

THESIS

ANALYSIS OF CONTAMINANT MASS IN PLACE IN TRANSMISSIVE AND LOW-K
ZONES

Submitted by

Eric Roads

Department of Civil and Environmental Engineering

In partial fulfillment of the requirements

For the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Summer 2020

Master's Committee:

Advisor: Tom Sale

Sybil Sharvelle
Sally Sutton

Copyright by Eric Michael Roads 2020

All Rights Reserved

ABSTRACT

ANALYSIS OF CONTAMINANT MASS IN PLACE IN TRANSMISSIVE AND LOW-K ZONES

Contaminant hydrology has been challenged by the common perception of homogeneous subsurface media. Previous sampling methods neglect the importance of differentiating between transmissive and low-k zones. Cryogenic core collection is a high-resolution sampling technique that can highlight the occurrence of transmissive and low-k zones as well as the distribution of contaminants in transmissive and low-k zones. Cryogenic core collection uses a CSU patented process that preserves core samples downhole using liquid nitrogen. Frozen cores are shipped to CSU on dry ice and always kept at -80° C. Cores are cut into subsamples and analyzed to determine geology, physical properties, contaminant concentrations, and microbial ecology. The data is processed into Excel™ and then stored in gINT™, a relational database. Herein, consideration is given to 390 feet of collected core from 31 boreholes from 5 hydrocarbon and 2 chlorinated solvent sites. Data analyses include comparisons within a site, intra-site comparisons, and between sites, inter-site comparisons.

Tools are developed in gINT™ to automate transformation of collected data into vibrant visual graphical outputs. First, for every borehole, a graphic is generated that includes a comprehensive panel of geology, contaminants of concern and fluid saturations properly presented by depth. Building on this, distributions of contaminants as a function of transmissive or low-k zones are resolved. Lastly, key attributes of mass distribution are compared across individual sites (intra-site comparisons) and between sites (inter-site comparisons).

Our analysis presents a first-ever quantification of distribution of contaminant mass in transmissive and low-k zones. The analysis begins with processing concentration data-by-depth to produce the total mass of contaminants in each borehole, the mass of contaminants in transmissive zones, and the mass of contaminants in low-k zones. The contaminant mass in a borehole is presented for each contaminant individually and as sum of all contaminants. The visualization of this data is not intuitive due to the ranges of contaminant mass in place. Hydrocarbons contaminated sites have contaminant masses that range from less than half a kilogram to about 30 kilograms of contaminants per m². Chlorinated solvent contaminated sites have contaminant masses that vary from less than 240 micrograms to right under 2.5 kilograms of contaminants per m².

The data is processed such that boreholes and sites with broad ranges of conditions can be compared. Data is presented as percent of contaminant mass in transmissive zones by borehole; the percent of contaminant mass in low-k zones by borehole, the percent of borehole that is transmissive, and percent of borehole that is low-k. Unlike previous data that required a y-axis formatted to a log scale, this data is visualized on a plot with the y-axis set at 0-100%. The fraction of a borehole that is low-k ranges between 0% and 94% with a median value of 52%. Secondly, the fraction of total contaminant mass stored in low-k zone ranges from 1% to 96% with a median value of 46%.

Illustrations of the tendency for mass storage in low-k zones are presented through difference in percent of borehole that is low-k and percent of contaminants in a borehole in low-k zones. The calculations defined a positive difference as preference for transmissive zones and a negative difference as preference for low-k zones. Data presented characterized the 18

hydrocarbon contaminated boreholes, 12 chlorinated solvent contaminated boreholes, and all 30 contaminated boreholes respectively. Key insights include

- Hydrocarbon contaminated boreholes showed statistically significant preference for low-k zones if the unit difference of percent of borehole that is low-k and percent of contaminants in a borehole in low-k zones was less than -24%.
- Chlorinated solvent contaminated boreholes showed statistically significant preference for low-k zones if the unit difference of percent of borehole that is low-k and percent of contaminants in a borehole in low-k zones was less than -11%.
- Remediated chlorinated solvent boreholes presented a preference for low-k zones where their non-remediated counterparts showed preference for transmissive zones..
- All contaminated boreholes showed statistically significant preference for low-k zones if the unit difference of percent of borehole that is low-k and percent of contaminants in a borehole in low-k zones was less than -19%.
- As an example, this thesis provides a unique documentation of benzene persisting in low-k zones. The presence or absence of benzene in low-k zones will have a large implication with respect to the longevity of benzene in monitoring wells and the efficacy of remedial measures that address the longevity of benzene in monitoring wells.

Overall, cryogenic core collection and advanced analytics provides a practical means of quantifying contaminant occurrence in transmissive and low-k zones and an improved basis for anticipating the benefits of site remedies.

ACKNOWLEDGEMENTS

Primary funding for this work came from sponsors of the University Consortium for Field Focus Groundwater Research including Chevron, ExxonMobil, and BP.

Special thanks to my advisor, Dr. Tom Sale, and committee members, Dr. Sharvelle and Dr. Sutton. Also, special thanks to my family and friends, especially my wife and parents who have been there for me through everything. I could not have finished this program without their help and support.

The data presented in this thesis was not collected or directly analyzed by the author but by members of the CCH team over many years. My primary contribution is organizing and provided methods for furthering analysis of contaminants in transmissive and low-k zones. Thus, it is very important that other individuals are acknowledged for their contributions. The following table summarizes each Site and the main contributors.

Site	Collection	Visual Analysis	Lab Analysis
A	Rick Johnson	Tom Sale & Eric Roads	Maria Irianni-Renno & Eric Roads
B	Maria Irianni-Renno & Tom Sale,	Tom Sale & Eric Roads	Maria Irianni-Renno & Eric Roads
C	Tom Sale	Tom Sale	Maria Irianni-Renno
D	Tom Sale	Tom Sale	Maria Irianni-Renno
E	Tom Sale & Maria Irianni-Renno	Tom Sale	Maria Irianni-Renno
F	Rick Johnson & Tom Sale	Tom Sale	Mitch Olson,
G	Rick Johnson & Tom Sale,	Tom Sale	Mitch Olson
H	Rick Johnson & Mitch Olson	Mitch Olson	Maria Irianni-Renno & Mitch Olson

TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	v
LIST OF TABLES.....	ix
LIST OF FIGURES.....	xi
LIST OF EQUATIONS.....	xiii
CHAPTER 1: INTRODUCTION & PROBLEM STATEMENT.....	1
1.1 Background Information	1
1.2 Objectives	6
1.3 Organization and Content	7
CHAPTER 2: METHODS.....	8
2.1 Sites	8
2.1.1 Site A.....	10
Use and COC.....	10
Depositional Environment.....	10
Core Collection.....	10
2.1.2 Site B.....	10
Use and COC.....	10
Depositional Environment.....	11
Core Collection.....	11
2.1.3 Site C.....	11
Use and COC.....	11
Depositional Environment.....	12
Core Collection.....	12
2.1.4 Site D.....	12
Use and COC.....	12
Depositional Environment.....	12
Core Collection.....	12
2.1.5 Site E.....	13
Use and COC.....	13
Depositional Environment.....	13

Core Collection	13
2.1.6 <i>Site F and Site G</i>	13
Use and COC	13
Depositional Environment.....	14
Core Collection	14
2.1.7 <i>Site H</i>	15
Use and COC	15
Depositional Environment.....	15
Core Collection	15
2.2 Core Collection and Processing	16
2.2.1 <i>Core Collection</i>	16
2.2.2 <i>Core Processing: Overview of Steps</i>	16
2.2.3 <i>Core Processing: Cutting plan</i>	17
2.2.4 <i>Core Processing: Cutting</i>	18
2.2.5 <i>Core Processing: Sample Preservation</i>	19
2.3 Sample analysis	22
2.3.1 <i>Visual</i>	22
2.3.2 <i>COC</i>	23
2.3.3 <i>Microbial</i>	23
2.4 Data Analysis	23
2.4.1 <i>Database: Need for gINT™ and Use of Excel™</i>	23
2.4.2 <i>Database: Standardization</i>	24
2.4.3 <i>Analytical: Transmissive – Low k</i>	25
2.4.4 <i>Analytical: Total Mass in Place in Borehole, Transmissive Zones, and Low-k Zones</i>	27
2.4.5 <i>Analytical: Fraction of Primary COC in Transmissive and Low-k Zones</i>	29
2.4.6 <i>Analytical: Intra-Site and Inter-Site Comparison</i>	32
CHAPTER 3: RESULTS	33
3.1 Intra-Site Analysis	33
3.1.1 <i>Intra-Site A</i>	33
3.1.1.1 <i>Contamination by Depth</i>	34
3.1.1.2 <i>Mass in Place Summary Analysis</i>	47
3.1.1.3 <i>Mass in Transmissive and Low-k Zones Summary Analysis</i>	48
3.1.2 <i>Intra-Site B</i>	54

3.1.2.1 Contamination by Depth	54
3.1.2.2 Mass in Place Summary Analysis	65
3.1.2.3 Mass in Transmissive and Low-k Zones Summary Analysis.....	65
3.1.3 <i>Intra-Site C</i>	70
3.1.3.1 Contamination by Depth	70
3.1.3.2 Mass in Place Summary Analysis	74
3.1.3.3 Mass in Transmissive and Low-k Zones Summary Analysis.....	75
3.1.4 <i>Intra-Site D</i>	79
3.1.4.1 Contamination by Depth	79
3.1.4.2 Mass in Place Summary Analysis	82
3.1.4.3 Mass in Transmissive and Low-k Zones Summary Analysis.....	83
3.1.5 <i>Intra-Site E</i>	87
3.1.5.1 Contamination by Depth	87
3.1.5.2 Mass in Place Summary Analysis	88
3.1.5.3 Mass in Transmissive and Low-k Zones Summary Analysis.....	89
3.1.6 <i>Intra-Site F</i>	93
3.1.6.1 Contamination by Depth	93
3.1.6.2 Mass in Place Summary Analysis	99
3.1.6.3 Mass in Transmissive and Low-k Zones Summary Analysis.....	99
3.1.7 <i>Intra-Site G</i>	102
3.1.7.1 Contamination by Depth	103
3.1.7.2 Mass in Place Summary Analysis	108
3.1.7.3 Mass in Transmissive and Low-k Zones Summary Analysis.....	108
3.1.8 <i>Intra-Site H</i>	111
3.1.8.1 Contamination by Depth	112
3.1.8.2 Mass in Place Summary Analysis	119
3.1.8.3 Mass in Transmissive and Low-k Zones Summary Analysis.....	119
3.2 Inter-Site Analysis	124
3.2.1 <i>Inter-Site: Hydrocarbon Boreholes</i>	124
3.2.1.1 Benzene & PCP.....	125
3.2.1.2 Total Petroleum Hydrocarbons.....	130
3.2.1.3 Methane	133
3.2.1.4 SUM COCs	138

3.2.2 <i>Inter-Site: Chlorinated Solvent Boreholes</i>	142
3.2.2.1 SUM CVOCs.....	142
3.2.3 <i>Inter-Site: All Boreholes</i>	148
3.2.3.1 SUM COCs	148
3.3 Discussion of Limitations	154
CHAPTER 4: CONCLUSION.....	156
4.1 Key findings	156
4.2 Implications for Site Characterization	158
4.3 Future Work	158
LITERATURE CITED.....	161

LIST OF TABLES

Table 1: Summary of Sites Included.....	9
Table 2: Core Intervals for Site A	10
Table 3: Core Intervals for Site B.....	11
Table 4: Core Intervals for Site C.....	12
Table 5: Core Intervals for Site D	13
Table 6: Core Interval for Site E	13
Table 7: Core Intervals for Site F	14
Table 8: Core Intervals for Site G	14
Table 9: Core Intervals for Site H	15
Table 10 : Description of subsample size, designation, preservation technique, and parameters for each Sample ID	21
Table 11: Total Mass of Contaminants at Site A.....	48
Table 12: Mass of PCP and Methane at Site A Divided into Zones.....	52
Table 13: Mass of TPH, GRO, and DRO at Site A Divided into Zones.....	52
Table 14: Percentage of Borehole that is Transmissive of Low-k and Percentage of PCP and Methane Mass in Zones at Site A	53
Table 15: Percentage of TPH, GRO, and DRO Mass in Zones at Site A	53
Table 16: Total Mass of Contaminants at Site B.....	65
Table 17: Mass of Benzene and Methane at Site B Divided into Zones.....	68
Table 18: Mass of TPH, GRO, and DRO at Site B Divided into Zones	68
Table 19: Percentage of Borehole that is Transmissive of Low-k and Percentage of Benzene and Methane Mass in Zones at Site B	69
Table 20: Percentage of TPH, GRO, and DRO Mass in Zones at Site B.....	69
Table 21: Total Mass of Contaminants at Site C.....	76
Table 22: Mass of Benzene and Methane at Site C Divided into Zones.....	76
Table 23: Mass of TPH, GRO, and DRO at Site C Divided into Zones	76
Table 24: Percentage of Borehole that is Transmissive of Low-k and Percentage of Benzene and Methane Mass in Zones at Site C	78
Table 25: Percentage of TPH, GRO, and DRO Mass in Zones at Site C.....	78
Table 26: Total Mass of Contaminants at Site D.....	84
Table 27: Mass of Benzene and Methane at Site D Divided into Zones	84
Table 28: Mass of TPH, GRO, and DRO at Site D Divided into Zones.....	84
Table 29: Percentage of Borehole that is Transmissive of Low-k and Percentage of Benzene and Methane Mass in Zones at Site D	86
Table 30: Percentage of TPH, GRO, and DRO Mass in Zones at Site D	86
Table 31: Total Mass of Contaminants at Site E.....	91
Table 32: Mass of Benzene, TPH, GRO, and DRO at Site E Divided into Zones	91
Table 33: Percentage of Borehole that is Transmissive of Low-k and Percentage of Benzene Mass in Zones at Site E	92
Table 34: Percentage of TPH, GRO, and DRO Mass in Zones at Site E.....	92

Table 35: Total Mass of Contaminants at Site F	101
Table 36: Mass of PCE, TCE, and Methane at Site F Divided into Zones	101
Table 37: Percentage of Borehole that is Transmissive of Low-k and Percentage PCE, TCE, and Methane Mass in Zones at Site F	102
Table 38: Total Mass of Contaminants at Site G.....	110
Table 39: Mass of DCE, TCE, and Methane at Site G Divided into Zones.....	110
Table 40: Percentage of Borehole that is Transmissive of Low-k and Percentage DCE, TCE, and Methane Mass in Zones at Site G	111
Table 41: Total Mass of Contaminants at Site H	119
Table 42: Mass of PCE, TCE, DCE, and VC at Site H Divided into Zones.....	122
Table 43: Percentage of Borehole that is Transmissive of Low-k and Percentage of Total COC Mass in Zones at Site H.....	123
Table 44: General Statistics for Percent of Borehole that is Transmissive and Low-k, Percent of Benzene in Zones, and the Deviation of the two Variables.	128
Table 45: General Statistics for Percent of Borehole that is Transmissive and Low-k, Percent of PCP in Transmissive and Low-k, and the Deviation of the two Variables.....	129
Table 46: General Statistics for Percent of Borehole that is Transmissive and Low-k, Percent of TPH in Zones, and the Deviation of the two Variables.	132
Table 47: General Statistics for Percent of Borehole that is Transmissive and Low-k, Percent of Methane in Zones, and the Deviation of the two Variables.	135
Table 48: Summary for Percentage of Borehole that is Transmissive or Low-k and Percentage of Contaminants in Zones for all Hydrocarbon Boreholes.....	137
Table 49: Summary for Percentage of Borehole that is Transmissive or Low-k, and Percentage of the Sum of Contaminants (Benzene/PCP+TPH) in Zones for all Hydrocarbon Boreholes.....	139
Table 50: General Statistics for Percent of Borehole that is Transmissive and Low-k, and Percent of Sum of all COCs (Benzene/PCP + TPH) in Zones for Hydrocarbon Boreholes.....	141
Table 51: Summary for Percentage of Borehole that is Transmissive or Low-k, Percentage of the Sum of Contaminants (Chlorinated Solvents) in Zones for all Chlorinated Solvent Boreholes.....	144
Table 52: General Statistics for Percent of Borehole that is Transmissive and Low-k, and Percent of Sum of all CVOCs (Chlorinated Solvents) in Zones for Chlorinated Solvent Boreholes.....	146
Table 53: Summary for Percentage of Borehole that is Transmissive or Low-k, and Percentage of the Sum of Contaminants (Benzene/PCP+TPH or Chlorinated Solvents) in Zones for all Boreholes.....	150
Table 54: General Statistics for Percent of Borehole that is Transmissive and Low-k, and Percent of Sum of all COCs (Benzene/PCP+TPH or Chlorinated Solvents) in Zones for all Boreholes.....	153

LIST OF FIGURES

Figure 1: Overall National Photo (Image From Google Earth).....	8
Figure 2: Diagrams of Cryogenically collected core Apparatus and Coring Process Kiaalhosseini et al. (2017).....	17
Figure 3: Example of a Cutting Plan	18
Figure 4: Core Getting Cut with Concrete Saw and Freshly Cut Core.....	19
Figure 5: Core Preservation Techniques.....	20
Figure 6: General overview of stations and subsamples (A,B,C,D, and E) for each Sample ID	21
Figure 7: Jars Set Up for Logging and a Jar Fluorescing Under UV.....	22
Figure 8: gINT™ USCS Graphic Choices.....	22
Figure 9: Standardization of Single Well Display.....	26
Figure 10: Core A1 Data by Depth Summary.....	35
Figure 11: Core A2 Data by Depth Summary.....	37
Figure 12: Core A3 Data by Depth Summary.....	39
Figure 13: Core A4 Data by Depth Summary.....	41
Figure 14: Core A5 Data by Depth Summary.....	43
Figure 15: Core A6 Data by Depth Summary.....	45
Figure 16: Core A7 Data by Depth Summary.....	47
Figure 17: Mass of Contamination at Site A Divided into Zones	52
Figure 18: Percentage of Mass in Zones at Site A Ordered from Transmissive to Low-k	53
Figure 19: Core B1 Data by Depth Summary	56
Figure 20: Core B2 Data by Depth Summary	57
Figure 21: Core B3 Data by Depth Summary	59
Figure 22: Core B4 Data by Depth Summary	60
Figure 23: Core B5 Data by Depth Summary	62
Figure 24: Core B6 Data by Depth Summary	63
Figure 25: Core B7 Data by Depth Summary	64
Figure 26: Mass of Contamination at Site B Divided into Zones.....	68
Figure 27: Percentage of Mass in Zones at Site B Ordered from Transmissive to Low-k.....	69
Figure 28: Core C1 Data by Depth Summary	72
Figure 29: Core C2 Data by Depth Summary	74
Figure 30: Mass of Contamination at Site C Divided into Zones.....	76
Figure 31: Percentage of Mass in Zones at Site C Ordered from Transmissive to Low-k.....	78
Figure 32: Core D1 Data by Depth Summary	80
Figure 33: Core D2 Data by Depth Summary	82
Figure 34: Mass of Contamination at Site D Divided into Zones	84
Figure 35: Percentage of Mass in Zones at Site D Ordered from Transmissive to Low-k	86
Figure 36: Core E1 Data by Depth Summary	88
Figure 37: Mass of Contamination at Site E Divided into Zones.....	91
Figure 38: Percentage of Mass in Zones at Site E Ordered from Transmissive to Low-k	92
Figure 39: Core F1 Data by Depth Summary.....	94

Figure 40: Core F2 Data by Depth Summary.....	96
Figure 41: Core F3 Data by Depth Summary.....	98
Figure 42: Mass of Contamination at Site F Divided into Zones.....	101
Figure 43: Percentage of Mass in Zones at Site F Ordered from Transmissive to Low-k.....	102
Figure 44: Core G1 Data by Depth Summary.....	104
Figure 45: Core G2 Data by Depth Summary.....	105
Figure 46: Core G3 Data by Depth Summary.....	107
Figure 47: Mass of Contamination at Site G Divided into Zones.....	110
Figure 48: Percentage of Mass in Zones at Site G Ordered from Transmissive to Low-k.....	111
Figure 49: Core H1 Data by Depth Summary.....	113
Figure 50: Core H3 Data by Depth Summary.....	114
Figure 51: Core H2 Data by Depth Summary.....	115
Figure 52: Core H4 Data by Depth Summary.....	116
Figure 53: Core H5 Data by Depth Summary.....	117
Figure 54: Core H6 Data by Depth Summary.....	118
Figure 55: Mass of Contamination at Site H Divided into Zones.....	122
Figure 56: Percentage of Total COC Mass in Zones at Site H Ordered from Transmissive to Low-k.....	123
Figure 57: Percentage of Benzene/PCP in Zones for All Hydrocarbon Boreholes.....	127
Figure 58: Percentage of TPH in Zones for All Hydrocarbon Boreholes.....	131
Figure 59: Percentage of Methane in Zones for All Hydrocarbon Boreholes.....	134
Figure 60: Box and Whisker Plot for The Difference Between Percent of Borehole that is Low-k and Percent of Total Benzene, PCP, TPH, or Methane in Low-k Zones.....	136
Figure 61: Summary for Percentage of Borehole that is Transmissive or Low-k and Percentage of the Sum of Contaminants (Benzene/PCP+TPH) in Zones for all Hydrocarbon Boreholes.....	140
Figure 62: Percentage of the Sum of all CVOCs (Chlorinated Solvents) in zones for all Chlorinated Solvent Boreholes.....	145
Figure 63: Percentage of the Sum of all CVOCs (Chlorinated Solvents) in zones for Site F/G Boreholes.....	147
Figure 64: Percentage of the Sum of all CVOCs (Chlorinated Solvents) in zones for Site H Boreholes.....	147
Figure 65: Percentage of the Sum of all COCs (Benzene/PCP+TPH or Chlorinated Solvents) in zones for all Boreholes.....	151
Figure 66: Box and Whisker Plots for Difference Between Percent of Borehole that is Low-k and Percent of Total Sum Of Contaminants in Low-k Zones Presented for Hydrocarbon, Chlorinated Solvent, and All Boreholes Respectively.....	152

LIST OF EQUATIONS

Equation 1: Mass in Place (M/L^2)	27
Equation 2: Bulk Density (M/L^3)	27
Equation 3: Total Mass in Place (M/L^2)	27
Equation 4: Total Mass in Place (M/L^2) in Transmissive Zones	28
Equation 5: Total Mass in Place (M/L^2) in Low-k Zones	28
Equation 6: Total Mass of Contaminants in Place (M/L^2)	28
Equation 7: Fraction of Sampled Borehole that is Transmissive (L/L)	29
Equation 8: Fraction of Sampled Borehole that is Low-k (L/L)	29
Equation 9: Fractions of Sampled Borehole equal 1 (L/L)	30
Equation 10: The fraction of contaminant of concern, COC_i , (M/M) in the transmissive zones of the borehole	30
Equation 11: The fraction of contaminant of concern, benzene, (M/M) in the transmissive zones of the borehole	30
Equation 12: The fraction of contaminant of concern, COC_i , (M/M) in the low-k zones of the borehole	31
Equation 13: The fraction of contaminant of concern, benzene, (M/M) in the low-k zones of the borehole	31
Equation 14: The fractions of contaminant of concern equals 1	31
Equation 15: Difference between the percent of the borehole that is low-k and the percent of contaminant or contaminants in low-k zones (L/L-M/M).....	31

CHAPTER 1: INTRODUCTION & PROBLEM STATEMENT

The emergence of cryogenic coring, as developed by Colorado State University Kiaalhosseini et al. (2017), is providing novel opportunities to resolve the mass and distribution of anthropogenic contaminants in shallow, unconsolidated soil-groundwater systems. Uniquely, cryogenic coring preserves physical properties of soil, pore liquids, pore gasses, volatile contaminants, and microbial ecology in-situ via rapid cryogenic freezing. Subsampling and analysis of cores at intervals of 2-10 inches provides high resolution data that facilitates estimated total mass in place, in all phases, in both transmissive and low permeability (low-k) zones. Furthermore, in-situ cryogenic freezing of core improves recovery of representative soil-fluid samples by 1) limiting sample losses due to sample dropping during collection and 2) helps control the movement of non-representative media (“sluff”) into empty augers between collection intervals. Recent publications supporting the use of cryogenic coring as outlined above include Johnson et al. (2012), Johnson et al. (2013), Sale et al. (2013), Sale et al. (2015), Irianni-Renno et al. (2015), Garj et al. (2017), Olson et al. (2017), and Kiaalhosseini et al. (2017).

1.1 Background Information

The primary historical impetus for collection and analysis of environmental samples from shallow, soil-specific groundwater systems includes the 1976 Resource Conservation and Recovery Act (RCRA) and the 1980 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The environmental movement achieved legal backing and required methods to sample contamination in groundwater systems.

Following Sale et al. (2016), the most common methods for sampling groundwater contamination is referred to as first generation (1G) site characterization techniques. 1G techniques date back to the 1980s Einarson et al. (2006) and include standard monitoring wells and grab soil samples Sale et al (2013). The limitations, Sale et al. (2013 & 2015), and Kiaalhosseini et al. (2016), are listed in the following text.

Standard monitoring well:

- In-well mixing of water and contaminants obscures actual contaminant, microbial, and physical distributions.
- Water sampled is from transmissive zones due to preferential flow from transmissive zones and, often, by design
- Little to no insight is gained with respect to condition in low-k zones

Grab sediment samples:

- Drainage of pore fluids.
- Disruption of in-situ soil structure.
- Loss of volatile contaminant.
- All contribute to limiting the validity of observed contaminant, microbial, and physical distributions.

The methods for 1G site characterization often fail to consider the vertical variation of physical, chemical, and biological distributions. They have very limited ability to differentiate contaminants in transmissive and low-k zones. Sampling methods from the 1980s and 1990s involved the use of these standard geotechnical sampling methods Einarson et al. (2006). In the early 90s, mathematical evidence began to emphasize the importance of contamination sorbed to

soils and in gas phases, even when the primary measurement is aqueous concentrations Feenstra et al. (1991). This emphasis, along with homogeneous geologic assumptions, presented the potential failings and possible limitations of 1G site characterization methods.

Many of the limitations of 1G methods were addressed by what is referred to as second generation (2G) site characterization tools. Common 2G site characterization include Membrane Interface Probes (MIPs), Rapid Optical Screening Techniques (ROST), Waterloo Profiler™, and rapid field-based high resolution subsampling of cores. The capabilities of each method are limited, and, very often, multiple methods are combined in the hope that at least one will work. The extent of application and purpose needs to be carefully determined before implementation. The limitations, Sale et al. (2013 & 2015) and Kiaalhosseini et al. (2017), are listed in the following text.

MIPs, ROST, Waterloo Profiler™, and other probes:

- Does not consider material sorbed to subsurface media.
- Not useful for every geologic system.
- ROST only works for fluorescing compounds and is not quantitative
- Does not match the detectability limits of laboratory equipment.
- High cost if multiple systems are needed

Complete sediment core

- Pore fluids drain when extracted.
- Recovery is limited with cohesionless soil
- Difficult to preserve in-situ biogeochemical properties, including microbial properties, all the way to laboratory analysis.

Even with these limitations, 2G site characterizations are crucial in understanding the impact of heterogeneous media. Heterogeneous media is documented extensively, Sudicky et al. (1985), Hess et al. (1992), Schincariol et al. (1997), Rivett et al. (2001), and Dentz & Carrera (2005). However, even in modern projects homogeneous assumptions are preferred for ease of use in site characterization models. This is unfortunate because the heterogeneity can be a prominent factor that determines the placement and concentration of contamination over time Haggerty and Gorelick (1995). The low-k zones have been found to back diffuse contaminants after the primary source zone is gone which can extend remediation timelines Chapman and Parker (2005). Methods like Discrete Fracture Network Parker et al. (2007) and the 14 Compartment Model Sale and Newell (2009) include considerations of heterogeneity, prominence in low-k, and different contaminant phases. These newer methods show the limitations of 2G site characterization techniques and the necessity of meeting microbial analysis requirements and low-k analysis requirements in the next generation of site characterization techniques.

Third generation (3G) site characterization techniques are advanced methods that push to maximize preservation of in-situ biogeochemical subsurface properties. So far, 3G site characterization techniques include cryogenic core collection and high-throughput analysis. The use of cryogenic processes to extract frozen core has been used for various geologic purposes since 1980, Cahoon & Reed (1995), Knaus & Cahoon (1990), Everest et al. (1980), and Petts et al. (1989). The first apparent use of cryogenic coring to measure contamination was in 1991 Durnford et al. (1991). However, it was the advancement in understanding of microbial communities and inability to sample low-k zones that promoted the advancement of a technically competent and, potentially, a commercially reliable method of cryogenic core collection Johnson et al. (2012), Johnson et al. (2013), Sale et al. (2013), Sale et al. (2015), Irianni-Renno et al.

(2015), Garj et al. (2017), Olson et al. (2017), and Kiaalhosseini et al. (2017). The methods and limitations of the current cryogenic core collection process are outlined in Sale et al. (2015).

Key limitations include:

- The method cannot collect subsurface media larger than the diameter of the drive shoe.
- Recovery percentages can drop in cobbles.
- Expense and time commitment can limit number of boreholes, and therefore spatial resolution, for any given project.

Cryogenic core collection has given our research team at Colorado State University the opportunity to analyze contaminant, microbial, and geologic distributions in shallow, soil ground water systems.

Work to date includes over 15 project sites with an assortment of DNAPL and/or LNAPL contamination. Key published work Sale et al. (2016), Olson et al. (2017), and Kiaalhosseini et al. (2017) presents the extensive capability of cryogenically collected core to analyze distributions of geologic properties, contaminant/dissolved ion/gas concentrations, microbial markers, and subsurface saturation percentages. Cryogenic core collection can also provide better site characterization for novel remediation actives like ZVI clay mixing Olson et al. (2017). Older cryogenic core collection data was created in and is presented through Excel's™ visualization tools which was very time-consuming Sale et al. (2016) Olson et al. (2017), and Kiaalhosseini et al. (2017). A relational database that included pre-programmed visual tools has become a critical tool for advancing future cryogenic core collection projects. After careful consideration, Bentley Academia's gINT™ was selected to meet the needs of cryogenically collected core data. Work in gINT™ began with meeting current needs of active projects. As

priorities were met, all available data from previous cryogenic projects was included into gINT™ with a large portfolio of option visual outputs. Standard output features for gINT™ are as follows. The first section includes geologic/observed data, followed by contaminant/methane concentrations by depth, and ending with geologic saturations percentages by depth. All contaminants have been programmed to have unique, standardized colors that are consistent across current and future output forms. Department research and cryogenic core collection projects continually recommended for future projects to analyze mass of contaminants in transmissive and low-k zones Sale et al. (2013), Sale et al. (2016), Olson et al. (2017), Kiaalhosseini et al. (2017), Garj et al. (2017). With the data storage and visualization efficiency from gINT™ and the calculation capabilities from Excel™, it is now possible to process the large amount of data from cryogenic core collection in a timely and effective manner. This leads to new methods for analysis of mass in transmissive and low-k zones like the one presented in this paper.

1.2 Objectives

The first objective of this thesis is to advance the visualization capability, through gINT™, for cryogenically collected core to professional levels.

The second objective is to pull together data from 7 different cryogenically sampled sites and analyze mass in place in transmissive and low-k zones

The third objective is to compare mass distributions in transmissive and low-k zones in each site individually (intra-site) and between sites (inter-site).

The final objective is to explore opportunities to use cryogenically collected core to better resolve the distribution of contamination in transmissive and low-k zones in support of better management of the sites.

1.3 Organization and Content

This report is divided into 5 Chapters. Methods are presented in Chapter 2. Results are presented in Chapter 3. Intra-site results and inter-site results are in Sections 3.1 and 3.2 respectively. The discussion of limitations is presented in Chapter 3 in section 3.3. Finally, conclusions are presented in Chapter 4. Key findings, implications for site characterization, and future work is presented in sections 4.1, 4.2, and 4.3 respectively.

CHAPTER 2: METHODS

The following presents methods including a description for each site, steps for core collection, steps for core processing, analytical methods, and data analysis.

2.1 Sites

A total of 7 unique cryogenic cored sites are considered in this thesis including sites in Wisconsin, Ohio, Missouri, Colorado, Wyoming, and Maryland. Figure 1 approximates the locations of each site. Table 1 presents the depositional environment, locations, depth to water table, industry use timeline, primary contaminants of concern (COC), and secondary COC for each site. Specific details as to site ownership, locations, etc. are not included reflecting the nascent nature of the methods and our desire to let the entities funding the work resolve the merits of the information.

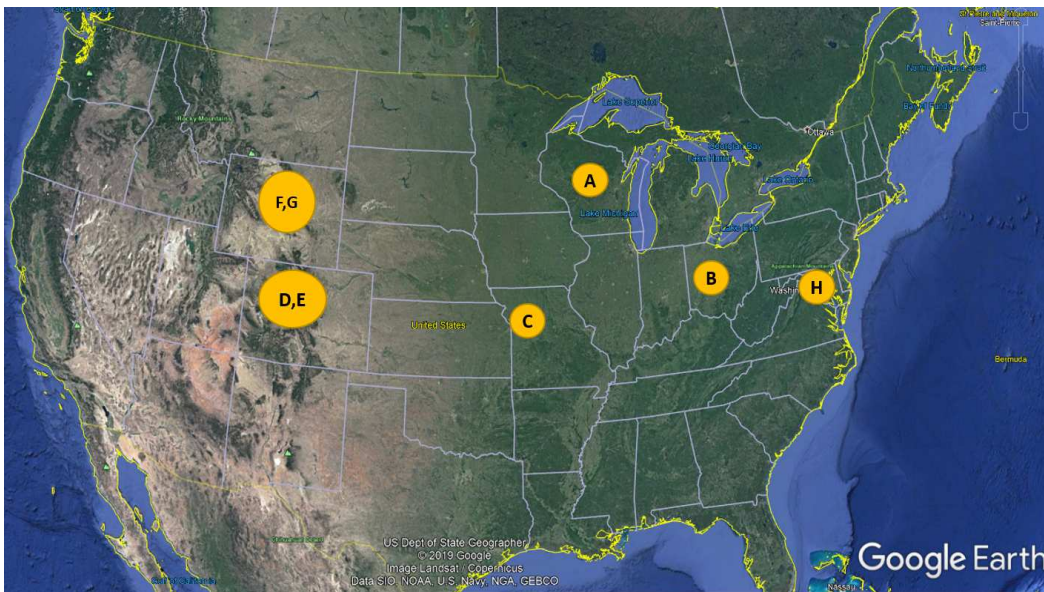


Figure 1: Overall National Photo (Image From Google Earth)

Table 1: Summary of Sites Included

Site	Depositional Environment	Region of Reference	Depth to Water Table	Active Industry Use	Primary COC	Secondary COC
A	<u>Glacial-Fluvial-</u> Sand and gravel with interbedded silt layers	Wisconsin	River Dependent; ~18-30ft bgs	Early 1900- March 1991	PCP in Carrier oil	DRO, GRO, Methane
B	<u>Glacial-Fluvial-</u> Sand and gravel with interbedded silt layers	Ohio	River Dependent; ~11-35ft bgs	1931- 1985	Benzene in Gasoline	DRO, GRO, Methane
C	<u>Fluvial Overbank Deposit-</u> Silt and sand beds	Missouri	River Dependent; ~12-17ft bgs	1904- 1985	Benzene in Gasoline	DRO, GRO, Methane
D	<u>Braided Stream Deposit-</u> Silt and sand overlying coarse sand and gravel	Colorado	~8-12ft bgs	Active	Benzene in Gasoline	DRO, GRO, Methane
E	<u>Braided Stream Deposit-</u> Silt and sand overlying coarse sand and gravel	Colorado	~8-12ft bgs	Active	Benzene in Gasoline	DRO, GRO, Methane
F & G	<u>Eolian Overlying Sandstone-</u> <u>Heterogenous layers</u> of conglomerate, sand, silt	Wyoming	11.5-25 ft	1900- present	F: TCE PCE G: TCE, DCE	Methane
H	<u>Tidal Estuary-</u> Fine Grained Sands and Silts	Maryland	River Dependent	~1960- ~1980s	PCE, TCE, DCE, VC	

2.1.1 Site A

Use and COC

Site A is a former wood-treating facility that ended operations in the 1990s. The site employed mineral carrier oil containing pentachlorophenol (PCP). The primary contaminant of concern (COC) is PCP and total petroleum hydrocarbons (TPH).

Depositional Environment

The geologic setting is a glacial outwash at the terminus of a former continental ice sheet. Sediments include interbedded layers of sand, gravel, and fine grained silts.

Core Collection

A total of seven cores were collected in an approximate 6 acre area. Core were collected in ~10-foot intervals about the water table as listed in Table 2.

Table 2: Core Intervals for Site A
Numerical values are good to 3 significant numbers

Core	Top (ft)	Bottom (ft)
A1	24.0	35.0
A2	24.5	35.0
A3	24.5	35.0
A4	29.5	35.0
A5	24.5	34.5
A6	24.5	27.0
A7	19.5	32.0

2.1.2 Site B

Use and COC

Site B is a former petroleum refinery that ended operations in 1985. Produced products include gasoline, jet fuels, diesel, and kerosene. The primary COCs are benzene and TPH. Site B is located on the floodplain of a major river.

Depositional Environment

The geologic setting is a glacial outwash at the terminus of a continental ice sheet. Sediments include interbedded layers of sand, gravel, and fine-grained silts.

Core Collection

A total of seven cores were collected in an approximate 100+ acre area. Core were collected as listed in Table 3. Cores B2 and B3 are duplicates of B1. Core B4 is a non-Cryogenically collected duplicate of B1. Cores B1-B4 and B5-B7 were completed in 2016 and 2018 respectively.

Table 3: Core Intervals for Site B
Numerical values are good to 3 significant numbers

	Core	Top(ft)	Bottom(ft)
	B1	0.00	33.5
Duplicate of B1	B2	21.5	33.5
Duplicate of B1	B3	21.5	31.5
Non-Frozen Duplicate of B1	B4	24.0	31.0
	B5	21.5	31.0
Small Missing Section of B7	B6	17.5	23.0
	B7	14.5	21.5

2.1.3 Site C

Use and COC

Site C is a former petroleum refinery that ended operations in 1982. Products produced include gasoline, jet fuel, kerosene, furnace oil, and petroleum coke. Primary COCs are benzene and TPH.

Depositional Environment

The geologic setting is a fluvial overbank deposit. Sediments include interbedded layers of silts and sands.

Core Collection

A total of two cores were collected in an approximate 1 acre area. Core were collected in duplicate intervals as listed in Table 4. Core C1 and C2 are duplicates.

Table 4: Core Intervals for Site C
Numerical values are good to 2 significant numbers

	Core Top (ft)	Bottom (ft)
C1	6.5	32
Duplicate of C1 C2	6.5	32

2.1.4 Site D

Use and COC

Site D is an active refinery. Products include liquefied petroleum gas, gasoline, jet fuel and asphalt. The primary COC is benzene and TPH.

Depositional Environment

The geologic setting of Site D is a braided stream deposit. Sediments include interbedded layers of sand and silt overlaying layers of coarse sand and gravel.

Core Collection

A total of two cores were collected in an approximate 1 acre area. Cores were collected in intervals from the ground surface to the water table as listed in Table 5. Core D1 contains no NAPL while D2 contains minor amount of LNAPL.

Table 5: Core Intervals for Site D
Numerical values are good to 3 significant numbers

Core	Top (ft)	Bottom (ft)
D1	0.0	14.5
D2	0.0	11.7

2.1.5 Site E

Use and COC

Site E is an active gas station in Colorado. Released products include gasoline and diesel. The primary COCs are benzene and TPH.

Depositional Environment

The geologic setting of Site E is a braided stream deposit. Sediments include interbedded layers of sand and silt overlaying layers of coarse sand and gravel.

Core Collection

A single core was collected in an approximate 15 acre area. Core was collected about the water table as listed in Table 6.

Table 6: Core Interval for Site E
Numerical values are good to 3 significant numbers

Core	Top (ft)	Bottom (ft)
E1	14.8	23.5

2.1.6 Site F and Site G

Use and COC

Site F & G are the same site. They are split into two separate categories because there are sampled at different times. The F designation is pre-remediation sampling and the G

designation is for the post-remediation sampling. The Site is an active Department of Defense facility in Wyoming. Historical operations have created multiple plumes containing chlorinated solvents. The primary COCs for Site F are trichloroethylene (TCE) and tetrachloroethylene (PCE) and for Site G are TCE and 1,2-dichloroethane (DCE).

Depositional Environment

The geologic setting of Site F & G is eolian silt overlying weathered portions of the Ogalla Formation. Sediments include interbedded layers of sand and silt overlaying layers of coarse sand and gravel.

Core Collection

A total of six cores were collected in an approximate 6 acre area. There are 3 cryogenically collected cores for Site F and Site G with depth intervals listed in Table 7 and Table 8 respectively. Core G1 is a post-remediation duplicate for the pre-remediated Core F1. Core G2 and G3 are post-remediation duplicates for the pre-remediated Core F3.

Table 7: Core Intervals for Site F

Numerical values are good to 3 significant numbers

Analog at G	Core	Top (ft)	Bottom (ft)
G1	F1	14.0	40.0
	F2	9.0	22.8
G2 & G3	F3	9.0	17.0

Table 8: Core Intervals for Site G

Numerical values are good to 3 significant numbers

Analog at F	Core	Top (ft)	Bottom (ft)
F1	G1	25.0	40.0
F2	G2	6.0	18.6
F2	G3	6.0	15.6

2.1.7 Site H

Use and COC

Site H is an active Department of Defense facility in Maryland. Source zone was removed around 1980. The primary COC for Site H are TCE, PCE, DCE, and vinyl chloride (VC).

Depositional Environment

The geologic setting is a tidal estuary. Sediments include a surface layer of fill and underneath interbedded layers of sand, gravel, and fine-grained silt. The remediation process modified the geology down to approximately 18 feet. A remedy of ZVI-Clay was employed at the site where deep soil techniques uniformly distribute bentonite clay and zero-valent iron in the subsurface.

Core Collection

A total of six cores were collected in an approximate 1-2 acre area. Core were collected in intervals from near surface down to the water table as listed in Table 9. The modified geology applies to cores H1, H2, H3 and H4. Cores H5 and H6 are sampled outside of the remediation area where the subsurface media has not been modified.

Table 9: Core Intervals for Site H
Numerical values are good to 3 significant numbers

Core	Top (ft)	Bottom (ft)
H1	3.0	22.0
H2	3.0	19.5
H3	7.0	19.5
H4	7.0	19.5
H5	3.0	19.5
H6	3.5	19.5

2.2 Core Collection and Processing

The following presents the procedure for collecting and processing cryogenic core. Additional details regarding collection and analysis of cryogenic core can be found in Sale et al. (2016), Olson et al. (2016) and Kiaalhosseini et al. (2017).

2.2.1 Core Collection

The process of cryogenically collecting 2.5-foot intervals of 2-1/4-inch inner diameter core is summarized in this section. On the left side of Figure 2 there is a cross-section of the cryogenic coring tools. On the right side of Figure 2 there is the diagram with steps 1, 2, and 3 of the cryogenic core collection process. Following Kiaalhosseini et al. (2017), the first step advances the augers and sample barrel to fill the sample liner with 2.5 feet of core. The second step injects liquid nitrogen to freeze the core inside the sample liner. Freezing generally is accomplished in four to six minutes. The third step produces a frozen plug at the bottom of the 2.5 feet interval and extracts the frozen core from the ground. Lastly, the fourth step removes the sample liner with core from the sample barrel. Once the core in the sample liner is removed from the sample barrel, it is placed in a large cooler surrounded by dry ice. The four steps are repeated until the targeted intervals are collected.

2.2.2 Core Processing: Overview of Steps

Core processing follows methods outlined in Sale et al. (2016), Kiaalhosseini et al. (2017), and Olson et al. (2016). Notable relevant advancements to core processing procedures are outlined in this section.

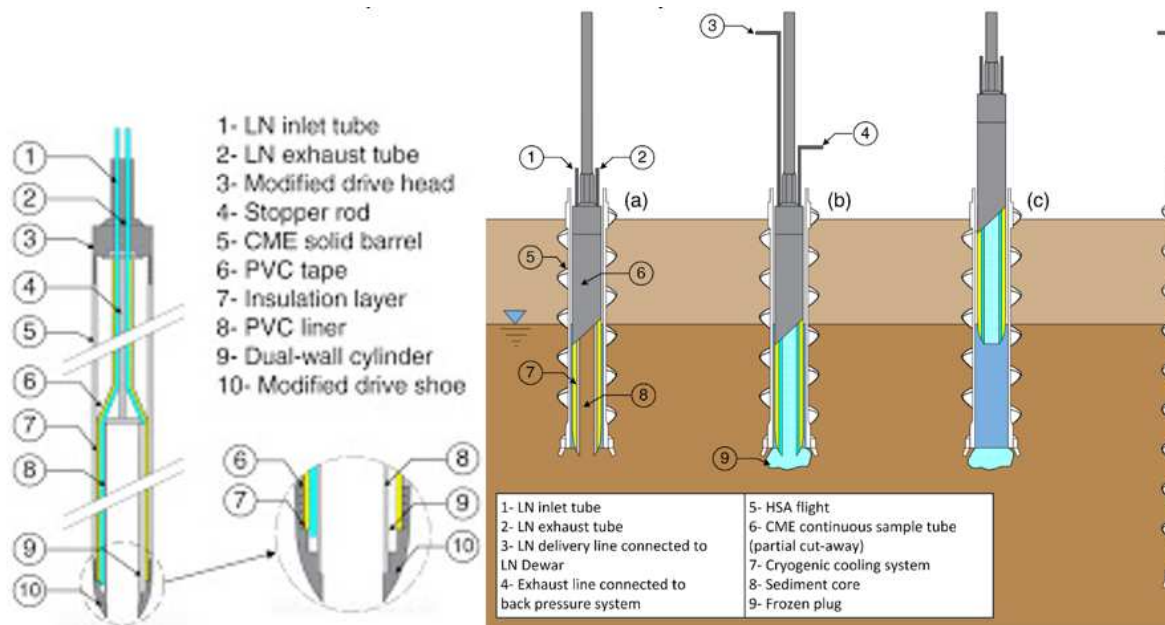


Figure 2: Diagrams of Cryogenically collected core Apparatus and Coring Process

2.2.3 Core Processing: Cutting plan

As a first step, a core cutting plan is advanced based on actual core recovery. Selected intervals for subsampling are based on 1) avoiding the ends of core where samples may be biased, 2) obtaining subsample over uniform intervals, and 3) addressing conditions at interfaces. Figure 3 provides an example of a cutting plan. The left side of Figure 3 lists 4 cryogenically collected cores at their respective depth interval. The top interval is 24-26.5 feet bgs. Included in Figure 3 is a scale, numbered 0-30 inches, moving right to left from the core's top. Figure 3 visualizes the collected core with light green for the depth to cut and light brown for the sample ID. Each sample ID has one-inch subsample referred to as "pucks". The project associated with this cutting plan wanted to increase their sampling resolution, highlighted in yellow, for the third cored interval (29-31.5 feet bgs) because it is in the zone targeted by Laser Induced Fluorescence (LIF).

		LIF - LNAPL		Bottom																Top																
Top	Bottom	Block	Sluff	Top	Bottom	30	29	28	27	#	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
ft.				28	30.5																															
24	26.5														0.17							25.083								24.583				24.083		
															4							3							2					1		
27	29																					26.75								27.083						
																						6							5							
29	31.5					31.417		31.08	31.00	30.92	30.83	30.75	30.67	30.58	###	30.42	30.33	###	30.17	30.083	30.00	29.92	###	29.75	29.67	29.58	29.50	29.42	29.33	29.25	###	29.083				
						18		17						16		15				14	13	12		11	10	9.0		8					7			
32	34					0.33																32.8			32.3									31.583		
						22																21			20									19		

Figure 3: Example of a Cutting Plan

2.2.4 Core Processing: Cutting

Cutting the frozen core has 3 key steps. The first step finds and removes the relevant section of frozen core from a -80 C° freezer. The second step positions an interval of frozen core on a chop saw in a hood. The third step cuts the core as shown in Figure 4. Figure 4 visualizes the saw making a 1-inch cut and a freshly cut core ready to be processed with the plastic liner intact. Sale et al. (2016), Kiaalhosseini et al. (2017), and Olson et al. (2016) outlined the use and definition of 1” frozen core sections as hockey “pucks”. There is a key modification that needs to be addressed. For each sample ID, we now cut two subsequent 1” “pucks” for each sample ID. These are referred to as Puck1 and Puck2. Puck1 is the top sample and is quartered for biogeochemical analyses (Subsample A), methanol extraction (Subsample B), and future analysis (Subsample D) as outlined in Sale et al. (2016), Kiaalhosseini et al. (2017), and Olson et al. (2016). The entire sample from Puck2 (Subsample C) will be used for visual observation and saturation calculations as outlined in Sale et al. (2016), Kiaalhosseini et al. (2017), and Olson et al. (2016). After Puck1 and Puck2 are cut for a sample ID, any remaining core is cut and archived (Subsample E).



Figure 4: Core Getting Cut with Concrete Saw and Freshly Cut Core

2.2.5 Core Processing: Sample Preservation

Each Sample ID is guaranteed to have subsamples A, B, C, and D with the possibility of a subsample E. Every subsample's size, preservation technique, and purpose is summarized in Table 10. During cutting, there are four work stations that each have a set responsibility as visualized in Figure 6. Following Figure 6, Station 1 cuts the core at planned intervals. Station 2 receives, removes plastic liner, and quarters Puck1 into subsamples A, B, and D. Subsample A is wrapped in foil and preserved in liquid nitrogen. Subsample B is preserved in 50 mL of methanol (Figure 5) for microbial and contaminant testing respectively. Any remaining material of Puck 1, subsample D, is sent to station 4 to be vacuum sealed as an archive sample. Station 3 preserves all of Puck2, Subsample C, in a 1-pint Ball™ jar for parameters outlined fully in Table 10. Finally, Station 4 vacuum seals remaining core from Puck1, Subsample D, and any remaining core between sample IDs, Subsample E, for future use (Figure 5). All vacuum sealed core is kept temporarily in dry ice coolers before being stored in -80C freezers.



Figure 5: Core Preservation Techniques

There is a notable, relevant advancement in methods from Sale et al. (2016), Kiaalhosseini et al. (2017), and Olson et al. (2016) at station 3. Previous methods outlined a quarter of a puck lowered into a ~100ml beaker of water. The results from these methods did not lead to consistently accurate analysis of fluid saturation as the quartered section was loose and did not retain its in-situ physical properties. Currently we take Puck2, with the plastic liner intact, and lower it into a 1 pint Ball™ pint jar filled with de-ionized water. Figure 13 shows the type of Ball pint jar used. The weight of the water being displaced by Puck2 is carefully measured. Using Puck2, as a full 1 inch “puck”, has 3 very positive attributes. The first is greater volumes of soil and water leads to easier weighting procedures. Additionally, the error associated with measuring the displaced water impacts large volumes much less. Finally, the intact plastic casing retains the in-situ pore space, saturations and other physical properties.

Table 10 : Description of subsample size, designation, preservation technique, and parameters for each Sample ID

Core Section Per Sample ID	Subsample & Size	Preservation Technique	Parameters
Puck1- Remove Plastic Liner	A-¼ Puck1	Wrapped in foil, stored temporarily in liquid nitrogen, and stored in -80°C Freezer until analyzed	Microbial Markers
	B-¼ Puck1	Placed into 50mL methanol and sealed in jar	Contamination Concentrations
	D-½ Puck1	Wrapped in foil, vacuumed sealed, stored temporarily on dry ice, and stored long term in -80°C Freezer	Future Analysis
Puck2- Plastic Liner Kept Intact	C-Puck 2	Placed in jar filled with deionized water	Geologic Properties Methane/Gas Sediment Characteristics NAPL Reflectiveness
Remaining Core- Plastic Liner Kept Intact	E- Variable Size	Wrapped in foil, vacuumed sealed, stored temporarily on dry ice, and stored long term in -80°C Freezer	Future Analysis Other CSU Department's Studies

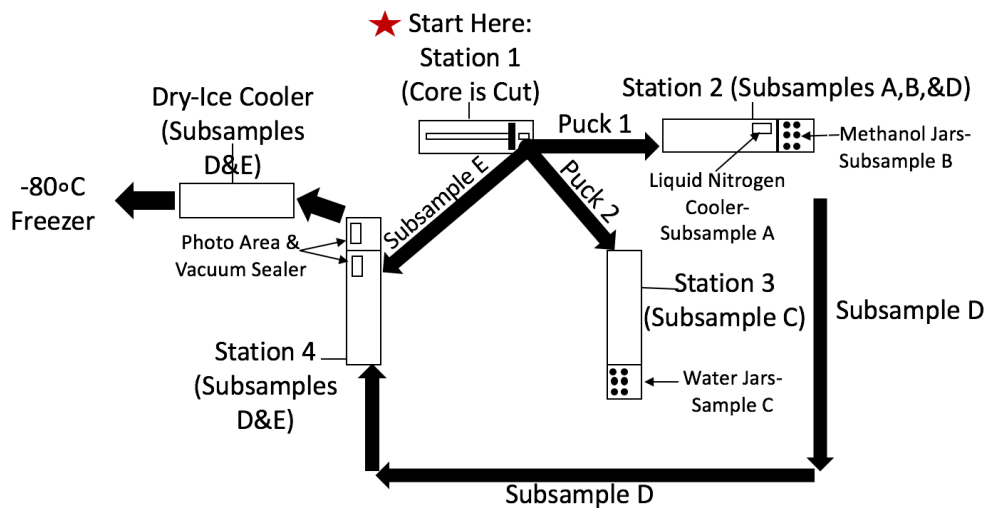


Figure 6: General overview of stations and subsamples (A, B, C, D, and E) for each Sample ID

2.3 Sample analysis

The following presents methods including the steps of visual logging, contaminant identification, and microbial identification outlined by Sale et al. (2016), Kiaalhosseini et al. (2017), and Olson et al. (2016).

2.3.1 Visual

The physical properties were evaluated by a Professional Geologist, Dr. Sale, in accordance with documented process in Sale et al. (2016), Kiaalhosseini et al. (2017), and Olson et al. (2016). Figure 7 shows jars ready to be logged and a jar with NAPL fluorescing under UV light. The properties are presented under USCS classification to reuse previously established graphic choices as outlined in Figure 8. I, Eric Roads, participated in identifying physical properties for sites since January 2019 in order to effectively evaluate previous reports and data.



Figure 7: Jars Set Up for Logging and a Jar Fluorescing Under UV

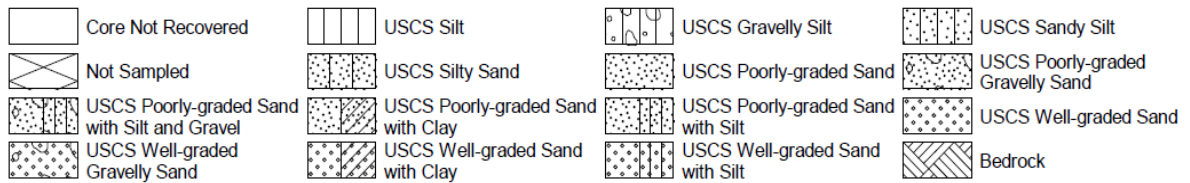


Figure 8: gINT™ USCS Graphic Choices

2.3.2 COC

COC analysis for chlorinated solvents and hydrocarbons follows methods outlined in Sale et al. (2016), Kiaalhosseini et al. (2017), and Olson et al. (2016). A Gas Chromatography Flame Ionization Detector measures the COCs in the methanol, Subsample B, and water jar, Subsample C, unless specified otherwise. As mentioned in (Sale et al. 2016), (Kiaalhosseini et al. 2017), and (Olson et al. 2016), each contaminant was freshly benchmarked using a known standard for every analysis. Benchmarks from previous projects were compared with new benchmarks for validity verification. The weights of all jars, fluids, samples, and plastic liners are meticulously recorded to solve calculations of porosity, water saturations, gas saturations, and NAPL saturations as outlined in Sale et al. (2016), Olson et al. (2016) and Kiaalhosseini et al. (2017).

2.3.3 Microbial

Microbial analysis for Subsample A, Subsample D, and Subsample E follows the methods outlined in (Sale et al. 2016), (Kiaalhosseini et al. 2017), Irianni-Renno and (Olson et al. 2016). Microbial data is not used in this thesis.

2.4 Data Analysis

The following presents methods for a relational database and primary visualization tool. This section further presents the methods for the analytical steps required to differentiate between transmissive and low-k zones, calculate mass in place in zones, calculate percentage of total mass in place, and provide intra-site and inter-site comparisons.

2.4.1 Database: Need for gINT™ and Use of Excel™

Cryogenically collected core creates large data sets that are best managed using a relational database. The program used to process data is Excel™. Excel™ allows for complex

equations and solutions to be quickly and easily applied to large sets of data. The program used to store this data needs to be a relational database. Access™ is a usable relational database based on Excel™. Unfortunately, Access™ does not have any preprogrammed visualization options that would meet our needs. Bentley Academia's™ program gINT™ is a relational database using the Access™ architecture. gINT™ includes easy-to-use, multifunctional, and highly modifiable capabilities to visualize data-by-depth. Thus, gINT™ is used exclusively for any data-by-depth visualization requirements for this thesis. Excel™ is still used to visually present mass in place data and statistic plots.

2.4.2 Database: Standardization

The purpose of gINT™ for cryogenically collected cores is to assemble all previous, current and future cryogenically collected cores to a single database that provides standardized data-by-depth visuals and allows for multiple cores from differing sites to be compared. The features and complexity of the visuals are developed on a project and purpose basis. This has led to many different visual features and archaic visualization outputs. For this project, there is one type of standardized gINT™ forms that will be used. Figure 9 is an example of this gINT™ form that outputs available information for a single core on a single sheet. Figure 9 includes a legend that is not included in gINT's™ output features but was added afterwards for descriptive simplicity. Notable features include a geology section that includes depths from surface (ft), Sample ID #, sediment color, USCS sediment graphics, NAPL visual response, transport designation, and water table depth. The NAPL response is colored with white for missing section, light grey for nothing and darker greys for increasing reflective response. The transport designation is between transmissive (blue) and low-k (black). The remaining gINT™ objects are

data-by-depth plots that use standardized, unique colors for each parameter. Due to various circumstances, certain sites do not have complete data sets to output all information and thus will have missing details.

2.4.3 Analytical: Transmissive – Low k

A key objective for this thesis is to resolve the distribution of contaminant mass in transmissive and low-k zones. The methods used to classify the transmissivity of sample are outlined in the following text. Using the visual logs of each Sample IDs, we review each borehole at a site to resolve transmissive and low-k zones. Conceptually, transmissive and low-k zones are thought to have at least a two order magnitude difference in hydraulic conductivity based on visual observations. If a difference of two orders of magnitude exists, the borehole has both transmissive and low-k zones. Two general conditions are observed in the cores and are presented in this thesis. The first is predominately sandy subsurface media. The first type of site defines the USCS classification silty sand and any particle smaller as low-k and the USCS classification fine sand and any particle larger as transmissive. The second type is predominately silt/clay subsurface media. The second type of site defines the USCS classification sandy silt and any particle smaller as low-k and the USCS classification silty sand and any particle larger as transmissive. This thesis presents the dividing point between the transmissive and low-k zones based on visual observations as opposed to actual measurements.

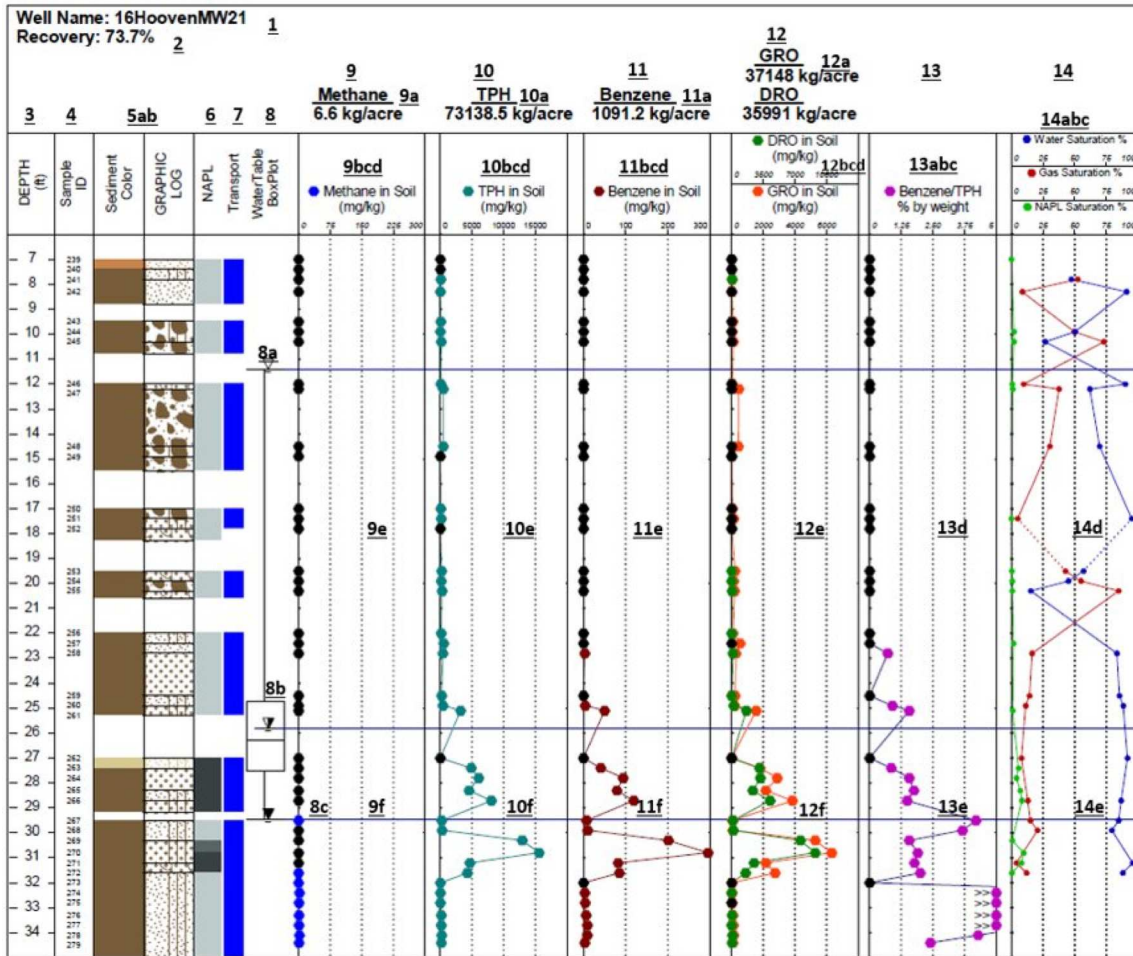


Figure 9: Standardization of Single Well Display

Each site was characterized based on an analysis of all the boreholes on site to determine a general distribution of subsurface media. In the future, consideration should be given to using cryogenic cores in laboratory studies to directly measure permeability.

2.4.4 Analytical: Total Mass in Place in Borehole, Transmissive Zones, and Low-k Zones

This section outlines the mathematical methods and equations used. The mass in place (M/L^2) for each Sample ID is defined as

Equation 1: Mass in Place (M/L^2)

$$\hat{\omega}_i = \omega_i * z_i * \rho_b$$

where ω_i is the mass of contaminant in mass of soil (M/M), z_i is the depth interval represented by the Sample ID (L), and ρ_b is the bulk density (M/L^3) of the Sample ID. $\rho_{b,i}$ is calculated for each Sample ID, unless information is unavailable or incomplete, and is defined as

Equation 2: Bulk Density (M/L^3)

$$\rho_{b,i} = \phi_i * \rho_{Quartz}$$

where ϕ_i is our calculated porosity (L^3/L^3) and ρ_{Quartz} is the density (M/L^3) of quartz (2.65 gm/cm³). The total mass in place (M/L^2) for the borehole is defined as

Equation 3: Total Mass in Place (M/L^2)

$$\hat{\omega}_{Total} = \sum_{i=1}^n \hat{\omega}_i$$

where n is the number of Sample IDs in the borehole, $\hat{\omega}_i$ is the mass in place (M/L²) for the selected parameters, and the operation sums all sample IDs for a borehole. The total mass in transmissive zones is defined as

Equation 4: Total Mass in Place (M/L²) in Transmissive Zones

$$\hat{\omega}_T = \sum_{i=if\ transmissive,1}^{n_{Transmissive}} \hat{\omega}_i$$

where $n_{Transmissive}$ is the number of Sample IDs in transmissive zones, “ $i = if\ transmissive, 1$ ” is selectively adding mass in transmissive zones only, $\hat{\omega}_i$ is the mass in place (M/L²) for the selected parameters, and the operation sums all transmissive sample IDs for a borehole. The total mass in low-k zones is defined as

Equation 5: Total Mass in Place (M/L²) in Low-k Zones

$$\hat{\omega}_{Lk} = \sum_{i=if\ low\ k,1}^{n_{Low\ k}} \hat{\omega}_i$$

where $n_{Low\ k}$ is the number of Sample IDs in low-k zones, “ $i = if\ low\ k, 1$ ” is selectively adding mass in low-k zones only, $\hat{\omega}_i$ is the mass in place (M/L²) for the selected parameters, and the operation sums all low-k sample IDs for a borehole. The total mass of all contaminants (M/L²) in the borehole is defined as

Equation 6: Total Mass of Contaminants in Place (M/L²)

$$\hat{\omega}_{Total,SUMCOC} = \sum_{i=1}^{n_{contaminants}} \hat{\omega}_{Total,i}$$

Where $n_{contaminants}$ is the number of number of contaminants measured in the borehole, $i = 1$ is adding the total mass of each contaminant, $\widehat{\omega}_{Total,i}$ is the total mass in place (M/L²) for the selected contaminant, and the operation sums all total contaminant masses for a borehole. Hydrocarbon boreholes sum benzene and TPH. Chlorinated solvent boreholes sum DCE, PCE, TCE, and/or VC.

The amount of core lost from drilling needs to be considered in assumptions in order for the mass in the hole to be continuous. Any lost length of core from the sampling procedure was divided evenly and the top half of lost core copies data from the point before it and the bottom half of lost core copies data from the point after it. This was done instead of ignoring losses or only using a single point because the data points before and after the lost core are usually significantly different.

2.4.5 Analytical: Fraction of Primary COC in Transmissive and Low-k Zones

The fraction of sampled borehole that is transmissive (L/L) is defined as

Equation 7: Fraction of Sampled Borehole that is Transmissive (L/L)

$$f_T = L_{transmissive} / L_{sampled}$$

where $L_{transmissive}$ (L) is the feet of core that is defines as transmissive and $L_{sampled}$ (L) is the total feet of core sampled. The fraction of sampled borehole that is low-k (L/L) is defined as

Equation 8: Fraction of Sampled Borehole that is Low-k (L/L)

$$f_{Lk} = L_{Low k} / L_{sampled}$$

where $L_{Low\ k}$ (L) is the feet of core that is defines as low-k and $L_{Sampled}$ (L) is the total feet of core sampled. The fraction of sampled borehole that is transmissive (L/L) and the fraction of sampled borehole that is low-k (L/L) are defined as

Equation 9: Fractions of Sampled Borehole equal 1 (L/L)

$$f_T + f_{Lk} = 1$$

where the sum of the two variables equals one. In this thesis percentages are the preferred method of data presentation. It is important to transform the mass in place (M/L^2) to fraction of mass (M/M) in each zone for each core. It is possible to compare mass in place (M) between sites and cores, but this paper needs to be able to compare cores that have drastically different masses of contamination, different depth intervals and different COCs. The fraction of contaminant of concern, COC_i , (M/M) in the transmissive zones of the borehole is defined as

Equation 10: The fraction of contaminant of concern, COC_i , (M/M) in the transmissive zones of the borehole

$$COC_i f_T = \hat{w}_T(COC_i) / \hat{w}_{Total}(COC_i)$$

Equation 11: The fraction of contaminant of concern, benzene, (M/M) in the transmissive zones of the borehole

$$COC_{benzene} f_T = \hat{w}_T(COC_{benzene}) / \hat{w}_{Total}(COC_{benzene})$$

where $\hat{w}_T(COC_i)$ is the mass of the COC_i per area (M/L^2) in the transmissive zones and $\hat{w}_{Total}(COC_i)$ is the total mass of the COC_i per area (M/L^2) in the borehole. The fraction of contaminant of concern, COC_i (M/M), that is in low-k zones of the borehole is defined as

Equation 12: The fraction of contaminant of concern, COC_i , (M/M) in the low-k zones of the borehole

$$COC_i f_{Lk} = \hat{\omega}_{Lk}(COC_i) / \hat{\omega}_{Total}(COC_i)$$

Equation 13: The fraction of contaminant of concern, benzene, (M/M) in the low-k zones of the borehole

$$COC_{benzene} f_{Lk} = \hat{\omega}_{Lk}(COC_{benzene}) / \hat{\omega}_{Total}(COC_{benzene})$$

where $\hat{\omega}_{Lk}(COC_i)$ is the mass of the COC_i per area (M/L^2) in the low-k zones and $\hat{\omega}_{Total}(COC_i)$ is the total mass of COC_i per area (M/L^2) in the borehole. The fraction of COC_i (M/M), that is in transmissive zones and the fraction of COC_i (M/M) that is in low-k zones is defined as

Equation 14: The fractions of contaminant of concern equals 1

$$COC_i f_T + COC_i f_{Lk} = 1$$

where the sum of the two variables equals one. In this thesis percentages are the preferred method of data presentation.

The focus of the statistics is on the difference between the percent of the borehole that is low-k and the percent of contaminant or contaminants in low-k zones (L/L-M/M). This is defined as

Equation 15: Difference between the percent of the borehole that is low-k and the percent of contaminant or contaminants in low-k zones (L/L-M/M)

$$\Delta f_{Lk, COC_i} f_{Lk} = \%f_{Lk} - \%COC_i f_{Lk}$$

Where f_{Lk} is the fraction of sampled borehole that is low-k (L/L) and $COC_i f_{Lk}$ is the fraction of COC_i (M/M) that is in low-k zones of the borehole. The difference is then put through a basic statistical analysis and plot as a box plot with extra visuals. All statistics are included in inter-site analysis. Intra-site analysis does not include statistics because only Site A and B would have enough boreholes, seven boreholes, for such analysis.

2.4.6 Analytical: Intra-Site and Inter-Site Comparison

The mass in place and percent mass in place will be used to provide comparisons of cores across a single site and across multiple sites. Every borehole and every site will have both mass in place data and percent of total mass in transmissive and low-k zones. The intra-site analysis will include a graphic and tabular summary of all boreholes and a site average specific to each site. The inter-site analysis will include selective borehole comparisons from differing sites and graphic and tabular summaries of all COCs at hydrocarbon sites, chlorinated solvent sites and all contaminated sites.

CHAPTER 3: RESULTS

This section presents the results for intra-site comparisons and inter-site comparisons. Results presented herein are good to no more than a single significant figure. Additional significant figures are retained to facilitate checking sums and future manipulation of values. The results for inter-site comparisons are presented on a site by site basis. They classify the subsurface media into transmissive or low k zones, outline key features of borehole concentrations by depth, calculate the mass of contaminants in zones, and calculate the percent of mass of contaminants in zones. The results for inter-site comparisons are presented on a contaminant basis extending across sites. Inter-site results present comparisons for hydrocarbon contaminated boreholes, comparisons for chlorinated solvent contaminated boreholes, and comparisons for all boreholes together. Inter-site results include relevant statistics accompanying mass in place visuals. As a special note, the principle objective of this work is to demonstrate methods for intra-site and inter-site comparisons of cryogenic core data. An exhaustive review of the basis for the conditions observed in transmissive and low-k subsurface media is beyond the scope of this thesis.

3.1 Intra-Site Analysis

Analysis begin with intra-site results. Sites A-H are presented in order with their respective boreholes.

3.1.1 Intra-Site A

Site A is a former wood treatment site where PCP was employed in a mineral carrier oil. The geologic setting is a glacial outwash at the terminus of an extinct continental ice sheet. At

Site A, media containing silt and finer media is characterized as low-k. All media without silt is characterized as transmissive.

3.1.1.1 Contamination by Depth

Figure 10 is an illustrative graphic from gINT™ that advances cryogenic coring data by including geologic and contaminant data-by depth for the cored interval from Borehole A1. Starting on the left, the geologic graphic includes depth from ground surface, Sample ID, sediment color, graphic log, NAPL visual, transport visual, and 3 points for water table data. The contaminant data-by-depth then plots methane, TPH, PCP, DRO, and GRO concentrations. Finally, this graphic plots the saturations percentages of water, gas, and NAPL. The key findings for borehole A1 include:

- 73% of the core was recovered.
- The zone targeted by LIF is largely characterized by transmissive zones with low-k zones present in areas of high contamination.
- A1 successfully bounds the zone targeted by LIF (26-32 feet bgs) inside the small cored interval (24-33.5 feet bgs).
- A1 has the most mass of contaminant PCP for all the boreholes collected from Site A with several, large off scale concentration spikes.
- There does not appear to be a correlation with concentration spikes of TPH and PCP.
- The percentage of gas increases past 50% below the water table at the depth of highest contamination (31 feet bgs). This could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017).

Borehole A1 has both transmissive and low-k zones and is a good representative of the LNAPL contamination of other boreholes at Site A. However, A1 is an outlier due to the high concentration of PCP observed. Like the other boreholes on site, the saturations percentages of water, gas, and LNAPL along with the presence of methane provide evidence for active microbial populations Garg et al (2017).

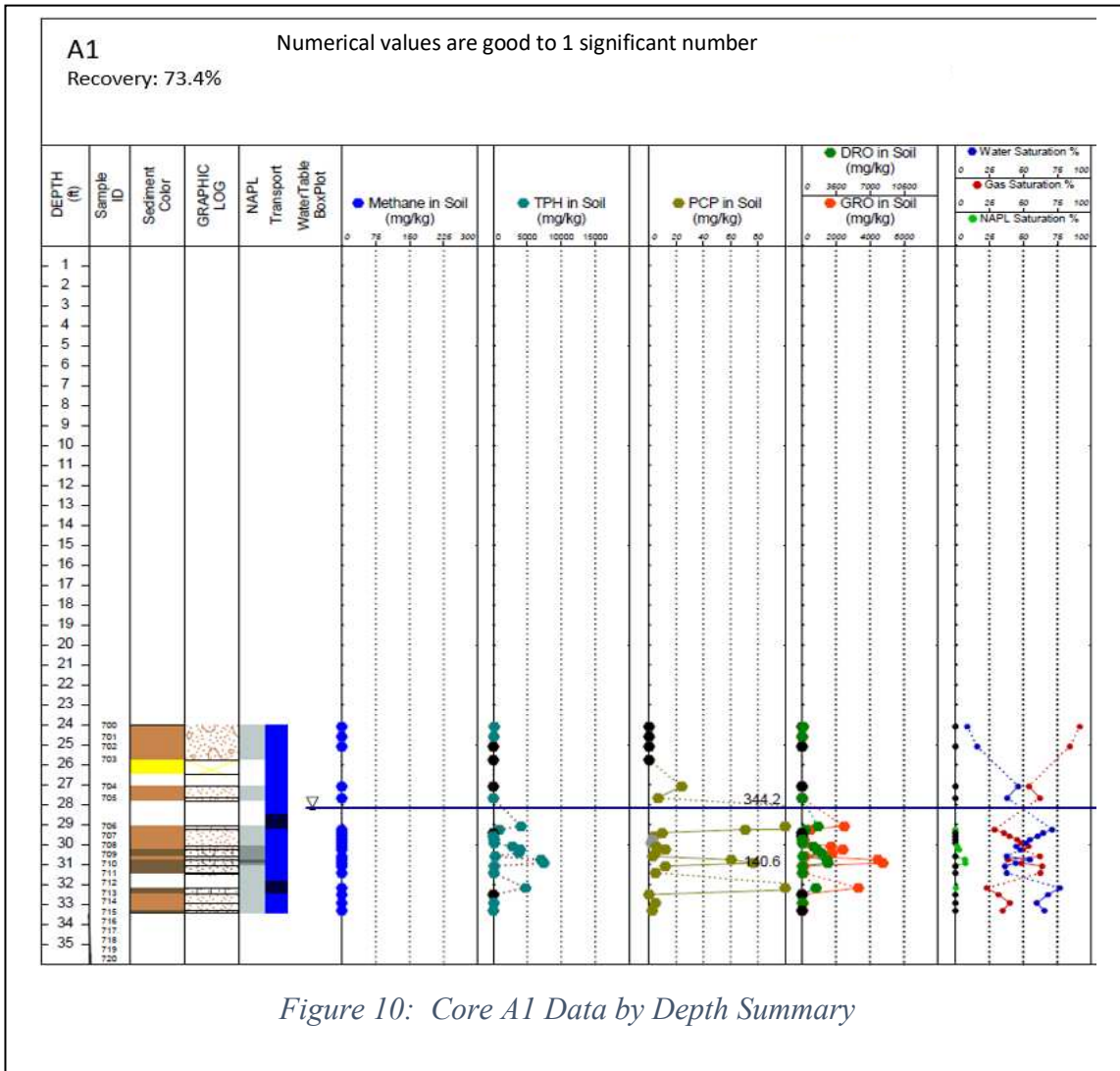


Figure 10: Core A1 Data by Depth Summary

Figure 11 is an illustrative graphic from gINT™ that follows the format of Figure 10.

The key findings for Borehole A2 include:

- 77% of the core was recovered.

- The zone targeted by LIF is largely characterized by transmissive zones with definitive low-k pockets throughout the cored interval.
- A2 successfully bounds the zone targeted by LIF (25-31.5 feet bgs) in the cored interval (21.5-33 feet bgs).
- A2 has almost no PCP contamination found. There is a single data point that positively measured PCP (21.5 feet bgs).
- The gas percentage below the water table pushes past 50% when the area has high contamination (25.5 feet bgs, 27.5 feet bgs, and 29.5 feet bgs) and 0.5%-5% NAPL saturation percentages. This could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017).

Borehole A2 has a similar trend for contamination that is seen in boreholes A3-A7. A2 has both transmissive and low-k zones and is a good representative of the LNAPL and PCP contamination of other boreholes at Site A. Like the other boreholes on site, the saturations percentages of water, gas, and LNAPL provide evidence for active microbial populations Garg et al (2017).

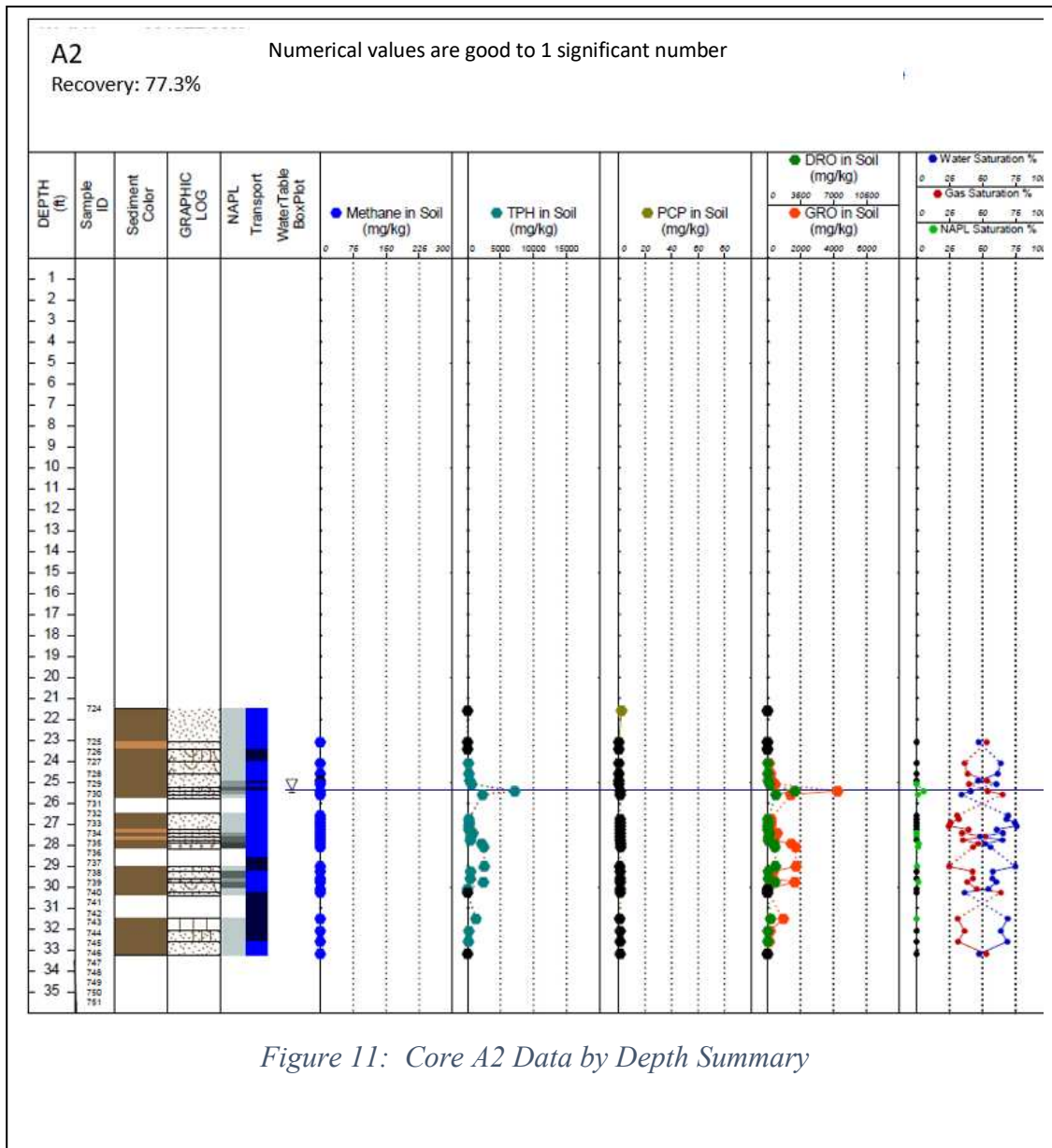


Figure 12 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole A3 include:

- 74% of the core was recovered.
- The zone targeted by LIF looks well represented by both transmissive and low-k zones throughout the cored interval.

- A3 successfully bounds the zone targeted by LIF (25-31.5 feet bgs) inside the cored interval (21.5-31.5 feet bgs).
- A3 has a small interval (24.5-26 feet bgs) that is PCP contaminated. It is still a magnitude less contamination than A1.
- Both times the gas saturation passes 50% there is a 1-4% NAPL saturation and high TPH concentrations at their respective depths. This could be evidence for pooling of natural source zone depletion (NSZD) gasses as they try to vertically move, Garg et al (2017) Kiaalhosseini et al. (2017).

Borehole A3 continues the trend in contamination that is seen in boreholes A2, and A4-A7. A3 is well represented by both transmissive and low-k zones and is a good representative of the LNAPL and PCP contamination of other boreholes at Site A. Like the other boreholes on site, the saturations percentages of water, gas, and LNAPL provide evidence for active microbial populations Garg et al (2017)

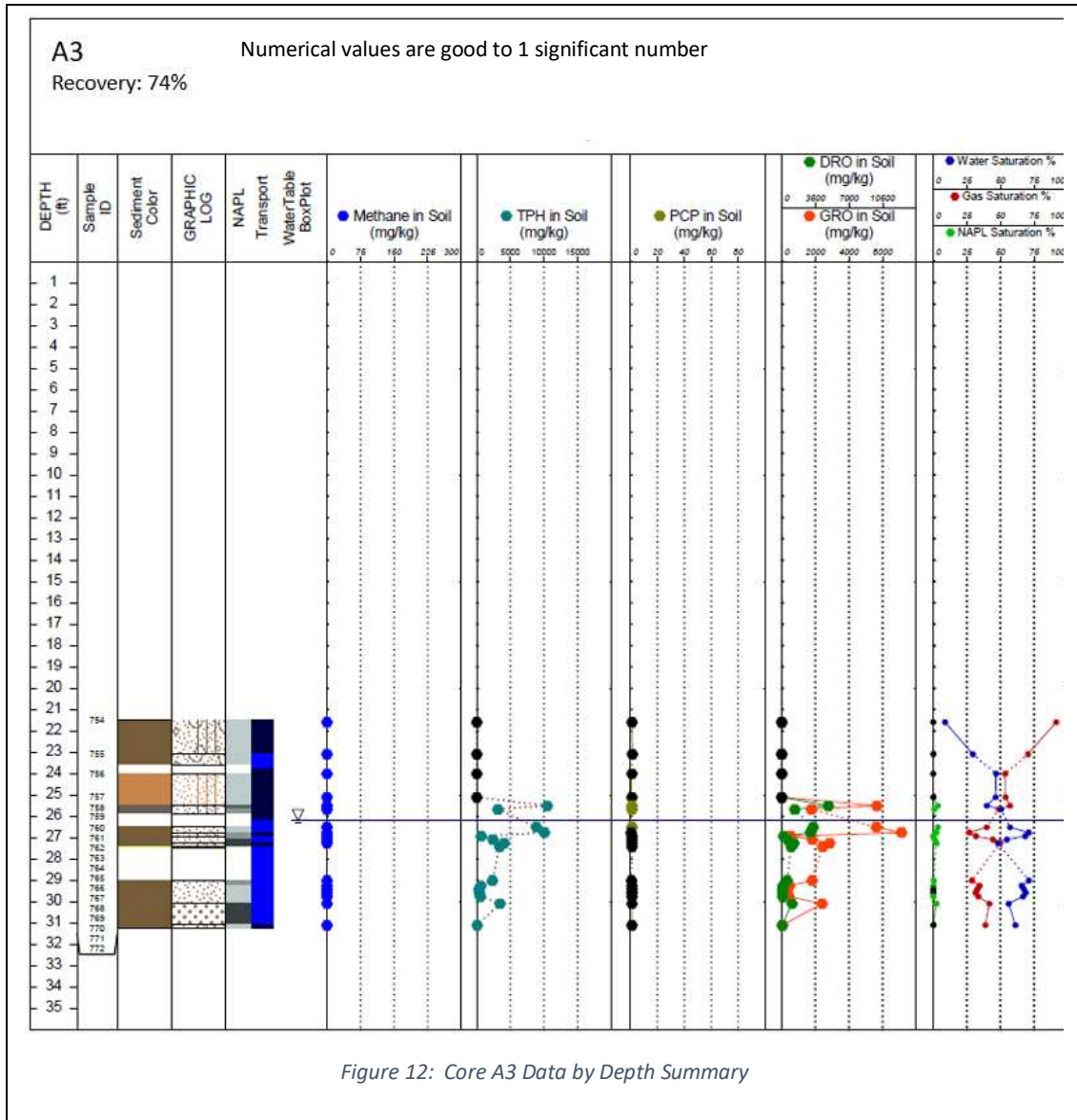


Figure 13 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole A4 include:

- 64% of the core was recovered.
- The core is evenly represented by transmissive and low-k zones. Transmissive zones dominate the top half where low-k zones dominate the bottom.

- A4 successfully bounds the zone targeted by LIF (25-28 feet bgs) in the cored interval (24-31 feet bgs).
- A4 has a small interval (24-27 feet bgs) that is contaminated with PCP. A4 has similar PCP distribution to core A3.
- TPH contamination is the largest on the site and it is mostly due to the calculated mass from a single data point at approximately 27 ft. This data point has been vetted extensively and is an accurate measurement. TPH is the sum of DRO and GRO and both constituents were found at very high concentrations. This data point is sampled from subsurface media that is classified as low-k.
- At 27 feet bgs, high gas percentages are expected because it is at the point of extreme contamination, but the gas percentage drops to its lowest at this point. This provides possible evidence for multiple microbial communities or proper vertical pathways for NSZD gasses to escape, Garg et al. (2017) & Kiaalhosseini et al. (2017).
- At 28 feet bgs, gas percentage crosses 50% for the first time and does not correlate with any contamination. This is below the extreme contamination and above a section of core lost during recovery and provides possible evidence for contaminant mass not being represented due to losses.

Borehole A4 continues the trend in contamination that is seen in boreholes A2, A3 and A5-A7. A4 is well represented by both transmissive and low-k zones and is a good representative of the LNAPL and PCP contamination of other boreholes at Site A. A4 does have the highest concentrations of LNAPL even though it was minor PCP concentrations. Like the other

boreholes on site, the saturations percentages of water, gas, and LNAPL provide evidence for active microbial populations Garg et al (2017).

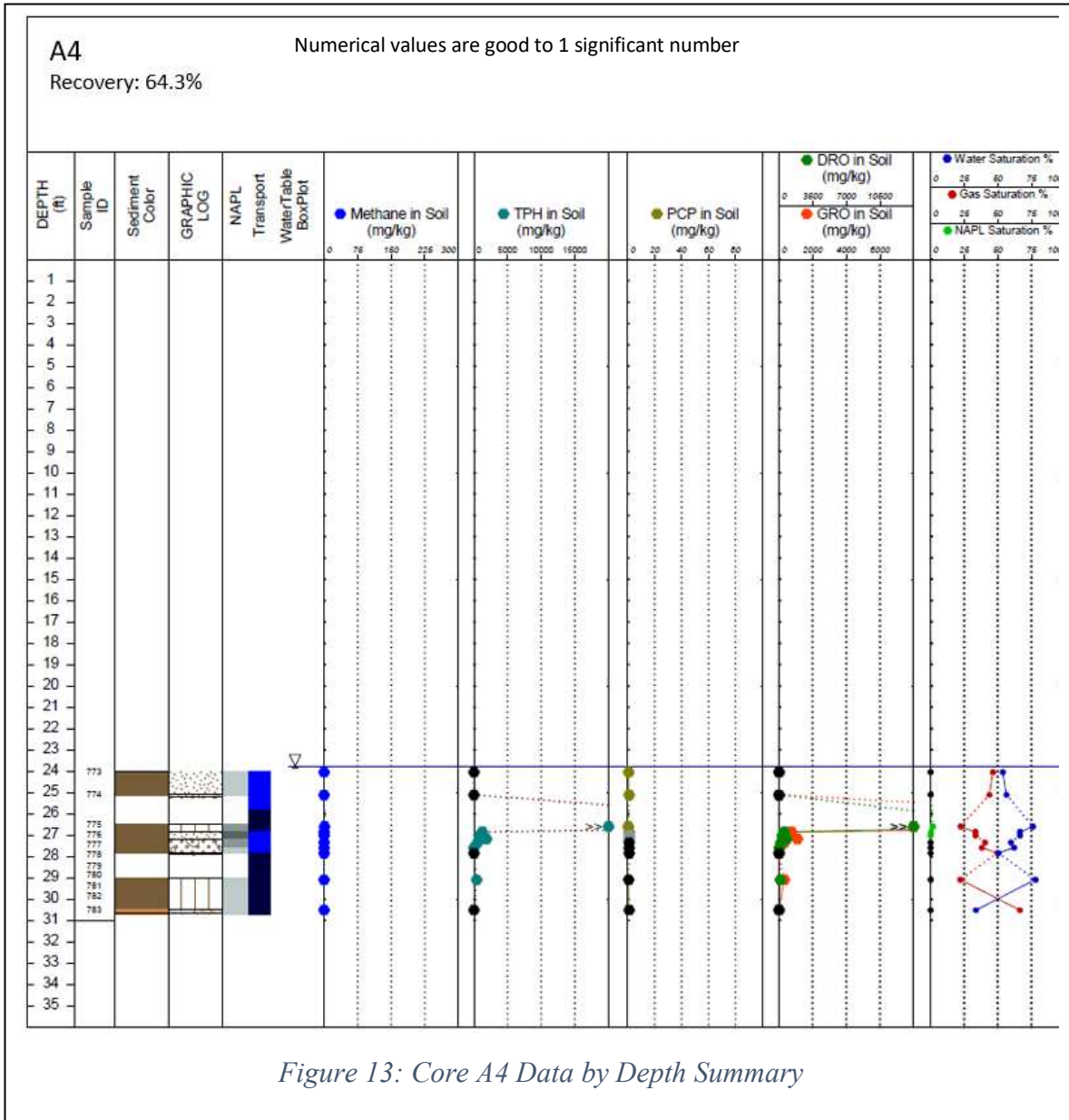


Figure 14 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole A5 include:

- 70% of the core was recovered.
- The core is evenly represented by transmissive and low k zones.
- A5 successfully bounds the zone targeted by LIF (24-28 feet bgs) in the cored interval (21.5-31 feet bgs).
- The contamination of PCP at A5 behaves similarly to A2. A5 has a single data point that positively measured PCP contamination at 25 feet bgs.
- At 25 feet bgs, gas saturation cross 50% saturation and there is a 1-4% LNAPL saturation and high TPH concentrations at depth. This could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017).
- At 27.5 feet bgs, there is a third point where gas percentage reaches 48% above a section of core that was not recovered. This could provide possible evidence that the section no recovered was contaminated.

Borehole A5 continues the trend in contamination that is seen in boreholes A2-A4, A6, and A7. A5 is evenly represented by both transmissive and low-k zones and is a good representative of the LNAPL and PCP contamination of other boreholes at Site A. Like the other boreholes on site, the saturations percentages of water, gas, and LNAPL provide evidence for active microbial populations Garg et al (2017).

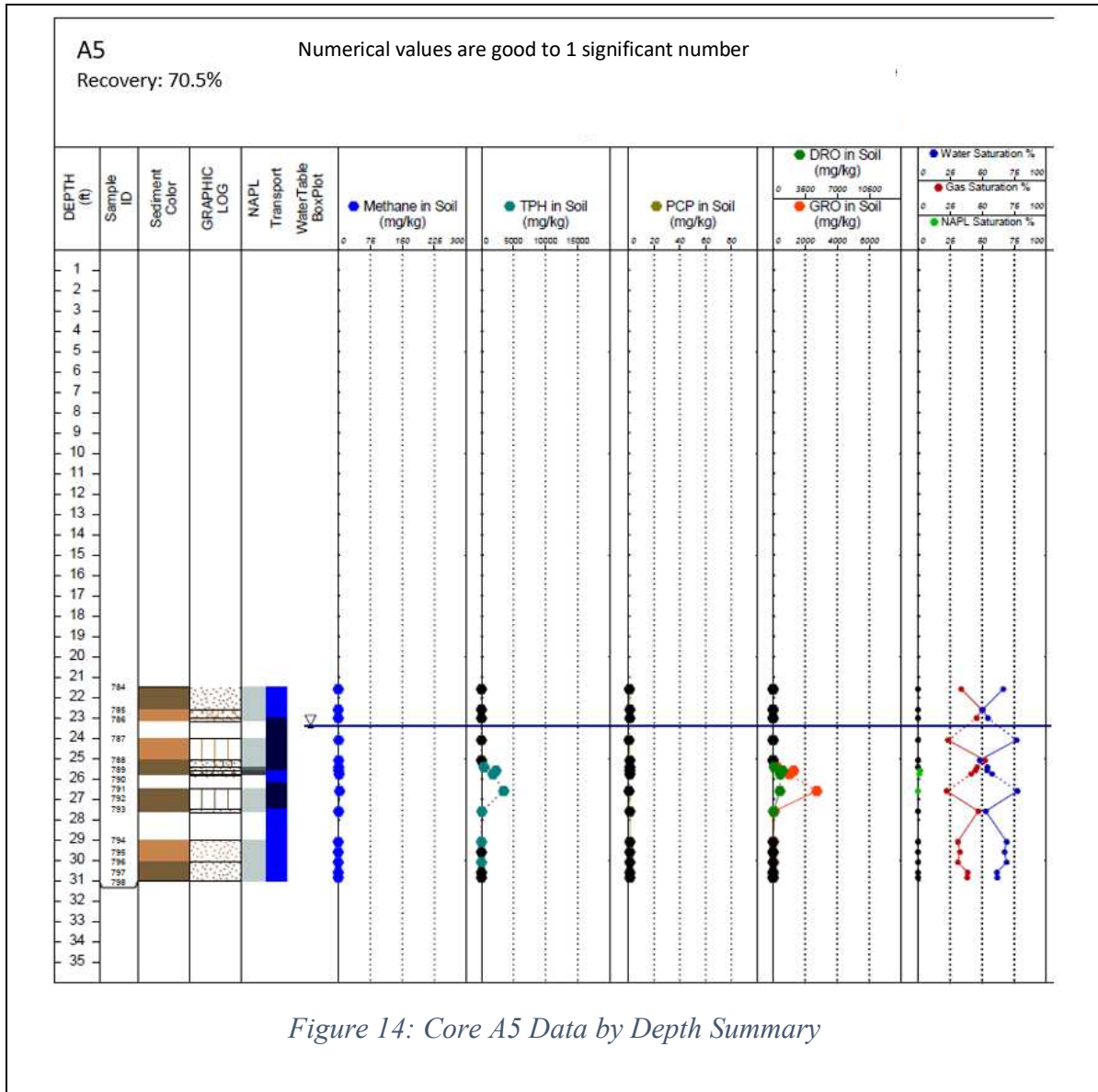


Figure 15 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole A6 include:

- 85% of the core was recovered.
- The borehole is dominated by transmissive zones with sporadic low-k zones.
- A6 bounds the zone targeted by LIF (18-22 feet bgs) in the cored interval (18-22 feet bgs).

- A6 has a small interval (19-21.5 feet bgs) that is PCP contaminated much like A3 and A4.
- At 18.5 feet bgs and 20 feet bgs, gases cross 50% saturation and correlate to a 1-4% NAPL saturation and high TPH concentrations at respective depths. This could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017).

Borehole A6 continues the trend in contamination that is seen in boreholes A2-A5 and A7. A6 is dominated by transmissive with low-k zones present. It is a good representative of the LNAPL and PCP contamination of other boreholes at Site A. Like the other boreholes on site, the saturations percentages of water, gas, and LNAPL provide evidence for active microbial populations Garg et al (2017).

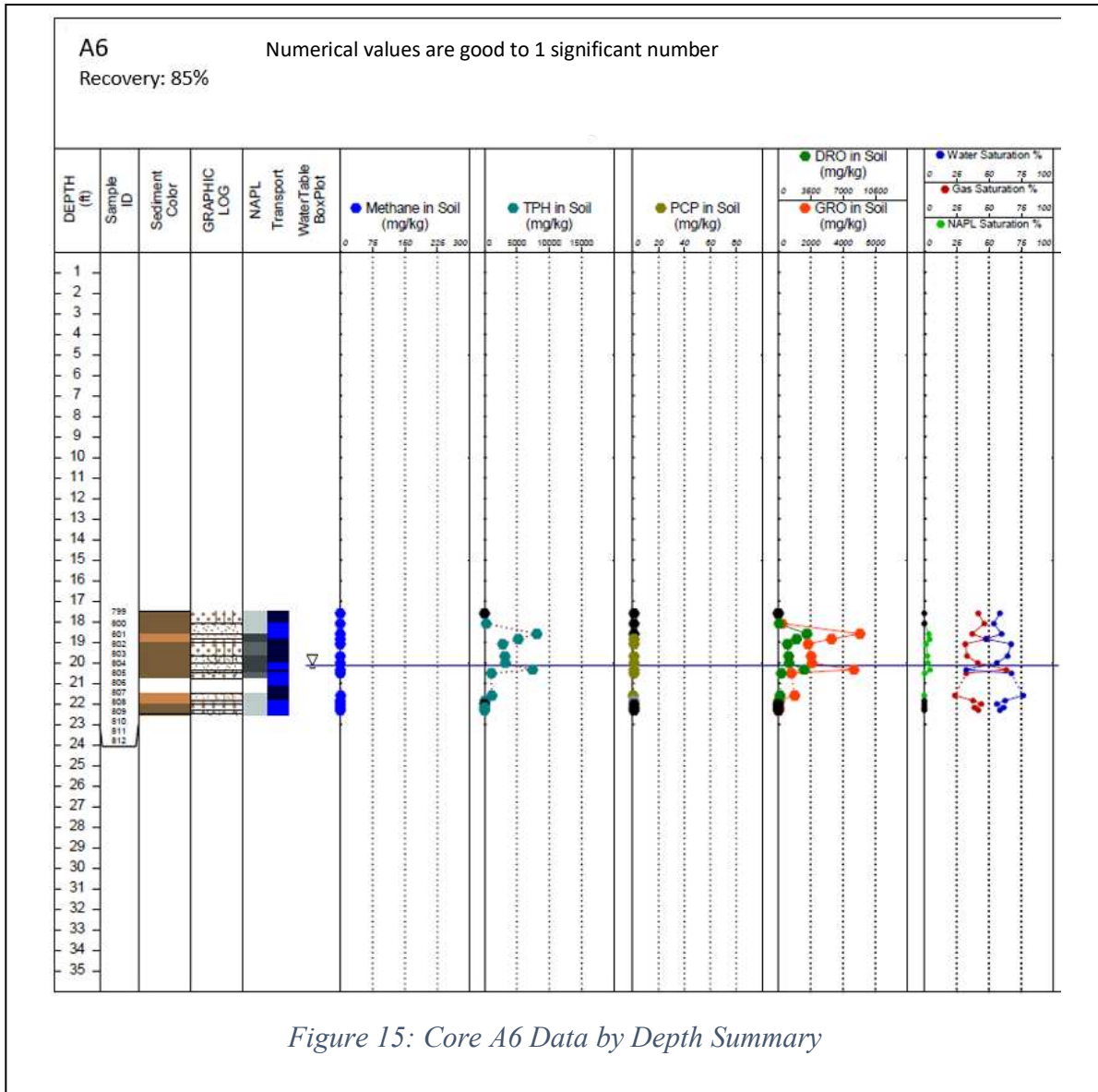
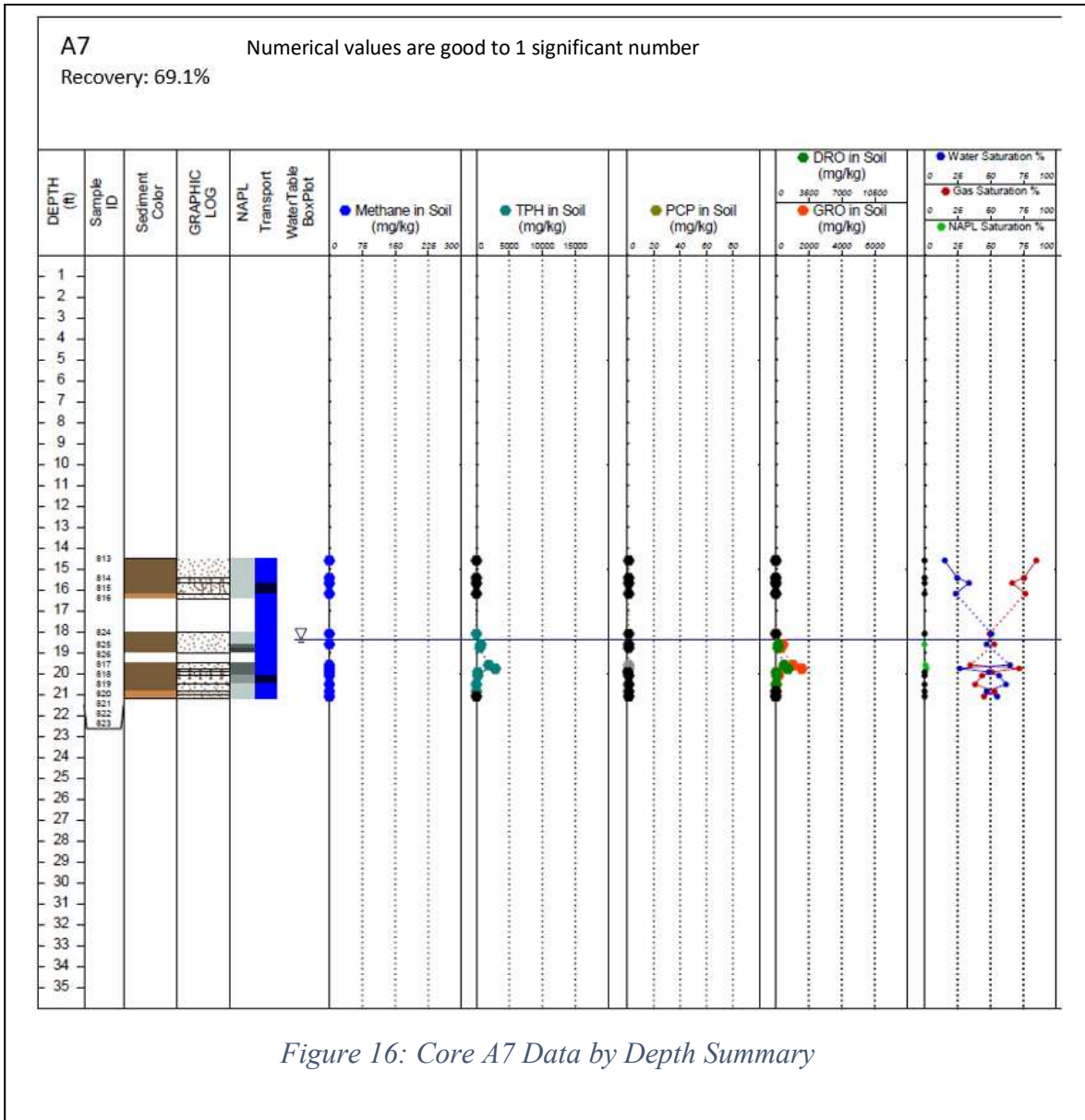


Figure 16 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole A7 include:

- 69% of the core was recovered.
- The core is mostly transmissive with small intervals of low k.

- A7 successfully bounds the zone targeted by LIF (18-20.5 feet bgs) inside the cored interval (14.5-21.5 feet bgs).
- A7 has almost no PCP contamination found similar to A2 and A5. There is a single data point that positively measured PCP (19.5 feet bgs). A7 has the smallest TPH contamination with a portion in low k zones.
- At 19.5 feet bgs , gases nearly reach 75% saturation and correlate to a 1-4% NAPL saturation and TPH concentrations of other boreholes at Site A. This could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017).
- At 21 feet bgs, there is a third point where gas percentage reaches 48%. It is unclear if this is a product of natural processes or a product of contamination below the sampled core.

Borehole A7 finishes the trend in contamination that is seen in boreholes A2-A6. A7 is dominated by transmissive with low-k zones present. Like the other boreholes on site, the saturations percentages of water, gas, and LNAPL provide evidence for active microbial populations Garg et al (2017).



3.1.1.2 Mass in Place Summary Analysis

Using the information presented from the previous paragraphs, the mass of contaminants are calculated using Equations 1-3. The key findings for mass of contaminants in the borehole (Table 11) include:

- The masses of TPH for all boreholes ranges between 1.18 kg/m² and 3.08 kg/m² (Table 11).

- Excluding outliers A4 and A7, TPH ranges between 2.96 kg/m² and 7.41 kg/ m² (Table 11).
- A1 is an outlier and is the only core with a large portion of PCP contamination at 0.19 kg/ m² (Table 11).
- All the cores, excluding A1, have a similar mass of PCP ranging between 0.0017 kg/ m² and 0.0042 kg/m² (Table 11).
- Methane is present in small consistent concentrations and has minimal representative mass in the borehole (Table 11). The high gas saturations promote the theory that active biodegradation is present in all cores including A1.

Table 11: Total Mass of Contaminants at Site A

Numerical values are good to 1 significant number.

Core	<u>PCP</u> kg/m ²	<u>Methane</u> kg/m ²	<u>TPH</u> kg/m ²	<u>GRO</u> kg/m ²	<u>DRO</u> kg/m ²	<u>SUM COC</u> kg/m ²
A1	1.95E-01	9.14E-05	5.06E+00	3.07E+00	1.98E+00	5.25E+00
A2	4.30E-03	2.89E-04	3.96E+00	2.69E+00	1.27E+00	3.97E+00
A3	3.65E-03	6.67E-05	7.56E+00	5.03E+00	2.53E+00	7.57E+00
A4	1.74E-03	3.88E-04	3.11E+01	1.71E+01	1.40E+01	3.11E+01
A5	2.75E-03	3.03E-03	2.99E+00	2.21E+00	7.76E-01	2.99E+00
A6	2.12E-03	2.89E-04	4.91E+00	3.22E+00	1.69E+00	4.91E+00
A7	3.36E-03	7.41E-05	1.19E+00	6.73E-01	5.16E-01	1.19E+00
Site A (AVG)	3.05E-02	6.10E-04	8.10E+00	4.85E+00	3.25E+00	8.13E+00

3.1.1.3 Mass in Transmissive and Low-k Zones Summary Analysis

The mass in transmissive and low-k zones is presented with two formats including 1) using equations 4 and 5 to calculate the mass in transmissive and low-k zones (M/L²) and 2) using Equations 6-10 to calculate the length of borehole that is transmissive/low-k (L/L) and to calculate the percent of total contaminant mass in transmissive/low-k zones (M/M). The key

findings for mass in transmissive and low-k zones (M/L^2) (Figure 17, Table 12, & Table 13) include:

- Site A has a large portion of the total mass of contaminants in low k zones (Figure 17, Table 12, & Table 13).
- Core A1 has over 0.14 kg/ m² PCP in low-k zones. Most of this mass comes from a single, vetted data point (Figure 17 & Table 12).
- All other cores besides A1, have PCP present in small masses in low-k zones (Figure 17 & Table 12).
- All cores, excluding A7, have less than 1 kg/m² THP in low-k zones. A4 has 29.6 kg/m² in low-k zones. The mass for A4 is largely attributed to a single, vetted data point. A7 has the least TPH contamination in core with less than 0.024 kg/m² TPH residing in low-k zones (Figure 17 & Table 13).
- The distribution of methane mass is similar throughout all boreholes. A4 and A5 are the only cores where methane prefers low-k zones (Table 12).

The average of Site A is useful to quantify total mass at the site in transmissive or low-k zones but it is not an accurate representation of any single core. For mass in place, it is much more beneficial to look at the boreholes independently than as a summary. The contaminants mass generally prefers transmissive zones but the contaminants mass in low-k zones is still possibly significant.

The mass of contaminant is now transformed into percentage of contaminant mass in subsurface zones (M/M). The key findings for percentage of contaminants in transmissive and low-k zones (Figure 18, Table 14, & Table 15) for Site A include.

- A1, A4, and A5 have a percentage of contaminant mass in low-k zones that does not correlate with the fraction of borehole that is low-k.
- A1 shows the strongest deviation across all contaminants from % f_{Lk} . A1 is the core where contaminants most prefer low-k zones.
- The distribution of TPH in transmissive and low-k zones at cores A1, A4, and A5 favors low-k zones, possibly significantly. The distribution of PCP in zones at core A1, A4, and A5 prefers transmissive zones.
- A4 and A5 have large TPH and methane deviations but small PCP deviations. PCP in these cores still prefers transmissive zones but >30% of the PCP mass is present in low-k.
- A2, A3, A6, and A7 have a percentage of contaminant mass in low k zones that correlates with the fraction that is low-k.
- A2 and A3 show slightly more deviation in (% f_{Lk} - % COC f_{Lk}) but % COC f_{Lk} is within a 10% deviation from % f_{Lk} . For both A2 and A3 the deviation (% f_{Lk} - % COC f_{Lk}) prefers transmissive zones over low-k zones.

Boreholes A1, A4, and A5 are very similar. The large mass of PCP at A1 and the large mass of TPH at A4 are each its own respective outlier. The boreholes at Site A present general contaminant preference for transmissive zones but still have a large portion of the total contaminant mass in low-k zones.

Many of the boreholes for Site A have similarities for concentration of contaminants by depth and total mass in place. There was not a direct correlation of PCP to TPH concentrations even though they are used together in industry practices. The recovery of cryogenically frozen core was also similar for all boreholes. The presence of cobbles made collecting continuous core

difficult with 65% to 85% core recovery. Overall, Site A provides a beneficial view into the distribution of contamination in subsurface media.

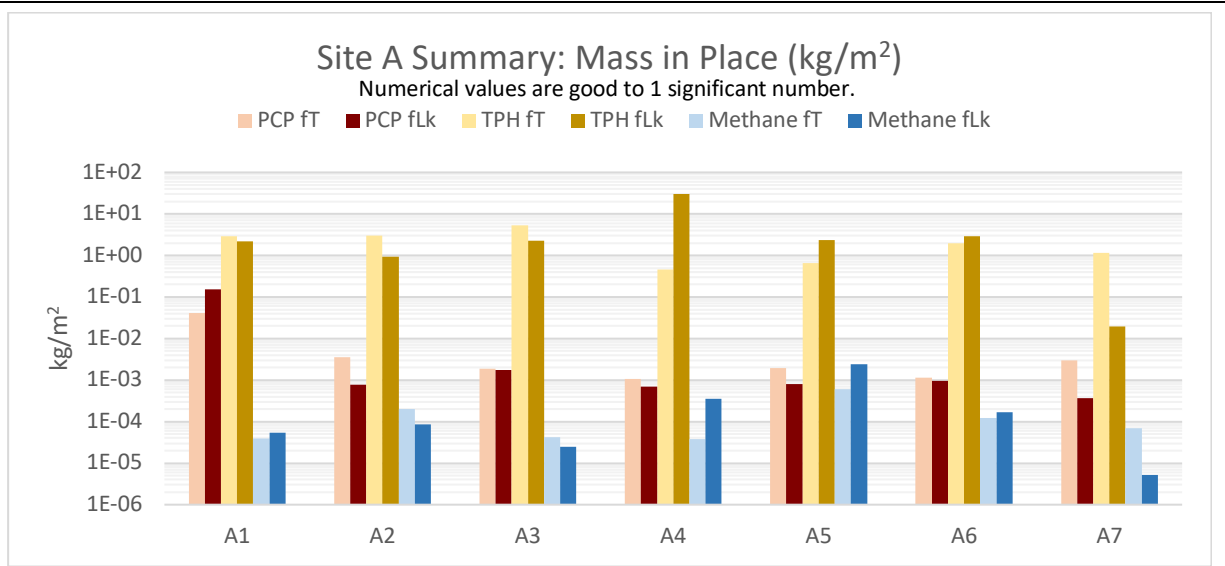


Figure 17: Mass of Contamination at Site A Divided into Zones

Table 12: Mass of PCP and Methane at Site A Divided into Zones
Numerical values are good to 1 significant number.

Core	PCP		Methane		SUM COCs	
	f _T	f _{Lk}	f _T	f _{Lk}	f _T	f _{Lk}
	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
A1	4.08E-02	1.55E-01	3.95E-05	5.44E-05	2.91E+00	2.35E+00
A2	3.52E-03	7.76E-04	2.03E-04	8.65E-05	3.04E+00	9.24E-01
A3	1.91E-03	1.75E-03	4.20E-05	2.47E-05	5.30E+00	2.27E+00
A4	1.06E-03	6.89E-04	3.95E-05	3.48E-04	4.58E-01	3.06E+01
A5	1.94E-03	8.08E-04	6.08E-04	2.42E-03	6.64E-01	2.32E+00
A6	1.15E-03	9.69E-04	1.21E-04	1.68E-04	1.98E+00	2.93E+00
A7	3.00E-03	3.63E-04	6.92E-05	4.94E-06	1.17E+00	2.01E-02
Site A (AVG)	7.63E-03	2.29E-02	1.61E-04	4.45E-04	2.22E+00	5.92E+00

Table 13: Mass of TPH, GRO, and DRO at Site A Divided into Zones
Numerical values are good to 1 significant number.

Core	TPH	TPH	GRO	GRO	DRO	DRO
	f _T	f _{Lk}	f _T	f _{Lk}	f _T	f _{Lk}
	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
A1	2.86E+00	2.19E+00	1.69E+00	1.38E+00	1.17E+00	8.14E-01
A2	3.04E+00	9.24E-01	2.04E+00	6.54E-01	1.00E+00	2.69E-01
A3	5.30E+00	2.26E+00	3.65E+00	1.39E+00	1.65E+00	8.77E-01
A4	4.57E-01	3.06E+01	2.74E-01	1.68E+01	1.83E-01	1.38E+01
A5	6.62E-01	2.32E+00	3.79E-01	1.83E+00	2.83E-01	4.93E-01
A6	1.97E+00	2.93E+00	1.29E+00	1.93E+00	6.80E-01	1.01E+00
A7	1.17E+00	1.97E-02	6.58E-01	1.51E-02	5.11E-01	4.69E-03
Site A (AVG)	2.21E+00	5.89E+00	1.43E+00	3.43E+00	7.83E-01	2.47E+00

Site A Summary by Borehole A1-A7 and Site A Total Ordered Transmissive to Low-k

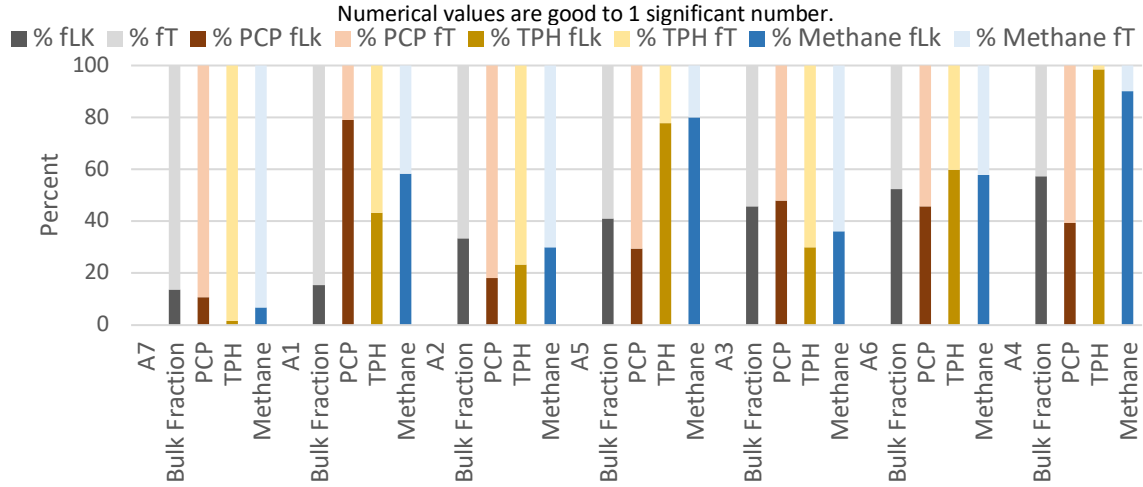


Figure 18: Percentage of Mass in Zones at Site A Ordered from Transmissive to Low-k

Table 14: Percentage of Borehole that is Transmissive of Low-k and Percentage of PCP and Methane Mass in Zones at Site A

Numerical values are good to 1 significant number.

Core	$\% f_T$	$\% f_{LK}$	$\% PCP f_T$	$\% PCP f_{LK}$	$\%$	
					Methane f_T	Methane f_{LK}
A1	84.50	15.50	20.90	79.10	41.73	58.27
A2	66.66	33.34	81.97	18.03	70.00	30.00
A3	54.15	45.85	52.13	47.87	63.80	36.20
A4	42.75	57.25	60.58	39.42	9.92	90.08
A5	58.92	41.08	70.55	29.45	20.04	79.96
A6	47.50	52.50	54.31	45.69	42.11	57.89
A7	86.25	13.75	89.18	10.82	93.16	6.84

Table 15: Percentage of TPH, GRO, and DRO Mass in Zones at Site A

Numerical values are good to 1 significant number.

Core	$\% TPH f_T$	$\% TPH f_{LK}$	$\% GRO f_T$	$\% GRO f_{LK}$	$\% DRO f_T$	$\% DRO f_{LK}$
A1	56.62	43.38	55.10	44.90	58.98	41.02
A2	76.69	23.31	75.70	24.30	78.79	21.21
A3	70.07	29.93	72.45	27.55	65.33	34.67
A4	1.47	98.53	1.61	98.39	1.31	98.69
A5	22.17	77.83	17.16	82.84	36.46	63.54
A6	40.23	59.77	40.16	59.84	40.36	59.64
A7	98.34	1.66	97.76	2.24	99.09	0.91

3.1.2 Intra-Site B

Site B is a former petroleum refinery. Primary COCs are benzene and TPH. A triplicate was collected in 2016, B1-3, along with a unfrozen core, B4. B1-4 came from an upgradient edge of an LNAPL body that is receding. The remaining 3 cores, B5-B7, were collected in 2018 from the middle of an extensive LNAPL body. B6 provides a missing section of B7 that is collected specifically from the interval missing from B7.

It includes 3 cryogenically collected cores (B1-B3) and a single unfrozen core (B4) sampled in 2016. Site B also includes 3 cryogenically collected cores sampled in 2018. The geologic setting is a glacial outwash at the terminus of an extinct continental ice sheet. At Site B, media containing silt and finer media is characterized as low-k. All media without silt is characterized as transmissive.

3.1.2.1 Contamination by Depth

Figure 19 is an illustrative graphic from gINT™ that advances cryogenic coring data by including geologic and contaminant data-by depth for the cored interval from Borehole B1. Starting on the left, the geologic graphic includes depth from ground surface, Sample ID, sediment color, graphic log, NAPL visual, transport visual, and 3 points for water table data with a year's worth of data presented in a boxplot. The contaminant data-by-depth then plots methane, TPH, benzene, DRO, and GRO concentrations. Next this graphic plots the percent ratio of concentrations of benzene over TPH. Finally, this graphic plots the saturations percentages of water, gas, and NAPL. The key findings for Borehole B1 include:

- 73% of the core was recovered.

- The zone targeted by LIF is largely characterized by low-k zones with transmissive zones dominating above zone targeted by LIF.
- Minor concentrations of methane were found at the bottom of core (29.5-35 feet bgs)
- B1 successfully bounds the zone targeted by LIF (25-32 feet bgs) inside the cored interval (0-35 feet bgs).
- Spikes in concentration of TPH correlate to spikes in concentration of benzene.
- Above 31.5 feet bgs, the % ratio of benzene to TPH where NAPL was visually observed under fluorescence is between 1.25-2.6%.
- Below 31.5 feet bgs, low concentrations of TPH produce high % ratio of benzene to TPH.
- B1 is the only borehole from 2016 with valid saturation data.

The interval of collection for Borehole B1 is much larger than the other boreholes from Site B. B1 provides a full view of contamination and subsurface media above of the zone targeted by LIF. B1 is a good representative of the contamination and geology of boreholes B2, B3, and B4. B1 is a good representative of the contamination at B5, B6, and B7 but not the geologic distribution. The saturations percentages of water, gas and NAPL along with the presence of methane provide evidence for active, biodegrading microbial populations (Garg et al. 2017). B1 is similar to B5, B6, and B7 because the saturations percentages of water, gas, and LNAPL correlate with the presence of methane.

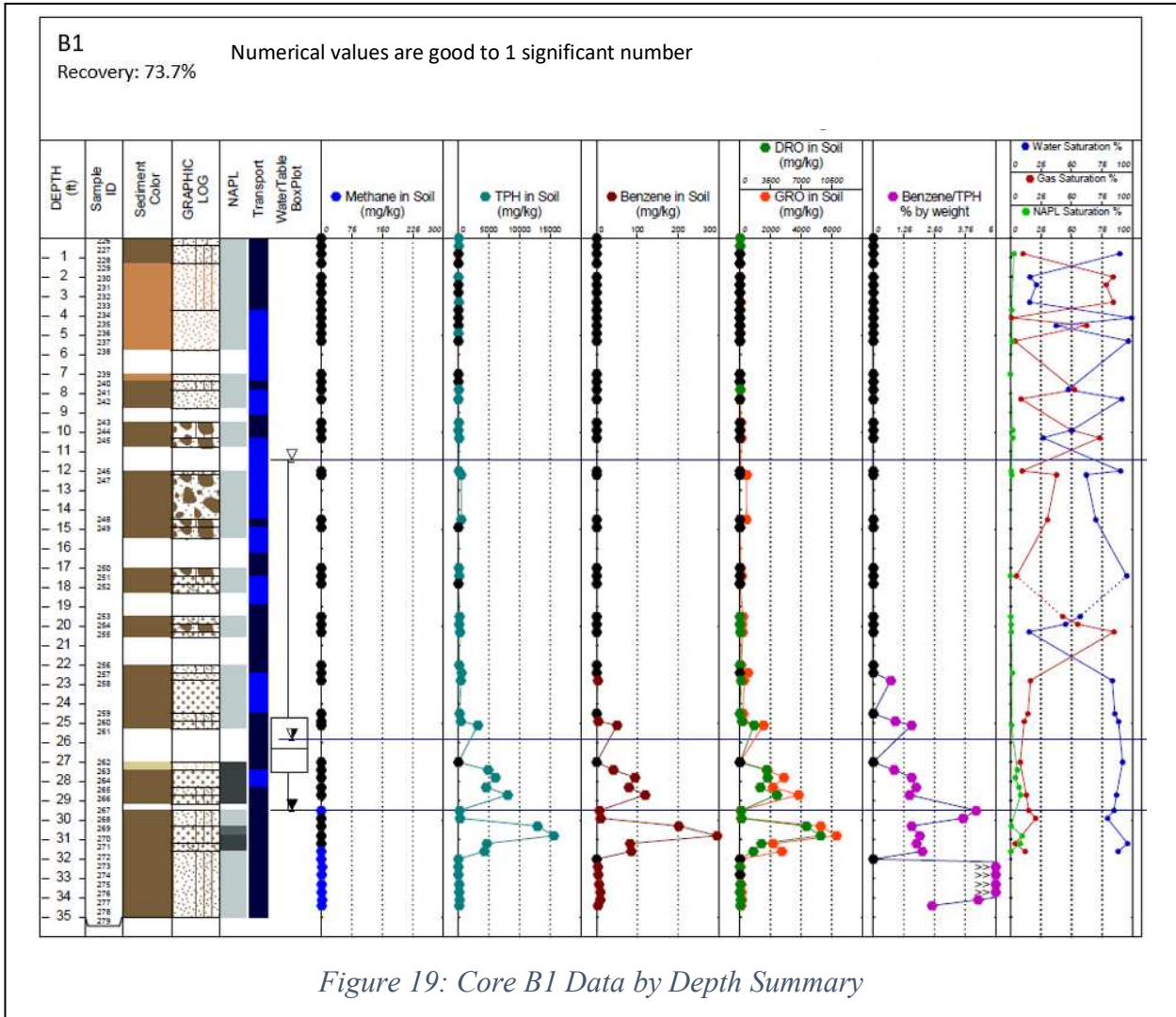


Figure 20 is an illustrative graphic from gINT™ that follows the format of Figure 19.

The key findings for Borehole B2 include:

- 87% of the core was recovered.
- The zone targeted by LIF is largely characterized by transmissive zones with small pockets of low-k zones throughout the cored interval.
- B2 successfully bounds the zone targeted by LIF (24-32.5 feet bgs) in the cored interval (24.5-35 feet bgs).

- The % ratio of benzene to TPH where NAPL was visually observed under fluorescence is between ~1.25-4%.
- The saturation percentages of water, gas, and NAPL were obtained before modifications were designed. The calculated percent saturation of water and gas is beyond possible limits (>100%) and the data was excluded.

The interval of collection for Borehole B2 is similar to B3. B2 is very similar in contamination and geology to B1, B3, and B4. The geology at B1, B2, B3, and B4 differs from B5, B6, and B7 in that it has a low-k zone at the bottom of the cored interval.

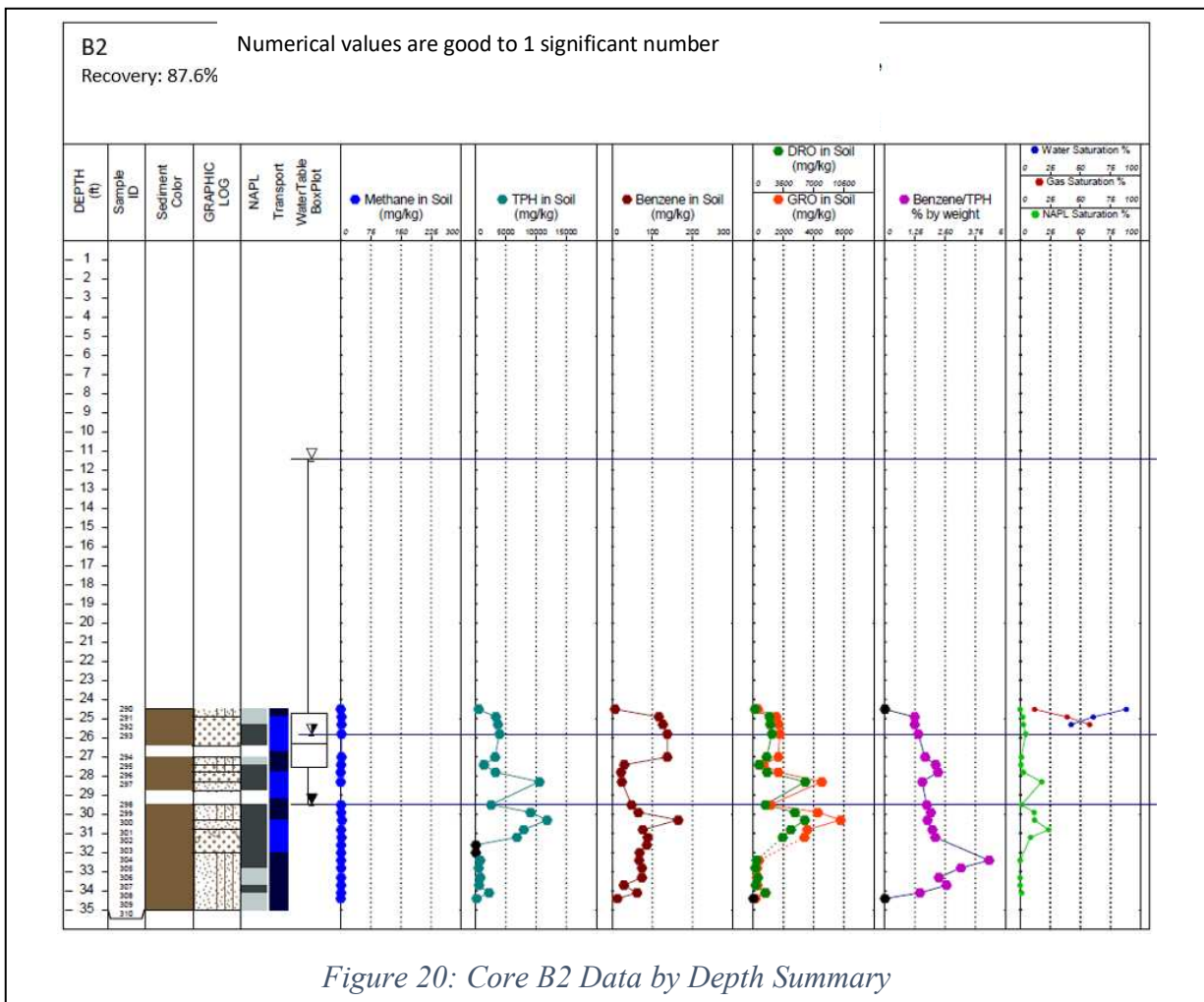


Figure 21 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole B3 include:

- 87% of the core was recovered.
- The zone targeted by LIF is largely characterized by transmissive zones with small pockets of low-k zones throughout the cored interval.
- B3 successfully bounds the zone targeted by LIF (25-32 feet bgs) inside the cored interval (24.5-35 feet bgs).
- B3 has the highest TPH concentrations at Site B.
- The % ratio of benzene to TPH where NAPL was visually observed under fluorescence is between ~1.25-5%.
- The saturation percentages of water, gas, and NAPL were obtained before modifications were designed. The calculated percent saturation of water and gas is beyond possible limits and the data was excluded.

The interval of collection for Borehole B3 is similar to B2. B3 is very similar in contamination and geology to B1, B2, and B4.

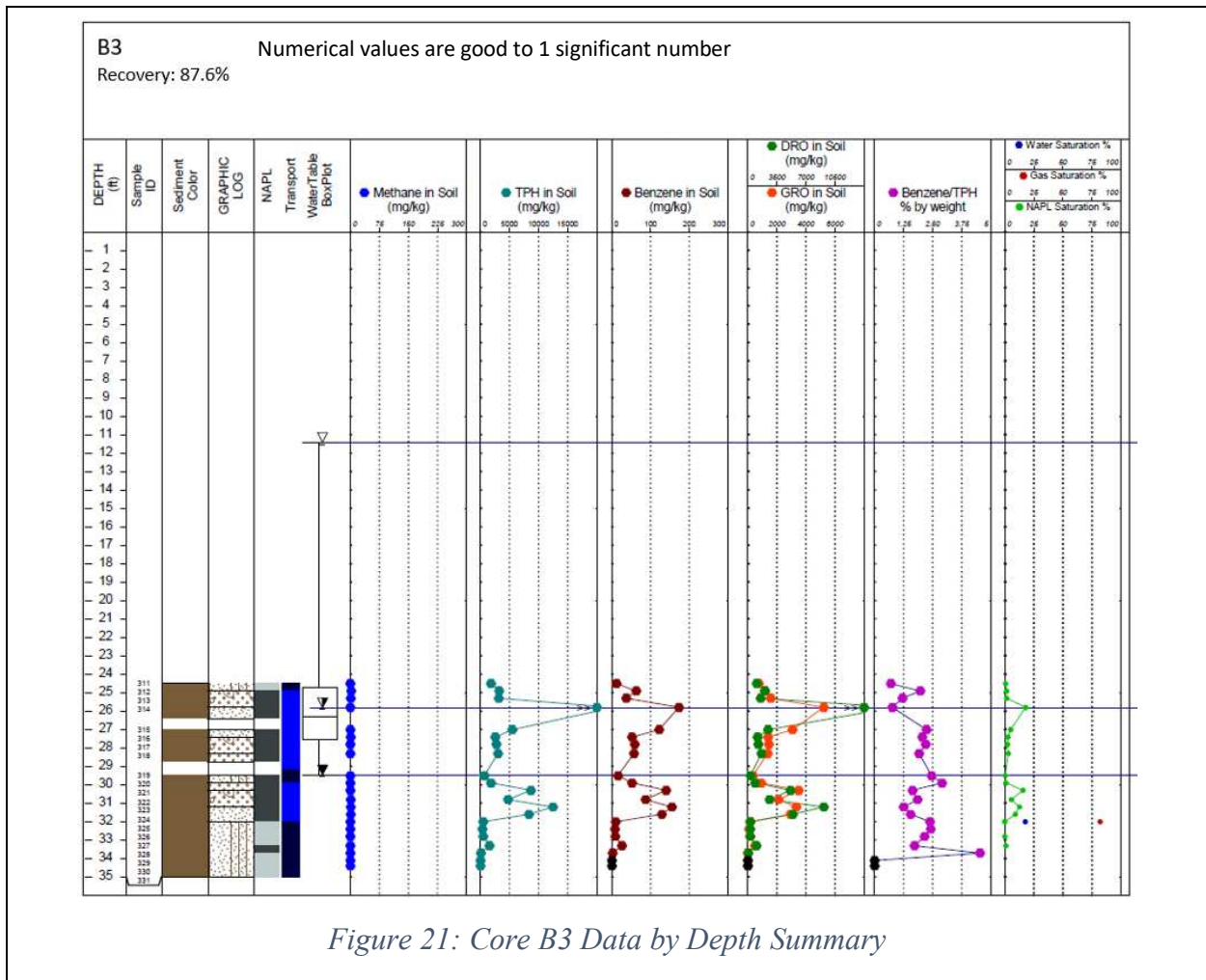


Figure 22 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole B4 include:

- 60% of the core was recovered.
- The core has both transmissive and low-k zones with low-k zones being more prevalent over the small interval of consideration.
- B4 unsuccessfully bounds the zone targeted by LIF in the cored interval (29-35 feet bgs).

- The % ratio of benzene to TPH where NAPL was visually observed under fluorescence is between ~1.25-3%.
- The saturation percentages of water, gas, and NAPL were obtained before modifications were designed. The calculated percent saturation of water and gas is beyond possible limits and the data was excluded.

The interval of collection for Borehole B4 is much smaller than the other boreholes from 2016. B4 has the least amount of contamination but the concentrations found in the small interval represent Site B well. B4 is very similar in contamination and geology to B1, B2, and B3. The geology at B1, B2, B3, and B4 does not match geology observed at B5, B6, and B7.

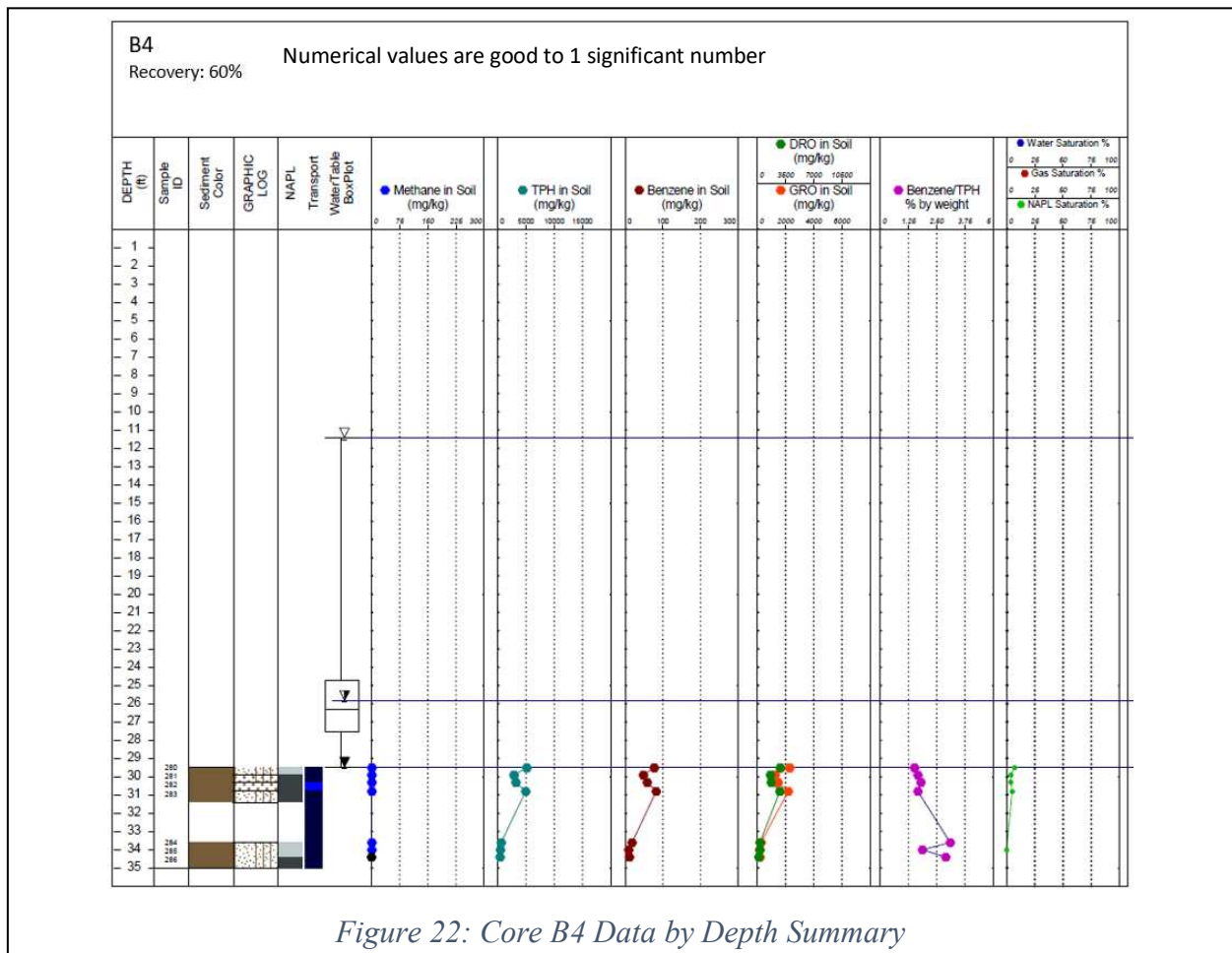


Figure 22: Core B4 Data by Depth Summary

Figure 23 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole B5 include:

- 93% of the core was recovered.
- The core is completely composed of transmissive zones.
- B5 partially captures the zone targeted by LIF (29-34.5+ feet bgs) in the cored interval (24.5-34.5 feet bgs).
- The % ratio of benzene to TPH where NAPL was visually observed under fluorescence is between ~1.5-5%.
- Spikes in concentrations of TPH and benzene correlate with spikes in percent saturation of gases.

B5 has gas saturations that could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017). B5 has contaminant concentrations that are representative of its location which is in the center of a large LNAPL plume in contrast to B1-B4 that are at the leading edge of the plume.

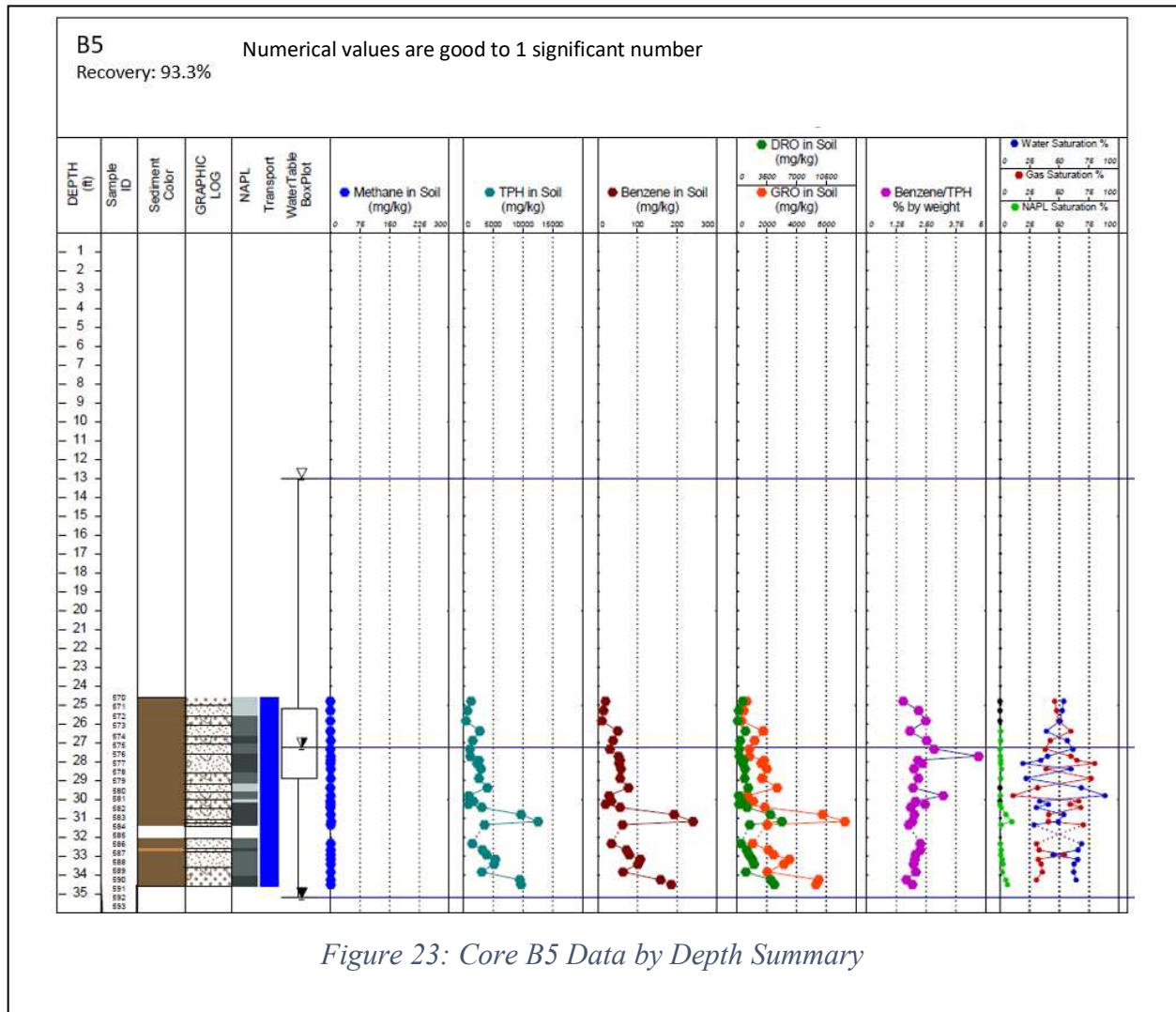


Figure 24 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole B6 include:

- B6 provides a missing section of B7 collected to represent core lost during recovery of B7.
- 100% of the core was recovered due to a small interval of collection.
- The core is completely represented by transmissive zones.
- It does not bound the zone targeted by LIF in the sampled interval

- Unable to provide percent saturation analysis from minimal data.

The contamination found in the interval has less overall mass, but the concentration of contaminants observed is typical for boreholes at Site B. The geologic distribution is only representative of boreholes B5 and B7. B6 is similar to B1, B5, and B7.

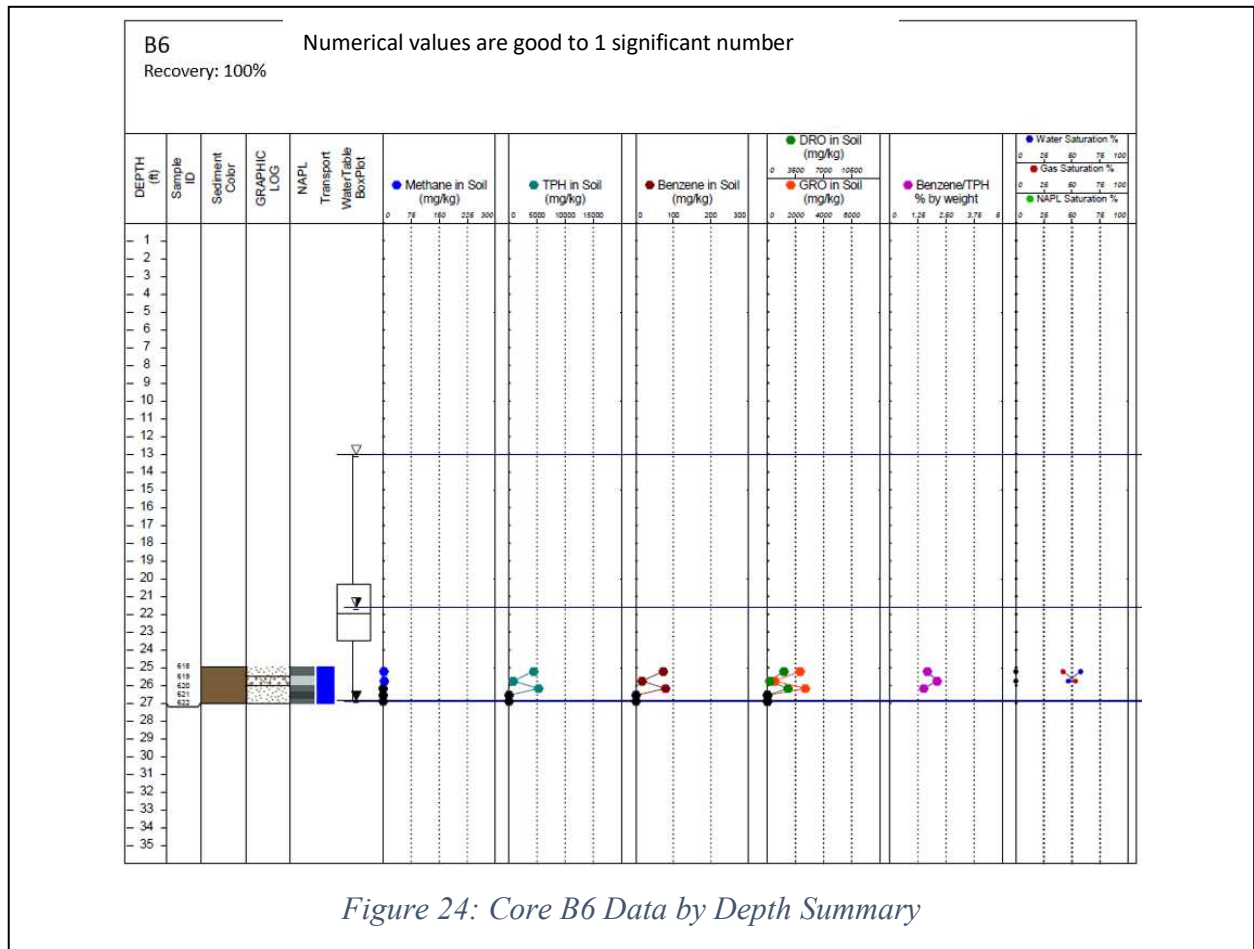
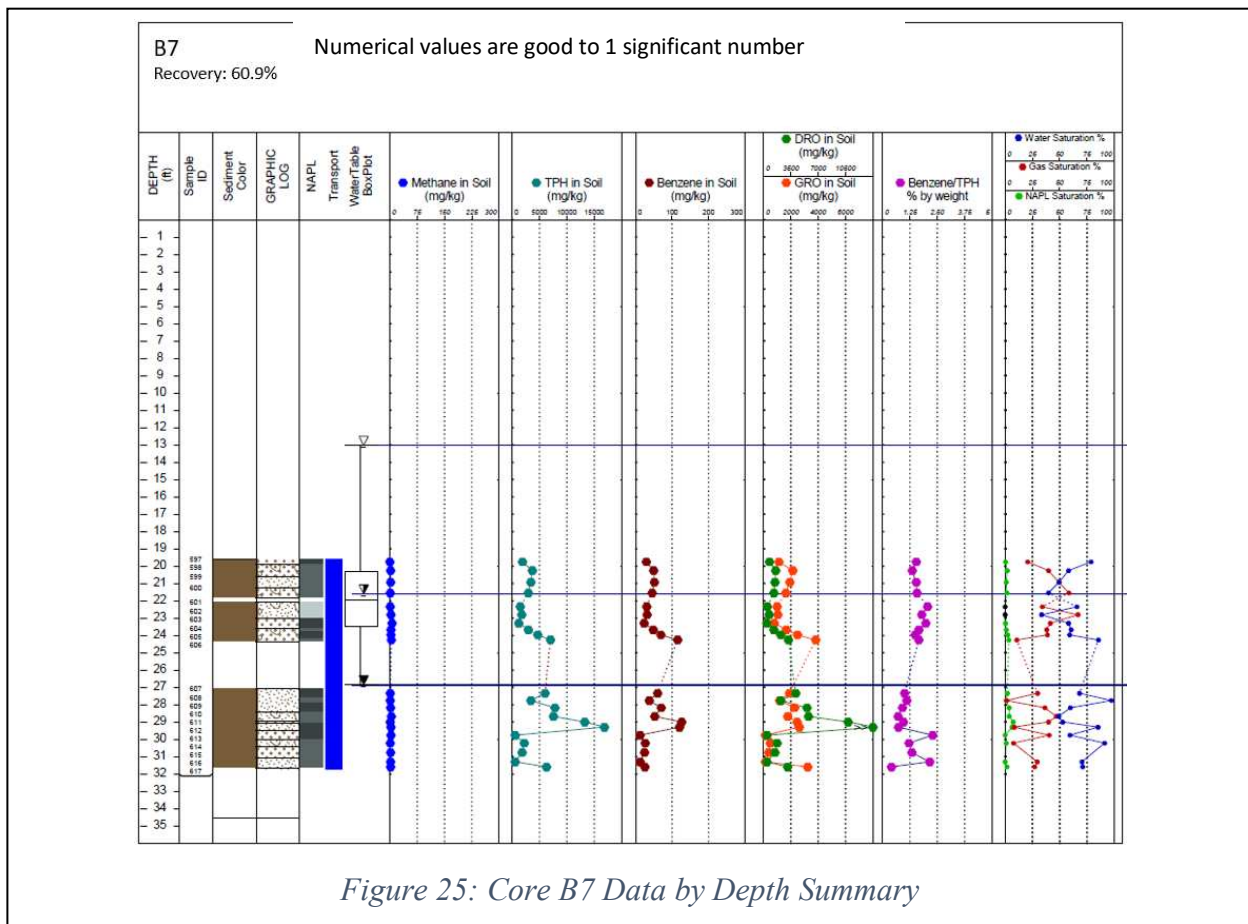


Figure 25 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole B7 include:

- 60% of the core was recovered.
- The core is completely represented by transmissive zones.

- B7 successfully bounds most of the zone targeted by LIF (23-31.5+ feet bgs) inside the cored interval (19.5-31.5 feet bgs).
- B7 has the most TPH contamination
- The % ratio of benzene to TPH where NAPL was visually observed under fluorescence is between ~0.5-2.8%.
- B7 has gas saturations that could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017). Spikes in concentrations of TPH and benzene correlate with spikes in percent saturation of gases.

B6 & B7 has contaminant concentrations that are representative of Site B but geologic distribution that are similar to B5.



3.1.2.2 Mass in Place Summary Analysis

Using the information presented from the previous paragraphs, the mass of contaminants are calculated using Equations 1-3. The key findings for mass of contaminants in the borehole (Table 16) include:

- The masses of TPH for all boreholes ranges between 2.47 kg/m² and 32.3 kg/m² (Table 16). Excluding small interval cores B4 and B7, TPH ranges between 15.3 kg/m² and 32.3 kg/m² (Table 16).
- The mass of benzene for all boreholes ranges between 0.039 kg/m² to 0.39 kg/m² (Table 16). Excluding small interval cores B4 and B7, benzene ranges between 0.24 kg/m² and 0.39 kg/m² (Table 16).

Table 16: Total Mass of Contaminants at Site B
Numerical values are good to 1 significant number.

Core	<u>Benzene</u> kg/m ²	<u>Methane</u> kg/m ²	<u>TPH</u> kg/m ²	<u>GRO</u> kg/m ²	<u>DRO</u> kg/m ²	<u>SUM COC</u> kg/m ²
B1	2.70E-01	1.64E-03	1.81E+01	9.18E+00	8.89E+00	1.83E+01
B2 (Duplicate of B1)	4.14E-01	6.62E-03	2.37E+01	1.10E+01	1.28E+01	2.42E+01
B3 (Duplicate of B1)	3.71E-01	2.37E-03	2.73E+01	9.39E+00	1.79E+01	2.77E+01
B4 (Duplicate of B1)	1.54E-01	2.23E-03	8.73E+00	3.86E+00	4.86E+00	8.88E+00
B5	3.13E-01	2.79E-03	1.55E+01	9.71E+00	5.77E+00	1.58E+01
B6 (Duplicate of B7)	4.03E-02	1.07E-03	2.51E+00	1.33E+00	1.19E+00	2.56E+00
B7	3.39E-01	1.41E-02	3.25E+01	1.36E+01	1.89E+01	3.29E+01
Site B (AVG)	2.71E-01	4.41E-03	1.83E+01	8.29E+00	1.01E+01	1.41E+01

3.1.2.3 Mass in Transmissive and Low-k Zones Summary Analysis

The mass in transmissive and low-k zones is presented with two formats including 1) using equations 4 and 5 to calculate the mass in transmissive and low-k zones (M/L²) and 2)

using Equations 6-10 to calculate the length of borehole that is transmissive/low-k (L/L) and to calculate the percent of total contaminant mass in transmissive/low-k zones (M/M). The key findings for mass in transmissive and low-k zones (M/L^2) (Figure 26, Table 17, & Table 18) include:

- Site A has a large portion of the total mass of contaminants in transmissive zones (Figure 26, Table 17, & Table 18).
- Boreholes B5-B7 are completely transmissive (Figure 26, Table 17, & Table 18).
- B1, B2, and B4 have a large portion of the total masses of benzene in low-k zones where B3 does not (Figure 26, Table 17, & Table 18). B1 has 13.8 kg/m² benzene in low-k zones (Figure 26, Table 17, & Table 18).
- B3, which is a duplicate representative of B1 & B2, less than 2.5 kilograms TPH per square meter in low-k zones (Figure 26, Table 17, & Table 18).

Defining boreholes B5, B6, and B7 as completely transmissive makes it nearly impossible to produce a Site B average that represents the distribution of contaminant mass in transmissive and low-k zones for the entire site.

The mass of contaminant is now transformed into percentage of contaminant mass in subsurface zones (M/M). The key findings for percentage of contaminants in transmissive and low-k zones (Figure 27, Table 19, & Table 20) for Site B include:

- B1, B2, and B3 have percentage of contaminant mass in low-k zones that does not correlate with the fraction of core that is low-k.
- Contaminants at B1 prefer low-k zones.
- Contaminants at B2 and B3 prefer transmissive zones.

- B4 has a percentage of contaminant mass in low k zones that correlates with the fraction of core that is low-k.
- Contaminants at B4 prefer each zone evenly.
- Contaminants at B5-B7 don't prefer any zone because the borehole is defined as completely transmissive.

The Site B average shows that contaminant preference favors transmissive zones. However, using Site B average has limitations because the classification of cores B5-B7 as transmissive makes producing an encompassing Site B summary difficult.

Many of the boreholes for Site B have similarities for concentration of contaminants by depth and total mass in place. However, there is a large discrepancy in geology between B1-B4 and B5-B7. It is not known why B5-B7 have no silts presents. Overall, Site B provides a beneficial view into the distribution of contamination in subsurface media and the discrepancies in the distribution of subsurface sediment.

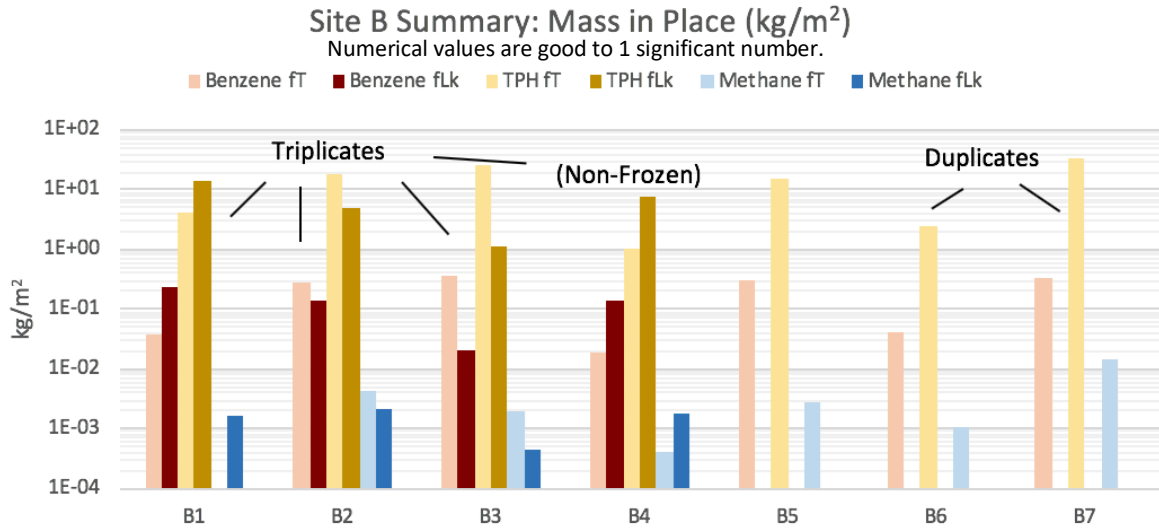


Figure 26: Mass of Contamination at Site B Divided into Zones

Table 17: Mass of Benzene and Methane at Site B Divided into Zones
Numerical values are good to 1 significant number.

	Benzene f _T	Benzene f _{Lk}	Methane f _T	Methane f _{Lk}	SUM COCs f _T	SUM COCs f _{Lk}
	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
Core						
B1	3.90E-02	2.31E-01	0.00E+00	1.64E-03	4.16E+00	1.42E+01
B2	2.78E-01	1.36E-01	4.44E-03	2.18E-03	1.90E+01	5.16E+00
B3	3.52E-01	1.99E-02	1.91E-03	4.57E-04	2.65E+01	1.17E+00
B4	1.84E-02	1.35E-01	4.03E-04	1.83E-03	1.04E+00	7.84E+00
B5	3.13E-01	0.00E+00	2.79E-03	0.00E+00	1.58E+01	0.00E+00
B6	4.03E-02	0.00E+00	1.07E-03	0.00E+00	2.56E+00	0.00E+00
B7	3.39E-01	0.00E+00	1.41E-02	0.00E+00	3.29E+01	0.00E+00
Site B (AVG)	1.97E-01	7.46E-02	3.54E-03	8.72E-04	1.46E+01	4.05E+00

Table 18: Mass of TPH, GRO, and DRO at Site B Divided into Zones
Numerical values are good to 1 significant number.

	TPH f _T	TPH f _{Lk}	GRO f _T	GRO f _{Lk}	DRO f _T	DRO f _{Lk}
	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
Core						
B1	4.13E+00	1.39E+01	2.32E+00	6.86E+00	1.80E+00	7.09E+00
B2	1.87E+01	5.02E+00	8.63E+00	2.35E+00	1.01E+01	2.67E+00
B3	2.62E+01	1.15E+00	8.94E+00	4.46E-01	1.72E+01	7.00E-01
B4	1.02E+00	7.71E+00	4.72E-01	3.39E+00	5.51E-01	4.31E+00
B5	1.55E+01	0.00E+00	9.71E+00	0.00E+00	5.77E+00	0.00E+00
B6	2.51E+00	0.00E+00	1.33E+00	0.00E+00	1.19E+00	0.00E+00
B7	3.25E+01	0.00E+00	1.36E+01	0.00E+00	1.89E+01	0.00E+00
Site B (AVG)	1.44E+01	3.97E+00	6.42E+00	1.86E+00	7.94E+00	2.11E+00

Numerical values are good to 1 significant number.
Site B Summary by Borehole B1-B7 and Site B Total Ordered Transmissive to Low-k

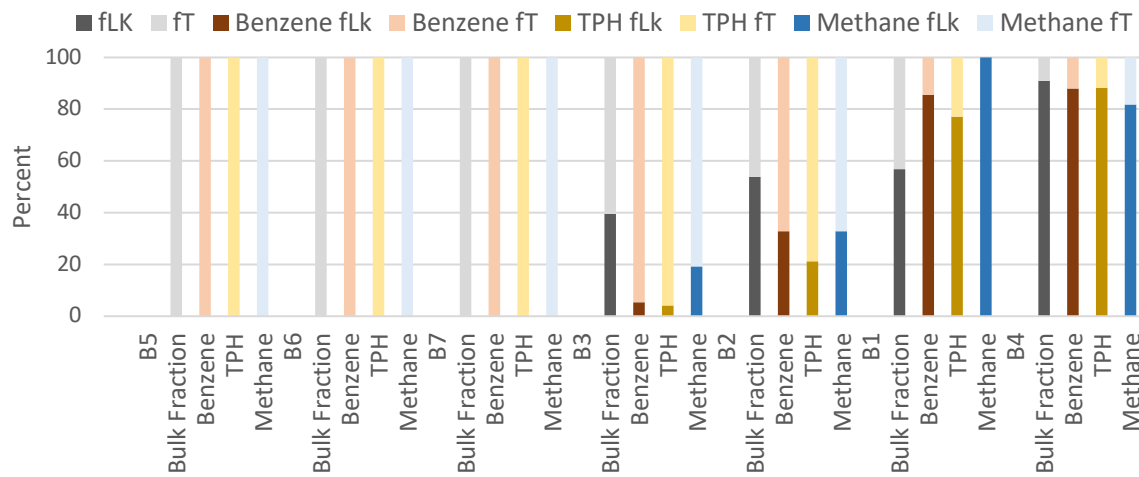


Figure 27: Percentage of Mass in Zones at Site B Ordered from Transmissive to Low-k

Table 19: Percentage of Borehole that is Transmissive of Low-k and Percentage of Benzene and Methane Mass in Zones at Site B
 Numerical values are good to 1 significant number.

Core	$\% f_T$	$\% f_{Lk}$	$\% \text{Benzene } f_T$	$\% \text{Benzene } f_{Lk}$	$\% \text{Methane } f_T$	$\% \text{Methane } f_{Lk}$
B1	43.14	56.86	14.46	85.54	0.00	100.00
B2	46.19	53.81	67.07	32.93	67.07	32.93
B3	60.48	39.52	94.64	5.36	80.71	19.29
B4	9.09	90.91	11.99	88.01	18.06	81.94
B5	100.00	0.00	100.00	0.00	100.00	0.00
B6	100.00	0.00	100.00	0.00	100.00	0.00
B7	100.00	0.00	100.00	0.00	100.00	0.00

Table 20: Percentage of TPH, GRO, and DRO Mass in Zones at Site B
 Numerical values are good to 1 significant number.

Core	$\% \text{TPH } f_T$	$\% \text{TPH } f_{Lk}$	$\% \text{GRO } f_T$	$\% \text{GRO } f_{Lk}$	$\% \text{DRO } f_T$	$\% \text{DRO } f_{Lk}$
B1	22.83	77.17	25.28	74.72	20.29	79.71
B2	78.85	21.15	78.63	21.37	79.05	20.95
B3	95.81	4.19	95.25	4.75	96.10	3.90
B4	11.72	88.28	12.20	87.80	11.33	88.67
B5	100.00	0.00	100.00	0.00	100.00	0.00
B6	100.00	0.00	100.00	0.00	100.00	0.00
B7	100.00	0.00	100.00	0.00	100.00	0.00

3.1.3 Intra-Site C

Site C is former petroleum refinery. Site C has two boreholes sampled as duplicates in 2016. The primary COCs are benzene and TPH. The geologic setting is a fluvial overbank deposit. At Site C, media defined as sandy silt and finer media is characterized as low-k. Media defined as silty sand and larger media is characterized as transmissive.

3.1.3.1 Contamination by Depth

Figure 28 is an illustrative graphic from gINT™ that advances cryogenic coring data by including geologic and contaminant data-by depth for the cored interval from Borehole C1. Starting on the left, the geologic graphic includes depth from ground surface, Sample ID, sediment color, graphic log, NAPL visual, transport visual, and 3 points for water table data. The contaminant data-by-depth then plots methane, TPH, benzene, DRO, and GRO concentrations. Next this graphic plots the percent ratio of concentrations of benzene over TPH. Finally, this graphic plots the saturations percentages of water, gas, and NAPL. The key findings for Borehole C1 include:

- 80% of the core was recovered.
- The geology of the contaminated zone is low-k dominated with several feet of transmissive bulk in the middle (12.5-13.5 feet bgs).
- The concentrations of methane in C1 are higher than other boreholes at other sites.
- Above the zone targeted by LIF (19 feet bgs), the spikes in concentration of methane correlate with spikes in concentrations of contaminants.
- The contamination is in and above the zone targeted by LIF (8-18 feet bgs).

- Between 7-19 feet bgs, the % ratio of benzene to TPH where NAPL was visually observed under fluorescence is between ~2.8-3.75%.
- Below the zone targeted by LIF (19-29 feet bgs), low concentrations of GRO produce 5-31% ratio of benzene to TPH and the zone is dominated by transmissive bulk.
- This borehole is characterized by a dominating (>90%) water saturation percentage throughout the borehole.

Borehole C1 is a hydrocarbon contaminated borehole with contamination and methane inside and out of the low-k dominated LIF targeted zone . C1 and C2 both have saturations percentages of water, gas, and LNAPL that correlate with presence of methane to provide evidence for active microbial populations. However, the high gas saturations that could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017).

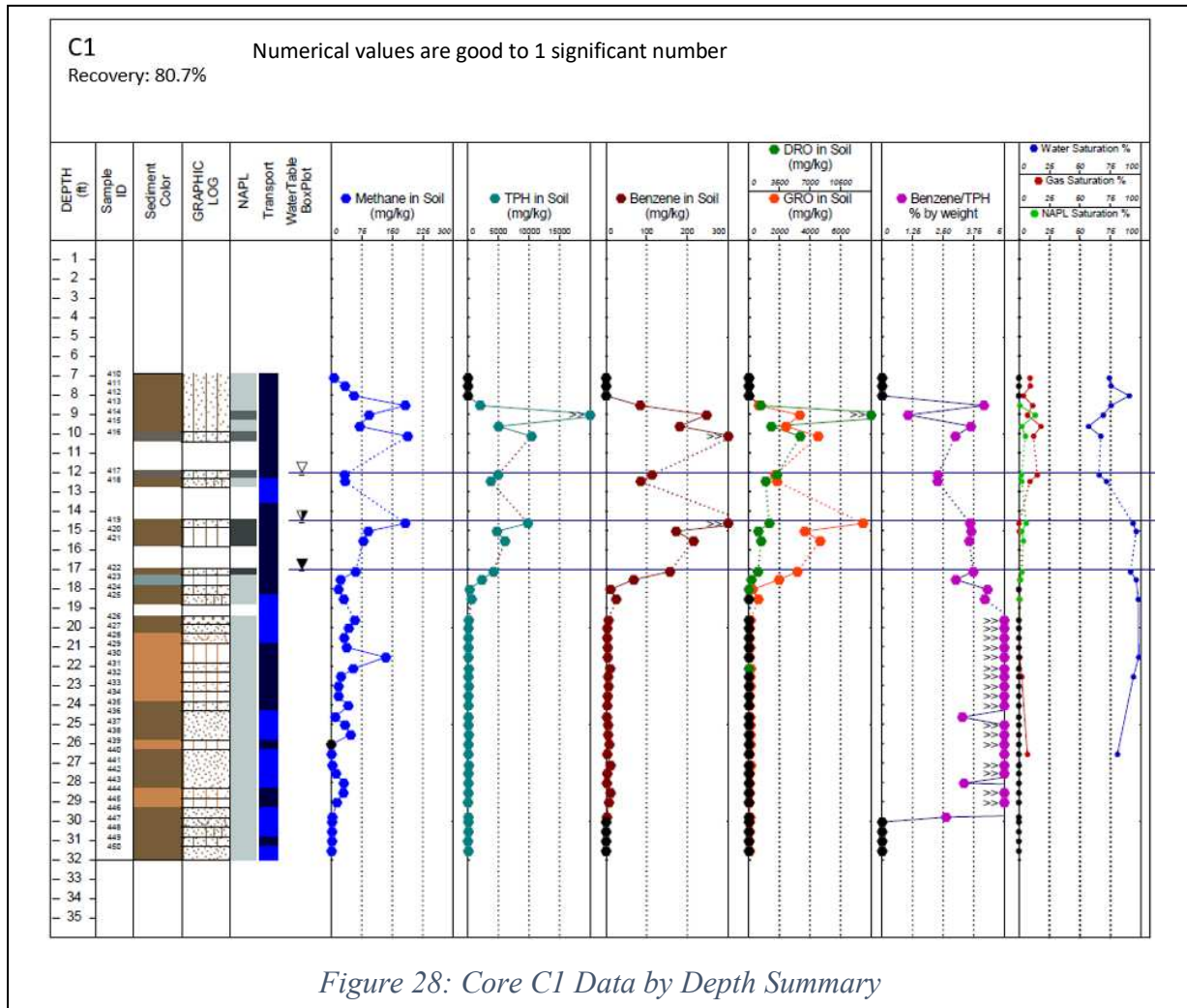


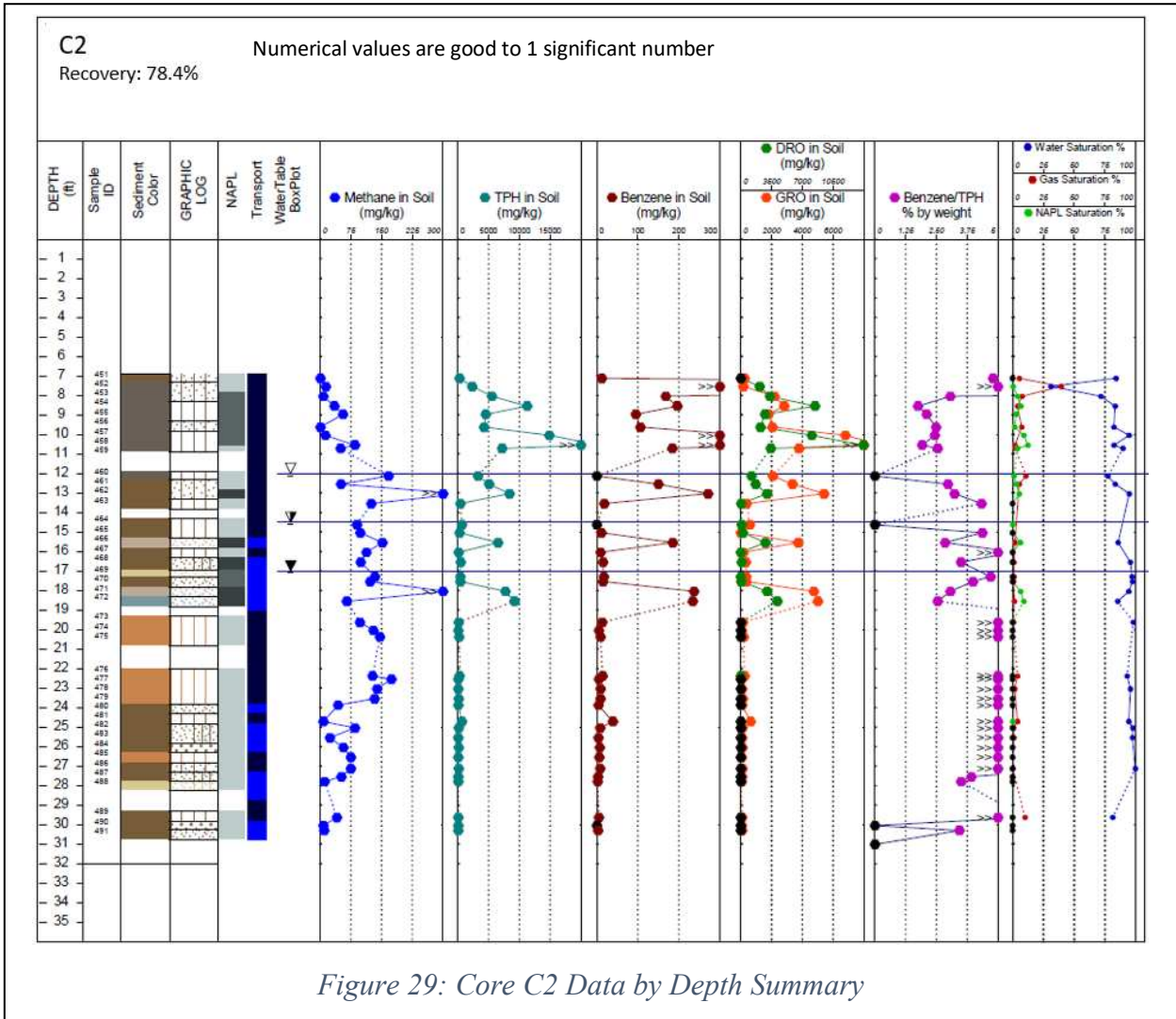
Figure 29 is an illustrative graphic from gINT™ that follows the format of Figure 28.

The key findings for Borehole C2 include:

- 78% of the core was recovered.
- The geology of the contaminated zone is low-k dominated with several feet of transmissive bulk at the bottom of the contaminated zone.
- Between 10-20 feet bgs, the spikes in concentration of methane correlate with spikes in concentrations of contaminants.

- Below 20 feet bgs, there is no contaminants but, the concentration of methane closely correlates with transmissivity of the bulk. This is illustrated with low-k zones at 19-23 feet bgs, 27 feet bgs and 30 feet bgs correlating with increases in concentrations of methane. This could provide evidence of different microbial communities in different geologic zones (Sale et al. 2017)
- The contamination is found in the zone targeted by LIF (7-20 feet bgs).
- There are large spikes of benzene near the top of sampled core (7-11 feet bgs).
- In the zone targeted by LIF (7-20 feet bgs), the % ratio of benzene to TPH where NAPL was visually observed under fluorescence is ~1.25-6%.
- Below 20 feet bgs, low concentrations of GRO produce a 5-11% ratio of benzene to TPH.
- This borehole is characterized by a large water saturation percentage throughout the core.

Borehole C2 is a hydrocarbon contaminated core with contamination and methane inside and out of the low-k dominated LIF targeted zone. C1 and C2 both have high gas saturations that could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017).



3.1.3.2 Mass in Place Summary Analysis

Using the information presented from the previous paragraphs, the mass of contaminants are calculated using Equations 1-3. The key findings for mass of contaminants in the borehole (Table 21) include:

- The total masses of TPH in C1 and C2 differ by 1% (Table 21).
- C2 has 20% more benzene mass and 57% more methane mass than C1 (Table 21).

- In both C1 and C2, methane is present in large concentrations and has a large representative mass (Table 21). Large amounts of methane can limit biodegradation if the methane does not have vertical off gassing pathways Garg et al. (2017).

3.1.3.3 Mass in Transmissive and Low-k Zones Summary Analysis

The mass in transmissive and low-k zones is presented with two key dimensions. 1) Uses equations 4 and 5 to calculate the mass in transmissive and low-k zones (M/L^2). 2) Uses Equations 6-10 to calculate the length of borehole that is transmissive/low-k (L/L) and to calculate the percent of total contaminant mass in transmissive/low-k zones (M/M). The key findings for mass in transmissive and low-k zones (M/L^2) (Figure 30, Table 22, & Table 23) include:

- Site C has a majority of contaminant mass in low-k zones (Table 23, Figure 30)
- C1 and C2 have tens of kg/m^2 of benzene and tens of kg/m^2 TPH in low-k zones (Table 22 & Table 23).
- Site C has a majority of methane mass in low-k zones (Figure 30).
- C1 and C2 each have over $0.54 kg/m^2$ methane in low-k zones (Table 22)

Duplicate Boreholes at Site C show strong similarities as listed above. The mass in low-k zones is greater than mass in transmissive zones for both C1 and C2 (Figure 30). The inter-site results will provide statistics to determine if this preference is significant.

Table 21: Total Mass of Contaminants at Site C

Numerical values are good to 1 significant number.

	<u>Benzene</u>	<u>Methane</u>	<u>TPH</u>	<u>GRO</u>	<u>DRO</u>	<u>SUM COC</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
C1	8.90E-01	6.37E-01	3.06E+01	1.64E+01	1.42E+01	3.15E+01
C2	1.09E+00	1.00E+00	2.95E+01	1.50E+01	1.45E+01	3.06E+01
Site C (AVG)	9.89E-01	8.21E-01	3.01E+01	1.57E+01	1.43E+01	3.10E+01

Boreholes C1 & C2 Duplicate Summary: Mass in Place (kg/m²)

Numerical values are good to 1 significant number.

■ Benzene fT ■ Benzene fLk ■ TPH fT ■ TPH fLk ■ Methane fT ■ Methane fLk

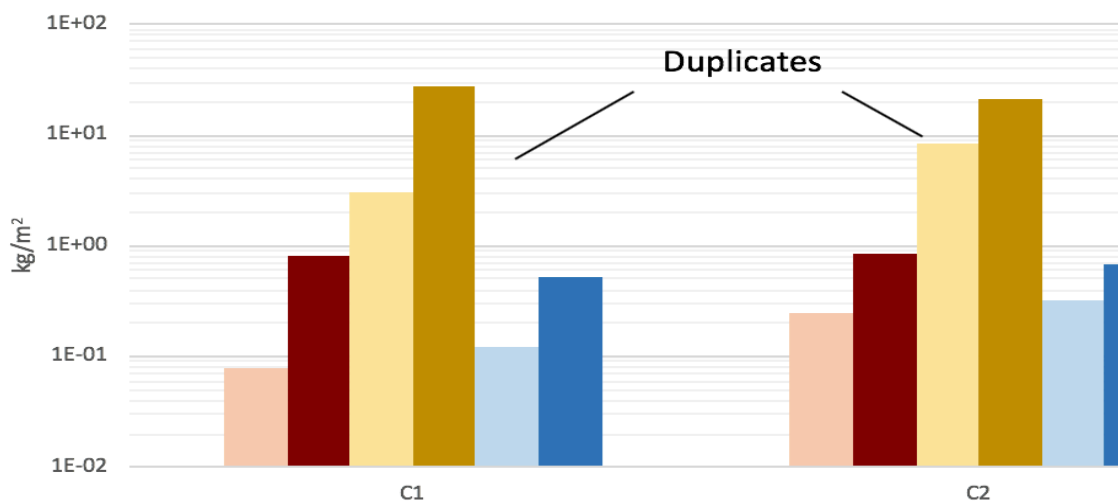


Figure 30: Mass of Contamination at Site C Divided into Zones

Table 22: Mass of Benzene and Methane at Site C Divided into Zones

Numerical values are good to 1 significant number.

	<u>Benzene</u>	<u>Benzene</u>	<u>Methane</u>	<u>Methane</u>	<u>SUM COCs</u>	<u>SUM COCs f</u>
	<u>f_T</u>	<u>f_{Lk}</u>	<u>f_T</u>	<u>f_{Lk}</u>	<u>f_T</u>	<u>Lk</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
C1	8.02E-02	8.10E-01	1.19E-01	5.18E-01	3.12E+00	2.84E+01
C2	2.43E-01	8.45E-01	3.22E-01	6.82E-01	8.82E+00	2.18E+01
Site C (AVG)	1.62E-01	8.27E-01	2.21E-01	6.00E-01	5.97E+00	2.51E+01

Table 23: Mass of TPH, GRO, and DRO at Site C Divided into Zones

Numerical values are good to 1 significant number.

	<u>TPH f_T</u>	<u>TPH f_{Lk}</u>	<u>GRO f_T</u>	<u>GRO f_{Lk}</u>	<u>DRO f_T</u>	<u>DRO f_{Lk}</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
C1	3.04E+00	2.75E+01	1.78E+00	1.46E+01	1.27E+00	1.29E+01
C2	8.57E+00	2.09E+01	5.07E+00	9.97E+00	3.50E+00	1.10E+01
Site C (AVG)	5.81E+00	2.42E+01	3.42E+00	1.23E+01	2.38E+00	1.19E+01

The mass of contaminant is now transformed into percentage of contaminant mass in subsurface zones (M/M). The key findings for percentage of contaminants in transmissive and low-k zones (Figure 31, Table 24, & Table 25) for Site C include:

- C1 has a percentage of contaminant mass in low-k zones that does not correlate with the fraction of C1 that is low-k. ($\%f_{LK} < \%COC_{LK}$)
- C1 is 62% low-k and the low-k zone has over 90% of the benzene and TPH mass. The distribution of contaminants at C1 prefers low-k zones.
- Unlike C1, C2 has a percentage of contaminant mass in low k zones that correlates with the fraction of C2 that is low-k. ($\%f_{LK} = \%COC_{LK}$)
- C2 is 68% low-k and has ~70% of TPH and methane and 77% benzene in low-k zones. The distribution of contaminants at C2 prefers each zone evenly.

Boreholes C1 and C2 have different distributions of contaminants in low-k zones. Inter-site results will provide statistics that will help determine if these distributions are significantly different.

Many of the results show similarities for C1 and C2 because of their proximity. The similarities are concentrations of contaminants by depth, total mass in place, and recovery losses. The key contrast at C1 and C2 is the distribution of mass of contaminants in transmissive and low-k zones. C1 has contamination that prefers low-k zones much more than C2. Site C provides a unique, beneficial view for this dataset by presenting the distribution of contamination in boreholes dominated by low-k zones.

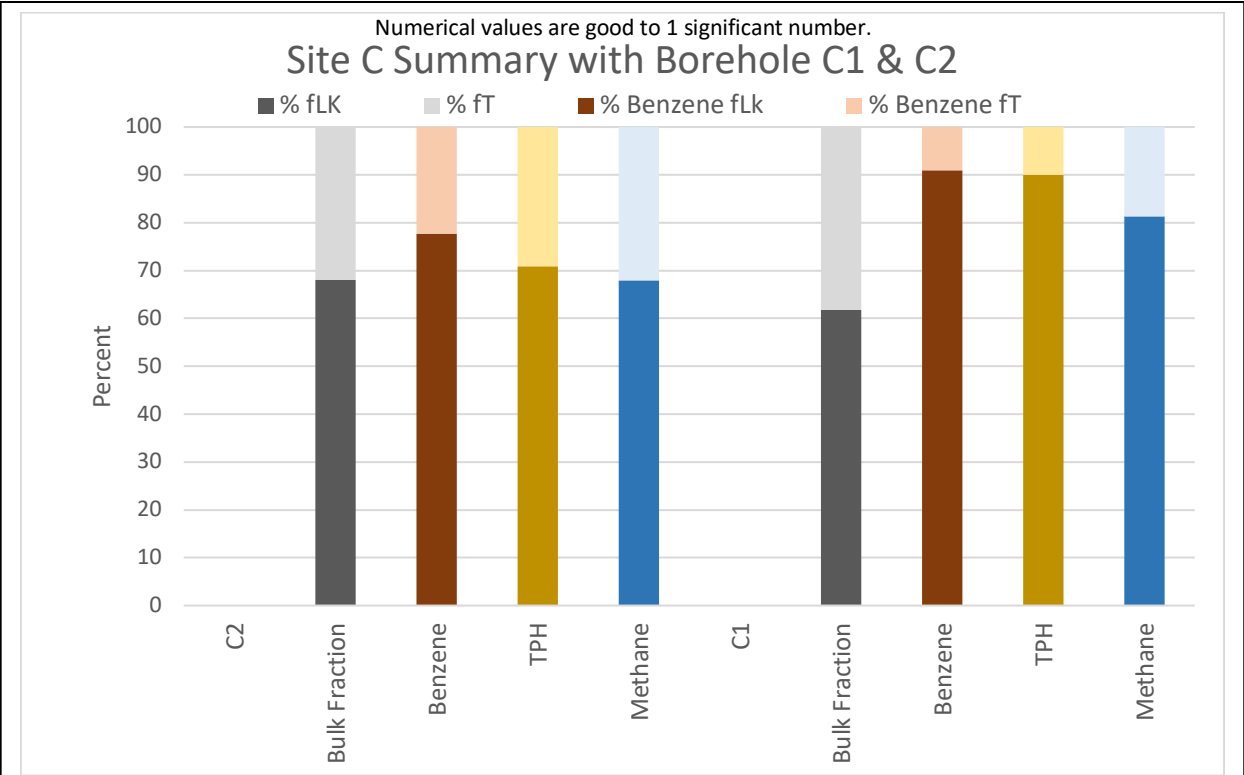


Figure 31: Percentage of Mass in Zones at Site C Ordered from Transmissive to Low-k

Table 24: Percentage of Borehole that is Transmissive of Low-k and Percentage of Benzene and Methane Mass in Zones at Site C

Numerical values are good to 1 significant number.

Core	$\% f_T$	$\% f_{LK}$	$\% \text{Benzene } f_T$	$\% \text{Benzene } f_{LK}$	$\% \text{Methane } f_T$	$\% \text{Methane } f_{LK}$
C1	38.17	61.83	9.01	90.99	18.71	81.29
C2	31.89	68.11	22.34	77.66	32.06	67.94

Table 25: Percentage of TPH, GRO, and DRO Mass in Zones at Site C

Numerical values are good to 1 significant number.

Core	$\% \text{TPH } f_T$	$\% \text{TPH } f_{LK}$	$\% \text{GRO } f_T$	$\% \text{GRO } f_{LK}$	$\% \text{DRO } f_T$	$\% \text{DRO } f_{LK}$
C1	9.95	90.05	10.83	89.17	8.94	91.06
C2	29.05	70.95	33.72	66.28	24.19	75.81

3.1.4 Intra-Site D

Site D is an active refinery. The primary COCs are benzene and TPH. The geologic setting of Site D is a braided stream deposit. At Site D, media containing silt and finer media is characterized as low-k. All media without silt is characterized as transmissive.

3.1.4.1 Contamination by Depth

Figure 32 is an illustrative graphic from gINT™ that follows the previous format but does not have any water table data available. The key findings for Borehole D1 include:

- 85% of the core was recovered.
- The geology of the borehole is split between transmissive and low-k zones.
- The concentrations of methane in D1 are typical with lower concentrations present.
- The concentrations of methane are centered around 4-14 feet bgs.
- There is no contamination in the borehole (0-14.5 feet bgs).

Borehole D1 has no NAPL and is divided by transmissive and low-k zones. D1 is a good benchmark for natural concentrations of methane and saturation percentages given no NAPL. D1 and D2 both have high gas saturations that could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017).

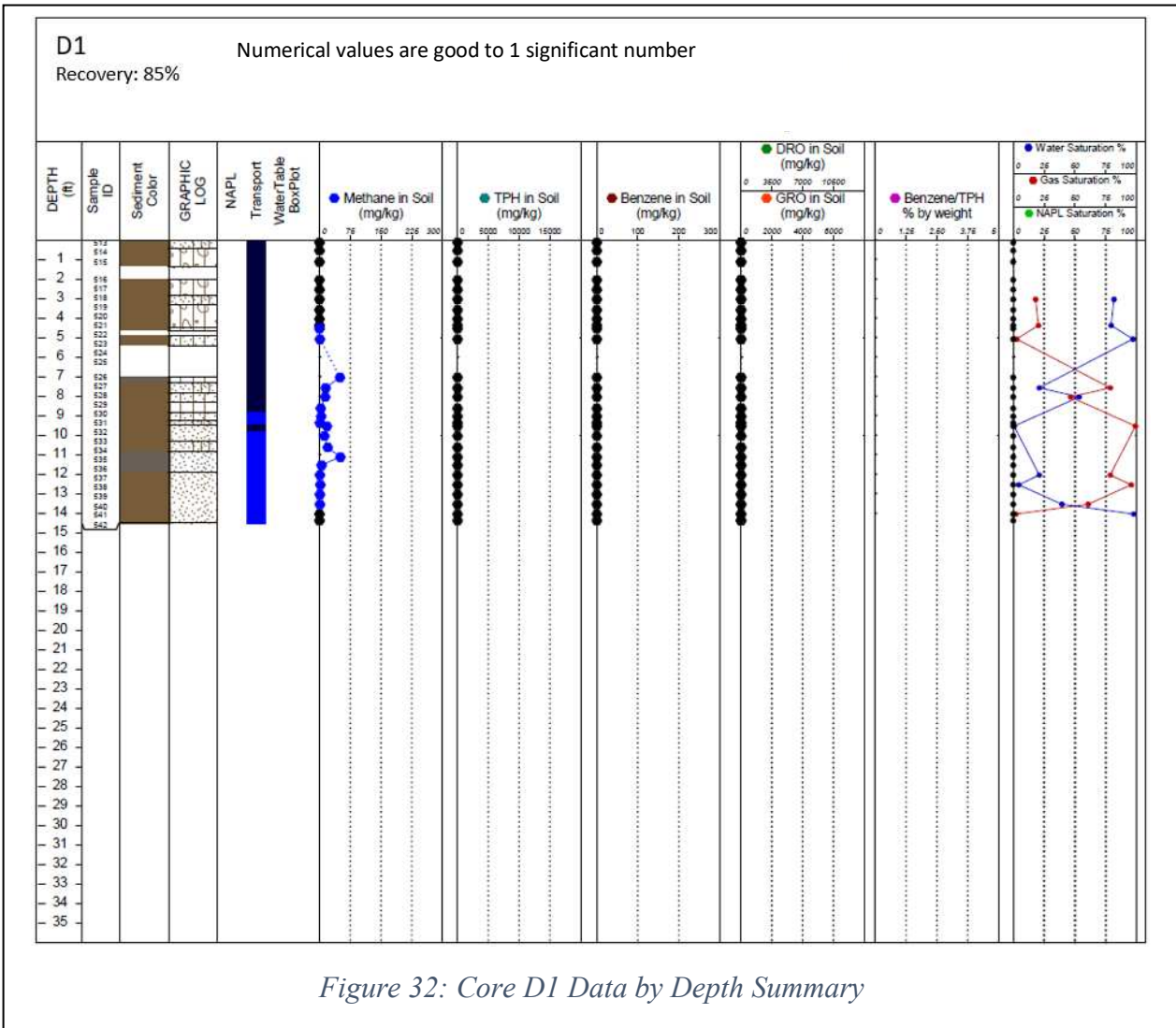


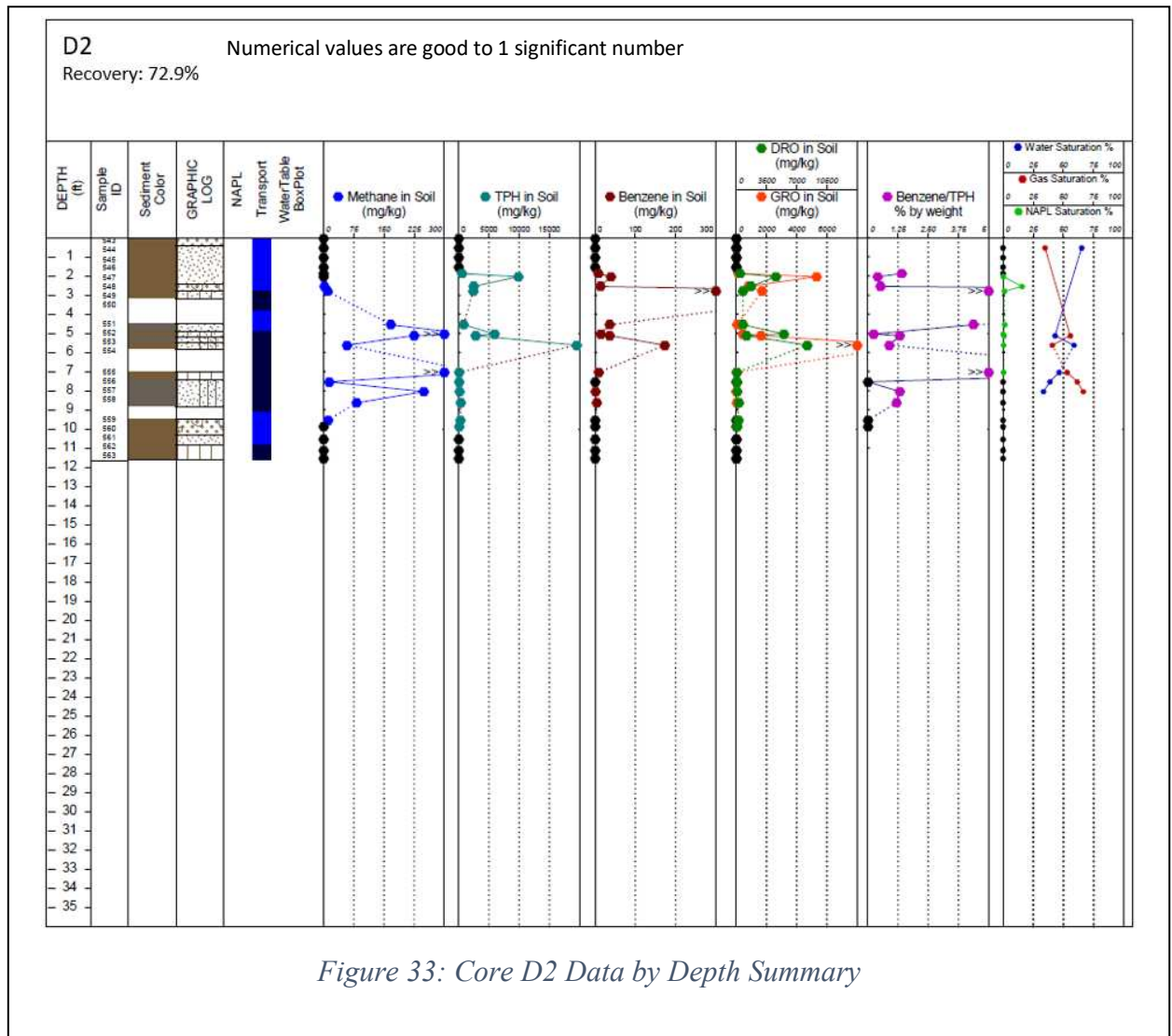
Figure 33 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole D2 include:

- 72% of the core was recovered.
- The geology of the contaminated zone is both low-k and transmissive.
- The contamination is found in the targeted zone (2-10 feet bgs).
- There is a large spike of benzene near the top of sampled core (3 feet bgs).

- D2 has contaminant concentrations where D1 has none.
- There is a general correlation with spikes in concentrations of methane with spikes in concentrations of contaminants.
- This data does not have visual NAPL reflectiveness and the ratio of benzene to TPH is limited in use.
- Excluding two points, the % ratio of benzene to TPH is 0-5%. At 2.5 feet bgs, there is a 29% ratio of benzene to TPH. At 7 feet bgs, there is a 12.8% ratio of benzene to TPH.
- This borehole is characterized by 30%-65% gas and water saturations throughout the core.

Borehole D2 is a hydrocarbon contaminated core with the contamination present in shallow subsurface media with greater concentrations of methane than the background concentrations.

D1 and D2 both have high gas saturations that could be evidence for natural attenuation, Garg et al (2017) Kiaalhosseini et al. (2017).



3.1.4.2 Mass in Place Summary Analysis

Using the information presented from the previous paragraphs, the mass of contaminants are calculated using Equations 1-3. The key findings for mass of contaminants in the borehole (Table 26) include:

- D2 has benzene and TPH mass (Table 26).

- In both D1 and D2, methane is present but has greater mass in areas of contamination at D2. D2 has 4.5x more methane mass than D1 (Table 26).

3.1.4.3 Mass in Transmissive and Low-k Zones Summary Analysis

The mass in transmissive and low-k zones is presented with two formats including 1) using equations 4 and 5 to calculate the mass in transmissive and low-k zones (M/L^2) and 2) using Equations 6-10 to calculate the length of borehole that is transmissive/low-k (L/L) and to calculate the percent of total contaminant mass in transmissive/low-k zones (M/M). The key findings for mass in transmissive and low-k zones (M/L^2) (Figure 34, Table 27, & Table 28) include:

- D2 has a large portion of the total contaminant mass in low-k zones (Figure 34). D2 has tens of kg/m^2 TPH in low-k zones and transmissive zones (Table 28). D2 has almost a quarter of kg/m^2 of benzene in low-k zones (Table 27).
- Methane at D2 prefers low-k zones where methane at D1 prefers each zone evenly (Figure 34 & Table 27).
- Site C has a majority of methane mass in low-k zones (Figure 34). C1 and C2 each have over $0.54 kg/m^2$ methane in low-k zones (Table 27).

Since a single core is clean, the D2 is the only borehole that will be used in inter-site comparisons with contaminants. D2 does demonstrate there is a large portion of the total mass of contaminants in low-k zones at site D.

Table 26: Total Mass of Contaminants at Site D

Numerical values are good to 1 significant number.

	<u>Benzene</u>	<u>Methane</u>	<u>TPH</u>	<u>GRO</u>	<u>DRO</u>	<u>SUM COC</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
D1	0.00E+00	5.27E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
D2	2.09E-01	2.40E-01	6.45E+00	3.08E+00	3.37E+00	6.66E+00

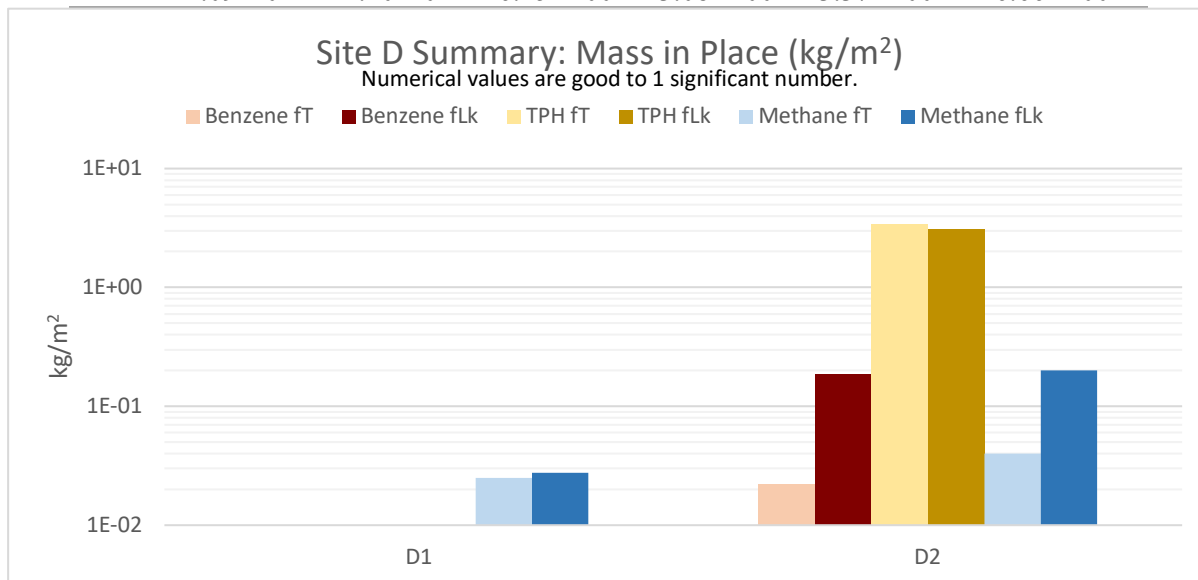


Figure 34: Mass of Contamination at Site D Divided into Zones

Table 27: Mass of Benzene and Methane at Site D Divided into Zones

Numerical values are good to 1 significant number.

	<u>Benzene f_T</u>	<u>Benzene f_{Lk}</u>	<u>Methane f_T</u>	<u>Methane f_{Lk}</u>	<u>SUM COCs f_T</u>	<u>SUM COCs f_{Lk}</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
D1	0.00E+00	0.00E+00	2.51E-02	2.76E-02	0.00E+00	0.00E+00
D2	2.20E-02	1.87E-01	4.01E-02	2.00E-01	3.42E+00	3.24E+00

Table 28: Mass of TPH, GRO, and DRO at Site D Divided into Zones

Numerical values are good to 1 significant number.

	<u>TPH f_T</u>	<u>TPH f_{Lk}</u>	<u>GRO f_T</u>	<u>GRO f_{Lk}</u>	<u>DRO f_T</u>	<u>DRO f_{Lk}</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
D1	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
D2	3.40E+00	3.05E+00	1.56E+00	1.52E+00	1.84E+00	1.53E+00

The mass of contaminant is now transformed into percentage of contaminant mass in subsurface zones (M/M). The key findings for percentage of contaminants in transmissive and low-k zones (Figure 35, Table 29, & Table 30) for Site D include:

- D2 has a percentage of contaminant mass in low-k zones that does not correlate with the fraction of D2 that is low-k.
- D1 is 69% low-k and has 52% of methane in low-k zones.
- D2 is 52% low-k and has 83% of methane and 89% benzene. Methane and benzene prefer low-k zones.
- D2 has 52% low-k and has 47% TPH in low-k zones. TPH prefers each zone evenly.

D2 is a good example where benzene prefers low-k zones and TPH prefers each zone evenly.

The preference of methane is interesting and is discussed further, along with Benzene and TPH, in inter-site results.

Site D is a hydrocarbon contaminated site that has a single contaminated borehole as representation. This makes it difficult to come to any general understanding of the site but gives very useful data to compare to other boreholes in the inter-site comparisons.

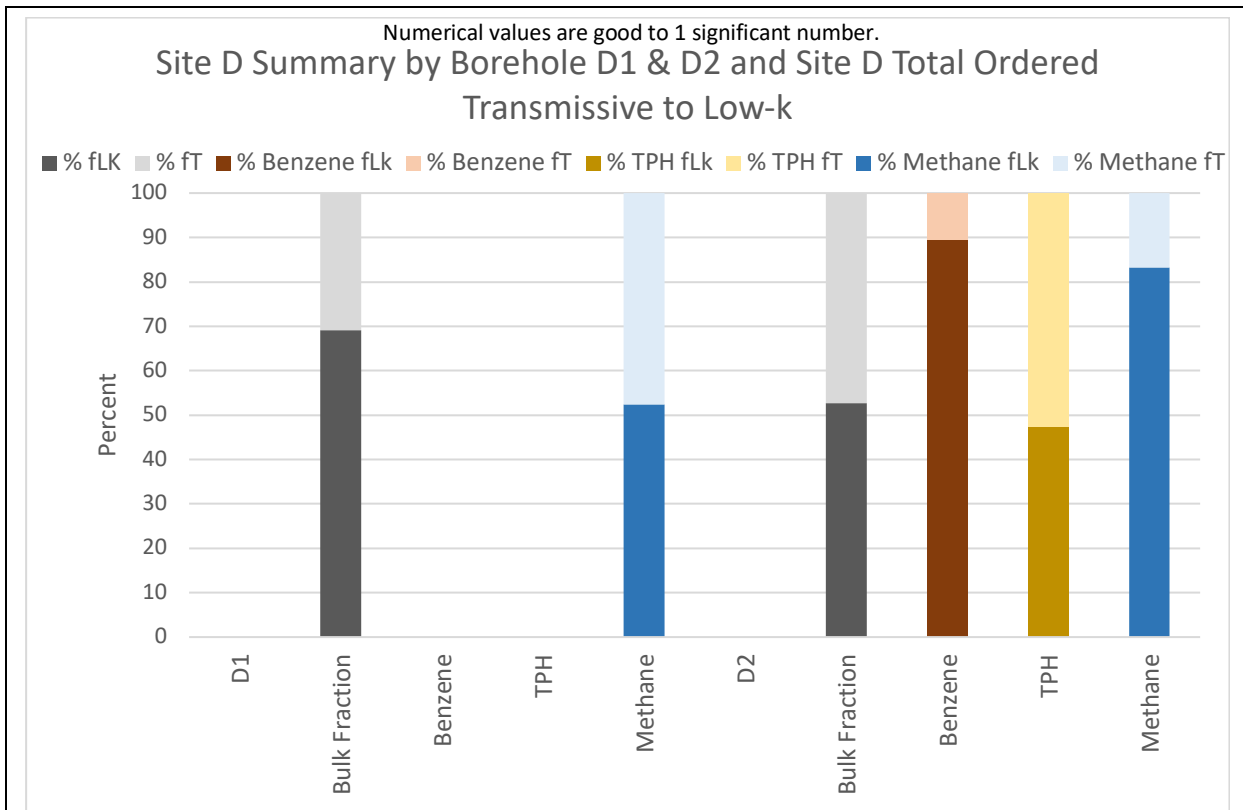


Figure 35: Percentage of Mass in Zones at Site D Ordered from Transmissive to Low-k

Table 29: Percentage of Borehole that is Transmissive of Low-k and Percentage of Benzene and Methane Mass in Zones at Site D

Numerical values are good to 1 significant number.

Core	$\% f_T$	$\% f_{LK}$	$\% \text{Benzene } f_T$	$\% \text{Benzene } f_{LK}$	$\% \text{Methane } f_T$	$\% \text{Methane } f_{LK}$
D1	30.83	69.17	0.00	0.00	47.66	52.34
D2	47.28	52.72	10.53	89.47	16.71	83.29

Table 30: Percentage of TPH, GRO, and DRO Mass in Zones at Site D

Numerical values are good to 1 significant number.

Core	$\% \text{TPH } f_T$	$\% \text{TPH } f_{LK}$	$\% \text{GRO } f_T$	$\% \text{GRO } f_{LK}$	$\% \text{DRO } f_T$	$\% \text{DRO } f_{LK}$
D1	0.00	0.00	0.00	0.00	0.00	0.00
D2	52.68	47.32	50.52	49.48	54.66	45.34

3.1.5 Intra-Site E

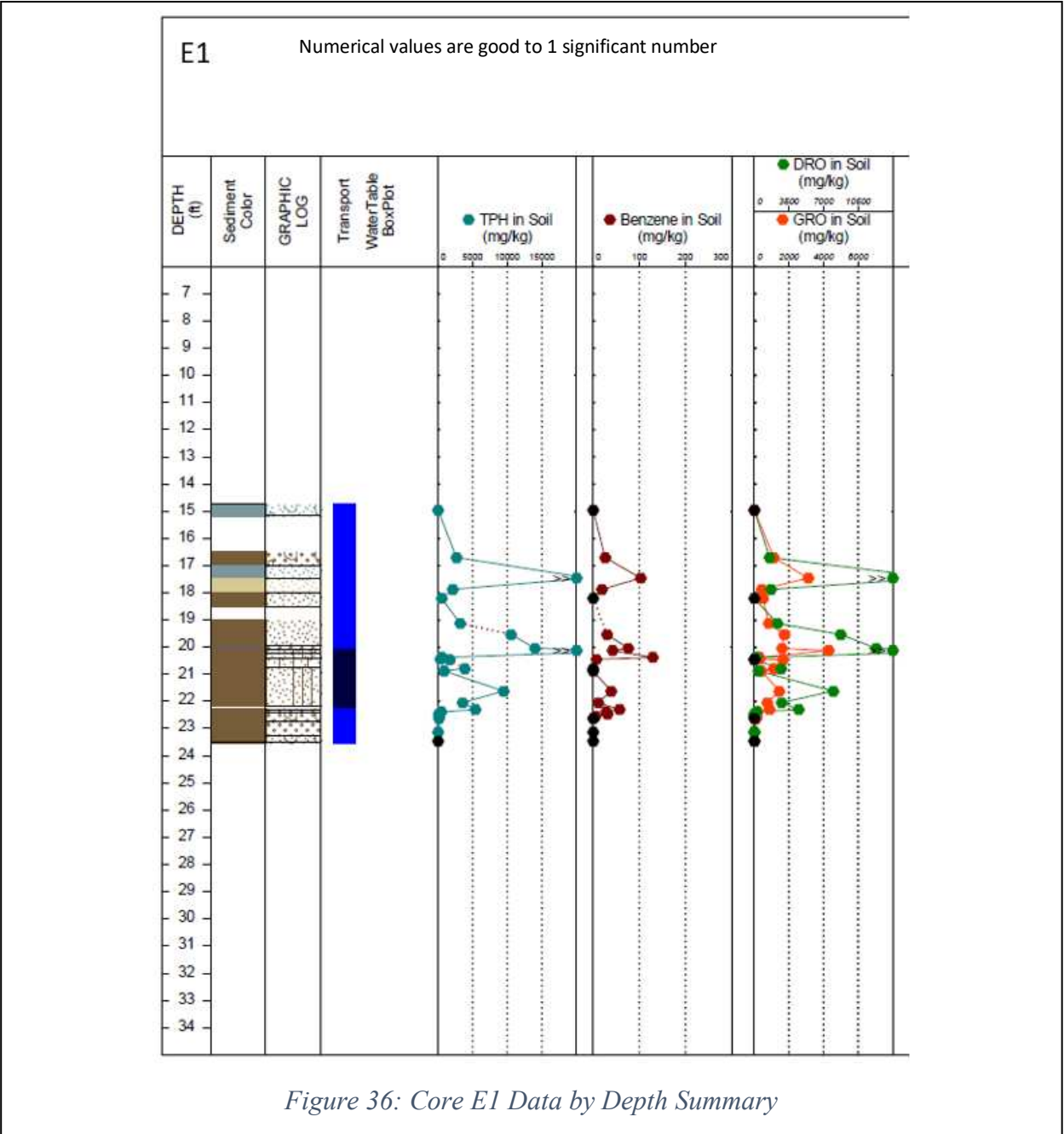
Site E is an active gas station. The primary COCs are benzene and TPH. The geologic setting of Site E is a braided stream deposit. At Site E, media containing silt and finer media is characterized as low-k. All media without silt is characterized as transmissive.

3.1.5.1 Contamination by Depth

Figure 36 is an illustrative graphic from gINT™ that advances cryogenic coring data by including geologic and contaminant data-by depth for the cored interval from Borehole E1. Starting on the left, the geologic graphic includes depth from ground surface, Sample ID, sediment color, graphic log, transport visual, no plotted water table data. The contaminant data-by-depth then plots methane, TPH, benzene, DRO, and GRO concentrations. The key findings for Borehole E1 include:

- The geology of the contaminated zone is transmissive dominated with several feet of low-k zones in the middle (20-22 feet bgs).
- The contamination is bound in the zone targeted by LIF (16.5-23 feet bgs) in the cored interval (14.8-23.5 feet bgs).

Borehole E1 is a hydrocarbon contaminated core with the contamination contained in the zone targeted by LIF which is dominated by low-k subsurface sediment. E1 is of limited use because the analysis is limited in scope.



3.1.5.2 Mass in Place Summary Analysis

Using the information presented from the previous paragraphs, the mass of contaminants are calculated using Equations 1-3. The key findings for mass of contaminants in the borehole (Table 31) include:

- E1 has a large total mass of TPH largely consisting of DRO (Table 31).

3.1.5.3 Mass in Transmissive and Low-k Zones Summary Analysis

The mass in transmissive and low-k zones is presented with two formats including 1) using equations 4 and 5 to calculate the mass in transmissive and low-k zones (M/L²) and 2) using Equations 6-10 to calculate the length of borehole that is transmissive/low-k (L/L) and to calculate the percent of total contaminant mass in transmissive/low-k zones (M/M). The key findings for mass in transmissive and low-k zones (M/L²) (Figure 37 & Table 32) include:

- E1 has a majority of contaminant mass in transmissive zones (Figure 37).
- E1 has tens of kg/m² TPH in low-k zones (Table 32) even though most of TPH mass is in transmissive zones.

The mass in E1 favors transmissive zones but there is still a portion of the total mass of contaminants in low-k zones (Figure 37).

The mass of contaminant is now transformed into percentage of contaminant mass in subsurface zones (M/M). The key findings for percentage of contaminants in transmissive and low-k zones (Figure 38, Table 33, & Table 34) for Site E include:

- E1 has a percentage of contaminant mass in low-k zones that does correlate with the fraction of E1 that is low-k.
- E1 is 24% low-k and has 30% benzene mass and 29% TPH mass in low-k zones. The contaminants prefer each zone evenly.

The distribution of mass in E1 is common and represents other hydrocarbon contaminated boreholes well.

Site E is a hydrocarbon contaminated site that allows us to get a singular glimpse through E1. The usefulness of this data is limited for intra-site analysis but can be utilized in inter-site analysis well.

Table 31: Total Mass of Contaminants at Site E

Numerical values are good to 1 significant number.

Core	<u>Benzene</u>	<u>TPH</u>	<u>GRO</u>	<u>DRO</u>	<u>SUM COC</u>
	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
E1	9.17E-02	1.81E+01	3.86E+00	1.43E+01	1.82E+01

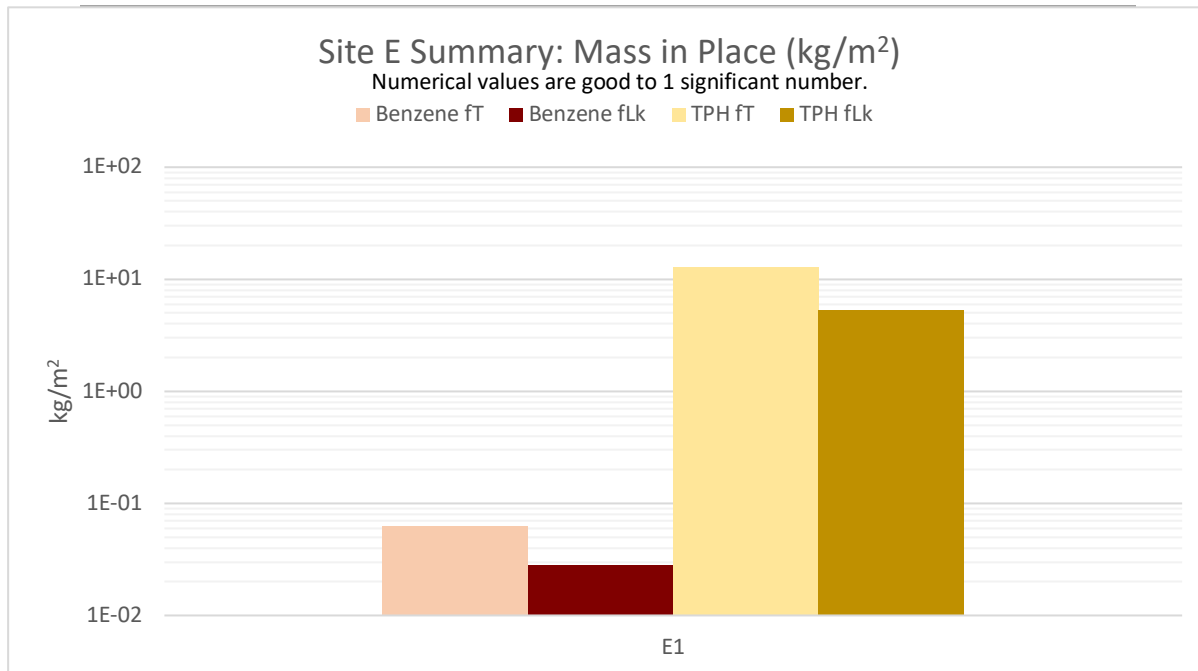


Figure 37: Mass of Contamination at Site E Divided into Zones

Table 32: Mass of Benzene, TPH, GRO, and DRO at Site E Divided into Zones

Numerical values are good to 1 significant number.

Core	<u>Benzene f_T</u>	<u>Benzene f_{Lk}</u>	<u>TPH f_T</u>	<u>TPH f_{Lk}</u>	<u>GRO f_T</u>	<u>GRO f_{Lk}</u>	<u>DRO f_T</u>	<u>DRO f_{Lk}</u>
	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
E1	6.34E-02	2.83E-02	1.28E+01	5.32E+00	2.65E+00	1.22E+00	1.02E+01	4.11E+00

	<u>SUM COCs</u>	<u>SUM COCs</u>
Core	<u>f_T</u>	<u>f_{Lk}</u>
	kg/m ²	kg/m ²
E1	1.29E+01	5.35E+00

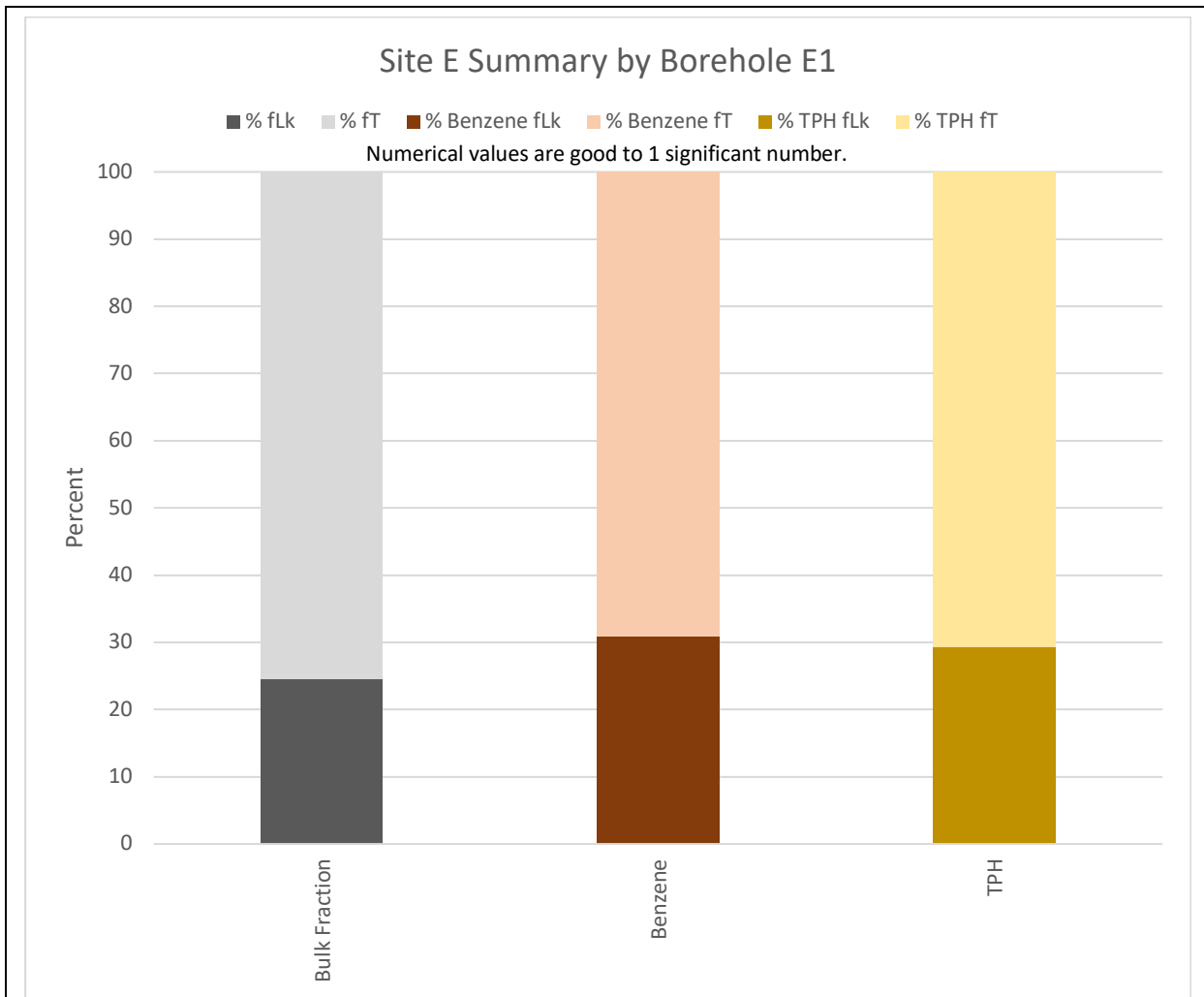


Figure 38: Percentage of Mass in Zones at Site E Ordered from Transmissive to Low-k

Table 33: Percentage of Borehole that is Transmissive of Low-k and Percentage of Benzene

Mass in Zones at Site E

Numerical values are good to 1 significant number.

Core	$\frac{\% f_T}{\% f_{Lk}}$	$\frac{\% Benzene f_T}{\% Benzene f_{Lk}}$
E1	75.43	69.15

Table 34: Percentage of TPH, GRO, and DRO Mass in Zones at Site E

Numerical values are good to 1 significant number.

Core	$\frac{\% TPH f_T}{\% TPH f_{Lk}}$	$\frac{\% GRO f_T}{\% GRO f_{Lk}}$	$\frac{\% DRO f_T}{\% DRO f_{Lk}}$
E1	70.63	68.53	71.20

3.1.6 Intra-Site F

Site F & G are the same site and it is an active DOD facility. The primary CVOCs for Site F are chlorinated solvents TCE and DCE which differ from Site G. The geologic setting of Site F & G is a braided stream deposit. At Site F & G, media containing silt and finer media is characterized as low-k. All media without silt is characterized as transmissive.

3.1.6.1 Contamination by Depth

Figure 39 is an illustrative graphic from gINT™ that advances cryogenic coring data by including geologic and contaminant data-by depth for the cored interval from Borehole F1. Starting on the left, the geologic graphic includes depth from ground surface, sediment color, graphic log, a single water table point, and transport visual. The contaminant data-by-depth then plots methane, PCE, TCE concentrations. The key findings for Borehole F1 include:

- The geology of the contaminated zone is transmissive dominated with many isolated sections of low-k zones throughout.
- The spikes in concentration of methane inversely correlate with spikes in concentrations of TCE at 29.5 feet bgs and 35.5 feet bgs.
- The contamination extends throughout the core interval (19-39 feet bgs) and beyond.
- The PCE concentrations remain at similar concentrations by depth.
- The TCE concentrations vary by depth with high concentrations at 33 feet bgs and 35 feet bgs.
- The spikes in concentration of methane inversely correlate with spikes in concentrations of TCE at 29.5 feet bgs and 35.5 feet bgs.

Borehole F1 is a chlorinated solvent contaminated core with varying concentrations of contaminants by depth. The shifting concentrations of methane could provide evidence for different, active microbial communities, Sale T. et al (2017).

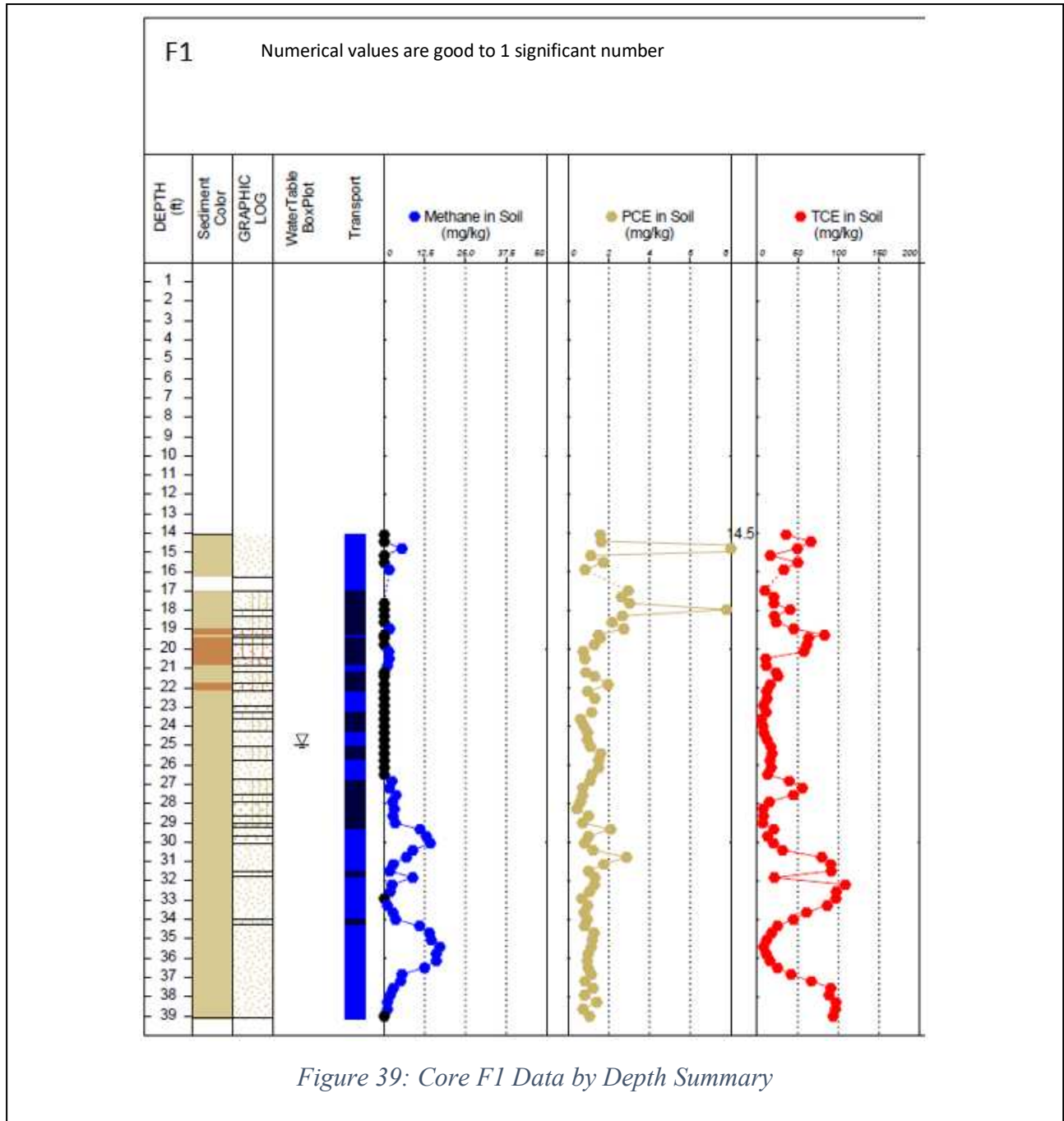


Figure 40 is an illustrative graphic from gINT™ that follows the format of Figure 39. The key findings for Borehole F2 include:

- The geology of the contaminated zone is transmissive dominated with many isolated sections of low-k zones throughout.
- No methane was found at any depth
- The contamination is found throughout the cored interval (9-23 feet bgs) and extends beyond.
- F2 has concentrations of PCE and TCE that remain at similar concentrations by depth.

Borehole F2 is a chlorinated solvent contaminated core with minor chlorinated solvent concentration by depth and no registered methane concentrations by depth. We believe the absence of methane correlates to methane being used as an electron acceptor in support of reductive dechlorination of TCE.

F2

Numerical values are good to 1 significant number

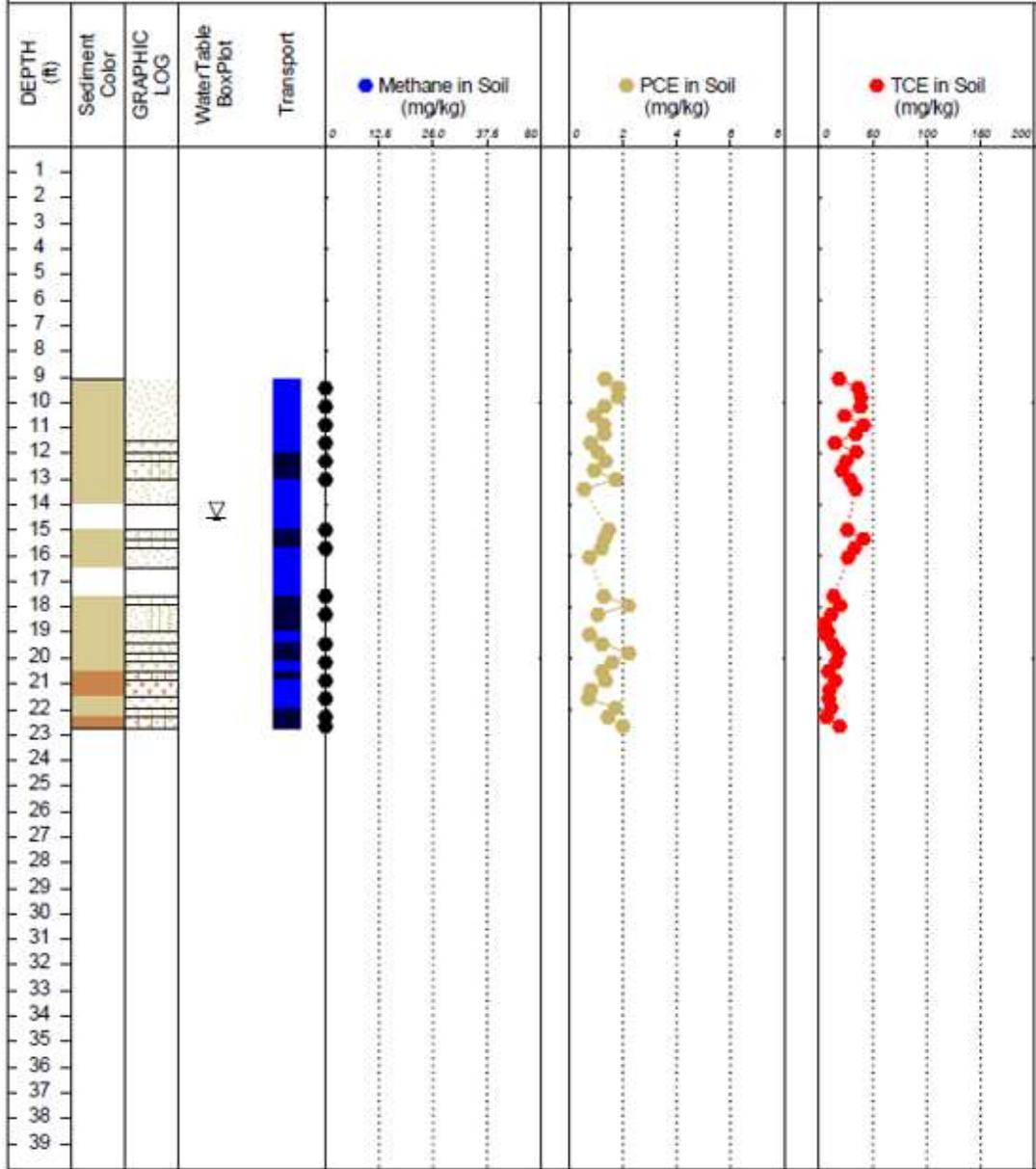


Figure 40: Core F2 Data by Depth Summary

Figure 41 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole F3 include:

- The geology of the contaminated zone is transmissive dominated with 2 isolated sections of low-k zones.
- Concentrations of methane are consistent throughout the borehole and do not correlate to any contaminant concentrations.
- The contamination is found throughout the cored interval (9-27 feet bgs) and extends beyond.
- Concentrations of PCE vary by depth but remain under 8 mg/kg.
- Concentrations of TCE vary between 0-400 mg/kg. High concentrations of TCE between 13-16 feet bgs.

Borehole F3 is a chlorinated solvent contaminated core with high chlorinated solvent concentrations in isolated depths and no correlations of methane to contaminants. The presence of methane could provide evidence for active microbial populations.

F3

Numerical values are good to 1 significant number

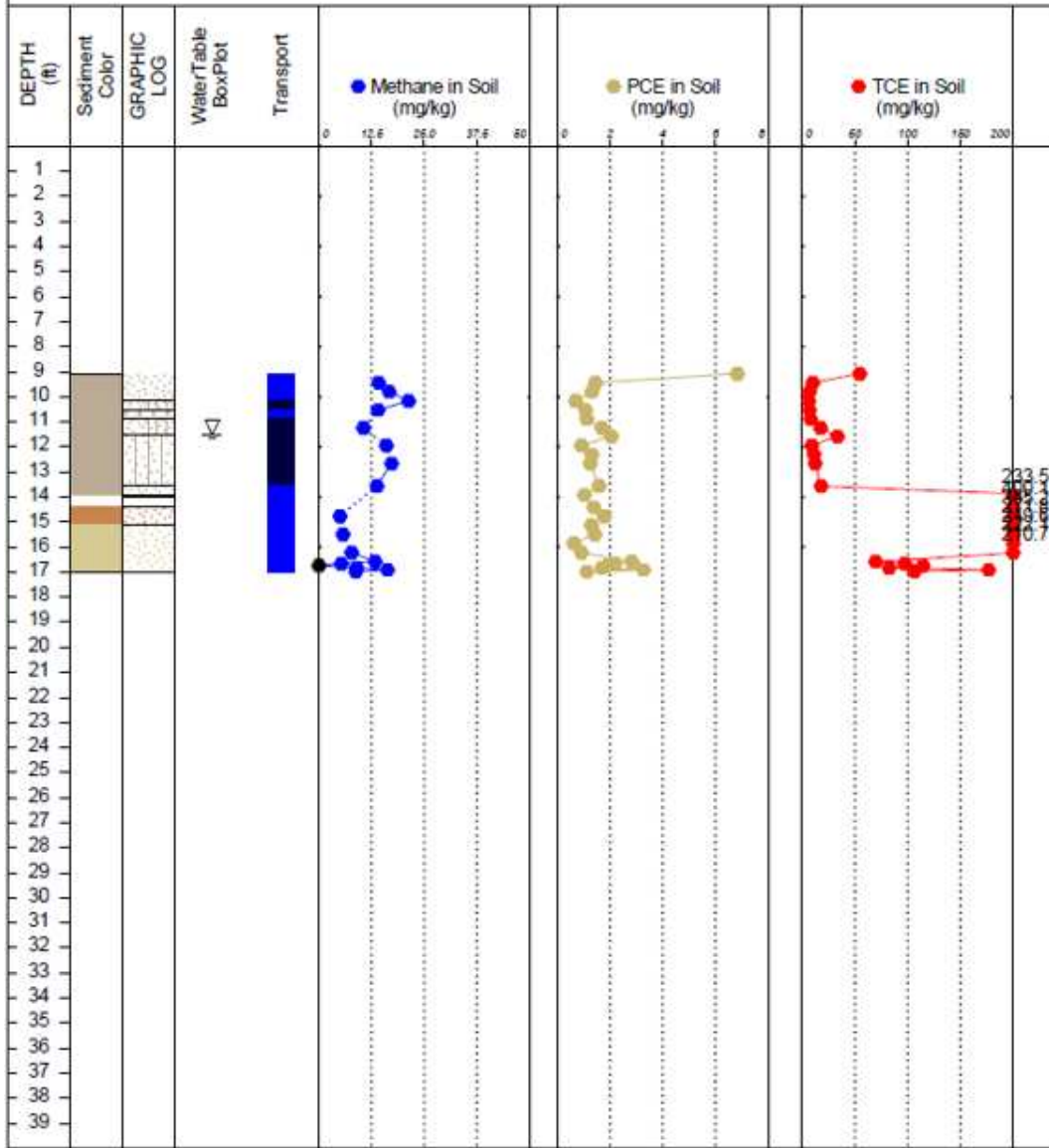


Figure 41: Core F3 Data by Depth Summary

3.1.6.2 Mass in Place Summary Analysis

Using the information presented from the previous paragraphs, the mass of contaminants are calculated using Equations 1-3. The key findings for mass of contaminants in the borehole (Table 35) include:

- F1, F2, and F3 have similar masses of PCE (Table 35).
- The total mass of TCE are similar for F1 and F3 at 0.49 kg/m² (Table 35).
- The total mass of TCE for F2 is approximately 30% the mass in F1 or F3 (Table 35).
- F2 has no recorded methane (Table 35).

3.1.6.3 Mass in Transmissive and Low-k Zones Summary Analysis

The mass in transmissive and low-k zones is presented with two formats including 1) using equations 4 and 5 to calculate the mass in transmissive and low-k zones (M/L²) and 2) using Equations 6-10 to calculate the length of borehole that is transmissive/low-k (L/L) and to calculate the percent of total contaminant mass in transmissive/low-k zones (M/M). The key findings for mass in transmissive and low-k zones (M/L²) (Figure 42 & Table 36) include:

- Site F has a majority of contaminant mass in transmissive zones (Figure 42).
- F1 and F2 have a large portion of the total mass of TCE in low-k zones (Table 36).
- Site F has a majority of methane mass in transmissive zones (Figure 42).
- F3 has almost all TCE mass in transmissive zones

The mass in transmissive zones is greater than mass in low-k zones while still having a large portion of the total mass in low-k for boreholes at Site F (Figure 42).

The mass of contaminant is now transformed into percentage of contaminant mass in subsurface zones (M/M). The key findings for percentage of contaminants in transmissive and low-k zones (Figure 43 & Table 37) for Site F include:

- F3 has a percentage of contaminant mass in low-k zones that does not correlate with the fraction of C1 that is low-k.
- F3 is 40% low-k and the low-k zone has over 21% of the PCE and 3% of TCE mass. The distribution of contaminants at F3 prefers transmissive zones.
- F1 and F2 have percentages of contaminant mass in low k zones that correlate with the fraction of their borehole that is low-k. Contaminant mass at F1 and F2 prefers each zone evenly.
- F1 is 37% low-k and has 42% of PCE and 30% TCE in low-k zones.
- F2 is 43% low-k and has 50% of PCE and 36% TCE in low-k zones.

Boreholes F1-F3 are very similar. Inter-site results present statistics that help determine if the boreholes from Site F shows any significant preference for zones. Site F is a chlorinated solvent contaminated site that allows us to view a site before remediation activities.

Boreholes from Site F allow a unique opportunity to measure distribution of contamination before remediation. Site F is one of the few sites to have the mass in place distributions that are observed to be very similar for F1-F3. Overall, Site F provides a beneficial view into the distribution of contamination in subsurface media before remediation activities.

Table 35: Total Mass of Contaminants at Site F
Numerical values are good to 1 significant number.

	<u>PCE</u>	<u>TCE</u>	<u>Methane</u>	<u>SUM CVOC</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²
F1	1.72E-02	4.34E-01	3.67E-02	4.96E-01
F3	7.61E-03	5.01E-01	3.48E-02	5.08E-01
F2	5.39E-03	9.55E-02	0.00E+00	1.60E-01
Site F (AVG)	1.01E-02	3.43E-01	2.38E-02	3.88E-01

Site F Summary: Mass in Place (kg/m²)

Numerical values are good to 1 significant number.

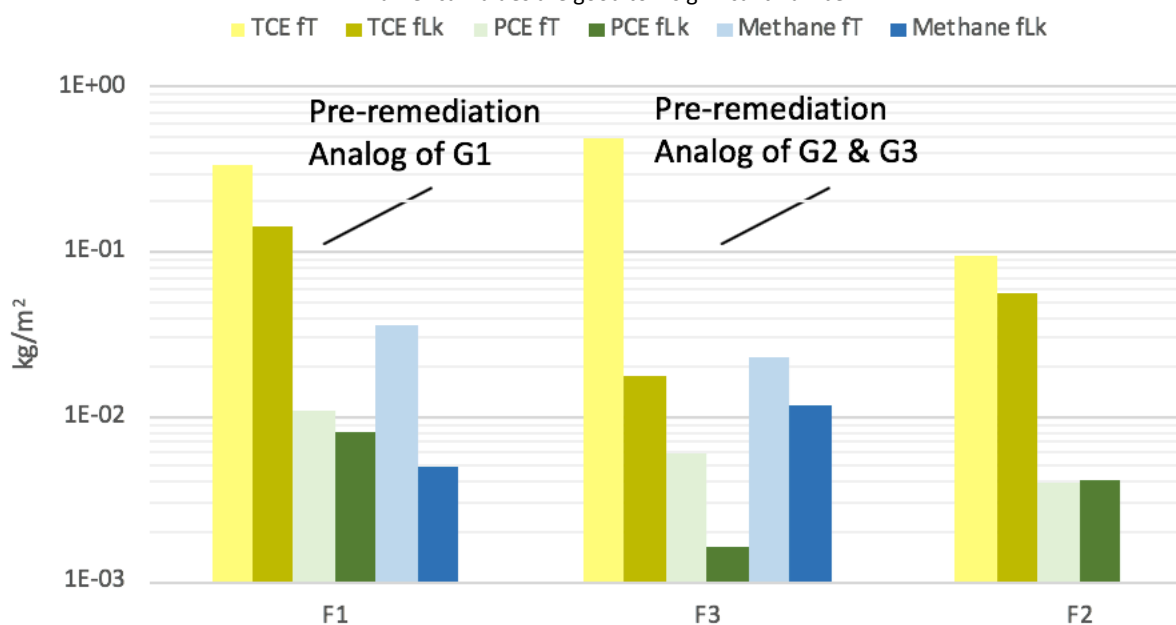


Figure 42: Mass of Contamination at Site F Divided into Zones

Table 36: Mass of PCE, TCE, and Methane at Site F Divided into Zones
Numerical values are good to 1 significant number.

	<u>PCE</u>	<u>PCE</u>	<u>TCE</u>	<u>TCE</u>	<u>Methane</u>	<u>Methane</u>	<u>SUM CVOC</u>	<u>SUM CVOC</u>
	<u>f_T</u>	<u>f_{Lk}</u>	<u>f_T</u>	<u>f_{Lk}</u>	<u>f_T</u>	<u>f_{Lk}</u>	<u>f_T</u>	<u>f_{Lk}</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
F1	9.97E-03	7.27E-03	3.02E-01	1.32E-01	3.21E-02	4.61E-03	3.43E-01	1.53E-01
F3	6.01E-03	1.60E-03	4.83E-01	1.74E-02	2.31E-02	1.16E-02	4.89E-01	1.90E-02
F2	3.12E-03	2.28E-03	6.36E-02	3.19E-02	0.00E+00	0.00E+00	9.97E-02	6.03E-02
Site F								
(AVG)	6.37E-03	3.71E-03	2.83E-01	6.04E-02	1.84E-02	5.41E-03	3.11E-01	7.74E-02

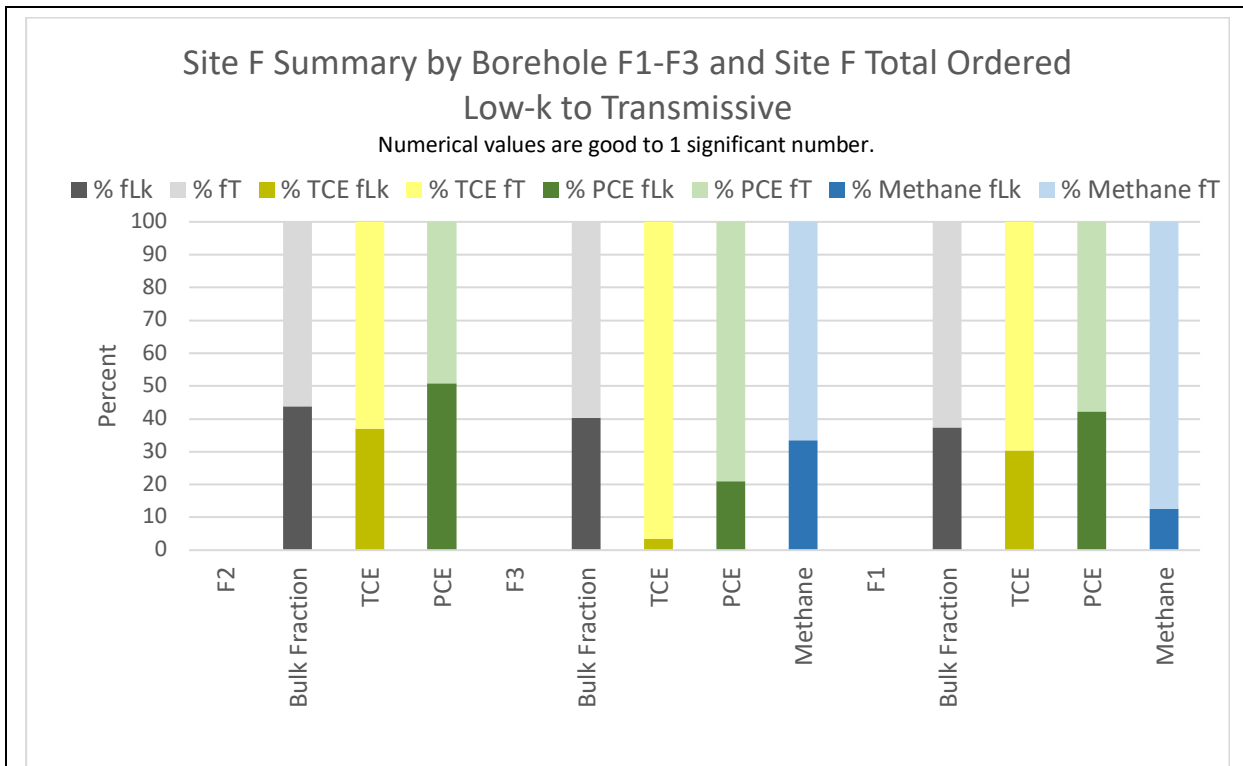


Figure 43: Percentage of Mass in Zones at Site F Ordered from Transmissive to Low-k

Table 37: Percentage of Borehole that is Transmissive of Low-k and Percentage PCE, TCE, and Methane Mass in Zones at Site F

Numerical values are good to 1 significant number.

Core	% f_T		% PCE		% TCE		% Methane	
	f_T	f_{Lk}	f_T	f_{Lk}	f_T	f_{Lk}	f_T	f_{Lk}
F1	62.60	37.40	57.83	42.17	69.65	30.35	87.43	12.57
F3	59.62	40.38	78.96	21.04	96.52	3.48	66.57	33.43
F2	56.29	43.71	49.26	50.74	63.03	36.97	0.00	0.00

3.1.7 Intra-Site G

Site F & G is an active DOD facility. The primary CVOCs at Site G are chlorinated solvents TCE and PCE. The geologic setting of Site F & G is a braided stream deposit. At Site

F & G, media containing silt and finer media is characterized as low-k. All media without silt is characterized as transmissive.

3.1.7.1 Contamination by Depth

Figure 44 is an illustrative graphic from gINT™ that advances cryogenic coring data by including geologic and contaminant data-by depth for the cored interval from Borehole G1. G1 is the post remediation analog of F1. Starting on the left, the geologic graphic includes depth from ground surface, sediment color, graphic log, no water table data, and transport visual. The contaminant data-by-depth then plots methane, DCE, TCE concentrations. The key findings for Borehole G1 include:

- The geology of the contaminated zone is low-k dominated with 2 small sections of transmissive zones.
- The concentrations of methane in G1 are high and consistent (~25 mg/kg)
- The increase in concentrations of methane correlates with increases in concentrations of DCE at 7.5 feet bgs and 16 feet bgs.
- The contamination extends throughout the core interval (7.5 feet bgs) and beyond the cored interval (15feet bgs +).
- The DCE concentrations have a small range of concentrations by depth (0-4 mg/kg).
- There is only one data point for TCE concentration (6.5feet bgs).

Borehole G1 is a chlorinated solvent contaminated core with varying concentrations of contaminants by depth. The presence of methane could provide evidence for active microbial populations.

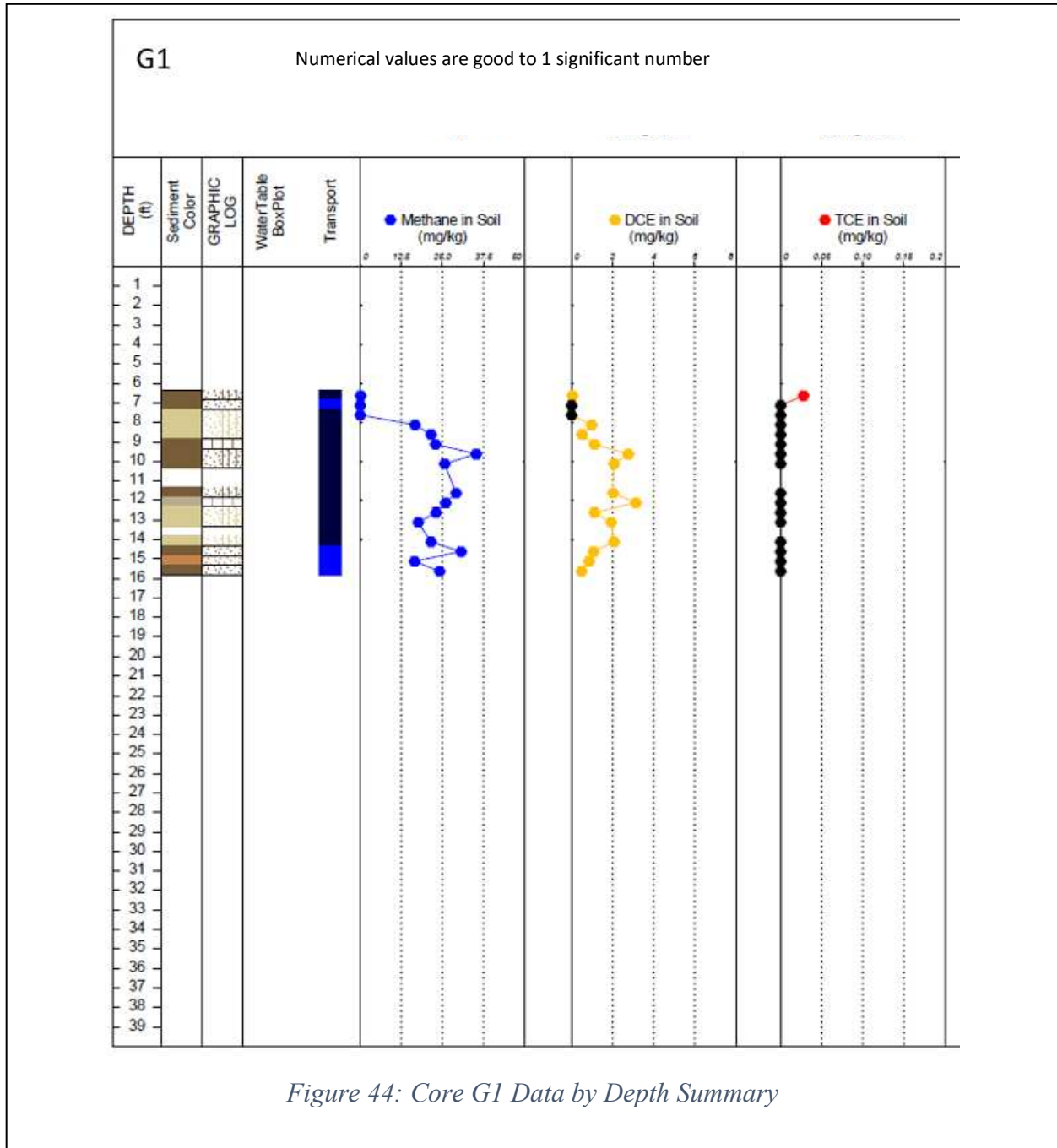


Figure 45 is an illustrative graphic from gINT™ that follows the format of Figure 44.

The key findings for Borehole G2 include:

- The geology of the contaminated zone is low-k dominated with several sections of transmissive zones.

- The contamination is found in very small concentrations throughout the cored interval (25.5-39 feet bgs).
- DCE and TCE remain at small concentrations (>0.2 mg/kg) by depth.

Borehole G2 is a chlorinated solvent contaminated core with minimal chlorinated solvent concentration at deeper depths. The presence of methane could provide evidence for active microbial populations.

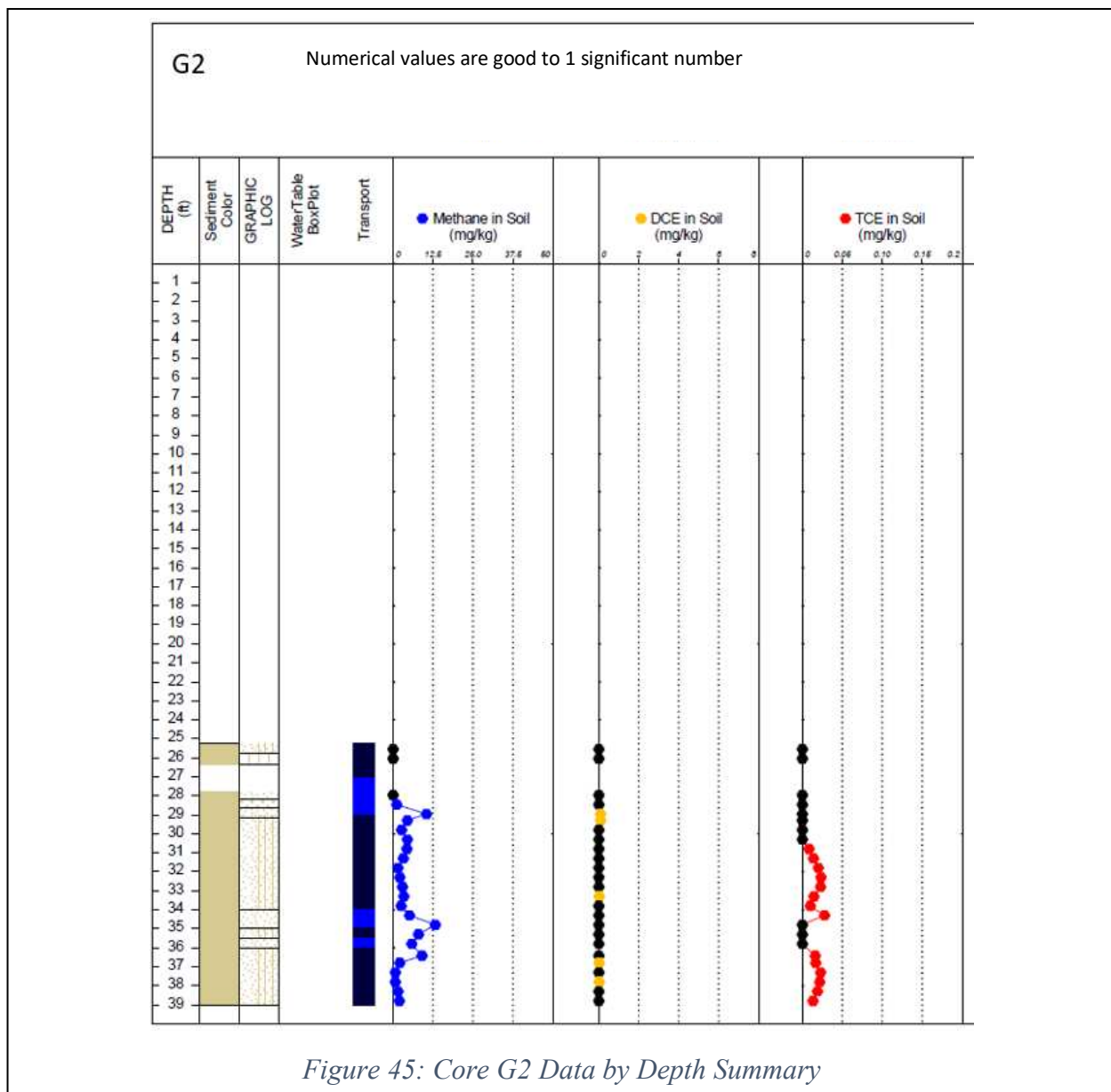


Figure 46 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole G3 include:

- The geology of the contaminated zone has both transmissive and low-k zones with low-k zones dominating the zone targeted by LIF.
- Concentrations of methane are inconsistent throughout the borehole.
- The contamination is found throughout the cored interval (8-19 feet bgs) and becomes minimal at the bottom of cored interval.
- Concentrations of DCE vary by depth but remain under 6 mg/kg.
- 3 insignificant data points for TCE concentration.

Borehole G3 is a chlorinated solvent contaminated core with small chlorinated solvent concentrations in isolated depths and no correlations of methane to contaminants. The presence of methane could provide evidence for active microbial populations.

G3

Numerical values are good to 1 significant number

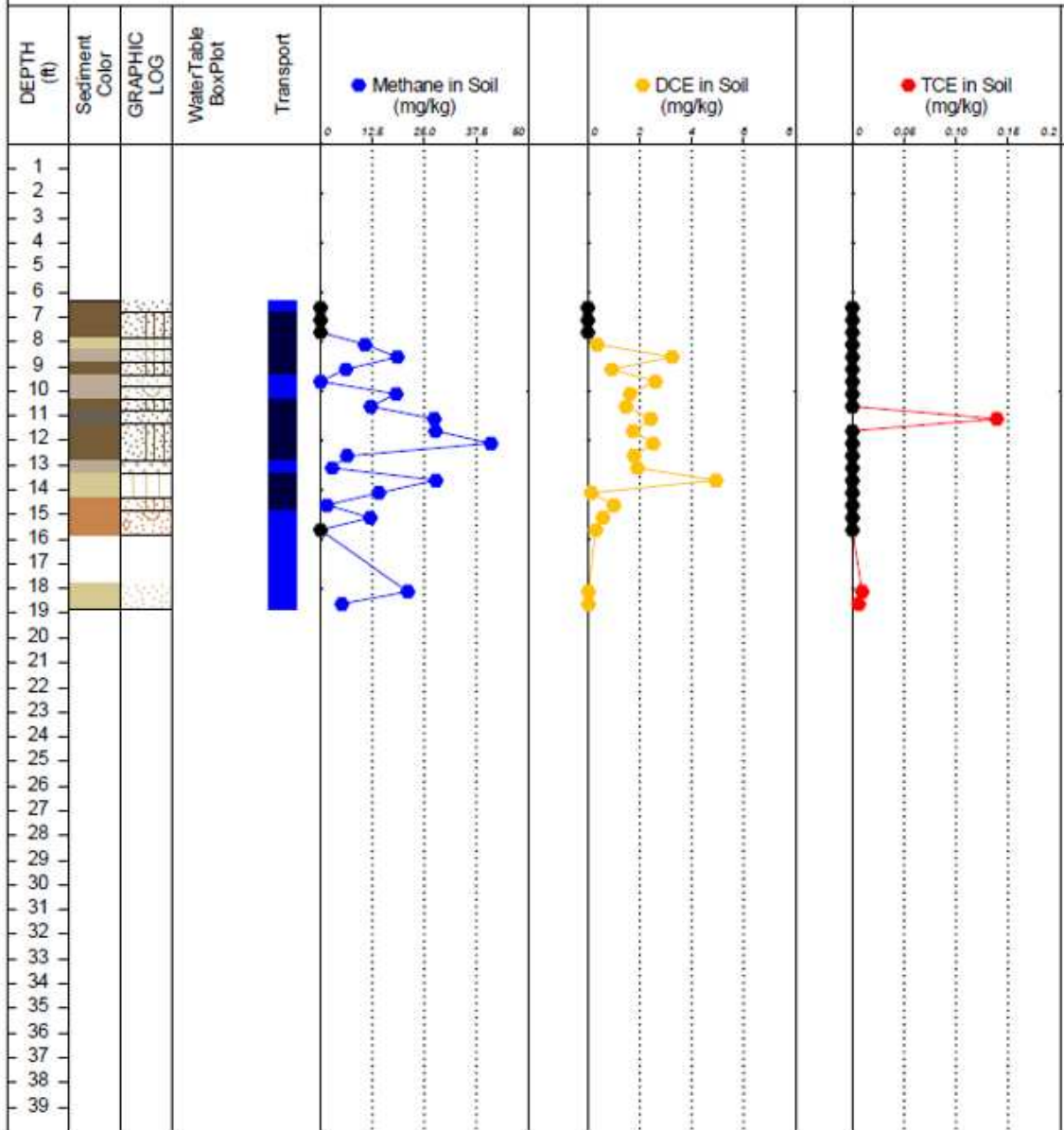


Figure 46: Core G3 Data by Depth Summary

3.1.7.2 Mass in Place Summary Analysis

Using the information presented from the previous paragraphs, the mass of contaminants are calculated using Equations 1-3. The key findings for mass of contaminants in the borehole (Table 38) include:

- G1, G2, and G3 have similar masses of TCE (Table 38).
- The total mass of DCE are similar for G2 and G3 at 0.007 kg/m² (Table 38).
- G1, G2, and G3 have methane present in expected amounts but with variation (Table 38).

3.1.7.3 Mass in Transmissive and Low-k Zones Summary Analysis

The mass in transmissive and low-k zones is presented with two formats including 1) using equations 4 and 5 to calculate the mass in transmissive and low-k zones (M/L²) and 2) using Equations 6-10 to calculate the length of borehole that is transmissive/low-k (L/L) and to calculate the percent of total contaminant mass in transmissive/low-k zones (M/M). The key findings for mass in transmissive and low-k zones (M/L²) (Figure 47 & Table 39) include:

- Site G has a majority of contaminant mass in low-k zones (Figure 47).
- G1 and G2 have the majority of a small amount of mass of TCE in low-k zones (Table 39).
- G2 and G3 have a large portion of the total mass of DCE in low-k zones (Table 39)
- Site G has a majority of methane mass in low-k zones (Figure 47).
- Site G has changed to prefer low-k zones after remediation of Site F.

The mass in low-k zones is greater than mass in transmissive zones for boreholes at Site G (Figure 47).

The mass of contaminant is now transformed into percentage of contaminant mass in subsurface zones (M/M). The key findings for percentage of contaminants in transmissive and low-k zones (Figure 48 & Table 40) for Site G include:

- G1, G2 and G3 have percentages of contaminant mass in low-k zones that do not correlate with the fraction, of their respective borehole, that is low-k.
- The mass of contaminants at Site G prefers low-k zones.

All boreholes have similar distributions while favoring low-k zones. Site G is a chlorinated solvent contaminated site that allows insight of subsurface contaminant distribution after remediation activities.

Boreholes from Site G allow a unique opportunity to measure distribution of contamination after remediation. Boreholes at Site G show strong similarities with each other. The similarities are concentrations of contaminants by depth, total mass in place, and mass of contaminants in zones. Unlike the pre-remediation samples, contaminants at Site G prefer low-k zones. Inter-site results will present statistics that will help determine if the difference in preference is significant or not. Site G provides a beneficial view into the distribution of contamination in subsurface media after remediation activities.

Table 38: Total Mass of Contaminants at Site G
Numerical values are good to 1 significant number

	<u>DCE</u>	<u>TCE</u>	<u>Methane</u>	<u>SUM CVOC</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²
G1	6.18E-05	8.65E-05	2.79E-02	1.48E-04
G2	8.01E-03	4.69E-05	8.45E-02	8.05E-03
G3	7.59E-03	7.41E-06	1.14E-01	7.59E-03
Site G (AVG)	5.22E-03	4.69E-05	7.56E-02	5.27E-03

Site G Summary: Mass in Place (kg/m²)

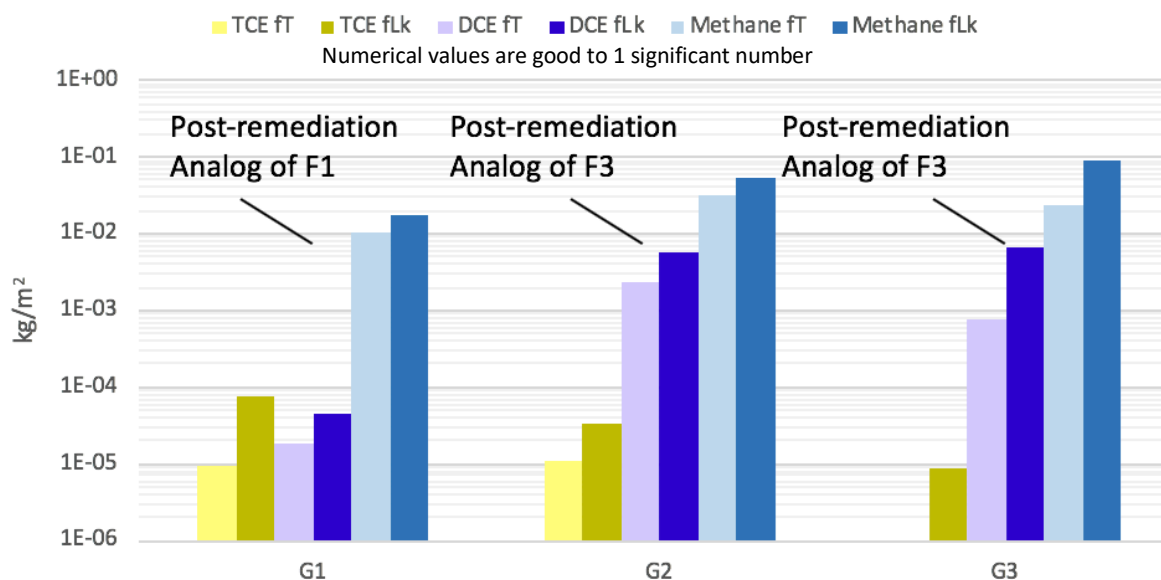


Figure 47: Mass of Contamination at Site G Divided into Zones

Table 39: Mass of DCE, TCE, and Methane at Site G Divided into Zones
Numerical values are good to 1 significant number

	<u>DCE</u>	<u>DCE</u>	<u>TCE</u>	<u>TCE</u>	<u>Methane</u>	<u>Methane</u>	<u>SUM</u>	<u>SUM</u>
	<u>f_T</u>	<u>f_{Lk}</u>	<u>f_T</u>	<u>f_{Lk}</u>	<u>f_T</u>	<u>f_{Lk}</u>	<u>f_T</u>	<u>f_{Lk}</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
G1	1.98E-05	4.45E-05	9.88E-06	7.66E-05	1.03E-02	1.77E-02	2.72E-05	1.21E-04
G2	2.40E-03	5.61E-03	1.24E-05	3.46E-05	3.19E-02	5.26E-02	2.41E-03	5.64E-03
G3	7.51E-04	6.83E-03	0.00E+00	7.41E-06	2.28E-02	9.16E-02	7.51E-04	6.84E-03
Site G (AVG)	1.06E-03	4.16E-03	7.41E-06	3.95E-05	2.17E-02	5.40E-02	1.06E-03	4.20E-03

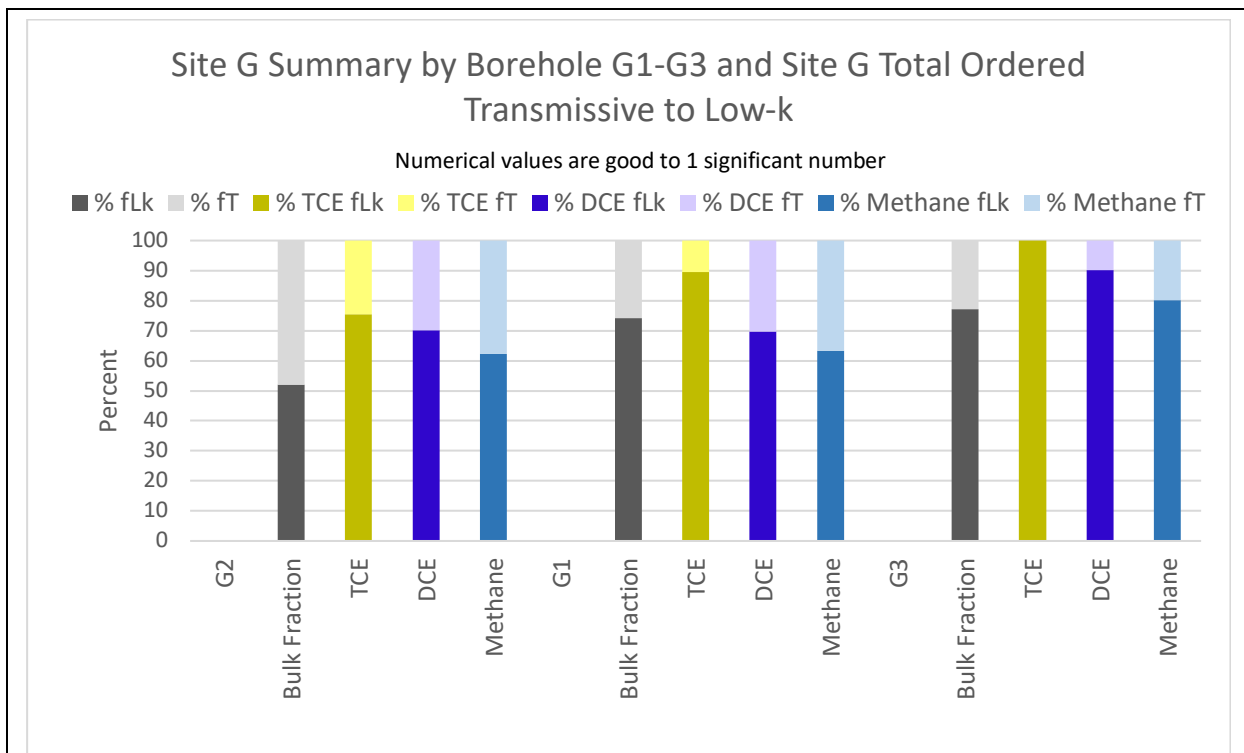


Figure 48: Percentage of Mass in Zones at Site G Ordered from Transmissive to Low-k

Table 40: Percentage of Borehole that is Transmissive of Low-k and Percentage DCE, TCE, and Methane Mass in Zones at Site G

Numerical values are good to 1 significant number

Core	% DCE		% DCE		% TCE		% Methane	% Methane
	f_T	f_{Lk}	f_T	f_{Lk}	f_T	f_{Lk}	f_T	f_{Lk}
G1	25.92	74.08	30.28	69.72	10.51	89.49	36.73	63.27
G2	48.00	52.00	29.94	70.06	24.48	75.52	37.76	62.24
G3	22.87	77.13	9.91	90.09	0.00	100.00	19.93	80.07

3.1.8 Intra-Site H

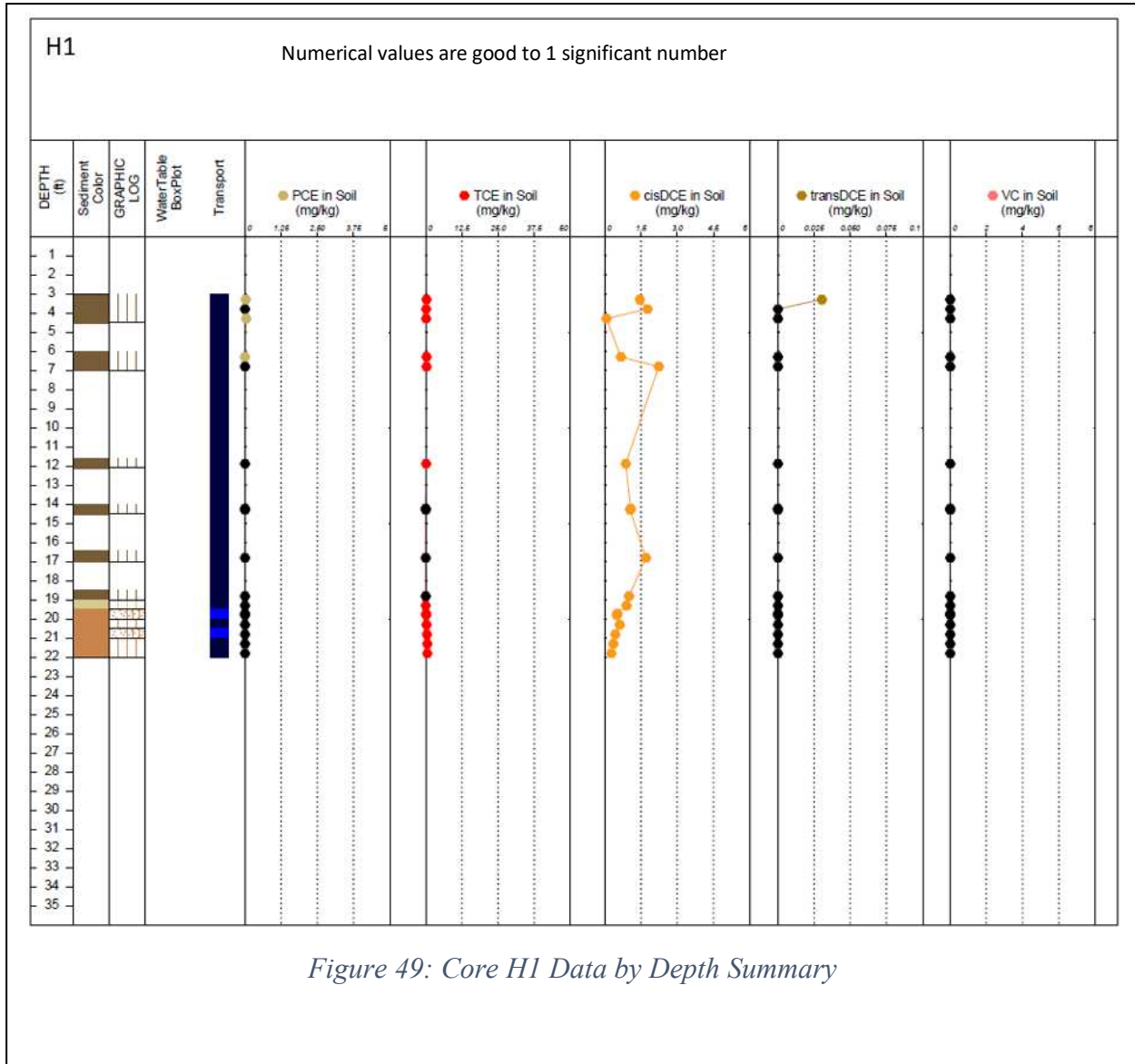
Site H is an active DOD facility. Boreholes H1-H4 are sampled in a remediated zone and H5 and H6 sampled outside the remediated zone. The primary CVOCs are the chlorinated solvents PCE, TCE, DCE, and VC. The geologic setting is a tidal estuary. At Site H, media defined as sandy silt and finer media is characterized as low-k. Media defined as silty sand and larger media is characterized as transmissive.

3.1.8.1 Contamination by Depth

Figure 49, Figure 50, Figure 51, & Figure 52 are illustrative graphics from gINT™ that advance cryogenic coring data by including geologic and contaminant data-by depth for the cored interval from the remediated Boreholes H1, H2, H3, and H4. Starting on the left, the geologic graphic includes depth from ground surface, sediment color, graphic log, no water table data, and transport visual. The contaminant data-by-depth then plots PCE, TCE, cis-DCE, trans-DCE, and VC concentrations. The key findings include:

- Recovery losses are significant for H1, H2, and H3.
- The geology of the contaminated zone is dominated by low-k zones with isolated sections of transmissive zones at depth for H1, H2, H3, and H4.
- At H1, the contamination extends throughout the core interval (3-22 feet bgs)
- At H2, the contamination extends throughout the core interval (3-19.8 feet bgs)
- At H3, the contamination extends throughout the core interval (7-19.5 feet bgs)
- At H4, the contamination is contained within the core interval (7-19.5 feet bgs)
- The PCE, TCE, trans-DCE, and VC concentrations are negligible for H1, H2, H3, and H4.
- At H1, the cis-DCE concentrations vary by depth but visibly decrease near the transmissive zones.
- At H2, the cis-DCE concentrations vary by depth and extend outside of the sampled zones
- At H3, the cis-DCE concentrations stay consistent by depth (~1.5 mg/kg).
- At H4, the cis-DCE concentrations stay consistent and low by depth.

Boreholes H1, H2, H3, and H4 are chlorinated solvent contaminated cores with minimal chlorinated solvent concentrations at depth. This promotes the notion that remediation was successful on site when compared to Boreholes H5 and H6.



H3

Numerical values are good to 1 significant number

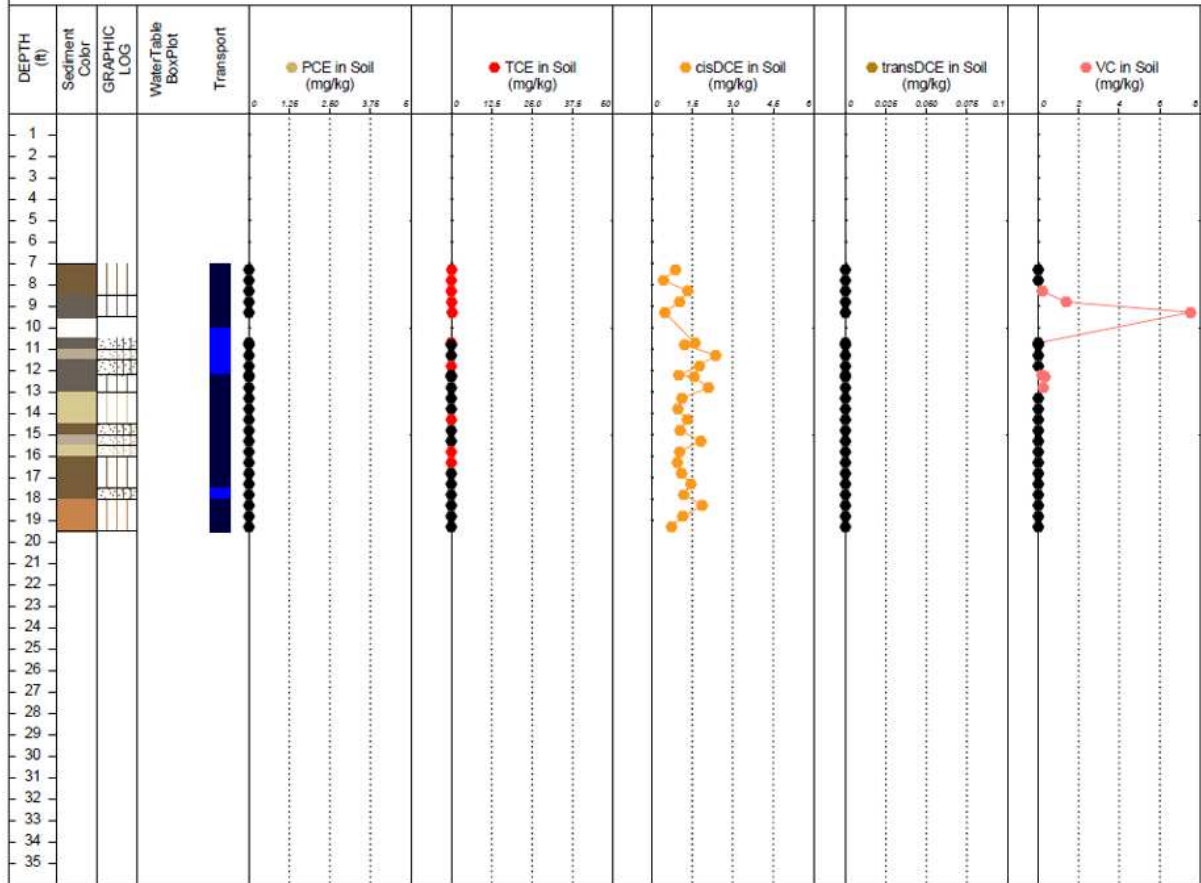


Figure 50: Core H3 Data by Depth Summary

H2

Numerical values are good to 1 significant number

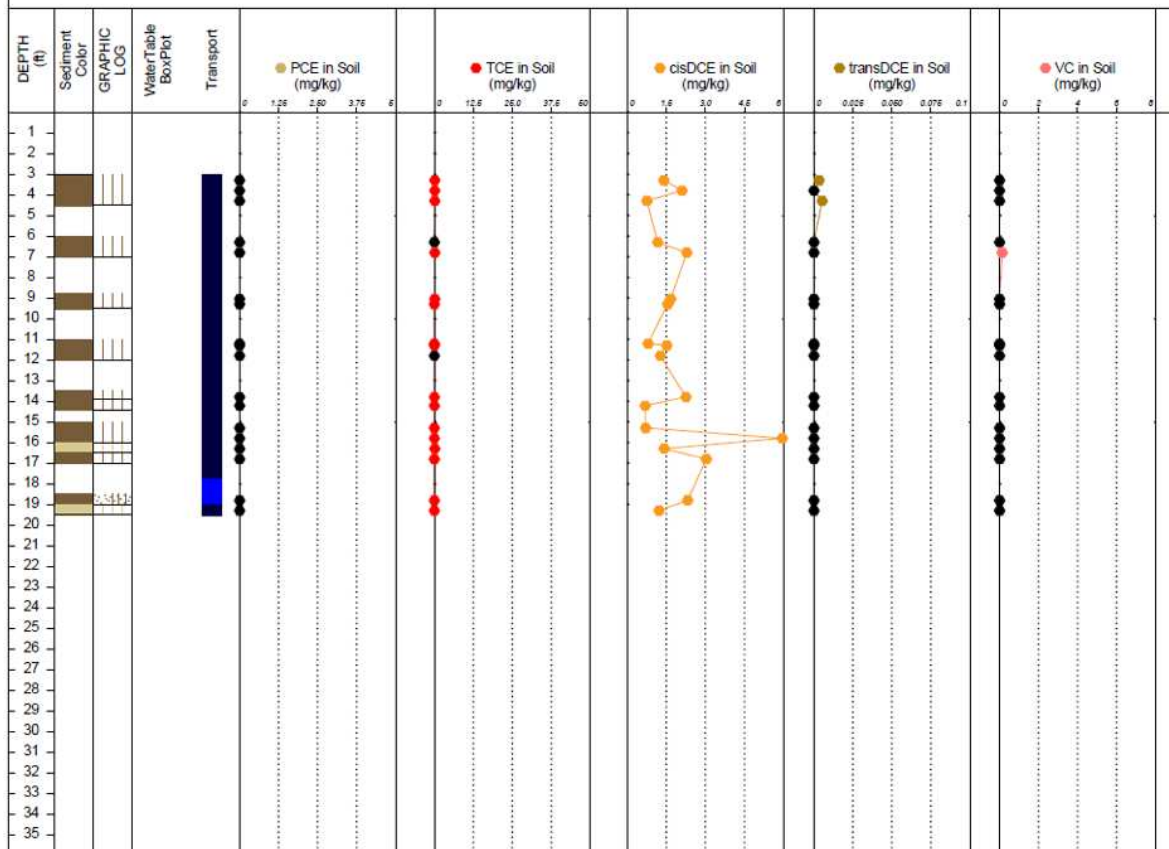


Figure 51: Core H2 Data by Depth Summary

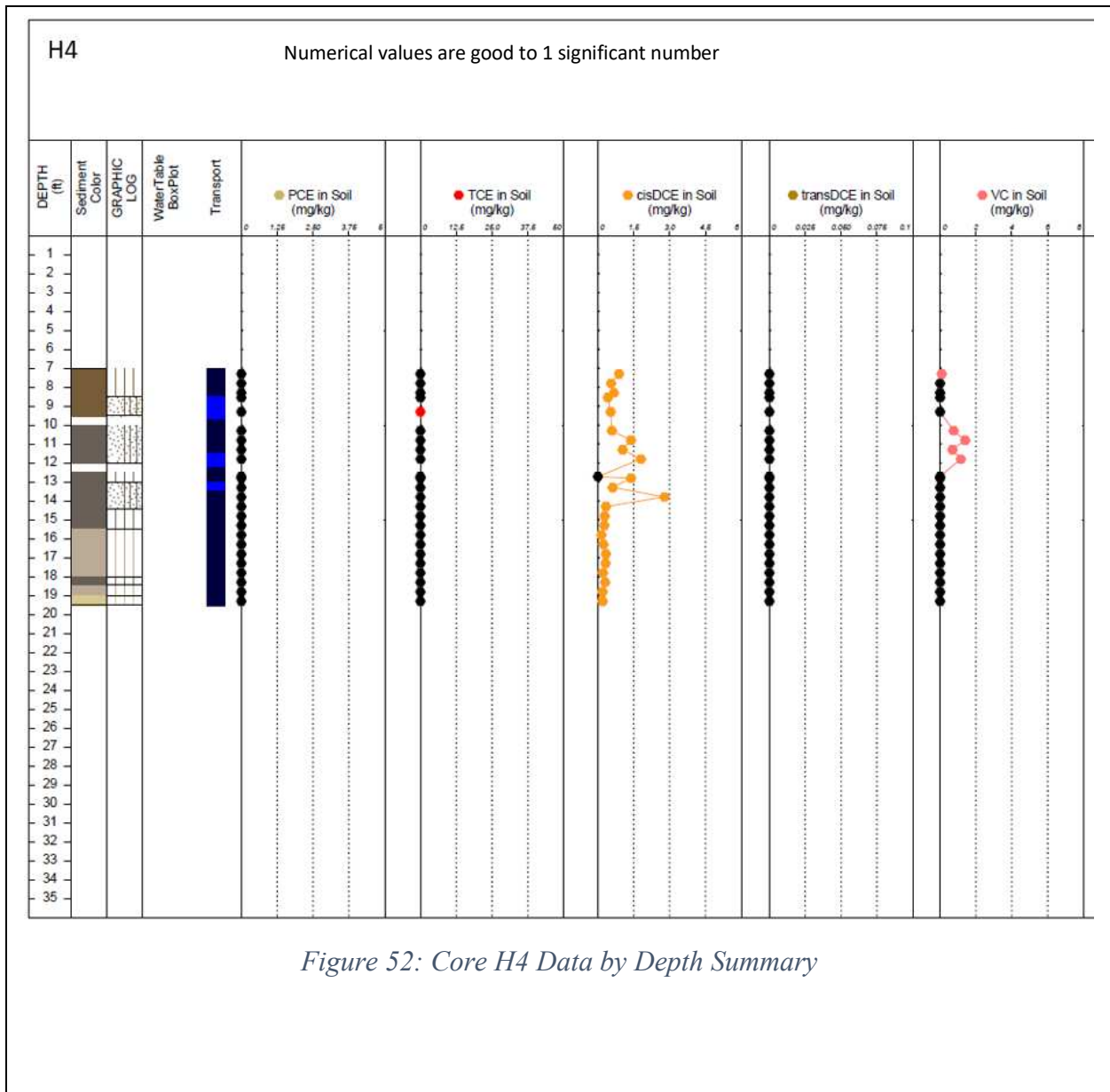


Figure 53 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole H5 include:

- The geology of the contaminated zone is dominated by low-k zones with isolated sections of transmissive zones.

- At H5, the contamination is within the core interval (7-19.5 feet bgs) and extends beyond the bottom of the interval.
- The PCE and VC concentrations are negligible or non-existent.
- The TCE and DCE concentrations have very high concentrations.

Borehole H5 is a chlorinated solvent contaminated core with high chlorinated solvent concentrations at depth.

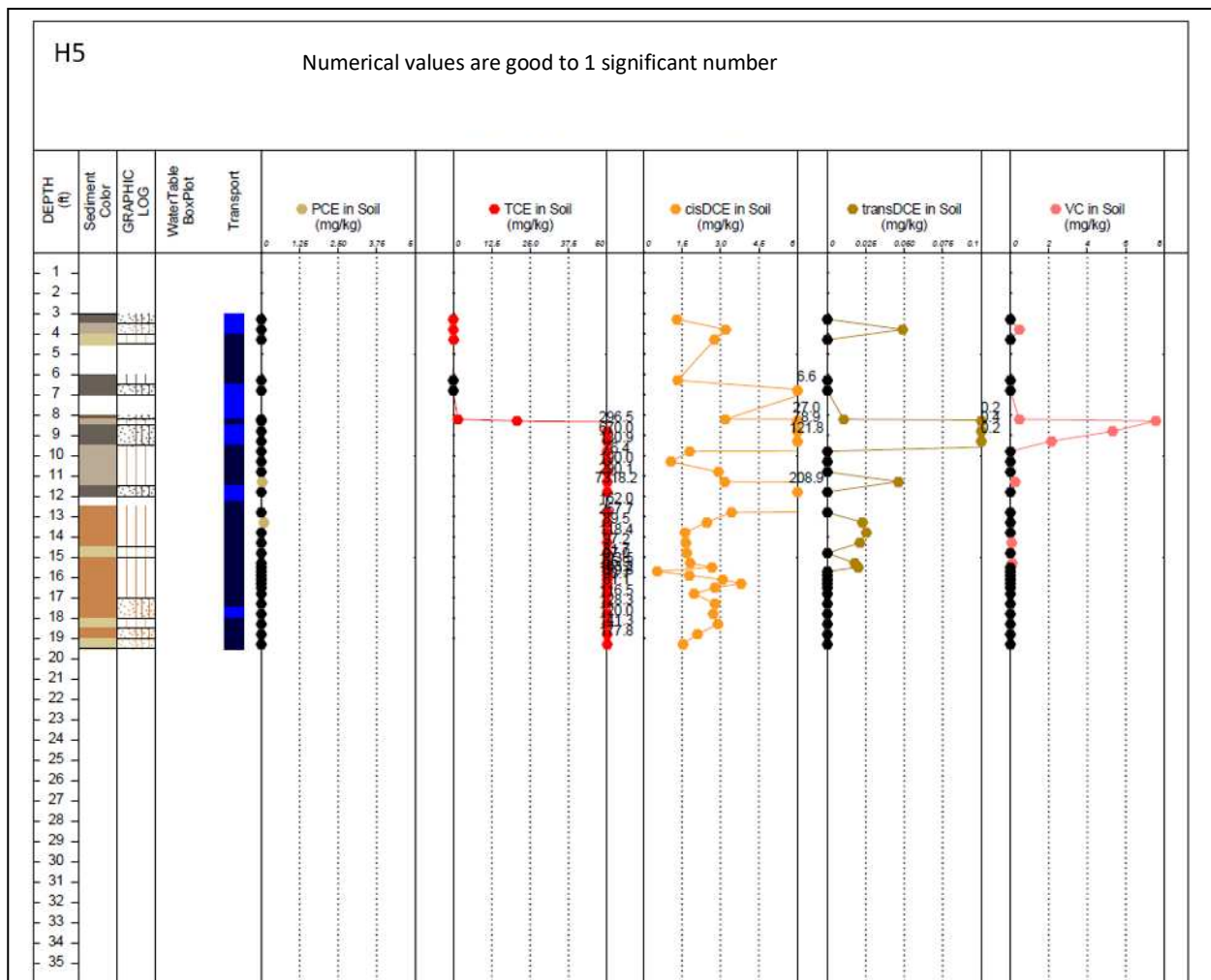
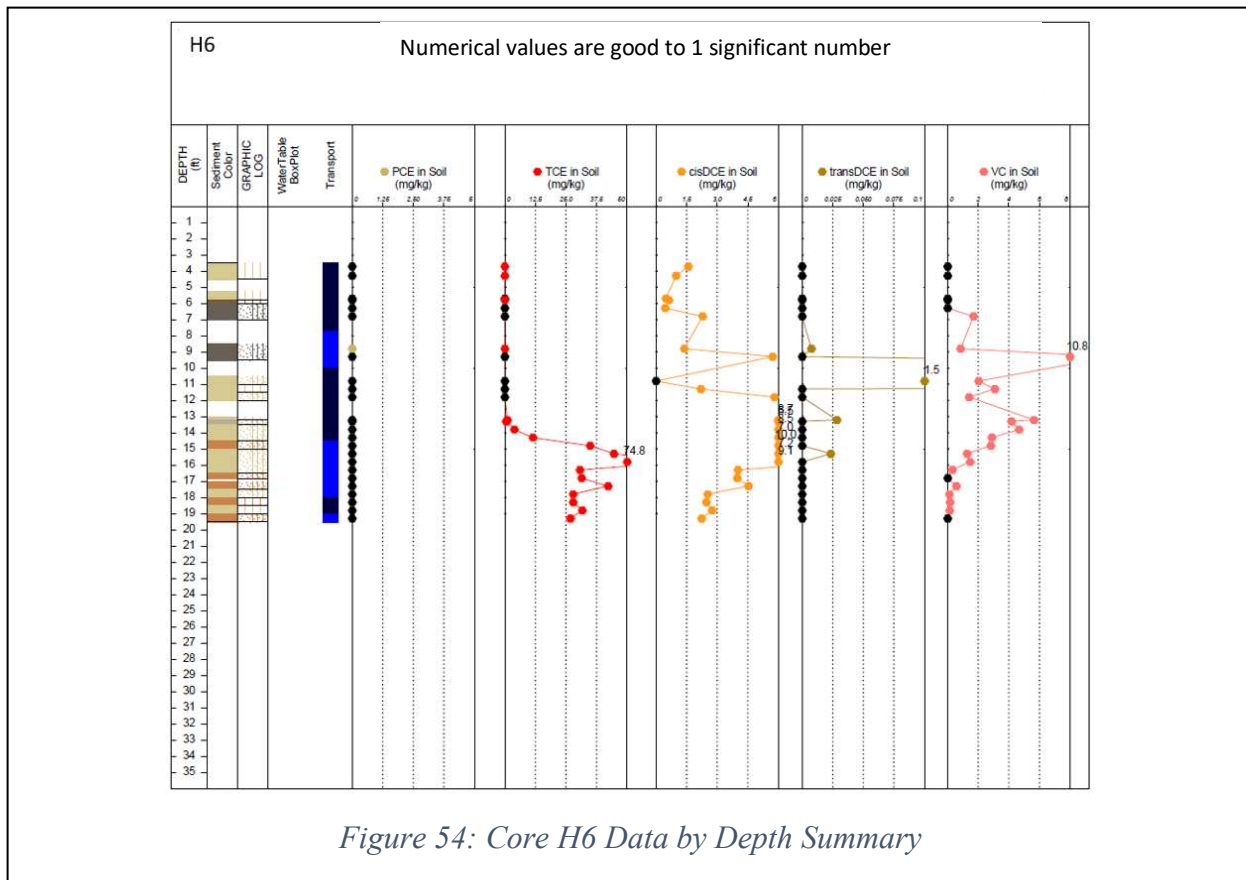


Figure 53: Core H5 Data by Depth Summary

Figure 54 is an illustrative graphic from gINT™ that follows the previous format. The key findings for Borehole H6 include:

- The geology of the contaminated zone is dominated by low-k zones with isolated sections of transmissive zones.
- At H6, the contamination is within the core interval (3.5-19.5 feet bgs) and extends beyond the bottom of the interval.
- The PCE concentrations are negligible or non-existent.
- The TCE, DCE, and VC concentrations are large.

Borehole H6 is a chlorinated solvent contaminated core with high chlorinated solvent concentrations at depth.



3.1.8.2 Mass in Place Summary Analysis

Using the information presented from the previous paragraphs, the mass of contaminants are calculated using Equations 1-3. The key findings for mass of contaminants in the borehole (Table 41) include:

- H1, H2, H3, and H4 have similar masses of contamination (Table 41).
- H1, H2, H3, and H4 only have mass for DCE (Table 41).
- H3 has an unusually high mass of VC (Table 41).
- H5 has a large mass of TCE at 14,000 kg/ace (Table 41).
- H6 has alarge portion of the total mass throughout (Table 41).
- PCE is irrelevant or non-existent (Table 41).

Table 41: Total Mass of Contaminants at Site H
Numerical values are good to 1 significant number.

	<u>PCE</u>	<u>TCE</u>	<u>DCE</u>	<u>VC</u>	<u>SUM CVOC</u>
Core	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²
H1	2.22E-05	1.27E-03	1.03E-02	0.00E+00	1.16E-02
H2	0.00E+00	4.27E-04	1.47E-02	9.64E-05	1.52E-02
H3	0.00E+00	3.68E-04	7.89E-03	7.97E-03	1.62E-02
H4	0.00E+00	1.24E-05	4.05E-03	1.26E-03	5.32E-03
H5	3.60E+00	1.50E-01	3.32E-03	3.76E+00	3.76E+00
H6	9.74E-02	3.06E-02	1.56E-02	1.44E-01	1.44E-01
Site H (AVG)	6.17E-01	3.63E-02	4.70E-03	6.58E-01	6.58E-01

3.1.8.3 Mass in Transmissive and Low-k Zones Summary Analysis

The mass in transmissive and low-k zones is presented with two formats including 1) using equations 4 and 5 to calculate the mass in transmissive and low-k zones (M/L²) and 2) using Equations 6-10 to calculate the length of borehole that is transmissive/low-k (L/L) and to

calculate the percent of total contaminant mass in transmissive/low-k zones (M/M). The key findings for mass in transmissive and low-k zones (M/L²) (Figure 55 & Table 42) include:

- H1, H2, H3, and H4 have more contaminant mass in low-k zones (Figure 55).
- H5 and H6 and more contaminant mass in transmissive zones
- H5 has a 2.96 kg/m² TCE in transmissive zones and 0.59 kg/m² TCE in low-k zones

The difference in total contaminant mass is very evident. With non-remediated boreholes H5 and H6 (Figure 55) having significantly more mass present than remediated boreholes H1, H2, H3, and H4.

The mass of contaminant is now transformed into percentage of contaminant mass in subsurface zones (M/M). The data presented here will be the sum of all mass of chlorinated solvents presented as SUM CVOC. This is because the contaminant masses were so variable and sporadic that it negatively affected the visual readability of the graphics. The key findings for percentage of contaminants in transmissive and low-k zones (Figure 56 & Table 43) include:

- The remediated Boreholes H1, H2, H3, and H4 have a percentage of contaminant mass in low-k zones that does correlate with the fraction of C1 that is low-k.
- Remediated cores have contaminants that prefer zones evenly
- Unlike the remediated cores, H5 and H6 have percentages of contaminant mass in low k zones that do not correlate with the fraction that is low-k.
- Non-remediated cores have contaminants that prefer transmissive zones.

Before remediation, Site H had contaminants that prefer transmissive zones. After remediation, Site H had contaminants that prefer zones evenly. This analysis, along with the differences of Site F & G, will be continued with statistics in inter-site results for chlorinated solvents. Site H

is a chlorinated solvent contaminated site that allows us to view a site before and after remediation activities.

The boreholes collected in the remediated area showed similarities across all factors. The boreholes collected outside the remediation area showed higher concentrations and masses with H5 being the most contaminated. Contaminants preferred transmissive zones outside the remediated area, and they preferred both zones evenly inside the remediated area.

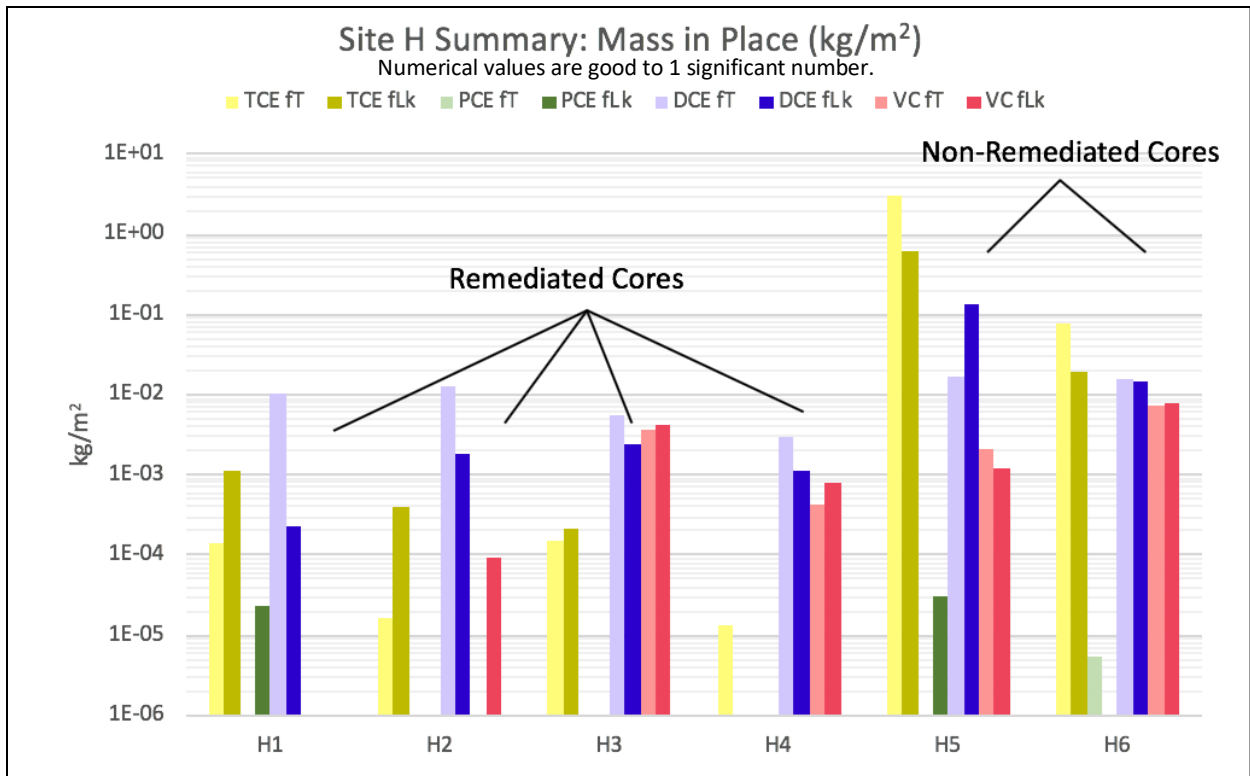


Figure 55: Mass of Contamination at Site H Divided into Zones

Table 42: Mass of PCE, TCE, DCE, and VC at Site H Divided into Zones
Numerical values are good to 1 significant number.

Core	<u>PCE</u>	<u>PCE</u>	<u>TCE</u>	<u>TCE</u>	<u>DCE</u>	<u>VC</u>	<u>VC</u>	
	<u>f_T</u>	<u>f_{Lk}</u>	<u>f_T</u>	<u>f_{Lk}</u>	<u>f_T</u>	<u>f_T</u>	<u>f_{Lk}</u>	
	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	kg/m ²	
H1	0.00E+00	2.22E-05	1.41E-04	1.13E-03	2.32E-04	1.01E-02	0.00E+00	0.00E+00
H2	0.00E+00	0.00E+00	1.73E-05	4.13E-04	1.89E-03	1.28E-02	0.00E+00	9.64E-05
H3	0.00E+00	0.00E+00	1.53E-04	2.13E-04	2.37E-03	5.53E-03	3.73E-03	4.24E-03
H4	0.00E+00	0.00E+00	1.24E-05	0.00E+00	1.13E-03	2.91E-03	4.35E-04	8.20E-04
H5	2.97E-05	3.00E+00	6.02E-01	1.34E-01	1.34E-01	1.63E-02	2.13E-03	1.19E-03
H6	0.00E+00	7.83E-02	1.91E-02	1.46E-02	1.46E-02	1.60E-02	7.54E-03	8.04E-03
Site H (AVG)	9.88E-06	5.13E-01	1.04E-01	2.57E-02	2.57E-02	1.06E-02	2.31E-03	2.40E-03

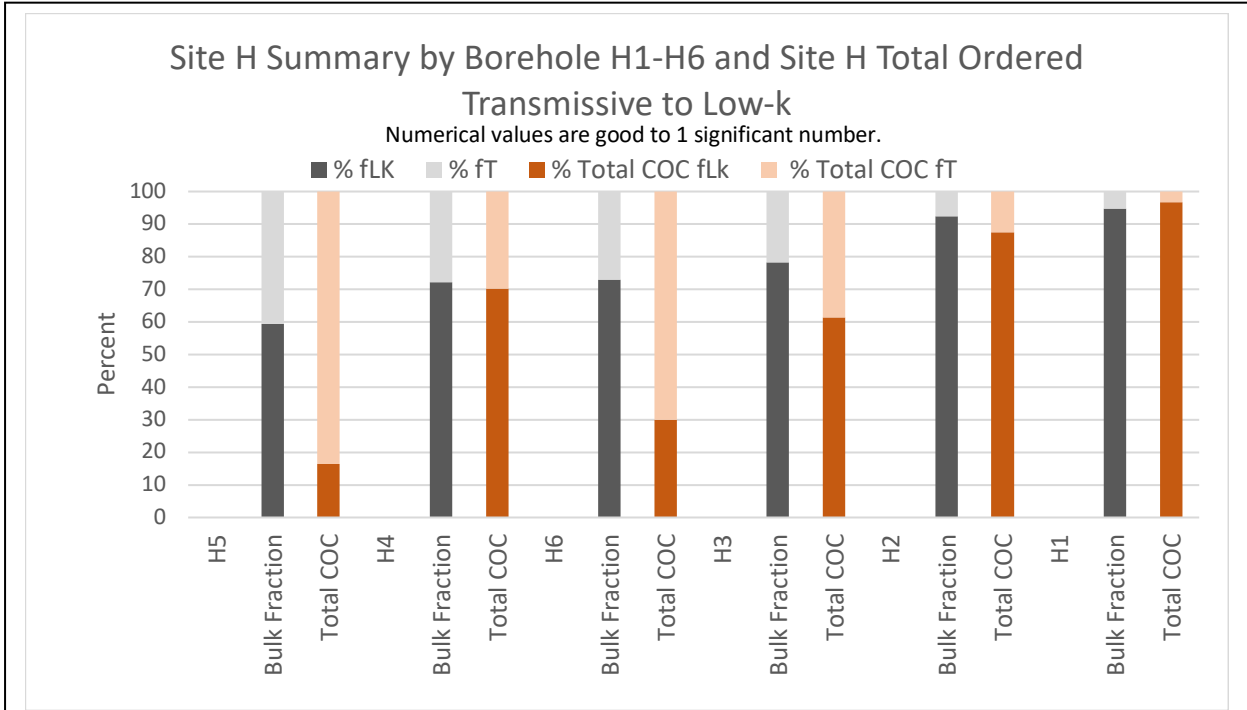


Figure 56: Percentage of Total COC Mass in Zones at Site H Ordered from Transmissive to Low-k

Table 43: Percentage of Borehole that is Transmissive of Low-k and Percentage of Total COC Mass in Zones at Site H

Numerical values are good to 1 significant number.

Core	$\% f_T$	$\% f_{LK}$	$\text{SUM CVOC } f_T$ (kg/m ²)	$\text{SUM CVOC } f_{LK}$ (kg/m ²)	$\% \text{ Total COC } f_T$	$\% \text{ Total COC } f_{LK}$
H1	5.26	94.74	3.73E-04	1.12E-02	3.22	96.78
H2	7.54	92.46	1.91E-03	1.33E-02	12.54	87.46
H3	21.68	78.32	6.25E-03	9.97E-03	38.54	61.46
H4	27.78	72.22	1.58E-03	3.74E-03	29.73	70.27
H5	40.55	59.45	6.19E-01	0.00E+00	83.52	16.48
H6	27.08	72.92	4.31E-02	0.00E+00	69.97	30.03

3.2 Inter-Site Analysis

The analysis is now moving from intra-site to inter-site analysis. Boreholes are grouped and presented based on contaminant types. The first group is hydrocarbon contaminated boreholes. Distribution of benzene, PCP, TPH, and methane mass in transmissive and low-k zones are presented with statistics. Figure 60 is the main visual of the statistical results for benzene, PCP, TPH, and methane. Figure 60 is presented after all hydrocarbon contaminants are discussed. Finally, the total mass of all contaminants in transmissive and low-k zones by borehole with statistics will finish the hydrocarbon results. Figure 66 is the main visual of the statistical results for the total mass of all contaminants in transmissive and low-k zones and is presented after the results for all boreholes is discussed. The second group is chlorinated solvent contaminated boreholes. The section includes the total mass of all contaminants in transmissive and low-k zones which includes statistics. Figure 66 is the main visual of the statistical results for the total mass of all chlorinated solvent contaminants in transmissive and low-k zones and is presented after the results for all boreholes is discussed. The final group is all boreholes together. This section includes the total mass of all contaminants in transmissive and low-k zones with statistics along with Figure 66 and will finish the inter-site results.

3.2.1 Inter-Site: Hydrocarbon Boreholes

The inter-site analysis presents hydrocarbon contaminated boreholes first. The hydrocarbon analysis begins with the distribution of benzene, PCP, TPH, and methane mass in transmissive/low-k zones for each borehole. Figure 60 is the main visual of the statistical results for the distribution of benzene, PCP, TPH, and methane mass in transmissive/low-k zones for each borehole. Finally, the total mass of all contaminants in transmissive and low-k zones with statistics will finish the hydrocarbon results. Figure 66 is the main visual of the statistical results

for the total mass of all contaminants in transmissive and low-k zones and is presented after the results for all boreholes is discussed.

3.2.1.1 Benzene & PCP

The distribution of benzene or PCP in transmissive and low-k zones is well documented at our hydrocarbon contaminated sites. Table 44 & Figure 58 presents the results from 19 boreholes. Figure 58 graphs the distribution of benzene or PCP. PCP is found only at Site A and benzene is found at Sites B-E. The deviation from percent of the borehole that is low-k to the percent of benzene/PCP in low-k zones is of greatest interest through inter-site results. The statistics include the difference and the absolute difference of the that deviation. The key features from Table 48, Figure 57, Table 44, & Table 45 include:

- Using the mean of % f_{Lk} and % Benzene/PCP f_{Lk} , Benzene and PCP have no general preference for either zone (Table 44 & Figure 60).
- A1, B1, B4, C1, and D2 all contain more than 70% of benzene or PCP in low-k zones (Figure 57)
- The deviation of (% f_{Lk} - % COC f_{Lk}) is more relevant than the absolute deviation because it considers negative numbers independently. A negative number says there is preference for low-k zones and a positive number says there is preference for transmissive zones. This is true for all inter-site deviation results (Table 44, Table 45, & Figure 60).
- The mean of (% f_{Lk} - % Benzene f_{Lk}) is -4.7% with a standard deviation of 21.2%. Boreholes B1, B2, C1, and D2 are one standard deviation from the mean and favor low-k zones. Borehole B3 is greater than a standard deviation from the mean and favors transmissive zones (Table 44, Table 45 & Figure 60).

- Using the mean and standard deviation, PCP may favor transmissive zones (Table 45 & Figure 60).
- The mean of ($\% f_{Lk} - \% PCP f_{Lk}$) is -1.6% with a standard deviation of 28.2%. Borehole A1 is a standard deviation from the mean and favors low-k zones (Figure 60).
- The statistical analysis is more relevant for benzene due to higher sample size (Table 44).
- The completely transmissive boreholes are included in the analysis (Table 44).
- The count difference is because D1 has no contamination and is not included in contaminants statistics (Table 44).

The statistics for all the boreholes show a general trend of equal preference for each zone. The varying individual borehole preferences for transmissive and low-k zones we have witnessed are valid. Understanding where a borehole lies in the distribution can provide additional information of contaminant preference. From the distributions, commonality between boreholes across sites can be resolved. Understanding contaminant distributions in transmissive and low-k zones can lead to better choice and application of remedial technologies.

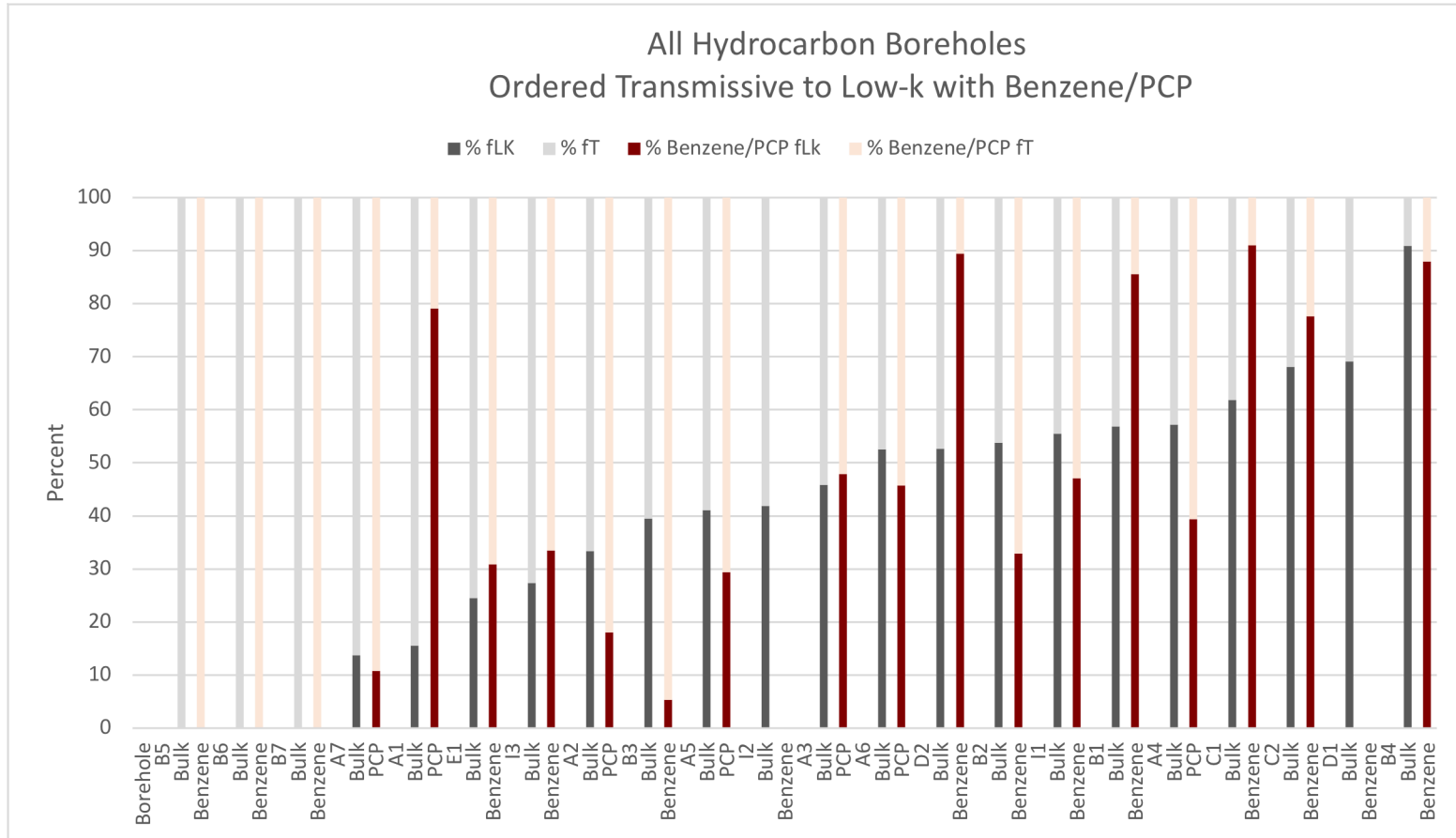


Figure 57: Percentage of Benzene/PCP in Zones for All Hydrocarbon Boreholes.

Numerical values are good to 1 significant number.

Table 44: General Statistics for Percent of Borehole that is Transmissive and Low-k, Percent of Benzene in Zones, and the Deviation of the two Variables.

Numerical values are good to 1 significant number.

	\bar{f}_T	\bar{f}_{LK}	<u>Benzene</u> \bar{f}_T	<u>Benzene</u> \bar{f}_{LK}	$\%f_{LK} - \%Benzene f_{LK}$	<u>Absolute</u> $\%f_{LK} - \%Benzene f_{LK}$
Mean	59.12	40.88	54.47	45.53	-4.77	15.31
Standard Error	5.97	5.97	12.30	12.30	6.41	4.46
Median	54.15	45.85	67.07	32.93	0.00	9.55
Mode	100.00	0.00	100.00	0.00	0.00	0.00
Standard Deviation	26.03	26.03	40.79	40.79	21.25	14.79
Sample Variance	677.34	677.34	1664.17	1664.17	451.53	218.89
Kurtosis	-0.65	-0.65	-2.15	-2.15	-0.15	-1.86
Skewness	0.19	-0.19	0.00	0.00	0.20	0.31
Range	90.91	90.91	90.99	90.99	70.92	36.76
Minimum	9.09	0.00	9.01	0.00	-36.76	0.00
Maximum	100.00	90.91	100.00	90.99	34.16	36.76
Sum	1123.22	776.78	599.19	500.81	-52.49	168.36
Count	19.00	19.00	11.00	11.00	11.00	11.00

Table 45: General Statistics for Percent of Borehole that is Transmissive and Low-k, Percent of PCP in Transmissive and Low-k, and the Deviation of the two Variables.
Numerical values are good to 1 significant number.

	<u>% PCP f_T</u>	<u>% PCP $f_{L,k}$</u>	<u>% $f_{L,k}$ - %PCP $f_{L,k}$</u>	<u>Absolute % $f_{L,k}$ - %PCP $f_{L,k}$</u>
Mean	61.37	38.63	-1.59	17.16
Standard Error	8.53	8.53	10.66	8.06
Median	60.58	39.42	6.81	11.63
Mode				
Standard Deviation	22.57	22.57	28.21	21.33
Sample Variance	509.32	509.32	795.64	454.97
Kurtosis	0.86	0.86	5.69	5.32
Skewness	-0.74	0.74	-2.32	2.22
Range	68.28	68.28	81.43	61.58
Minimum	20.90	10.82	-63.60	2.02
Maximum	89.18	79.10	17.83	63.60
Sum	429.61	270.39	-11.11	120.13
Count	7.00	7.00	7.00	7.00

3.2.1.2 Total Petroleum Hydrocarbons

The distribution of TPH in transmissive and low-k zones is well documented at our hydrocarbon contaminated sites. Table 48 and Figure 58 presents the TPH results of 19 boreholes and Table 46 & Figure 60 presents statistics. Figure 57 graphs the distribution of TPH and is best described with statistics along with key features. They include:

- Using the mean of % f_{Lk} and % TPH f_{Lk} , TPH has no general preference for either zone (Table 46 & Figure 60).
- The mean of (% f_{Lk} - % TPH f_{Lk}) is -3.0% with a standard deviation of 21.4%. Boreholes A1, A4, A5, and C1 are one standard deviation from the mean and favor low-k zones. Boreholes B2 and B3 are greater than a standard deviation from the mean and favor transmissive zones (Table 46 & Figure 60).
- A4, A5, B1, and C1 contain more than 70% TPH in low-k zones and show preference to low-k zones (Figure 58).
- A3, A7, B2, and B3 show preference for transmissive zones (Figure 58)
- There is a balance of preference for transmissive and low-k zones looking at individual boreholes, but it is important apply statistical significance.

The statistics for all the boreholes show a general trend of equal contaminant preference for each zone. Understanding TPH contamination in zones relative to other boreholes can provide additional information with cross-site borehole analysis. This can lead to better choices regarding site management decisions.

All Hydrocarbon Boreholes Ordered Transmissive to Low-k with TPH

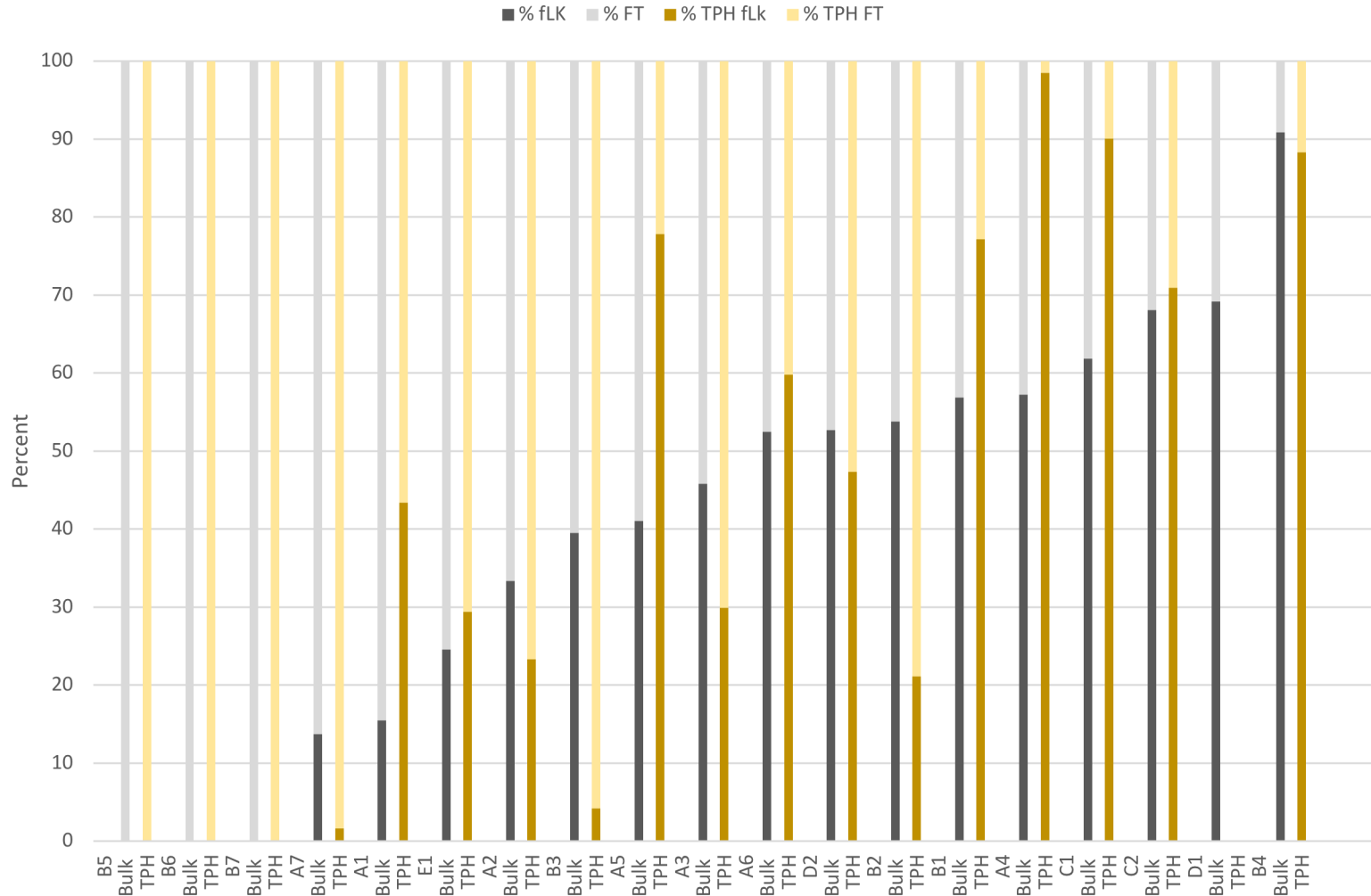


Figure 58: Percentage of TPH in Zones for All Hydrocarbon Boreholes.

Numerical values are good to 1 significant number.

Table 46: General Statistics for Percent of Borehole that is Transmissive and Low-k, Percent of TPH in Zones, and the Deviation of the two Variables.
Numerical values are good to 1 significant number.

	f_T	f_{LK}	TPH f_T	TPH f_{LK}	$\%f_{LK} - \%TPH f_{LK}$	<u>Absolute $\%f_{LK} - \%TPH$</u> f_{LK}
Mean	59.12	40.88	57.62	42.38	-3.07	15.74
Standard Error	5.97	5.97	8.24	8.24	5.05	3.39
Median	54.15	45.85	63.35	36.65	0.00	11.06
Mode	100.00	0.00	100.00	0.00	0.00	0.00
Standard Deviation	26.03	26.03	34.97	34.97	21.43	14.38
Sample Variance	677.34	677.34	1222.74	1222.74	459.14	206.66
Kurtosis	-0.65	-0.65	-1.47	-1.47	-0.31	-1.32
Skewness	0.19	-0.19	-0.19	0.19	-0.10	0.51
Range	90.91	90.91	98.53	98.53	76.61	41.28
Minimum	9.09	0.00	1.47	0.00	-41.28	0.00
Maximum	100.00	90.91	100.00	98.53	35.33	41.28
Sum	1123.22	776.78	1037.12	762.88	-55.27	283.40
Count	19.00	19.00	18.00	18.00	18.00	18.00

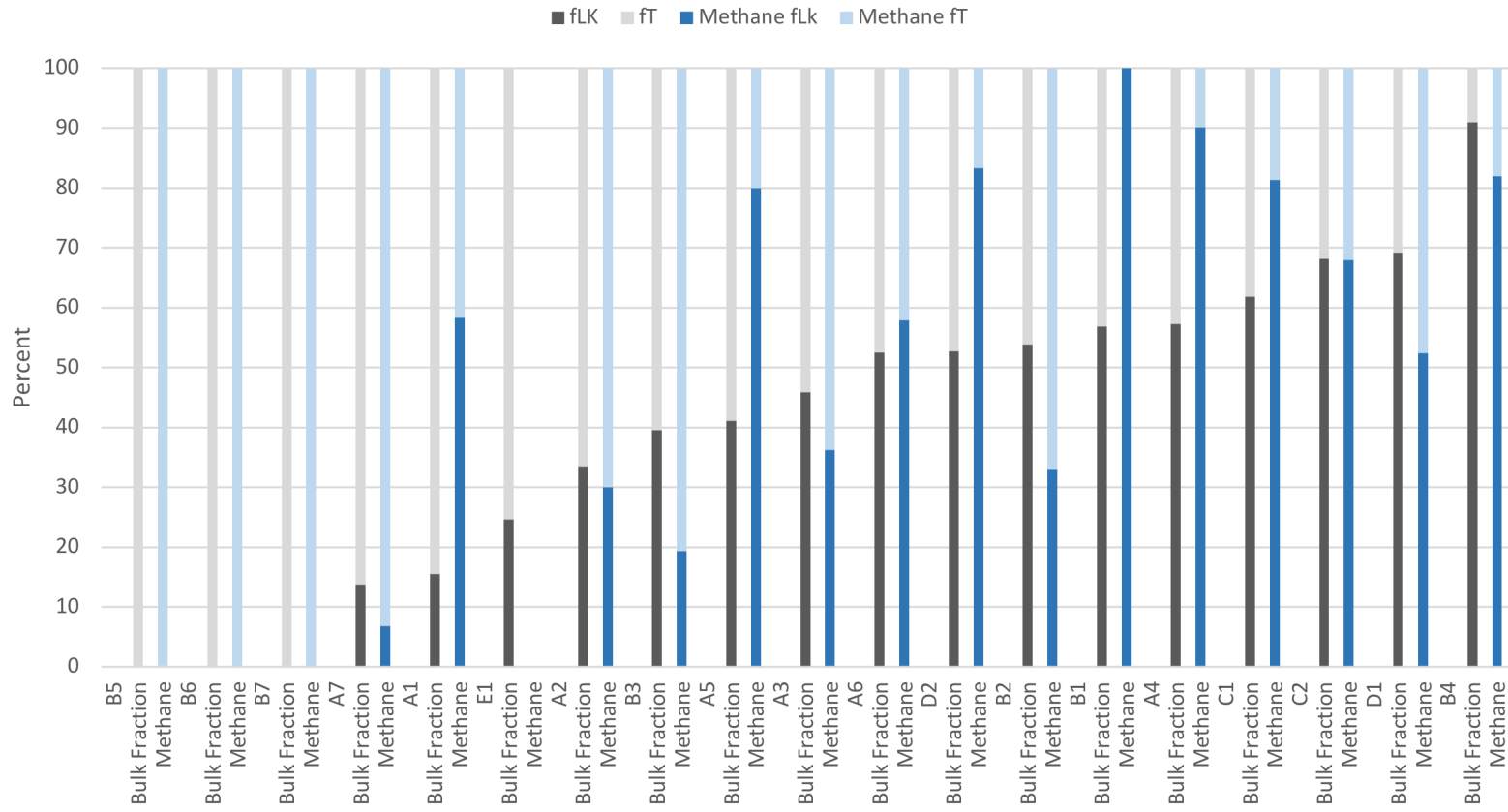
3.2.1.3 Methane

The distribution of methane in zones documented to evaluate the probable activity of biodegradation. Table 48 and Figure 59 presents the methane results of 19 boreholes and Table 47 & Figure 60 presents statistics. Methane can provide a means to judge the activity of the subsurface microbial community and/or the degree to which NSZD reactions are depleted by interactions with atmospheric conditions, Garg et al. (2017). Methane moves around much more freely in transmissive zones than low-k zones. Low-k zones can also trap and inhibit the movement of methane. Large masses of methane contained in low-k zones could inhibit local biodegradation, Garg et al. (2017). Also, high gas saturations could be evidence for pooling of NSZD gasses as they try to vertically move, Garg et al (2017), and similarly high gas saturations are described in detail in Kiaalhosseini et al. (2017). Figure 69 graphs the distribution of methane and is best described with statistics along with key features. They include:

- Using the mean of % f_{Lk} and % methane f_{Lk} , methane has no general preference for either zone (Table 47 & Figure 60).
- A1, A4, A5, B1, C1, and D2 have most of their methane mass in low-k zones
- The mean of (% f_{Lk} - % Methane f_{Lk}) is -7.0% with a standard deviation of 21.8%. Boreholes A1, A4, A5, B1, and D2 are one standard deviation from the mean and favor low-k zones. Boreholes B2 and B3 are greater than a standard deviation from the mean and favor transmissive zones (Table 47 & Figure 60).

The statistics for all the boreholes show a general trend of equal preference for each zone. Understanding methane's preference for transmissive or low-k zones in your borehole can provide additional information of NSZD presence and limitations Garg et al. (2017). Cross-site borehole analysis can lead to better choice and application of remedial technologies.

All Hydrocarbon Boreholes Ordered Transmissive to Low-k with Methane



Numerical values are good to 1 significant number.

Figure 59: Percentage of Methane in Zones for All Hydrocarbon Boreholes.

Table 47: General Statistics for Percent of Borehole that is Transmissive and Low-k, Percent of Methane in Zones, and the Deviation of the two Variables.

Numerical values are good to 1 significant number.

	$\% f_T$	$\% f_{LK}$	$\% \text{Methane } f_T$	$\% \text{Methane } f_{LK}$	$\% f_{LK} - \% \text{Methane } f_{LK}$	Absolute $\% f_{LK} - \% \text{Methane } f_{LK}$
Mean	59.12	40.88	48.51	46.22	-7.00	16.67
Standard Error	5.97	5.97	8.06	8.02	5.14	3.61
Median	54.15	45.85	42.11	52.34	0.00	13.24
Mode	100.00	0.00	100.00	0.00	0.00	0.00
Standard Deviation	26.03	26.03	35.13	34.95	21.83	15.30
Sample Variance	677.34	677.34	1234.10	1221.39	476.43	234.23
Kurtosis	-0.65	-0.65	-1.37	-1.50	-1.09	-1.06
Skewness	0.19	-0.19	0.22	-0.08	-0.56	0.56
Range	90.91	90.91	100.00	100.00	64.02	43.14
Minimum	9.09	0.00	0.00	0.00	-43.14	0.00
Maximum	100.00	90.91	100.00	100.00	20.87	43.14
Sum	1123.22	776.78	921.74	878.26	-126.06	300.01
Count	19.00	19.00	19.00	19.00	18.00	18.00

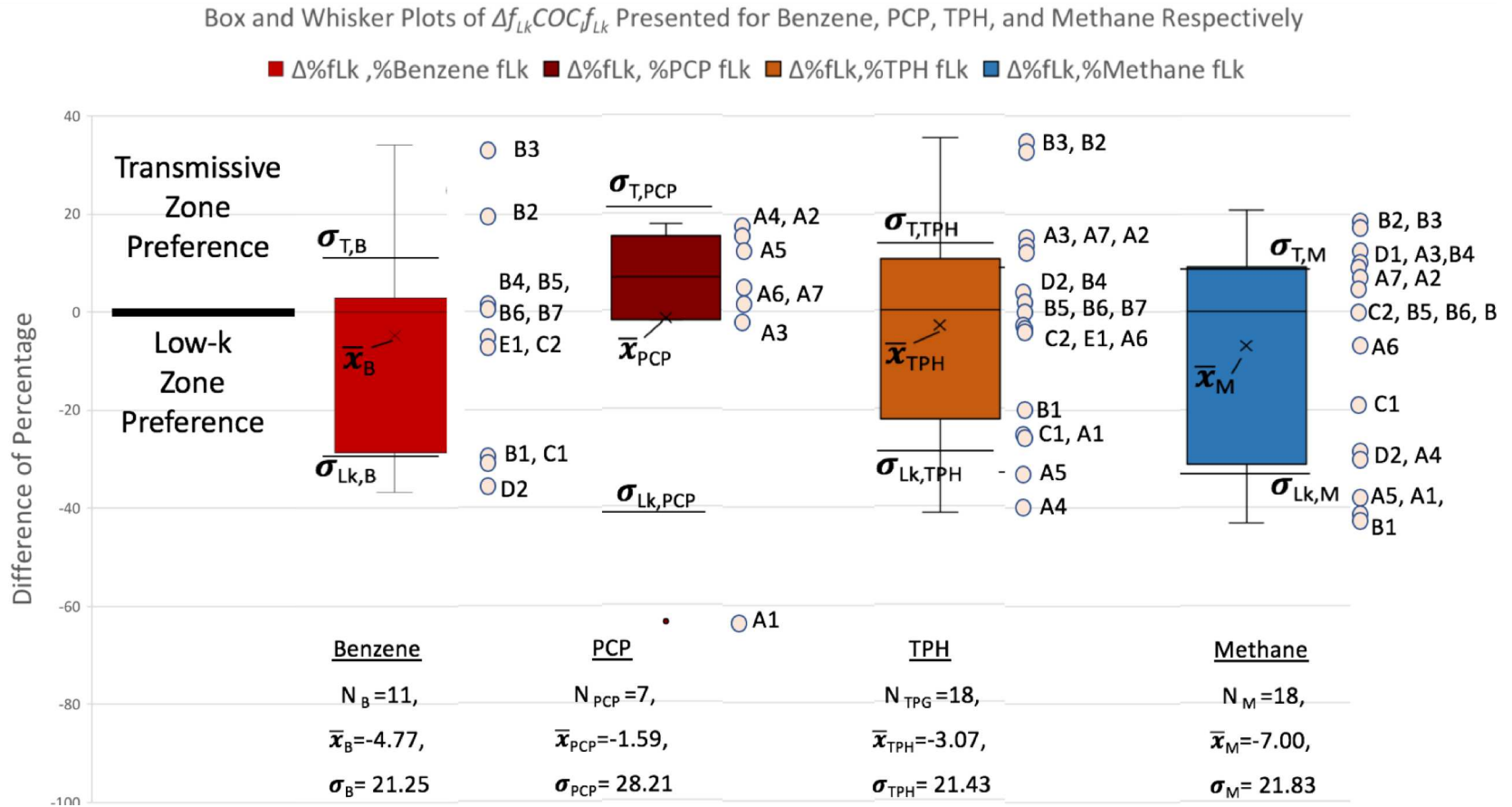


Figure 60: Box and Whisker Plot for The Difference Between Percent of Borehole that is Low-k and Percent of Total Benzene, PCP, TPH, or Methane in Low-k Zones

Numerical values are good to 1 significant number.

Table 48: Summary for Percentage of Borehole that is Transmissive or Low-k and Percentage of Contaminants in Zones for all Hydrocarbon Boreholes.

Numerical values are good to 1 significant number.

Core	<u>% f_T</u>	<u>% f_{LK}</u>	<u>% Benzene f_T</u>	<u>% Benzene f_{LK}</u>	<u>% TPH f_T</u>	<u>% TPH f_{LK}</u>	<u>% PCP f_T</u>	<u>% PCP f_{LK}</u>
E1	75.43	24.57	69.15	30.85	70.63	29.37		
B1	43.14	56.86	14.46	85.54	22.83	77.17		
B2	46.19	53.81	67.07	32.93	78.85	21.15		
B3	60.48	39.52	94.64	5.36	95.81	4.19		
B4	9.09	90.91	11.99	88.01	11.72	88.28		
B5	100.00	0.00	100.00	0.00	100.00	0.00		
B6	100.00	0.00	100.00	0.00	100.00	0.00		
B7	100.00	0.00	100.00	0.00	100.00	0.00		
A1	84.50	15.50			56.62	43.38	20.90	79.10
A2	66.66	33.34			76.69	23.31	81.97	18.03
A3	54.15	45.85			70.07	29.93	52.13	47.87
A4	42.75	57.25			1.47	98.53	60.58	39.42
A5	58.92	41.08			22.17	77.83	70.55	29.45
A6	47.50	52.50			40.23	59.77	54.31	45.69
A7	86.25	13.75			98.34	1.66	89.18	10.82
C1	38.17	61.83	9.01	90.99	9.95	90.05		
C2	31.89	68.11	22.34	77.66	29.05	70.95		
D1	30.83	69.17	0.00	0.00	0.00	0.00		
D2	47.28	52.76	10.53	89.47	52.68	47.32		

3.2.1.4 SUM COCs

The results here are an attempt to categorize all contaminant mass in zones by borehole for all hydrocarbon boreholes. This allows for hydrocarbon contaminated boreholes to be compared with chlorinated solvent contaminated boreholes later in inter-site results. The COCs summed in each hydrocarbon borehole are Benzene, PCP and/or TPH. The results for Table 49, Figure 61, Table 50, & Figure 66 include:

- The masses are added together so the defining mass, TPH, dominates the mass total.
- The SUM COC mass (kg/m^2) for each borehole varies so much that the median is a fraction of the mean. The standard deviation includes negative mass. The sample variance is very large which means the data is very spread out and outliers would need to be identified. This is a trend that repeats itself for all SUM COC inter-site results in the following sections (Table 50 & Figure 66). This large variation is a underlying cause for the development of these methods.
- Comparing the mean and the standard deviation for % f_{Lk} and % SUM COCs f_{Lk} , SUM COC has no general preference for either zone (Table 50 & Figure 66).
- The mean of (% f_{Lk} - % COC f_{Lk}) is -3.25% with a standard deviation of 21.4%.
Boreholes A1, A4, A5, and C1 are one standard deviation from the mean and prefer low-k zones. Boreholes A3, B2 and B3 are greater than a standard deviation from the mean and prefer transmissive zones (Table 50 & Figure 66).
- A3 was not a standard deviation away from the mean in the TPH results. This provides evidence that the SUM COC calculation does present unique results even with a dominating contaminant mass.

The statistics for the percent of mass in zones presents a usable distribution. It provides a unique analysis for hydrocarbon contaminated boreholes. It also sets up hydrocarbon contaminated boreholes to be easily compared with chlorinated solvent contaminated boreholes.

Table 49: Summary for Percentage of Borehole that is Transmissive or Low-k, and Percentage of the Sum of Contaminants (Benzene/PCP+TPH) in Zones for all Hydrocarbon Boreholes.

Numerical values are good to 1 significant number.

Core	$\% f_T$	$\% f_{Lk}$	<u>% SUM COC</u>	<u>% SUM COC</u>
			f_T	f_{Lk}
E1	75.43	24.57	70.63	29.37
B1	43.14	56.86	22.71	77.29
B2	46.19	53.81	78.65	21.35
B3	60.48	39.52	95.79	4.21
B4	9.09	90.91	11.72	88.28
B5	100.00	0.00	100.00	0.00
B6	100.00	0.00	100.00	0.00
B7	100.00	0.00	100.00	0.00
A1	84.50	15.50	55.30	44.70
A2	66.66	33.34	76.70	23.30
A3	54.15	45.85	70.06	29.94
A4	42.75	57.25	1.47	98.53
A5	58.92	41.08	22.22	77.78
A6	47.50	52.50	40.24	59.76
A7	86.25	13.75	98.31	1.69
C1	38.17	61.83	9.92	90.08
C2	31.89	68.11	28.81	71.19
D1	30.83	69.17		
D2	47.28	52.72	51.36	48.64

Numerical values are good to 1 significant number.

All Hydrocarbon Boreholes Ordered Transmissive to Low-k with SUM COC

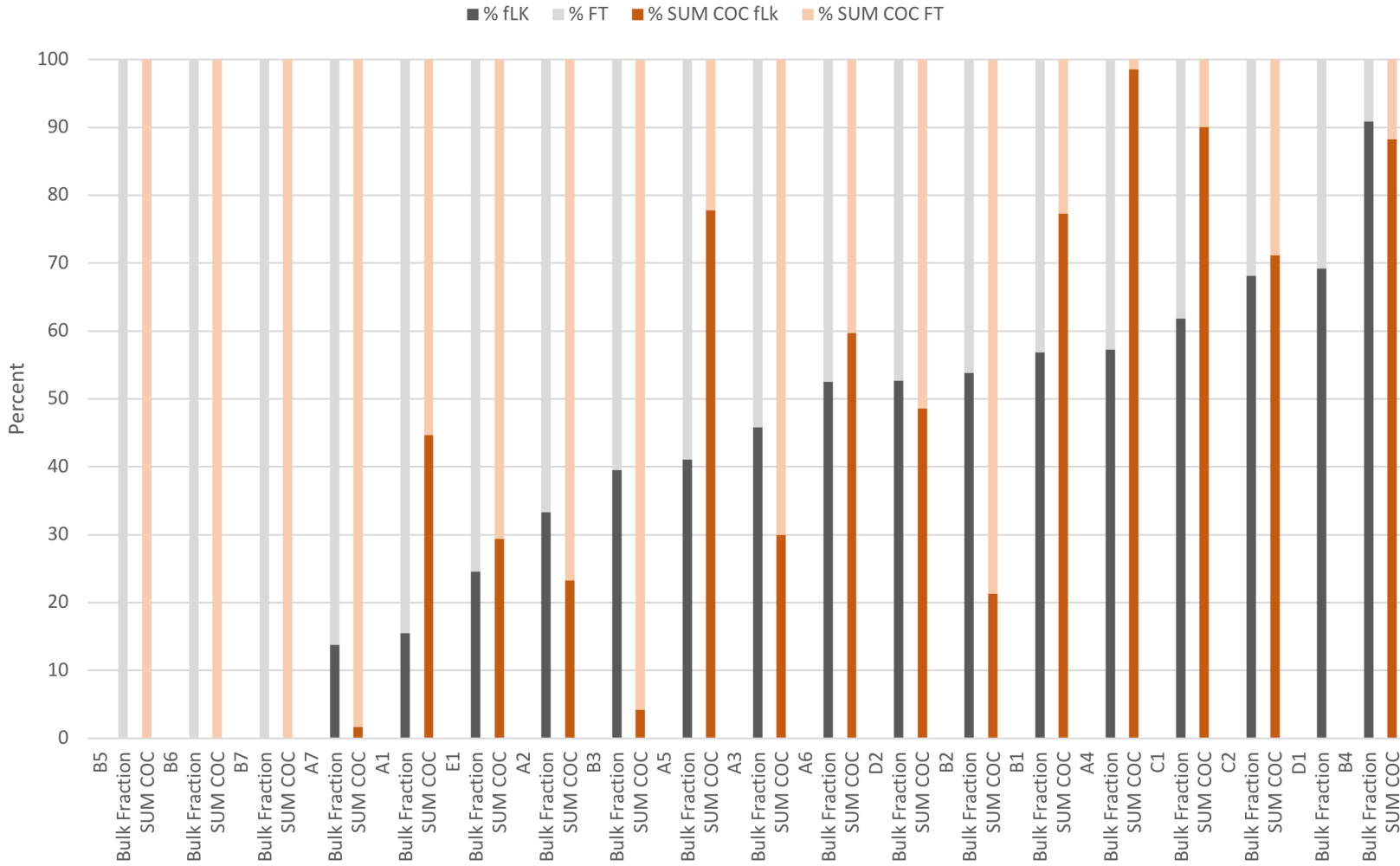


Figure 61: Summary for Percentage of Borehole that is Transmissive or Low-k and Percentage of the Sum of Contaminants (Benzene/PCP+TPH) in Zones for all Hydrocarbon Boreholes.

Table 50: General Statistics for Percent of Borehole that is Transmissive and Low-k, and Percent of Sum of all COCs (Benzene/PCP + TPH) in Zones for Hydrocarbon Boreholes.

Numerical values are good to 1 significant number.

	<u>% f_T</u>	<u>% f_{LK}</u>	<u>% SUM COCs f_T</u>	<u>% SUM COCs f_{Lk}</u>	<u>%f_{Lk} - %SUM COC f_{Lk}</u>	<u>Absolute %f_{Lk} - %SUM COC f_{Lk}</u>
Mean	59.12	40.88	57.44	42.56	-3.25	15.75
Standard Error	5.97	5.97	8.25	8.25	5.06	3.41
Median	54.15	45.85	62.68	37.32	0.00	11.05
Mode	100.00	0.00	100.00	0.00	0.00	0.00
Standard Deviation	26.03	26.03	34.99	34.99	21.47	14.48
Sample Variance	677.34	677.34	1224.34	1224.34	461.03	209.56
Kurtosis	-0.65	-0.65	-1.48	-1.48	-0.32	-1.36
Skewness	0.19	-0.19	-0.18	0.18	-0.09	0.50
Range	90.91	90.91	98.53	98.53	76.59	41.27
Minimum	9.09	0.00	1.47	0.00	-41.27	0.00
Maximum	100.00	90.91	100.00	98.53	35.31	41.27
Sum	1123.22	776.78	1033.88	766.12	-58.51	283.50
Count	19.00	19.00	18.00	18.00	18.00	18.00

3.2.2 Inter-Site: Chlorinated Solvent Boreholes

The inter-site analysis will continue with results for chlorinated solvent contaminated boreholes. The section includes the total mass of all contaminants in transmissive and low-k zones which includes statistics. Figure 66 is the main visual of the statistical results for the total mass of all contaminants in transmissive and low-k zones and is presented after the results for all boreholes is discussed.

3.2.2.1 SUM CVOCs

It is important to provide the similar analysis to chlorinated solvent contaminated boreholes so they can be compared with hydrocarbon contaminated boreholes. The distribution of the total sum of CVOCs adds all chlorinated solvents mass for each zone. Table 51 and Figure 62 presents the results of the 12 chlorinated solvent contaminated boreholes. Figure 63 presents the change in distribution from before and after remediation activities at Site F/G. Figure 64 presents the difference in distribution from non-remediated and remediated boreholes at Site H. Table 51 and Figure 62 are best described with statistics from Table 52 & Figure 66 along with key features from Figure 63 and Figure 64. They include:

- The boreholes are more represented by low-k zones
- Comparing the mean of % f_{Lk} and % SUM CVOC f_{Lk} , there is a small preference of transmissive zones (Table 52 & Figure 66).
- The mass comparisons follow the trend mentioned previously.
- The mean of (% f_{Lk} - % CVOC f_{Lk}) is 9.9% with a standard deviation of 20.8%.

Boreholes G2 and G3 (Post-Remediation boreholes) are one standard deviation from the mean and favor low-k zones (Table 52 & Figure 66).

- Boreholes F3, H5, and H6 (pre-remediated and non-remediated boreholes) are greater than a standard deviation from the mean and favor transmissive zones.
- Pre-remediation, Site F-boreholes have contamination that prefers transmissive zones (Figure 63)
- Post-remediation, Site G-boreholes have contamination that prefers low-k zones (Figure 63).
- Non-remediated boreholes from Site H have contamination that strongly prefers transmissive zones (Figure 64).
- Remediated boreholes from Site H have contamination that strongly changes preference from transmissive zones to equal preference of zones (Figure 64).

The statistics for the chlorinated solvent contaminated boreholes show non-remediated contaminated boreholes favor transmissive zones and remediated boreholes change significantly to prefer low-k zones. Understanding and applying these methods can lead to better choice and application of remedial technologies.

Table 51: Summary for Percentage of Borehole that is Transmissive or Low-k, Percentage of the Sum of Contaminants (Chlorinated Solvents) in Zones for all Chlorinated Solvent Boreholes.

Numerical values are good to 1 significant number.

	<u>% fT</u>	<u>% fLk</u>	<u>% Sum CVOC</u> <u>fT</u>	<u>% Sum CVOC</u> <u>fLk</u>
F1	62.60	37.40	69.20	30.80
F3	59.62	40.38	96.26	3.74
F2	56.29	43.71	62.33	37.67
G1	25.92	74.08	18.83	81.17
G2	48.00	52.00	29.91	70.09
G3	22.87	77.13	9.90	90.10
H1	5.26	94.74	3.22	96.78
H2	7.54	92.46	12.54	87.46
H3	21.68	78.32	38.54	61.46
H4	27.78	72.22	29.73	70.27
H5	40.55	59.45	83.52	16.48
H6	27.08	72.92	69.97	30.03

All Chlorinated Solvent Boreholes: Total CVOC in zones Ordered Transmissive to Low-k

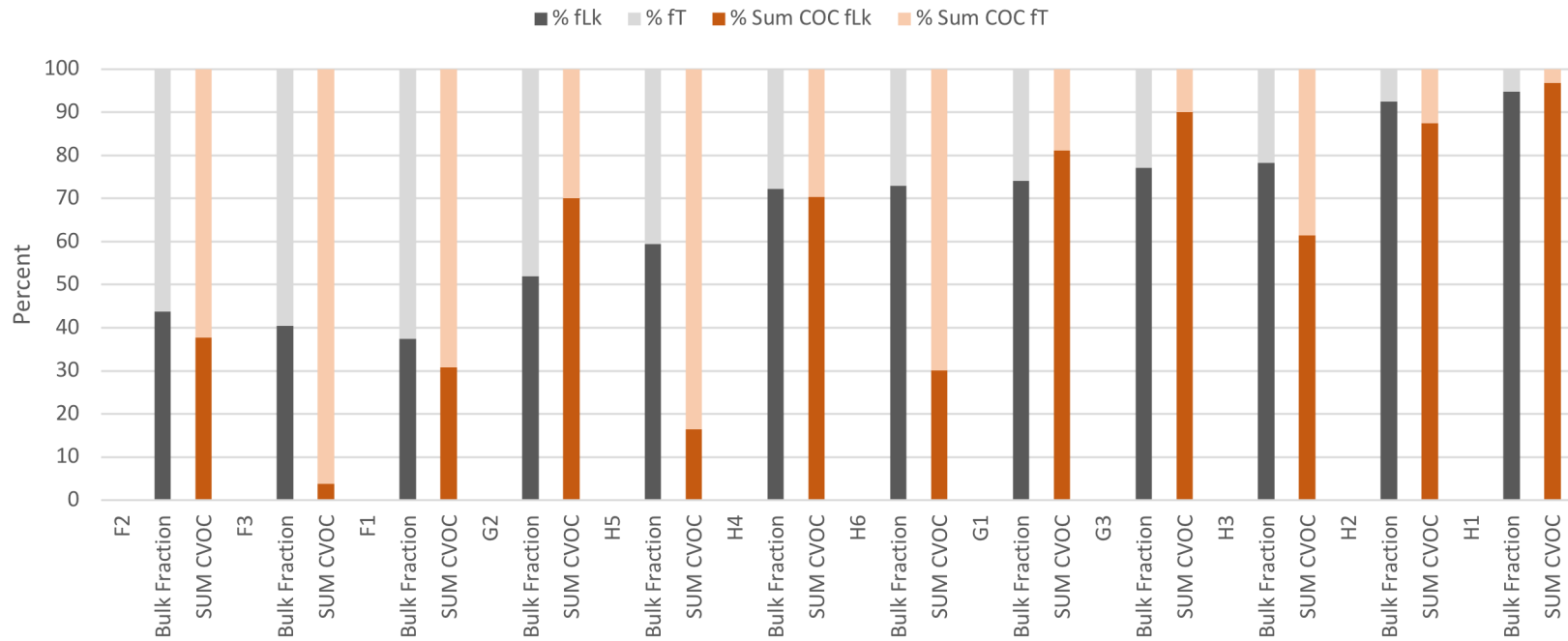


Figure 62: Percentage of the Sum of all CVOCs (Chlorinated Solvents) in zones for all Chlorinated Solvent Boreholes.

Numerical values are good to 1 significant number.

Table 52: General Statistics for Percent of Borehole that is Transmissive and Low-k, and Percent of Sum of all CVOCs (Chlorinated Solvents) in Zones for Chlorinated Solvent Boreholes.
Numerical values are good to 1 significant number.

	$\% f_T$	$\% f_{LK}$	$\frac{\% \text{SUM}}{\text{CVOC } f_T}$	$\frac{\% \text{SUM}}{\text{CVOC } f_{LK}}$	$\frac{\% f_{LK} - \% \text{SUM}}{\text{CVOC } f_{LK}}$	$\frac{\text{Absolute } \% f_{LK} - \% \text{SUM}}{\text{CVOC } f_{LK}}$
Mean	33.76	66.24	43.66	56.34	9.90	16.60
Standard Error	5.62	5.62	9.05	9.05	6.03	4.49
Median	27.43	72.57	34.22	65.78	5.52	10.02
Mode						
Standard Deviation	19.45	19.45	31.36	31.36	20.88	15.57
Sample Variance	378.42	378.42	983.43	983.43	436.01	242.43
Kurtosis	-1.16	-1.16	-1.33	-1.33	-0.81	-0.65
Skewness	0.16	-0.16	0.33	-0.33	0.60	0.97
Range	57.33	57.33	93.04	93.04	61.06	41.02
Minimum	5.26	37.40	3.22	3.74	-18.09	1.95
Maximum	62.60	94.74	96.26	96.78	42.97	42.97
Sum	405.17	794.83	523.95	676.05	118.78	199.15
Count	12.00	12.00	12.00	12.00	12	12

Pre- to Post-Remediation of Chlorinated Solvents at Site F/G: Total CVOCs in Zones Ordered Pre to Post-Remediation

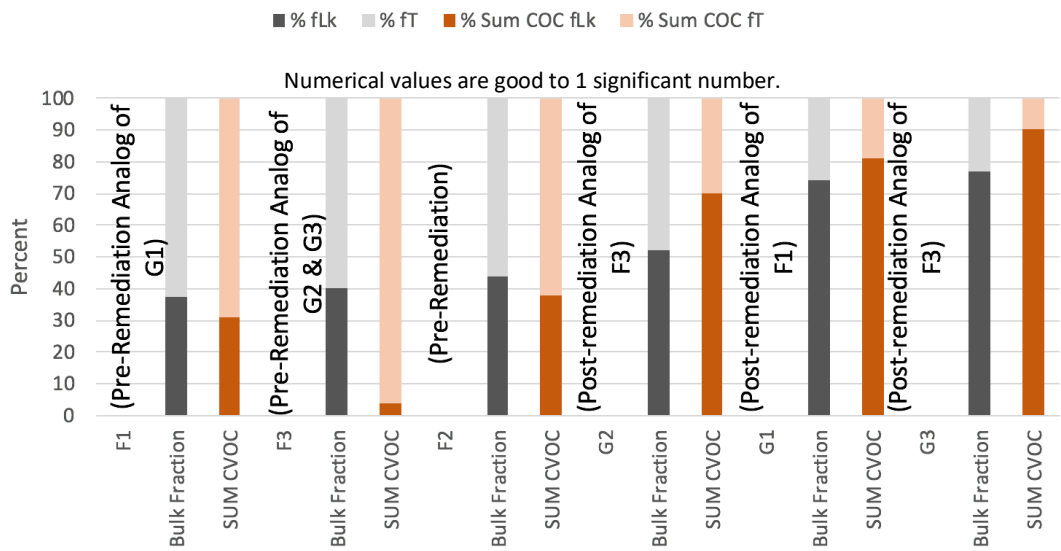


Figure 63: Percentage of the Sum of all CVOCs (Chlorinated Solvents) in zones for Site F/G Boreholes.

Non-Remediated vs Post-Remediation at Site H: Total CVOCs in Zones Non-Remediated to Post-Remediation

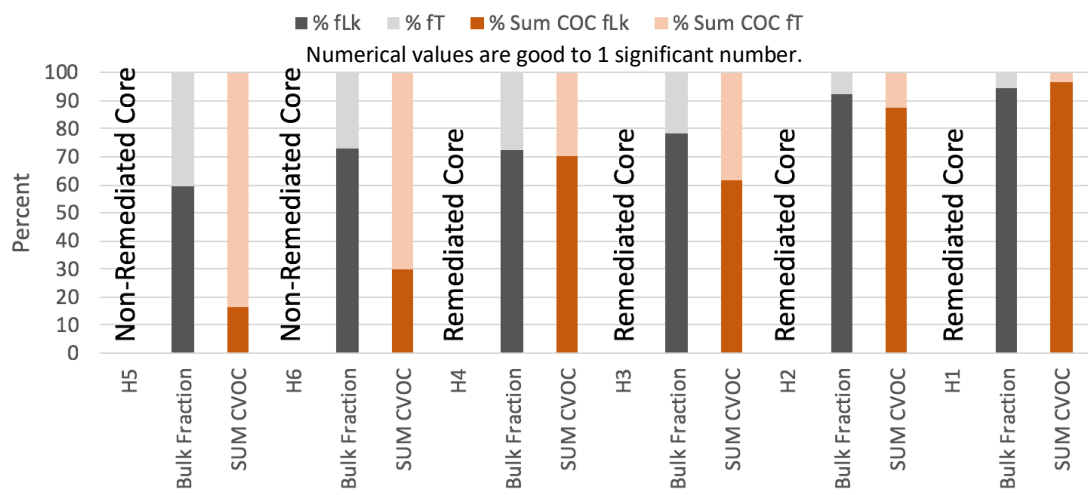


Figure 64: Percentage of the Sum of all CVOCs (Chlorinated Solvents) in zones for Site H Boreholes.

3.2.3 Inter-Site: All Boreholes

The inter-site analysis will finish with all contaminated boreholes analyzed together for the distribution of contamination mass in transmissive and low-k zones. This section includes Figure 66 which is the primary graphic for visualizing relevant statistic information for the total mass of contaminants in transmissive and low-k zones for hydrocarbon, chlorinated solvent, and all boreholes.

3.2.3.1 SUM COCs

Every borehole from both hydrocarbon and chlorinated solvent contaminated sites is compared. The distribution of the total sum of COCs and CVOCs (now labeled COCs) includes the boreholes calculated previously in hydrocarbon and chlorinated solvent results. Table 53 and Figure 65 presents the results of the 31 contaminated boreholes and are best described with statistics (Table 54 & Figure 66) along with key features. They include:

- Using the mean and the standard deviation for $\%f_{Lk}$ and $\% \text{ SUM COC } f_{Lk}$, the contaminant for each borehole has no statistically relevant preference for either zone (Table 54 & Figure 66).
- The mean and median values of the $\% \text{ SUM COC}$ are within 2% of each other (Table 54 & Figure 66).
- The statistical results for masses (kg/m^2) in zones follow the trend mention previously. (Table 54 & Figure 66).
- The mean of $(\% f_{Lk} - \% \text{ COC } f_{Lk})$ is 2.0% with a standard deviation of 21.8%. Boreholes A1, A4, A5, B1, and C1 are one standard deviation from the mean and favor low-k zones. Boreholes B2, B3, F3, H5, and H6 are greater than a standard deviation from the mean and favor transmissive zones (Table 54 & Figure 66).

- Actual boreholes show a variety of preference. Boreholes that have contamination preference for low-k zones are balanced by boreholes that have contamination preference for transmissive zones (Figure 65) in the statistical analysis.

The statistics for all the boreholes present insight into comparing boreholes with different contaminants. The results found in the other sections are still presented and valid here. It will be mentioned again later but it is unfortunate that the data set does not include a post-remediated hydrocarbon site. Understanding the relationship between contaminants and low-k zones is essential and can lead to better choice and application of remedial technologies.

Table 53: Summary for Percentage of Borehole that is Transmissive or Low-k, and Percentage of the Sum of Contaminants (Benzene/PCP+TPH or Chlorinated Solvents) in Zones for all Boreholes.

Numerical values are good to 1 significant number.

	<u>% f_T</u>	<u>% f_{LK}</u>	<u>% SUM COC f_T</u>	<u>% SUM COC f_{LK}</u>
B5	100.00	0.00	100.00	0.00
B6	100.00	0.00	100.00	0.00
B7	100.00	0.00	100.00	0.00
A7	86.25	13.75	98.31	1.69
A1	84.50	15.50	55.30	44.70
E1	75.43	24.57	70.63	29.37
A2	66.66	33.34	76.70	23.30
F2	56.29	43.71	62.33	37.67
F3	59.62	40.38	96.26	3.74
F1	62.60	37.40	69.20	30.80
B3	60.48	39.52	95.79	4.21
A5	58.92	41.08	22.22	77.78
A3	54.15	45.85	70.06	29.94
G2	48.00	52.00	29.91	70.09
A6	47.50	52.50	40.24	59.76
D2	47.28	52.72	51.36	48.64
B2	46.19	53.81	78.65	21.35
B1	43.14	56.86	22.71	77.29
A4	42.75	57.25	1.47	98.53
H5	40.55	59.45	83.52	16.48
C1	38.17	61.83	9.92	90.08
C2	31.89	68.11	28.81	71.19
D1	30.83	69.17		
H4	27.78	72.22	29.73	70.27
H6	27.08	72.92	69.97	30.03
G1	25.92	74.08	18.83	81.17
G3	22.87	77.13	9.90	90.10
H3	21.68	78.32	38.54	61.46
B4	9.09	90.91	11.72	88.28
H2	7.54	92.46	12.54	87.46
H1	5.26	94.74	3.22	96.78

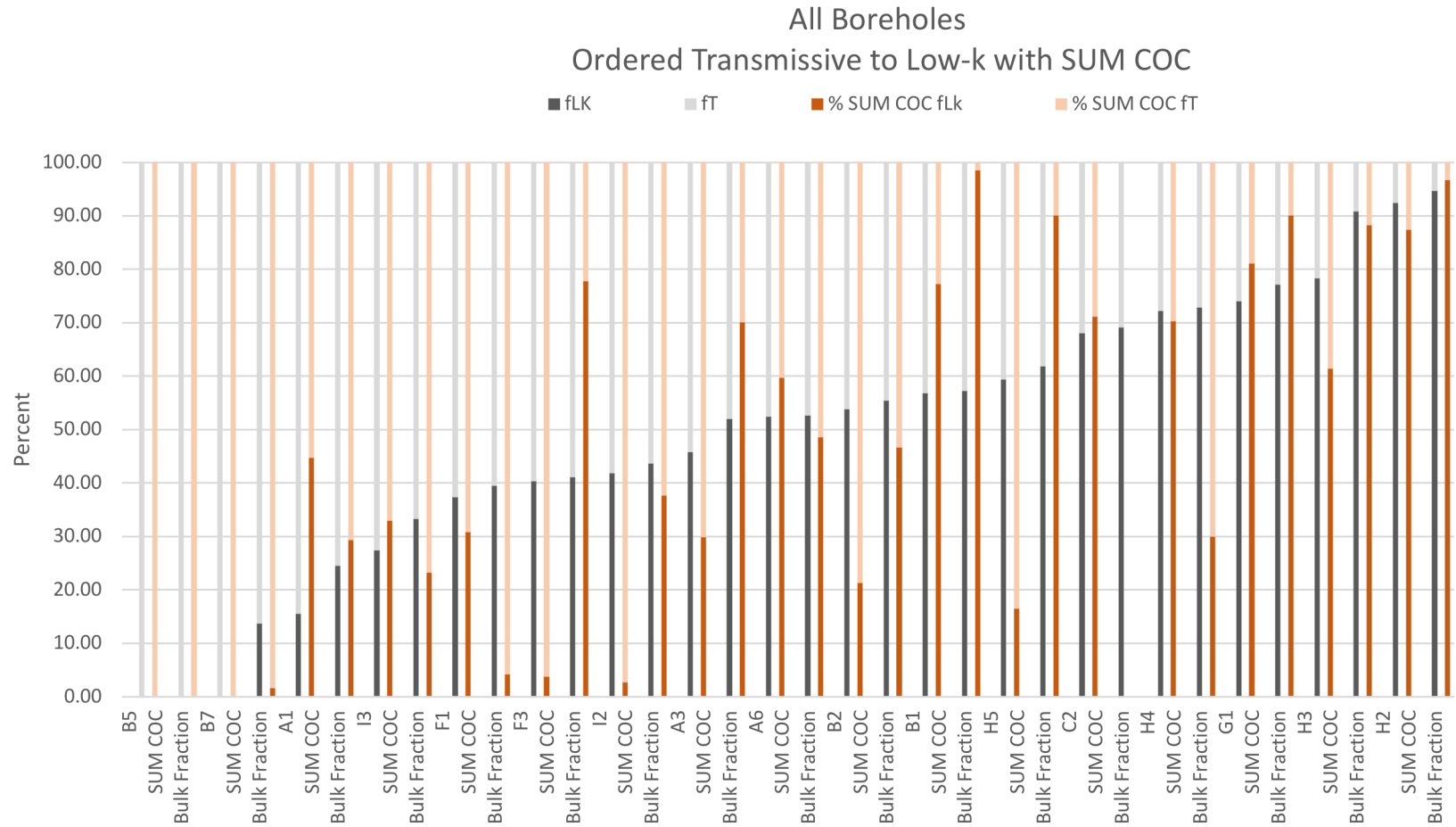


Figure 65: Percentage of the Sum of all COCs (Benzene/PCP+TPH or Chlorinated Solvents) in zones for all Boreholes.

Numerical values are good to 1 significant number.

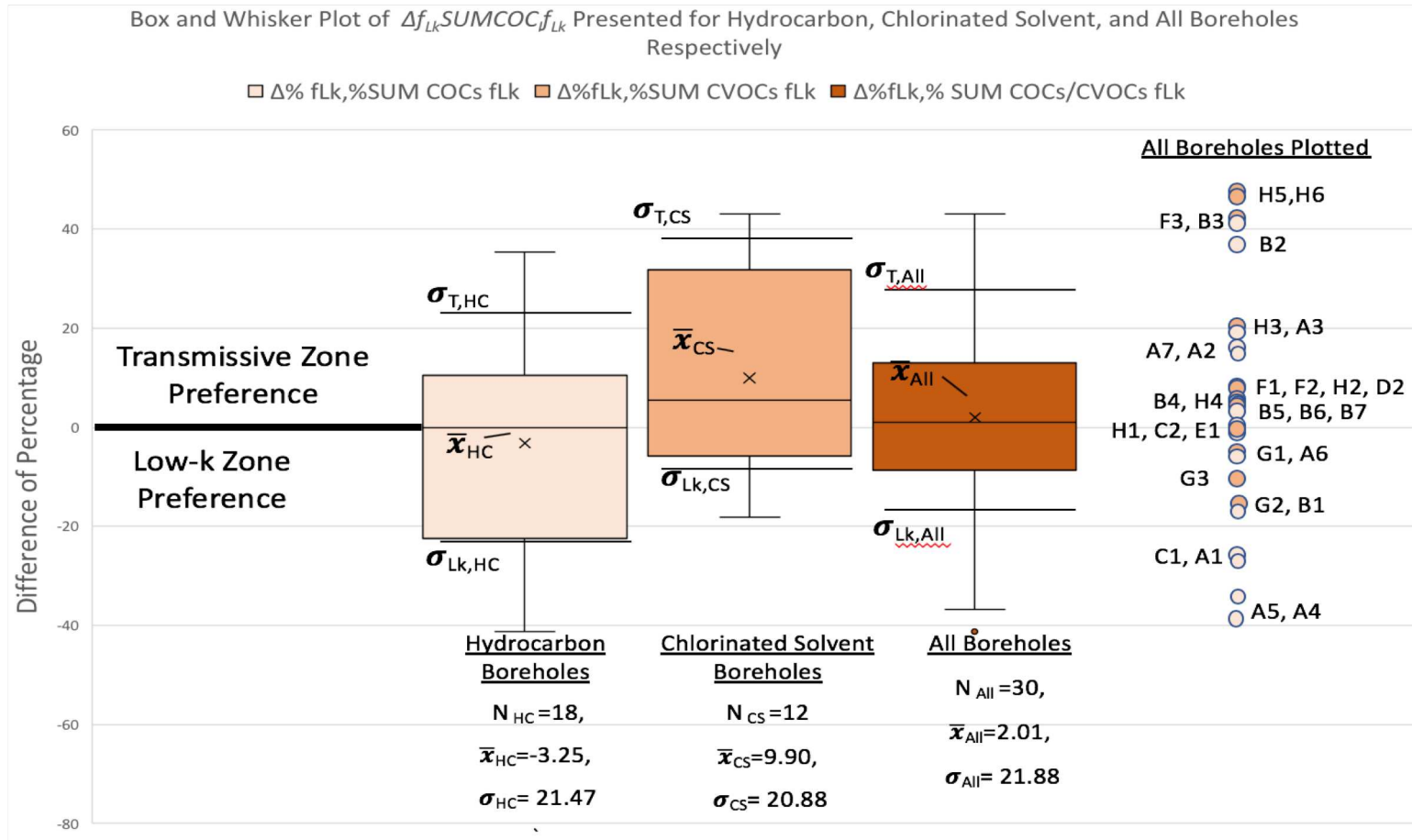


Figure 66: Box and Whisker Plots for Difference Between Percent of Borehole that is Low-k and Percent of Total Sum Of Contaminants in Low-k Zones Presented for Hydrocarbon, Chlorinated Solvent, and All Boreholes Respectively

Table 54: General Statistics for Percent of Borehole that is Transmissive and Low-k, and Percent of Sum of all COCs (Benzene/PCP+TPH or Chlorinated Solvents) in Zones for all Boreholes.

Numerical values are good to 1 significant number.

	<u>% f_T</u>	<u>% f_{Lk}</u>	<u>% SUM COC f_T</u>	<u>% SUM COC f_{Lk}</u>	<u>%f_{Lk} - %SUM COC f_{Lk}</u>	<u>Absolute %f_{Lk} - %SUM COC f_{Lk}</u>
Mean	49.30	50.70	51.93	48.07	2.01	16.09
Standard Error	4.76	4.76	6.16	6.16	3.99	2.68
Median	47.28	52.72	53.33	46.67	0.98	11.05
Mode	100.00	0.00	100.00	0.00	0.00	0.00
Standard Deviation	26.51	26.51	33.73	33.73	21.88	14.66
Sample Variance	702.73	702.73	1137.85	1137.85	478.57	214.98
Kurtosis	-0.41	-0.41	-1.46	-1.46	-0.14	-1.06
Skewness	0.39	-0.39	0.05	-0.05	0.10	0.67
Range	94.74	94.74	98.53	98.53	84.24	42.97
Minimum	5.26	0.00	1.47	0.00	-41.27	0.00
Maximum	100.00	94.74	100.00	98.53	42.97	42.97
Sum	1528.39	1571.61	1557.83	1442.17	60.27	482.65
Count	31.00	31.00	30.00	30.00	30.00	30.00

3.3 Discussion of Limitations

There are several limitations to the results that need to be discussed. There are limitations from core recovery, natural methane concentrations, and this paper's methods. They are:

Limitations: Recovery

- Varies based on subsurface media. Subsurface objects larger than the diameter of the drive shoe prevent further sampling.
- Site A was filled with cobbles and made it difficult to get full recovery. It also made designing a cutting plan and cutting the core significantly more difficult.

Limitations: Methane

- The presence of methane can be natural in the environment. Any correlation made between contaminant degradation and methane concentration could instead be natural background concentrations.

Limitations: COC Method

- We visually observe subsurface media suspended in water rather than performing standard geotechnical analysis. This is due to the limited sample size per sample ID and the dangerous contamination in each sample.
- The method has been modified since the first cryogenically cored samples were taken. New methods have better sampling resolution and detail along with added experience across participants. Inter-site comparisons take data produced under different methods with different contaminants.

- As mentioned in Sale et al (2016), the data for Site F has several detections of chlorinated solvents below readable limits but are interpreted as the posted concentrations. Those results are included.
- Intra-Site descriptive statistics are not produced for any individual site because many sites do not have enough boreholes to provide a sample size for such analysis.
- Some gINT forms are incomplete because the data was not available at the time of writing.
- Cannot apply data to a greater site picture or anything of greater significance than the borehole sampled

These limitations do affect the overall application of the analysis to a site characterization model.

It is also outside of the scope of this research to consider the implications of the method on the classification of contamination at each site.

CHAPTER 4: CONCLUSION

The overarching objectives completed in this research are:

- Advanced the visualization capability, through gINT™, for cryogenically collected core to professional, automated levels.
- Compared mass distributions in transmissive and low-k zones in each site individually (intra-site) and between sites (inter-site) for all boreholes.
- Explored opportunities to use cryogenically collected core to better resolve the distribution of contamination in transmissive and low-k zones in support of better site management decisions.

4.1 Key findings

The key findings are summarized in the following text.

gINT™ Forms are Successful

- The gINT™ forms have been successful and are being used in current and future projects. The forms are more often cannibalized into new forms as dictated by clients. However, the formatting, colors, and other key features have remained consistent.
- Improved data-by-depth visualizations to a professional level.

Method Was Successful

- The method was able to produce inter-site data that could be easily analyzed with descriptive statistics.
- The overall validity of the identification of transmissive and low-k zones needs to be developed further.
- The contaminant mass present in each borehole varies widely and it can be difficult to apply statistics to such a large range of mass. Thus, the statistical analysis of mass (kg/m²) in place was not usable. However, defining mass as "percent of total in zones" allows for the data to be bound in 0-100% scale. This presents the ability for boreholes from different sites and COCs to be compared in a single analysis.

Remediation changed COCs preference form transmissive zones towards low-k zones for Chlorinated Solvent Sites

- Site F/G changed after remediation efforts. This is an expected change and was apparent in the analysis. There was a statistically significant change from CVOCs pre-remediation preference for transmissive zones to CVOCs post-remediation preference for low-k zones.
- Site H has statistically significant difference between remediated boreholes and non-remediated boreholes. This was an expected change and was apparent in the analysis. Non-remediated boreholes significantly preferred transmissive zones and remediated boreholes showed and equal preference for each zone.

4.2 Implications for Site Characterization

It is important that this method can have greater use and applicability. The implications for site characterization are:

- The methods can be used for intra-site and inter-site comparisons.
- Boreholes can also be compared to other boreholes outside of their respective sites.
- This greater understanding can lead to better choice and design for remediation activities.
- Methods for identification of transmissive and low-k zones needs to be further developed

4.3 Future Work

The following text provides a list of beneficial future work.

- Develop methods to properly and scientifically measure the permeability of subsurface sediment at resolutions in inches. It is recommended that the assumed hydraulic conductivity values be verified via spot checks on representative samples. The spot checks can utilize Subsample E or “E-cores” that have been stored for future use.
- Continue to add new sites and boreholes using the methods provided in order to broaden the statistical analysis.
- Return to Sites A-E after remediation efforts to obtain post-remediation hydrocarbon data that includes NSZD data. This could provide helpful insight to see if the post-remediation hydrocarbon data correlates to post-remediation chlorinated solvent data.
- Expand analysis on the remediation efficiency at chlorinated solvent sites using a quantitative approach. The evaluation of the remediation activities in this thesis needs to

consider much more quantitative detail in the remediation processes for reductive dichlorination at Site F,G and ZVI clay mixing at Site H.

- Provide borehole specific estimates of how much contaminant mass was there historically. These boreholes are decades away from contaminant releases and have become mid/late-stage site contamination. This means that many of the issues present when the source was on have disappeared and the remaining contamination is minimal in comparisons of volume. However, even with the limited mass, there is still significant health and safety considerations that need to be addressed. Providing a timeline of mass depletion that considers remediation action and time could provide essential evidence to parties promoting remediation technologies and/or NSZD.
- Provide site specific estimates of how much mass would need to be lost in order to see a statistically valid change in total contaminant mass at a site. Site B and Site C are of current interest to our department at the moment and could provide a basis for future sites.
- Expand the methods to include microbial analysis and markers
- Expand the methods to include chemical and solution properties. This can include, but not limited to, dissolved ion concentrations, hydraulic conductivity, pH, ORP, and other dissolved gasses.
- Expand the analysis to include in depth, statistical considerations of the percent ratio of benzene/TPH by borehole, site, and all applicable boreholes. The analysis should follow some of the methods outlined in this thesis, but designing a novel analysis for benzene/TPH might need to be considered. This would include an expanded analysis into

benzene's persistence in low-k zones, selectively considering transmissive and low-k zones, and determining the longevity of contamination.

- Expand the analysis to include “why” hydrocarbons, chlorinated solvents and gases (methane) present the distributions we are observing. This would require the use of a statistical analysis, such as a principle compartment analysis, to determine the governing processes that control contaminant mass in subsurface media. This would look at factors including TDS, redox potential, temperature, microbial markers, other contamination, and more. This is not an exhaustive list and many factors would need to be vetted. Our current hypothesis is that it is redox driven, however, this is speculative and needs to be further verified.
- Utilize the graphics and information in this thesis to provide a more comprehensive view of subsurface media and the contamination that lies therein. This information can help with decisions regarding remediation activities. As an example, this thesis provides unique documentation of benzene in low- k zones. An absence or presence of benzene in low k zones is likely to have large implication with respect to the longevity of benzene in monitoring wells and the efficacy of remedial measures that address the longevity of benzene in respective monitoring wells.
- Combine the methods presented in this thesis with methods for monitoring natural attenuation of contaminants Askarani et al. (2018), Askarani & Sale (2020). The methods presented in this thesis can provide mass in place at a point in time. If we have mass in place numbers from two points in time compared with constant subsurface monitoring techniques it could be possible to provide further evidence for natural degradation rates and convince regulators to change traditional monitoring standards.

LITERATURE CITED

- Askarani K.K. and Sale T. (2020). "Thermal estimation of natural source zone depletion rates without background correction". *Water research*, 169, p.115245. <https://doi.org/10.1016/j.watres.2019.115245>
- Cahoon D.R., Lynch J.C., Knaus R.M. (1996). "Improved Cryogenic Coring Device for Sampling Wetland Soils". *Journal of Sedimentary Research*. Vol 66 No 5.
- Cahoon D.R., Reed D.J., Day J.W. (1995). "Estimating shallow subsidence in microtidal salt marshes of the southeastern United States: Kay and Barghoorn revisited" *Marine Geology* 128 I-9.
- Chapman S.W. and Parker B.L. (2005). "Plume Persistence Due to Aquitard Back Diffusion Following Dense Nonaqueous Phase Liquid Removal or Isolation", *Water Resource Research*, Vol. 41, No. 12, W12411.
- Cherry J. A., Parker B. L., Bradbury K. R., Eaton T. T., Gotkowitz M. B., and Hart D. J. (2006). "Contaminant Transport Through Aquitards: A State of the Science Review". AWWA Research Foundation, Denver, CO, USA.
- Dentz M. and Carrera, J. (2005). "Effective solute transport in temporally fluctuating flow through heterogenous media". *Water Resources Research*. Vol 41, Issue 8.
- Durnford D., Brookman J., Billica J., and Milligan J. (1991). "LNAPL distribution in a cohesionless soil: a field investigation and cryogenic sampler". *Ground Water Monitoring and Remediation*, 11(3), 115-122.
- Einarson M.D. and Mackay D.M. (2001). "Predicting the impacts of groundwater contamination." *Environmental Science and Technology* 35, no. 3: 67A-73A.
- Everest F. H., McLemore C. E., and J. F. Ward. (1980). "An improved tri-tube cryogenic gravel sampler. U.S. Forest Service Pacific Northwest Forest and Range Experiment Station Research Note PNW-350".
- Feenstra S, Mackay D. M., and Cherry J. A., (1991). "A method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples." *Groundwater & Environmental Services INC*.
- Garg S., Newell C., Kulkarni P., King D., Adamson D., Irianni-Renno M., and Sale T. (2017). "Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change." *Groundwater Monitoring & Remediation* 37(3): 62-81
- Haggerty R. & Grelick S. M. (1995). "Multiple-Rate Mass Transfer for Modeling Diffusion and Surface Reactions in Media with Pre-Scale Heterogeneity." *Water Resources Research* Vol 31, Issue 10.

- Irianni Renno M., Akhbari D., Olson M.R., Byrne A.P., Lefevre E., Zimbron J., Lyverse M., Sale T., and Long S.K. (2015). "Comparison of bacterial and archaeal communities in depth resolved zones in an LNAPL body. In preparation for submission to Applied Microbiology and Biotechnology".
- Johnson R.L., Simon H.S., Brow C.N., and Johnson,R.O.B. (2012). "Cryogenic collection of complete subsurface samples for molecular biological analysis". Strategic Environmental Research and Development Program, US DOD, ER-1559.
- Johnson R.L., Brow C.N., Johnson R.O.B., and Simon H.M. (2013). "Cryogenic core collection and preservation of subsurface samples for biomolecular analysis". *Groundwater Monitoring & Remediation*, 33(2), 38-43.
- Karimi Askarani K., Stockwell E.B., Piontek K.R. and Sale T.C. (2018). "Thermal monitoring of natural source zone depletion. *Groundwater Monitoring & Remediation*", 38(3), pp.43-52. <https://doi.org/10.1111/gwmr.12286>
- Kiaalhosseini S., Johnson R., Rogers R., Irianni-Renno M., Olson M., Lyverse M., and Sale T. (2017). "Cryogenic Core Collection (C3) from Unconsolidated Subsurface Media". *Groundwater Monitoring & Remediation* 36(4): 41-49.
- Olson M., Clayton W., Sale T., Long S., Irianni-Renno M., Johnson R. (2017). "Evaluating Long-Term Impacts of Soil-Mixing Source-Zone Treatment using Cryogenic Core Collection". ESTCP Project ER-201587. June 2017.
- Petts, G.E., Thoms, M.C., Brittan, K. and Atkin, B. (1989). "A freeze-coring technique applied to pollution by fine sediments in gravel-bed rivers". *Science of the Total Environment*. 84, pp. 259-272. doi:10.1016/0048-9697(89)90388-4.
- Rivett MO., Feenstra S., Cherry,JA. (2001). "A controlled field experiment on groundwater contamination by multicomponent DNAPL: creation of the emplaced-source and overview of dissolved plume development." *Journal of Contaminant Hydrology*. Volume 49, Issues 1-2 pgs 111-149.
- Sale T. and Newell C. (2010). "The Dependence of Plumes On Source Zones, Chapter 7 In Situ Remediation Of Chlorinated Solvent Plumes". New York, pp.85-117.
- Sale T. and Newell C. J. (2011). "A Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvent Sites". ESTCP Project ER-05 30. Environmental Security Technology Certification Program, Washington DC.
- Sale T., Parker B.L., Newell C. J., and Devlin J.F.. (2013). "State-of-the-science Review Management of Contaminants Stored in Low Permeability Zones." SerDP Project ER-1740.
- Sale T.C., Kiaalhosseini S., Olson M., & Johnson R.L. (2015). "Management of contaminants stored in low permeability zones: a state-of-the-science review, part II, third-generation (3G) site characterization: cryogenic core collection and high-throughput core analysis." U.S. Department

of Defense (DOD), Strategic Environmental Research and Development Program (SERDP), ER-1740.

Sale T., Kiaalhosseini S., Olson M., Johnson R., and Rogers R. (2016). "Third-Generation 3G Site Characterization: Cryogenic Core Collection and High-Throughput Core Analysis. An Addendum to Management of Contaminants Stored in Low Permeability Zones: A State-of-the-Science Review. SERDP Project ER-1740. July 2016."

Schincariol RA., Schwartz FW., Mendoza CA. (1997). "Instabilities in variable density flows: Stability and sensitivity analyses for homogeneous and heterogeneous media." *Water Resources Research*. Volume 33, Issue 1.

Sudicky E.A., Gillham R.W., Frind E.O. (1985). "Experimental investigation of solute transport in stratified porous media" 1. The nonreactive case, *Water Resources Research* 21, 1035–1041.