evaluate the precision of sample analysis and to assess whether the sample measurements are within acceptable limits (U.S. Department of Energy, 2002). The RPD equation utilized is as follows:

$$\text{RPD}(\%) = \frac{|X_1 - X_2|}{X_{ave}} \times 100\%$$

where: X_1 and X_2 = analytical sample concentrations being compared
X_{ave} = mean concentration of X_1 and X_2

To apply the RPD calculation above to sampling data collected by the alternative sampling technologies it is assumed that X_1 is the concentration for the alternative technology and X_2 is one of the industry standard concentrations for the parameter being compared. As the different well types were installed within close proximity (approximately one metre) of each other, this calculation assumes that lateral spatial variability in analyte concentration is negligible, thus the RPD represents the variability between the different technologies and this can be used to assess the ability of the alternative technology to accurately measure groundwater concentrations.

To demonstrate the numerical use of the RPD equation using the sample data collected from the research sites, the following example has been calculated:

The bicarbonate results for the depth interval 3 to 4 metres at Site 1 for the February sampling event (Table 3.15) are:

Bailer sampled well (3.0 to 3.5 m) = 198 mg/L
Waterra sampled well (3.2 to 4.3 m) = 152 mg/L
Waterra sampled well (3.2 to 4.8 m) = 180 mg/L
Diffusion sampler (3.1 to 3.7 m) = 162 mg/L
Diffusion sampler (3.8 to 4.4 m) = 164 mg/L

The RPD calculation and comparison for the shallow diffusion sampler (3.1 to 3.7 m) follows:

X_1 in the RPD calculation is the bicarbonate concentration for the alternative sampling technology, which in this case is the shallow diffusion sampler (3.1 to 3.7 m).

$$X_1 = 162 \text{ mg/L}$$

X_2 is the bicarbonate concentration for the industry standard. In this case there are three concentrations that X_2 may take in the RPD calculation.

The first option for X_2 is the bailer bicarbonate concentration:

$$X_2 = 198 \text{ mg/L}$$

As a result, the X_{ave} value is:

$$X_{ave}^{1} = (X_1 + X_2) / 2 = (162 \text{ mg/L} + 198 \text{ mg/L}) / 2 = 180 \text{ mg/L}$$

Thus the RPD value for the bailer sampled result is:

$$RPD_1\,(\%) = \frac{| X_1 - X_2 |}{X_{ave}^{1}} \times 100\% = \frac{| 162 \text{ mg/L} - 198 \text{ mg/L} |}{180 \text{ mg/L}} \times 100\% = 20.0\%$$

The second option for X_2 is the Waterra (3.2 to 4.3 m) bicarbonate concentration:

$$X_2 = 152 \text{ mg/L}$$

As a result, the X_{ave} value is:

$$X_{ave}^{2} = (X_1 + X_2) / 2 = (162 \text{ mg/L} + 152 \text{ mg/L}) / 2 = 157 \text{ mg/L}$$

Thus the RPD value for the shallow Waterra result (3.2 to 4.3 m) is:

$$RPD_2\,(\%) = \frac{| X_1 - X_2 |}{X_{ave}^{2}} \times 100\% = \frac{| 162 \text{ mg/L} - 152 \text{ mg/L} |}{157 \text{ mg/L}} \times 100\% = 6.4\%$$

The third option for X_2 is the Waterra (3.2 to 4.8 m) bicarbonate concentration:

$$X_2 = 180 \text{ mg/L}$$

As a result, the X_{ave} value is:

$$X_{ave}^3 = (X_1 + X_2) / 2 = (162 \text{ mg/L} + 180 \text{ mg/L}) / 2 = 171 \text{ mg/L}$$

Thus the RPD value for the deeper Waterra result (3.2 to 4.8 m) result is:

$$RPD_3 (\%) = \frac{| X_1 - X_2 |}{X_{ave}^3} \times 100\% = \frac{| 162 \text{ mg/L} - 180 \text{ mg/L} |}{171 \text{ mg/L}} \times 100\% = 10.5\%$$

So the RPD for the shallow diffusion sampler (3.1 to 3.7 m) becomes:

$$RPD_{Ave} (\%) = \frac{RPD_1 + RPD_2 + RPD_3}{3} = \frac{20.0\% + 6.4\% + 10.5\%}{3} = 12.3\%$$

In order to assess if the diffusion sampler RPD value is reasonable or acceptable, it should be compared to the RPD for the industry standard results. As a result the industry standard RPD must be calculated and this is done by:

There are three industry standard results to be compared, so for the first RPD calculation X_1 is the bicarbonate concentration for the bailer sampled well:

$$X_1 = 198 \text{ mg/L}$$

X_2 is the bicarbonate concentration for the shallow Waterra sampled well (3.2 to 4.3 m):

$$X_2 = 152 \text{ mg/L}$$

As a result, the X_{ave} value is:

$$X_{ave}^1 = (X_1 + X_2) / 2 = (198 \text{ mg/L} + 152 \text{ mg/L}) / 2 = 175 \text{ mg/L}$$

So the first RPD value for the industry standard results is:

$$RPD_1 (\%) = \frac{| X_1 - X_2 |}{X_{ave}^1} \times 100\% = \frac{| 198 \text{ mg/L} - 152 \text{ mg/L} |}{175 \text{ mg/L}} \times 100\% = 26.3\%$$

For the second RPD calculation, X_1 now becomes the bicarbonate concentration for the shallow Waterra sampled well (3.2 to 4.3 m):

$$X_1 = 152 \text{ mg/L}$$

And X_2 becomes the other bicarbonate concentration for the deeper Waterra sampled well (3.2 to 4.8 m):

$$X_2 = 180 \text{ mg/L}$$

As a result, the X_{ave} value is:

$$X_{ave}^2 = (X_1 + X_2) / 2 = (152 \text{ mg/L} + 180 \text{ mg/L}) / 2 = 166 \text{ mg/L}$$

So the second RPD value for the industry standard results is:

$$RPD_2\ (\%) = \frac{| X_1 - X_2 |}{X_{ave}^2} \times 100\% = \frac{| 152 \text{ mg/L} - 180 \text{ mg/L} |}{166 \text{ mg/L}} \times 100\% = 16.9\%$$

For the third RPD calculation X_1 once again becomes the bicarbonate concentration for the bailer sampled well:

$$X_1 = 198 \text{ mg/L}$$

And X_2 remains the bicarbonate concentration for the deeper Waterra sampled well (3.2 to 4.8 m):

$$X_2 = 180 \text{ mg/L}$$

As a result, the X_{ave} value is:

$$X_{ave}^3 = (X_1 + X_2) / 2 = (198 \text{ mg/L} + 180 \text{ mg/L}) / 2 = 189 \text{ mg/L}$$

So the second RPD value for the industry standard results is:

$$RPD_3\ (\%) = \frac{| X_1 - X_2 |}{X_{ave}^3} \times 100\% = \frac{| 198 \text{ mg/L} - 180 \text{ mg/L} |}{189 \text{ mg/L}} \times 100\% = 9.5\%$$

So the RPD for the industry standard results becomes:

$$RPD_{Ave}\,(\%) = \frac{RPD_1 + RPD_2 + RPD_3}{3} = \frac{26.3\% + 9.5\% + 16.9\%}{3} = 17.6\%$$

The fact that the average RPD for the diffusion sampler (12.3%) is lower than the average RPD for the industry standard results (17.6%) indicates that the bicarbonate concentrations measured by the shallow diffusion sampler were representative and that the diffusion sampler was capable of accurately measuring bicarbonate within the groundwater.

Sand Pack and Well Volume Calculations

To accurately calculate the volume of the sand pack around the well, the volume of space that the well itself occupies must be calculated and subtracted from the volume of the borehole that the well was installed. This is done as follows:

The outer diameter of the multilevel well is 1.7 inches = 0.04318 metres.

$$\text{Area} = \Pi \text{ x } r^2 = \Pi \text{ x } (0.04318 \text{ m}/2)^2$$
$$\text{Area} = 0.001464 \text{ m}^2$$

As the typical sand pack height is 0.6 metres, the volume becomes:

$$\text{Volume} = \text{Area x Height} = 0.001464 \text{ m}^2 \text{ x } 0.6 \text{ m}$$
$$\text{Volume} = 0.0008763 \text{ m}^3$$

Knowing that there is 1000 Liters of water per one cubic metre (m^3) we get a volume in liters of:

$$\text{Volume} = 0.0008763 \text{ m3 x } 1000 \text{ L/m}$$
$$\text{Volume}_{(\text{Well})} = 0.8786 \text{ L}$$

Assuming that a six inch borehole would exist for the well to be installed if a six inch solid stem auger or the inner diameter of an eight inch hollow stem auger were used, the following borehole area can be calculated:

6 inches = 0.1524 metres.

$$\text{Area} = \Pi \text{ x } r^2 = \Pi \text{ x } (0.1524 \text{ m}/2)^2$$
$$\text{Area} = 0.01824 \text{ m}^2$$

For the typical sand pack height of 0.6 metres for the multilevel well installation, the volume for the borehole becomes:

$$\text{Volume} = \text{Area x Height} = 0.01824\ \text{m}^2 \text{ x } 0.6\ \text{m}$$
$$\text{Volume} = 0.01094\ \text{m}^3 \text{ x } 1000\ \text{L/m}$$
$$\text{Volume}_{(\text{Borehole})} = 10.9448\ \text{L}$$

To determine the volume of the sand pack that exists around the well, the two volumes must be subtracted to give:

$$\text{Volume}_{(\text{Sand Pack})} = \text{Volume}_{(\text{Borehole})} - \text{Volume}_{(\text{Well})}$$
$$\text{Volume}_{(\text{Sand Pack})} = 10.9448\ \text{L} - 0.8786\ \text{L}$$
$$\text{Volume}_{(\text{Sand Pack})} = 10.06\ \text{L}$$

Assuming a void ratio of 0.4 for the sand used in well construction, the volume available for groundwater to occupy becomes:

$$\text{Volume}_{(\text{Groundwater})} = \text{Volume}_{(\text{Sand Pack})} \text{ x } 0.4 = 10.06\ \text{L x } 0.4$$
$$\text{Volume}_{(\text{Groundwater})} = 4.02\ \text{L}$$

To determine the range of volumes that exist within the multilevel wells at both sites, the groundwater must be reviewed to assess within which wells the smallest and largest volumes exist. The groundwater data is as follows:

Site	Well ID	Water Level (mTOC)	Well Depth (mTOC)	Height of Water in Well (m)
1	ML1	2.45	2.89	0.44
	ML2	2.46	3.73	1.27
	ML3	4.06	4.94	0.88
	ML4	4.06	5.93	1.87
3	34-ML2	2.64	3.55	0.91
	34-ML3	2.64	4.55	1.91
	34-ML4	2.64	5.29	2.65
3	35-ML1	3.06	3.46	0.40
	35-ML2	3.06	4.44	1.38
	35-ML3	3.06	5.44	2.38
	35-ML4	3.06	6.58	3.52

Note: mTOC = metres below top of casing
Height of Water in Well = Well Depth – Water Level
October groundwater data was used as this was presented at both sites

The largest volume that would exist within one of the ½ inch channels would be for the channel with the largest Height of Water in Well. For all the locations investigated during this research program, this existed for ML4 at Well Cluster 35 at Site 3 (3.52 m).

As the well diameter is 0.5 inches = 0.0127 metres, so the area becomes (assuming circular well for ease of calculation):

$$\text{Area} = \Pi \text{ x } r^2 = \Pi \text{ x } (0.0127 \text{ m}/2)^2$$
$$\text{Area} = 0.0001267 \text{ m}^2$$

The largest well volume would be for the largest Height of Water in Well, which occurred at ML4 of Well Cluster 35 at Site 3, which gives the following volume:

$$\text{Well Volume}_{(\text{Largest})} = \text{Area x Height} = 0.0001267 \text{ m}^2 \text{ x } 3.52 \text{ m}$$
$$\text{Well Volume}_{(\text{Largest})} = 0.0004459 \text{ m}^3 \text{ x } 1000 \text{ L/m}$$
$$\text{Well Volume}_{(\text{Largest})} = 0.4459 \text{ L} = 0.45 \text{ L}$$

The smallest well volume would be for the smallest Height of Water in Well value, which occurred at ML1 of Well Cluster 35 at Site 3 (0.40 m), which gives the following volume:

$$\text{Well Volume}_{(\text{Largest})} = \text{Area x Height} = 0.0001267 \text{ m}^2 \text{ x } 0.40 \text{ m}$$
$$\text{Well Volume}_{(\text{Largest})} = 0.00005067 \text{ m}^3 \text{ x } 1000 \text{ L/m}$$
$$\text{Well Volume}_{(\text{Largest})} = 0.05067 \text{ L} = 0.050 \text{ L}$$

Ionic Diffusion Calculations

Research using a variety of dissolved gases found that the following equation could numerically estimate the rates of equilibration when compared against the results of several experimental trials. As a result, the equation was utilized to assess the rate of equilibration for dissolved iron during the field installation. The assumptions made in the numerical calculation have been described below.

$$Cs(t) = Cr*H\ [1-e\hat{}^{(-(Dm*A*t)/(Vm*Lm))}] \qquad \text{(Sanford et al., 1996)}$$

where: Cs(t)= concentration within sampler at time t after deployment [M/L^3]
Cr= concentration in formation water [M/L^3]
Dm= effective constituent diffusion coefficient for membrane [L^2/T]
H= solute dimensionless Henry's Law Constant [unitless]
A= surface area of diffusion membrane [L^2]
t= time deployment [T]
Vm= volume of membrane [L^3]
Lm= membrane thickness [L]
Note: M=mass L=length T=time

Typical commercial passive diffusion sampler Dm ranges are: Dm= 0.5×10^{-7} to 5×10^{-7} cm^2/s (Divine and McCray, 2004)

As the sampler is filled with water, Henry's Law Constant goes to unity H=1 (Divine and McCray, 2004)

The volume of the membrane is limited by the protective PVC pipe that surrounds it in the sampler.
The PVC pipe has 1.5 inch inner diameter (1.1610 inches from pipe chart = 4.0894 cm)

$$\text{Area} = \Pi*r^2$$
$$= \Pi*(4.0894/2)^2$$
$$= 13.13 \ cm^2$$

The membrane was approximately 60 cm in length, so the volume is:

$$Vm = \text{Area x Length}$$
$$= 13.1343 \times 60$$
$$= 788.06 \ cm^3$$

Nominal membrane thickness for 6000 to 8000 MWCO membrane is 87 μm, so:

$$Lm = 0.0087 \ cm$$

The surface area of the diffusion membrane (uncovered) would be 770.83 m^2, but the protective PVC pipe around the membrane had 0.95 cm holes drilled throughout the pipe to allow equilibration. So the total surface area of membrane exposure is approximately:

A= 35.44 cm^2 (Based on 50 holes drilled into the PVC pipe to allow equilibration)

The diffusion samplers were usually installed for about 21 days.

t= 1814400 seconds

The iron concentrations measured by the Waterra sampler from the same well as the diffusion samplers were installed were:

Location	Date	Iron Conc.		Corresponding Dialysis Iron Conc. Sampler 1	Sampler 2	
Site 1	Feb	10.5	mg/L	3.4	5.2	mg/L
Site 2						
Well Cluster 34	Oct	10.1	mg/L	5.4	5.7	mg/L
	Feb	3.3	mg/L	2.2	1.1	mg/L
Well Cluster 35	Oct	49.4	mg/L	33.8	37.7	mg/L
	Feb	31.1	mg/L	0.06	0.07	mg/L

The Waterra iron concentrations will be used for Cr values in the equation.

The Cs(t) for the various Cr values over the range of diffusion coefficients available are as follows:

Location	Date	Cr	Cs(t) for Dm=0.5x10-7 cm^2/s	Cs(t) for Dm=5x10-7 cm^2/s
Site 1	Feb	10.5 mg/L	3.9 mg/L	10.4 mg/L
Site 2				
Well Cluster 34	Oct	10.1 mg/L	3.8 mg/L	10.0 mg/L
	Feb	3.3 mg/L	1.2 mg/L	3.3 mg/L
Well Cluster 35	Oct	49.4 mg/L	18.5 mg/L	48.9 mg/L
	Feb	31.1 mg/L	11.6 mg/L	30.8 mg/L

References

Divine, C.E. and McCray, J.E. 2004. Environmental Science and Technology. **38**: 1849-1857.
Sanford, W.E., Shropshire, R.G. and Solomon, D.K. 1996. Water Resources Res. **32** (6): pg 1635.

APPENDIX F:

Sampling Technology Summary Result Tables for Selected Parameters of Interest in a MNA Program

Summary Data Result Tables

The tables (Table F1 to F16) have the data split for the selected sampling events into the different parameters of interest to a MNA program: cations, anions, metals and hydrocarbon results. To assess the ability of the alternative sampling methods and well types to measure discrete depth intervals, the sample results should be compared over short depth intervals (2 to 3 metres, 3 to 4 metres and 4 to 6 metres). This method of comparison reduces the likelihood that vertical variations in the groundwater geochemistry are responsible for the sample variability; therefore the differences in the sample results in each table should likely be caused by the sampling method or well type being compared.

The common sample collection methods (5 cm, 3 m screened PVC monitoring wells sampled by bailer and Waterra samplers), span two or more sampling intervals. Therefore, these samples may have come from a particular depth interval or a combination of depth intervals. This is because there is no control over the zone from which the groundwater recharges within the screened portion of the well during purging and sampling. This fact must be considered when comparing data collected from these well types or sampling methods because this may be the explanation for the results matching well with other sampling technologies for one depth interval and not another.

Table F1. October Cation Sample Results Comparison (Site 1).

MAGNESIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technology	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	5.7	22	90	51	45	30	33	5	16	16	22	20	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	7.1	0	71	30	24	8	54	17	6	6	0	1	22	22
		ML2	2.5	3.2	15	71	0	44	50	64	114	86	76	76	71	73	90	90
		ML3	3.7	4.4	9.6	30	44	0	6	22	80	46	36	36	30	31	51	51
		ML4	5.0	5.4	9.0	24	50	6	0	16	75	40	29	29	24	25	45	45
	Peristaltic	DP1	2.1	3.0	7.7	8	64	22	16	0	61	25	14	14	8	10	30	30
		DP2	2.8	3.7	4.1	54	114	80	75	61	0	38	48	48	54	52	33	33
		DP3	3.8	4.7	6.0	17	86	46	40	25	38	0	11	11	17	15	5	5
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	6.7	6	76	36	29	14	48	11	0	0	6	4	16	16
	Diffusion (Deep)	3m S	4.1	4.7	6.7	6	76	36	29	14	48	11	0	0	6	4	16	16
	BarCad (Shallow)	3m S	2.7	3.7	7.1	0	71	30	24	8	54	17	6	6	0	1	22	22
	BarCad (Deep)	3m S	3.3	4.3	7.0	1	73	31	25	10	52	15	4	4	1	0	20	20

CALCIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technologies	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	26	30	96	51	42	38	26	4	24	27	21	27	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	35	0	72	23	13	8	55	26	6	3	9	3	30	30
		ML2	2.5	3.2	74	72	0	51	60	64	115	93	77	74	79	74	96	96
		ML3	3.7	4.4	44	23	51	0	10	15	75	48	29	26	32	26	51	51
		ML4	5.0	5.4	40	13	60	10	0	5	67	39	19	16	22	16	42	42
	Peristaltic	DP1	2.1	3.0	38	8	64	15	5	0	62	34	14	11	17	11	38	38
		DP2	2.8	3.7	20	55	115	75	67	62	0	30	49	52	46	52	26	26
		DP3	3.8	4.7	27	26	93	48	39	34	30	0	20	23	17	23	4	4
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	33	6	77	29	19	14	49	20	0	3	3	3	24	24
	Diffusion (Deep)	3m S	4.1	4.7	34	3	74	26	16	11	52	23	3	0	6	0	27	27
	BarCad (Shallow)	3m S	2.7	3.7	32	9	79	32	22	17	46	17	3	6	0	6	21	21
	BarCad (Deep)	3m S	3.3	4.3	34	3	74	26	16	11	52	23	3	0	6	0	27	27

SODIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technologies	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	4.5	139	179	158	156	27	2	145	9	11	46	59	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	25	0	107	41	36	124	138	11	134	133	111	100	139	139
		ML2	2.5	3.2	83	107	0	74	79	173	179	99	178	177	168	164	179	179
		ML3	3.7	4.4	38	41	74	0	5	146	157	30	154	153	136	128	158	158
		ML4	5.0	5.4	36	36	79	5	0	144	155	25	152	151	133	125	156	156
	Peristaltic	DP1	2.1	3.0	5.9	124	173	146	144	0	25	130	19	17	20	34	27	27
		DP2	2.8	3.7	4.6	138	179	157	155	25	0	144	6	8	44	57	2	2
		DP3	3.8	4.7	28	11	99	30	25	130	144	0	140	139	118	109	145	145
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	4.9	134	178	154	152	19	6	140	0	2	38	52	9	9
	Diffusion (Deep)	3m S	4.1	4.7	5.0	133	177	153	151	17	8	139	2	0	36	50	11	11
	BarCad (Shallow)	3m S	2.7	3.7	7.2	111	168	136	133	20	44	118	38	36	0	14	46	46
	BarCad (Deep)	3m S	3.3	4.3	8.3	100	164	128	125	34	57	109	52	50	14	0	59	59

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F2. October Anion Sample Results Comparison (Site 1).

BICARBONATE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technology	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	120	24	39	32	31	36	28	39	20	20	21	27	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	153	0	15	8	7	12	51	16	4	5	3	3	24	24
		ML2	2.5	3.2	178	15	0	8	8	3	65	1	19	20	18	13	39	39
		ML3	3.7	4.4	165	8	8	0	1	4	58	8	12	12	11	5	32	32
		ML4	5.0	5.4	164	7	8	1	0	5	57	9	11	12	10	4	31	31
	Peristaltic	DP1	2.1	3.0	172	12	3	4	5	0	62	4	16	16	15	9	36	36
		DP2	2.8	3.7	90.8	51	65	58	57	62	0	65	47	47	48	53	28	28
		DP3	3.8	4.7	179	16	1	8	9	4	65	0	20	20	19	13	39	39
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	147	4	19	12	11	16	47	20	0	1	1	7	20	20
	Diffusion (Deep)	3m S	4.1	4.7	146	5	20	12	12	16	47	20	1	0	1	7	20	20
	BarCad (Shallow)	3m S	2.7	3.7	148	3	18	11	10	15	48	19	1	1	0	6	21	21
	BarCad (Deep)	3m S	3.3	4.3	157	3	13	5	4	9	53	13	7	7	6	0	27	27

SULFATE

Comparison Group	Sampling Method	Well Type	*Sample Interval (mbgs)*		*Concentration (mg/L)*	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technologies	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	0.1	199	200	200	200	171	100	194	133	143	196	197	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	46.0	0	148	68	62	189	197	147	196	195	126	110	199	199
		ML2	2.5	3.2	306	148	0	107	111	198	200	191	199	199	187	183	200	200
		ML3	3.7	4.4	93.0	68	107	0	7	194	199	172	198	197	159	150	200	200
		ML4	5.0	5.4	87.0	62	111	7	0	194	199	170	198	197	157	147	200	200
	Peristaltic	DP1	2.1	3.0	1.3	189	198	194	194	0	125	138	89	74	156	164	171	171
		DP2	2.8	3.7	0.3	197	200	199	199	125	0	184	50	67	189	191	100	100
		DP3	3.8	4.7	7.1	147	191	172	170	138	184	0	174	169	39	61	194	194
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	0.5	196	199	198	198	89	50	174	0	18	182	186	133	133
	Diffusion (Deep)	3m S	4.1	4.7	0.6	195	199	197	197	74	67	169	18	0	178	183	143	143
	BarCad (Shallow)	3m S	2.7	3.7	10.5	126	187	159	157	156	189	39	182	178	0	24	196	196
	BarCad (Deep)	3m S	3.3	4.3	13.3	110	183	150	147	164	191	61	186	183	24	0	197	197

CHLORIDE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technologies	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	4.7	19	67	29	23	14	7	2	4	7	2	6	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	5.7	0	49	10	3	5	26	17	24	26	21	13	19	19
		ML2	2.5	3.2	9.4	49	0	39	46	54	72	65	71	72	69	61	67	67
		ML3	3.7	4.4	6.3	10	39	0	7	15	36	27	33	36	31	23	29	29
		ML4	5.0	5.4	5.9	3	46	7	0	9	29	21	27	29	25	17	23	23
	Peristaltic	DP1	2.1	3.0	5.4	5	54	15	9	0	20	12	18	20	16	8	14	14
		DP2	2.8	3.7	4.4	26	72	36	29	20	0	9	2	0	4	13	7	7
		DP3	3.8	4.7	4.8	17	65	27	21	12	9	0	6	9	4	4	2	2
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	4.5	24	71	33	27	18	2	6	0	2	2	11	4	4
	Diffusion (Deep)	3m S	4.1	4.7	4.4	26	72	36	29	20	0	9	2	0	4	13	7	7
	BarCad (Shallow)	3m S	2.7	3.7	4.6	21	69	31	25	16	4	4	2	4	0	8	2	2
	BarCad (Deep)	3m S	3.3	4.3	5.0	13	61	23	17	8	13	4	11	13	8	0	6	6

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F3. October Metals Sample Results Comparison (Site 1).

MANGANESE																		
Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technology	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	0.72	95	129	78	68	42	57	59	44	39	73	78	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	2.03	0	49	21	32	59	134	136	57	62	27	21	95	95
		ML2	2.5	3.2	3.34	49	0	68	78	101	157	158	99	103	73	68	129	129
		ML3	3.7	4.4	1.65	21	68	0	12	40	122	124	37	43	6	1	78	78
		ML4	5.0	5.4	1.47	32	78	12	0	29	114	116	26	31	5	11	68	68
	Peristaltic	DP1	2.1	3.0	1.10	59	101	40	29	0	93	95	3	3	34	39	42	42
		DP2	2.8	3.7	0.40	134	157	122	114	93	0	3	95	91	118	122	57	57
		DP3	3.8	4.7	0.39	136	158	124	116	95	3	0	97	93	120	123	59	59
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	1.13	57	99	37	26	3	95	97	0	5	31	37	44	44
	Diffusion (Deep)	3m S	4.1	4.7	1.07	62	103	43	31	3	91	93	5	0	37	42	39	39
	BarCad (Shallow)	3m S	2.7	3.7	1.55	27	73	6	5	34	118	120	31	37	0	6	73	73
	BarCad (Deep)	3m S	3.3	4.3	1.64	21	68	1	11	39	122	123	37	42	6	0	78	78

IRON																		
Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technologies	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	3.09	57	120	180	180	28	191	189	92	98	22	28	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	5.54	0	151	189	189	30	195	194	41	48	76	30	57	57
		ML2	2.5	3.2	0.77	151	0	131	131	137	167	158	166	169	105	136	120	120
		ML3	3.7	4.4	0.16	189	131	0	0	185	78	56	193	193	176	185	180	180
		ML4	5.0	5.4	0.16	189	131	0	0	185	78	56	193	193	176	185	180	180
	Peristaltic	DP1	2.1	3.0	4.11	30	137	185	185	0	193	191	69	75	49	1	28	28
		DP2	2.8	3.7	0.07	195	167	78	78	193	0	25	197	197	189	193	191	191
		DP3	3.8	4.7	0.09	194	158	56	56	191	25	0	196	196	186	191	189	189
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	8.40	41	166	193	193	69	197	196	0	8	109	69	92	92
	Diffusion (Deep)	3m S	4.1	4.7	9.08	48	169	193	193	75	197	196	8	0	114	76	98	98
	BarCad (Shallow)	3m S	2.7	3.7	2.48	76	105	176	176	49	189	186	109	114	0	49	22	22
	BarCad (Deep)	3m S	3.3	4.3	4.08	30	136	185	185	1	193	191	69	76	49	0	28	28

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F4A. October Hydrocarbon Sample Results Comparison (Site 1).

BENZENE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technology	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	0.0027	11	63	158	168	30	148	118	26	23	30	11	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	0.0030	0	54	154	165	40	153	124	15	13	40	0	11	11
		ML2	2.5	3.2	0.0052	54	0	127	143	89	171	153	39	42	89	54	63	63
		ML3	3.7	4.4	0.0233	154	127	0	30	168	193	188	148	149	168	154	158	158
		ML4	5.0	5.4	0.0315	165	143	30	0	176	195	191	160	161	176	165	168	168
	Peristaltic	DP1	2.1	3.0	0.0020	40	89	168	176	0	133	96	55	52	0	40	30	30
		DP2	2.8	3.7	0.0004	153	171	193	195	133	0	55	159	158	133	153	148	148
		DP3	3.8	4.7	0.0007	124	153	188	191	96	55	0	133	132	96	124	118	118
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	0.0035	15	39	148	160	55	159	133	0	3	55	15	26	26
	Diffusion (Deep)	3m S	4.1	4.7	0.0034	13	42	149	161	52	158	132	3	0	52	13	23	23
	BarCad (Shallow)	3m S	2.7	3.7	0.0020	40	89	168	176	0	133	96	55	52	0	40	30	30
	BarCad (Deep)	3m S	3.3	4.3	0.0030	0	54	154	165	40	153	124	15	13	40	0	11	11

ETHYLBENZENE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technologies	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	0.052	75	70	125	185	99	125	147	57	51	63	84	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	0.115	0	129	162	193	29	162	174	21	27	124	10	75	75
		ML2	2.5	3.2	0.025	129	0	70	170	144	70	103	115	112	8	134	70	70
		ML3	3.7	4.4	0.012	162	70	0	143	171	0	40	154	152	77	165	125	125
		ML4	5.0	5.4	0.002	193	170	143	0	195	143	120	192	191	172	194	185	185
	Peristaltic	DP1	2.1	3.0	0.154	29	144	171	195	0	171	180	49	55	140	19	99	99
		DP2	2.8	3.7	0.012	162	70	0	143	171	0	40	154	152	77	165	125	125
		DP3	3.8	4.7	0.008	174	103	40	120	180	40	0	168	167	109	176	147	147
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	0.093	21	115	154	192	49	154	168	0	6	110	31	57	57
	Diffusion (Deep)	3m S	4.1	4.7	0.088	27	112	152	191	55	152	167	6	0	106	36	51	51
	BarCad (Shallow)	3m S	2.7	3.7	0.027	124	8	77	172	140	77	109	110	106	0	130	63	63
	BarCad (Deep)	3m S	3.3	4.3	0.127	10	134	165	194	19	165	176	31	36	130	0	84	84

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F4B. October Hydrocarbon Sample Results Comparison (Site 1).

TOTAL XYLENES

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technologies	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	0.040	89	46	86	172	111	96	133	81	78	46	97	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	0.104	0	122	147	189	30	153	171	9	13	122	11	89	89
		ML2	2.5	3.2	0.025	122	0	44	157	139	56	103	117	114	0	129	46	46
		ML3	3.7	4.4	0.016	147	44	0	137	159	13	67	142	140	44	152	86	86
		ML4	5.0	5.4	0.003	189	157	137	0	192	129	91	188	187	157	190	172	172
	Peristaltic	DP1	2.1	3.0	0.140	30	139	159	192	0	164	178	38	42	139	19	111	111
		DP2	2.8	3.7	0.014	153	56	13	129	164	0	55	149	147	56	157	96	96
		DP3	3.8	4.7	0.008	171	103	67	91	178	55	0	169	168	103	174	133	133
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	0.095	9	117	142	188	38	149	169	0	4	117	20	81	81
	Diffusion (Deep)	3m S	4.1	4.7	0.091	13	114	140	187	42	147	168	4	0	114	24	78	78
	BarCad (Shallow)	3m S	2.7	3.7	0.025	122	0	44	157	139	56	103	117	114	0	129	46	46
	BarCad (Deep)	3m S	3.3	4.3	0.116	11	129	152	190	19	157	174	20	24	129	0	97	97

PHC F1-BTEX

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]												
						Alternative Sampling Technologies											Industry Standard Technologies	
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	Shallow BarCad	Deeper BarCad	Bailer	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.0	3.5	2.1	10	90	90	182	25	27	165	10	10	150	50	0	0
Alternative Well Types	Peristaltic	ML1	1.7	2.3	1.9	0	81	81	180	35	17	162	0	0	145	59	10	10
		ML2	2.5	3.2	0.8	81	0	0	156	109	67	120	81	81	91	126	90	90
		ML3	3.7	4.4	0.8	81	0	0	156	109	67	120	81	81	91	126	90	90
		ML4	5.0	5.4	0.1	180	156	156	0	186	176	67	180	180	100	189	182	182
	Peristaltic	DP1	2.1	3.0	2.7	35	109	109	186	0	51	172	35	35	160	26	25	25
		DP2	2.8	3.7	1.6	17	67	67	176	51	0	156	17	17	137	75	27	27
		DP3	3.8	4.7	0.2	162	120	120	67	172	156	0	162	162	40	178	165	165
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	1.9	0	81	81	180	35	17	162	0	0	145	59	10	10
	Diffusion (Deep)	3m S	4.1	4.7	1.9	0	81	81	180	35	17	162	0	0	145	59	10	10
	BarCad (Shallow)	3m S	2.7	3.7	0.3	145	91	91	100	160	137	40	145	145	0	168	150	150
	BarCad (Deep)	3m S	3.3	4.3	3.5	59	126	126	189	26	75	178	59	59	168	0	50	50

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F5. February Cation Sample Results Comparison (Site 1).

MAGNESIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	9.6	61	-	14	84	69	22	25	0	29	42	28
	Waterra - MW1	3m S - MW1	3.2	4.8	7.2	86	-	42	59	42	7	4	29	0	13	
	Waterra - MW2	3m S - MW2	3.2	4.3	6.3	96	-	54	47	29	20	17	42	13	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	18	0	-	48	129	117	80	82	61	86	96	81
		ML3	3.7	4.4	-	-	-	-	-	-	-	-	-	-	-	-
		ML4	5.0	5.4	11	48	-	0	95	80	35	38	14	42	54	37
	Peristaltic	DP2	2.8	3.7	3.9	129	-	95	0	19	66	63	84	59	47	64
		DP3	3.8	4.7	4.7	117	-	80	19	0	48	46	69	42	29	47
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	7.7	80	-	35	66	48	0	3	22	7	20	16
	Diffusion (Deep)	3m S	3.8	4.4	7.5	82	-	38	63	46	3	0	25	4	17	15

CALCIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	43.4	68	-	11	80	65	16	17	0	19	34	23
	Waterra - MW1	3m S - MW1	3.2	4.8	36.0	84	-	29	64	48	3	1	19	0	15	
	Waterra - MW2	3m S - MW2	3.2	4.3	30.9	96	-	44	50	34	18	17	34	15	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	88.1	0	-	58	130	120	81	83	68	84	96	83
		ML3	3.7	4.4	-	-	-	-	-	-	-	-	-	-	-	-
		ML4	5.0	5.4	48.4	58	-	0	89	75	26	28	11	29	44	28
	Peristaltic	DP2	2.8	3.7	18.6	130	-	89	0	17	66	65	80	64	50	64
		DP3	3.8	4.7	22.0	120	-	75	17	0	51	50	65	48	34	49
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	37.1	81	-	26	66	51	0	2	16	3	18	12
	Diffusion (Deep)	3m S	3.8	4.4	36.5	83	-	28	65	50	2	0	17	1	17	12

SODIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	5.7	155	-	141	9	84	15	13	0	13	13	9
	Waterra - MW1	3m S - MW1	3.2	4.8	6.5	150	-	134	22	73	2	0	13	0	0	
	Waterra - MW2	3m S - MW2	3.2	4.3	6.5	150	-	134	22	73	2	0	13	0	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	45	0	-	31	159	105	149	150	155	150	150	151
		ML3	3.7	4.4	-	-	-	-	-	-	-	-	-	-	-	-
		ML4	5.0	5.4	33	31	-	0	146	81	133	134	141	134	134	136
	Peristaltic	DP2	2.8	3.7	5.2	159	-	146	0	92	24	22	9	22	22	18
		DP3	3.8	4.7	14	105	-	81	92	0	72	73	84	73	73	77
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	6.6	149	-	133	24	72	0	2	15	2	2	6
	Diffusion (Deep)	3m S	3.8	4.4	6.5	150	-	134	22	73	2	0	13	0	0	4

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F6. February Anion Sample Results Comparison (Site 1).

BICARBONATE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	198	11	-	19	75	45	20	19	0	10	26	18
	Waterra - MW1	3m S - MW1	3.2	4.8	180	2	-	9	67	36	11	9	10	0	17	
	Waterra - MW2	3m S - MW2	3.2	4.3	152	15	-	8	51	19	6	8	26	17	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	177	0	-	8	65	34	9	8	11	2	15	9
		ML3	3.7	4.4	-	-	-	-	-	-	-	-	-	-	-	-
		ML4	5.0	5.4	164	8	-	0	58	27	1	0	19	9	8	12
	Peristaltic	DP2	2.8	3.7	90	65	-	58	0	33	57	58	75	67	51	64
		DP3	3.8	4.7	125	34	-	27	33	0	26	27	45	36	19	34
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	162	9	-	1	57	26	0	1	20	11	6	12
	Diffusion (Deep)	3m S	3.8	4.4	164	8	-	0	58	27	1	0	19	9	8	12

SULFATE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	0.1	200	-	200	0	187	189	186	0	179	173	126
	Waterra - MW1	3m S - MW1	3.2	4.8	1.8	197	-	192	179	50	69	40	179	0	25	
	Waterra - MW2	3m S - MW2	3.2	4.3	1.4	198	-	194	173	73	90	63	173	25	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	257	0	-	97	200	195	194	196	200	197	198	198
		ML3	3.7	4.4	-	-	-	-	-	-	-	-	-	-	-	-
		ML4	5.0	5.4	89	97	-	0	200	187	184	188	200	192	194	195
	Peristaltic	DP2	2.8	3.7	0.1	200	-	200	0	187	189	186	0	179	173	117
		DP3	3.8	4.7	3.0	195	-	187	187	0	21	11	187	50	73	103
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	3.7	194	-	184	189	21	0	31	189	69	90	116
	Diffusion (Deep)	3m S	3.8	4.4	2.7	196	-	188	186	11	31	0	186	40	63	96

CHLORIDE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	6.8	23	-	16	39	29	41	39	0	37	29	24
	Waterra - MW1	3m S - MW1	3.2	4.8	4.7	59	-	21	2	8	4	2	37	0	8	
	Waterra - MW2	3m S - MW2	3.2	4.3	5.1	51	-	13	10	0	13	10	29	8	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	8.6	0	-	39	61	51	63	61	23	59	51	44
		ML3	3.7	4.4	-	-	-	-	-	-	-	-	-	-	-	-
		ML4	5.0	5.4	5.8	39	-	0	23	13	25	23	16	21	13	17
	Peristaltic	DP2	2.8	3.7	4.6	61	-	23	0	10	2	0	39	2	10	17
		DP3	3.8	4.7	5.1	51	-	13	10	0	13	10	29	8	0	12
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	4.5	63	-	25	2	13	0	2	41	4	13	19
	Diffusion (Deep)	3m S	3.8	4.4	4.6	61	-	23	0	10	2	0	39	2	10	17

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F7. February Metals Sample Results Comparison (Site 1).

MANGANESE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	1.26	112	85	33	105	96	74	61	0	17	22	26
	Waterra - MW1	3m S - MW1	3.2	4.8	1.06	123	99	49	92	83	59	45	17	0	39	
	Waterra - MW2	3m S - MW2	3.2	4.3	1.57	96	66	11	120	112	92	80	22	39	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	4.48	0	35	88	168	164	154	148	112	123	96	111
		ML3	3.7	4.4	3.13	35	0	57	156	151	137	129	85	99	66	83
		ML4	5.0	5.4	1.75	88	57	0	127	120	100	89	33	49	11	31
	Peristaltic	DP2	2.8	3.7	0.39	168	156	127	0	12	39	53	105	92	120	106
		DP3	3.8	4.7	0.44	164	151	120	12	0	27	41	96	83	112	97
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	0.58	154	137	100	39	27	0	14	74	59	92	75
	Diffusion (Deep)	3m S	3.8	4.4	0.67	148	129	89	53	41	14	0	61	45	80	62

IRON

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	9.37	14	91	126	93	119	93	58	0	11	15	17
	Waterra - MW1	3m S - MW1	3.2	4.8	10.50	25	100	133	101	126	102	68	11	0	26	
	Waterra - MW2	3m S - MW2	3.2	4.3	8.07	1	79	116	80	109	81	44	15	26	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	8.16	0	80	117	81	109	82	45	14	25	1	13
		ML3	3.7	4.4	3.50	80	0	49	2	38	3	39	91	100	79	90
		ML4	5.0	5.4	2.13	117	49	0	47	12	46	83	126	133	116	125
	Peristaltic	DP2	2.8	3.7	3.44	81	2	47	0	36	1	40	93	101	80	91
		DP3	3.8	4.7	2.39	109	38	12	36	0	35	74	119	126	109	118
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	3.41	82	3	46	1	35	0	41	93	102	81	92
	Diffusion (Deep)	3m S	3.8	4.4	5.18	45	39	83	40	74	41	0	58	68	44	56

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F8A. February Hydrocarbon Sample Results Comparison (Site 1).

BENZENE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	0.0036	93	93	161	160	127	57	53	0	18	11	19
	Waterra - MW1	3m S - MW1	3.2	4.8	0.0030	106	107	167	153	116	40	35	18	0	29	
	Waterra - MW2	3m S - MW2	3.2	4.3	0.0040	84	85	157	164	133	67	62	11	29	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	0.0098	0	1	109	184	170	132	129	93	106	84	94
		ML3	3.7	4.4	0.0099	1	0	109	184	170	133	130	93	107	85	95
		ML4	5.0	5.4	0.0334	109	109	0	195	191	177	176	161	167	157	162
	Peristaltic	DP2	2.8	3.7	0.0004	184	184	195	0	67	133	136	160	153	164	159
		DP3	3.8	4.7	0.0008	170	170	191	67	0	86	90	127	116	133	125
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	0.0020	132	133	177	133	86	0	5	57	40	67	55
	Diffusion (Deep)	3m S	3.8	4.4	0.0021	129	130	176	136	90	5	0	53	35	62	50

ETHYLBENZENE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	0.0597	40	144	170	167	169	79	76	0	23	31	36
	Waterra - MW1	3m S - MW1	3.2	4.8	0.075	61	154	175	173	175	97	95	23	0	53	
	Waterra - MW2	3m S - MW2	3.2	4.3	0.044	9	126	160	156	159	50	48	31	53	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	0.0399	0	121	156	152	155	42	40	40	61	9	36
		ML3	3.7	4.4	0.0098	121	0	67	58	65	91	93	144	154	126	141
		ML4	5.0	5.4	0.0049	156	67	0	10	2	137	138	170	175	160	168
	Peristaltic	DP2	2.8	3.7	0.0054	152	58	10	0	8	131	133	167	173	156	165
		DP3	3.8	4.7	0.0050	155	65	2	8	0	135	137	169	175	159	168
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	0.0260	42	91	137	131	135	0	3	79	97	50	75
	Diffusion (Deep)	3m S	3.8	4.4	0.0267	40	93	138	133	137	3	0	76	95	48	73

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F8B. February Hydrocarbon Sample Results Comparison (Site 1).

TOTAL XYLENES

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	0.0388	10	103	151	163	180	60	55	0	57	1	38
	Waterra - MW1	3m S - MW1	3.2	4.8	0.0700	66	140	171	179	189	108	104	57	0	57	
	Waterra - MW2	3m S - MW2	3.2	4.3	0.0390	10	104	151	164	180	60	55	1	57	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	0.0352	0	96	147	160	178	51	46	10	66	10	29
		ML3	3.7	4.4	0.0124	96	0	79	104	144	51	56	103	140	104	115
		ML4	5.0	5.4	0.0054	147	79	0	32	92	118	121	151	171	151	158
	Peristaltic	DP2	2.8	3.7	0.0039	160	104	32	0	64	137	140	163	179	164	169
		DP3	3.8	4.7	0.0020	178	144	92	64	0	165	167	180	189	180	183
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	0.0210	51	51	118	137	165	0	5	60	108	60	76
	Diffusion (Deep)	3m S	3.8	4.4	0.0221	46	56	121	140	167	5	0	55	104	55	71

PHC F1-BTEX

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]										
						Alternative Sampling Technologies							Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	3.0	3.5	5.6	145	167	180	150	167	111	95	0	85	60	92
	Waterra - MW1	3m S - MW1	3.2	4.8	13.9	176	186	192	178	186	159	150	85	0	129	
	Waterra - MW2	3m S - MW2	3.2	4.3	3.0	108	143	164	116	143	61	40	60	129	0	
Alternative Well Types	Peristaltic	ML2	2.5	3.2	0.9	0	57	100	12	57	56	76	145	176	108	143
		ML3	3.7	4.4	0.5	57	0	50	46	0	105	120	167	186	143	165
		ML4	5.0	5.4	0.3	100	50	0	91	50	137	148	180	192	164	178
	Peristaltic	DP2	2.8	3.7	0.8	12	46	91	0	46	67	86	150	178	116	148
		DP3	3.8	4.7	0.5	57	0	50	46	0	105	120	167	186	143	165
Alternative Sampling Methods	Diffusion (Shallow)	3m S	3.1	3.7	1.6	56	105	137	67	105	0	22	111	159	61	110
	Diffusion (Deep)	3m S	3.8	4.4	2.0	76	120	148	86	120	22	0	95	150	40	95

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F9. October Cation Sample Results Comparison (Site 2 - Well Cluster 34).

MAGNESIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	155	17	29	46	12	41	7	17	32	0	34	22	23
	Waterra - MW1	3m S - MW1	2.1	4.6	219	17	6	12	46	7	41	18	3	34	0	13	
	Waterra - MW2	3m S - MW2	2.2	4.6	193	5	7	25	34	20	29	5	10	22	13	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	184	0	12	30	29	25	24	1	15	17	17	5	13
		ML3	3.5	4.1	207	12	0	18	41	13	36	12	3	29	6	7	14
		ML4	4.5	4.6	248	30	18	0	58	5	53	30	15	46	12	25	28
	Peristaltic	DP2	2.2	3.0	137	29	41	58	0	53	5	29	43	12	46	34	31
		DP3	3.2	4.0	236	25	13	5	53	0	48	25	10	41	7	20	23
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	144	24	36	53	5	48	0	24	39	7	41	29	26
	Diffusion (Deep)	3m S	2.7	3.3	183	1	12	30	29	25	24	0	15	17	18	5	13
	BarCad	3m S	3.6	4.6	213	15	3	15	43	10	39	15	0	32	3	10	15

CALCIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	39.1	56	141	158	32	112	39	58	85	0	96	77	65
	Waterra - MW1	3m S - MW1	2.1	4.6	111	46	69	99	119	22	63	43	13	96	0	23	
	Waterra - MW2	3m S - MW2	2.2	4.6	88.0	23	88	116	102	44	41	21	10	77	23	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	69.7	0	106	130	84	66	18	2	33	56	46	23	42
		ML3	3.5	4.1	227	106	0	37	156	49	119	104	80	141	69	88	99
		ML4	4.5	4.6	329	130	37	0	168	82	140	129	109	158	99	116	124
	Peristaltic	DP2	2.2	3.0	28.4	84	156	168	0	132	69	86	110	32	119	102	84
		DP3	3.2	4.0	138	66	49	82	132	0	82	64	34	112	22	44	59
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	58.0	18	119	140	69	82	0	21	51	39	63	41	48
	Diffusion (Deep)	3m S	2.7	3.3	71.4	2	104	129	86	64	21	0	31	58	43	21	41
	BarCad	3m S	3.6	4.6	97.4	33	80	109	110	34	51	31	0	85	13	10	36

SODIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	262	7	12	25	18	6	10	9	10	0	22	3	17
	Waterra - MW1	3m S - MW1	2.1	4.6	327	15	10	3	40	16	32	13	12	22	0	25	
	Waterra - MW2	3m S - MW2	2.2	4.6	254	10	15	28	15	9	7	12	13	3	25	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	281	0	5	18	25	1	17	2	3	7	15	10	11
		ML3	3.5	4.1	295	5	0	13	30	6	21	3	2	12	10	15	12
		ML4	4.5	4.6	337	18	13	0	43	19	34	16	15	25	3	28	19
	Peristaltic	DP2	2.2	3.0	218	25	30	43	0	24	9	27	28	18	40	15	25
		DP3	3.2	4.0	278	1	6	19	24	0	16	3	4	6	16	9	10
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	238	17	21	34	9	16	0	18	20	10	32	7	16
	Diffusion (Deep)	3m S	2.7	3.3	286	2	3	16	27	3	18	0	1	9	13	12	11
	BarCad	3m S	3.6	4.6	290	3	2	15	28	4	20	1	0	10	12	13	12

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F10. October Anion Sample Results Comparison (Site 2 - Well Cluster 34).

BICARBONATE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	1520	17	0	8	11	17	13	11	6	0	19	9	13
	Waterra - MW1	3m S - MW1	2.1	4.6	1840	2	19	27	30	2	31	8	13	19	0	10	
	Waterra - MW2	3m S - MW2	2.2	4.6	1670	7	9	18	20	7	22	2	3	9	10	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	1800	0	17	25	28	0	29	6	11	17	2	7	9
		ML3	3.5	4.1	1520	17	0	8	11	17	13	11	6	0	19	9	9
		ML4	4.5	4.6	1400	25	8	0	3	25	4	19	15	8	27	18	18
	Peristaltic	DP2	2.2	3.0	1360	28	11	3	0	28	1	22	17	11	30	20	21
		DP3	3.2	4.0	1800	0	17	25	28	0	29	6	11	17	2	7	9
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	1340	29	13	4	1	29	0	24	19	13	31	22	22
	Diffusion (Deep)	3m S	2.7	3.3	1700	6	11	19	22	6	24	0	5	11	8	2	7
	BarCad	3m S	3.6	4.6	1620	11	6	15	17	11	19	5	0	6	13	3	7

SULPHATE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	1.2	88	199	200	18	199	195	195	198	0	199	198	149
	Waterra - MW1	3m S - MW1	2.1	4.6	379	197	52	109	199	12	121	119	60	199	0	51	
	Waterra - MW2	3m S - MW2	2.2	4.6	224	195	97	140	198	63	82	80	9	198	51	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	3.1	0	198	199	102	197	187	188	194	88	197	195	160
		ML3	3.5	4.1	648	198	0	66	199	41	150	148	104	199	52	97	116
		ML4	4.5	4.6	1280	199	66	0	200	100	173	172	145	200	109	140	150
	Peristaltic	DP2	2.2	3.0	1.0	102	199	200	0	199	196	196	198	18	199	198	138
		DP3	3.2	4.0	429	197	41	100	199	0	129	127	71	199	12	63	91
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	93.2	187	150	173	196	129	0	3	75	195	121	82	133
	Diffusion (Deep)	3m S	2.7	3.3	96.3	188	148	172	196	127	3	0	72	195	119	80	131
	BarCad	3m S	3.6	4.6	205	194	104	145	198	71	75	72	0	198	60	9	89

CHLORIDE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	59.1	63	9	14	97	1	10	25	4	0	15	7	10
	Waterra - MW1	3m S - MW1	2.1	4.6	69.0	48	25	2	109	17	6	10	12	15	0	8	
	Waterra - MW2	3m S - MW2	2.2	4.6	63.6	56	17	7	103	9	2	18	4	7	8	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	113	0	71	50	139	64	54	39	59	63	48	56	56
		ML3	3.5	4.1	53.8	71	0	23	90	8	19	35	13	9	25	17	17
		ML4	4.5	4.6	67.9	50	23	0	108	15	4	12	10	14	2	7	7
	Peristaltic	DP2	2.2	3.0	20.4	139	90	108	0	96	105	116	100	97	109	103	103
		DP3	3.2	4.0	58.3	64	8	15	96	0	11	27	5	1	17	9	9
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	65.1	54	19	4	105	11	0	16	6	10	6	2	6
	Diffusion (Deep)	3m S	2.7	3.3	76.3	39	35	12	116	27	16	0	22	25	10	18	18
	BarCad	3m S	3.6	4.6	61.3	59	13	10	100	5	6	22	0	4	12	4	6

Note:
3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F11. October Metals Sample Results Comparison (Site 2 - Well Cluster 34).

MANGANESE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	0.336	119	171	172	143	63	150	152	139	0	166	126	125
	Waterra - MW1	3m S - MW1	2.1	4.6	3.590	92	18	22	194	139	43	37	63	166	0	83	
	Waterra - MW2	3m S - MW2	2.2	4.6	1.480	11	98	100	185	79	45	50	23	126	83	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	1.330	0	106	108	184	70	55	60	34	119	92	11	74
		ML3	3.5	4.1	4.300	106	0	4	195	148	59	54	79	171	18	98	96
		ML4	4.5	4.6	4.460	108	4	0	195	150	63	57	82	172	22	100	98
	Peristaltic	DP2	2.2	3.0	0.056	184	195	195	0	168	191	191	188	143	194	185	174
		DP3	3.2	4.0	0.644	70	148	150	168	0	113	117	98	63	139	79	94
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	2.330	55	59	63	191	113	0	6	22	150	43	45	79
	Diffusion (Deep)	3m S	2.7	3.3	2.470	60	54	57	191	117	6	0	28	152	37	50	80
	BarCad	3m S	3.6	4.6	1.870	34	79	82	188	98	22	28	0	139	63	23	75

IRON

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	21.2	97	94	175	146	132	119	115	156	0	71	139	100
	Waterra - MW1	3m S - MW1	2.1	4.6	10.1	32	27	151	102	79	61	55	118	71	0	90	
	Waterra - MW2	3m S - MW2	2.2	4.6	3.82	63	67	93	15	13	34	40	38	139	90	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	7.31	0	5	136	76	50	30	24	95	97	32	63	64
		ML3	3.5	4.1	7.66	5	0	138	80	55	35	29	98	94	27	67	63
		ML4	4.5	4.6	1.40	136	138	0	81	103	118	121	60	175	151	93	140
	Peristaltic	DP2	2.2	3.0	3.29	76	80	81	0	28	49	54	23	146	102	15	88
		DP3	3.2	4.0	4.37	50	55	103	28	0	21	27	50	132	79	13	75
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	5.40	30	35	118	49	21	0	6	70	119	61	34	71
	Diffusion (Deep)	3m S	2.7	3.3	5.72	24	29	121	54	27	6	0	75	115	55	40	70
	BarCad	3m S	3.6	4.6	2.61	95	98	60	23	50	70	75	0	156	118	38	104

Note:
3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F12A. October Hydrocarbon Sample Results Comparison (Site 2 - Well Cluster 34).

BENZENE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	0.0380	153	182	181	27	194	138	104	171	0	92	145	106
	Waterra - MW1	3m S - MW1	2.1	4.6	0.0140	95	154	152	70	184	67	15	129	92	0	80	
	Waterra - MW2	3m S - MW2	2.2	4.6	0.0060	18	108	104	131	164	15	67	67	145	80	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	0.0050	0	94	90	141	157	33	82	50	153	95	18	89
		ML3	3.5	4.1	0.0018	94	0	5	177	100	118	148	50	182	154	108	148
		ML4	4.5	4.6	0.0019	90	5	0	175	104	115	145	45	181	152	104	146
	Peristaltic	DP2	2.2	3.0	0.0290	141	177	175	0	192	122	83	163	27	70	131	76
		DP3	3.2	4.0	0.0006	157	100	104	192	0	168	181	133	194	184	164	180
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	0.0070	33	118	115	122	168	0	53	80	138	67	15	73
	Diffusion (Deep)	3m S	2.7	3.3	0.0120	82	148	145	83	181	53	0	120	104	15	67	62
	BarCad	3m S	3.6	4.6	0.0030	50	50	45	163	133	80	120	0	171	129	67	122

ETHYLBENZENE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	0.459	26	124	180	23	84	99	3	13	0	21	48	32
	Waterra - MW1	3m S - MW1	2.1	4.6	0.564	45	136	184	2	100	114	24	33	21	0	28	
	Waterra - MW2	3m S - MW2	2.2	4.6	0.750	71	150	188	26	120	131	51	60	48	28	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	0.355	0	107	175	48	62	78	22	13	26	45	71	48
		ML3	3.5	4.1	0.107	107	0	127	137	54	37	122	116	124	136	150	137
		ML4	4.5	4.6	0.024	175	127	0	184	155	147	180	178	180	184	188	184
	Peristaltic	DP2	2.2	3.0	0.577	48	137	184	0	102	115	26	36	23	2	26	17
		DP3	3.2	4.0	0.187	62	54	155	102	0	19	81	73	84	100	120	102
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	0.155	78	37	147	115	19	0	96	89	99	114	131	115
	Diffusion (Deep)	3m S	2.7	3.3	0.444	22	122	180	26	81	96	0	10	3	24	51	26
	BarCad	3m S	3.6	4.6	0.403	13	116	178	36	73	89	10	0	13	33	60	35

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F12B. October Hydrocarbon Sample Results Comparison (Site 2 - Well Cluster 34).

TOTAL XYLENES

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	4.20	72	184	186	3	175	80	2	94	0	7	8	6
	Waterra - MW1	3m S - MW1	2.1	4.6	3.90	66	183	185	10	173	73	10	88	7	0	1	
	Waterra - MW2	3m S - MW2	2.2	4.6	3.86	65	183	184	11	173	72	11	88	8	1	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	1.97	0	168	171	75	150	8	74	26	72	66	65	68
		ML3	3.5	4.1	0.17	168	0	11	184	46	165	184	159	184	183	183	183
		ML4	4.5	4.6	0.16	171	11	0	186	57	168	186	163	186	185	184	185
	Peristaltic	DP2	2.2	3.0	4.31	75	184	186	0	176	82	0	96	3	10	11	8
		DP3	3.2	4.0	0.28	150	46	57	176	0	147	176	138	175	173	173	174
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	1.81	8	165	168	82	147	0	81	18	80	73	72	75
	Diffusion (Deep)	3m S	2.7	3.3	4.29	74	184	186	0	176	81	0	96	2	10	11	7
	BarCad	3m S	3.6	4.6	1.51	26	159	163	96	138	18	96	0	94	88	88	90

PHC F1-BTEX

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]											
						Alternative Sampling Technologies								Industry Standard Technologies			
						ML2	ML3	ML4	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.2	5.2	5.2	135	141	192	147	185	141	101	38	0	6	49	37
	Waterra - MW1	3m S - MW1	2.1	4.6	4.9	132	138	192	144	184	138	97	43	6	0	55	
	Waterra - MW2	3m S - MW2	2.2	4.6	8.6	158	162	195	166	191	162	134	12	49	55	0	
Alternative Well Types	Peristaltic	ML2	2.6	3.1	1.0	0	11	164	22	133	11	52	153	135	132	158	142
		ML3	3.5	4.1	0.9	11	0	160	12	127	0	62	158	141	138	162	147
		ML4	4.5	4.6	0.1	164	160	0	156	67	160	178	195	192	192	195	193
	Peristaltic	DP2	2.2	3.0	0.8	22	12	156	0	120	12	72	162	147	144	166	152
		DP3	3.2	4.0	0.2	133	127	67	120	0	127	158	190	185	184	191	187
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.0	2.7	0.9	11	0	160	12	127	0	62	158	141	138	162	147
	Diffusion (Deep)	3m S	2.7	3.3	1.7	52	62	178	72	158	62	0	127	101	97	134	111
	BarCad	3m S	3.6	4.6	7.6	153	158	195	162	190	158	127	0	38	43	12	31

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F13. October Cation Sample Results Comparison (Site 2 - Well Cluster 35).

MAGNESIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	82.9	35	53	121	50	53	46	31	53	47	58	0	14	58	39
	Waterra - MW1	3m S - MW1	2.7	5.3	72.0	21	39	112	37	40	32	17	40	33	45	14	0	45	
	Waterra - MW2	3m S - MW2	2.6	5.3	45.7	24	6	77	8	5	13	29	5	12	0	58	45	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	58.2	0	18	96	16	19	11	5	19	12	24	35	21	24	27
		ML2	3.7	4.3	48.4	18	0	81	2	1	7	23	1	6	6	53	39	6	32
		ML3	4.7	5.2	20.4	96	81	0	83	81	87	100	81	86	76	121	112	77	103
		ML4	5.9	6.2	49.5	16	2	83	0	3	5	21	3	4	8	50	37	8	32
	Peristaltic	DP1	2.2	2.9	48.0	19	1	81	3	0	8	24	0	7	5	53	40	5	33
		DP2	3.3	4.0	51.9	11	7	87	5	8	0	16	8	1	13	46	32	13	30
		DP3	4.2	5.0	60.9	5	23	100	21	24	16	0	24	17	29	31	17	29	25
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	48.0	19	1	81	3	0	8	24	0	7	5	53	40	5	33
	Diffusion (Deep)	3m S	3.4	4.0	51.4	12	6	86	4	7	1	17	7	0	12	47	33	12	31
	BarCad	3m S	4.3	5.3	45.5	24	6	76	8	5	13	29	5	12	0	58	45	0	35

CALCIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	185	46	94	105	46	73	96	33	84	74	72	0	27	84	57
	Waterra - MW1	3m S - MW1	2.7	5.3	141	19	72	84	19	49	74	6	61	50	47	27	0	60	
	Waterra - MW2	3m S - MW2	2.6	5.3	75.6	42	13	27	42	12	15	55	0	11	14	84	60	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	116	0	54	67	0	30	56	14	42	31	29	46	19	42	36
		ML2	3.7	4.3	66.4	54	0	14	54	25	2	67	13	24	27	94	72	13	60
		ML3	4.7	5.2	57.7	67	14	0	67	39	12	79	27	38	40	105	84	27	72
		ML4	5.9	6.2	116	0	54	67	0	30	56	14	42	31	29	46	19	42	36
	Peristaltic	DP1	2.2	2.9	85.6	30	25	39	30	0	27	43	13	1	2	73	49	12	45
		DP2	3.3	4.0	65.2	56	2	12	56	27	0	68	15	26	29	96	74	15	61
		DP3	4.2	5.0	133	14	67	79	14	43	68	0	55	44	42	33	6	55	31
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	75.5	42	13	27	42	13	15	55	0	11	14	84	61	0	48
	Diffusion (Deep)	3m S	3.4	4.0	84.6	31	24	38	31	1	26	44	11	0	3	74	50	11	45
	BarCad	3m S	4.3	5.3	87.0	29	27	40	29	2	29	42	14	3	0	72	47	14	44

SODIUM

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	137	21	37	136	20	32	2	35	19	18	7	0	1	5	3
	Waterra - MW1	3m S - MW1	2.7	5.3	139	19	36	135	19	33	4	36	21	20	6	1	0	4	
	Waterra - MW2	3m S - MW2	2.6	5.3	144	16	33	133	15	36	7	40	24	23	2	5	4	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	169	0	17	124	1	52	23	55	40	39	14	21	19	16	19
		ML2	3.7	4.3	200	17	0	113	17	67	40	70	56	55	31	37	36	33	35
		ML3	4.7	5.2	722	124	113	0	124	152	137	153	146	145	132	136	135	133	135
		ML4	5.9	6.2	168	1	17	124	0	51	23	54	39	38	13	20	19	15	18
	Peristaltic	DP1	2.2	2.9	100	52	67	152	51	0	29	4	13	13	38	32	33	36	34
		DP2	3.3	4.0	134	23	40	137	23	29	0	33	17	16	9	2	4	7	4
		DP3	4.2	5.0	96	55	70	153	54	4	33	0	16	17	42	35	36	40	37
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	113	40	56	146	39	13	17	16	0	1	26	19	21	24	21
	Diffusion (Deep)	3m S	3.4	4.0	114	39	55	145	38	13	16	17	1	0	25	18	20	23	20
	BarCad	3m S	4.3	5.3	147	14	31	132	13	38	9	42	26	25	0	7	6	2	5

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F14. October Anion Sample Results Comparison (Site 2 - Well Cluster 35).

BICARBONATE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	1250	16	31	39	32	42	48	68	57	51	49	0	8	47	32
	Waterra - MW1	3m S - MW1	2.7	5.3	1150	7	22	31	24	34	40	60	50	43	41	8	0	39	
	Waterra - MW2	3m S - MW2	2.6	5.3	772	32	17	9	16	5	0	22	11	4	2	47	39	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	1070	0	15	23	17	27	33	54	43	36	34	16	7	32	18
		ML2	3.7	4.3	919	15	0	8	2	12	18	39	28	21	19	31	22	17	23
		ML3	4.7	5.2	845	23	8	0	7	4	9	31	20	13	11	39	31	9	26
		ML4	5.9	6.2	902	17	2	7	0	11	16	38	26	20	18	32	24	16	24
	Peristaltic	DP1	2.2	2.9	812	27	12	4	11	0	5	27	16	9	7	42	34	5	27
		DP2	3.3	4.0	770	33	18	9	16	5	0	22	11	4	2	48	40	0	29
		DP3	4.2	5.0	617	54	39	31	38	27	22	0	11	18	20	68	60	22	50
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	692	43	28	20	26	16	11	11	0	7	9	57	50	11	39
	Diffusion (Deep)	3m S	3.4	4.0	741	36	21	13	20	9	4	18	7	0	2	51	43	4	33
	BarCad	3m S	4.3	5.3	756	34	19	11	18	7	2	20	9	2	0	49	41	2	31

SULFATE

Comparison Group	Sampling Method	Well Type	Sample Intervsl (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	0.8	32	182	200	197	126	165	199	120	120	182	0	12	184	126
	Waterra - MW1	3m S - MW1	2.7	5.3	0.9	20	179	200	197	118	161	199	127	127	180	12	0	182	
	Waterra - MW2	3m S - MW2	2.6	5.3	19	178	13	193	142	138	78	178	196	196	9	184	182	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	1.1	0	175	200	196	104	153	199	138	138	176	32	20	178	77
		ML2	3.7	4.3	17	175	0	194	148	130	67	181	195	195	4	182	179	13	125
		ML3	4.7	5.2	1140	200	194	0	164	199	197	111	200	200	194	200	200	193	198
		ML4	5.9	6.2	112	196	148	164	0	188	172	98	199	199	146	197	197	142	179
	Peristaltic	DP1	2.2	2.9	3.5	104	130	199	188	0	81	196	178	178	133	126	118	138	127
		DP2	3.3	4.0	8.3	153	67	197	172	81	0	190	191	191	70	165	161	78	135
		DP3	4.2	5.0	327	199	181	111	98	196	190	0	200	200	180	199	199	178	192
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	0.2	138	195	200	199	178	191	200	0	0	195	120	127	196	148
	Diffusion (Deep)	3m S	3.4	4.0	0.2	138	195	200	199	178	191	200	0	0	195	120	127	196	148
	BarCad	3m S	4.3	5.3	17	176	4	194	146	133	70	180	195	195	0	182	180	9	124

CHLORIDE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	78.3	36	62	75	47	37	55	97	54	53	54	0	52	49	35
	Waterra - MW1	3m S - MW1	2.7	5.3	46.1	17	11	26	5	15	4	52	2	2	3	52	0	3	
	Waterra - MW2	3m S - MW2	2.6	5.3	47.6	13	15	29	2	12	7	55	5	5	6	49	3	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	54.4	0	28	42	12	1	20	67	19	18	19	36	17	13	22
		ML2	3.7	4.3	41.1	28	0	14	16	27	8	41	9	10	9	62	11	15	29
		ML3	4.7	5.2	35.6	42	14	0	30	41	22	27	24	24	23	75	26	29	43
		ML4	5.9	6.2	48.4	12	16	30	0	10	9	56	7	6	8	47	5	2	18
	Peristaltic	DP1	2.2	2.9	53.7	1	27	41	10	0	19	66	17	17	18	37	15	12	22
		DP2	3.3	4.0	44.4	20	8	22	9	19	0	48	2	2	1	55	4	7	22
		DP3	4.2	5.0	27.2	67	41	27	56	66	48	0	50	50	49	97	52	55	68
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	45.1	19	9	24	7	17	2	50	0	1	1	54	2	5	20
	Diffusion (Deep)	3m S	3.4	4.0	45.4	18	10	24	6	17	2	50	1	0	1	53	2	5	20
	BarCad	3m S	4.3	5.3	44.8	19	9	23	8	18	1	49	1	1	0	54	3	6	21

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F15. October Metals Sample Results Comparison (Site 2 - Well Cluster 35).

MANGANESE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	3.81	54	136	113	20	106	155	135	80	62	40	0	17	60	50
	Waterra - MW1	3m S - MW1	2.7	5.3	4.51	38	144	124	36	118	162	144	93	77	56	17	0	75	
	Waterra - MW2	3m S - MW2	2.6	5.3	2.06	105	95	64	41	55	125	94	23	2	20	60	75	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	6.64	0	160	145	72	140	173	160	121	107	90	54	38	105	66
		ML2	3.7	4.3	0.73	160	0	37	124	46	42	1	77	93	110	136	144	95	125
		ML3	4.7	5.2	1.06	145	37	0	99	10	76	36	43	62	82	113	124	64	100
		ML4	5.9	6.2	3.13	72	124	99	0	91	147	124	62	44	21	20	36	41	32
	Peristaltic	DP1	2.2	2.9	1.17	140	46	10	91	0	84	45	33	53	74	106	118	55	93
		DP2	3.3	4.0	0.48	173	42	76	147	84	0	43	110	123	136	155	162	125	147
		DP3	4.2	5.0	0.74	160	1	36	124	45	43	0	76	92	110	135	144	94	124
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	1.64	121	77	43	62	33	110	76	0	20	43	80	93	23	65
	Diffusion (Deep)	3m S	3.4	4.0	2.01	107	93	62	44	53	123	92	20	0	23	62	77	2	47
	BarCad	3m S	4.3	5.3	2.53	90	110	82	21	74	136	110	43	23	0	40	56	20	39

IRON

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	65.6	117	155	197	170	54	141	188	64	54	165	0	28	143	100
	Waterra - MW1	3m S - MW1	2.7	5.3	49.4	97	143	196	162	27	126	185	38	27	154	28	0	128	
	Waterra - MW2	3m S - MW2	2.6	5.3	10.9	45	28	184	70	110	4	139	102	110	52	143	128	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	17.2	0	71	190	106	75	41	159	65	75	92	117	97	45	86
		ML2	3.7	4.3	8.22	71	0	180	44	129	32	123	122	128	25	155	143	28	109
		ML3	4.7	5.2	0.44	190	180	0	169	195	185	127	195	195	174	197	196	184	193
		ML4	5.9	6.2	5.25	106	44	169	0	151	73	91	146	151	19	170	162	70	134
	Peristaltic	DP1	2.2	2.9	37.8	75	129	195	151	0	108	180	11	0	142	54	27	110	64
		DP2	3.3	4.0	11.3	41	32	185	73	108	0	141	100	108	56	141	126	4	90
		DP3	4.2	5.0	1.97	159	123	127	91	180	141	0	178	180	106	188	185	139	171
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	33.8	65	122	195	146	11	100	178	0	11	137	64	38	102	68
	Diffusion (Deep)	3m S	3.4	4.0	37.7	75	128	195	151	0	108	180	11	0	142	54	27	110	64
	BarCad	3m S	4.3	5.3	6.37	92	25	174	19	142	56	106	137	142	0	165	154	52	124

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F16A. October Hydrocarbon Sample Results Comparison (Site 2 - Well Cluster 35).

BENZENE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	0.120	16	166	181	181	22	30	197	40	21	12	0	18	6	16
	Waterra - MW1	3m S - MW1	2.7	5.3	0.100	34	160	177	177	40	12	196	57	39	6	18	0	25	
	Waterra - MW2	3m S - MW2	2.6	5.3	0.128	10	168	182	182	16	36	197	34	14	19	6	25	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	0.141	0	171	184	184	6	45	197	24	5	28	16	34	10	20
		ML2	3.7	4.3	0.011	171	0	59	59	173	156	167	177	172	162	166	160	168	165
		ML3	4.7	5.2	0.006	184	59	0	0	185	175	143	187	184	179	181	177	182	180
		ML4	5.9	6.2	0.07010	67	146	168	168	73	24	194	88	71	41	52	35	58	49
	Peristaltic	DP1	2.2	2.9	0.150	6	173	185	185	0	51	197	18	1	34	22	40	16	26
		DP2	3.3	4.0	0.089	45	156	175	175	51	0	196	68	50	17	30	12	36	26
		DP3	4.2	5.0	0.001	197	167	143	143	197	196	0	198	197	196	197	196	197	197
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	0.180	24	177	187	187	18	68	198	0	20	52	40	57	34	44
	Diffusion (Deep)	3m S	3.4	4.0	0.148	5	172	184	184	1	50	197	20	0	33	21	39	14	25
	BarCad	3m S	4.3	5.3	0.106	28	162	179	179	34	17	196	52	33	0	12	6	19	12

ETHYLBENZENE

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	0.680	80	187	191	191	34	59	198	69	103	89	0	111	55	77
	Waterra - MW1	3m S - MW1	2.7	5.3	0.196	39	157	170	170	84	62	194	51	11	28	111	0	65	
	Waterra - MW2	3m S - MW2	2.6	5.3	0.386	28	177	184	184	22	4	197	16	55	39	55	65	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	0.292	0	170	180	180	49	24	196	12	29	12	80	39	28	49
		ML2	3.7	4.3	0.023	170	0	39	39	181	176	152	174	161	167	187	157	177	174
		ML3	4.7	5.2	0.016	180	39	0	0	187	184	132	182	173	177	191	170	184	182
		ML4	5.9	6.2	0.034	159	36	73	73	174	167	165	163	147	154	181	141	168	164
	Peristaltic	DP1	2.2	2.9	0.480	49	181	187	187	0	26	197	37	75	59	34	84	22	47
		DP2	3.3	4.0	0.371	24	176	184	184	26	0	197	12	52	35	59	62	4	41
		DP3	4.2	5.0	0.003	196	152	132	132	197	197	0	196	194	195	198	194	197	196
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	0.330	12	174	182	182	37	12	196	0	40	24	69	51	16	45
	Diffusion (Deep)	3m S	3.4	4.0	0.219	29	161	173	173	75	52	194	40	0	17	103	11	55	56
	BarCad	3m S	4.3	5.3	0.260	12	167	177	177	59	35	195	24	17	0	89	28	39	52

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

Table F16B. October Hydrocarbon Sample Results Comparison (Site 2 - Well Cluster 35).

TOTAL XYLENES

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	10.300	114	195	197	197	28	129	199	51	92	126	0	116	103	79
	Waterra - MW1	3m S - MW1	2.7	5.3	2.740	3	182	187	187	96	21	196	77	33	16	116	0	18	
	Waterra - MW2	3m S - MW2	2.6	5.3	3.280	15	185	189	189	81	38	197	61	15	34	103	18	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	2.810	0	182	188	188	94	23	196	74	31	19	114	3	15	44
		ML2	3.7	4.3	0.131	182	0	37	37	193	178	135	192	187	179	195	182	185	187
		ML3	4.7	5.2	0.090	188	37	0	0	195	185	111	194	191	185	197	187	189	191
		ML4	5.9	6.2	0.132	182	1	38	38	193	178	135	192	187	179	195	182	185	187
	Peristaltic	DP1	2.2	2.9	7.750	94	193	195	195	0	111	199	23	68	108	28	96	81	68
		DP2	3.3	4.0	2.230	23	178	185	185	111	0	195	93	53	4	129	21	38	62
		DP3	4.2	5.0	0.026	196	135	111	111	199	195	0	198	197	196	199	196	197	197
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	6.140	74	192	194	194	23	93	198	0	46	90	51	77	61	63
	Diffusion (Deep)	3m S	3.4	4.0	3.830	31	187	191	191	68	53	197	46	0	49	92	33	15	47
	BarCad	3m S	4.3	5.3	2.330	19	179	185	185	108	4	196	90	49	0	126	16	34	59

PHC F1-BTEX

Comparison Group	Sampling Method	Well Type	Sample Interval (mbgs)		Concentration (mg/L)	Calculated Relative Percent Difference (RPD) Result [%]													
						Alternative Sampling Technologies										Industry Standard Technologies			
						ML1	ML2	ML3	ML4	DP1	DP2	DP3	Shallow Diff.	Deeper Diff.	BarCad	Bailer	Waterra MW1	Waterra MW2	Industry Standard Ave.
Common Sample Collection	Bailer	3m S	2.8	5.3	76	196	182	198	198	194	195	199	190	194	197	0	172	191	156
	Waterra - MW1	3m S - MW1	2.7	5.3	5.7	151	48	174	174	130	140	193	100	130	162	172	0	104	
	Waterra - MW2	3m S - MW2	2.6	5.3	1.8	77	64	127	127	40	57	179	5	40	100	191	104	0	
Alternative Well Types	Peristaltic	ML1	2.6	3.3	0.8	0	126	67	67	40	22	156	81	40	29	196	151	77	141
		ML2	3.7	4.3	3.5	126	0	159	159	98	111	189	59	98	141	182	48	64	98
		ML3	4.7	5.2	0.4	67	159	0	0	100	86	120	130	100	40	198	174	127	166
		ML4	5.9	6.2	0.3	91	168	29	29	120	108	100	145	120	67	198	180	143	174
	Peristaltic	DP1	2.2	2.9	1.2	40	98	100	100	0	18	169	45	0	67	194	130	40	121
		DP2	3.3	4.0	1.0	22	111	86	86	18	0	164	62	18	50	195	140	57	131
		DP3	4.2	5.0	0.1	156	189	120	120	169	164	0	180	169	143	199	193	179	191
Alternative Sampling Methods	Diffusion (Shallow)	3m S	2.7	3.4	1.9	81	59	130	130	45	62	180	0	45	104	190	100	5	99
	Diffusion (Deep)	3m S	3.4	4.0	1.2	40	98	100	100	0	18	169	45	0	67	194	130	40	121
	BarCad	3m S	4.3	5.3	0.6	29	141	40	40	67	50	143	104	67	0	197	162	100	153

Note: 3m S - indicates that the well type is an industry standard three meter screened well (five centimeter diameter, PVC).
ML - indicates multilevel well type.
DP - indicates drive point well type.
Diff. - indicates diffusion sampler.

1. See Appendix E for a detailed example RPD calculation.

APPENDIX G:

Sampling Technology Figures for Selected Parameters of Interest in a MNA Program

Sampling Technology Figures

The figures have been plotted for each MNA parameter of interest for October and February at Site 1 (Figures G1 to G24) and for October at Site 2 for Well Cluster 34 and 35 (Figure G25 to G48). This figure format allows the ability of the alternative well types and sampling methods to collect discrete interval samples to be assessed. MNA parameter concentrations measured by all technologies are compared over various sample depth intervals on a single plot; allowing depth dependent trends to be observed.

The plots have an abbreviated sampling technology name and the depth interval over which the sample was collected along the y-axis. The abbreviations used are ML (multilevel well), DP (drive point well), Bail (bailer sampled three metre screen well), Wat. (Waterra sampled three metre screen well), BC (BarCad System) and Diff (diffusion sampler). For the common sample collection methods having wells with longer screened intervals, the sample depth interval indicated along the y-axis shows the upper limit of the sample interval to be the depth where the water surface existed within the screened portion of the well at the time of sampling. This was the sample interval indicated because this was the depth interval over which the sample could have been collected, as the sample could not have come from the entire three metre screen interval for the well.

All the plots have a logarithmic x-axis because of the large variations in concentrations measured for many of the parameters. The concentration values have been added to the right of the bar for easier comparison.

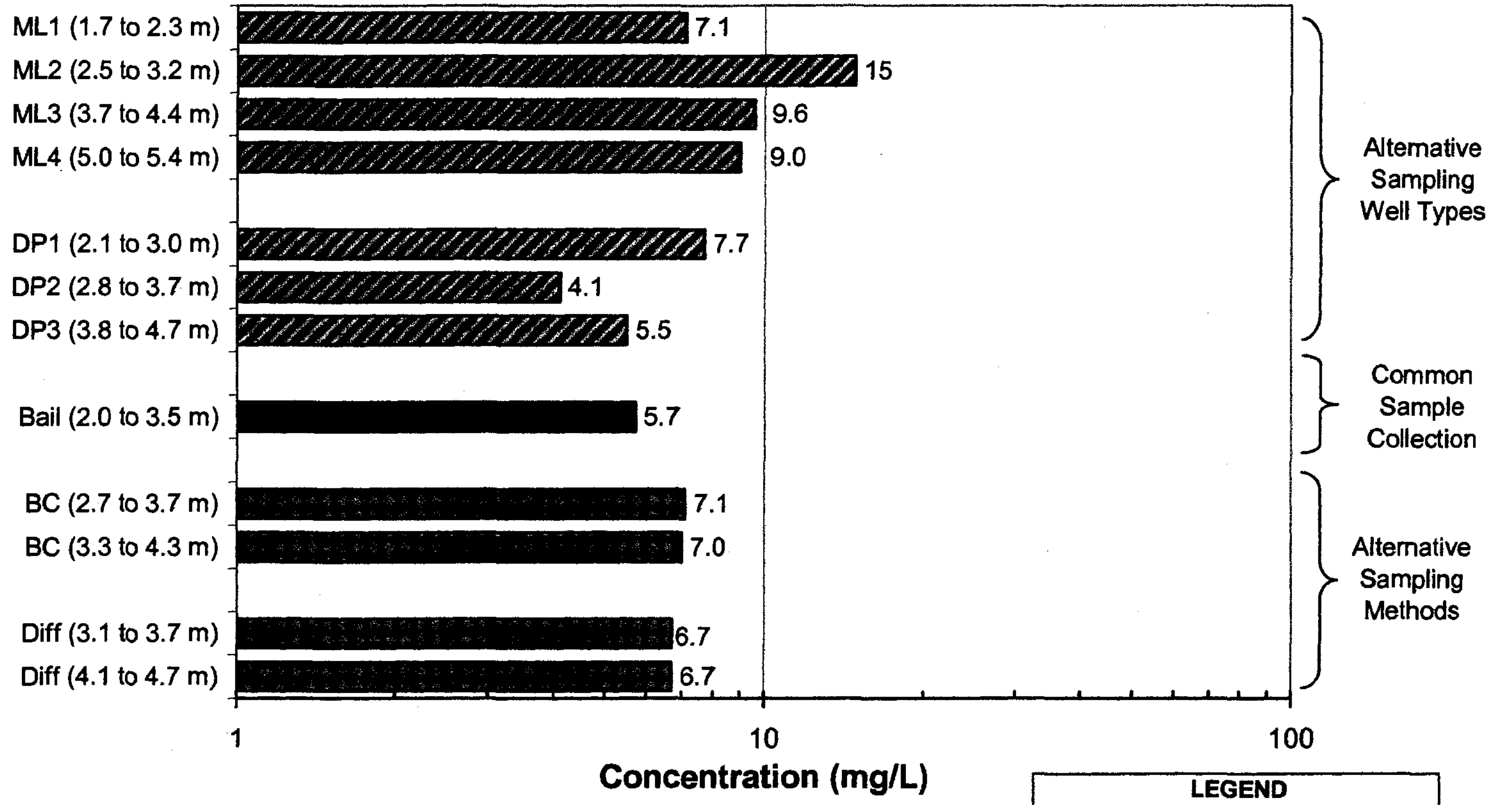


Figure G1. Magnesium Concentration Comparison (October, Site 1)

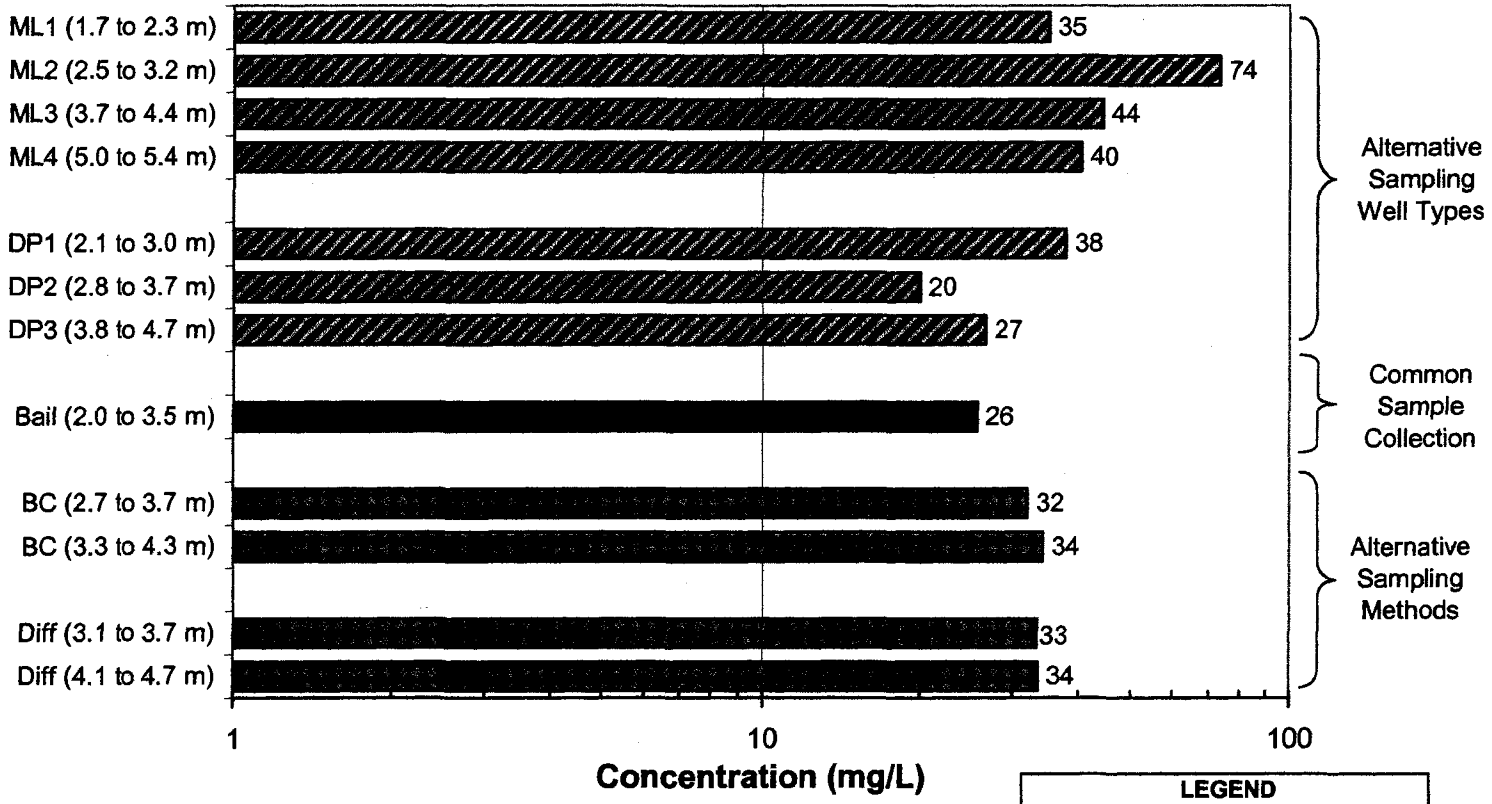


Figure G2. Calcium Concentration Comparison (October, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

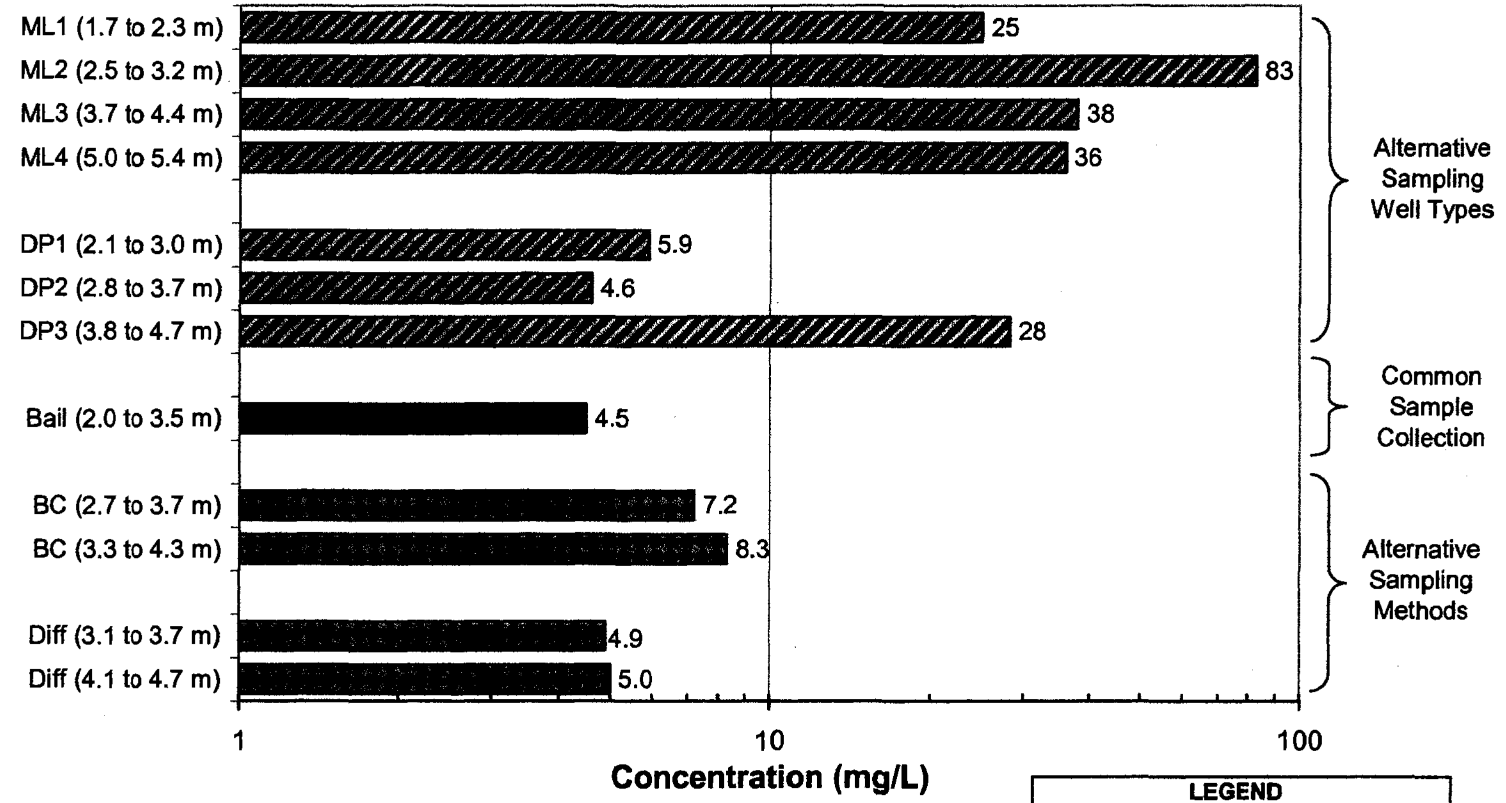


Figure G3. Sodium Concentration Comparison (October, Site 1)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

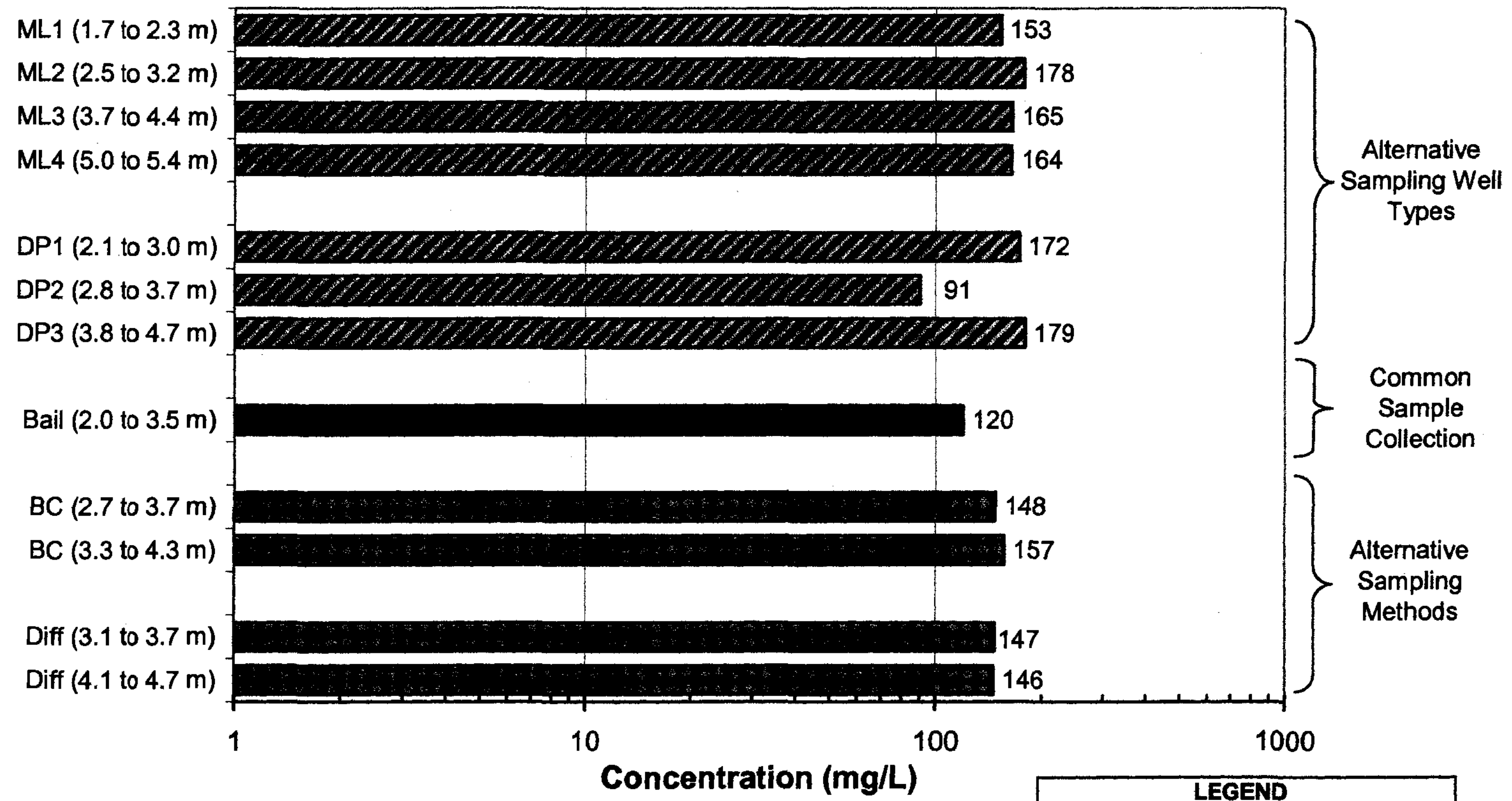


Figure G4. Bicarbonate Concentration Comparison (October, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

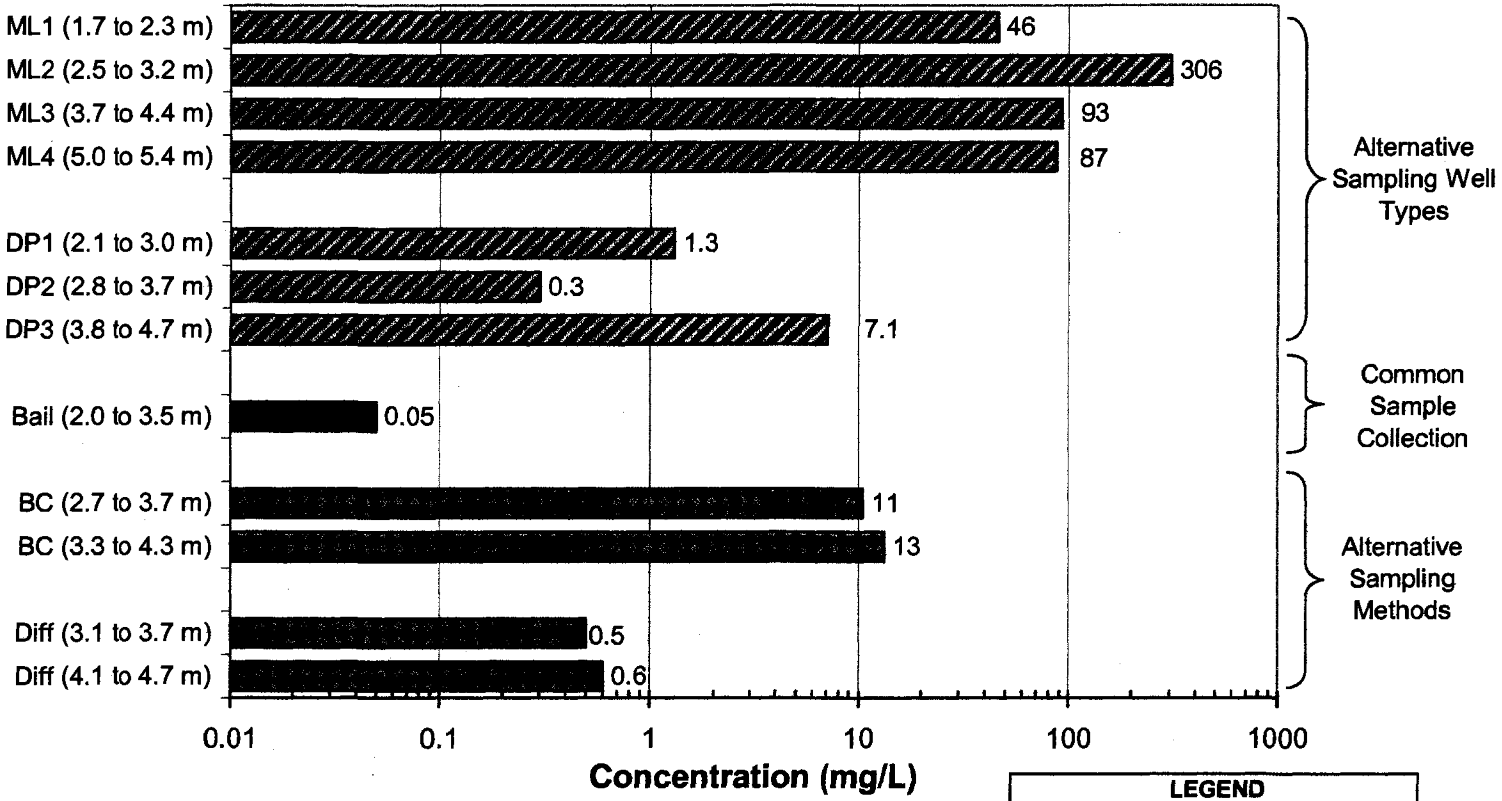


Figure G5. Sulfate Concentration Comparison (October, Site 1)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

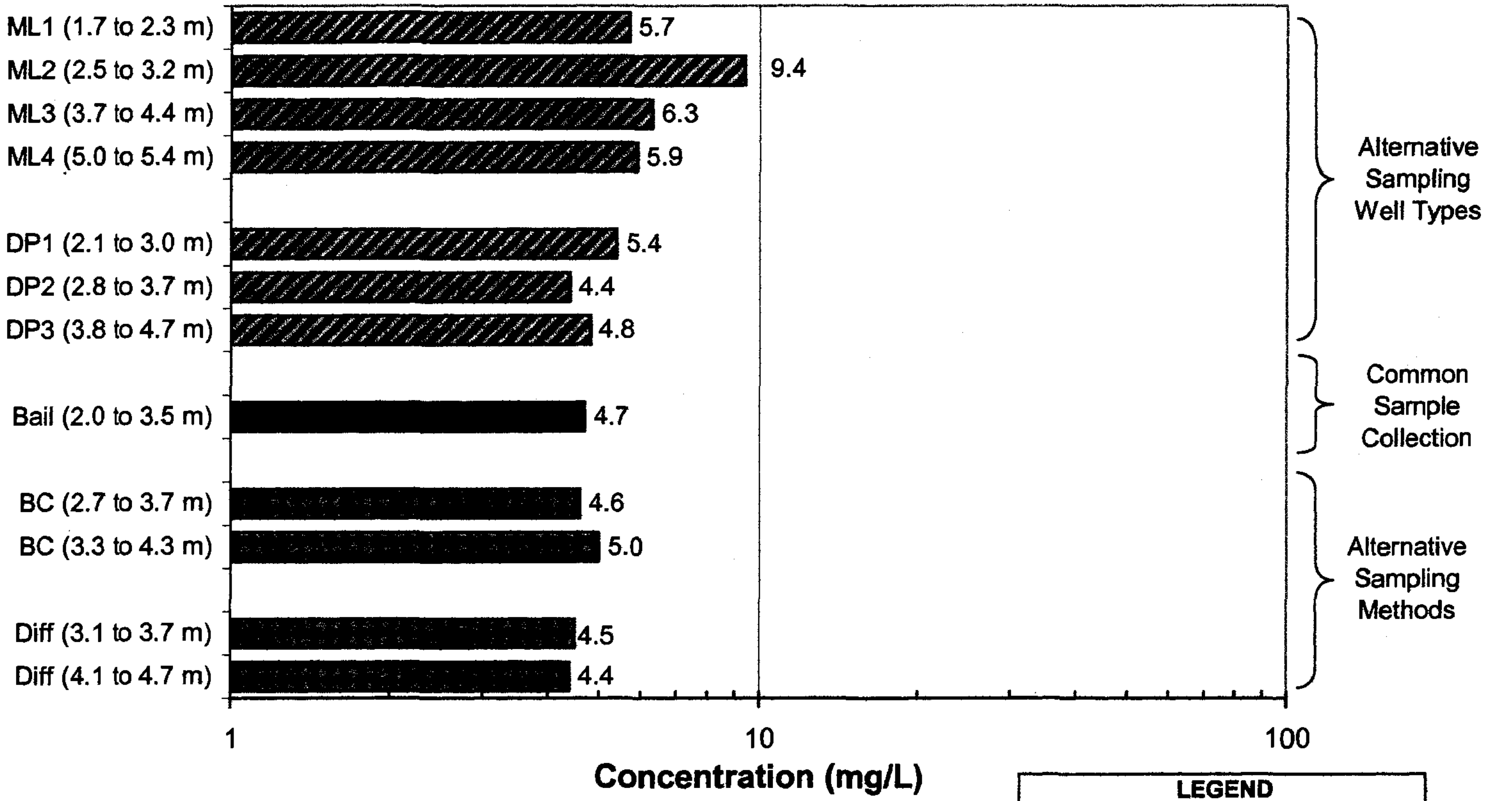


Figure G6. Chloride Concentration Comparison (October, Site 1)

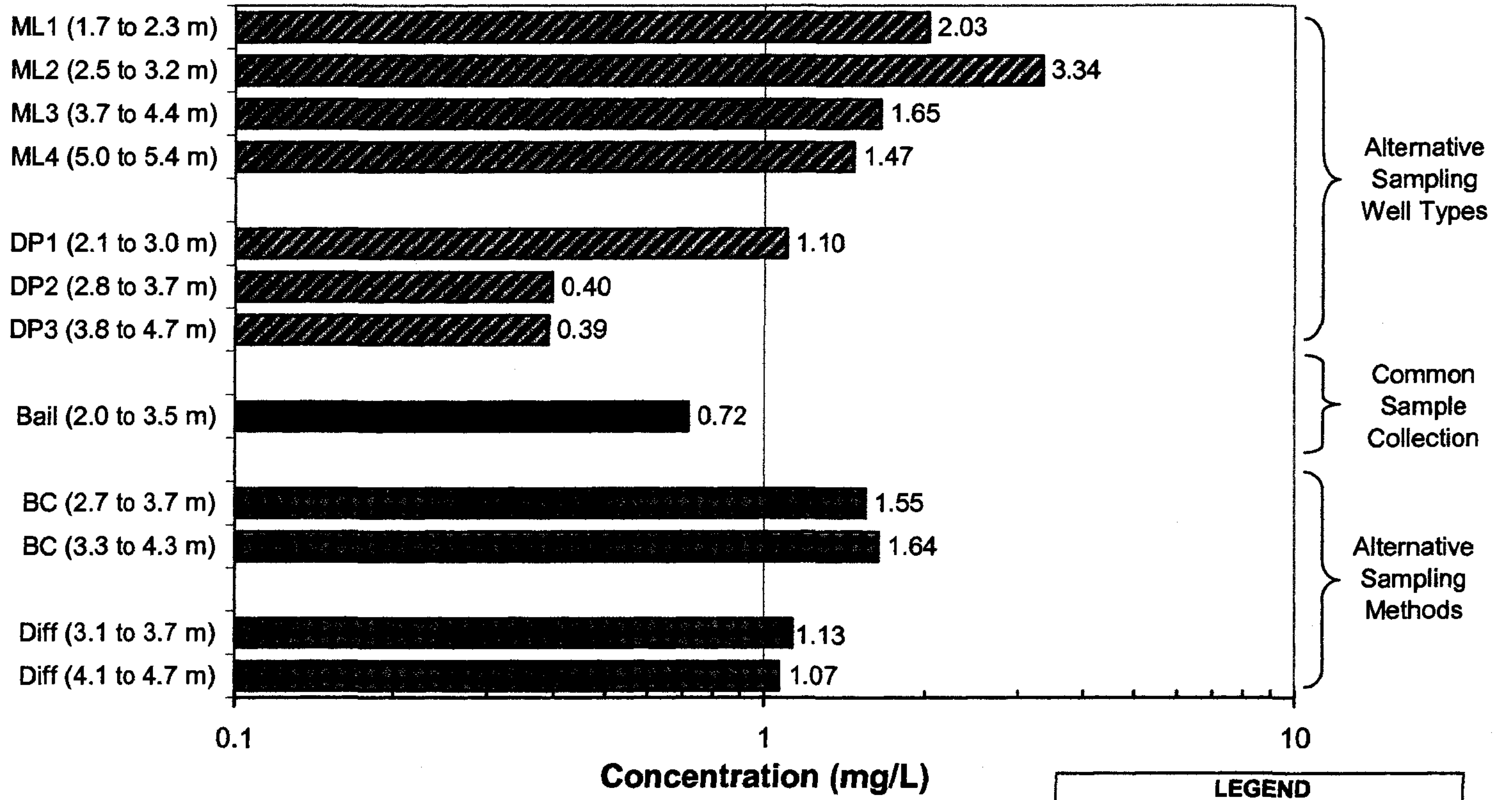


Figure G7. Manganese Concentration Comparison (October, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

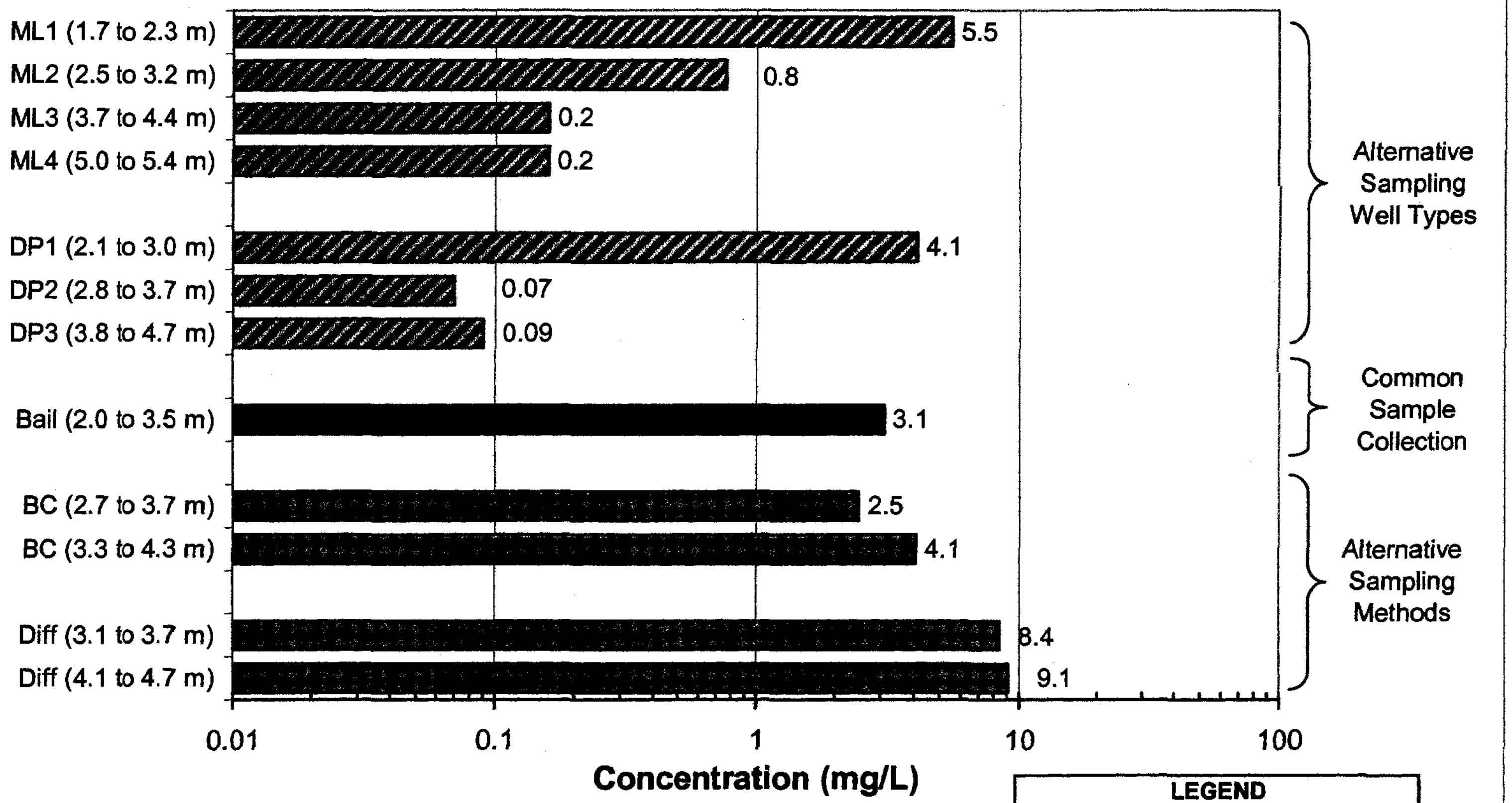


Figure G8. Iron Concentration Comparison (October, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

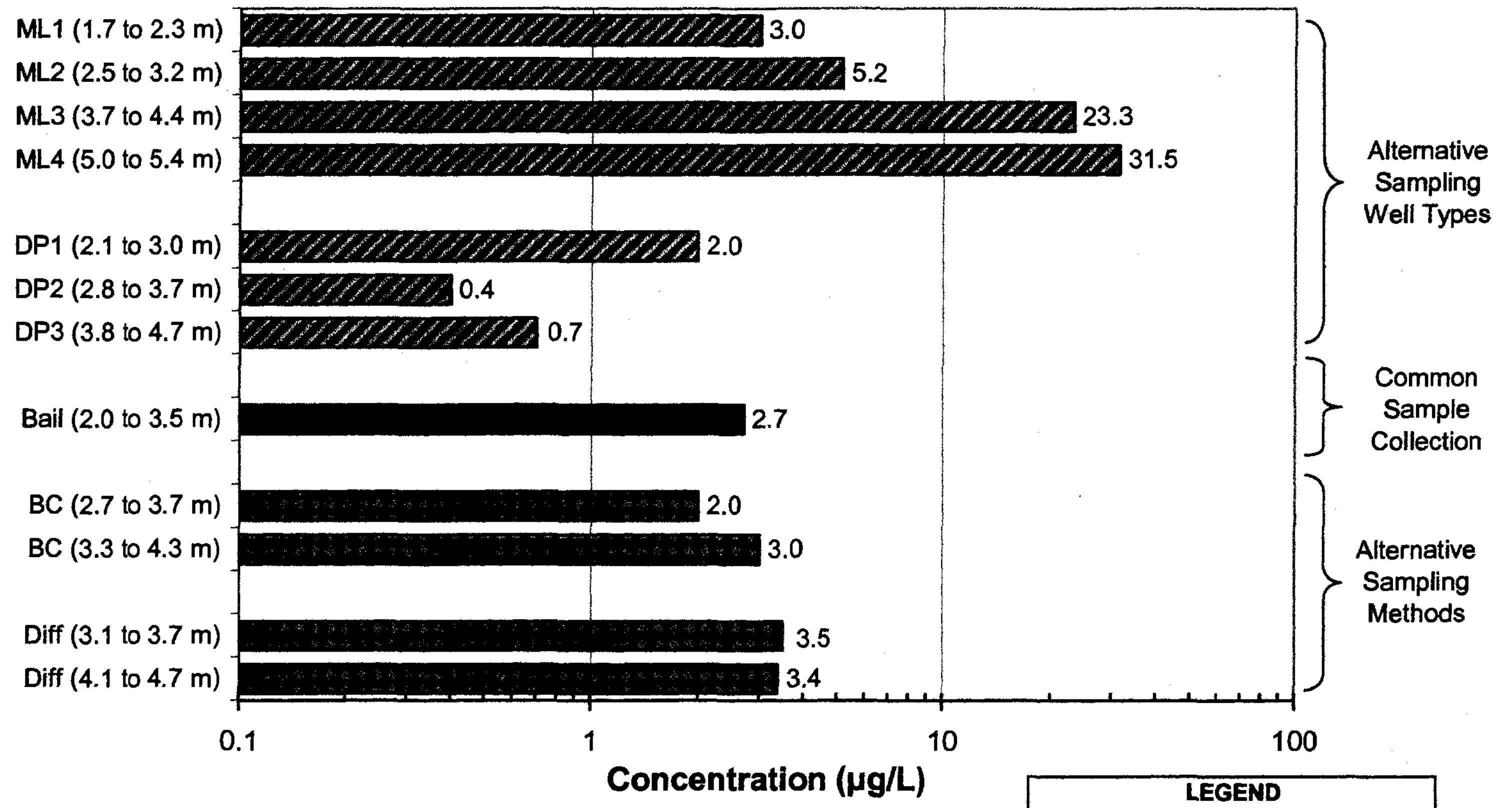


Figure G9. Benzene Concentration Comparison (October, Site 1)

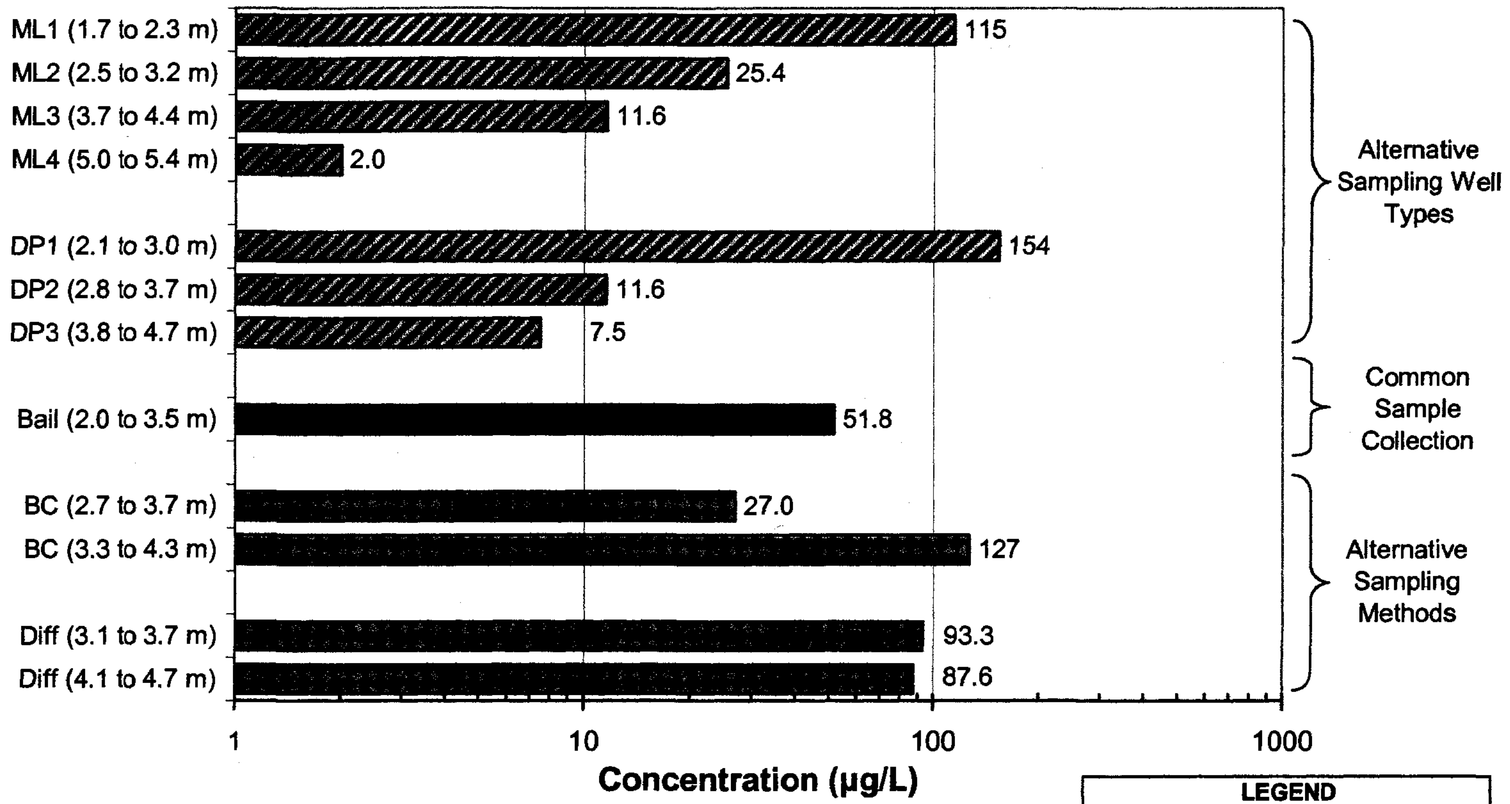


Figure G10. Ethylbenzene Concentration Comparison (October, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

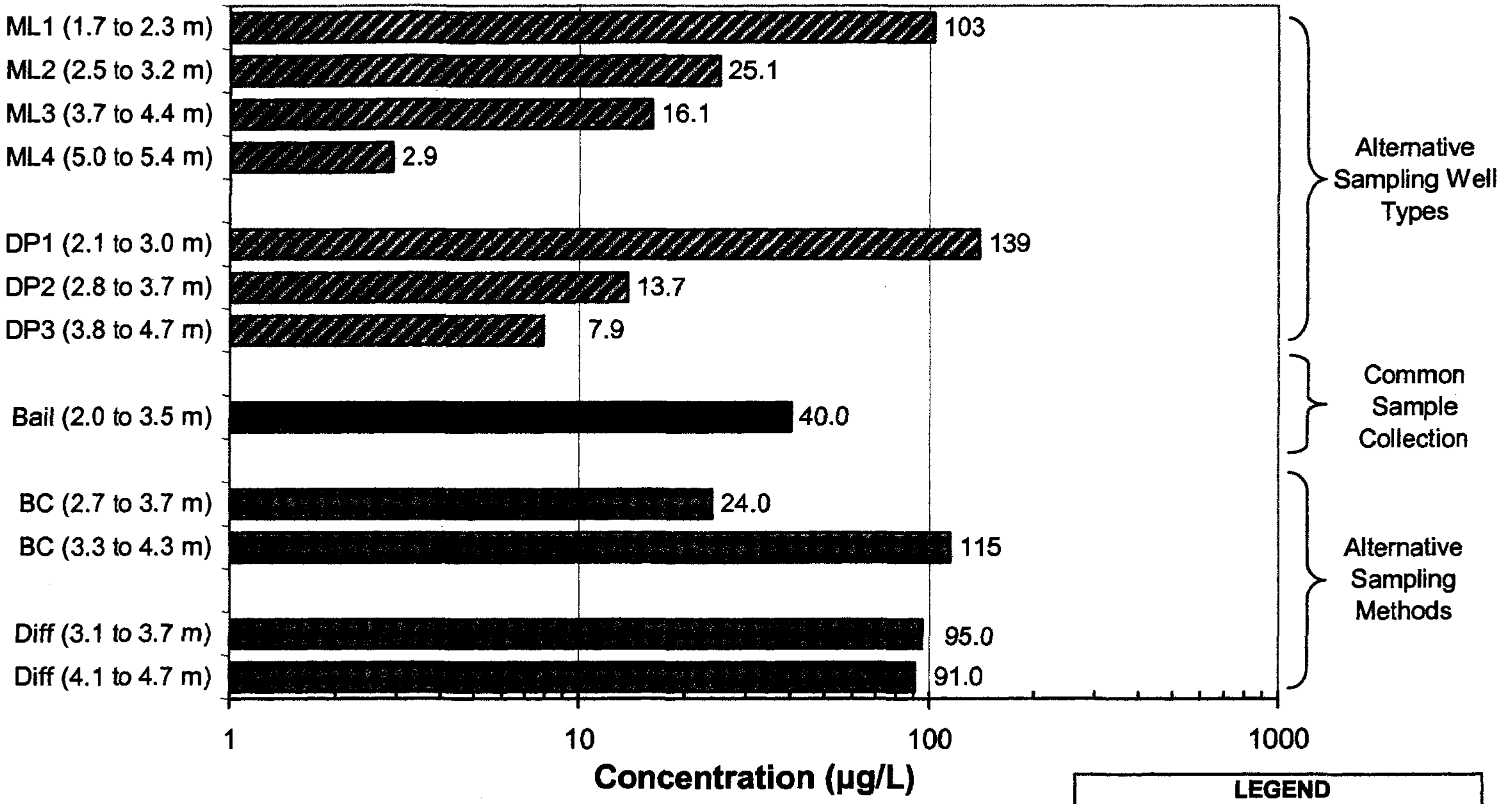


Figure G11. Total Xylenes Concentration Comparison (October, Site 1)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

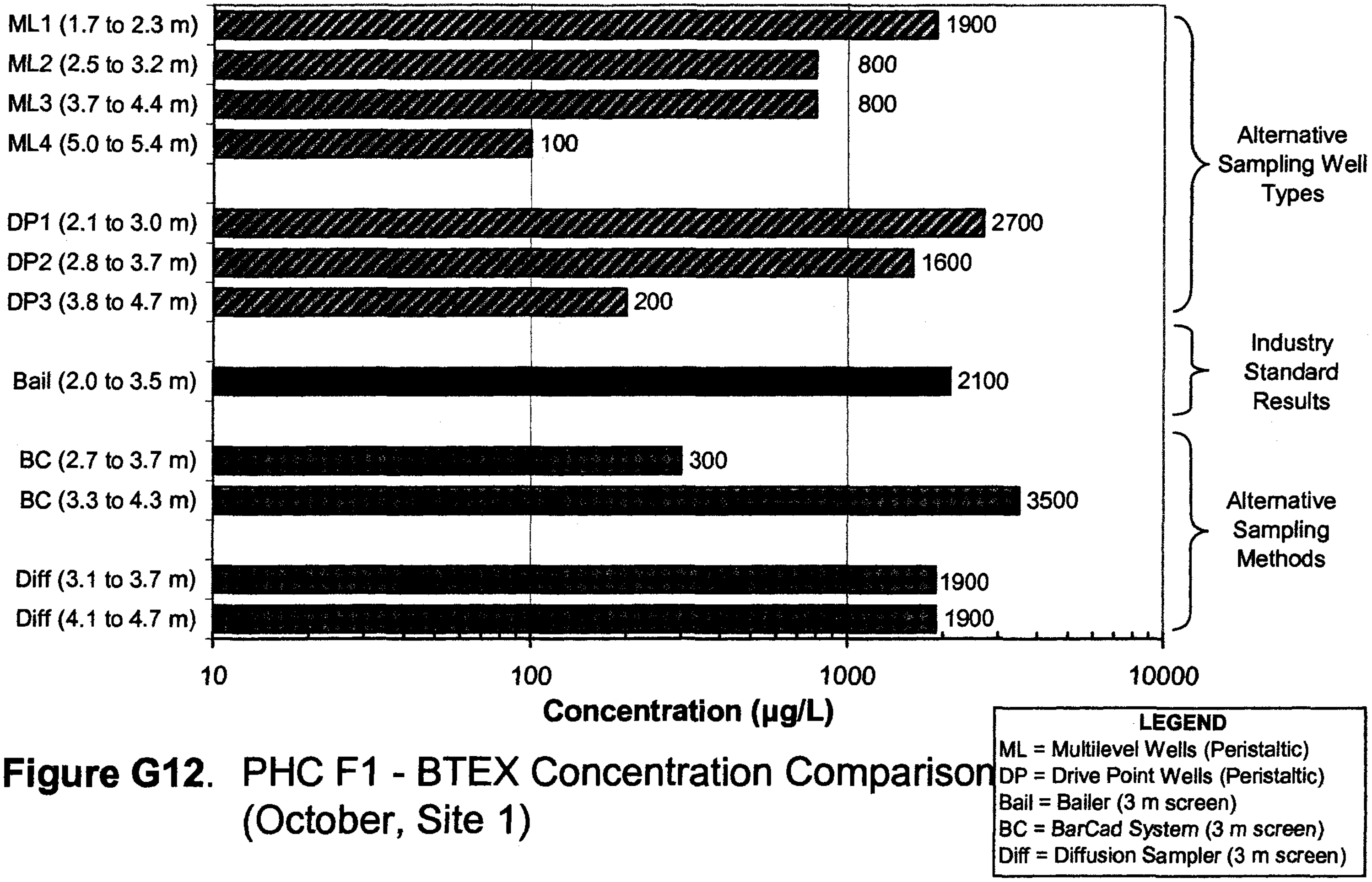


Figure G12. PHC F1 - BTEX Concentration Comparison (October, Site 1)

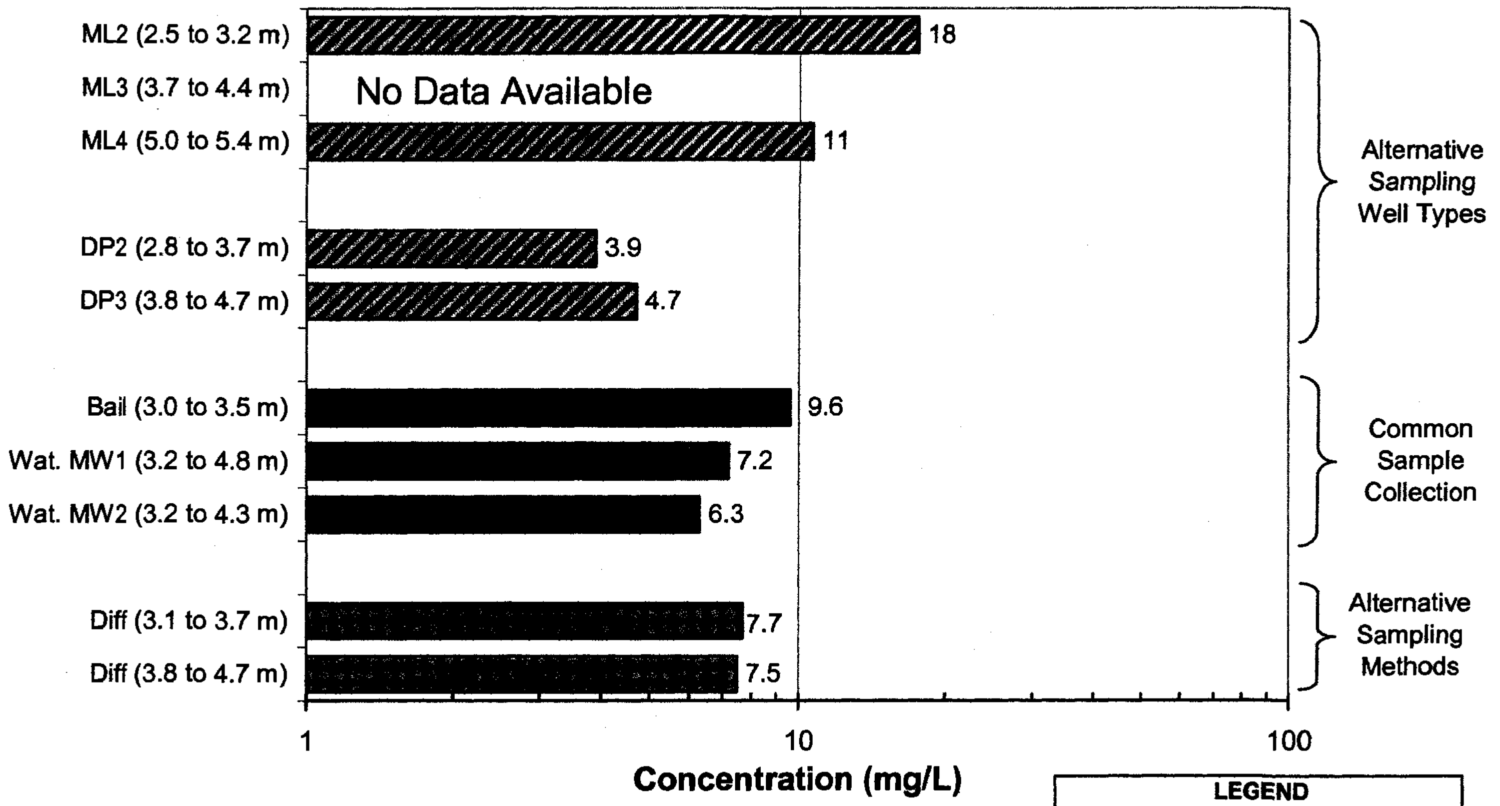


Figure G13. Magnesium Concentration Comparison (February, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
Diff = Diffusion Sampler (3 m screen)

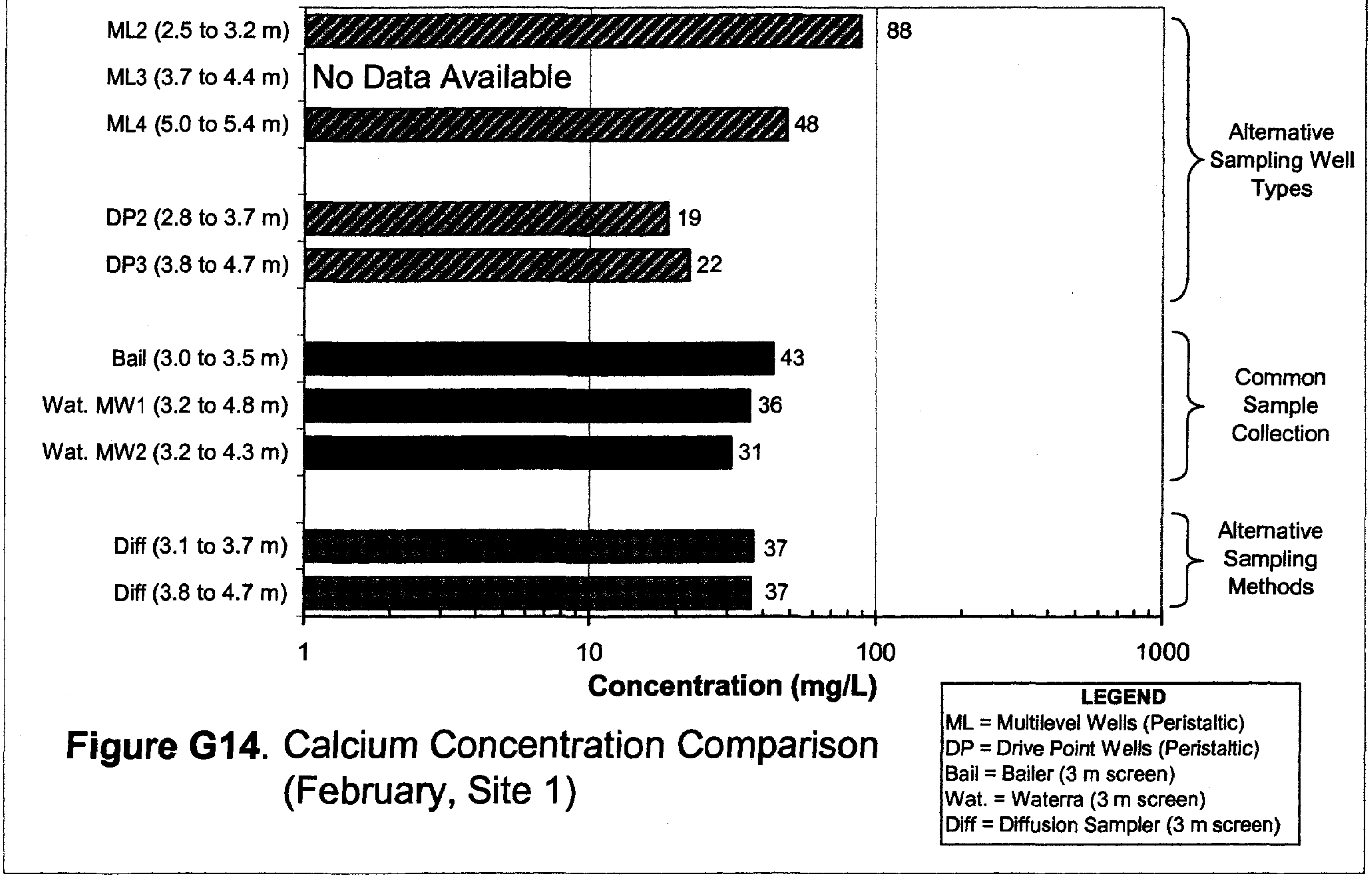


Figure G14. Calcium Concentration Comparison (February, Site 1)

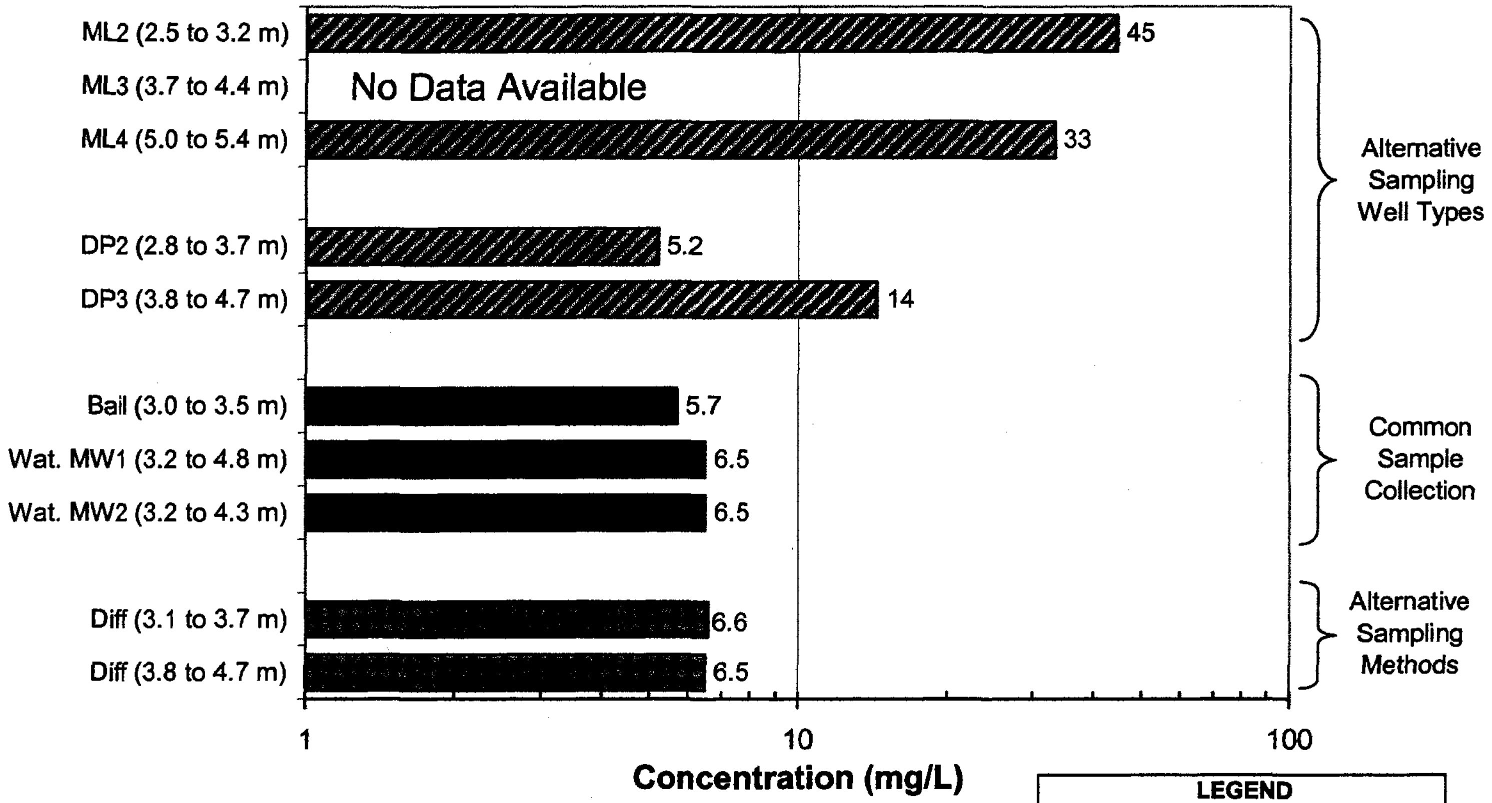


Figure G15. Sodium Concentration Comparison (February, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
Diff = Diffusion Sampler (3 m screen)

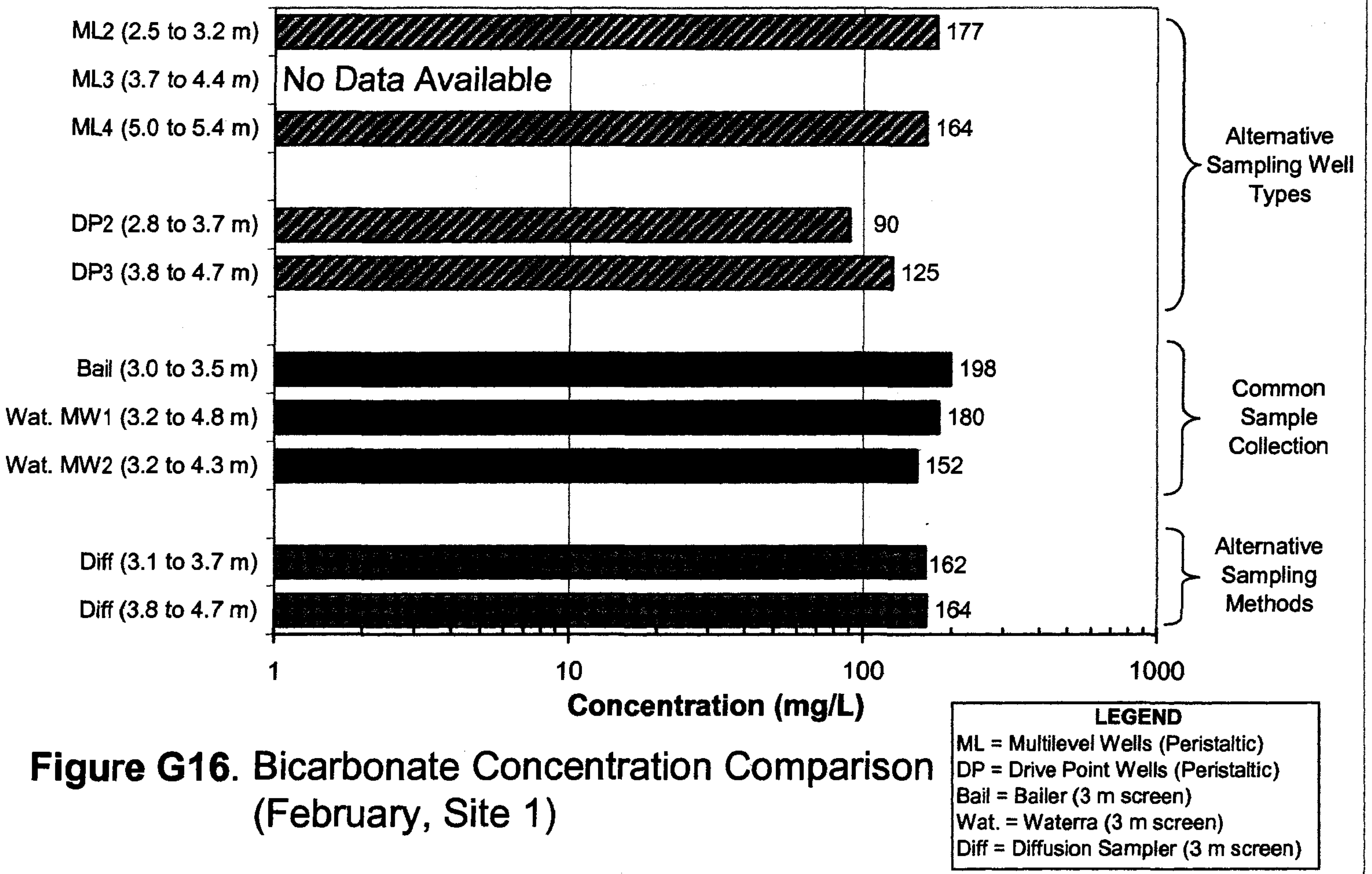


Figure G16. Bicarbonate Concentration Comparison (February, Site 1)

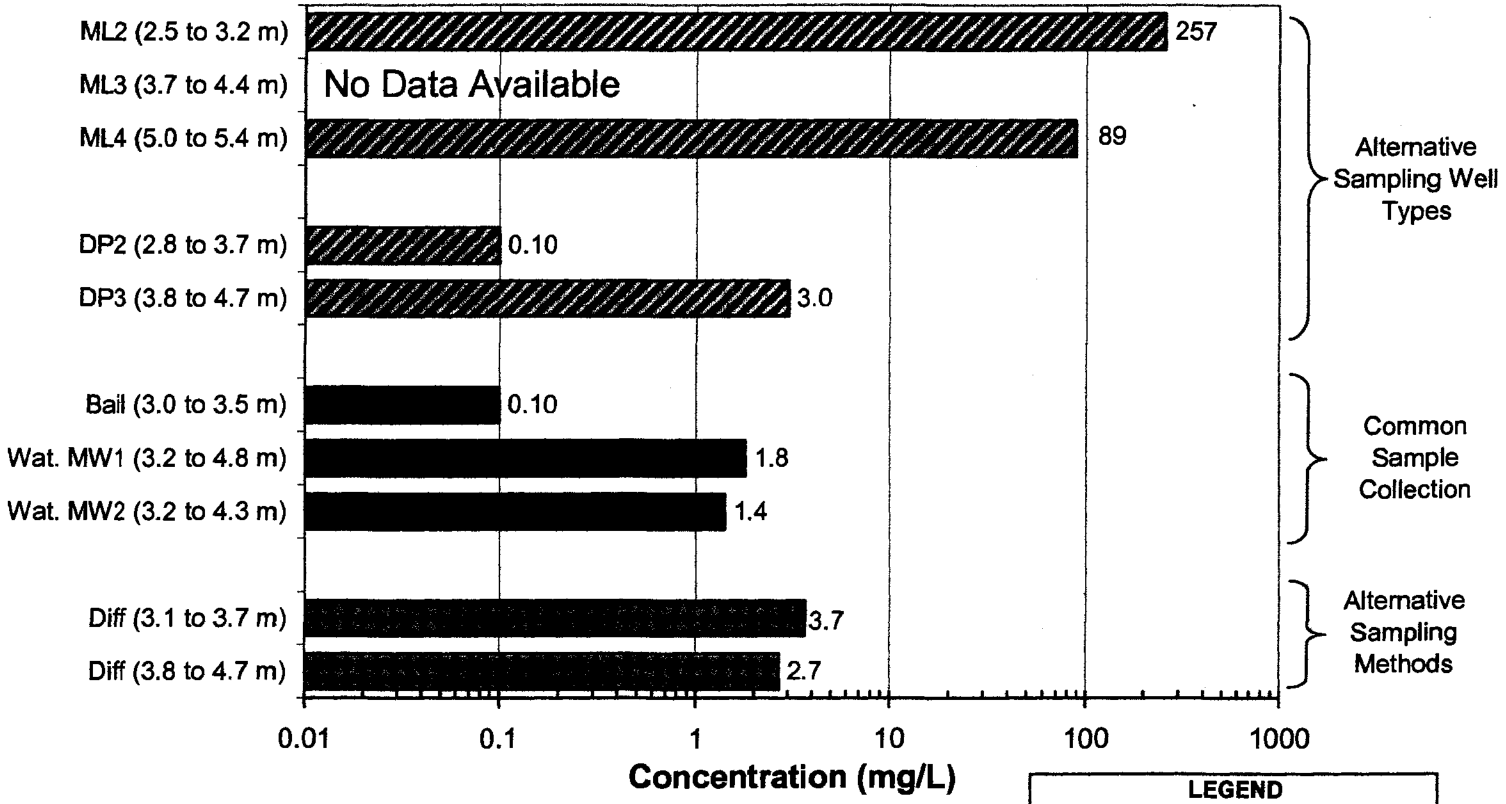


Figure G17. Sulfate Concentration Comparison (February, Site 1)

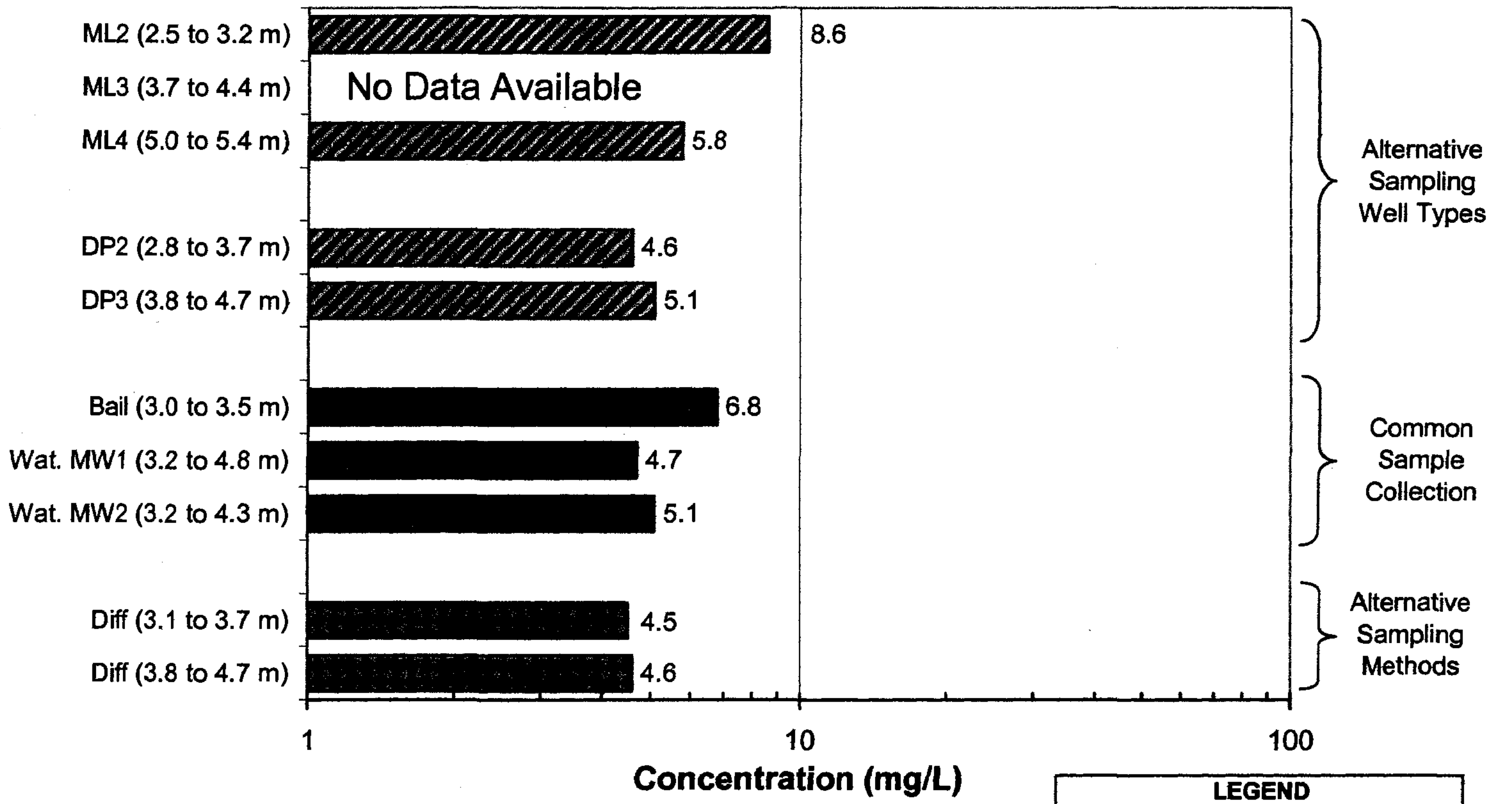


Figure G18. Chloride Concentration Comparison (February, Site 1)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
Diff = Diffusion Sampler (3 m screen)

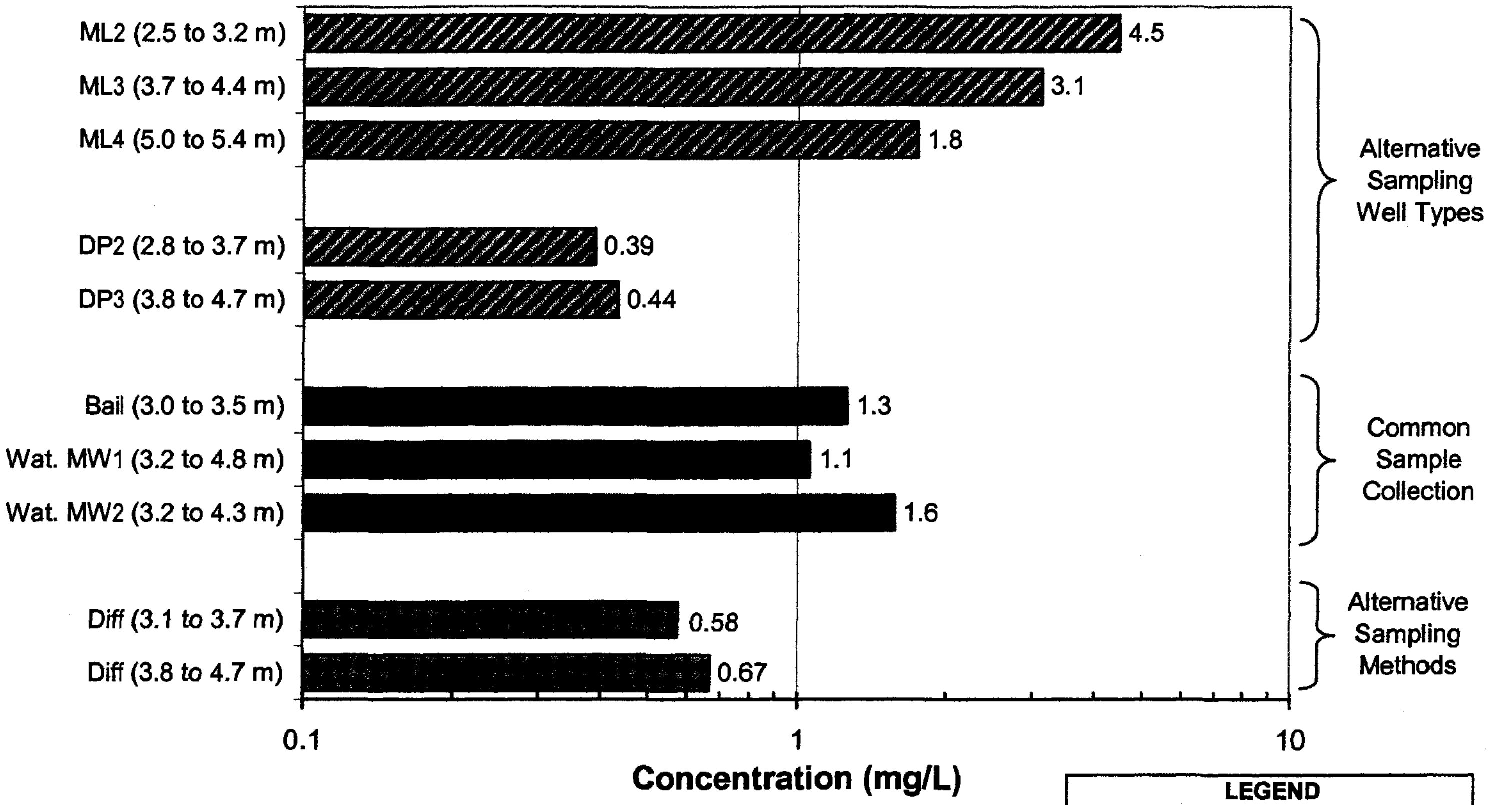


Figure G19. Manganese Concentration Comparison (February, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
Diff = Diffusion Sampler (3 m screen)

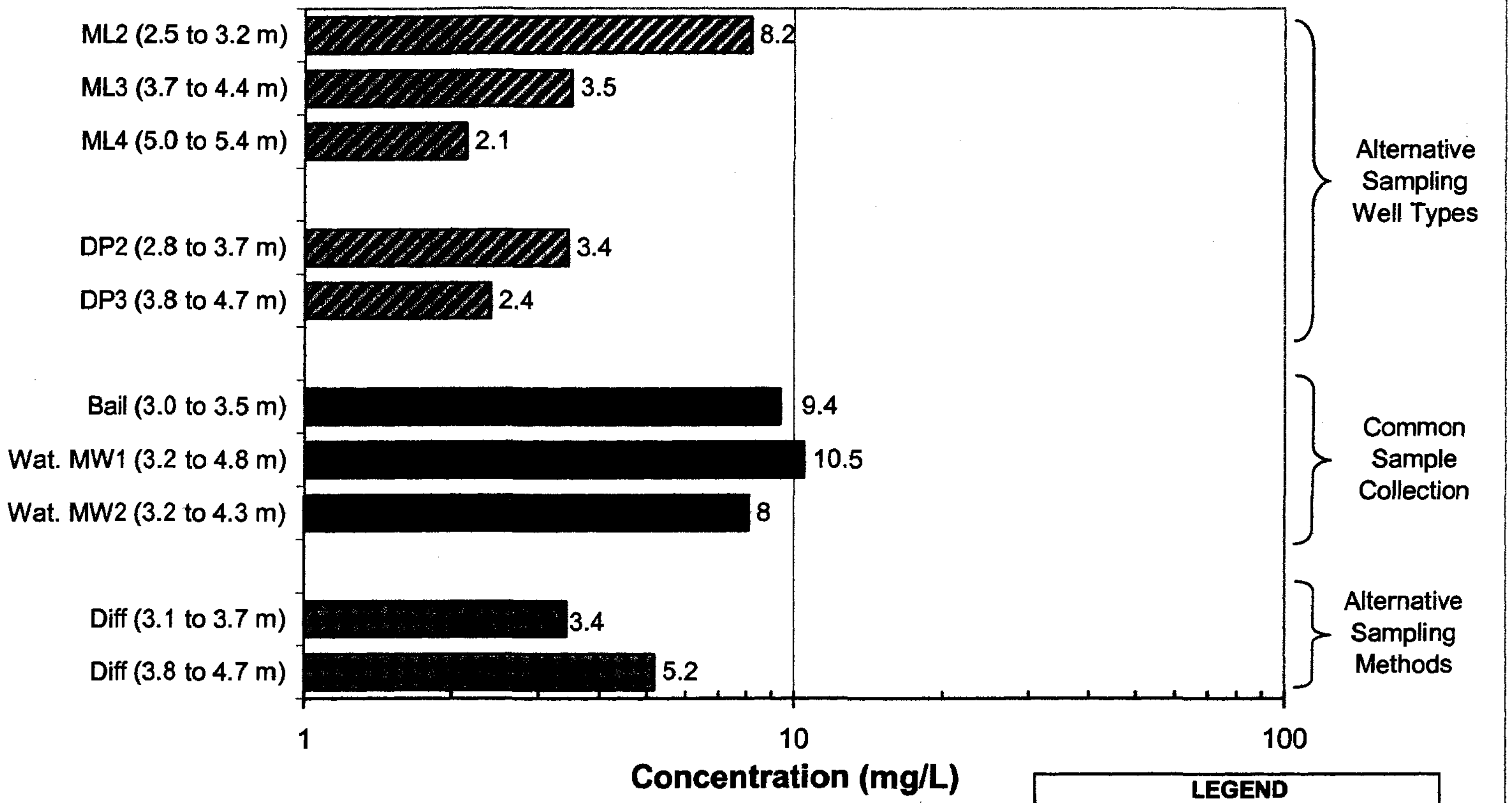


Figure G20. Iron Concentration Comparison (February, Site 1)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
Diff = Diffusion Sampler (3 m screen)

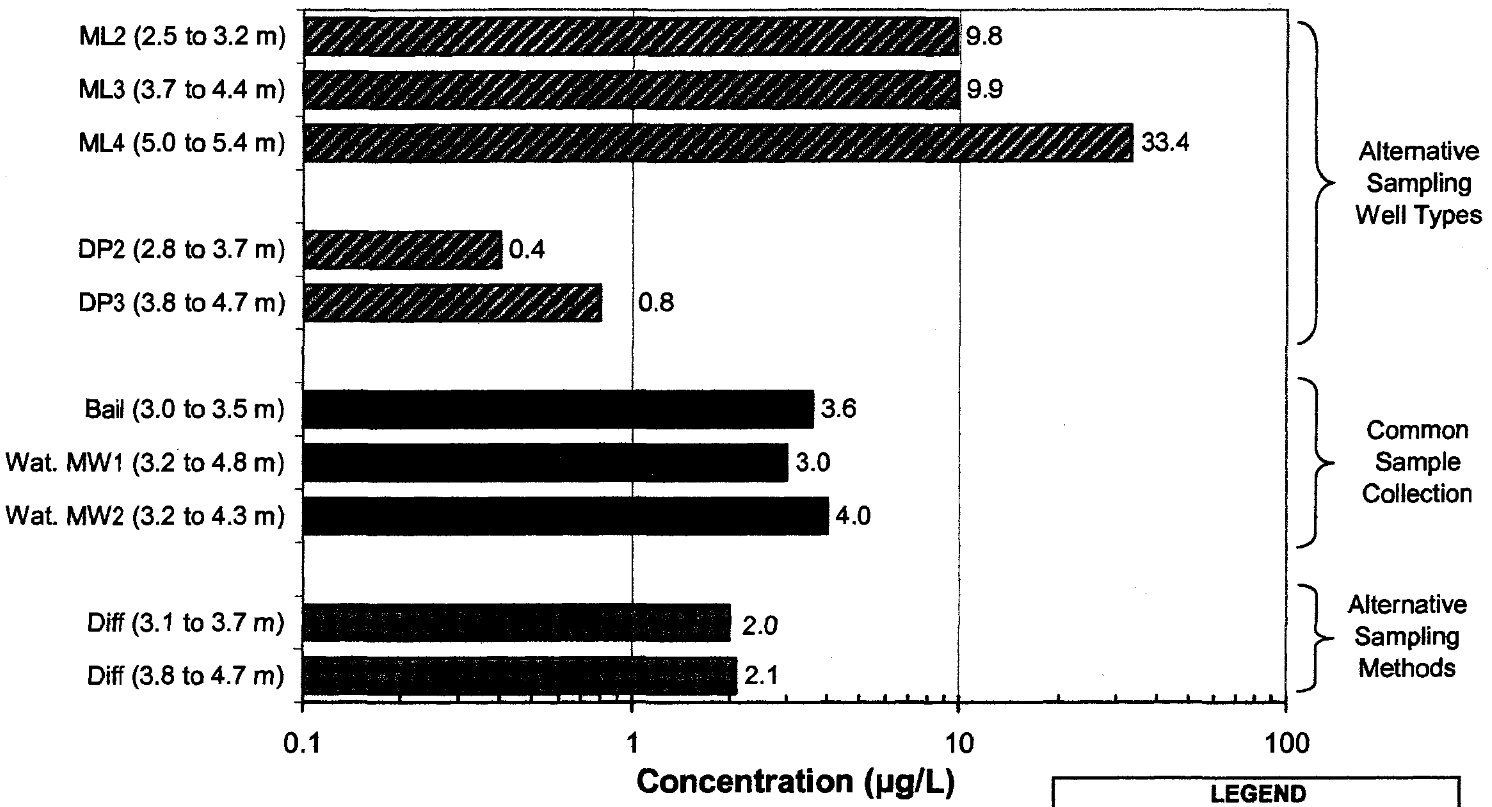


Figure G21. Benzene Concentration Comparison (February, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
Diff = Diffusion Sampler (3 m screen)

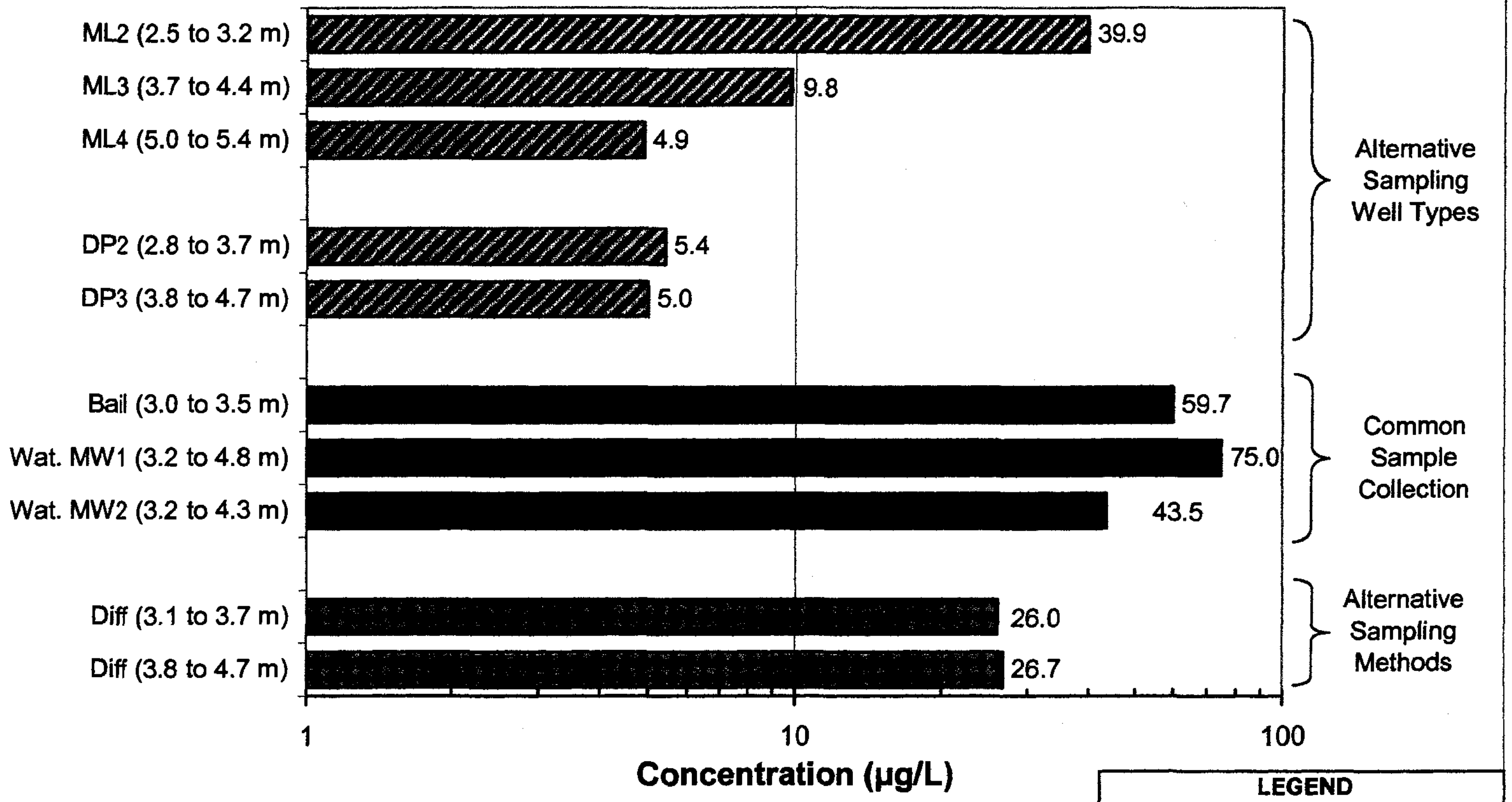


Figure G22. Ethylbenzene Concentration Comparison (February, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
Diff = Diffusion Sampler (3 m screen)

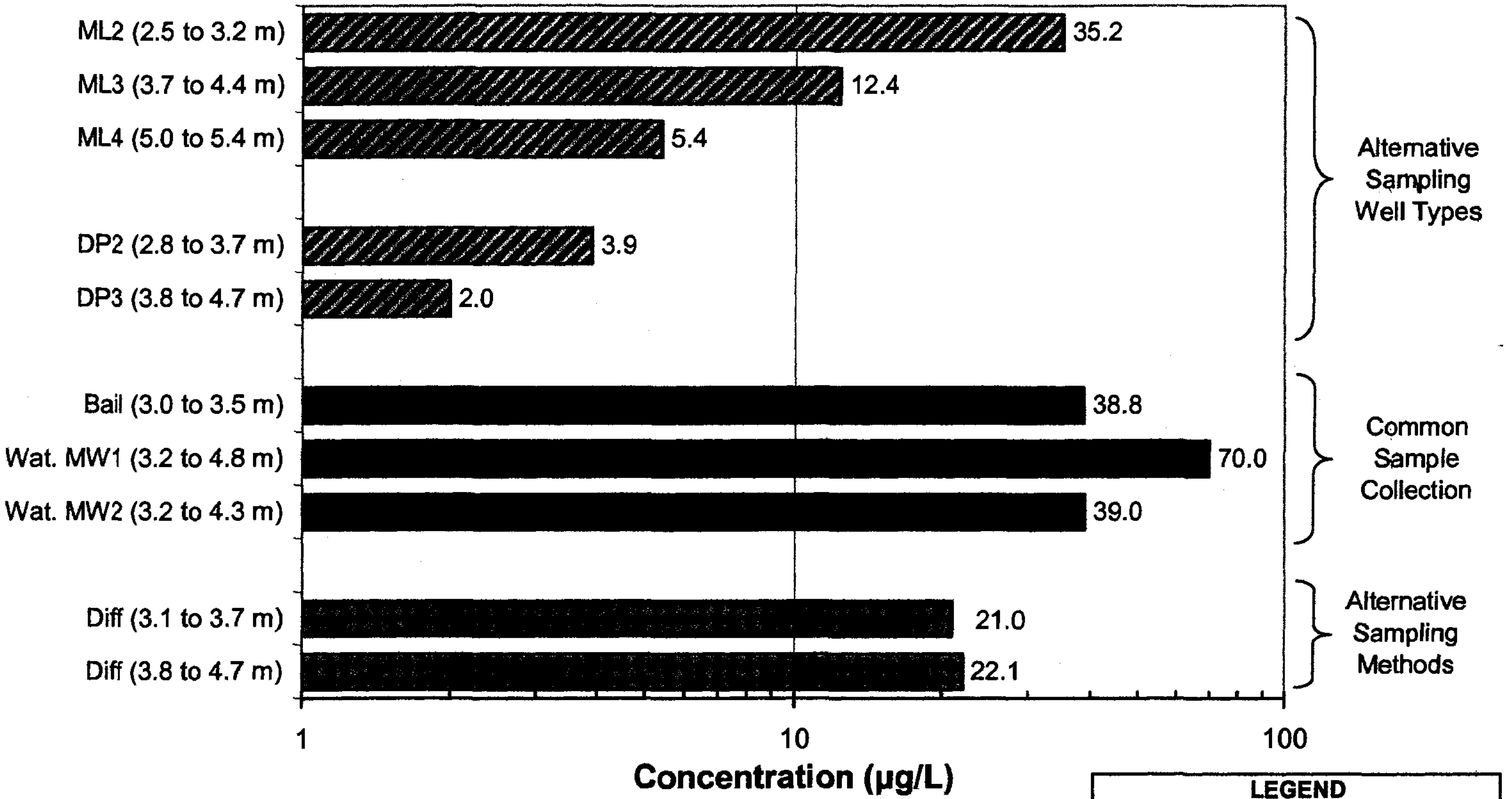


Figure G23. Total Xylenes Concentration Comparison (February, Site 1)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
Diff = Diffusion Sampler (3 m screen)

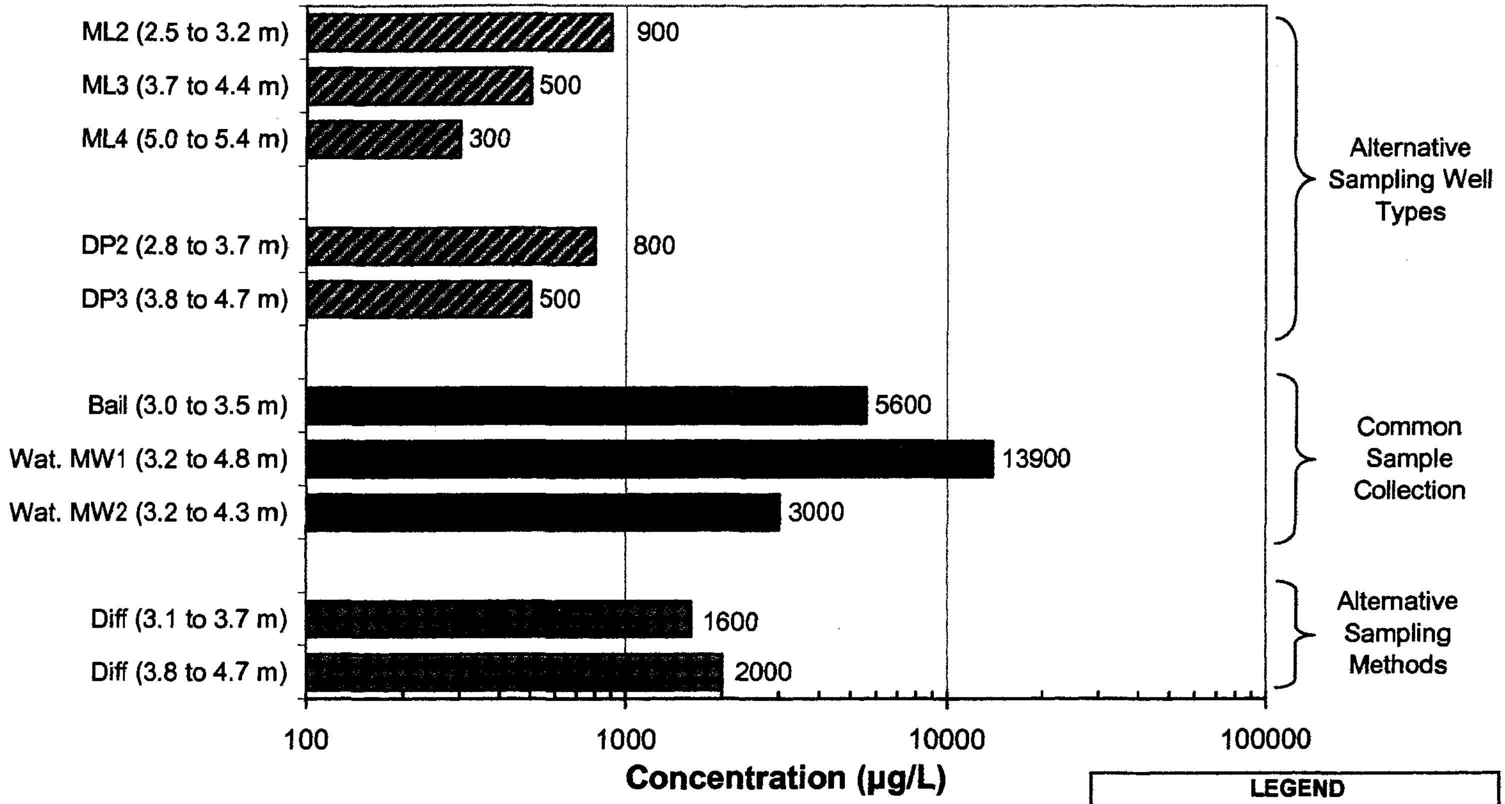


Figure G24. PHC F1 - BTEX Concentration Comparison (February, Site 1)

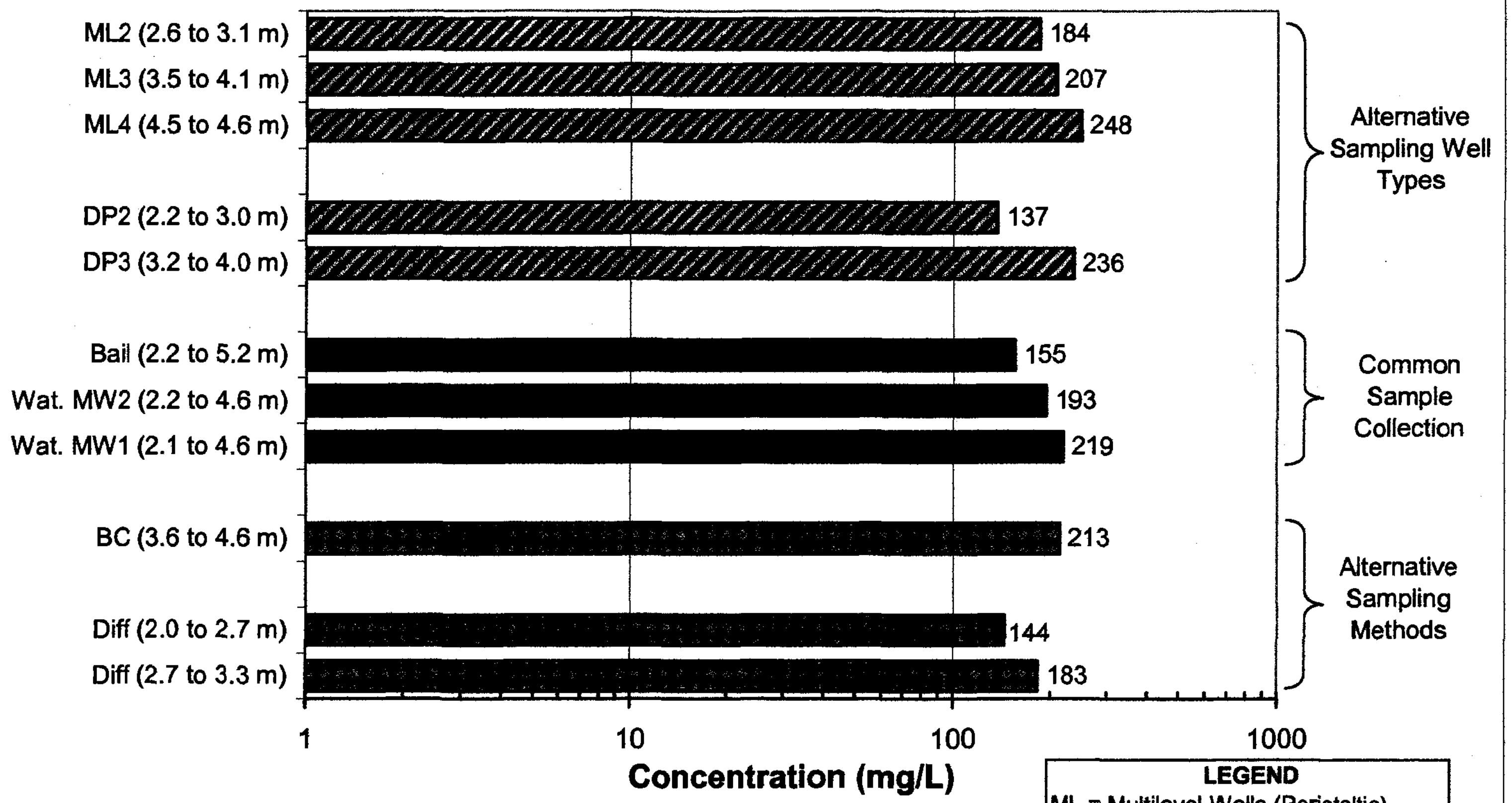
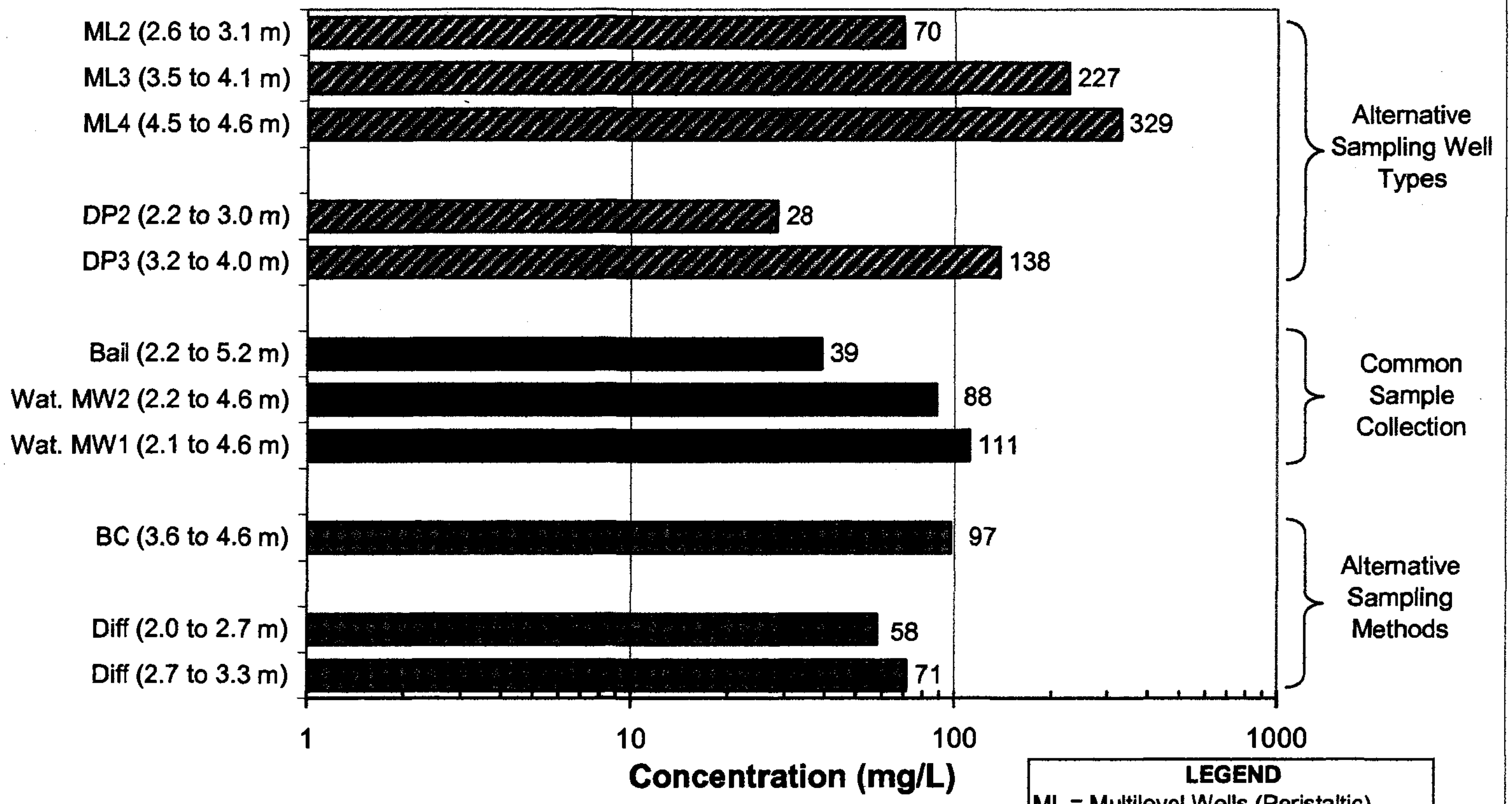


Figure G25. Magnesium Concentration Comparison (October, Site 2 - Well Cluster 34)



LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

Figure G26. Calcium Concentration Comparison (October, Site 2 - Well Cluster 34)

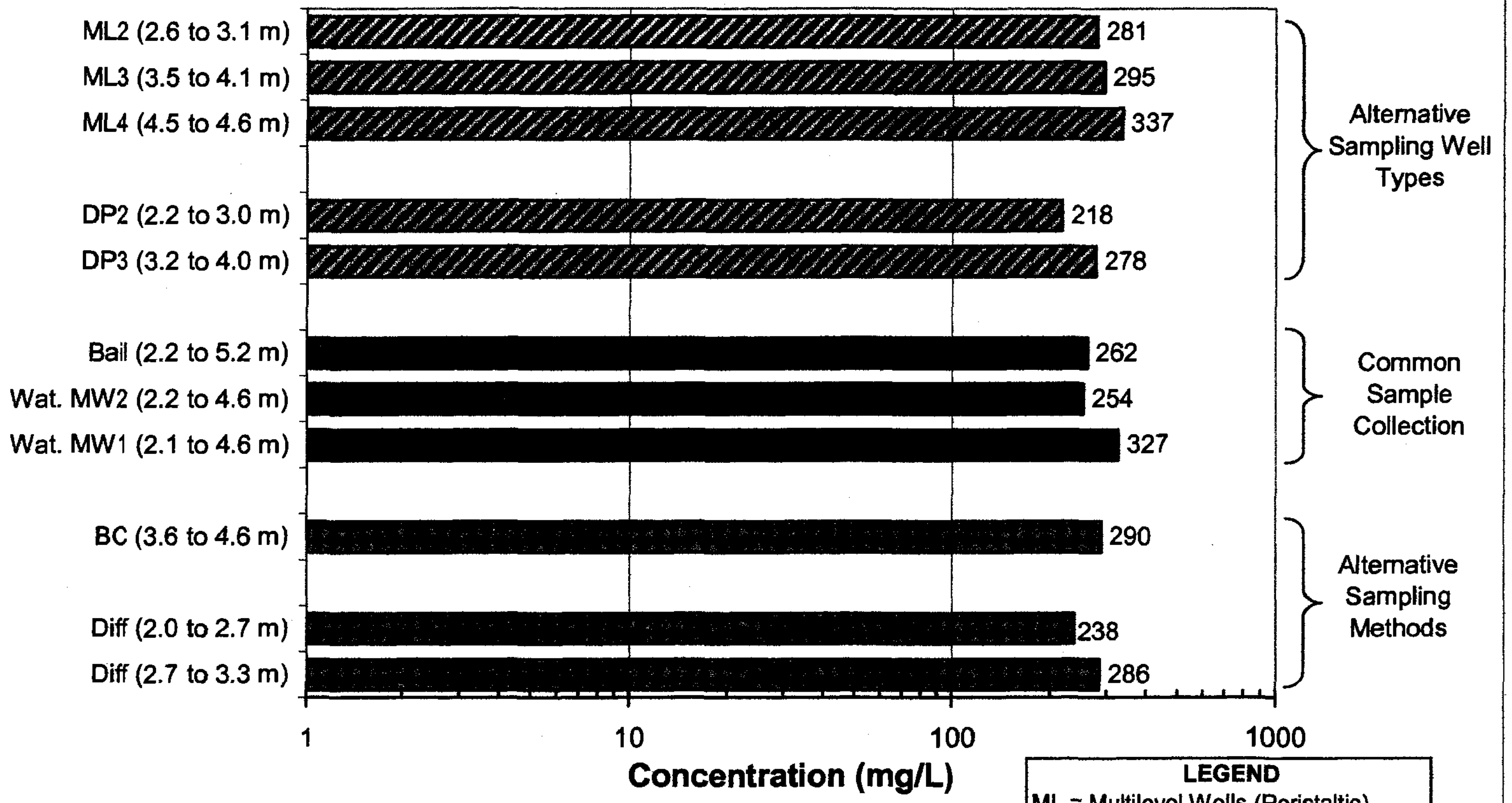


Figure G27. Sodium Concentration Comparison (October, Site 2 - Well Cluster 34)

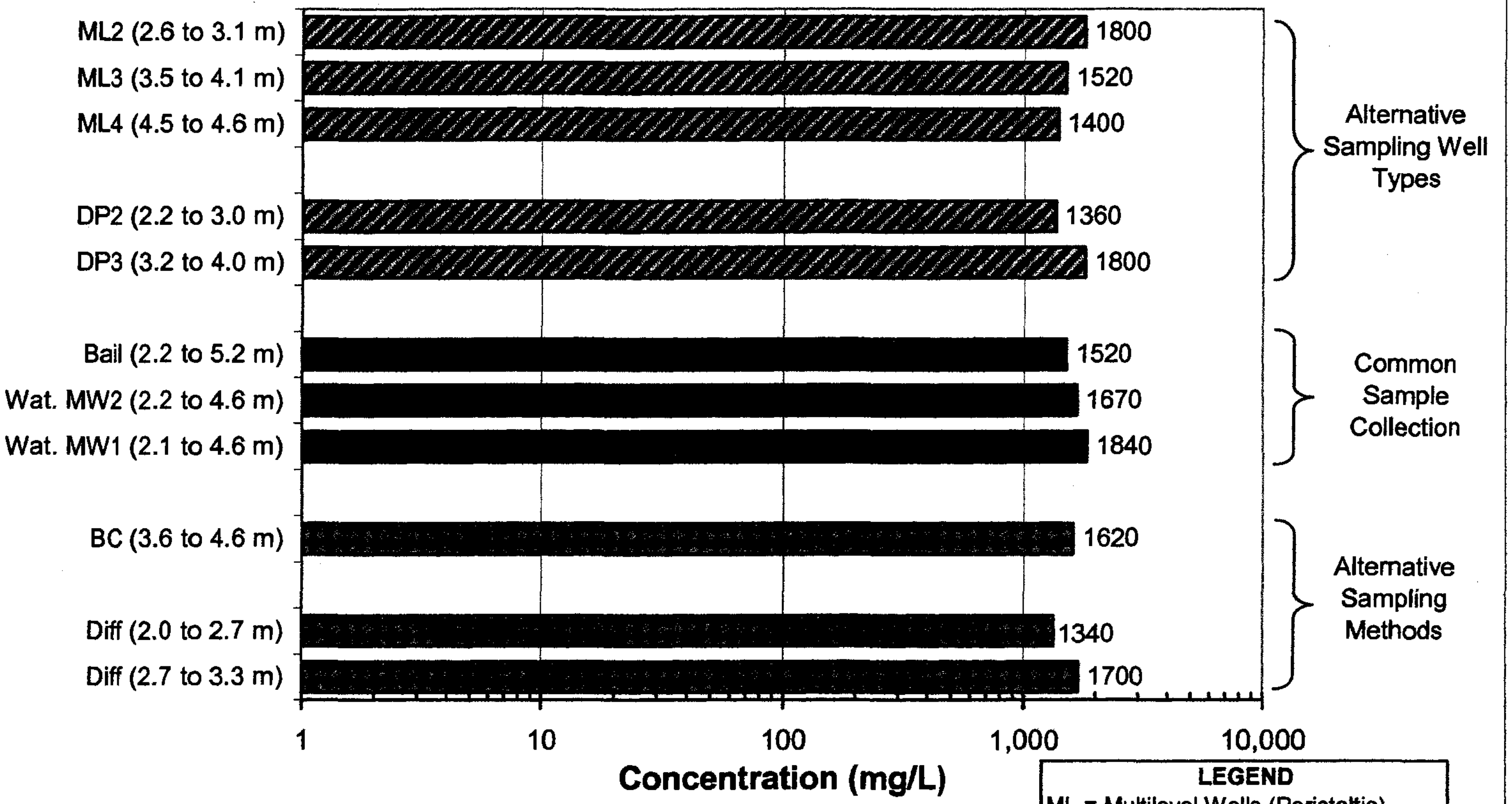


Figure G28. Bicarbonate Concentration Comparison (October, Site 2 - Well Cluster 34)

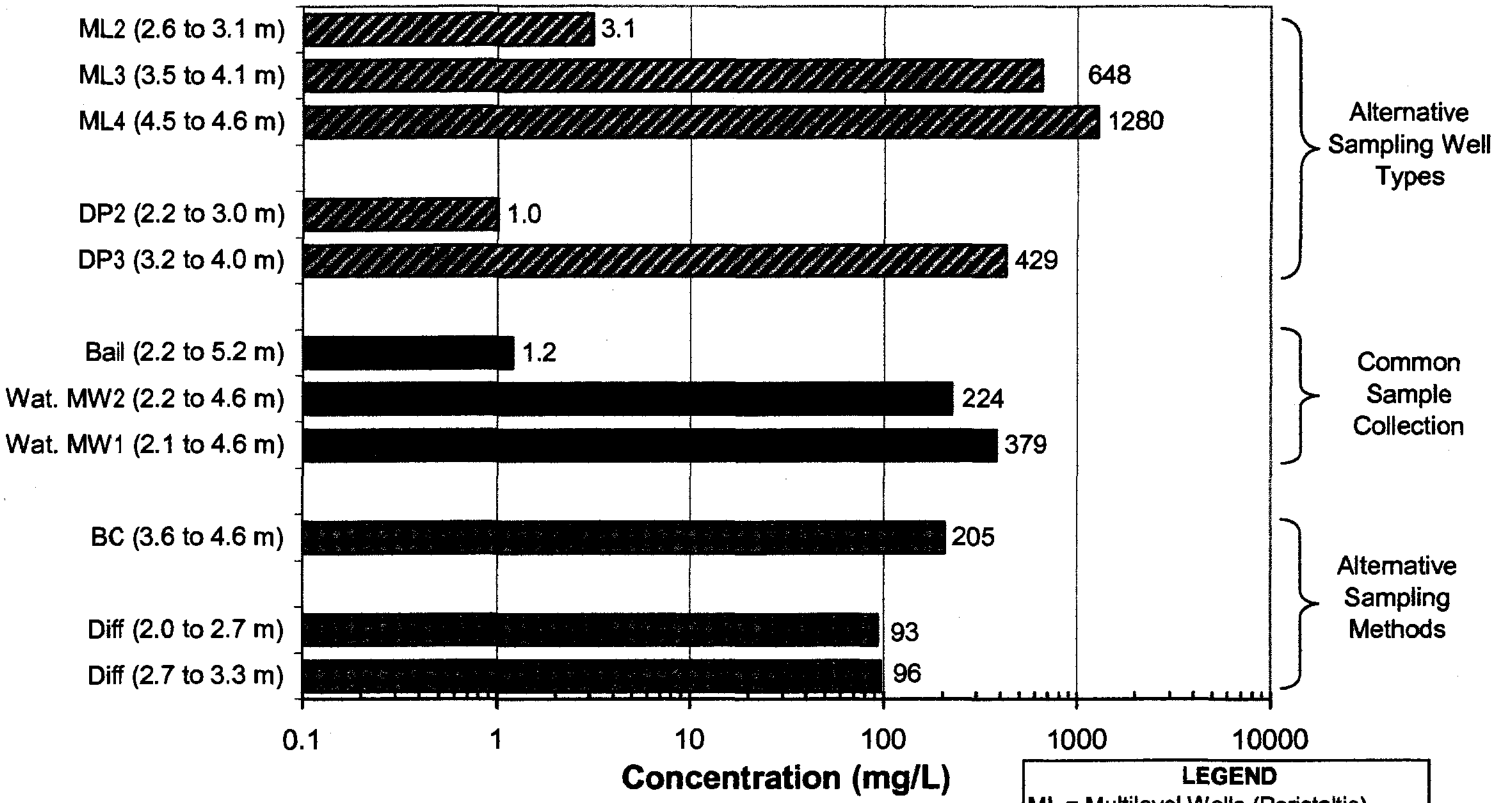


Figure G29. Sulfate Concentration Comparison
(October, Site 2 - Well Cluster 34)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

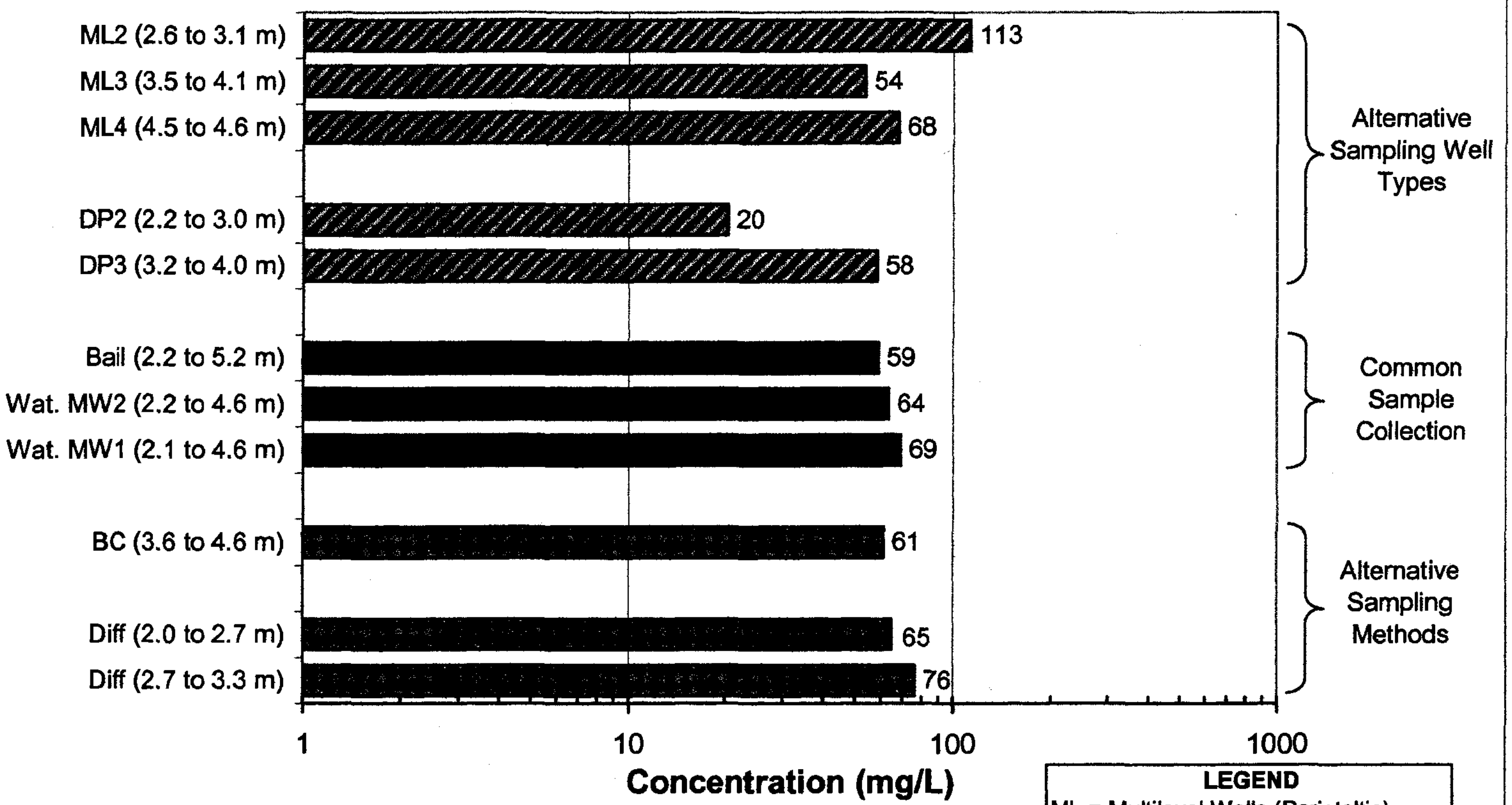


Figure G30. Chloride Concentration Comparison (October, Site 2 - Well Cluster 34)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

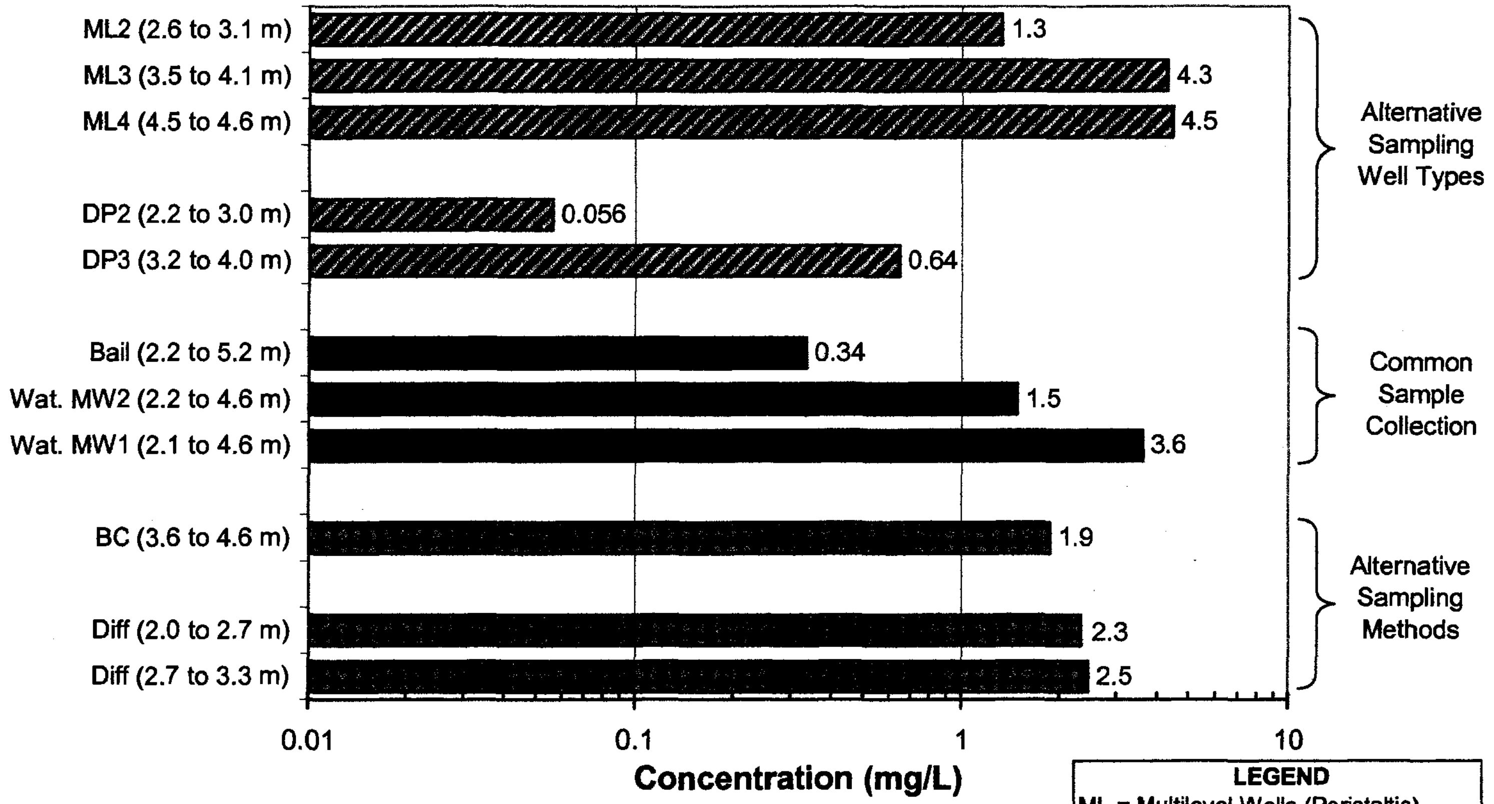


Figure G31. Manganese Concentration Comparison (October, Site 2 - Well Cluster 34)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

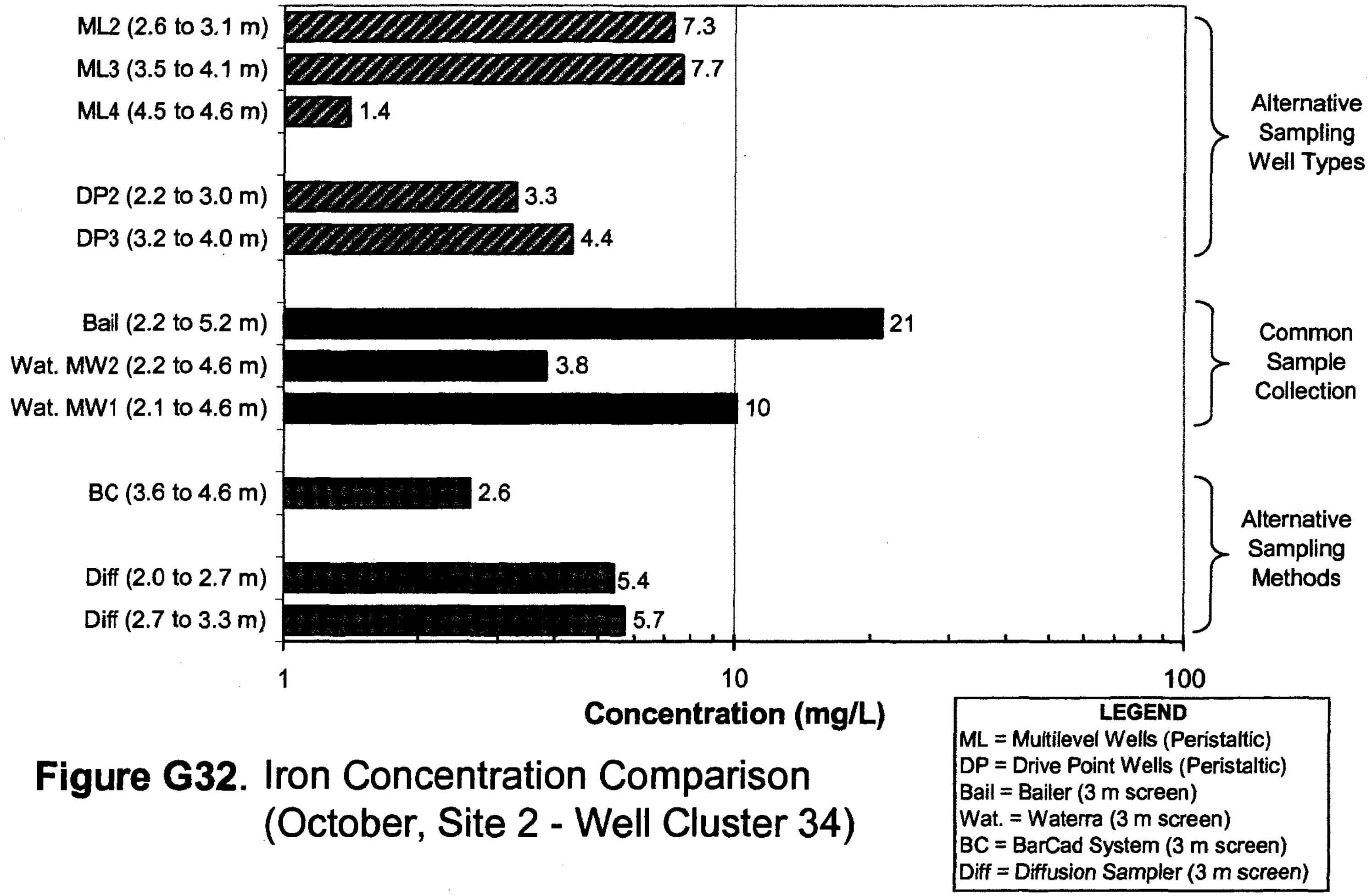


Figure G32. Iron Concentration Comparison (October, Site 2 - Well Cluster 34)

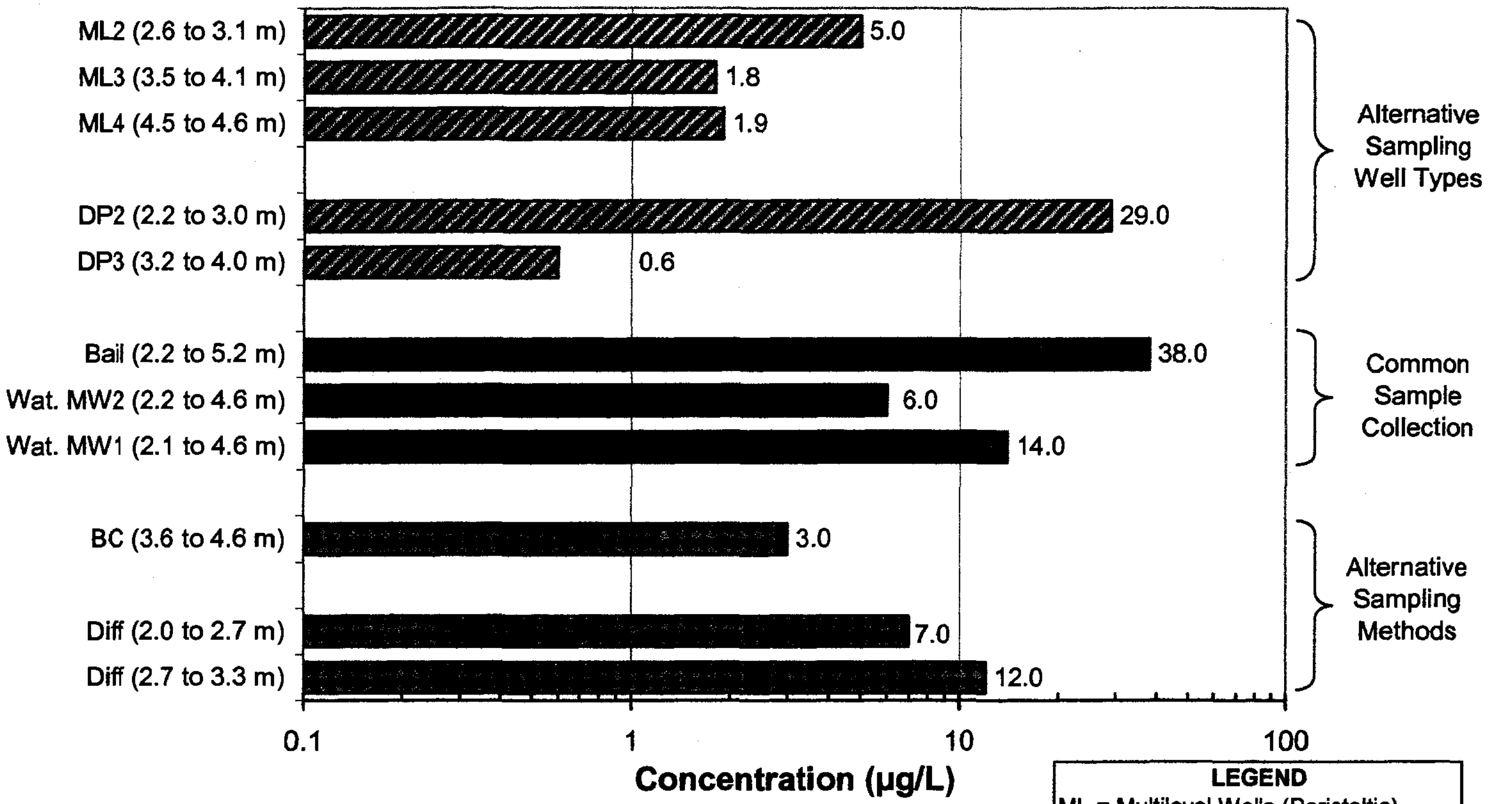


Figure G33. Benzene Concentration Comparison (October, Site 2 - Well Cluster 34)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

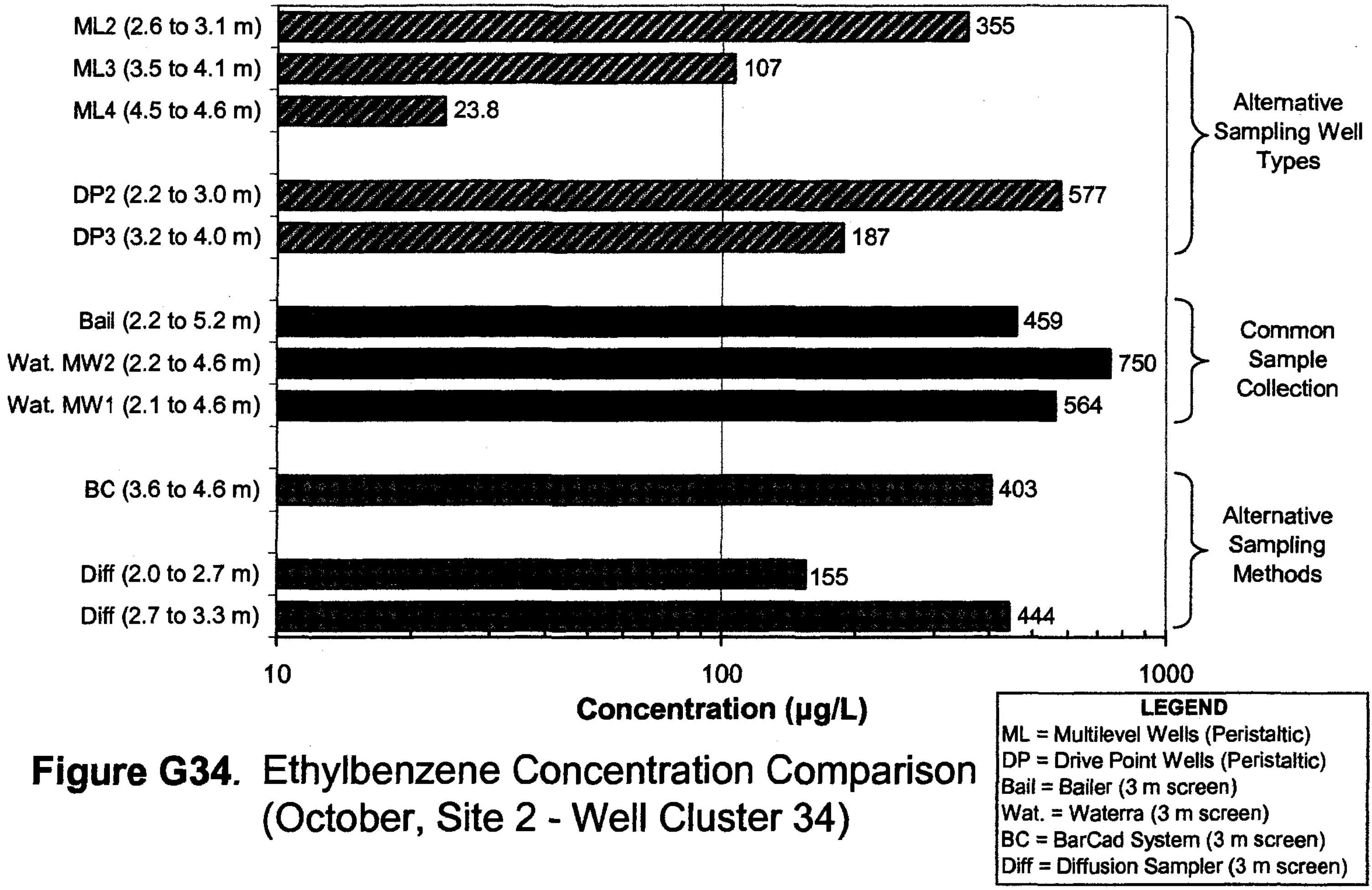


Figure G34. Ethylbenzene Concentration Comparison (October, Site 2 - Well Cluster 34)

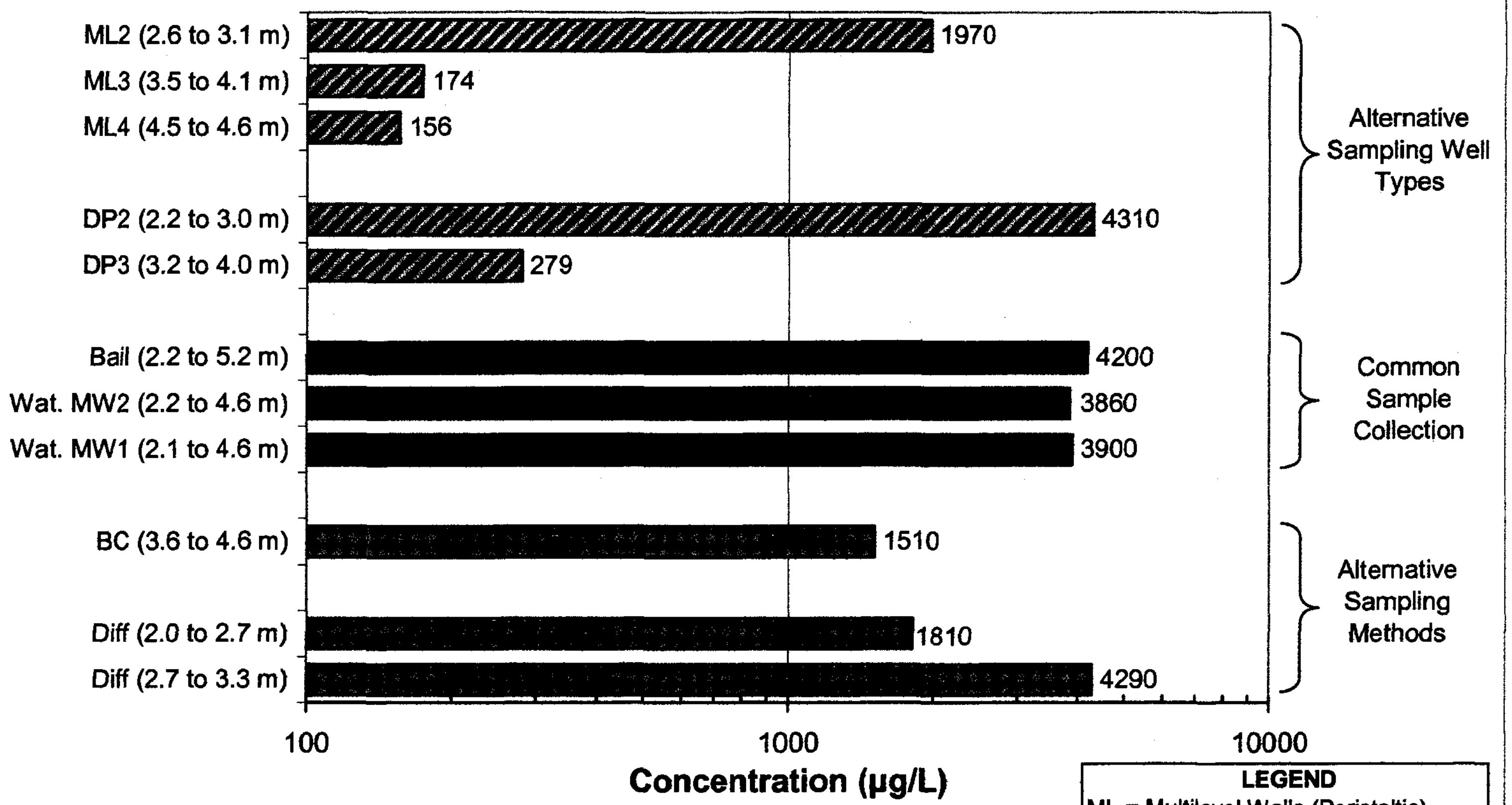


Figure G35. Total Xylenes Concentration Comparison (October, Site 2 - Well Cluster 34)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

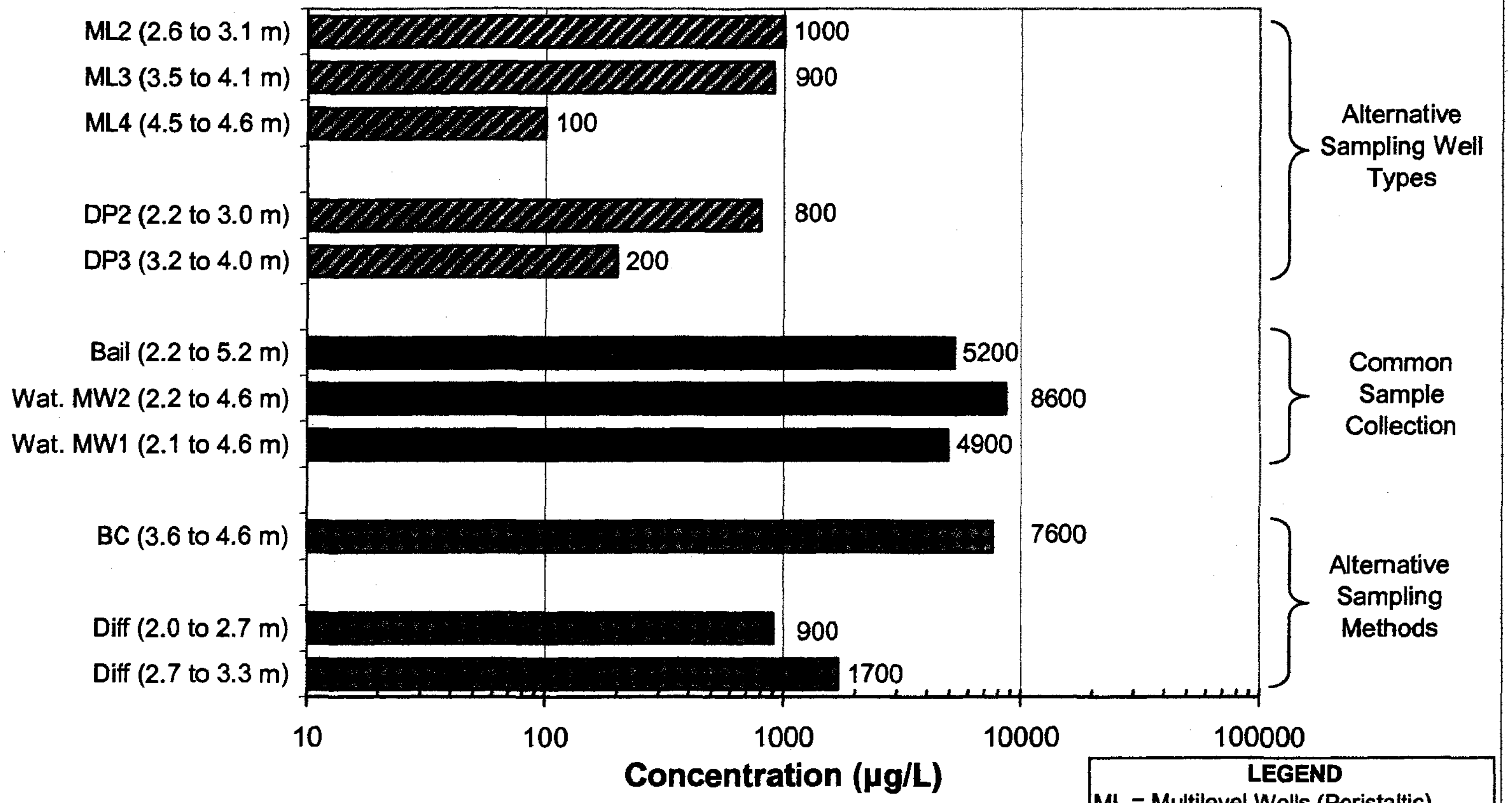


Figure G36. PHC F1 - BTEX Concentration Comparison (October, Site 2 - Well Cluster 34)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

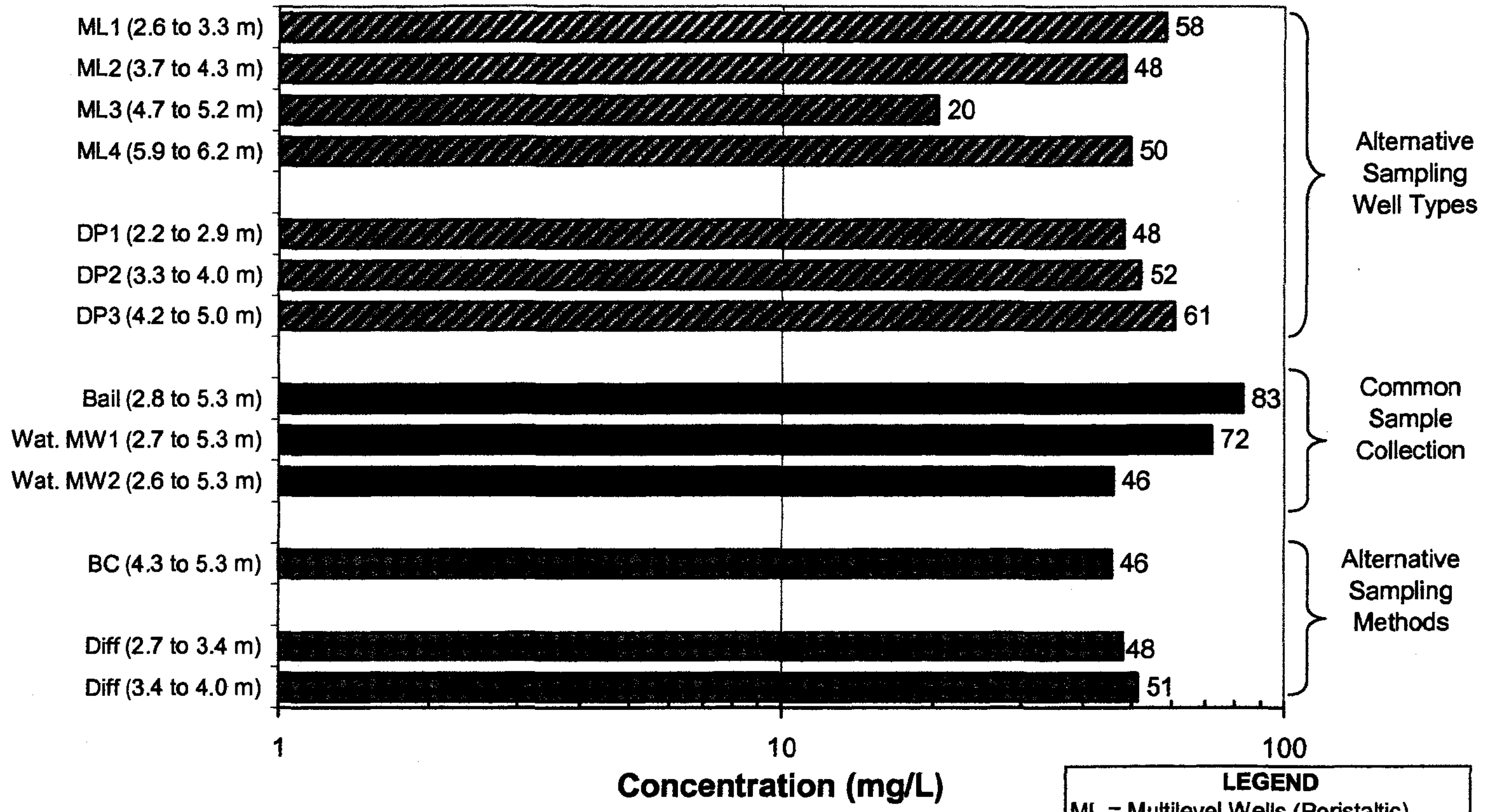


Figure G37. Magnesium Concentration Comparison (October, Site 2 - Well Cluster 35)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

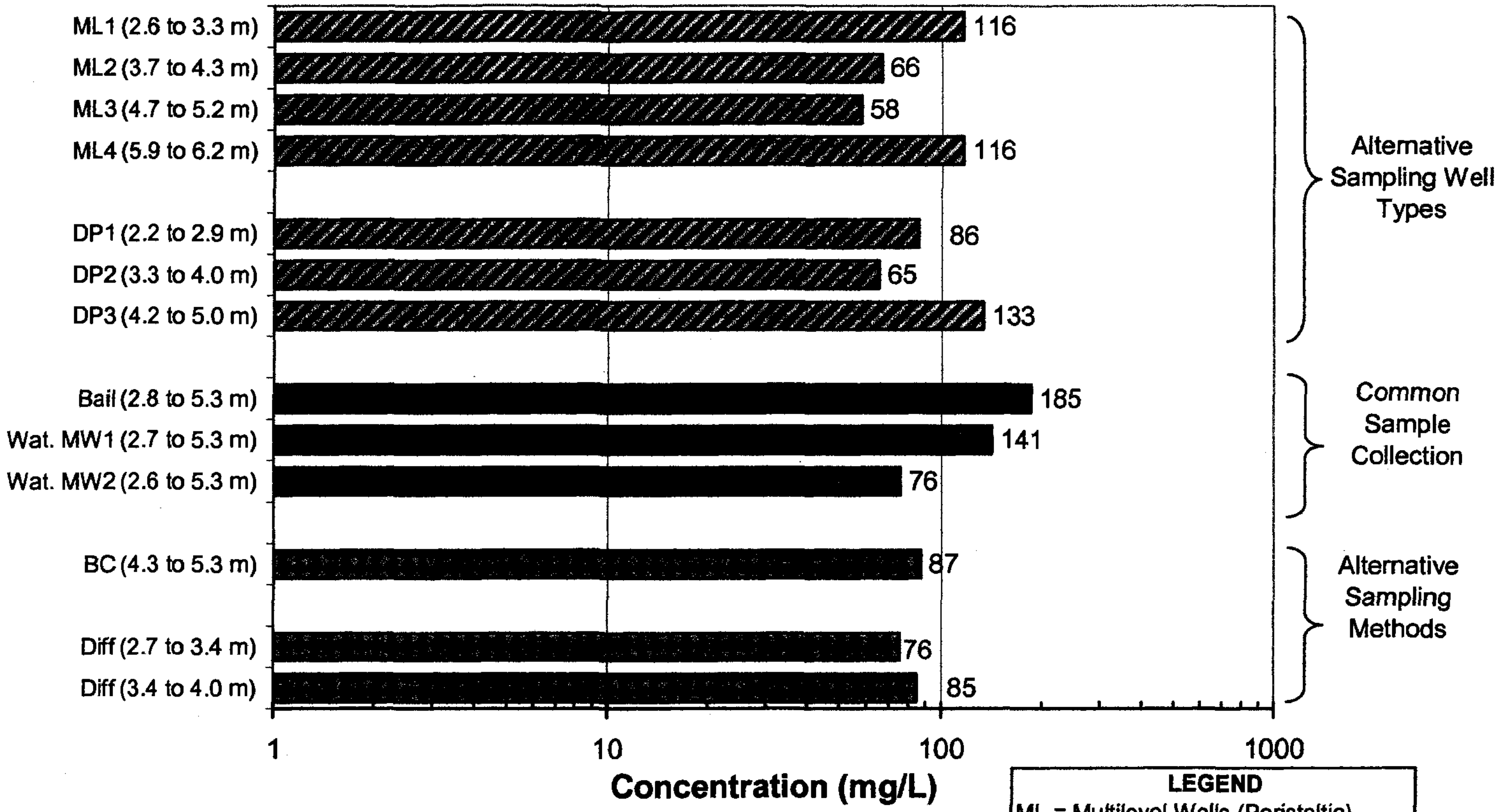


Figure G38. Calcium Concentration Comparison (October, Site 2 - Well Cluster 35)

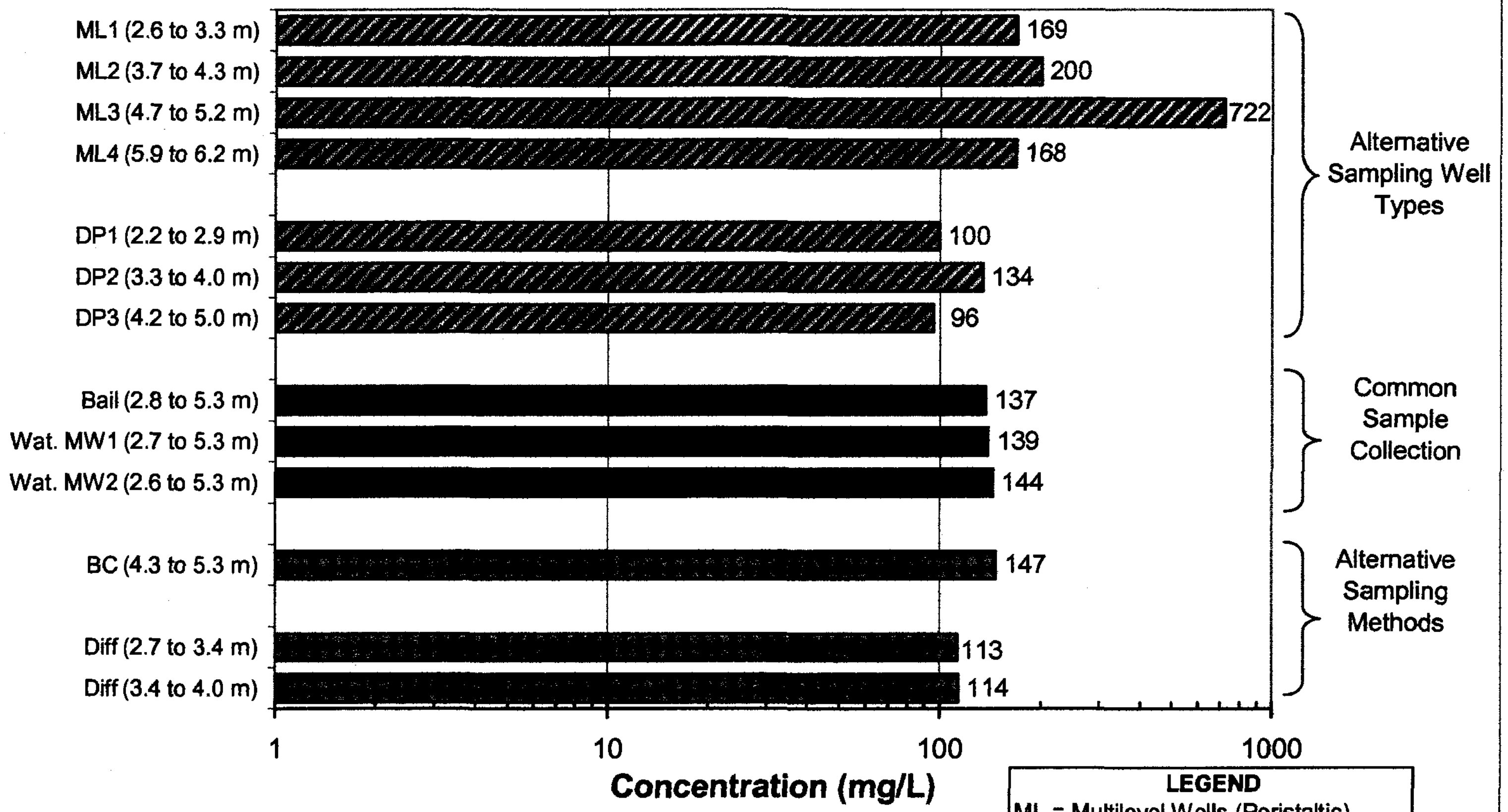


Figure G39. Sodium Concentration Comparison (October, Site 2 - Well Cluster 35)

LEGEND
ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

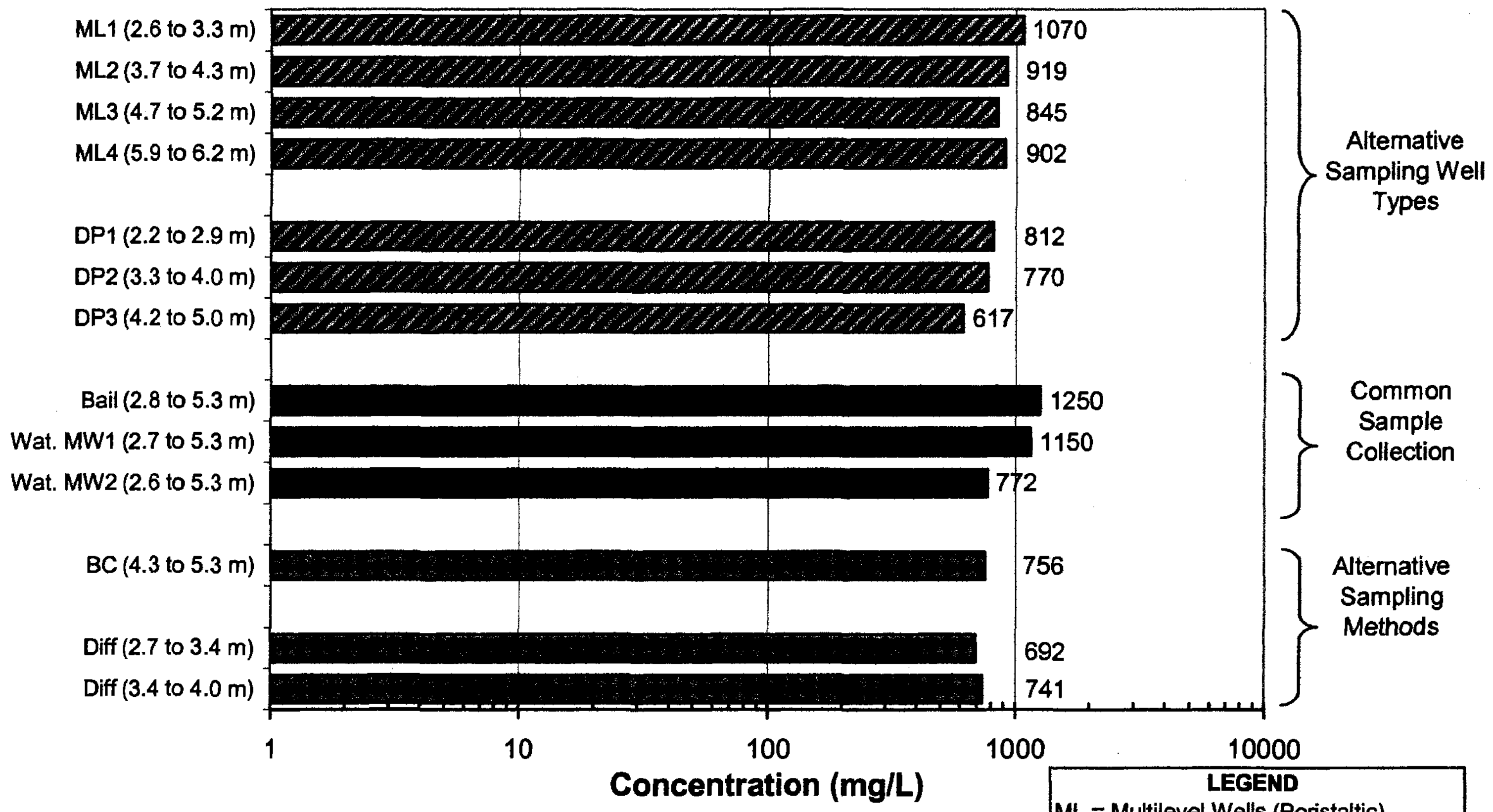


Figure G40. Bicarbonate Concentration Comparison (October, Site 2 - Well Cluster 35)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

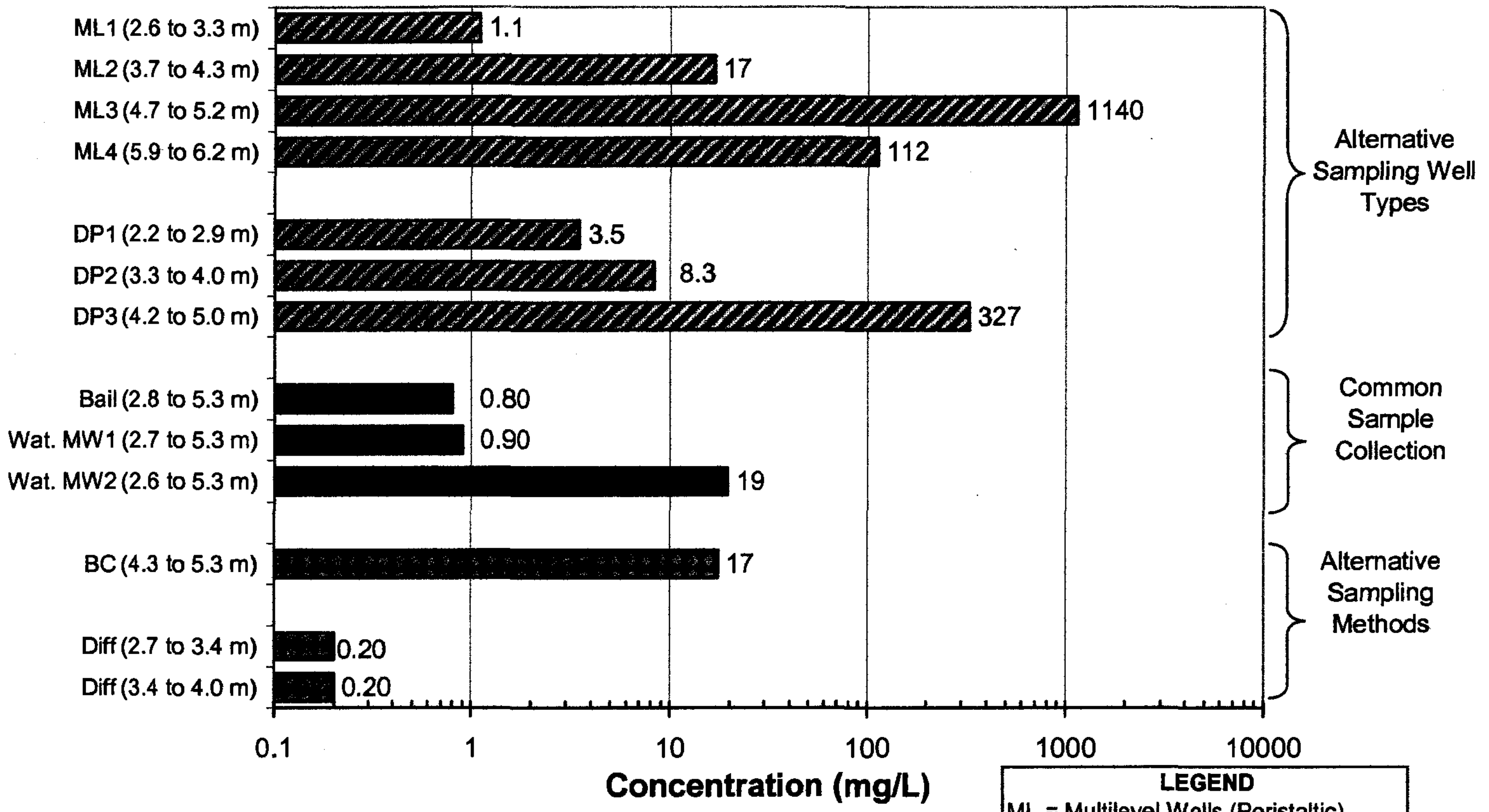


Figure G41. Sulfate Concentration Comparison (October, Site 2 - Well Cluster 35)

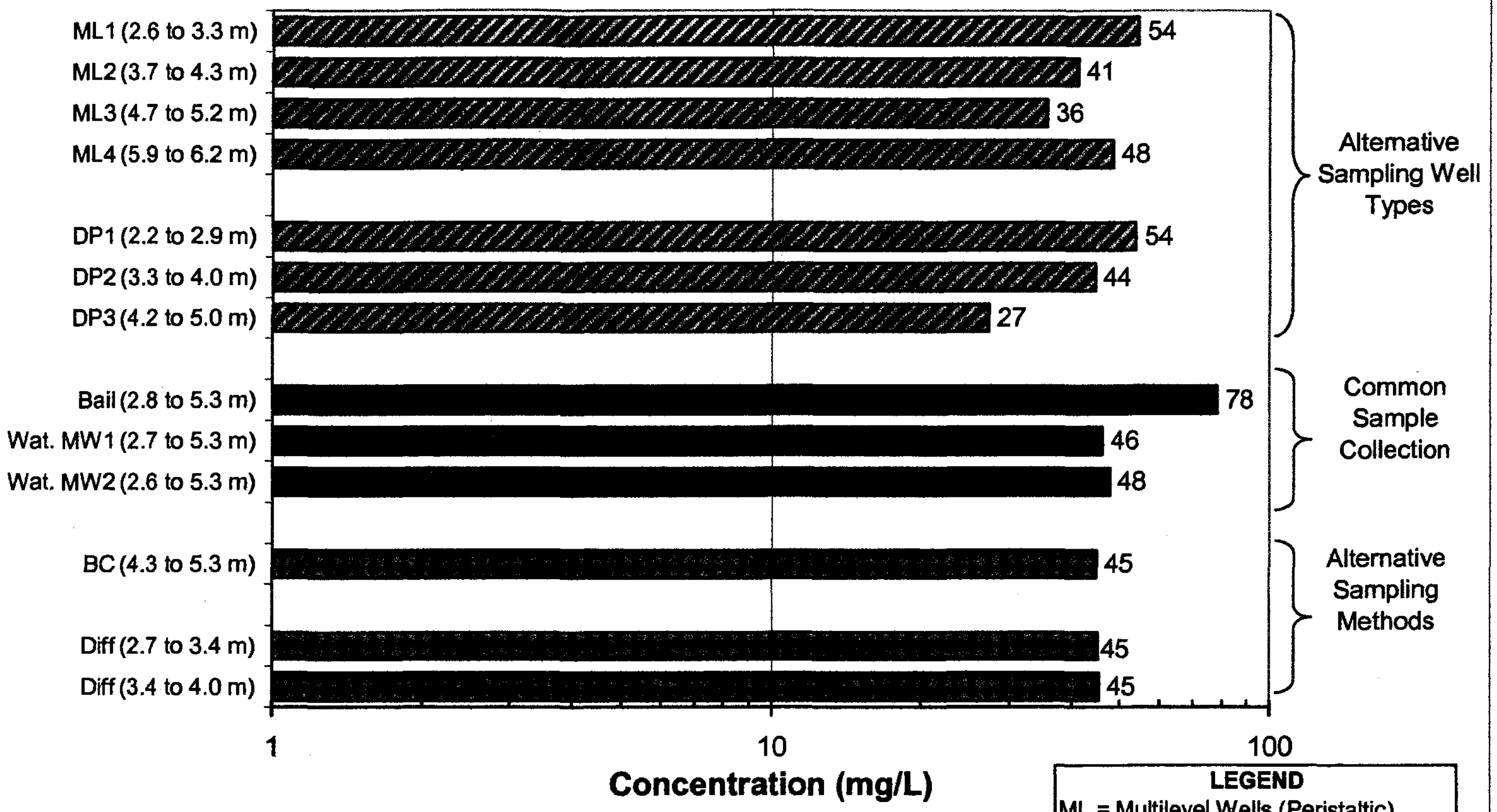


Figure G42. Chloride Concentration Comparison (October, Site 2 - Well Cluster 35)

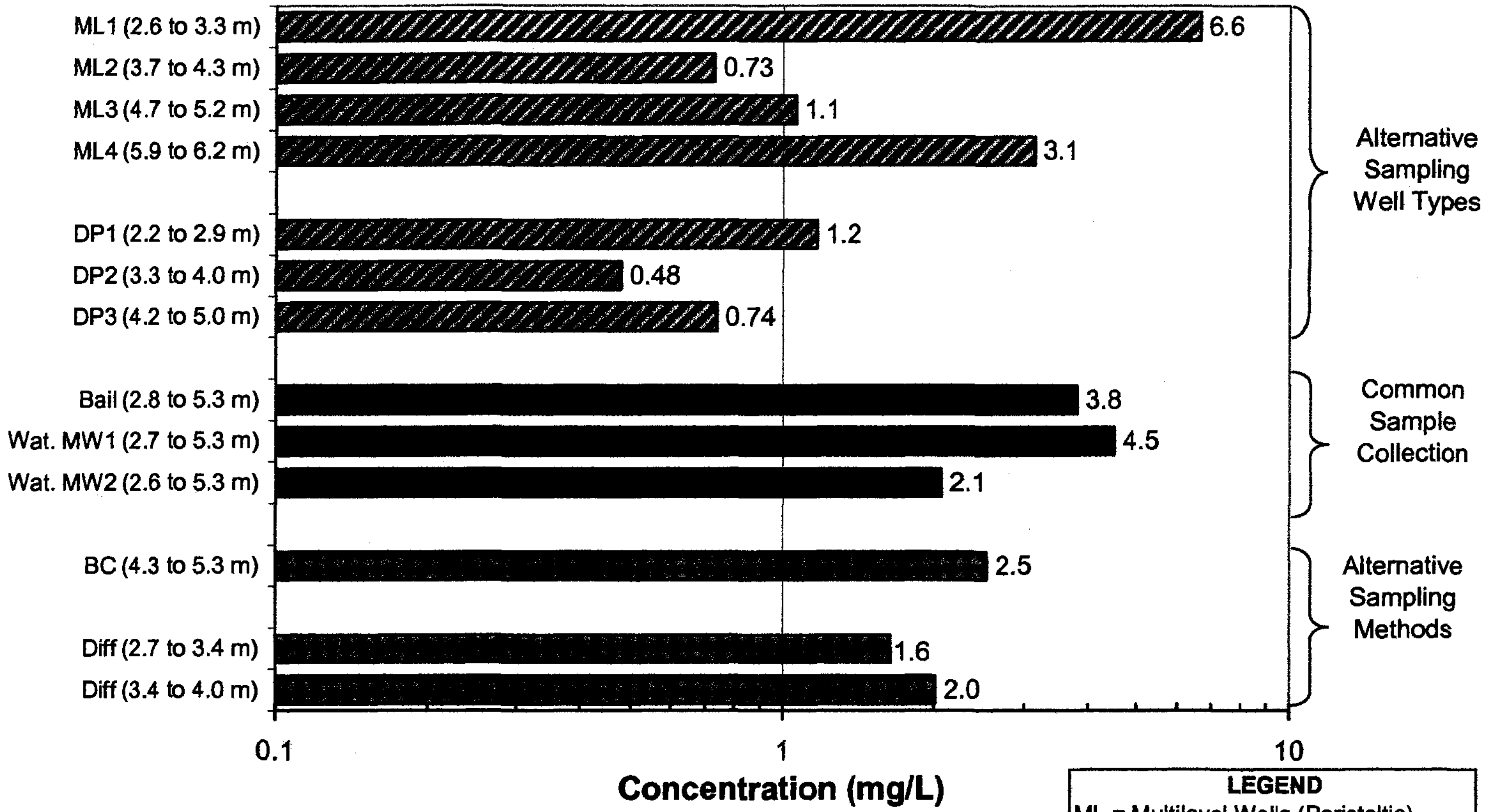


Figure G43. Manganese Concentration Comparison (October, Site 2 - Well Cluster 35)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

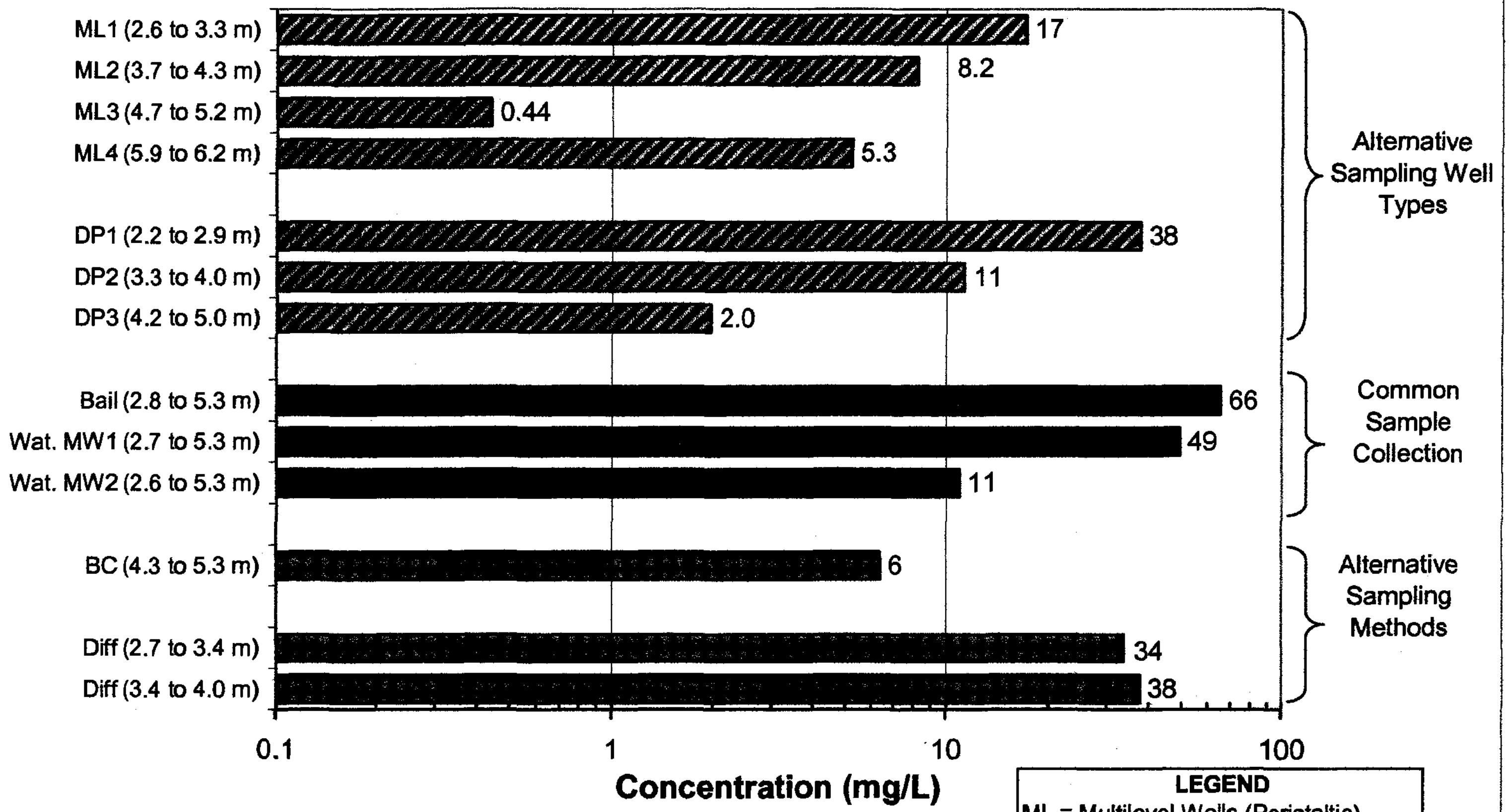


Figure G44. Iron Concentration Comparison (October, Site 2 - Well Cluster 35)

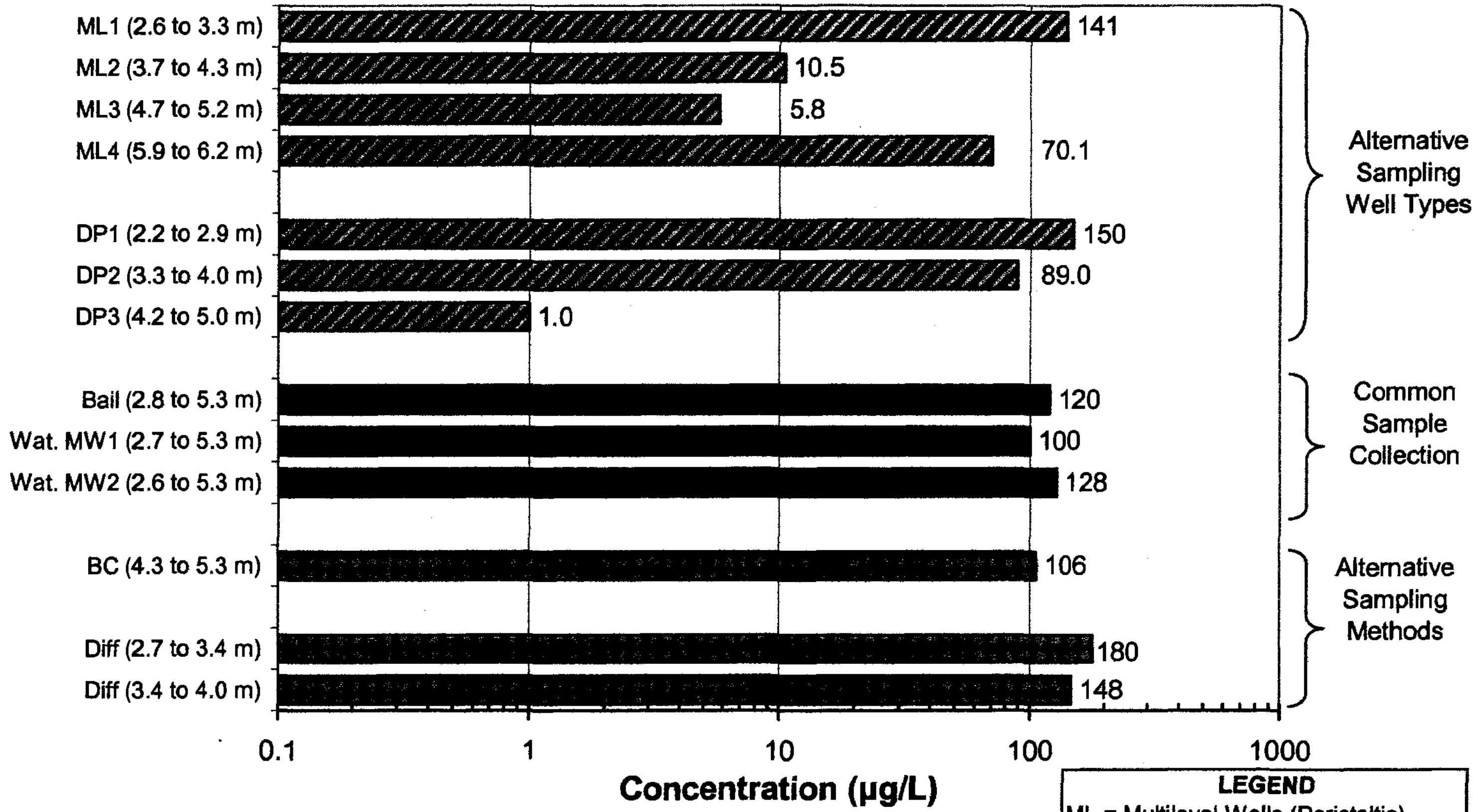


Figure G45. Benzene Concentration Comparison (October, Site 2 - Well Cluster 35)

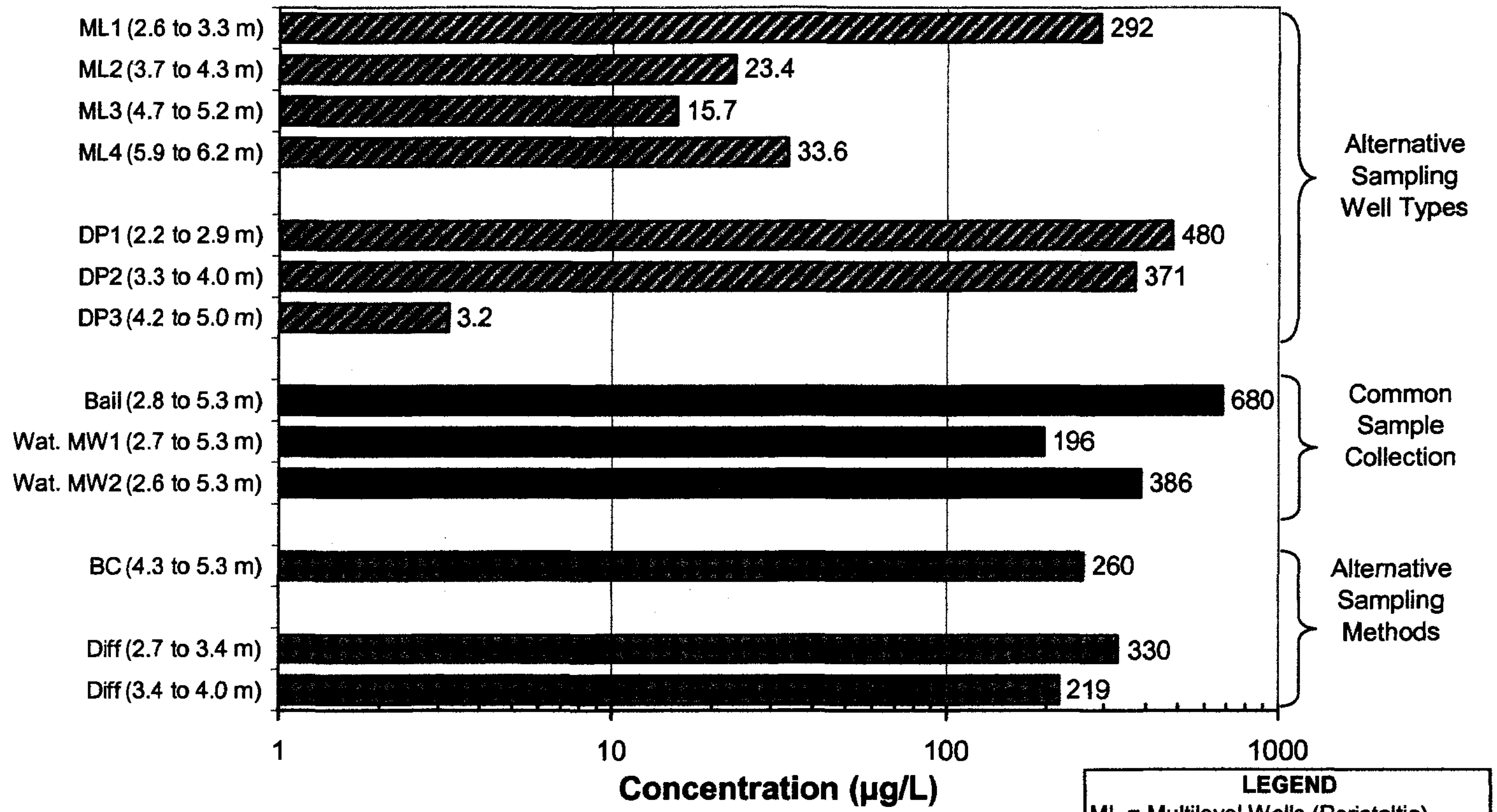


Figure G46. Ethylbenzene Concentration Comparison (October, Site 2 - Well Cluster 35)

LEGEND

ML = Multilevel Wells (Peristaltic)
DP = Drive Point Wells (Peristaltic)
Bail = Bailer (3 m screen)
Wat. = Waterra (3 m screen)
BC = BarCad System (3 m screen)
Diff = Diffusion Sampler (3 m screen)

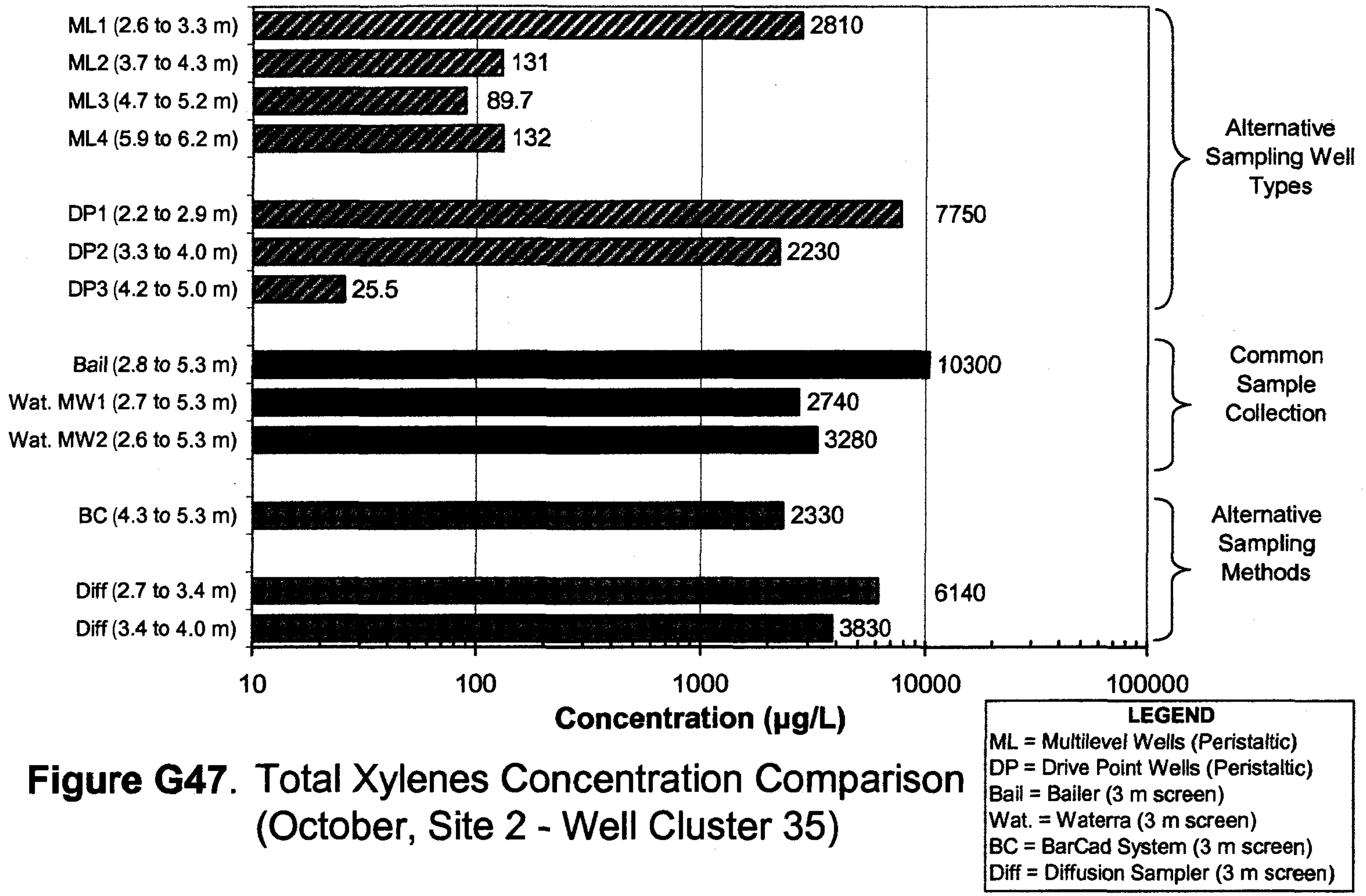


Figure G47. Total Xylenes Concentration Comparison (October, Site 2 - Well Cluster 35)

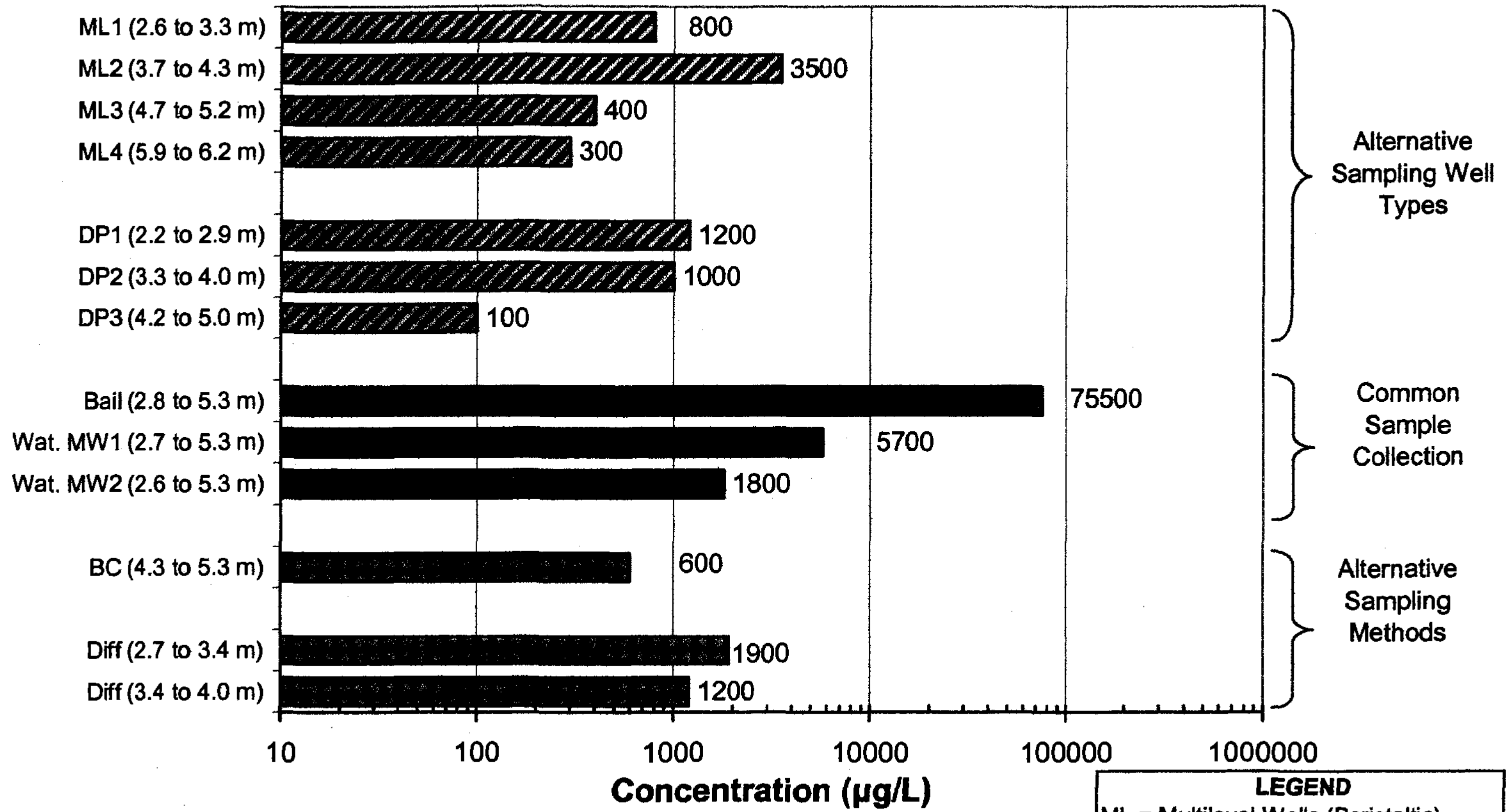


Figure G48. PHC F1 - BTEX Concentration Comparison (October, Site 2 - Well Cluster 35)