

**The Effect of Age on Petroleum Hydrocarbon
Contaminants in Soil for Bioventing Remediation**

**By
Mei Xiao**

**A Thesis
presented to
The University of Guelph**

**In partial fulfilment of requirements
for the degree of
Master of Science
in
Environmental Engineering**

Guelph, Ontario, Canada

© Mei Xiao, April, 2018

ABSTRACT

THE EFFECT OF AGE ON PETROLEUM HYDROCARBON CONTAMINANTS IN SOIL FOR BIOVENTING REMEDIATION

Mei Xiao
University of Guelph, 2018

Advisor:
Professor Richard G Zytner

An investigation was completed on the effects of petroleum contaminant aging in bioventing, a low cost and non-destructive *in situ* remediation method. Predicting site closure times remains a challenge in field applications, where the aged compounds are known to be sorbed into the soil, decreasing their bioavailability. Wet soil spiked with a known concentration of synthetic gasoline was aged in a refrigerator for 300 days. 150 g respirometers and 80 kg bioventing reactor degradation experiments were performed. After aging, a constant degradation rate at the 80 kg scale, varying from $0.12 d^{-1}$ to $0.133 d^{-1}$, was observed. In the 150 g respirometer, there was an increase in biodegradation rate, from $0.0787 d^{-1}$ to $0.1943 d^{-1}$. Microbial acclimatization during the aging process of wet soil was a key factor in both experiment.

ACKNOWLEDGEMENTS

This project would not have been possible without the help and support from all the important people I have received over the past two years. Sincere thanks to my supervisor, Dr. Richard Zytner, whose guidance and understanding throughout the entire project has helped me understand that any problem can be solved. His knowledge and experience were essential in the success of this project. I would also like to thank my advisory committee, Dr. Bassim Abbassi, whose valuable suggestions and feedback elevated this study and reminded me to take a step back to examine the problem with a different point of view. Furthermore, many thanks to the Natural Science and Engineering Research Council (NSERC) of Canada for providing the funding for this research project.

To Joanne Ryks and Ryan Smith, I owe all my gratitude for providing support and assistance during the experimental phase of the project. Their suggestions and technical knowledge were an immeasurable help. Many thanks to Professors Hung Lee and Zeny Feng for their insights on microbiology and statistical analyses respectively, who helped to point me in the right direction, and to Lucia Costanzo, from the Data Resource Center, who was infinitely patient in answering all my statistical questions.

I would like to thank the friends I've made during this journey; the joyful memories and mutual commiseration brought life into these few years as I transplanted myself into a new city. I cherish these connections and hope they remain strong as we part ways. To my friends and family who have supported me from afar, thank you for your continual understanding and encouragement. And to my best friend and the light of my life, thank you for always being there for me, for supporting my every decision, for everything.

LIST OF ACRONYMS

BTEX	Benzene, toluene, ethylbenzene, xylene
C:N	Carbon to nitrogen ratio, weight basis
CFU	Colony-forming units
CI	Confidence Interval
FCSAP	Federal Contaminated Sites Action Plan
FID	Flame ionization detector
GC	Gas chromatograph
k_d	Degradation rate coefficient
k_p	Sorption coefficient
k_{oc}	Soil organic carbon-water partitioning coefficient
k_{ow}	Octanol-water partition coefficient
LOD	Lower detection limit
MC	Moisture Conte
MeCl	Methylene Chloride, CH ₂ Cl ₂
MW	Molecular weight
NAPL	Non-aqueous phase liquid
OM	Organic matter content of soil
PAH	Polycyclic aromatic hydrocarbons
PDB	Petroleum degrading bacteria
PHC	Petroleum hydrocarbon
SVE	Soil vapour extraction
THB	Total heterotrophic bacteria
TPH	Total petroleum hydrocarbon
TSA	Tryptic soy agar
US EPA	United States Environmental Protection Agency
UST	Underground storage tank

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	III
LIST OF ACRONYMS	IV
LIST OF FIGURES	VIII
LIST OF TABLES.....	IX
CHAPTER 1: INTRODUCTION.....	1
1.1 Objective of this study	2
1.2 Layout of the thesis.....	3
CHAPTER 2: LITERATURE REVIEW.....	4
2.1 Petroleum hydrocarbon as hazardous waste	4
2.2 Fate of petroleum hydrocarbon in the environment.....	5
2.2.1 <i>Non-aqueous phase liquid (NAPL)</i>	6
2.2.2 <i>Dissolution into the groundwater</i>	6
2.2.3 <i>Air volatilization</i>	7
2.2.4 <i>Sorption onto soil particles</i>	7
2.3	8
2.4 Treatment technologies	8
2.4.1 <i>Excavation</i>	8
2.4.2 <i>Soil vapour extraction</i>	9
2.4.3 <i>Bioventing</i>	10
2.5 Bioventing factors.....	11
2.6 Scale up factors	12
2.7 Aging factor	14
2.7.1 <i>Aging process</i>	14
2.7.2 <i>Bioavailability</i>	15
2.7.3 <i>Contaminant type</i>	16
2.7.4 <i>Laboratory-scale aging</i>	17
2.7.5 <i>Challenges</i>	17
CHAPTER 3: LIST OF EXPERIMENTS.....	18
CHAPTER 4: EXPERIMENTAL METHODS	20
4.1 Synthetic Gasoline	20
4.2 Soil Collection	21
4.2.1 <i>Delhi Soil</i>	21
4.2.2 <i>Elora Soil</i>	22
4.3 Soil Preparation.....	22
4.3.1 <i>Sifting</i>	22
4.3.2 <i>Soil Spiking</i>	22
4.3.3 <i>Aging</i>	23
4.3.4 <i>Nutrient Addition</i>	23
4.4 80 kg reactor	24
4.4.1 <i>Reactor Characteristic</i>	24
4.4.2 <i>Loading, maintenance, and sampling of the reactor</i>	25
4.5 150 g respirometer	26
4.6 Preparation of Controls	27
CHAPTER 5: ANALYTICAL METHODS.....	29
5.1 PHC.....	29
5.1.1 <i>Methylene Chloride Extraction</i>	29

5.1.2	<i>Off Gases</i>	29
5.2	Gas Chromatography with Flame Ionization Detector	30
5.2.1	<i>Overview and Setup</i>	30
5.2.2	<i>Creation of Standards and Calibration Curves</i>	31
5.3	Respiration	32
5.3.1	<i>Oxygen Usage</i>	32
5.3.2	<i>Carbon dioxide production</i>	33
5.4	Soil pH	33
5.5	Soil Water Content.....	33
5.6	Microbial plate counting	34
CHAPTER 6: EXPERIMENT QUALITY ASSURANCE/QUALITY CONTROL.....		36
6.1	80 kg reactor	36
6.1.1	<i>Soil Water Content</i>	36
6.1.2	<i>Oxygen Levels</i>	37
6.1.3	<i>Off gas Monitoring</i>	38
6.1.4	<i>Microbial Count</i>	40
6.2	150 g Respirometer	41
6.2.1	<i>Soil Water content</i>	41
6.2.2	<i>Soil pH</i>	42
6.2.3	<i>Carbon Dioxide Production</i>	43
6.2.4	<i>Biotic and Abiotic Controls</i>	45
6.3	Biodegradation Rates Processing and Statistical Methods	46
6.3.1	<i>Calibration Curve</i>	46
6.3.2	<i>Coefficient of Variation – GC-FID</i>	48
6.3.3	<i>Lower Detection Limit</i>	49
6.3.4	<i>Coefficient of Variation – Soil Mixing</i>	50
6.3.5	<i>Data Validation</i>	51
6.3.6	<i>Degradation Rate Coefficient</i>	51
CHAPTER 7: BIODEGRADATION RATE RESULTS AND DISCUSSION		53
7.1	Extraction Efficiencies	53
7.1.1	<i>Overall TPH</i>	53
7.1.2	<i>Compounds</i>	54
7.2	150 g Respirometers.....	56
7.2.1	<i>Short-Term Aging</i>	56
7.2.2	<i>Long-term aging</i>	59
7.3	80 kg bioventing reactor	60
7.3.1	<i>Single-stage biodegradation rates</i>	61
7.3.2	<i>Expanded bioventing reactor</i>	63
7.3.3	<i>Long-term aging</i>	65
7.3.4	<i>Scale-Up Factor</i>	67
CHAPTER 8: CONCLUSION		69
CHAPTER 9: RECOMMENDATIONS		72
REFERENCES		73
APPENDIX A: SAMPLE CALCULATIONS		77
A.1:	Nutrient Amendment Calculation	77
A.2:	Sample data processing, from GC-FID output to contaminant concentration in soil	78
APPENDIX B: EXPERIMENTAL CONDITIONS – DATA.....		81
B.1:	Biotic Control Data	81
B.2:	Delhi-270-80kg – Operating Conditions.....	82
B.3:	Delhi-300-80kg – Operating Conditions.....	90
B.4:	150g Experiments – Operating Conditions	95

<i>B.4-1 Delhi-270-150g and Delhi-300-150g</i>	95
<i>B.4-2 Long-Term Aging</i>	96
<i>B.4-3 Short-Term Aging</i>	98
<i>B4-4: Microbial Data</i>	101
APPENDIX C: BIODEGRADATION RATE – DATA	102
Full degradation rate coefficient table with statistical analysis	102
Delhi-270-150g.....	105
Delhi-270-80kg.....	106
Delhi-300-150g.....	108
Delhi-300-80kg.....	110
Elora-270-80kg.....	117
Delhi-LT-150g.....	118

LIST OF FIGURES

Figure 2.1: Federal contaminated sites distribution by contaminant type where 59% (including PAH, BTEX, and PHC) are due to petroleum-based products. (TBCS, 1994)	4
Figure 4.1: 80 kg bioventing reactor setup	24
Figure 4.2: 150 g respirometer setup	27
Figure 6.1: Soil water content during the Delhi-270-80kg experiment	36
Figure 6.2 : Soil water content during the Delhi-300-80kg experiment	36
Figure 6.3: Oxygen levels for Delhi-270-80kg and Delhi300-80kg experiments.....	37
Figure 6.4: TPH captured in off gases for Delhi-270-80kg and Delhi-300-80kg experiments.....	38
Figure 6.5: Difference in TPH composition between the extracted compounds and the compounds captured in the off gases at the start of the experiments. Values averaged between the Delhi-270-80kg and Delhi-300-80kg experiment.	40
Figure 6.6: Soil Water content for Delhi-270-150g and Delhi-300-150g experiment.....	41
Figure 6.7: pH level differences between Delhi and Elora soil for short term aging experiments (soil contaminant age between 0 and 30 days)	42
Figure 6.8: pH readings in the KOH tubes in experiments Delhi-270-150g and Delhi-300-150g	44
Figure 6.9: KOH pH for short-term experiments with Delhi and Elora soil.....	44
Figure 6.10: Bioventing experiment for the Delhi-LT-150g experiment after 305 days of aging, for autoclaved aged soil (abiotic control) and regularly aged soil	45
Figure 6.11: Sample output from the GC-FID. Five syngas compounds can be seen at 5.9 (isooctane), 7.2 (toluene), 8.4 (m-xylene), 9.4 (mesitylene), and 11.6 (naphthalene) minutes.	47
Figure 6.12: Sample calibration curve for run mx170731. Linear regression plotted for all five syngas compounds, intercept forced at zero.	47
Figure 6.13: Coefficient of Variation at different concentrations for different TPH compounds for standard solutions run in the GC-FID between March 2017 and November 2017, with total sample size $n \geq 79$ for all compounds.....	48
Figure 6.14: Data distribution between concentrations of 0 to 2 mg/kg _{soil} for all data collected with the GC-FID.....	49
Figure 7.1: Decrease in TPH concentration with increase in age for contaminants in Delhi soil for all 150 g-scale bioventing experiments, showing a zeroth order decrease in extractability with increased aging.	53
Figure 7.2: Decrease in syngas concentration between 0 and 305 days of aging, more prominent for isooctane, toluene, and m-xylene and minimal in mesitylene and naphthalene	55
Figure 7.3: Change in relative syngas composition between 0 days aged and 305 days aged TPH	56
Figure 7.4: Individual compounds concentration results from Elora-A-30-150g over 30 days of bioventing in 150 g respirometers. An increase in mesitylene at day 11 is notable	58
Figure 7.5: Change in degradation rate coefficients (k_d) for Delhi soil (150 g) from age 0 to 10 month, plotted with a linear regression and 95% confidence intervals (CI)	59

Figure 7.6: Comparison between single stage and two-stage degradation rates for Delhi-300-80kg, selecting day 14 as the break point between stage one and stage two. Regression model details in Table 7.4	63
Figure 7.7: Delhi-300-80kg results, showing the effects of sampling location on TPH concentration and biodegradation rate	64
Figure 7.8: Delhi-300 initial TPH concentration for the 150 g experiment and for different location in the 80 kg reactor	65
Figure 7.9: Degradation rate coefficient in 80 kg bioventing reactor for different contaminant age.	66

LIST OF TABLES

Table 2.1: Summary of 30-day bioventing degradation rate constant for Delhi (Loamy Sand) and Elora (Silt Loam) soil using 150 g, 4kg, and 80 kg of soil from past research and experiments	14
Table 3.1: List of experiments	18
Table 4.1 Synthetic gasoline composition	20
Table 4.2: Physical soil characteristics for Delhi and Elora soil.....	21
Table 5.1: Standard solution preparation with synthetic gasoline and MeCl.....	32
Table 6.1: TPH volatilized during 80 kg experiments	39
Table 7.1: K_{ow} values and molecular weight of synthetic gasoline compounds	55
Table 7.2: Summary of k_d values for short term aging experiments	57
Table 7.3: Degradation rates for Delhi soil at different scales.....	62
Table 7.4: Fit comparison between one-stage and two-stage degradation rate for first order degradation rates in Figure 7.6	62
Table 7.5: Degradation rate coefficient and scale up factors for Delhi soil.....	68

CHAPTER 1: INTRODUCTION

Petroleum hydrocarbon contamination in soil is a threat to both human health and the environment and is one of the most common source of contaminants in the soil. As of March 2011, 15 000 of the 22 000 federal contaminated sites remain open and require remediation, causing an estimated financial liability of \$4.2 billion (OAGC, 2012). Many of these sites have not been audited financially, and could significantly increase the cost estimate. Of these open sites, over half are due to petroleum products (TBCS, 1994), often caused by diesel fuel due to spills during the transportation and transfer of fuels and leaks from underground storage tanks.

Many of the sites have contaminated soil, which cause a threat to human health due to the BTEX (benzene, toluene, ethylbenzene, and xylene) compounds present in fuel. Some polycyclic aromatic hydrocarbons (PAH) have also been found to be cancerous in mammalian tissues (ATSDR, 1995a). In order to reduce the impact of these contaminants, it is important to develop cost effective methods of remediation. A technique that shows a lot of promise in the field of remediation is bioventing. It is an *in situ* technique that relies on bacteria, whose growth is stimulated via the addition of nitrogen and oxygen to the soil, to degrade the contaminants.

Bioventing still present challenges surrounding the estimation of degradation rates and remediation times. Laboratory experiments often use soil that has been freshly spiked, which is not a realistic representation as most remediation sites contain contaminants that have been in contact with the soil for an extended period. With time, petroleum products can become sorbed into the soil and this bonding made it difficult for the bacteria to access, thus lowering the rate of biodegradation. As such, it is important to understand the effect of “age” on bioventing.

This project will seek to determine the degradation rates for bioventing of soil that has been spiked with petroleum hydrocarbon and aged for up to 300 days. Bioventing processes will be performed in a 150 g respirometer and 80 kg reactor to determine the effects of aging on scale. This work will be a continuation

of the research performed by several students at the University of Guelph using different scaled reactors. Shewfelt et al. (2005) and Eyvazi and Zytner (2009) have done work using 150 g soil samples, optimizing the process and developing a correlation to estimate the degradation rate constant. Khan and Zytner (2013) performed extensive work with 4 kg scale reactors and his work was continued by Mosco and Zytner (2017), using 80 kg reactors, determining the scale-up factors.

1.1 Objective of this study

There is currently a gap in knowledge on the effects of aged contaminants on the biodegradation rate for petroleum hydrocarbons, despite the numerous contaminated sites that have been contaminated in the past, where petroleum contaminants have been sequestered into the soil matrix with time. To better predict the remediation rates, it is important to factor in the age of the contaminant and how it will affect the bioavailability of the petroleum hydrocarbons for the microbial communities. As such, additional work to support the research done by Shewfelt et al. (2005), Eyvazi and Zytner (2009), Khan and Zytner (2013) and Mosco and Zytner (2017) is required to improve predictions for site closure times when using bioventing. These past experiments were performed using freshly spiked soil. Replicating these experiments with aged contaminants will allow for the effects of short and long-term aging to be examined to determine the effect of aging on the biodegradation rates.

Contaminant extractability and sorption will be measured throughout the aging process. In addition, the rate of remediation for the 150 g respirometer and 80 kg reactor will be compared to each other to develop a preliminary scale-up factor due to the number of experiments needed, which can then be used in the field to better estimate the time required to remediate a contaminated site. Two soil types will be used to have comparable data with past experiments. This will advance the knowledge in the field of bioventing. For this research project, the objectives are as follows:

- (1) Determine the effects of aging on contaminant extractability over time
- (2) Perform bioventing remediation at two different scales (150 g and 80 kg) using the methods developed by Eyvazi and Zytner (2009) and Mosco (2016) using soil with aged contaminants to qualify the changes with time
- (3) Develop a scale-up factor for similar soil at two different scales
- (4) Qualify the impact of the aging process on bioventing degradation rates

1.2 Layout of the thesis

This thesis contains nine chapters and three appendices. Chapter 1 briefly introduces the research topic and the main objectives of this study. Chapter 2 will present a review the literature on the current knowledge of aged petroleum hydrocarbons contaminants in the soil and bioventing remediation. The list of experiments performed during this research is present in Chapter 3. Chapter 4 will detail the experimental methods used to prepare the soil and the experiment, whereas the different analytical methods are described in Chapter 5. The experimental conditions are recorded in Chapter 6 and the biodegradation rate results are presented in Chapter 7, followed by the conclusions of this study in Chapter 8. Recommendations for future studies are in Chapter 9, and followed by a list of references.

Appendix A contains detailed calculations necessary during this research project. Appendix B and list the raw data set for the experimental condition and Appendix C summarizes the biodegradation rates along with the statistical analyses performed on the data.

CHAPTER 2: LITERATURE REVIEW

2.1 Petroleum hydrocarbon as hazardous waste

The use of petroleum hydrocarbon in Canada is ubiquitous and it affects everyone's daily lives. They are a source of raw material and energy, used in climate control, transportation, and work (CCME, 2008). However, petroleum hydrocarbon also accounts for the largest source of contaminant in Canada, with 22,000 federal contaminated sites in Canada (OAGC, 2012). The Federal Contaminated Sites Action Plan (FCSAP), a 15-year 4.2-billion-dollar program for the assessment and remediation of contaminated sites, reports that over 59% of the contaminations comes from petroleum products. This includes aliphatic petroleum hydrocarbons (PHC), BTEX (Benzene, Toluene, Ethylbenzene, Xylene), and polycyclic aromatic hydrocarbons (PAH) (TBCS, 1994). Figure 2.1 shows the breakdown of all federal contaminated sites. For this research, these petroleum products will be referred to as total petroleum hydrocarbon (TPH).

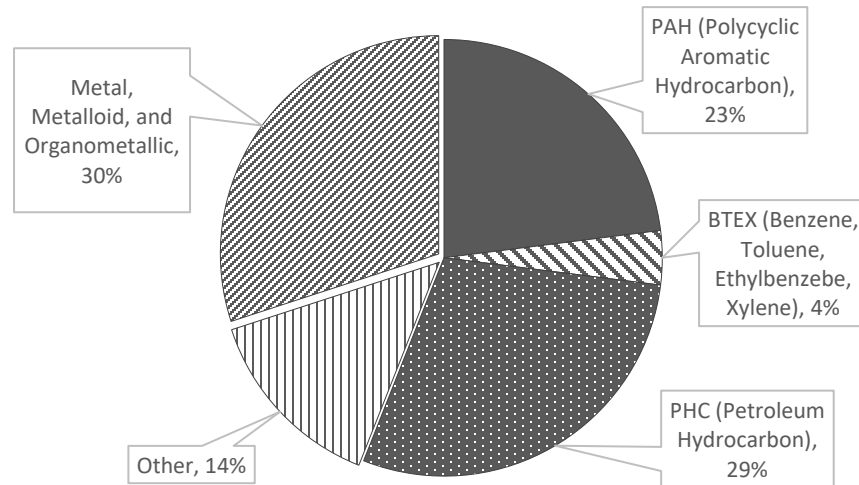


Figure 2.1: Federal contaminated sites distribution by contaminant type where 59% (including PAH, BTEX, and PHC) are due to petroleum-based products. (TBCS, 1994)

Many of these sites are a result of spills and leaks, especially in more populated areas where there are many old underground storage tanks (UST). In the past, these tanks were often made of bare steel, which have since corroded, allowing its contents to leak into the soil. The United States Environmental Protection Agency (US EPA) estimates that around 25% of the 2 million UST were releasing petroleum hydrocarbons into the soil and groundwater before new standards and regulations were implemented (Hinchee and Ong,

1992; US EPA, 2013). Overall, a third of the UTS installed before 1990 are either currently leaking or expected to be leaking in the future (AEP, 2015).

There have been efforts to mitigate the risk of leaks through the Canadian Environmental Protection Act, 1999, the Storage Tank Systems for Petroleum Products and Allied Petroleum Products Regulations (MoJ, 2008). However, as the regulation only applies to petroleum storage tanks that belong to the federal house or if they are located on federal or aboriginal land, it excludes all UTS used for residential, commercial, and industrial purposes. This is a serious threat to human health as, once released into the soil and groundwater, TPH are classified hazardous waste.

Human exposure is possible through three different pathways: inhalation in the air; ingestion through water, food, or soil; and physical contact. Exposure can cause toxic health effects, causing damage to the human nervous system along with potential carcinogenic effect, especially products comprised of BTEX. Acute exposure can cause headaches, dizziness, irritation, and tremors, while prolonged chronic exposure to benzene has been linked to the reduction of red and white blood cell production from bone marrow, along with cases of leukemia (WHO, 2010). Due to the small chemical structures of BTEX compounds, they tend to have a higher solubility than other petroleum hydrocarbon products, they are more susceptible to travelling through the aquifer, contaminating the groundwater.

PAH have also been found to have toxic, mutagenic, and cancerous properties in mammals. The lipophilic tendencies of PAH have led to these compounds to accumulate in fatty tissues such as in the kidney, liver, or body fat. Though the residence time tend to be short – a couple of days before they are eliminated through urine and feces – continuous exposure to the contaminants can result in long term health defects (ATSDR, 1995b).

2.2 Fate of petroleum hydrocarbon in the environment

The migration of petroleum hydrocarbons in soil is greatly affected by the characteristics of both the soil and the contaminant. Due to the complex nature and diverse properties of petroleum hydrocarbon

along with the variety of soil heterogeneities, it is difficult to give a specific prediction of the movement of the contaminant in soil.

Petroleum hydrocarbons can travel through the soil as a plume, be dissolved and transported with the groundwater, or volatilize into the air. In addition, the contaminants can ‘age’ in the soil as they are sorbed onto the solid soil phase, rendering them less mobile than they would be in the other three phases.

2.2.1 *Non-aqueous phase liquid (NAPL)*

NAPL describes a mass of contaminants which have aggregated together in the form of a plume due to their hydrophobicity, and migrate through the soil driven by both gravitational and advection forces. Migration in the unsaturated zone can be affected by many parameters, from the property of the soil and of the contaminants forming the NAPL. Furthermore, the volume of the spill, how quick the spill happened, and the age of the spill will all affect the movement of the NAPL. Overall, soils with a more porous texture and a strong hydraulic gradient will experience a higher speed of contaminant migration.

2.2.2 *Dissolution into the groundwater*

Though TPH are mostly hydrophobic contaminants, when they are in contact with water, there is a migrate into the aqueous phase. The octanol-water partition coefficient (k_{ow}) describes the concentration of contaminants in the octanol phase (NAPL) to the water phase, as seen in Equation 1, and helps us better understand the quantities that are migrated. This number is usually extremely high in petroleum products (Piwoni and Keeley, 1990) and is different for every compound. The k_{ow} is crucial in the remediation rates of TPH in groundwater but plays a less significant role when focusing strictly on the soil’s unsaturated zone.

$$k_{ow} = \frac{\text{Concentration}_{\text{Octanol}}}{\text{Concentration}_{\text{water}}} \quad [1]$$

2.2.3 *Air volatilization*

Many small petroleum hydrocarbon chains have a high vapour pressure, so there is a tendency for them to vaporize. There is potential for highly volatile contaminants, such as toluene, to be released into the atmosphere due to passive volatilization (Gidda T. et al., 2011), which can be a source of human health risk as this compound is both flammable and toxic. However, this volatility can also be harnessed for in-situ remediation techniques for unsaturated soil, where the rate can be increased to extract the contaminants as off gases.

2.2.4 *Sorption onto soil particles*

Contaminants can enter the solid phase of the soil through sorption, which encompasses two different processes: adsorption and absorption. Adsorption is the process in which the contaminants concentrates on the surface of the adsorbent and accounts for a majority of the sorption in soil. Absorption is the phenomenon where the adsorbate is taken into the volume of the solid matrix. This can occur via diffusion and can cause irreversible retention of the contaminants when they have travelled into the micropores in the soil (Loibner et al., 2006). Desorption occurs when the bond between the adsorbate and the soil is broken and the contaminant is free to travel and migrate to other areas of the soil.

The rate of sorption and desorption can be described using the Freundlich isotherm, an empirical equation that describes the relationship between the concentration of the contaminant on the surface of the soil and of the surrounding environment (Zytner, 1994). As adsorption is the dominant process for sorption, an increase surface area of the adsorbent can increase the rate of sorption. As such, soils with a higher distribution of smaller particles, such as silt and clay heavy soils, often see a slower migration of TPH contaminants due to sorption. Furthermore, soils with higher silt and clay content also invariably contain a larger fraction of soil organic matter (OM). The OM content in soil is a key factor that influences the sorption and retention rate of BTEX due to its hydrophobic nature, which attracts the petroleum waste.

Though overall retention times will vary depending on the exact soil and contaminant characteristics, the sorption coefficient (k_p) and the soil organic carbon-water partitioning coefficient (k_{oc}), described by Equations 2 and 3, can provide essential information on the distribution of the contaminants (Piwoni and Keeley, 1990), especially when the contaminants have been aged, allowing for not only adsorption, but also absorption to occur between the TPH molecules and the soil particles. It is also influenced by the soil retention capacity, also known as the water holding capacity, which describes the amount of water a soil can hold, and is a function of soil texture and soil organic matter content. A high soil retention capacity increases the contact time, and thus the sorption, between a contaminant in its aqueous phase and the solid soil matrix.

$$k_p = \frac{\text{Concentration}_{\text{solid phase}}}{\text{Concentration}_{\text{solution}}} \quad [2]$$

$$k_{oc} = \frac{\text{Sorption Coefficient } (k_p)}{\text{Fraction Organic Carbon}} \quad [3]$$

2.3

2.4 Treatment technologies

Many soil remediation techniques are available for petroleum hydrocarbons in the unsaturated zone of the soil, including chemical, physical, and biological treatment methods. They are often divided between *ex situ* and *in situ* techniques, depending on the location of the remediation process.

2.4.1 Excavation

Ex situ techniques require the physical removal of the contaminated soil where it will be remediated off site. This method allows for a rapid removal of the contaminants from the site and can allow a wider range of remediation methods to be performed at the cost of both environmental and economical drawbacks. The cost of soil excavation, transport, and storage can be high for larger spill areas. Furthermore, the soil chemistry and biology is disrupted as the excavated area is filled with foreign soil. Overall, this method is preferred in areas where the contaminated site must be remediated rapidly for immediate redevelopment (Kuppusamy et al., 2016).

2.4.2 Soil vapour extraction

In situ techniques focus on remediating the soil on site and are often less expensive but more time consuming. One popular technique for the remediation of TPH is soil vapour extraction (SVE), which takes advantage of the high vapour pressure of the contaminants. This method uses a series of pumps and wells to increase the air circulation in the soil, stimulating the volatilization of the chemicals, which are then extracted with a vacuum (Wilson, 1995).

A phenomenon that can be observed in SVE remediation sites is the effects of tailing and rebound. Tailing describes the rapid slowdown of remediation effectiveness due to mass transfer resistance; the concentration of petroleum hydrocarbons being extracted drops rapidly after the initial withdrawal of the easily accessed contaminant. This is due to preferential flow in the soil which causes a large concentration to be initially withdrawn before a rapid decrease is expected. Lower-level concentrations can then be observed due to an increase in mass transfer resistance, often stagnating at a concentration higher than acceptable according to most environmental cleanup standards.

Rebound refers to the rapid increase in the level of contaminants after the remediation process has ended, which is mainly caused by equilibrium conditions being attained. Rebound can also be due to the upwelling of the groundwater table (Rathfelder et al., 2000) as the vacuum draws the water table higher under the well, filling the soil gas pores with water and limiting gas flow around the contaminated area. This can cause remediation efforts to be prematurely terminated as low TPH concentrations are present in the off gases, while higher levels remain present in the soil. Both tailing and rebound can cause the treatment time to be extended, sometimes an entire order of magnitude longer, while also keeping the contaminant levels above clean-up levels (US EPA, 1996).

2.4.3 Bioventing

Bioventing is a remediation technique that shows a lot of promise in the field, using similar technologies to SVE but relying on biodegradation for the removal of petroleum hydrocarbon contamination. Though natural biodegradation tends to be much slower than physical methods of contaminant removal, with major difficulties in estimating cleanup times (Bezerra and Zytner, 2003), bioventing seeks to provide optimal conditions to the microbial population through the increase in oxygen content along with an addition of nutrients to break down the semi-volatile petroleum hydrocarbons.

This is an *in situ*, low-impact remediation technique, where pre-existing indigenous bacteria are stimulated for biodegradation. In addition, bioventing is a low-cost method that requires minimal technology and monitoring past the setup phase, making it ideal for contaminated sites with petroleum hydrocarbon contamination with low accessibility.

A successful bioventing remediation should follow SVE in order to take advantage of the rapid extraction of contaminants before tailing occurs (McClure and Sleep, 1996), as neither tailing nor rebound effects have been observed when conducting bioventing experiments (Lee et al., 2001). Since injection and extraction wells are used in both SVE and bioventing, the conversion from one technique to the other is effortless.

There are many challenges in accurately predicting the degradation rates of these contaminants, which are based on individual site conditions. These variabilities, along with the complex nature of biodegradation in the soil, lead to difficulties in providing a timeframe for these operations, potentially resulting in higher costs than planned. Many laboratory-scale experiments have been performed to increase the efficiency of bioventing. Biological growth is often a factor difficult to predict in the environment as it is affected by several factors, including the oxygen level in the soil, water content, nitrogen application rate, along with particle size distribution (Bezerra and Zytner, 2003; Eyvazi and Zytner, 2009; Khan and Zytner, 2013; Rathfelder et al., 2000; Shewfelt et al., 2005).

2.5 Bioventing factors

Field tests to determine bioventing degradation rates have found that many factors affect biodegradation, including soil type, contaminant composition, and contaminant age. Degradation rates were also found to vary seasonally as temperatures and water content in the soil changed (Hinchee and Ong, 1992). The variations present during field experiments make it difficult to understand how each factor affects the rates of biodegradation. As such, most bioventing research has been done in a laboratory-scale for better environmental control. Optimal bioventing conditions were extensively tested in the small-scale reactors, developed by Shewfelt and modified by Eyvazi (Eyvazi and Zytner, 2009; Shewfelt et al., 2005).

To promote bacterial growth which, in turn, increases biodegradation, environmental factors can be optimized by varying the levels of nutrients, water, and oxygen present in the system. The process was found to be nutrient-limited (Brook et al., 2001; Shewfelt et al., 2005), where a Carbon:Nitrogen (C:N) ratio of 10:1 using ammonium nitrate as the amendment was required for ideal aerobic bacterial degradation. Water content did not significantly alter biodegradation rates but a 50-70% soil water content of its water holding capacity is suggested to ensure sufficient water content while not limiting the air flow through the system (Shewfelt et al., 2005).

While initial TPH concentration alone did not seem to affect biodegradation rates, soil with long-term contamination have been suggested to contain bacteria that have been acclimatized to the elevated levels of petroleum concentration, thus exhibiting a higher rate of biodegradation in the sealed reactors. However, the inoculation of contaminated soil with bacteria or bacteria-rich amendments to promote higher quality of microbial activity do not appear to significantly improve biodegradation rates (Huesemann, 2004; Møller et al., 1996).

The composition of soil along with its organic matter content are important influences of biodegradation rates due to their intrinsic link with bioavailability, which is defined as the quantity of contaminants that the microbes can access in the soil. This is affected by the migration of contaminants as

they are most accessible in their gaseous or aqueous phase, as opposed to the NAPL or solid phase (Reid et al., 2000). For soils with high organic matter content, and thus, a larger k_{oc} , more of the contaminants are expected to be sorbed onto the soil where they are less bioavailable. In fact, for smaller aliphatic and ringed petroleum hydrocarbon, biodegradation rates depend on desorption rates from the soil (Jonsson et al., 2007).

Equation 4 was developed to describe the effects of soil type physio-chemical properties on the biodegradation rate constant in 150g respirometers (Eyvazi and Zytner, 2009).

$$\ln(k_d) = 2.803 PDP + 0.210 \times Sand + 4.886 \times OM - 0.094 \times Clay - 0.004 (SW \times Sand) - 0.021 (Sand \times PDP) - 0.632 (OM \times PDP) + 0.004 (SW \times Clay) - 23.5 \quad [4]$$

where

- k_d : biodegradation rate constant (day^{-1})
- PDP: initial petroleum degrading microbial population in the soil (log CFU/g)
- SW: soil water content (%)
- Sand: soil sand content (%)
- Clay: soil clay content (%)
- OM: soil organic matter content (%)

This correlation was developed for bench-scale respirometers undergoing ideal bioventing conditions by observing the exponential regressions between the different soil characteristics and highlights the effects of soil composition on the rate of biodegradation.

2.6 Scale up factors

While *in situ* test are preferable to lab scale ones as they are much more representative (Hinchee and Ong, 1992), it is not always possible due limitations of access and background knowledge of the contaminated site. In addition, there are more variables at play that are difficult to control, which in turn make it difficult to pinpoint how each factor influences bioventing degradation rates. Nevertheless, the goal of laboratory-scale experiments is for the knowledge to be eventually transferred and applied in the field. This requires the development of scale-up factors, which ensure that values, such as the biodegradation rate constant found in a laboratory environment, are representative at larger scales.

These differences can be due to the complexities found in undisturbed soils that are difficult to recreate *ex situ*. Furthermore, not only do heterogeneities in the soil become more important at larger scales, larger bioventing systems benefit from creating an expanded reactor when air is injected into the system as it allows for some of the TPH to volatilize into the air, which can then be biodegraded in the surrounding soil, ultimately increasing the rate of biodegradation (US EPA, 1995).

To investigate these scale-up factors, larger-scaled bioventing reactors were developed at the University of Guelph, using similar techniques, contaminants, and soil types as the small-scaled respirometers, allowing for a direct comparison to be made for the larger 4 kg (Khan et al., 2015) and 80 kg (Mosco, 2016) experiments.

When comparing the degradation rates measured for the larger (4 kg and 80 kg) reactor with the expected degradation rates in the smaller 150 g respirometer, an average scale up factor of 2.3 was calculated. Furthermore, a two-stage degradation rate was observed in the larger reactors, where the transition from stage one to stage two would occur around the eight-day mark (Khan and Zytner, 2013). Stage one was characterized by a much higher degradation rate constant than the second stage, where the bacteria process the easily accessible petroleum hydrocarbons, followed by the slower second stage, where the less bioavailable contaminants are now being degraded.

Equation 5 describes the stage two degradation rate correlation developed by Khan and Zytner following the 4 kg bioventing experiments.

$$\ln(k_{stg2}) = 0.0234 \times \text{Silt} - 0.0355 \times \text{Clay} - 0.385 \times \text{OM} + 0.825 \times \text{PDP} - 0.048 \times \text{SW} - 6.774 \quad [5]$$

where

- k_{stg2} : stage 2 biodegradation rate constant (day^{-1})
- PDP: initial petroleum degrading microbial population in the soil ($\log \text{CFU/g}$)
- SW: soil water content (%)
- Silt: soil silt content (%)
- Clay: soil clay content (%)
- OM: soil organic matter content (%)

A summary of the biodegradation rate constant at different scales are reported in Table 2.1, where the degradation factors for two different soils (Delhi, a loamy sand; and Elora, a silt loam) are presented. The scale-up factor was calculated by comparing the second stage degradation rates of the 4kg and 80 kg reactors with that of the 150 g reactor.

Table 2.1: Summary of 30-day bioventing degradation rate constant for Delhi (Loamy Sand) and Elora (Silt Loam) soil using 150 g, 4kg, and 80 kg of soil from past research and experiments

Soil Type	Stage	150 g reactor ¹	4kg reactor ²	80 kg reactor ³	80 kg reactor (aged) ³	Scale-Up Factor
Delhi	1 (0-8 days)		0.598	0.2795	0.081	2.7
	2 (8-30 days)	0.045	0.123	0.121	0.053	
Elora	1 (0-8 days)		0.460	0.387		1.9
	2 (8-30 days)	0.040	0.075	0.0745		

Data obtained from 1(Eyvazi & Zytner, 2009); 2(Khan & Zytner, 2013); and 3(Mosco & Zytner, 2017)

2.7 Aging factor

2.7.1 Aging process

When contaminants are present in the soil for prolonged periods of time, they are considered “aged”. This process is inevitable as it is not always possible to detect leaks and spills immediately, but it can affect many remediation methods. The adsorbed contaminant particles become more tightly bound with the soil matrix and absorption through diffusion start to become more significant as well.

Soil with more organic matter content tend to exhibit a greater sorption effect of the contaminant when aged. In fact, intra-organic matter diffusion can cause non-equilibrium sorption with BTEX (Alexander, 2000; Reid et al., 2000). Overall, aging can be described as the movement of compounds into less accessible sites over time, causing a reduction in its extractability. The sorption of the contaminants into the soil along with the diffusion into the micro- and nano-pores cause a decrease in bioavailability as the degrading organisms have a harder time accessing the substances when they are in the solid phase.

This aging process can mask the true effects of bioremediation as the sequestered contaminants could mask as contaminants being degraded, when they are still present in the soil, but simply in less extractable state (Northcott and Jones, 2001).

Many interactions between the soil and the petroleum compounds are involved in the process of aging and it depends on a variety of factors, including soil organic matter nature and amount, soil pore size and texture, along with the initial pollutant concentration and the processing of the soil by the indigenous microorganisms (Reid et al., 2000). Environmental factors, such as changes in temperatures along with the wetting and drying of soil, also contribute to the aging process (Schreck et al., 2011).

2.7.2 Bioavailability

When adopting biological remediation methods, such as bioventing, it is important to consider the bioavailability of aged contaminants. The rate-limiting factor can often be the rate of desorption, especially for PAH compounds with higher molecular weights (MW) (Cuypers et al., 2001; Huesemann et al., 2005; Jonsson et al., 2007). As such, aged contaminants are not only less biodegradable to microorganisms, they are also less bioavailable to ecological receptors and less extractable to mild solvents, making detection more challenging as well (Huesemann et al., 2002; Northcott and Jones, 2001). In fact, it has been found that in aged sites a portion of contaminants are easily accessible to the microorganisms, and thus can be degraded rapidly, while other contaminants are strongly sorbed onto the soil and cannot be biodegraded without additional mechanical mixing or stirring (Eriksson et al., 2000).

Due to the decrease in bioavailability and extractability with age, it is much more difficult to estimate the risks associated with these contaminants when testing for petroleum compounds in a pre-existing site. The sorbed portion become less mobile and less bioavailable with time and less likely for the surrounding microbiome to uptake the contaminants. Nevertheless, there are long-term risks associated with aged contaminant to both human health and the environment. Strongly sequestered particles can be released back into the environment following the weathering of sediments over time, which can subsequently affect the surrounding ecosystem (Reid et al., 2000). Research on the bioavailability and biodegradation of petroleum hydrocarbons are limited, with little work done on the effects of decreased bioavailability on the actual TPH degradation rates.

2.7.3 Contaminant type

The biodegradability in aged soil also changed with contaminant type. Overall, alkanes are more susceptible to desorption, and so more are bioavailable, than PAH. In fact, biodegradation rates for alkane hydrocarbons can be higher than the abiotic desorption, which infers that there exists a biological desorption process. It is hypothesized that biosurfactants produced by the microbial colonies allow the increase in uptake of alkane molecules in soils with low organic matter content (Huesemann et al., 2003).

Within PAH contaminants, low MW compounds will biodegrade faster than high MW compounds, as a stall in the rate of biodegradation can be observed after a week of bioventing for larger MW compounds (Cuypers et al., 2001; Huesemann et al., 2002; Zytner et al., 2006). Small PAH molecules with few aromatic rings biodegrade as fast as they are being desorbed from the soil and are mass-transfer limited, suggesting that the biosurfactants are not very suitable for ringed molecules. Larger PAH molecules with more than four rings, however, showed a degradation rate slower than the rate of desorption, alluding to microbial processing being the limiting factor instead. These heavier contaminants might require other substances to trigger cometabolism in order to be biodegradable (Onwurah, 2004).

For over all TPH, it has been observed that when there is a strong NAPL phase present, the degradation rate between aged soil and freshly contaminated soil can be similar (Huesemann et al., 2003), whereas other experiments have found that after just 4 months of aging smaller concentrations of TPH, lower degradation rates can be observed (Mosco, 2016). Regardless, the choice of petroleum hydrocarbon used to simulate gasoline and diesel is important when designing laboratory-scale experiments: a mixture of TPH should be used to better represent the overall change in biodegradation behaviours, which vary depending on their MW and k_{ow} . (Kreamer and Stetzenbach, 1990; Northcott and Jones, 2001).

2.7.4 Laboratory-scale aging

A standard methodology for aging soil in a laboratory setting has not been developed as the aging conditions often depends on the research question. Some methods encourage biodegradation to occur during the aging process, leaving the soil in open air for the duration of the experiment. This mimics *in situ* soil conditions before any remediation processes can be performed and resulted in 61% of the original 20% PHC to be degraded in the first 210 days of aging without the need for any addition (Tang et al., 2012).

For faster aging processes, the soil can be put through multiple cycles of higher and lower temperature to simulate the daily and seasonal changes which can encourage the sorption and sequestration of the contaminants. This can be done in a greenhouse with ambient temperature control, or by using active heating and cooling systems (Schreck et al., 2011; Udovic and Lestan, 2009).

Other experiments have allowed the soil to age without any change in temperature or water content, where the soil is kept either at room or lower temperatures (Huesemann et al., 2002; Mosco, 2016). A lower temperature would discourage any biodegradation processes to occur during the aging process as the microbe's metabolism would be suppressed, preventing any major losses in TPH before the remediation process.

2.7.5 Challenges

Little work has been done on quantifying the effects of contaminant age on biodegradation rates. Many *in situ* and laboratory-scale experiments have concentrated their work on determining the bioavailability of contaminants in aged sites, but do not address the rate of change according to age. This research aims to fill that gap by examining detail of the effects of contaminant age on the rate of biodegradation within the same soil, when put through similar remediation processes. This information will help determine the urgency in which new spills should be remediated, and to qualify the challenges that exist in completing bioremediation due to age and its effect on sorption increase and bioavailable decrease.

CHAPTER 3: LIST OF EXPERIMENTS

The experiments that were conducted over the course of this research are listed in Table 3.1. The experiment names follow the convention of *soil type-age-size*. Two types of soil, characterized in section 4.2 , were used: Delhi and Elora. The age of the soil is listed in days and the size represents one of two experimental setups, 150 g respirometers or an 80 kg reactor, where 150 g and 80 kg of soil respectively is used during the experiment.

Table 3.1: List of experiments

	NAME	SOIL	SIZE	AGE (DAYS)
LONG-TERM AGING				0
				0
				64
	Delhi-LT-150g	Delhi	150 g	132
				177
				217
				245
				305
SHORT-TERM AGING	Delhi-0-150g			0
	Delhi-15-150g	Delhi	150 g	15
	Delhi-30-150g			30
	Elora-0-150g			0
	Elora-15-150g	Elora	150 g	15
	Elora-30-150g			30
	EloraA-0-150g			0
	EloraA-15-150g	Elora-A	150 g	15
	EloraA-30-150g			30
80 KG	Delhi-270-80kg	Delhi	80 kg	270
	Delhi-300-80kg			300
	Delhi-270-150g	Delhi	150 g	270
	Delhi-300-150g			300

The 30-day experiment took soil spiked with petroleum hydrocarbons and wet-aged at 15% water content between 0 and 300 days and remediated it using bioventing. Soils were sampled periodically to determine TPH concentration during the bioventing process to calculate biodegradation rates.

To determine the effects of long-term aging, the Delhi-LT-150g experiments used Delhi-type soil that was spiked and stored in 1L glass mason jars to be aged. Every other month, two jars of aged soil were used to run the bioventing experiment at the 150 g scale. This would allow the degradation rates to be tracked for different contaminant ages, given similar bioventing conditions. Furthermore, the initial petroleum hydrocarbon concentration could be measured before each experiment to examine the effects of age on contaminant extractability and bioavailability.

For short-term aging effects, three soil types; Delhi, Elora, and Elora-A; were similarly spiked and aged in glass jars for 0, 15, and 30 days. Elora-A consisted of the Elora-type soil which has been aged in the past for over 250 days, until the contaminants were no longer extractable due to aging, and then re-spiked. Aging has been shown to have an effect on extraction efficiencies of petroleum hydrocarbon within 14 days (Jain et al., 1992) and short term experiments would determine whether the change in extraction efficiencies affect biodegradation rates.

The 80 kg experiments were performed in the 80 kg reactor, using soil that was spiked and aged in aluminium-lined containers. Two runs, Delhi-270-80kg and Delhi-300-80kg, were performed one after the other, aged at 270 and 300 days respectively. To ensure adequate comparison between 80 kg and 150 g respirometers could be done and to develop a scale-up factor between the two experiments, Delhi-270-150g and Delhi-300-150g are experiments performed concurrently, using the smaller reactors.

CHAPTER 4: EXPERIMENTAL METHODS

This project is a continuation of many works done at the University of Guelph. For the data collected in this experiment to be comparable with past results, the experimental setups for the 150 g and 80 kg reactors were based on the methodologies by Eyvazi (2011) and Mosco (2016) respectively. Ideal nitrogen and water content level for the bioventing setups were developed by Shewfelt et al. (2005)

4.1 Synthetic Gasoline

A mix of five petroleum compounds (24.9 wt% isooctane, 36.0 wt% toluene, 23.9 wt% m-xylene, 11.9 wt% mesitylene, and 3.2 wt% naphthalene) were used to represent the Canada Wide Standard for petroleum hydrocarbon. This mixture was based on previous work with Imperial Oil Ltd (Bezerra and Zytner, 2003; Shewfelt et al., 2005). By using a prepared mix of compounds rather than a commercial product, the number of chemicals present were minimized and the composition of the synthetic gasoline could be carefully monitored during the bioventing process, allowing for the compounds to be analysed individually. The same mix of petroleum hydrocarbons was used by Eyvazi and Zytner (2009) and Mosco (2016) to allow for consistency when comparing degradation rates.

Table 4.1 Synthetic gasoline composition

Chemical Compound	% weight	Manufacturer	Supplier	Catalog Number
Isooctane (HPLC)	36.1	Fisher Chemical	Fisher Scientific	O 296-4
Toluene (HPLC)	23.9	Fisher Chemical	Fisher Scientific	T290-4
m-xylene, UN1307	11.9	Thomas Scientific	Fisher Scientific	NC0572923
Mesitylene, 99%, Extra Pure	24.9	ACROS Organics™	Fisher Scientific	125580010
Naphthalene (Crystalline/Certified)	3.2	Fisher Chemical	Fisher Scientific	N134-500

All work was performed under a fume hood due to the potentially hazardous nature of the chemical compounds. The synthetic gasoline was created by weighting each individual compound using a Mettler AJ100L scale using the recipe in Table 4.1. As naphthalene was the only chemical in its solid phase, it was weighted first and transferred into a 1L glass beaker, followed by the other liquid compounds. The

compounds were mixed to dissolve the naphthalene crystals and transferred into 500mL amber glass bottles. 24 hours prior to use, the synthetic gasoline would be placed in the freezer to cool.

4.2 Soil Collection

The effects of contaminant mobility, and thus biodegradation rates, is affected by the soil composition. Two soil types were used in this experiment to better characterize the effects of aging on in different soils. Soil from Delhi and Elora Research Station were selected as they have been used extensively in past bioventing experiments by Eyvazi and Zytner (2009), Khan and Zytner (2013), and Mosco (2016) and have been well characterized, with the results summarized in Table 4.2.

Table 4.2: Physical soil characteristics for Delhi and Elora soil

Soil Name	Sand (%)	Silt (%)	Clay (%)	Organic Matter (%)	Water Holding Capacity (%)	Bulk Density (kg/m³)	Texture
Delhi	84.9	9.8	5.3	1.1	25	1550	Loamy Sand
Elora	31	50.8	18.2	3	30	1350	Silt Loam

4.2.1 Delhi Soil

Historically, Delhi soil was collected from the Delhi Research Station located at 711 Schafer Road, Delhi, ON, operated by Agriculture and Agri-Food Canada (AAFC). However, operations have been closed since December 2012 and the land has since been sold to Titan Trailers of Delhi. Following both phone and e-mail contact, Mrs Sandy Kloefer (Kloefer, 2016), owner and management executive at Titan Trailers, granted permission to access the site for soil collection. Samples were collected on May 26th, 2016 from directly across the main administration building. The soil was excavated to 15-30 cm from the surface, around 3 meters from the road on the east side of the field and was collected in large poly bags using a shovel. Around 250 kg of soil was collected and transported back to the University of Guelph, in room THRN1113A to air dry.

4.2.2 Elora Soil

The Elora Research Station, located at 6182 2nd Line, Pilkington Twp. R.R. #2 Ariss, ON, is operated by the University of Guelph under Dave Kells (Kells, 2016), the station manager. On June 8th, 2016, Mr. Kells had prepared an area where the soil had been recently turned. The soil was directly collected and placed in poly bags using a shovel. Around 250 kg of soil was collected and transported back to the University of Guelph, where the soil was air-dried in the bags in room THRN1113A.

4.3 Soil Preparation

4.3.1 Sifting

To prepare the soil for contamination and aging, the soil was dried in room THRN1113A at the University of Guelph in permeable poly bags, where the natural air flow removed all moisture at room temperature. The soil was then sifted through a USCS Number 10 sieve with a 2 mm mesh size to remove any gravel and large organic material, such as grasses and roots that were unintentionally collected in the field. Larger clumps of soil were carefully broken up using a rubber mallet. To prevent any respiratory issues from small airborne soil particles, a dust mask was worn during the soil preparation phase.

4.3.2 Soil Spiking

To prepare the soil for aging, the dried and sieved soil had to be spiked with the synthetic gasoline and brought to the appropriate water content level to mimic field conditions, hence the term wet aging. A level of 50-70% of the soil's water holding capacity (WHC) was determined to be the ideal soil water content for bioventing (Shewfelt et al., 2005) and was thus used to calculate the water that was to be added to the soil. The WHC of Delhi soil was measured to be 25%, whereas Elora soil had a WHC of 30%. Enough water was added to each soil to bring the water content to 15%, which is 60% and 50% of the WHC of the Delhi and Elora soil respectively (Eyvazi, 2011). The soil was spiked at $4000 \text{ mg}_{\text{synthetic gasoline}}/\text{kg}_{\text{soil}}$.

A mechanical soil mixer, designed and built by Mosco (2016), was used to homogenize the soil. Four paint cans, 1 gallon (3.79 L) in size, could be tumbled in unison to uniformly mix the contents. 4000 g

of soil, 600 g of water, and 16 g of synthetic gasoline were weighed using a Mettler PJ1220 scale and placed in a paint can and mixed for 20 minutes, when the soil looked uniformly mixed. Samples taken at separate locations in the paint can after the mixing process confirmed homogeneity, as discussed in Chapter 6.3.4 .

4.3.3 Aging

To age the soil, the spiked wet soil was placed in large 40L plastic totes, lined with aluminium foil to prevent any losses of the petroleum hydrocarbon. The bins were filled and sealed with tape before being transferred into a large cooling room in THRN1105, which was kept at a temperature of 4 °C. This lowered temperature would reduce the volatilization and microbial activity within the soil to prevent too much biodegradation to occur before the soil was needed. Once a box was unsealed, the soil was not reused as the handling of the soil would cause unwanted volatilization of the synthetic gasoline. This aging process is not representative of field aging, as it lacks the variance in temperature and water content from being exposed to the elements, but allows for controlled aging to occur over the course of over 300 days to provide time for sorption to take place.

Additional experiments that required smaller quantities of soil used glass mason jars, with lids lined with aluminium foil, to store the spiked soil. These smaller aging containers were also placed in a 4 °C environment for the duration of the aging process.

4.3.4 Nutrient Addition

Before the soil could be effectively bioremediated, nutrients in the form of nitrogen is required to stimulate the microorganisms. The optimal C:N ratio was determined to be 10:1 from past research (Shewfelt et al., 2005). Assuming that half of the spiked synthetic gasoline would remain in the soil after the mixing and handling of the soil, a starting concentration of 2000 mg_{synthetic gasoline}/kg was used to calculate the necessary nitrogen addition (Mosco and Zytner, 2017).

Considering the composition of the synthetic gasoline used to spike the soil, the ratio of 40.6:59.4 C:H molecules are present in the system. Using the molecular weight of the molecules and knowing that

the desired C:N ratio is 10:1, 178 mg/kg nitrogen was calculated. Ammonium chloride (NH_4Cl) was used as the nitrogen amendment, leading to 680mg of NH_4Cl needed for each kilogram of soil. Full calculations can be found in Appendix A:

The required amount of NH_4Cl was measured on a Mettler AJ100L scale and dissolved in a small quantity of water before being amended to the soil. The soil was then mixed for 20 minutes to ensure an even distribution of nutrients prior to the start of the experiments.

4.4 80 kg reactor

4.4.1 Reactor Characteristic

The 80 kg reactor, built by Mosco, was used to run large-scale experiments, and is shown in Figure 4.1. The reactor is composed of an 80L stainless steel drum ($O.D. = 41.3\text{ cm}$ and $height = 51.4\text{ cm}$) purchased from General Container Corporation, Newark, NJ, with a mesh outer layer to allow air flow through the system. A hollow and permeable vertical tube ran down the center of the drum as a vacuum well. Full details of the construction and parts are available in Mosco (2016). The lid of the drum is slightly depressed and seals using three 1.5" C-clamps. Fifteen sampling ports are spread along the drum in three

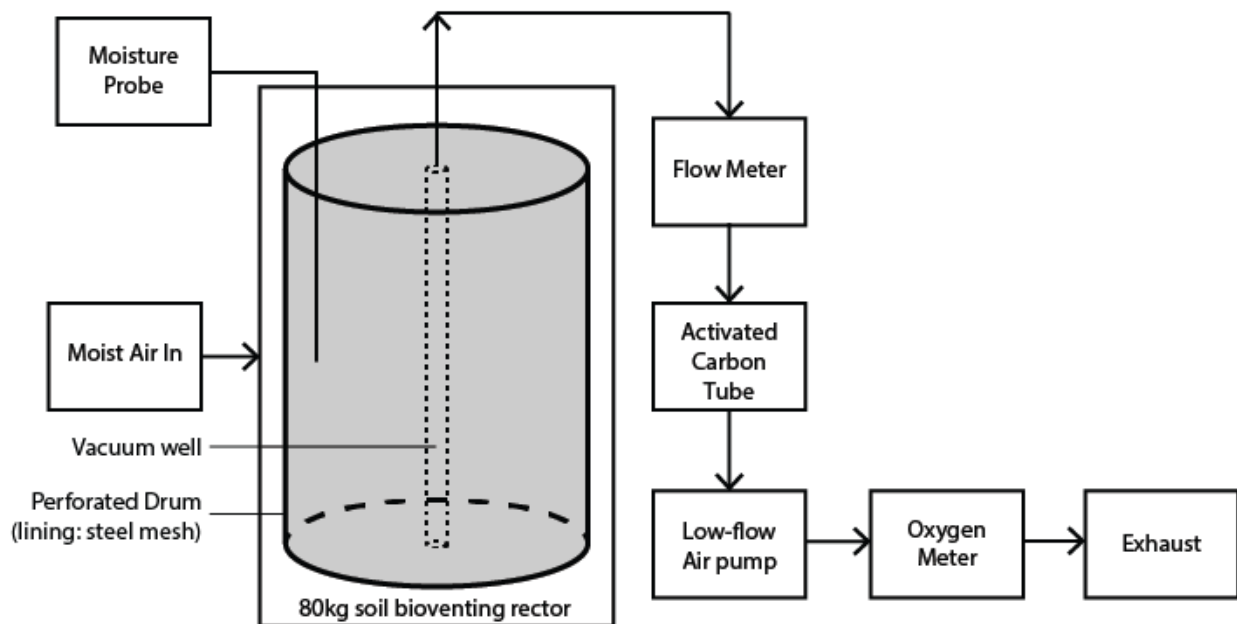


Figure 4.1: 80 kg bioventing reactor setup

rows and five columns, 72° from each other horizontally and 18.7 *cm* apart vertically. The sampling ports are typically sealed with plugs, which are removed during the sampling process.

The reactor was placed in a Plexiglass® enclosure to minimize dry air flow into the system and to keep the system under negative pressure. A flow meter, oxygen monitor, and activated carbon tube were connected to the vacuum's exhaust to measure for air flow and oxygen levels in the off gases, while capturing any volatilized TPH. A bubbler was used to increase the water content of the intake air, acting as a humidifier.

4.4.2 Loading, maintenance, and sampling of the reactor

The reactor was loaded by placing the aged and amended soil in batches. To ensure that the density is even, the inside of the reactor was marked to indicate where every 8kg of soil should fill. The soil was lightly compacted at each layer, which would ensure equal air flow through the system and to prevent any short circuiting. At around the halfway point, moisture content probes were placed into the reactor, one near the outer edge of the reactor and one closer to the center, to monitor moisture losses over time, before the rest of the soil was loaded.

Due to the nature of the setup, moisture loss was expected during the experiment. As such, to ensure optimal conditions for the microbes in the reactor, a cotton wrap was placed around the outside of the reactor and moistened daily using a spray bottle. Furthermore, the intake air was humidified using a bubbler to help keep water content at appropriate levels, read using moisture probes.

The air flow through the system was kept at 8.9mL/min to achieve ideal oxygenation in the system while minimizing volatilization. This was calculated by Mosco (2016) to allow for 0.5 pore volume exchanges for each 24 hour period. A Gilian-Sensidyne (LFS-113DC) low flow pump and an Omega (FMA-5606ST) Micro Flow Meter was used to create and monitored the flow rate throughout the experiment.

To sample the soil, a probe, built by the University of Guelph's Physics Workshop uses a hollow rod to take soil cores from the sampling ports in the reactor. The sampling location was varied throughout the experiment to minimize short-circuiting in the reactor and to reduce any location bias. The sampled soil was placed onto aluminium weighing dishes before they are weighted and transferred into the appropriate containers to measure for TPH, pH, and soil water content. Any volatilization was captured through a carbon-filled tube and analyzed for off-gases. The 80 kg reactor was kept at 20°C, the ambient temperature of the lab, under vented conditions.

4.5 150 g respirometer

One-liter glass bottles were used as respirometers. Due to the number of experiments completed, different bottles were used – one liter mason jars and small-necked jars with vented rubber stoppers, the latter of which can be seen in Figure 4.2. Before loading the soil, a Potassium Hydroxide (KOH) mixture 3%w/v was created using deionized water to capture the carbon dioxide formed during microbial respiration to ensure the system was kept under negative pressure, avoiding volatilization.

For the respirometers, 150 g of the aged and amended soil was loaded into the respirometers. Test tubes containing 20 mL of the KOH mixture were placed into the bottles before the system was capped and sealed using silicon grease. The KOH tube would capture any carbon dioxide created during microbial respiration. This would ensure that the bottle was under negative pressure so when the bottles were aerated, no contaminant would be lost through volatilization. The negative pressure was confirmed when the system was vented, the lids of the mason jar showed a depression and an auditory cue could be heard when opening the vent in the rubber-capped jar.

The respirometers were kept at 25 °C in an incubator for the duration of the experiment. The bottles were vented every two days during the first ten days of the experiment, and then every five days for the next twenty days, to ensure proper oxygenation. To sample the soil, the respirometer was sacrificed as it was opened and unsealed. The KOH tube was carefully removed and then sealed with parafilm for pH measurement, while the soil was transferred into appropriate containers for analysis.

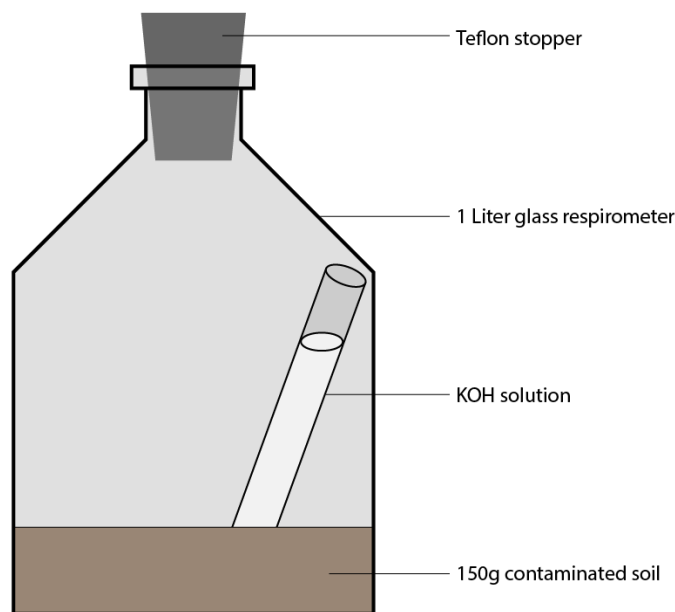


Figure 4.2:150 g respirometer setup

4.6 Preparation of Controls

Experimental controls are powerful tools to identify other environmental effects on the bioventing experiments. Negative controls eliminate independent variables to observe its effect on the dependant variable. As biodegradation depends on both the microbe population and the TPH in the soil, two controls were set up. The abiotic control sterilizes the soil of any living microorganisms and was performed by autoclaving the soil five times over five days for 90 minutes. The soil was then spiked and aged in glass mason jars. The biotic control used soil that was had optimal water content and C:N ratio, but without the

addition of TPH. The soil was stored in the same location as the spiked samples and were run concurrently during many of the Delhi-LH-150g aging experiments. Due to the extensive soil requirements for the 80 kg experiments, no controls were run at that scale.

CHAPTER 5: ANALYTICAL METHODS

5.1 PHC

5.1.1 *Methylene Chloride Extraction*

Prior to the extraction, a sufficient quantity of methylene chloride (MeCl, CH_2Cl_2) was placed in a freezer to chill. Small 40 mL amber bottles were prepared by threading the vials with Teflon tape to minimize any losses through volatilization. Around 3 g of the sampled soil, taken from either the 80 kg reactor using the custom sampling tool or from the 150 g respirometers, was transferred into the 40mL amber bottles, weighed using a Mettler AJ100L scale. The exact weight of the soil was recorded.

To reduce the water content in the soil and improve extraction efficiencies, anhydrous sodium sulfate was added at a 1:1 (w:w) basis and manually shaken by inversion a few times to distribute the product. 10 mL of MeCl was then added using a glass pipette, which acted as the solvent in the extraction procedure. For soils with lower expected concentration of TPH, such as soil that has undergone several months of aging or near the end of the bioventing experiment, 5 mL of solvent was used for more accurate TPH concentration reading.

The bottles were placed on a multi-wrist shaker for one hour on medium speed before being stored in the freezer overnight to allow the soil particles to settle. The next day, 2 mL of the supernatant was pipetted into GC vials, which were then capped, crimped, and stored in the freezer until they were analyzed. As both MeCl and synthetic gasoline are prone to volatilization and the crimp camps of the vials are not completely air tight, the samples should not be stored for extended periods of time before analysis.

5.1.2 *Off Gases*

The 80 kg bioventing reactor was under negative pressure for most of the experiment. Therefore, the only losses in TPH are due to biodegradation, sorption, or volatilization. To better quantify the overall losses in TPH and to ensure that the off gases did not disrupt the air pumps and monitoring devices down the line, the off gases were captured before reaching the vacuum pump. ORBO™-32 sorbent tubes (Sigma-

Aldrich, Cat No. 20267-U), filled with two chambers of activated carbon, were connected to the line. The carbon tubes were exchanged and extracted daily to calculate the daily volatilization taking place in the 80 kg reactor.

The ORBO™-32 sorbent tubes contained two layers of activated carbon separated by a foam separator – the main layer and the backup layer. The backup layer would ensure that any contaminants in the off gases that was not captured by the main layer, due to an excess in TPH concentration, would not reach the vacuum pump. The backup sorbent layer should not contain any contaminants for low volatilization systems.

To extract the activated carbon, the glass tubes were carefully broken using an ORBO™ Tube Cutter (Sigma-Aldrich, Cat No. 20596). The two layers of sorbent were placed in two separate 40 mL amber vials and 4 mL of MeCl was added. The samples were shaken on a multi-wrist shaker for 1 hour before being stored in a freezer overnight. The next day, 2 mL of the supernatant was transferred into GC vials and stored in the freezer before analysis.

5.2 Gas Chromatography with Flame Ionization Detector

5.2.1 Overview and Setup

A Gas Chromatography with Flame Ionization Detector (GC-FID) was used to analyze the samples that were extracted using MeCl. The GC-FID (Hewlett-Packard 5890 Series II) at the University of Guelph has been used in past experiments to measure TPH in similar experiments (Eyvazi and Zytner, 2009; Khan and Zytner, 2013; Mosco, 2016). Using this device, the five components in the synthetic gasoline could be identified and measured by comparing the outputs to a calibration curve.

The GC-FID was used to analyze the total petroleum hydrocarbons in the soil samples taken from both the 80 kg and 150 g respirometers, along with the activated carbon sorbent tubes. The device was equipped with an auto sampler (Hewlett-Packard 7673). The machine was fitted with a J&W Scientific DB5 capillary column. It was 30 m long with an ID of 0.32 mm, and with a film thickness of 1 μ m. Grade

5.0 helium was used as a carrier gas and the split column pressure was set at 12.5psi (Eyvazi and Zytner, 2009; Khan and Zytner, 2013; Mosco, 2016).

The operating temperature of the injector was set at 225 °C and the FID was set at 275 °C. The oven ramp program starts at a temperature of 35 °C, at which point the the auto-injection system would inject 1 μ L of sample into the device. The system would hold this temperature for 3.5 minutes before gradually ramping the temperature up at 25 °C/*min* until reaching the operating temperature of 225 °C. That temperature was held for 5 minutes, for a complete runtime of 15.2 minutes. Between each injection, the syringe used to transfer the samples was washed and rinsed with methanol to prevent any transferring of residual TPH into the next injection in the syringe (Eyvazi and Zytner, 2009; Khan and Zytner, 2013; Mosco, 2016).

It was noted that some errors due to faults in the sampler (“unable to retrieve vial from tray” and “door open or injector not mounted”) would cause a pause in the analysis. This required a manual restart of the auto-injection process. Furthermore, the auto-sampler injector would occasionally fail in the injection without causing an error, which would result in a blank output from the GC-FID. These data points were removed from the data set.

5.2.2 *Creation of Standards and Calibration Curves*

Calibration curves were necessary to calculate the concentration of TPH in the solvent, extracted from the soils contaminated with petroleum hydrocarbon. Calibration curves are created by running several samples of known concentration, standard solutions, to relate the area response curve output from the GC-FID to contaminant concentrations.

The standard solutions were created by diluting the synthetic gasoline, detailed in Chapter 4.1 , with the MeCl solvent used to extract the petroleum products from the soil samples, as detailed in Table 5.1. The solutions were stored in 40mL glass amber bottles, threaded with Teflon tape and kept at freezing temperatures to minimize losses through volatilization. All solutions were kept in the freezer for 24 hours

before the creation of the standards to minimize volatilization and work was done under a fume hood. A Mettler AJ100L was used to measure the initial synthetic gasoline. Glass pipette tubes and graduated cylinders were used to mix and prepare the standard solutions. Larger batches of standards were stored in 500mL amber glass bottles at room temperature. Working volumes would be transferred in smaller 40mL amber glass bottles and stored in the freezer. 2mL of each standard were transferred into GC vials before analysis. Calibration curves were created by running a set of standards before and after any samples with unknown TPH concentrations to account for any volatilization that happens during the analysis.

Table 5.1: Standard solution preparation with synthetic gasoline and MeCl

Desired Concentration			Volume of Solution	Remaining Volume
2000 mg/L	200 mg synthetic gasoline	Add 100 mL MeCl	100 mL	35 mL
1000 mg/L	50 mL of 2000 mg/L	Add 50 mL MeCl	100 mL	50 mL
750 mg/L	15 mL of 2000 mg/L	Add 25 mL MeCl	40 mL	40 mL
500 mg/L	50 mL of 1000 mg/L	Add 50 mL MeCl	100 mL	65 mL
250 mg/L	20 mL of 500 mg/L	Add 20 mL MeCl	40 mL	40 mL
100 mg/L	10 mL of 500 mg/L	Add 40 mL MeCl	50 mL	45 mL
10 mg/L	5 mL of 100 mg/L	Add 45 mL MeCl	50 mL	45 mL

5.3 Respiration

5.3.1 Oxygen Usage

Biodegradation relies on microorganism activity in the soil to break down petroleum compounds, where $Organic\ Matter + O_2 \rightarrow H_2O + CO_2 + Energy$. The bacteria present in the bioventing reactor can degrade organic matter, including the petroleum compounds, through respiration, using oxygen (O_2) and producing water (H_2O) and carbon dioxide (CO_2). Ideally, both oxygen and carbon dioxide measurements throughout the experiment would allow for precise quantification of the respiration that occurs during the bioventing process, allowing for stoichiometric calculations of the degradation rate. The 80 kg reactor setup allowed only for oxygen measurements, where the air pumped out of the reactor was fed into a 6 L glass jar, in which an Opogee Oxygen Meter was installed. Oxygen levels ($\pm 0.1\%$) were recorded daily and monitored for any significant decreases during the experiments.

5.3.2 Carbon dioxide production

The 150 g respirometers setups included a vial of KOH (3% w/v) to capture any carbon dioxide created by the respiration of the microorganisms in the soil, where $KOH + CO_2 \rightarrow KHCO_3$ and $KHCO_3 + KOH \rightarrow K_2CO_3 + H_2O$. This results in a decrease in pH in the KOH that is related to the respiration and biodegradation in the respirometer. An Oakton pH700 pH meter was used to measure alkalinity of the KOH throughout the bioventing process. The meter was calibrated using buffers solutions at pH 7.0, 10.0, and 12.45.

5.4 Soil pH

Extreme soil pH can have inhibitory effects on the microbial degradation. Optimal pH range depends on the exact soil type, but studies have found that some inhibition can occur around pH 8.5 (Dibble and Bartha, 1979). Soil pH was frequently measured during the bioventing experiment to ensure no drastic changes were occurring in the soil.

To make a 1:5 soil:water slurry, 6 g of sampled soil was mixed with 30 mL of water in a 40 mL amber bottle. The mixture was placed in a multi-wrist shaker for 1 hour on medium speed before the pH of the slurry was measured using an Oakton pH 700 benchtop meter.

5.5 Soil Water Content

Although a large range of soil water is adequate for ideal biodegradation condition, 50% of a soil's water holding capacity is suggested to allow adequate water availability for the microorganism without limiting the air flow in the reactor (Shewfelt et al., 2005). To monitor the water content in the 80 kg reactor, two soil moisture sensors (SMS-BTA) connected to a Vernier LabQuest®2 were placed in the center layer of the reactor, one near the outer edge of the drum and the other near the vacuum tube. The device was calibrated for volumetric water content and is rated for an accuracy range of $\pm 4\%$ typical. To convert from volumetric water content to gravimetric water content, the results from the moisture probe was divided by the bulk density of the soil, given in Table 4.2.

The probes were set to record water content data every three hours for the Delhi-270-80kg experiment. However, due to the limitations of the data logger, the logs had to be reset often as only a limited number of data points could be recorded in a single session. As the change in water content were found to be gradual, the interval between data collection was extended to twelve hours for the Delhi-300-80kg experiment to allow for longer data collection time before the LabQuest® data logger had to be reset.

The water content in the 150 g respirometers could not be measured using the moisture probes due to the small quantity of soil used. Furthermore, oven drying the soil was not recommended due to the contaminants present in the soil which could not be contained during the drying process. The mass of a weighing boat is measured and recorded using a Mettler AJ100L scale. Around 10 g of the sampled soil is added to the weighing boat and both the wet weight and the dry weight, following 48 hours of air drying under a fume hood, was recorded. The water content was calculated using Equation 6

$$MC\% = \frac{W_{water}}{W_{Dry\ soil}} * 100\% = \frac{W_{moist\ soil+tin} - W_{dry\ soil+tin}}{W_{Dry\ soil+tin} - W_{tin}} * 100\% \quad [6]$$

5.6 Microbial plate counting

Bioventing remediation rely on the native microbial populations in the soil to biodegrade the TPH contaminants. To ensure that the microbes are indeed present in the soil before and after the experiment, microbial plate counting was performed. This methodology extracts all of the microbes from the soil and dilutes the solvent until a countable number of microbes can be seen when spread onto a petri dish. A tryptic soy agar (TSA) medium was used to incubate and grow the microbes. To minimize contamination from the environment, the following procedure was performed under a fume hood in a sterile environment.

24 hours before sampling the soil, a solution of sodium pyrophosphate (NaPP) was prepared by mixing 1 g of NaPP to 1L of ultra-pure water in an autoclave-safe bottle. The mixture was stirred on a magnetic stirring plate until all the powder was dissolved and then autoclaved for 25 minutes at 121°C in a SANYO Autoclave MLS-3781 L. The autoclaved solution was then cooled to room temperature until use.

To prepare the TSA medium, a ratio of 40 g TSA to 1 L ultra-pure water was mixed in an autoclave-safe bottle and gently shaken to dissolve the TSA powder. The solution was autoclaved for 25 minutes at 121°C and then placed in a 57°C Fisherbrand™ Isotemp™ Digital-Control Water Bath (Model 205) until ready to be poured. Around 25 mL of the solution is poured into a petri plate and covered immediately to avoid contamination. The plates are ready to use when the solution has solidified at room temperature.

In a 250 mL Erlenmeyer flask, a 5 g soil sample was collected and measured before adding 45 mL of NaPP. The solution was mixed on a Big Bill Orbital Mixer at 300 rpm for 1 hour to detach the microorganisms from the soil. A serial dilution was then performed, where 100 μL of soil solution was pipetted into a 15 mL centrifugal tube with 900 μL of the NaPP solution. The mixture was vortexed using a Fisher Scientific Vortex Mixer for 1 minutes and repeated as necessary until a dilution of 10^7 was achieved.

The prepared TSA plates were then inoculated with 100 μL of the diluted sample. A sterilized plastic disposable spreader was used to evenly spread the sample, taking care to avoid the edges of the petri dish. The plates were then inverted and incubated at 25°C. The number of colonies would be visible and countable after 48 hours, and then confirmed after 72 hours in the incubator. All waste were properly disposed of in a Biohazard Waste Autoclaved Bag.

CHAPTER 6: EXPERIMENT QUALITY ASSURANCE/QUALITY CONTROL

6.1 80 kg reactor

6.1.1 Soil Water Content

The soil water content, measured using a Vernier LabQuest®2 data logger with soil moisture probes recorded the water content for both the Delhi-270-80kg and the Delhi-300-80kg experiments. The water content level of the two runs are shown in Figure 6.1 and Figure 6.2. The gaps in the data are due to user error of the data logger, which would stop logging data after reaching its maximum logging capacity before the system was manually reset.

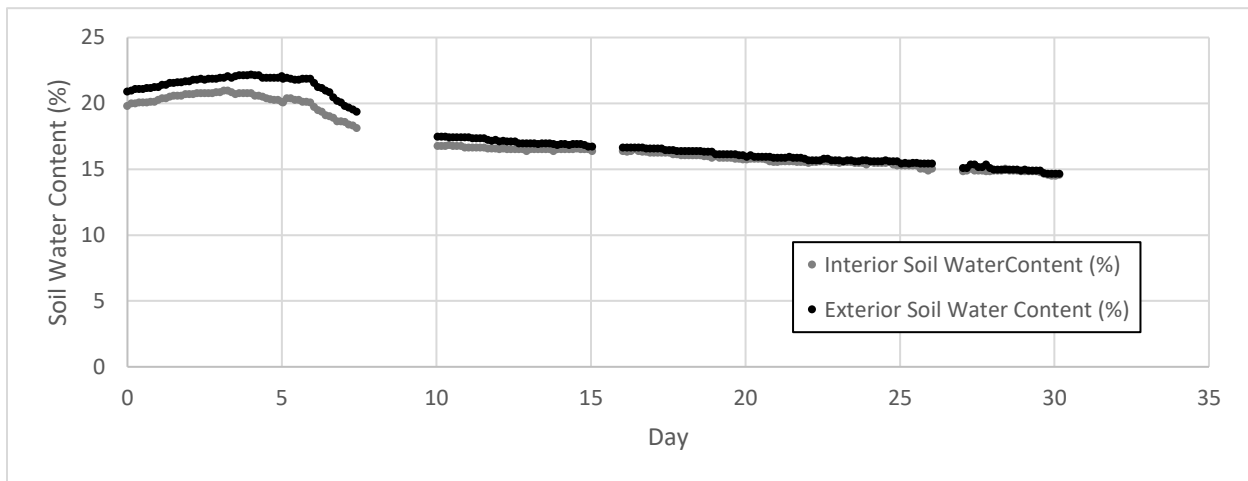


Figure 6.1: Soil water content during the Delhi-270-80kg experiment

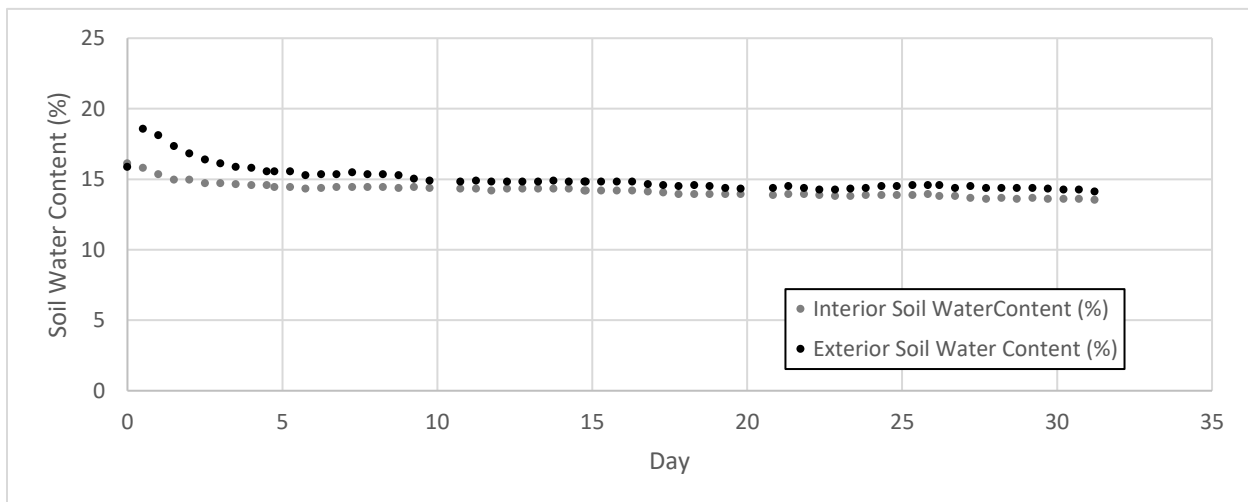


Figure 6.2 : Soil water content during the Delhi-300-80kg experiment

Figure 6.1 and Figure 6.2 show that the soil water content was at around 15%, which was sufficient to allow for adequate aeration of the soil while providing enough moisture for bacterial growth. During the Delhi-270-80kg run, the initial soil water content was high due to an error while mixing the soil. The system was not sprayed to allow for the reactor to dry out during the first week of the experiment. Overall, the water content levels in the Delhi-300-80kg soil were in the appropriate range for ideal biodegradation rates.

It is to be noted that the water levels at the start of the experiment were higher than the water content of the soil prior to the aging process. The increase in water content is a sign of respiration occurring while the soil was being aged at 4°C, despite the lowered temperature.

6.1.2 Oxygen Levels

Oxygen levels were recorded daily in the 80 kg reactor, which can be seen in Figure 6.3. The oxygen levels in the air were at around 21%. In the Delhi-270-80kg run, when the water content levels were high, so were the oxygen levels due to a lack of microbial respiration, leading to a lack of biodegradation during that time. Otherwise, the oxygen levels were consistent during most of the experiment.

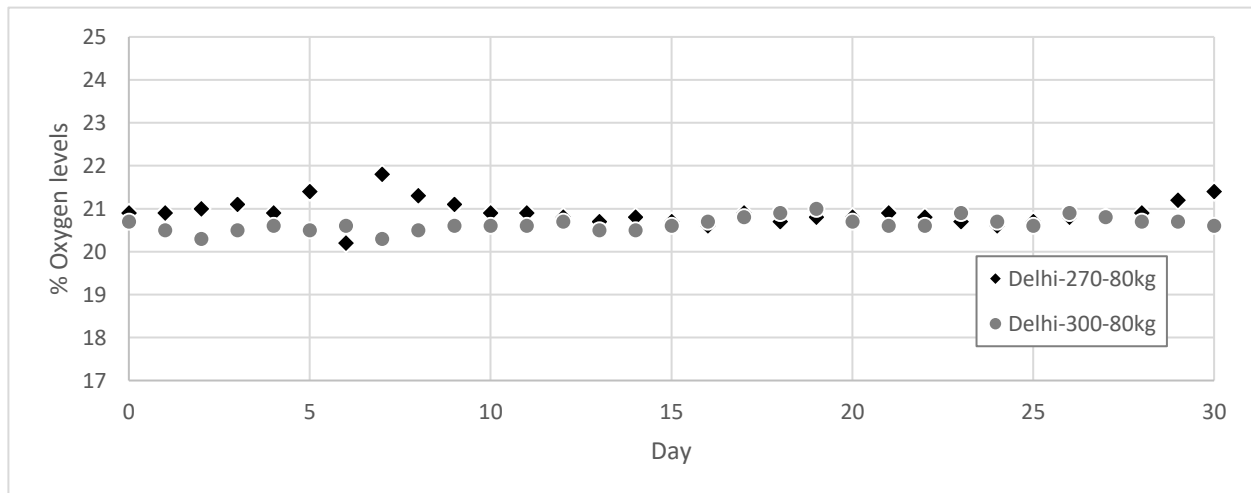


Figure 6.3: Oxygen levels for Delhi-270-80kg and Delhi300-80kg experiments

When comparing the oxygen levels in past experiments performed by Mosco (2016) using the same reactor with freshly contaminated soil, a sharp decrease in oxygen levels was seen during the first day of the experiment, before gradually increasing from 18.5 to 19.5% throughout the rest of the experiment. The immediate decrease in oxygen was due to the microbes activating from the sudden presence of water, nutrients, and TPH in the soil during the spiking of the soil. This was not seen in the aged experiments, though a small dip was present in the Delhi-300-80kg experiment due to the microbes already being active during the aging process. Overall, the soil water levels were adequate for microbial activity and the petroleum contaminants could be used as a source of food. These results are consistent with the soil water content findings.

6.1.3 Off gas Monitoring

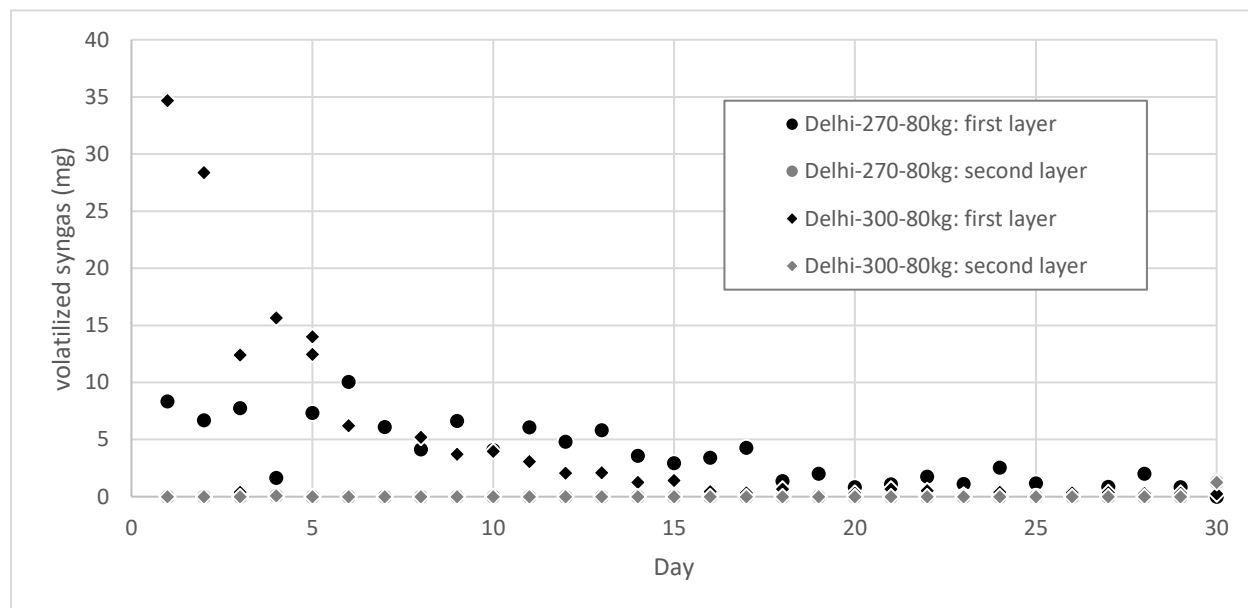


Figure 6.4: TPH captured in off gases for Delhi-270-80kg and Delhi-300-80kg experiments

Off gases were captured using activated carbon to measure any losses of TPH through volatilization. The capture tube had two layers of activated carbon, where the first layer would capture all the petroleum hydrocarbon and the second layer acted as a backup in case of higher contaminant concentration than the first layer can accommodate.

There were only few instances of extractable TPH in the second layer of the activated carbon tube. For most of the runs, the first layer of activated carbon captured all the volatilized synthetic gasoline. Up to 35 mg of TPH was captured during the first day of the Delhi-300-80kg experiment, and each subsequent day saw a decrease in the amount of petroleum products volatilized. Comparable results were seen in the Delhi-270-80kg experiment, though due to the low air flow and high water content during the start of the experiment, the volatilization was also low.

At the start of the experiment, a total of 8670 mg and 5447 mg of synthetic gasoline were present in the Delhi-270-80kg and Delhi-300-80kg experiment respectively after being packed into the reactor. The cumulative losses due to volatilization is 109.8 and 160.8 mg during the two experiments, which represent 1.27% and 2.95% of the synthetic gasoline in the system respectively, as seen in Table 6.1. These small losses were acceptable for these experiments.

Table 6.1: TPH volatilized during 80 kg experiments

Experiment	Delhi-270-80kg	Delhi-300-80kg
TPH extracted from the soil at the start of the experiment	108.37 mg/kg _{soil}	68.08 mg/kg _{soil}
Total TPH in 80 kg reactor	8670 mg	5447 mg
Cumulative losses due to volatilization	109.8 mg	160.8 mg
Percent TPH volatilized during experiment	1.27%	2.95%

The composition of the extracted TPH in the soil and in the activated carbon also differed quite significantly, as seen in Figure 6.5. Whereas naphthalene and mesitylene were the most prevalent in the TPH extracted from the soil, the volatilized compounds were mostly composed of mesitylene and m-xylene, with no naphthalene present at all. These trends were expected.

The difference in properties, such as volatility and molecular weight, of the five compounds determine the proportion of the hydrocarbon is present in the off-gases. In remediation processes that rely on volatilization for remediation, such as in SVE, the composition of the off gases in relation to the

composition of the contaminants will affect remediation rates. The bioventing experiments used very low air flow and volatilization rates, so the results may not be representative to SVE conditions.

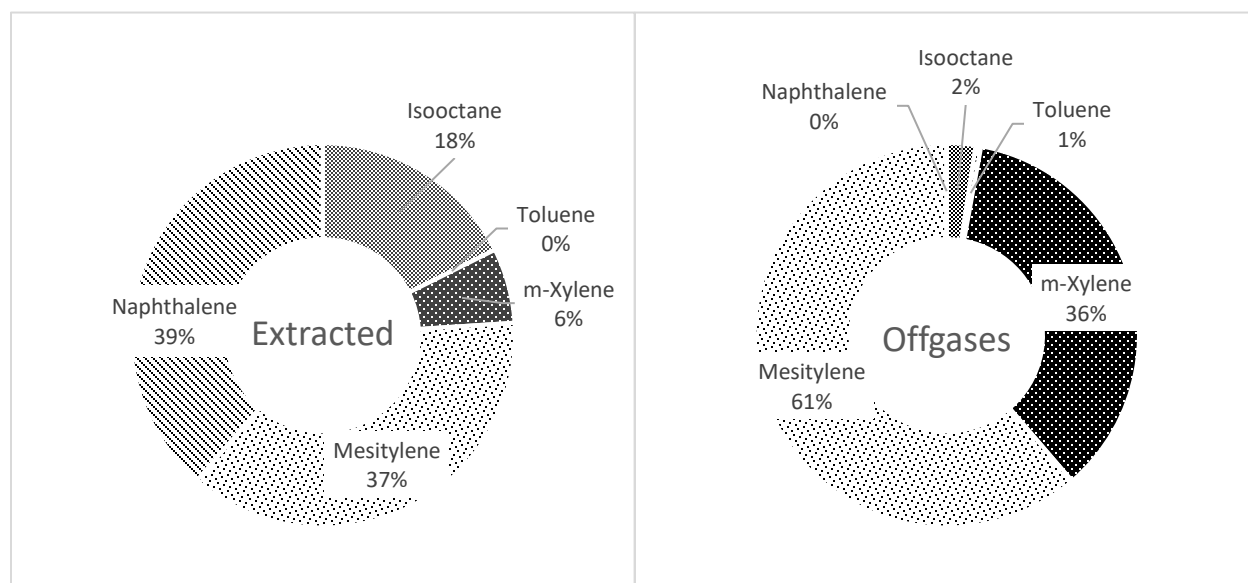


Figure 6.5: Difference in TPH composition between the extracted compounds and the compounds captured in the off gases at the start of the experiments. Values averaged between the Delhi-270-80kg and Delhi-300-80kg experiment.

6.1.4 Microbial Count

The bioventing remediation process assumes that the native bacteria in the soil are biodegrading and removing the TPH contaminants, it was important to confirm the presence of these microbes. The number of colony-forming units (CFU) can estimate the quantity of viable bacteria in a given sample. The full results for the number of total heterotrophic bacteria (THB) are available in Appendix B:

Overall, the number of CFU in 5g of soil was approximately 5×10^7 CFU in both the Delhi and Elora soil. The CFU remained stable throughout the duration of the experiment and between the different experiments. These results are consistent with past experiments performed by Mosco (2016) and Eyvazi (2011). Despite the increase in nutrients in the soil, the number of microbes did not increase significantly due to the small quantities of TPH present in the reactor, causing a restriction in the food source for the biodegrading microorganisms.

Some experiments did not have microbial plate counting analysis due to time constraints. Furthermore, TSA determines the number of overall bacteria in a sample; a different growth medium, such as a Bushnell-Hass(BH) medium mixed with synthetic gasoline, would have allowed for the number of petroleum-degrading bacteria (PDB) to be enumerated. A few BH plates were tested but due to longer time constraints, where two weeks of incubation were required, not enough data was collected. Nevertheless, there is sufficient evidence from past work done with similar soil (Eyvazi and Zytner, 2009; Khan and Zytner, 2013; Mosco, 2016) along with strong degradation rates to assume that there is presence of petroleum-degrading bacteria in the THB. In fact, the aging process likely increased the number of PDB during the acclimatization process, allowing the bacteria to adapt to a petroleum-rich environment.

6.2 150 g Respirometer

6.2.1 Soil Water content

The moisture levels measured in the 150 g respirometer experiments remained consistent throughout the experiments. A sample of the water content data is displayed in Figure 6.6. The rest of the data can be found in Appendix B:

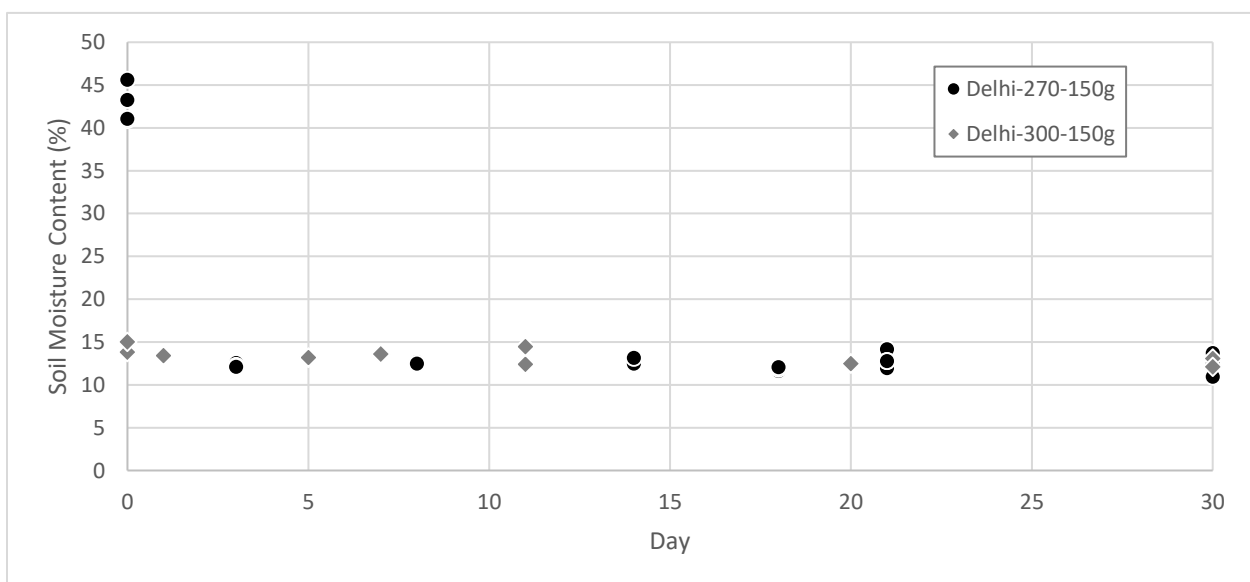


Figure 6.6: Soil Water content for Delhi-270-150g and Delhi-300-150g experiment

The high water content at the start of the Delhi-270 experiment is visible in the 150 g scale as well, since the same soil was used, but the levels naturally drop down to the 15% range by the third day in the respirometer. All other experiments showed water content levels of around 15% for the entirety of the bioventing process. Due to respiration, an increase in water content was expected despite the closed system, and the excess moisture appeared as visible condensation in the respirometers.

6.2.2 Soil pH

Soil pH was measured during all the 150 g experiments. A sample set of results can be seen in Figure 6.7 and the rest of the data is present in Appendix B: The pH of the soil remains stable during the length of the experiment and any variance could be attributed to the difficulties in sampling a soil slurry; the pH would change depending on the state of the slurry and how much of the soil sediment had settled. To keep all measurements consistent, the soil slurry was constantly mixed by hand while sampling the pH.

Soil texture affected pH levels, as Delhi soil was found to be more acidic (pH ~7.13) than Elora soil (pH~8.27), as seen in Figure 6.7. The high pH level in Elora soil would suggest slight bacterial growth inhibition, resulting in poor biodegradation rates when compared to Delhi soil. This was the case when comparing the degradation rate results, which will be further discussed in section 7.2.1 below.

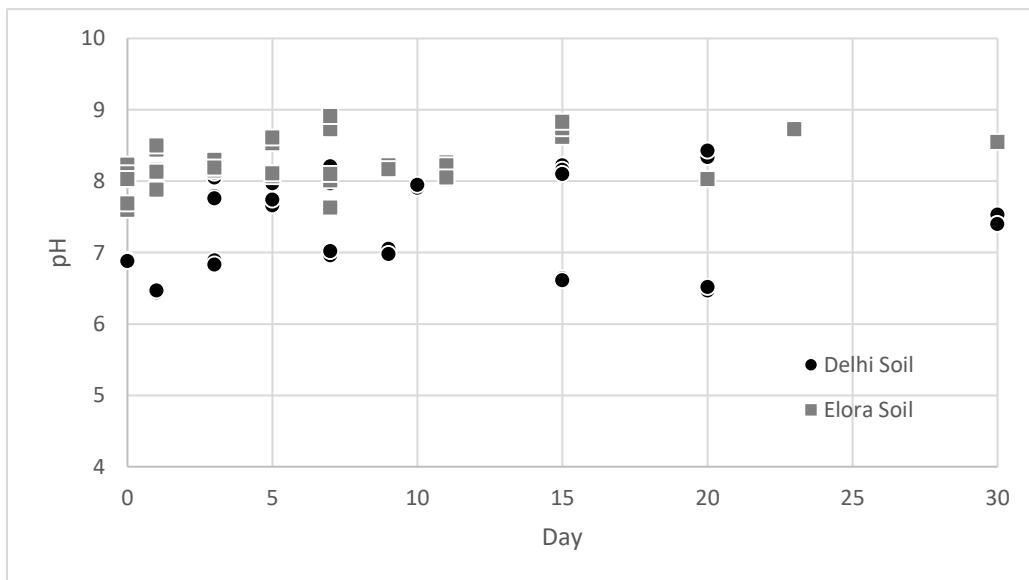


Figure 6.7: pH level differences between Delhi and Elora soil for short term aging experiments (soil contaminant age between 0 and 30 days)

Slight changes in pH with age was also observed in the long-term aging experiments, where freshly contaminated samples were found to be more acidic (pH ~ 6.0) than soil that has been aged (pH ~ 7.5), but the overall difference in pH was small and within the viable range for the microorganisms. The buffers used to calibrate the pH meters were for pH 7.0, 10.0, and 12.45. As such, the pH levels measured below 7.0 would suffer from increased variance.

6.2.3 Carbon Dioxide Production

A sample of the pH readings in experiments Delhi-270-150g and Delhi-300-150g of the KOH vials used to capture the carbon dioxide produced from microbial respiration are represented in Figure 6.8. There was only a minor change in the pH in these two experiments throughout the duration of the experiment, despite evidence of biodegradation. These results are typical when compared with the pH readings of the other 150 g experiments, which are available Appendix B: Other experiments show a notable decrease in the pH levels, representing a significant capture of carbon dioxide by the KOH, as seen in Figure 6.9, when looking at the data from short term experiments. Experiments using Elora soil exhibited more consistent carbon dioxide capture than the experiments using Delhi soil. The production of carbon dioxide was a positive indication that respiration, and thus biodegradation, was occurring during the experiments.

The use of a pH meter was not the most suitable tool to accurately measure pH at such high ranges. The calibration was performed using buffers of pH 7.0, 10.0, and 12.45; the typical pH levels for the KOH vials was over pH 13.0. More accurate readings of the pH levels can be achieved a titration procedure, using HCl and an indicator such as phenolphthalein. However, past experiments at the 150 g scale has determined that it is not a suitable method for determining biodegradation rates (Eyvazi, 2011). Therefore, the pH meter was chosen for more time saving pH measurements despite the lower accuracy.

The KOH tube in the respirometer was present to ensure that the system was kept under negative pressure so when the bottles were vented, minimal losses due to volatilization would occur as air would flow into the system, and not out. In addition, they were used as a qualitative assessment of the respirometers, rather than quantitative biodegradation rate measuring tool.

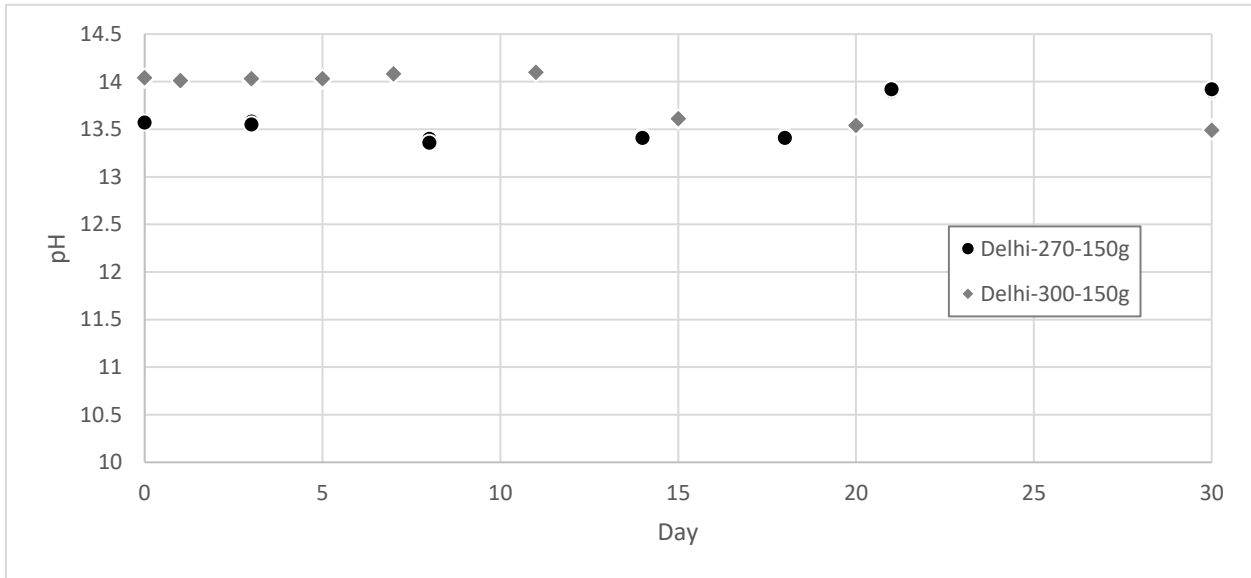


Figure 6.8: pH readings in the KOH tubes in experiments Delhi-270-150g and Delhi-300-150g

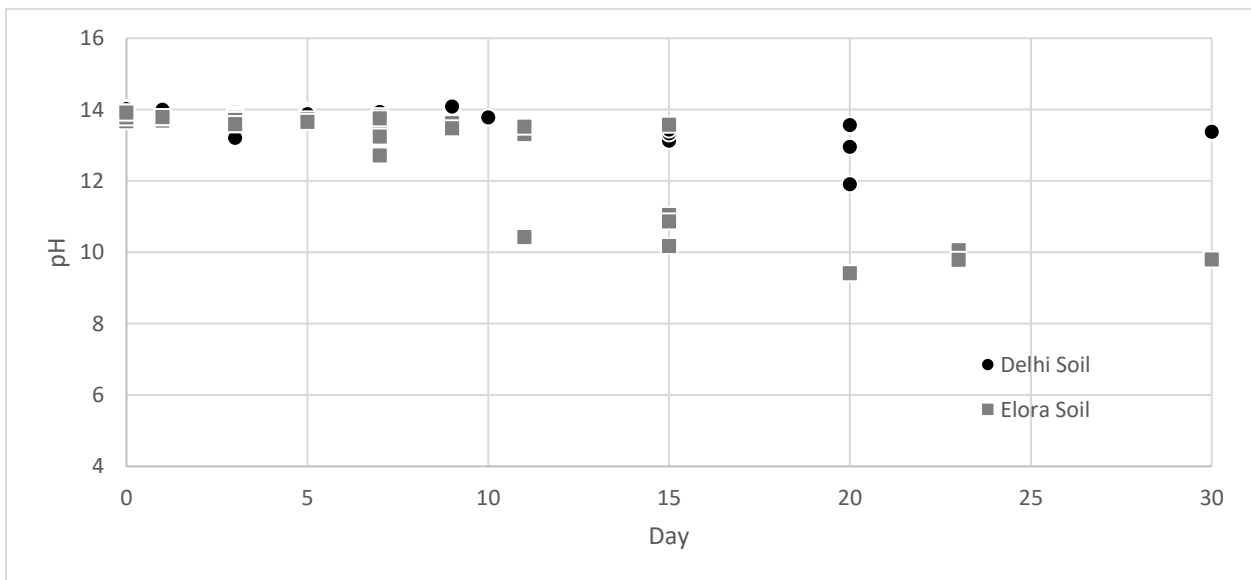


Figure 6.9: KOH pH for short-term experiments with Delhi and Elora soil

6.2.4 Biotic and Abiotic Controls

Biotic controls were run in tandem to many of the 150 g experiments, where the soil was mixed and amended in the same way as the soil used in the experiment, but without the spiking of TPH. This ensured that there was nothing in the method for the mixing, aging, and bioventing process that would produce false positive readings. None of the biotic controls had any extractable TPH at any age, confirming that there was no transfer in petroleum products through volatilization or diffusion, nor was there any chemical used in the extraction process that would show up as petroleum products in the GC-FID. The data for the blank results is available in Appendix B:

The experiments using the autoclaved soil, named Delhi-LT-150g-BLANK showed obvious signs that the abiotic control failed. No microbial presence should have been found in the abiotic control, but inoculation likely occurred during the initial mixing and spiking phase. The long aging process of 300 days would have been sufficient for the number of CFU in the abiotic control to recover, leading to similar biodegradation rates when compared to similarly aged soil, as seen in Figure 6.10. Microbial plating for these experiments were not available due to time constraints.

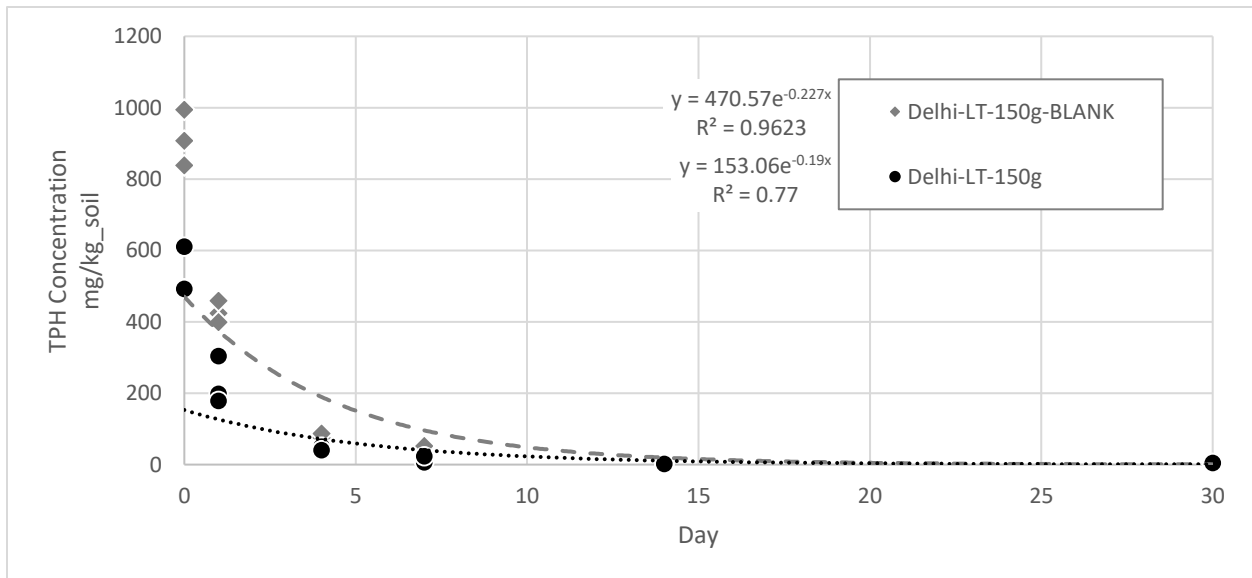


Figure 6.10: Bioventing experiment for the Delhi-LT-150g experiment after 305 days of aging, for autoclaved aged soil (abiotic control) and regularly aged soil

The starting concentration is different between the two experiments, which could be due to a difference in the initial spiking and mixing of the TPH or a change in the initial microbial presence affecting the aging process. The soil that was not autoclaved would have a larger variety of microbes present in the soil, allowing for the bacteria most suited to environments with petroleum hydrocarbon to thrive. In contrast, the abiotic control soil would have only small numbers of initial CFU, resulting in less ideal degradation of the TPH during the aging process. Nevertheless, the biodegradation rates ended up being statistically similar ($k_d = 0.227$ for the abiotic control, compared to $k_d = 0.190$) during the 30-day bioventing experiment.

6.3 Biodegradation Rates Processing and Statistical Methods

6.3.1 Calibration Curve

The output from the GC-FID used for this experiment consists of the time and area of the detected peaks, with each peak representing a different compound in the synthetic gasoline make up. A sample output is seen in Figure 6.11. The first small peak, followed by the large peak, at around four minutes represents the MeCl used as the extractant. The following five large peaks at 5.9, 7.2, 8.4, 9.4, and 11.6 minutes represent the five synthetic gasoline compounds (isooctane, toluene, m-xylene, mesitylene, and naphthalene respectively).

Using a series of standards, ran before and after the samples to take into consideration the slight volatilization of MeCl, calibration curves were created to convert the area under the curve of each peak into concentrations. Every compound was interpolated individually to determine the linear relationship between the area outputted by the GC and the corresponding concentration. As seen in Figure 6.12, a linear interpolation with a zero intercept was derived to avoid any negative values at lower concentrations. With the calibration curve, the concentration of unknown samples can be calculated using the given area.

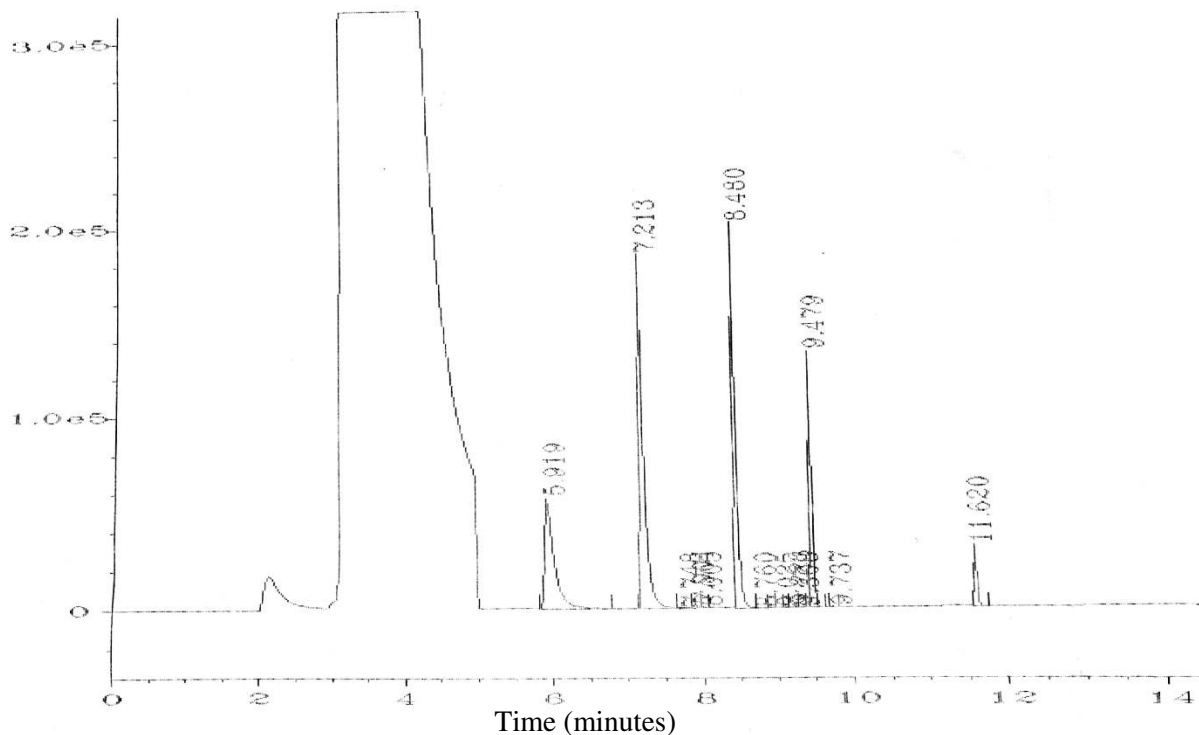


Figure 6.11: Sample output from the GC-FID. Five syngas compounds can be seen at 5.9 (isooctane), 7.2 (toluene), 8.4 (m-xylene), 9.4 (mesitylene), and 11.6 (naphthalene) minutes.

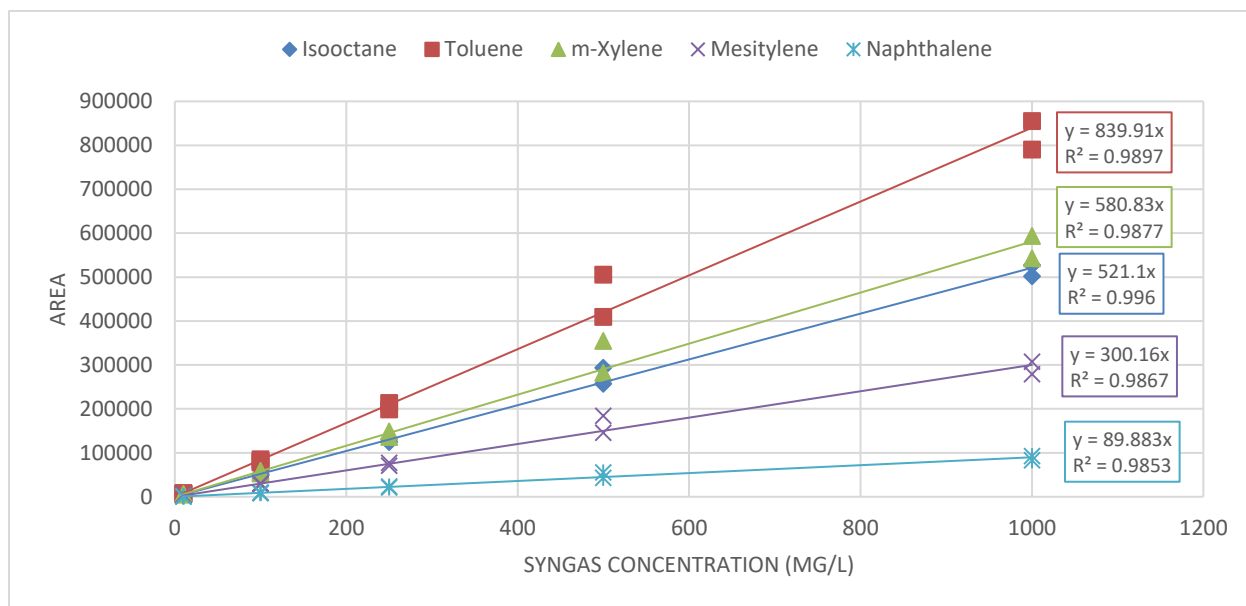


Figure 6.12: Sample calibration curve for run mx170731. Linear regression plotted for all five syngas

6.3.2 Coefficient of Variation – GC-FID

Also known as the relative standard deviation, the coefficient of variation (CV) quantifies the variation in a data set and measures the dispersion around the mean value. It is calculated using Equation 7 and allows a better understanding of the variation present in the collected data.

$$CV = \frac{\text{sample standard deviation}}{\text{sample mean}} \quad [7]$$

Small variations between replicates are expected, either during the extraction process of the TPH or due to the natural variations that occur during the use of the GC-FID. Standards were run multiple times during the experiment to create calibration curves, using known concentrations of TPH, and they were used to calculate the CV at different concentrations. Since CV are representative only when there is a large sample size, a small section of the data, collected before the GC-FID was recalibrated in February 2017, was omitted from the calculations. After recalibration, $n \geq 79$ standards were run between the dates of March 2017 and November 2017. These values, found in Appendix C, were pooled together to calculate the CV for each concentration, as seen in Figure 6.13, to determine the variance in the GC-FID over different concentration ranges for each compound.

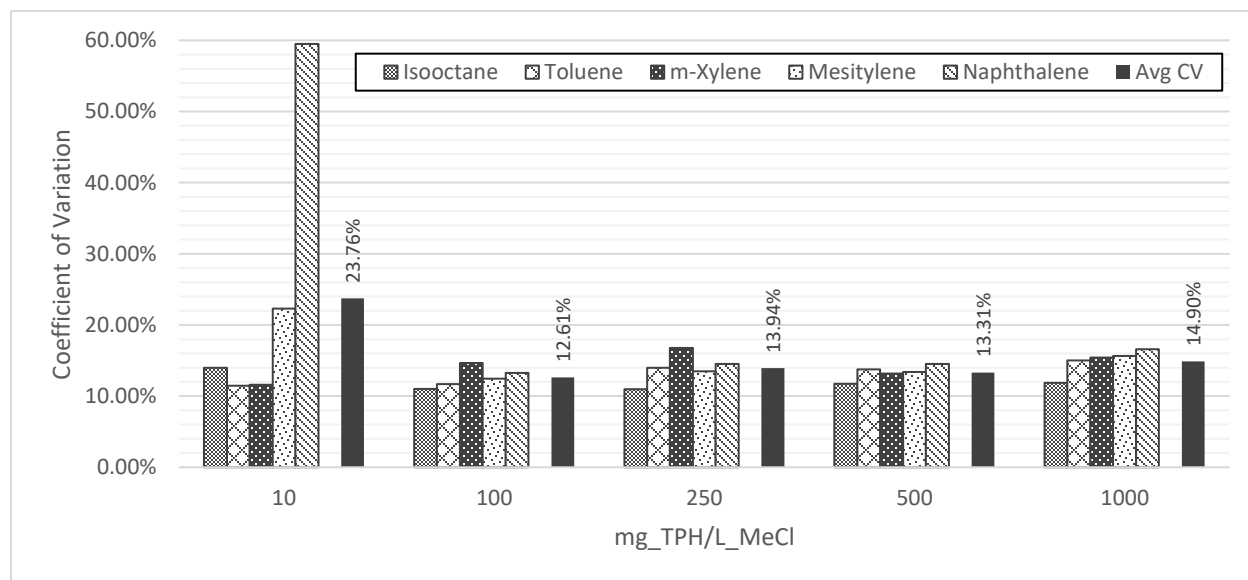


Figure 6.13: Coefficient of Variation at different concentrations for different TPH compounds for standard solutions run in the GC-FID between March 2017 and November 2017, with total sample size $n \geq 79$ for all compounds

On average, the CV of the compounds in the standard solution is 14%, with the notable exception seen in the measurement of naphthalene at $10 \text{ mg}_{TPH}/L_{MeCl}$, which represents approximately $17 \text{ mg}_{TPH}/\text{kg}_{soil}$. This larger variance is due to the small amount of naphthalene in the overall makeup of the synthetic gasoline (3.2% by weight), resulting in low concentrations that are near the lower detection limit of the GC-FID. This means that the machine measures data consistently across most of the concentration range of interest, but struggles at lower concentrations. Different soil properties have different typical CV values, which would affect the biodegradation rates. Soil organic matter content have an average CV value between 21-41%, whereas pesticide absorption has values between 12-31% (Warrick, 2001). Therefore, a CV of 14% is acceptable for the analysis of petroleum hydrocarbon in soil.

6.3.3 Lower Detection Limit

Knowing that the samples being run through the GC-FID approach the lower detection limit (LOD) of the device, the data distribution was plotted from concentrations between 0 and $2 \text{ mg}_{PHC}/\text{kg}_{soil}$ in a histogram in Figure 6.14. It can be observed that only 25 data points were present between 0 and $0.3 \text{ mg}/\text{kg}_{soil}$, whereas 50 samples were present between 0.3 and $0.4 \text{ mg}/\text{kg}_{soil}$. Furthermore, 1553 samples were read as $0 \text{ mg}/\text{kg}_{soil}$, which represent not only the samples where the contaminants were no longer extractable due to biodegradation or sorption, but also all samples with concentration below the LOD limit of the GC-FID. This is consistent to the concentration at which naphthalene showed a much higher CV, calculated in section 6.3.2 at $0.32 \text{ mg}/\text{kg}_{soil}$.

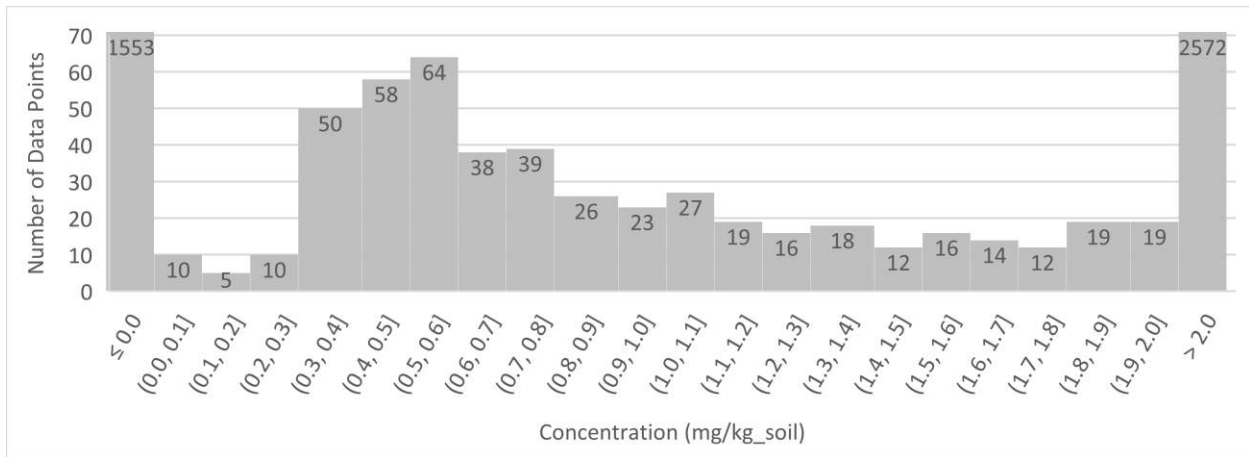


Figure 6.14: Data distribution between concentrations of 0 to 2 $\text{mg}/\text{kg}_{soil}$ for all data collected with the GC-FID

The loss of data at low concentration due to the LOD increases the uncertainty in the results, causing degradation rates can be overestimated, which can in turn underestimate the remediation time necessary. In addition, using the extraction methodology described in this research, the LOD of the Hewlett-Packard 7673 is higher than the cleanup standards in Canada (MoE, 2011), which suggests that adjustments are necessary for future research when examining soil with very low TPH concentrations.

To overcome the LOD limit of the analytical machine, samples with low TPH were extracted with a smaller volume of MeCl. Other changes to the extraction method were attempted on samples with no detectable TPH. The contact time between the solvent and the soil was increased by allowing the vials to shake on a multi-wrist shaker for a longer period. There was a slight increase in extractable TPH in the samples, but the extended shaking process could potentially increase volatilization rates since the samples were kept at room temperature. Furthermore, different solvents were tested, including the use of acetone instead of MeCl (Schwab et al., 1999), with no significant improvement in TPH concentration. There was no change in the method apart from a decrease in MeCl, from 10 mL to 5 mL, to double the concentration.

6.3.4 Coefficient of Variation – Soil Mixing

Both the 80 kg reactor and the 150 g respirometers assumed that the TPH was mixed and distributed homogeneously at the start of the experiment, but limitations of scale required the soil mixing process to be done in smaller 4kg batches. Each batch used both the Mettler AJ100L and Mettler PJ1220 scale to weigh the soil, water, synthetic gasoline, and nitrogen in 4L cans before they were sealed and tumbled for 20 minutes. Two batches of soil were mixed and handled for the same amount of time before samples were taken at various locations in the mixing can to measure for TPH. The data for the samples are available in Appendix C.

An average of 17% CV was calculated using Equation 7, with no real difference between the compounds making up the synthetic gasoline. Human error in measurement along with the precision of the scale ($\pm 0.0001g$ and $\pm 0.1g$ respectively) causes variation between not only the different batches of soil,

but within a single batch itself. This variation will cause slight differences in the initial TPH concentration between the 150 g respirometers and between separate locations of the 80 kg bioventing reactor. These errors are reasonable considering the natural variation and heterogeneity found within soil, along with the CV determined for the measurement of the TPH.

6.3.5 Data Validation

A limited number of total experiments could be run due to time and space constraints; each experiment lasted 30 days and there was a restriction in the number of concurrent due to the size of the 80 kg reactor and the size of the incubator to fit the 150 g respirometers. Nevertheless, measures were taken to ensure that limited data collected would be robust.

Triplicate samples were taken for each 150 g respirometer for the extraction and measurement of TPH. Furthermore, two 150 g respirometer bottles were sacrificed for each data point, for a total of 6 discrete readings. In the 80 kg reactor, though no true replicates were taken, multiple samples were taken at different location each day. In addition, the 80 kg experiments were run twice with minor delay in between to try and mitigate the effects of age between the Delhi-270 and Delhi-300 experiments.

6.3.6 Degradation Rate Coefficient

A first order degradation rate is expected when using a biological process such as bioventing, which past studies have confirmed (Eyvazi and Zytner, 2009; Khan and Zytner, 2013; Mosco, 2016). An exponential degradation rate coefficient (k_d) was thus expected for the experiments performed in this research project. The raw data for the concentration of synthetic gasoline was processed by taking the natural logarithm for every value. For the data points where the concentration was measured to be zero, they were changed to $10^{-1} \text{ mg/kg}_{soil}$. The k_d for each experiment could then be calculated as the slope of a linear regression, as seen in Equation 8, which describes a first order biodegradation rate.

$$\frac{C}{C_0} = e^{-kt} \qquad \ln\left(\frac{C}{C_0}\right) = -kt \qquad [8]$$

where

C = TPH concentration

C₀ = initial TPH concentration

-k = degradation rate coefficient (*k_d*)

t = time

To validate the assumption of an exponential decay for aged soil, the *p*-value and adjusted *r*-square (*r*_{adj}²) values were measured for every linear regression. A *p*-value of < 0.05 indicates that the null hypothesis that there is no significant trend between time and TPH concentration is rejected. The *r*_{adj}² value indicates the fit of the linear regression to the data, where a high value demonstrates a better fit than a lower fit. The full data set and the associates slopes, *p*-values, and *r*_{adj}² values can be found in Appendix C:

Overall, 90.15% of the linear regression had a *p*-value of < 0.05. When examining the fit, 18.2% of the regressions had an average to poor fit, (*r*_{adj}² between 0.3 – 0.55) and 59.1% had a good fit (*r*_{adj}² > 0.55). The high *p*-value and lower *r*_{adj}² indicates that though there is a statistically significant change in TPH concentration during the bioventing experiment and the exponential decay model is accepted, not every variance in the data can be accounted for.

CHAPTER 7: BIODEGRADATION RATE RESULTS AND DISCUSSION

7.1 Extraction Efficiencies

7.1.1 Overall TPH

Data from the DELHI-LT-150g were used to examine the effects of long-term aging under wet conditions on contaminant bioavailability and extractability. An increase in sorption, resulting in a decrease in extractable TPH, was expected in both aging setups. An initial spiking concentration of 4000 mg/kg was chosen to ensure that the initial concentrations were around 2000 mg/kg in the un-aged experiments.

There was a notable decline in extractability of TPH in Delhi soil, as seen in the decrease in measurable TPH on the first day of a bioventing experiment, as represented in Figure 7.1. These losses, attributed to a combination of contaminant sorption and biodegradation, which occurred at 4°C with minimal to no airflow, yet follow similar trends to soil aged in the open air. 61% losses were observed within 210 days by (Tang et al., 2012), compared to the ~70% losses seen during the wet aging of Delhi soil, despite a difference in aging method along with both soil and petroleum composition.

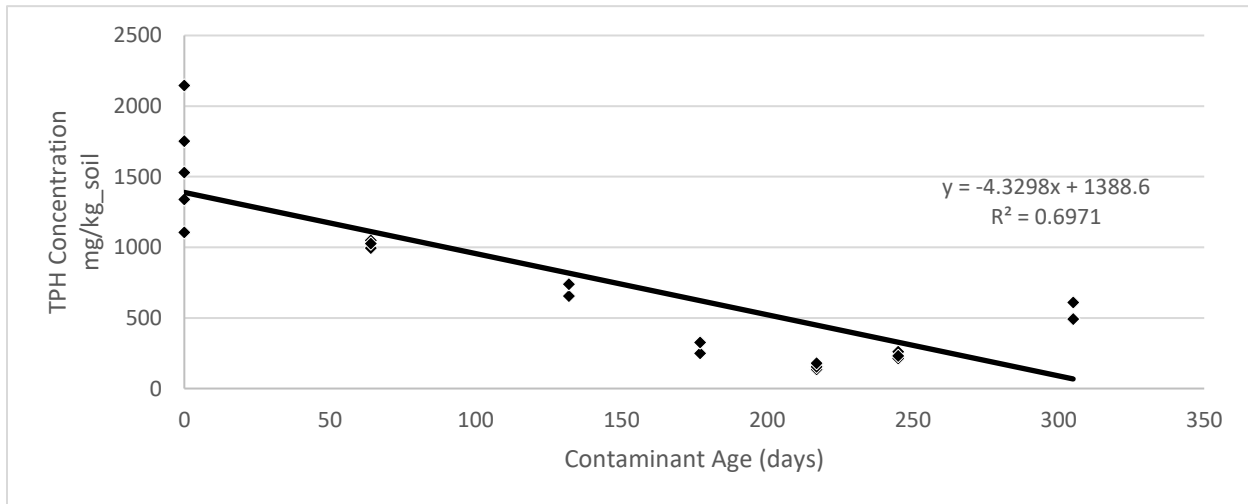


Figure 7.1: Decrease in TPH concentration with increase in age for contaminants in Delhi soil for all 150 g-scale bioventing experiments, showing a zeroth order decrease in extractability with increased aging.

This implies that even in less than ideal conditions, the extractability of contaminants can decrease rapidly over time, which will limit the bioavailability of the compounds when opting for biological remediation methods. It is important to note, however, that these results assume a single spill event homogeneously distributed throughout the soil in a closed environment, preventing any additional contaminant migration to occur in or out of the system, which is not representative of an actual spill or leakage event.

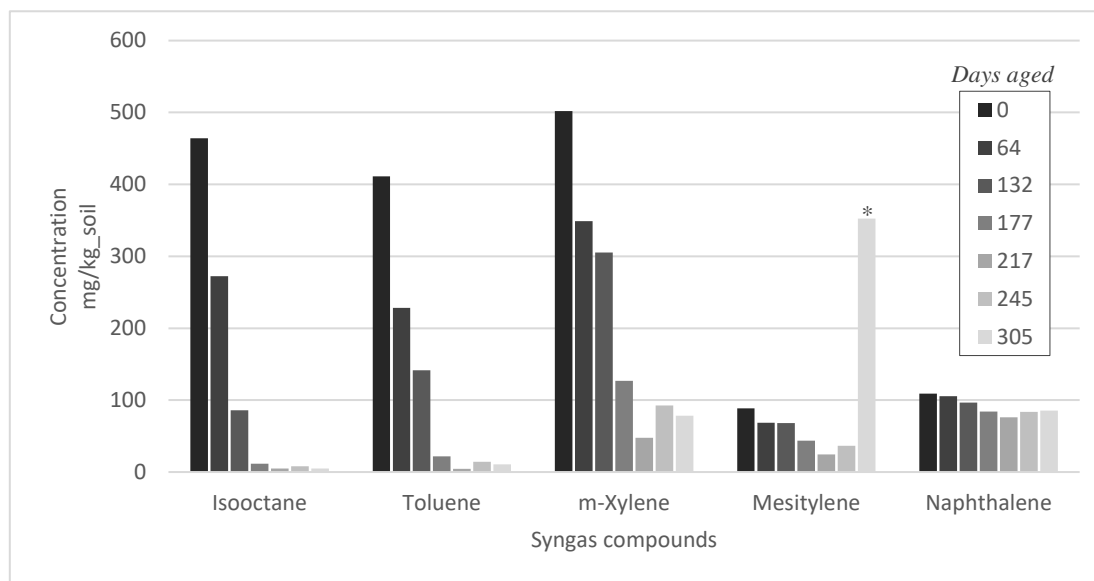
When examining the effects of aging on Elora soil, very little TPH could be extracted from the soil after 270 days of aging, implying that the compounds became so tightly bound that the MeCl extraction was no longer strong enough to break the bonds. Stronger extraction methods were attempted, resulting in some detectable compounds near the concentration of the LOD of the GC-FID. This result is consistent with the knowledge that soil with higher silt and clay particles such as Elora, a silt loam, will exhibit stronger sorption than Delhi, a loamy sand. For future aging experiments, it is recommended for the soil to be spiked at a higher concentration to allow for higher initial TPH values in long-term aged soil.

7.1.2 Compounds

The aging of TPH contaminants in soil affect not only the concentration, but also the composition of the synthetic gasoline. The concentration of the five compounds making up the synthetic gasoline are plotted over time in Figure 7.2 and shows a clear and significant decrease in contaminant concentration for isooctane, toluene, and m-xylene, but only small decrease for mesitylene and naphthalene. These results support the literature which states compounds with low K_{ow} values, such as toluene, are more likely to sorb onto the soil particles than PAH molecules like naphthalene. This same trend also reflects the biodegradability of these compounds, where alkanes were more susceptible to biodegradation than PAH (Zytner et al., 2006)

The extractability of compounds is not directly proportional to the K_{ow} values shown in Table 7.1, most notably with isooctane's high K_{ow} while exhibiting a loss in extraction efficiency like that of toluene.

This suggests that there are more processes that affect contaminant sorption, such as molecular weight and shape of the petroleum compounds. Furthermore, biodegradation also plays a significant role during the aging process, in addition to the sorption of contaminants into the soil matrix.



*aberrant value, extracted concentration over three times higher than spiked concentration

Figure 7.2: Decrease in syngas concentration between 0 and 305 days of aging, more prominent for isooctane, toluene, and m-xylene and minimal in mesitylene and naphthalene

Table 7.1: K_{ow} values and molecular weight of synthetic gasoline compounds

	<i>Isooctane</i>	<i>Toluene</i>	<i>m-Xylene</i>	<i>Mesitylene</i>	<i>Naphthalene</i>
log K_{ow}	4.3	2.65 ¹ 2.73 ²	3.20 ²	3.53 ²	3.3 ¹²
Molecular Weight g/mol	114.2	92.1	106.2	120.2	128.2

1(Yong, 2000), 2(Sangster, 1989)

It is clear from Figure 7.2 that there is a change in the synthetic gasoline composition over time, which will in turn affect biodegradation rates in the system during bioventing. There is a rapid and sharp decrease in isooctane and toluene until they are only extractable in small concentrations after 177 days of aging. This contrasts with mesitylene and naphthalene, which show little decline in contaminant concentration over the 305-day aging period. The change in synthetic gasoline composition can be visualized in Figure 7.3. The synthetic gasoline used to spike the soil was composed of 29% isooctane and 26% toluene, which dropped down to 1 and 2% respectively of the synthetic gasoline present in the soil

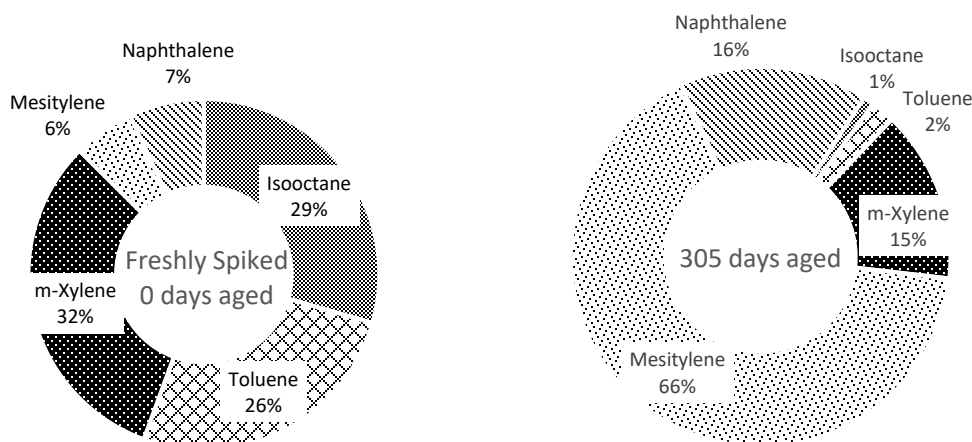


Figure 7.3: Change in relative syngas composition between 0 days aged and 305 days aged TPH

after 305 days of aging. Mesitylene, which represented 6% of the synthetic gasoline and naphthalene, which was only 7%, rose to 66 and 16% respectively after 305 days wet-aged as their concentrations did not decrease much. In freshly spiked soil, the degradation rate of toluene and isooctane would dominate the TPH degradation rate, whereas these two compounds are not as prevalent in aged soil. These results confirm that there is preferential sorption and biodegradation of some compounds during the wet-aging process.

7.2 150 g Respirometers

7.2.1 Short-Term Aging

Short term studies on hydrocarbon extractability in soils showed a decrease within a month of aging due to sorption and biodegradation (Jain et al., 1992). This section will discuss 30-day bioventing degradation rates for short term aging, using results from experiments Delhi-0-150g, Delhi-15-150g, Delhi-30-150g, Elora-0-150g, Elora-15-150g, Elora-30-150g, EloraA-0-150g, EloraA-15-150g, and EloraA-30-150g. The Delhi and Elora experiments used freshly spiked soil and aged for 0, 15, and 30 days respectively. The Elora-A used soil, wet-aged for over 250 days, and then re-spiked and aged for 0, 15, and 30 days. The degradation rate coefficients (k_d) for these experiments are summarized in Table 7.2 below. Within these experiments, the r_{adj}^2 values for the measurement of k_d was very poor for the Delhi-0-150g and Elora-15-150g experiments and so they were not included in the analysis.

Table 7.2: Summary of k_d values for short term aging experiments

Synthetic gasoline Age	Delhi	Elora	Elora-A
0 days	0.0337*	0.2050	0.2002
15 days	0.1114	0.0633*	0.0110
30 days	0.1771	0.1138	0.0966

**poor r_{adj}^2 values, values not robust*

Due to the small number of runs (three per soil type), very few coefficients were calculated, resulting in statistical tests like the t-test to be inconclusive or non-significant. However, these effects still provide interesting discussion points on short-term aging as, with only 30 days of aging, evidence of an increasing k_d with an increase in contaminant age can be seen between the Delhi runs. In the Elora soils, the opposite trend can be seen, where the setups with aged contaminants have a lower k_d than their unaged counterparts. The different soil types may react differently to the aging process, but more data is needed for conclusive results.

The runs between Elora and Elora-A were examined carefully to determine if spiking previously contaminated soil (Elora-A) would affect the degradation process. This re-contaminated could represent a second spill event in a contaminated site. Though the degradation rates between the two were similar, visually, the Elora-A runs tended to exhibit an increase in TPH concentration, mostly due to the mesitylene in the soil, at the 11-day mark, as seen in Figure 7.4. Though small increases were also seen in the Elora soil, it was much more prevalent in the Elora-A. It is hypothesized that the desorption of the compounds at a faster rate than the biodegradation causes this phenomenon. The previously aged contaminants, which were not available for extraction, had a notable effect in the increase in mesitylene at that time, either by acting as a chemical surfactant or by allowing the bacteria to acclimatize better to the TPH in the soil, causing an increase of biological surfactants to be produced. More work is needed to further explore the effects of spiking already contaminated soil to better understand the interactions at play.

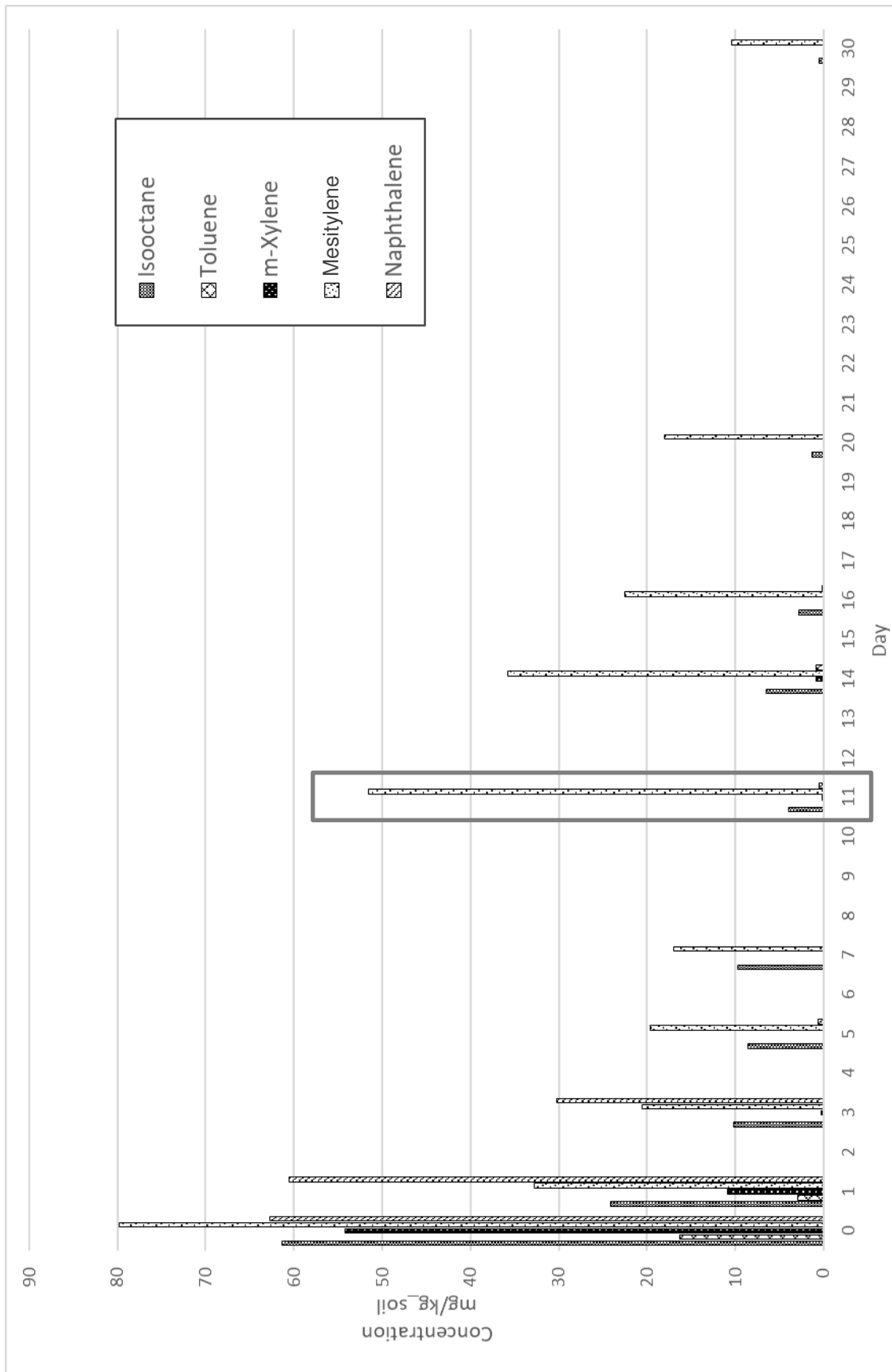


Figure 7.4: Individual compounds concentration results from Elora-A-30-150g over 30 days of bioventing in 150 g respirometers. An increase in mesitylene at day 11 is notable

Overall, little effect can be seen in the degradation rate of TPH under short term aging. This could mean that there is no need for remediation to be applied immediately as long as the source of contamination and the plume has been contained, such as after the contaminated soil has been excavated from the site. However, these results are inconclusive and more work needs to be done to confirm the findings.

7.2.2 Long-term aging

The petroleum hydrocarbon in many contaminated sites have been aged for extended periods of time as, especially in the cases of leaking UT.; Property owners might not detect the leak until several months, if not years later. The effects of long-term aging are thus interesting to study to understand the change in biodegradation rates, if all other conditions are kept similar, to highlight the importance of early detection and remediation.

Numerous 150 g experiments performed throughout this study, run under similar conditions, with the only variable being the age of the contaminants. The k_d calculated for the degradation of TPH are plotted in Figure 7.5 along with a 95% confidence interval, which show an increasing k_d with increasing age. Furthermore, the regression was analyzed in R, a statistical software, to extract the p -value and the

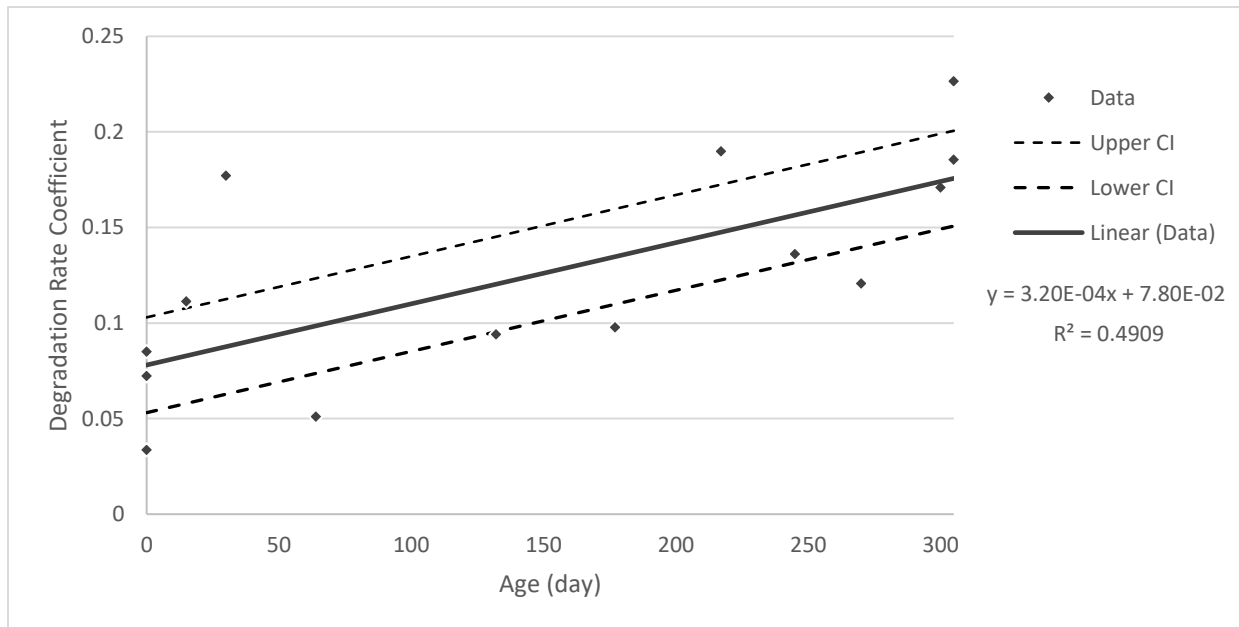


Figure 7.5: Change in degradation rate coefficients (k_d) for Delhi soil (150 g) from age 0 to 10 month, plotted with a linear regression and 95% confidence intervals (CI)

r_{adj}^2 , which to test for significance. The null hypothesis states that there is no effect of age on the k_d values. A p -value of 0.005 was calculated, rejecting the null hypothesis ($p < 0.05$). An r_{adj}^2 value of 0.449 indicates an adequate fit, considering the expected variances in the data set.

A statistically significant increase in k_d , from $0.079 d^{-1}$ for freshly spiked soil to $0.194 d^{-1}$ for soil aged for over 300 days, indicates a more rapid degradation rate with aged soil, which infers that the 150 g respirometers perform more optimally with aged contaminants. This is consistent with past observations done at the 150 g scale (Eyvazi and Zytner, 2009) and is likely due to the acclimatization of the bacteria in the system, allowing for them to perform under sub-optimal conditions.

Knowing that the bench-scale 150 g respirometers do not run optimally under fresh-spiked soil conditions, the importance of proper scale-up factors become apparent. However, the scale-up factors that have been developed for freshly contaminated soil might not be sufficient in describing the degradation rates for aged contaminants. The subsequent chapters will examine the effects of aging in larger-scale reactors.

7.3 80 kg bioventing reactor

The limitation of bench-scale experiments lies in their inaccurate depiction of field-scale sites, especially in soil science, where many large-scale interactions cannot be replicated. Furthermore, 150 g respirometers rely on passive air flow for the supply of oxygen, rather than an active pumping system that is more commonly used in bioventing. An 80 kg bioventing reactor is used in this experiment, which was developed by Mosco (2016), to relate the results of the 150 g respirometer experiments to the field.

Both Elora and Delhi experiments were planned for the 80 kg bioventing reactor experiments to develop a scale-up factor for the two soil types. However, following an aging period of 250 days, the initial contaminants present in the Elora soil at concentrations close to or below the LOD of the GC-FID, resulting in no extractable TPH within a week of the bioventing process. As such, degradation rates were not

calculated and the experiment was terminated after seven days. The higher silt and OM content in the Elora soil caused more of the spiked synthetic gasoline to be sorbed into the solid phase than expected. The data set for the first few days can be found in Appendix C:

Delhi-270 and Delhi-300 were run at the 80 kg scale, along with concurrent 150 g respirometer experiments which used the same aged soil. Though there is a small age difference of 30 days between Delhi-270 and Delhi-300, the other conditions were set to be similar for the two runs to be considered replicates. Unfortunately, a setup error resulted in a larger initial water content in the Delhi-270 experiments, which slower biodegradation rates as the airflow was less than optimal during the first days.

7.3.1 *Single-stage biodegradation rates*

A two-stage biodegradation rate was observed in previous bioventing work done with freshly spiked soil at the 4 kg and at the 80 kg scale reactors (Khan and Zytner, 2013; Mosco, 2016), with stage two beginning at around 8 days after the start of the bioventing process. Dry-aged Delhi soil (120 days) also had a similar two-stage biodegradation rate, albeit for a smaller rate change between the two stages. These values, along with the single-phase degradation rate observed in the 150 g respirometers, are reported in Table 7.3. It was hypothesized that the easily accessible contaminants were biodegraded during the first week, whereas the second stage represented the less bioavailable TPH which were rate-limited by the desorption process. This followed the observations that contaminants biodegraded at two different rates, where the bioavailable portion was degraded within the first 20 days using bioaugmentation, whereas the less bioavailable substances required more extensive remediation methods (Eriksson et al., 2000).

In addition, lag was observed in dry-aged soil, where the decrease in TPH was delayed by a few days due to the microbes being in a dormant state during the aging process. Whereas in dry-aging, dry soil is spiked and aged, wet-aging spikes the same dried soil but also brings the soil water content up to 15% prior to being aged. This allows for the microbes to remain active during the aging process and to avoid any time lag during the experiments.

Table 7.3: Degradation rates for Delhi soil at different scales

Reactor size	150 g ¹	4kg ²	80 kg ³	80 kg ³	Delhi-270 80 kg	Delhi-300 80 kg
Age (days)	--	--	--	120	270	300
Stage 1 (0-8d)	--	0.598	0.2795	0.081	--	--
Stage 2 (8-30d)	0.045	0.123	0.118	0.053	0.124	0.132

1 (Eyvazi and Zytner, 2009) 2(Khan and Zytner, 2013) 3(Mosco, 2016)

When attempting to fit a two-stage degradation rate onto the Delhi-270 and Delhi-300 TPH data, the statistical software R was used to test different break points via trial and error to calculate the combination with the best r_{adj}^2 value. As seen in Table 7.4, a much better fit was calculated for a single-stage biodegradation rate. The best break point for a two-stage degradation rate coefficient was determined to be at day 14, where $k_{d_{stg1}} = 0.2366$ and $k_{d_{stg2}} = 0.0431$, representing a non-trivial change in degradation rate. Both regression lines had a p -value of < 0.05 , rejecting the null hypothesis. However, the r_{adj}^2 values were both extremely poor, at 0.2936 for $k_{d_{stg1}}$ and an abysmal 0.03028 for $k_{d_{stg2}}$, compared to 0.4740 for a single stage k_d .

Table 7.4: Fit comparison between one-stage and two-stage degradation rate for first order degradation rates in Figure 7.6

Stage	k_d	r_{adj}^2
Single Stage: 0-30	0.1327	0.4740
Stage 1: 0-14	0.2366	0.2936
Stage 2: 14-30	0.0431	0.03028

The associated trendlines can be seen in Figure 7.6, where both the single and two-stage degradation rates were plotted. Detailed statistical analyses for the three fits can be found Appendix C: The longer aging process could have reduced the amount of easily degradable TPH, which are responsible for the two-stage degradation process.

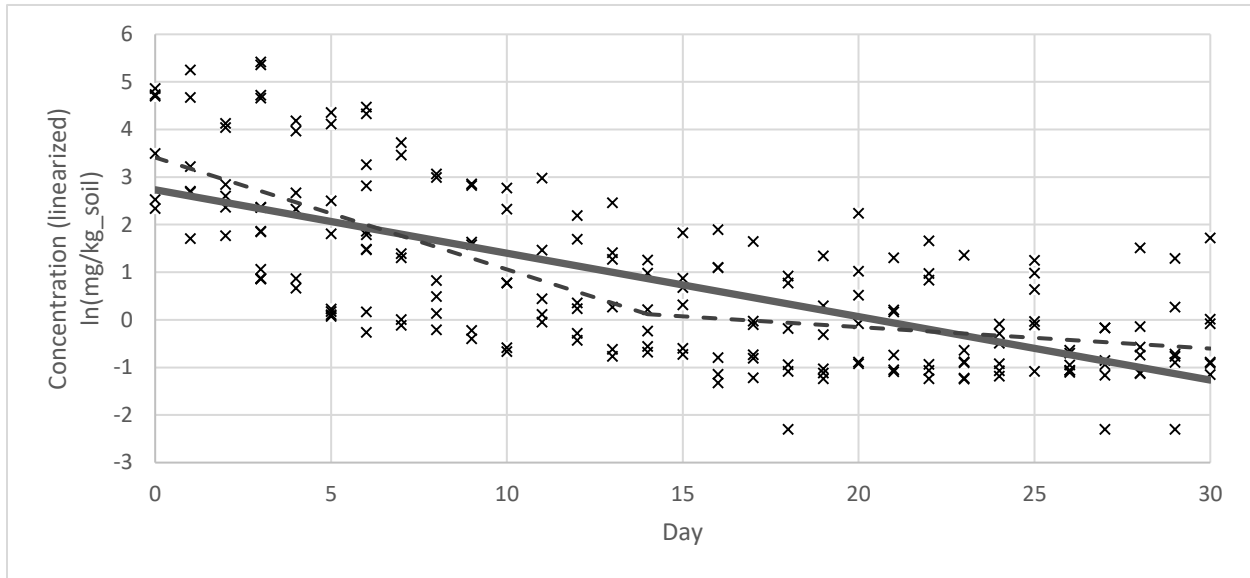


Figure 7.6: Comparison between single stage and two-stage degradation rates for Delhi-300-80kg, selecting day 14 as the break point between stage one and stage two. Regression model details in Table 7.4

7.3.2 Expanded bioventing reactor

The bioventing reactor was constructed from a stainless steel drum with a height of 51.4 cm ($20\frac{1}{4}$ in) and an I.D. of 40.6cm (16 in), with sampling ports distributed evenly along the drum in 3 rows by 5 columns. Daily samples were taken for the measurement of TPH at three different layers of the reactor during the Delhi-300 experiment to investigate the differences in degradation rates at different depths. In the field, biological remediation methods decrease in efficacy at lower depths due to inadequate aeration (Hinchee and Leeson, 1996).

When plotting the TPH over the 30-day experiment, the location of the sample affects not only the TPH concentration, where the samples taken at the top of the reactor have a higher concentration on TPH than the samples at the middle and bottom of the reactor, but also the k_d , where $k_{d_{top}} = 0.1836 d^{-1} > k_{d_{mid}} = 0.1281 d^{-1} > k_{d_{bot}} = 0.880 d^{-1}$, as seen in Figure 7.7.

The initial difference in concentration were caused by the method in which the reactor was loaded, where $4 \times 4\text{kg}$ batches of soil was mixed, loaded, and packed into the reactor, every 30 minutes as the subsequent batches are being processed. This would cause more volatilization to occur for the soil that was loaded first, at the bottom of the reactor, which was exposed to the open air for longer periods of time. Furthermore, the soil at the bottom of the reactor had to be loaded from the top and was allowed to drop down. This mechanical tumbling could also have increase the TPH being volatilization. When comparing initial TPH composition at the beginning of the experiment for the three locations of the Delhi-300-80kg with Delhi-300-150g, the top of the reactor had the most similar composition and concentration, as seen in Figure 7.8. The methodology of loading the reactor thus caused a significant difference in initial TPH.

The overall decrease in k_d with reactor depth can be caused by a combination of multiple factors. The contaminants lost due to volatilization during the handling of the soil were the fraction of the synthetic gasoline that were sorbed less strongly into the soil. The microbiome was then left with strongly sorbed contaminants that were less bioavailable. Therefore, with less available TPH, the microbial population growth stalled and caused a decrease in the biodegradation rates.

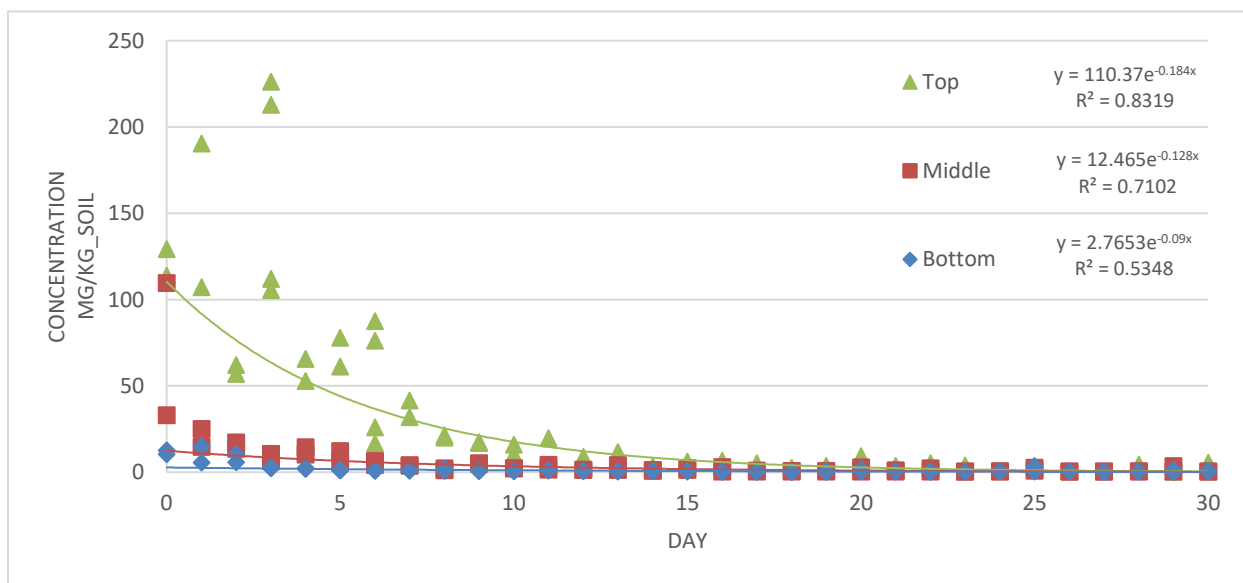


Figure 7.7: Delhi-300-80kg results, showing the effects of sampling location on TPH concentration and biodegradation rate

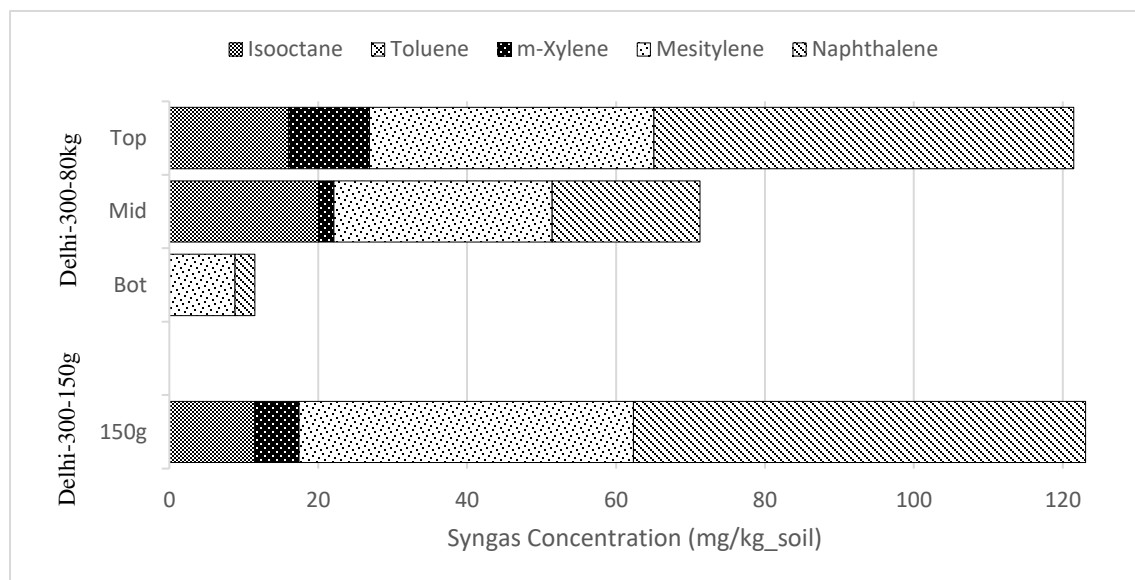


Figure 7.8: Delhi-300 initial TPH concentration for the 150 g experiment and for different location in the 80 kg reactor

The expanded reactor showed that as the contaminants are being desorbed, volatilization occurs and the contaminants migrate through the bioventing system to feed and nourish the bacteria population in the top layers of the reactor. In addition, gravity could have caused an increase in water content near the bottom of the reactor, restricting air flow and causing less-than-ideal bioventing condition.

Finally, though a lot of care was put into the construction and design of the 80 kg reactor, there is a possibility that the airflow throughout the system is not even, favoring the top layers of soil, resulting in faster bioventing degradation rates. Some or all of the listed factors would have caused a gradient in total microbial population during the bioventing process. Unfortunately, microbial analysis was not performed for the different locations of the bioventing reactor at the time, which would be suggested for future experiments involving the 80 kg reactor.

7.3.3 Long-term aging

The long-term changes in bioventing degradation rates at the 80 kg reactor scale is possible by comparing the Delhi-270-80kg and Delhi-300-80kg runs with the stage-two degradation data collected by Mosco (2016), which were run under similar condition with the same soil. Though a decrease in k_d at the 4-month mark was observed ($0.053 d^{-1}$), as seen in Figure 7.9, no significant change in degradation rate

can be seen for the Delhi-270-80kg ($0.124 d^{-1}$) and Delhi-300-80kg ($0.133 d^{-1}$), experiments at the 9 and 10 months of aging respectively, when compared to soils with freshly spiked contaminants ($0.12d^{-1}$). The null hypothesis could not be rejected for the linear trend between the data points. Despite the drastic decrease in starting TPH concentration, there was only a minor change in the actual degradation rates.

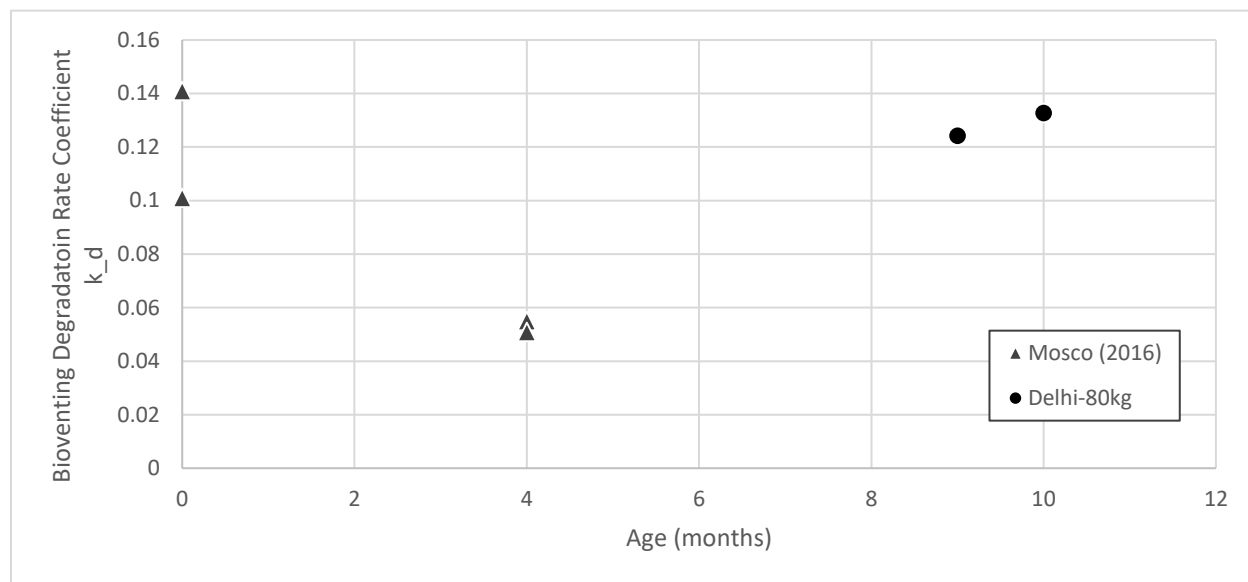


Figure 7.9: Degradation rate coefficient in 80 kg bioventing reactor for different contaminant age.

For a contaminant aging process between 4 and 9 months, not only did the degradation rate change from a two-stage process to a single stage process, as detailed in chapter 7.3.1 , but the decrease in k_d observed by Mosco (2016) was no longer present. It is notable that the aging process was different between the soil aged for 4 months and the soil aged for 9-10 months; the soil used in the 4-month aging experiment was spiked at 8000 mg/kg of synthetic gasoline and aged under dry conditions, whereas the soil used in the Delhi-270 and Delhi-300 experiments were spiked at 4000 mg/kg synthetic gasoline with a soil water content of 15%.

The process of wet-aging would have allowed more acclimatization to occur, as the water content in the soil would allow for microbial growth. Furthermore, it would allow an easier access to the contaminants, allowing the microbial community to grow under high TPH concentration environments to increase biodegradation rates, compensating for the contaminant sorption that occurs during the aging

process. In contrast, the bacteria are in a dormant state during a dry-aging process, as the soil was dried and only amended with water after the aging process, and the microbial population would not have the time to develop. This highlights the influence of the aging environment on remediation times and the complexities of biological systems. More data points are needed to obtain more thorough results, examining the effects of age at a finer resolution, for longer aging times, and for different aging conditions.

7.3.4 Scale-Up Factor

A challenge for all lab-based work is to relate their findings to a field level. With an increase in scale, there is an increase in complexities and heterogeneities which can affect the predicted model. A reactor with 150 g of soil will thus react differently than a reactor with 80 kg, and different at the field scale as well. This is especially true as bench-top respirometers do not use active air flow due to the small amount of soil present.

This was shown in during past experiments where scale-up factors were developed to compare the bioventing degradation rate coefficients for freshly spiked soil at three different scales: 150 g, 4kg, and 80 kg. It was found that there was no statistical difference in the degradation rates of the 4kg and 80 kg scale reactors, and a scale up factor of 2.7 for Delhi soil and 1.9 for Elora soil was observed for the 150 g respirometers (Khan et al., 2015; Mosco, 2016). This was due to an increase in efficiencies between the respirometers and the large-scale bioventing reactor. Whereas there is an active venting system in the larger experiments, created by the low-flow air pump, the respirometer had a closed environment with no air flow. As such, the oxygen could only be transmitted to the lower layers of soil through diffusion.

The Delhi-270 and Delhi-300 experiments were performed at both the 80 kg and 150 g scale to allow for a scale-up factor to be determined when aging is present. The different k_d and scale up factors are available in Table 7.5. Only second-stage degradation rates were reported, as they are more representative for long-term bioventing remediation systems to determine site closure times.

Table 7.5: Degradation rate coefficient and scale up factors for Delhi soil

Reactor size	150 g ¹	80 kg ³	80 kg ³	150g	80 kg	Scale-Up Factor 80kg	
Age (days)	0	0	120 (dry-aged)	270-300 (wet-aged)	270-300 (wet-aged)	0	270-300 (wet-aged)
Stage 1 (0-8d)	--	0.2795	0.081		--	--	--
Stage 2 (8-30d)	0.045	0.118	0.053	0.146	0.128	2.7 ³	0.88

1 (Eyvazi and Zytner, 2009) 2(Khan and Zytner, 2013) 3(Mosco, 2016)

No significant scale-up factor was calculated for the aged Delhi soil. The change between the 150 g and 80 kg scale was statistically insignificant, given the low number of data points and high variance in degradation rates. This would imply that the 150 g respirometers are performing at ideal rates, despite the lack of air flow through the system. The effects of age on bioventing is complex, with sorption and desorption processes acting alongside biodegradation. One of the experiments in the DELHI-LT-150g series, wet-aged for approximately 130 days, had a degradation rate of 0.094 d⁻¹, compared to 0.053 d⁻¹, the degradation rate of the same soil dry-aged for 120 days by Mosco (2016) for a scale up factor of 0.56. This smaller scale-up factor is likely due to the different aging techniques, which increased the degradation rate at the 150 g scale due to the wet-aging, and decreased the rates for the dry-aged experiment. Based on the work completed, more research is needed to quantify the difference between the two aging techniques and their effect on biodegradation rates.

In addition, whether the scale-up factor will remain insignificant after longer aging time or if the scale-up factor would decrease until the 150 g respirometers perform at a more efficient rate than 80 kg reactors requires additional research and experimentation to determine. The implications of a lack of scale-up factor means that benchtop bioventing experiments are sufficient for the estimation of bioventing processes in the field for wet aged soil. Larger-scale reactors, which require more soil and a more complex setup, would no longer be necessary. This would allow for estimations of *in situ* contaminated sites to be performed at any location without the need for specialized equipment, nor large quantities of soil to test.

CHAPTER 8: CONCLUSION

Petroleum hydrocarbon in its various forms is the leading contaminant in Canada. Due to the common use of petroleum compounds, a background level of exposure is expected, especially in urban areas with many gasoline and diesel service stations. However, unintended spills and leaks into the environment, one of the leading causes of petroleum contaminated soils, can become the source of additional exposure, which can lead to health complications if left untreated.

This research project focused on bioventing, an *in situ* biological remediation process for petroleum contamination in the unsaturated zone of the soil. Bioventing treatment amends the soil with nitrogen and increases the air flow in the soil, which stimulates the native microorganisms to optimize the biodegradation rates to remove the contaminants. *In situ* treatments are low-impact and low-cost as they avoid expensive excavation fees, though longer remediation times are often necessary. In addition, bioventing does not suffer from tailing and rebound, nor does it require the treatment of off gases when compared soil vapour extraction, another common remediation technique for petroleum compounds.

Bioventing is still a recent technology and estimating remediation times can be challenging in the field. Different soil and contaminant properties can all affect degradation rates, which will in turn change the remediation time necessary for site cleanup. The sorption of contaminants in the soil with time, also known as aging, can decrease the extractability of the compounds, which have been linked to the bioavailability of the compounds to the microorganisms. More knowledge is need on the effects of aging, along with different aging processes.

Experiments were performed on loamy sand (Delhi) and silt loam (Elora) soils, aged at 4°C under 15% water content and spiked with 4000 mg_{synthetic gasoline}/kg_{soil}. The results showed that the amount of extractable petroleum products decrease significantly with time. In fact, after 270 days of aging, the Elora-type soil showed less than 100 mg/kg_{soil} extractable petroleum hydrocarbon. Both sorption and microbial biodegradation likely caused the steep reduction in petroleum products. The aging process also changed the

composition of the TPH due to different compounds' tendency to be sorbed onto the soil or biodegraded by the microbes due to different K_{ow} values, molecular weight, and compound shapes of the five compounds used in the experiment; isooctane, toluene, m-xylene, mesitylene, and naphthalene.

Microbial acclimatization plays a key role during the wet-aging of contaminants in soil. The lengthy aging process allows ample time for the microorganisms to adapt to a petroleum-rich environment. Petroleum-degrading bacteria would likely dominate over the other microorganisms in the soil due to food availability, which would ultimately increase in biodegradation rates. Dry-aging, on the other hand, causes the microorganisms to remain dormant, only stimulating them after the aging process where both water and nutrients are mixed into the spiked and aged soil. Dry-aging also causes a time-lag to be observed due to the microbes only recently being activated by the addition of water in the soil after the aging process. This was not present in the experiments that were wet-aged, where there was already active microbes present in the aged soils.

The effects of microbial acclimatization was seen in the bioventing experiments at the 150 g respirometer and 80 kg reactor scale, using methods adapted from past experiments performed using freshly spiked soil. At the 150 g scale, the respirometers showed an increase in biodegradation rate with an increase in age due to the acclimatization of the microbes, from $0.079 d^{-1}$ to $0.194 d^{-1}$ over the course of 300 days of aging. These respirometers do not run under ideal conditions due to the lack of active venting in the system, but still provide reasonable estimates. In contrast, the degradation rates at the 80 kg scale did not change with aging ($k_d = 0.12d^{-1}$ at 0 days aged, $0.124 d^{-1}$ and $0.133 d^{-1}$ at 270 and 300 days aged) due to the competing effects of sorption decreasing the bioavailability of the contaminants and acclimatization increasing the desorption and biodegradation rates. In contrast, dry-aged soil showed a significant decrease in degradation rate after 120 days aged ($k_d = 0.053d^{-1}$). A single-stage biodegradation rate was observed with wet-aged soil, rather than a two-stage degradation rate in freshly spiked soils and dry-aged soil.

The increase in degradation rate at the 150 g scale and the stabilization at the 80 kg scale resulted in a lack of significant scale up effect between the two experiments performed on the same soil. Large-scale experiments might not be necessary for future work if the results from bench-scale respirometers improve with soil age. This would allow for more experiments to be performed as large reactors suffer from the downside of requiring more resources to operate. Furthermore, different degradation rates were observed in the 80 kg reactor at separate locations: $0.184 d^{-1}$, $0.128 d^{-1}$, and $0.088d^{-1}$ at the top, middle, and bottom third of the reactor respectively. The initial TPH concentration also varied due to the method used to load the reactor causing the soil at the bottom of the reactor to be exposed to air and volatilization for longer periods of time than the soil at the top of the reactor. Coupled with the expanded reactor effect, where volatilized compounds travel up through the reactor to be biodegraded in the top layers of soil, causing an increase in microbial population and biodegradation rate, a gradient occurred in the 80 kg reactor.

No significant results were seen for the degradation rates in the short-term aging experiments due to the small number of experiments, but there is evidence of contaminants being desorbed quicker than they are being degraded around the 10-day mark of the experiments using Elora soil. A slight increase in contaminants can be observed, especially when examining the data from the Elora-A series, where soil spiked and aged for over 300 days is re-spiked and re-aged, such as in the event of a second spill.

Overall, aging affects biodegradation rates in several aspects, changing sorption and desorption rates and affecting microbial biodegradation. The aging process and the soil properties both affect the overall bioventing remediation rates. More research is needed to pinpoint the exact effects of age to better estimate site closure times in the field.

CHAPTER 9: RECOMMENDATIONS

Further research into the effects of aging in petroleum hydrocarbon bioventing degradation rates would allow for better understanding of overall remediation rates. Different aging processes should be examined, such as dry-aging and wet-aging, to better understand how water content changes the rate of sorption and desorption in the soil. It is recommended for future research to spike the soil at much higher TPH concentration to allow for the contaminants to be aged without reaching the LOD of analytical devices for extractable petroleum compounds. Furthermore, abiotic controls during aging would allow the sorption to be quantified during the aging process, which would in turn allow the biodegradation to be quantified as well.

A wider range of petroleum products can be used to spike the soil, either as a single contaminant type or as a solution, to better understand how aging is affected by the different compound properties. In fact, the effects of age on real gasoline mix rather than the synthetic gasoline used in this research would confirm if the results derived from these experiments are applicable to field studies. More rigorous microbial analysis to qualify the change in microorganism quantity and composition during the aging process, or even in separate locations of the 80 kg reactor, would help understand the complex nature of biodegradation.

Scale-up factors between the 150 g and the 80 kg scale should be confirmed for other aging times before retiring the large-scaled reactor – a wider range of ages would allow for the effects of age on biodegradation to be highlighted, similar to the long-term experiments performed on the 150 g respirometers in this research. It would be interesting to see at what point the two-stage degradation rate becomes a single stage rate, and when the scale-up factor is no longer present between the two experiments. Longer aging times of over a year would have to be tested to see if the scale-up factor stays negligible or if the biodegradation rate in the 150 g reactor continues to increase.

REFERENCES

- AEP (2015). Petroleum Storage Tanks | AEP - Environment and Parks.
- Alexander, M. (2000). Aging, Bioavailability, and Overestimation of Risk from Environmental Pollutants. *Environ. Sci. Technol.* *34*, 4259–4265.
- ATSDR (1995a). Toxicological Profile for Polycyclic Aromatic Hydrocarbons.
- ATSDR (1995b). Public Health Statement: Total Petroleum Hydrocarbons (TPH).
- Bezerra, S.M., and Zytner, R. (2003). Bioventing of gasoline-contaminated soil: Some aspects for optimization.
- Brook, T.R., Stiver, W.H., and Zytner, R.G. (2001). Biodegradation of Diesel Fuel in Soil Under Various Nitrogen Addition Regimes. *Soil Sediment Contam. Int. J.* *10*, 539–553.
- CCME (2008). Canada-Wide Standards for Petroleum Hydrocarbons (PHC) in Soil (CCME).
- Cuypers, C., Clemens, R., Grotenhuis, T., and Rulkens, W. (2001). Prediction of Petroleum Hydrocarbon Bioavailability in Contaminated Soils and Sediments. *Soil Sediment Contam.* *10*, 459–482.
- Dibble, J.T., and Bartha, R. (1979). Effect of environmental parameters on the biodegradation of oil sludge. *Appl. Environ. Microbiol.* *37*, 729–739.
- Eriksson, M., Dalhammar, G., and Borg-Karlson, A.-K. (2000). Biological degradation of selected hydrocarbons in an old PAH/creosote contaminated soil from a gas work site. *Appl. Microbiol. Biotechnol.* *53*, 619–626.
- Eyvazi, M.J. (2011). An empirical correlation to estimate the bioventing degradation rate constant. University of Guelph.
- Eyvazi, M.J., and Zytner, R.G. (2009). A Correlation to Estimate the Bioventing Degradation Rate Constant. *Bioremediation J.* *13*, 141–153.
- Gidda T., Stiver W. H., and Zytner R. G. (2011). Measuring Aqueous-Air and Sorbed-Aqueous Mass Transfer Coefficients for Application in Soil Vapor Extraction. *J. Environ. Eng.* *137*, 880–888.
- Hinchee, R.E., and Leeson, A. (1996). *Soil Bioventing: Principles and Practice* (CRC Press).
- Hinchee, R.E., and Ong, S.K. (1992). A rapid in situ respiration test for measuring aerobic biodegradation rates of hydrocarbons in soil. *J. Air Waste Manag. Assoc.* *42*, 1305–1312.
- Huesemann, M. (2004). *Biodegradation and Bioremediation of Petroleum Pollutants in Soil*.
- Huesemann, M.H., Hausmann, T.S., and Fortman, T.J. (2002). Microbial Factors Rather Than Bioavailability Limit the Rate and Extent of PAH Biodegradation in Aged Crude Oil Contaminated Model Soils. *Bioremediation J.* *6*, 321–336.
- Huesemann, M.H., Hausmann, T.S., and Fortman, T.J. (2003). Assessment of bioavailability limitations during slurry biodegradation of petroleum hydrocarbons in aged soils. *Environ. Toxicol. Chem.* *22*, 2853–

2860.

Huesemann, M.H., Hausmann, T.S., and Fortman, T.J. (2005). Leaching of BTEX from Aged Crude Oil Contaminated Model Soils: Experimental and Modeling Results. *Soil Sediment Contam.* *14*, 545–558.

Jain, D.K., Lee, H., and Trevors, J.T. (1992). Effect of addition of *Pseudomonas aeruginosa* UG2 inocula or biosurfactants on biodegradation of selected hydrocarbons in soil. *J. Ind. Microbiol.* *10*, 87–93.

Jonsson, S., Persson, Y., Frankki, S., van Bavel, B., Lundstedt, S., Haglund, P., and Tysklind, M. (2007). Degradation of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils by Fenton's reagent: A multivariate evaluation of the importance of soil characteristics and PAH properties. *J. Hazard. Mater.* *149*, 86–96.

Kells, D. (2016). Email: dkells@uoguelph.ca. Tel: (519) 846-5521.

Khan, A.A., and Zytner, R.G. (2013). Degradation Rates for Petroleum Hydrocarbons Undergoing Bioventing at the Meso-Scale. *Bioremediation J.* *17*, 159–172.

Khan, A.A., Zytner, R.G., and Feng, Z. (2015). Establishing Correlations and Scale-Up Factor for Estimating the Petroleum Biodegradation Rate in Soil. *Bioremediation J.* *19*, 32–46.

Kloeper, S. (2016). Email: sandyk@titantrailers.com. Tel: (519) 688-4826.

Kreamer, D.K., and Stetzenbach, K.J. (1990). Development of a Standard, Pure-Compound Base Gasoline Mixture for Use as a Reference in Field and Laboratory Experiments. *Ground Water Monit. Remediat.* *10*, 135–145.

Kuppusamy, S., Palanisami, T., Megharaj, M., Venkateswarlu, K., and Naidu, R. (2016). Ex-Situ Remediation Technologies for Environmental Pollutants: A Critical Perspective. In *Reviews of Environmental Contamination and Toxicology Volume 236*, P. de Voogt, ed. (Cham: Springer International Publishing), pp. 117–192.

Lee, J.-Y., Lee, C.-H., Lee, K.-K., and Choi, S.-I. (2001). Evaluation of Soil Vapor Extraction and Bioventing for a Petroleum-Contaminated Shallow Aquifer in Korea. *Soil Sediment Contam. Int. J.* *10*, 439–458.

Loibner, A., Jensen, J., Ter Laak, T., Celis, R., and Hartnik, T. (2006). Sorption and ageing of soil contamination. *Ecol. Risk Assess. Contam. Land—decision Support Site Specif. Investig.* RIVM Rep.

McClure, P.D., and Sleep, B.E. (1996). Simulation of Bioventing for Soil and Ground-Water Remediation. *J. Environ. Eng.* *122*, 1003–1012.

MoE (2011). Soil, Ground Water and Sediment Standards for Use Under Part XV.1 of the Environmental Protection Act (Ministry of the Environment).

MoJ (2008). Storage Tank Systems for Petroleum Products and Allied Petroleum Products Regulations (Minister of Justice).

Møller, J., Winther, P., Lund, B., Kirkebjerg, K., and Westermann, P. (1996). Bioventing of diesel oil-contaminated soil: Comparison of degradation rates in soil based on actual oil concentration and on respirometric data. *J. Ind. Microbiol.* *16*, 110–116.

Mosco, M.J. (2016). Large Scale Bioventing Degradation Rates of Petroleum Hydrocarbon and Determination of Scale-up Factors. University of Guelph.

Mosco, M.J., and Zytner, R.G. (2017). Large-scale bioventing degradation rates of petroleum hydrocarbons and determination of scale-up factors. *Bioremediation J.* 21, 149–162.

Northcott, G.L., and Jones, K.C. (2001). Partitioning, Extractability, and Formation of Nonextractable PAH Residues in Soil. 1. Compound Differences in Aging and Sequestration. *Environ. Sci. Technol.* 35, 1103–1110.

OAGC (2012). Chapter 3—Federal Contaminated Sites and Their Impacts.

Onwurah, I.N.E. (2004). Modelling Cometabolism of Petroleum Hydrocarbon Pollutants in Soil by *Azotobacter vinelandii* in the Obligate Presence of *Pseudomonas sp.* *Bull. Environ. Contam. Toxicol.* 73, 690–697.

Piwoni, M.D., and Keeley, J.W. (1990). Basic Concepts of Contaminant Sorption at Hazardous Waste Sites (EPA).

Rathfelder, K.M., Lang, J.R., and Abriola, L.M. (2000). A numerical model (MISER) for the simulation of coupled physical, chemical and biological processes in soil vapor extraction and bioventing systems. *J. Contam. Hydrol.* 43, 239–270.

Reid, B.J., Jones, K.C., and Semple, K.T. (2000). Bioavailability of persistent organic pollutants in soils and sediments—a perspective on mechanisms, consequences and assessment. *Environ. Pollut.* 108, 103–112.

Sangster, J. (1989). Octanol-Water Partition Coefficients of Simple Organic Compounds. *J. Phys. Chem. Ref. Data.*

Schreck, E., Foucault, Y., Geret, F., Pradere, P., and Dumat, C. (2011). Influence of soil ageing on bioavailability and ecotoxicity of lead carried by process waste metallic ultrafine particles. *Chemosphere* 85, 1555–1562.

Schwab, A.P., Su, J., Wetzel, S., Pekarek, S., and Banks, M.K. (1999). Extraction of Petroleum Hydrocarbons from Soil by Mechanical Shaking. *Environ. Sci. Technol.* 33, 1940–1945.

Shewfelt, K., Lee, H., and Zytner, R.G. (2005). Optimization of nitrogen for bioventing of gasoline contaminated soil. *J. Environ. Eng. Sci.* 4, 29–42.

Tang, J., Lu, X., Sun, Q., and Zhu, W. (2012). Aging effect of petroleum hydrocarbons in soil under different attenuation conditions. *Agric. Ecosyst. Environ.* 149, 109–117.

TBCS (1994). Federal Contaminated Sites Inventory.

Udovic, M., and Lestan, D. (2009). Pb, Zn and Cd mobility, availability and fractionation in aged soil remediated by EDTA leaching. *Chemosphere* 74, 1367–1373.

US EPA (1995). Bioventing Principles and Practice Volume II: Bioventing Design.

US EPA (1996). Pump and Treat Ground-Water Remediation: A Guide for Decision Makers and Practitioners (United States Environmental Protection Agency).

US EPA (2013). Underground Storage Tanks (USTs).

Warrick, A.W. (2001). Soil Physics Companion (CRC Press).

WHO (2010). Exposure to Benzene: A Major Public Health Concern (Geneva, Switzerland: World Health Organization).

Wilson, D.J. (1995). Modeling of in situ techniques for treatment of contaminated soils: soil vapor extraction, sparging, and bioventing. Model. Situ Tech. Treat. Contam. Soils Soil Vap. Extr. Sparging Bioventing.

Yong, R.N. (2000). Geoenvironmental Engineering: Contaminated Soils, Pollutant Fate, and Mitigation (CRC Press).

Zytner, R.G. (1994). Sorption of benzene, toluene, ethylbenzene and xylenes to various media. J. Hazard. Mater. 38, 113–126.

Zytner, R.G., Salb, A.C., and Stiver, W.H. (2006). Bioremediation of Diesel Fuel Contaminated Soil: Comparison of Individual Compounds to Complex Mixtures. Soil Sediment Contam. Int. J. 15, 277–297.

APPENDIX A: SAMPLE CALCULATIONS

A.1: Nutrient Amendment Calculation

A 10:1 C:N ratio (by weight) is optimal for bioventing. Ammonium chloride NH_4Cl was used as the nitrogen source. In Table A-1, the synthetic gasoline composition in moles were calculated to determine the overall ratio of C:H molecules. The C:H ratio by weight could then be calculated using the molecular weights of carbon and hydrogen

Table A-1: calculation of C:H ratio by weight of synthetic gasoline

Synthetic gasoline Compound	%	Composition	C	H		C×%	H×%	
Isooctane	24.9	C_8H_{16}	8	16		1.992	3.984	
Toluene	36.1	C_7H_8	7	8		2.527	2.888	
m-xylene	23.9	C_8H_{10}	8	10		1.912	2.39	
Mesitylene	11.9	C_9H_{16}	9	16		1.071	1.904	
Naphthalene	3.2	$C_{10}H_8$	10	8		0.32	0.256	Σ
Σ Mole:						7.822	11.422	19.244
C:H ratio (by mole) in synthetic gasoline						0.4065	0.5935	100%
Convert mole to weight (g)						4.878	0.594	5.471
C:H ratio (by weight) in synthetic gasoline						0.892	0.108	100%

$$\text{Molecular weight of C: } \frac{12g}{mol}, \quad 12g * 0.406 = 4.878g$$

$$\text{Molecular weight of H: } \frac{1g}{mol}, \quad 1g * 0.594 = 0.594g$$

$$\text{Total weight} = 4.878 + 0.595 = 5.471g$$

$$\text{Weight Ratio C:H} = \frac{4.878}{5.471} : \frac{0.594}{5.471} = 0.892: 0.108$$

Assuming $2000 \text{ mg}_{\text{syngas}}/\text{kg}_{\text{soil}}$, the amount of carbon, by weight, was calculated to be $1783 \text{ mg}_C/\text{kg}_{\text{soil}}$, thus requiring $178 \text{ mg}_N/\text{kg}_{\text{soil}}$ to be added to the system. The nitrogen is amended to the soil in the form of ammonium chloride, which is 26.17% nitrogen by weight. As such, $680 \text{ mg}_{\text{NH}_4\text{Cl}}/\text{kg}_{\text{soil}}$ was required to achieve a 10:1 C:N ratio in the soil after aging.

$$\text{for } \frac{2000 \text{ mg}_{\text{syngas}}}{\text{kg}_{\text{soil}}}, C = 0.892 * 2000 = \frac{1783 \text{ mg}_C}{\text{kg}_{\text{soil}}}$$

$$\text{for 10:1 C:N (weight)}, \frac{178 \text{ mg}_N}{\text{kg}_{\text{soil}}}$$

$$\text{Molecular weight of } \text{NH}_4\text{Cl}: \frac{53.491 \text{ g}}{\text{mol}}, \quad \text{NH}_4\text{Cl is 26.17 wt\% N}$$

$$\frac{178 \text{ mg}_N}{\text{kg}_{\text{soil}}} \div \frac{100 \text{ mg}_{\text{NH}_4\text{Cl}}}{26.17 \text{ mg}_N} = \frac{680.17 \text{ mg}_{\text{NH}_4\text{Cl}}}{\text{kg}_{\text{soil}}}$$

A.2: Sample data processing, from GC-FID output to contaminant concentration in soil

To calculate the extracted contaminant and its concentration in soil, a calibration curve was created by plotting synthetic gasoline of known concentration against the area under the curve as outputted by the GC-FID, as seen in Figure A-1 and Table A-3. The linear interpolation was set to intercept at zero, in order to prevent any negative values and the slopes were recorded. The data output from the GC-FID, as seen in Table A-2, was then processed using the calculated slopes.

Table A-2: Output for sample run in file:MX170731

Sample	Soil (g)	MeCl (mL)	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
007F0201	2.9900	5	10135	22250	152252	60136	154603
008F0201	3.0095	5	9778	17808	121862	49261	129467
009F0201	2.9935	5	10483	19352	130148	55201	139430

Table A-3: Calibration curve data for MX170731

Concentration mg_{syngas} L_{MeCl}	Peak 1 Isooctane	Peak 2 Toluene	Peak 3 m-Xylene	Peak 4 Mesitylene	Peak 5 Naphthalene
10	4680	7485	5260	4138	743
10	4878	8138	5733	3238	857
10	4699	7997	5686	3065	873
100	48934	77981	53468	28632	8110
100	50133	81009	56057	29187	8652
100	51595	84944	59140	30744	9208
250	124677	198747	136521	70994	20900
250	130511	213332	148494	77006	23082
500	257368	409649	281605	145410	43100
500	293430	505790	354614	184221	55405
1000	501947	790030	542567	279051	83128
1000	527317	854818	593302	307179	92669
SLOPE	521.10	839.91	580.38	300.16	89.883

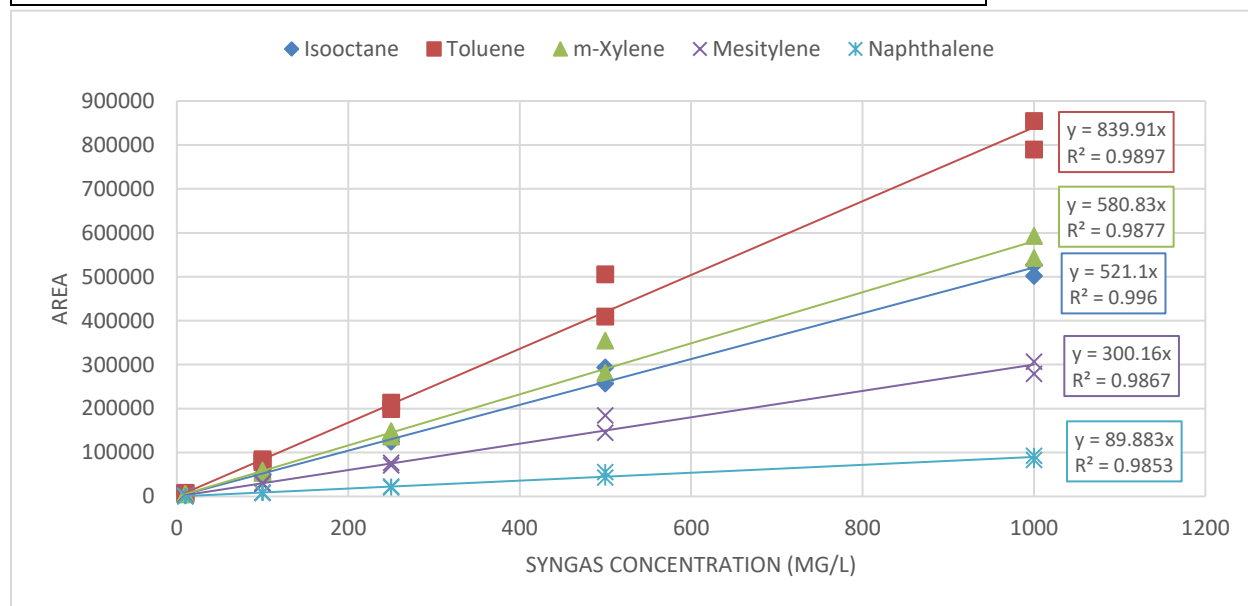


Figure A-1: Calibration curve for MX170731

Taking sample 007F0201, the area output was converted into concentration ($mg_{compound}/L_{MeCl}$) using the slopes calculated from the calibration curve. This was then converted into the desired concentration (mg_{syngas}/kg_{soil}) as seen in Table A-4 using the following equations:

$$\begin{aligned} \text{Concentration} \left(\frac{mg_{syngas}}{L_{MeCl}} \right) &= \frac{\text{Area}}{\text{Slope}} \\ \text{Concentration} \left(\frac{mg_{compound}}{L_{MeCl}} \right) &= \left(\frac{mg_{syngas}}{L_{MeCl}} \right) \times (\% \text{syngas composition}) \\ \text{Concentration} \left(\frac{mg_{syngas}}{kg_{soil}} \right) &= \left(\frac{mg_{compound}}{L_{MeCl}} \right) \times \frac{MeCl(L)}{soil(Kg)} = \left(\frac{mg_{compound}}{L_{MeCl}} \right) \times \frac{5}{2.99} \end{aligned}$$

Table A-4: Data processing for sample 007F0201 in file MX170731

SAMPLE 007F0201	PEAK 1 ISOCTANE	PEAK 2 TOLUENE	PEAK 3 M-XYLENE	PEAK 4 MESITYLENE	PEAK 5 NAPHTHALENE
SYNTHETIC GASOLINE COMPOSITION	24.90%	36.10%	23.90%	11.90%	3.20%
CALIBRATION CURVE SLOPE	521.10	839.91	580.82	300.16	89.883
OUTPUT (AREA)	10135	22250	152252	60136	154603
CONCENTRATION (MG_{COMPOUND}/L_{MECL})	4.843	9.563	62.650	23.841	55.041
CONCENTRATION (MG_{SYNTHETIC GASOLINE}/KG_{SOIL})	8.099	15.992	104.766	3.868	92.042

Table A-5: Processed data for file:MX170731

Sample	Soil (g)	MeCl (mL)	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
007F0201	2.9900	5	8.0984	15.9920	104.7655	39.8683	92.0427
008F0201	3.0095	5	7.7625	12.7164	83.3106	32.4469	76.5786
009F0201	2.9935	5	8.3667	13.8928	89.4509	36.5537	82.9124

The processed data with the appropriate concentrations are shown in Table A-5. The full list of processed data available in Appendix C.

APPENDIX B: EXPERIMENTAL CONDITIONS – DATA

B.1: Biotic Control Data

Table B-1: Data for biotic controls run during Delhi-LT-150g experiments

FILE NAME	VIAL NUMBER	VIAL NAME	EXTRACTION DATE	TOTAL TPH	NOTES
mx161212	011F0201	M0D30-02	2016-12-07	95.4654	
mx161212	012F0201	M0D30-02	2016-12-07	99.3682	
mx161212	013F0201	M0D30c-01	2016-12-07	0.0000	Control
mx161212	014F0201	M0D30c-03	2016-12-07	0.0000	Control
mx170223	016F0201	M0D30-01	2017-02-09	280.6418	
mx170223	017F0201	M0D30-02	2017-02-09	138.3196	
mx170223	018F0201	M0D30-01C	2017-02-09	0.0000	Control
mx170223	019F0201	M0D30-02C	2017-02-09	0.0000	Control
mx170223	020F0201	M0D30-03C	2017-02-09	0.0000	Control
mx170223	021F0201	M2D30-01	2017-02-09	58.3715	
mx170223	022F0201	M2D30-02	2017-02-09	285.3022	
mx170223	023F0201	M2D30-03	2017-02-09	212.0857	
mx170223	024F0201	M2D30-01C	2017-02-09	0.0000	Control
mx170223	025F0201	M2D30-02C	2017-02-09	0.0000	Control
mx170223	026F0201	M2D30-03C	2017-02-09	0.0000	Control
mx170605	054F0801	May-D30-1	2017-06-05	6.9465	
mx170605	055F0801	May-D30-2	2017-06-05	7.8781	
mx170605	056F0801	May-D30-3	2017-06-05	7.5483	
mx170605	057F0801	May-D30-4	2017-06-05	0.0000	Control
mx170605	058F0801	May-D30-5	2017-06-05	0.0000	Control
mx170605	059F0801	May-D30-6	2017-06-05	0.0000	Control
mx170523	007F0101	D30-1A	2017-04-21	17.5146	
mx170523	008F0101	D30-2A	2017-04-21	18.7340	
mx170523	009F0101	D30-3A	2017-04-21	17.5394	
mx170523	010F0101	D30-1	2017-04-21	0.0000	Control
mx170523	011F0101	D30-2	2017-04-21	0.0000	Control
MX170716	047F0301	June-150-D30-1	2017-07-12	0.7057	
MX170716	048F0301	June-150-D30-2	2017-07-12	0.5885	
MX170716	049F0301	June-150-D30-3	2017-07-12	0.4801	
MX170716	050F0301	June-150-D30-B1	2017-07-12	0.0000	Control
MX170716	051F0301	June-150-D30-B2	2017-07-12	0.0000	Control
MX170716	052F0301	June-150-D30-B3	2017-07-12	0.0000	Control

B.2: Delhi-270-80kg – Operating Conditions

Table B-2: Off gases for Delhi-270-80kg experiments

Extraction Date	Isooctane	Toluene	m-xylene	Mesitylene	Naphthalene	Total off gases (mg/kg carbon)	Total synthetic gasoline (mg)
2017-05-14	23598.78	13879.87	25906.99	19912.26	259.1597	83557.06	8.355706
2017-05-15	20789.65	11503.82	20865.95	13797	38.66021	66995.08	6.699508
2017-05-16	23027.82	10775.32	25321.66	18295.53	71.95095	77492.27	7.749227
2017-05-17	5922.954	2279.381	4186.362	4021.638	0	16410.33	1.641033
2017-05-18	21941.1	6350.579	23534.18	21589.12	59.80768	73474.79	7.347479
2017-05-19	33983.32	5184.582	29083.42	32335.01	33.73682	100620.1	10.06201
2017-05-20	23927.57	1698.184	15945.98	19561.37	0	61133.1	6.11331
2017-05-21	17086.97	635.5271	10449.77	13320.24	0	41492.5	4.14925
2017-05-22	25373.8	616.4952	16631.93	23816.24	41.25408	66479.72	6.647972
2017-05-23	17082.59	229.6398	9562.093	14109.45	0	40983.78	4.098378
2017-05-24	23434.28	197.4321	12534.02	22873.7	1769.836	60809.27	6.080927
2017-05-25	17460.61	111.4884	9473.871	21072.04	0	48118.01	4.811801
2017-05-26	23600.96	104.1685	10341.86	24328.18	0	58375.18	5.837518
2017-05-27	14089.9	44.97074	5461.355	16217.73	0	35813.96	3.581396
2017-05-28	11858.42	36.60646	4187.191	13189.79	0	29272.01	2.927201
2017-05-29	13277.65	35.09347	4002.615	16715.83	0	34031.19	3.403119
2017-05-30	16699.12	34.79873	4185.987	22023.27	0	42943.18	4.294318
2017-05-31	6073.037	0	1097.7	6476.303	0	13647.04	1.364704
2017-06-01	9062.007	0	1511.783	9640.59	0	20214.38	2.021438
2017-06-02	4028.641	0	561.3739	3766.809	0	8356.823	0.835682
2017-06-03	5305.419	0	627.3177	4974.038	0	10906.78	1.090678
2017-06-04	9412.963	0	880.2627	7421.198	0	17714.42	1.771442
2017-06-05	4916.827	0	527.3103	5796.845	0	11240.98	1.124098
2017-06-06	12312.35	0	1225.058	11943.86	0	25481.27	2.548127
2017-06-07	5618.481	0	448.8995	5780.193	0	11847.57	1.184757

2017-06-08	1125.937	0	79.5520 6	1174.822	0	2380.311	0.238031
2017-06-09	4107.168	0	236.354	4452.012	0	8795.534	0.879553
2017-06-10	10324.91	0	423.753	9532.17	0	20280.83	2.028083
2017-06-11	4430.954	0	148.419 8	3722.595	0	8301.969	0.830197
2017-06-12	0	0	0	0	7.214956	0	0

Table B-3: Oxygen levels during the Delhi-270-80kg experiment

DATE	DAY	O2 (%)
13-May	0	20.9
14-May	1	20.9
15-May	2	21
16-May	3	21.1
17-May	4	20.9
18-May	5	21.4
19-May	6	20.2
20-May	7	21.8
21-May	8	21.3
22-May	9	21.1
23-May	10	20.9
24-May	11	20.9
25-May	12	20.8
26-May	13	20.7
27-May	14	20.8
28-May	15	20.7
29-May	16	20.6
30-May	17	20.9
31-May	18	20.7
01-Jun	19	20.8
02-Jun	20	20.8
03-Jun	21	20.9
04-Jun	22	20.8
05-Jun	23	20.7
06-Jun	24	20.6
07-Jun	25	20.7
08-Jun	26	20.8
09-Jun	27	20.8
10-Jun	28	20.9
11-Jun	29	21.2
12-Jun	30	21.4

Table B-4: Volumetric Water Content and Gravimetric Water Content during the Delhi-270-80kg experiment

DELHI 270 RUN TIME		VOLUMETRIC WATER CONTENT (%)		GRAVIMETRIC WATER CONTENT (%)	
Hours	Days	Interior	Exterior	Interior	Exterior
0	0	30.7	32.4	19.80645	20.90323
3	0.125	31	32.5	20	20.96774
6	0.25	31	32.7	20	21.09677
9	0.375	31.1	32.7	20.06452	21.09677
12	0.5	31.1	32.7	20.06452	21.09677
15	0.625	31.1	32.8	20.06452	21.16129
18	0.75	31.2	32.8	20.12903	21.16129
21	0.875	31.2	32.9	20.12903	21.22581
24	1	31.4	32.9	20.25806	21.22581
27	1.125	31.6	33.2	20.3871	21.41935
30	1.25	31.6	33.2	20.3871	21.41935
33	1.375	31.8	33.4	20.51613	21.54839
36	1.5	31.9	33.4	20.58065	21.54839
39	1.625	31.9	33.5	20.58065	21.6129
42	1.75	31.9	33.5	20.58065	21.6129
45	1.875	32.1	33.6	20.70968	21.67742
48	2	32.1	33.6	20.70968	21.67742
51	2.125	32.1	33.8	20.70968	21.80645
54	2.25	32.2	33.8	20.77419	21.80645
57	2.375	32.2	33.9	20.77419	21.87097
60	2.5	32.2	33.8	20.77419	21.80645
63	2.625	32.2	33.9	20.77419	21.87097
66	2.75	32.2	33.9	20.77419	21.87097
69	2.875	32.3	33.9	20.83871	21.87097
72	3	32.3	34	20.83871	21.93548
75	3.125	32.5	34	20.96774	21.93548
78	3.25	32.5	34.2	20.96774	22.06452
81	3.375	32.3	34	20.83871	21.93548
84	3.5	32.1	34.2	20.70968	22.06452
87	3.625	32.2	34.3	20.77419	22.12903
90	3.75	32.2	34.3	20.77419	22.12903
93	3.875	32.2	34.3	20.77419	22.12903
96	4	32.2	34.4	20.77419	22.19355
99	4.125	31.9	34.3	20.58065	22.12903
102	4.25	31.9	34.3	20.58065	22.12903
105	4.375	31.8	34	20.51613	21.93548
108	4.5	31.6	34	20.3871	21.93548
111	4.625	31.5	34	20.32258	21.93548
114	4.75	31.4	34	20.25806	21.93548
117	4.875	31.4	34	20.25806	21.93548
120	5	31.2	34.2	20.12903	22.06452

121	5.041667	31.1	33.9	20.06452	21.87097
124	5.166667	31.6	34	20.3871	21.93548
127	5.291667	31.6	33.9	20.3871	21.87097
130	5.416667	31.4	33.8	20.25806	21.80645
133	5.541667	31.4	33.8	20.25806	21.80645
136	5.666667	31.2	33.9	20.12903	21.87097
139	5.791667	31.2	33.9	20.12903	21.87097
142	5.916667	31.1	33.9	20.06452	21.87097
145	6.041667	30.6	33.4	19.74194	21.54839
148	6.166667	30.2	32.9	19.48387	21.22581
151	6.291667	30	32.8	19.35484	21.16129
154	6.416667	29.6	32.5	19.09677	20.96774
157	6.541667	29.5	32.3	19.03226	20.83871
160	6.666667	29.3	31.7	18.90323	20.45161
163	6.791667	28.9	31.3	18.64516	20.19355
166	6.916667	28.9	31.1	18.64516	20.06452
169	7.041667	28.8	30.7	18.58065	19.80645
172	7.166667	28.5	30.5	18.3871	19.67742
175	7.291667	28.4	30.3	18.32258	19.54839
178	7.416667	28.1	30	18.12903	19.35484
241	10.04167	26	27.1	16.77419	17.48387
244	10.16667	26	27.1	16.77419	17.48387
247	10.29167	26	27.1	16.77419	17.48387
250	10.41667	26.1	27	16.83871	17.41935
253	10.54167	26	27	16.77419	17.41935
256	10.66667	26	27	16.77419	17.41935
259	10.79167	26	27	16.77419	17.41935
262	10.91667	25.8	27	16.64516	17.41935
265	11.04167	25.8	27	16.64516	17.41935
268	11.16667	25.8	26.9	16.64516	17.35484
271	11.29167	25.8	26.9	16.64516	17.35484
274	11.41667	25.8	26.9	16.64516	17.35484
277	11.54167	25.8	26.9	16.64516	17.35484
280	11.66667	25.7	26.7	16.58065	17.22581
283	11.79167	25.7	26.6	16.58065	17.16129
286	11.91667	25.7	26.7	16.58065	17.22581
289	12.04167	25.6	26.5	16.51613	17.09677
292	12.16667	25.7	26.6	16.58065	17.16129
295	12.29167	25.6	26.5	16.51613	17.09677
298	12.41667	25.6	26.5	16.51613	17.09677
301	12.54167	25.6	26.5	16.51613	17.09677
304	12.66667	25.6	26.3	16.51613	16.96774
307	12.79167	25.6	26.3	16.51613	16.96774
310	12.91667	25.4	26.3	16.3871	16.96774
313	13.04167	25.6	26.3	16.51613	16.96774

316	13.16667	25.6	26.3	16.51613	16.96774
319	13.29167	25.6	26.2	16.51613	16.90323
322	13.41667	25.6	26.3	16.51613	16.96774
325	13.54167	25.6	26.3	16.51613	16.96774
328	13.66667	25.6	26.3	16.51613	16.96774
331	13.79167	25.4	26.2	16.3871	16.90323
334	13.91667	25.6	26.1	16.51613	16.83871
337	14.04167	25.6	26.2	16.51613	16.90323
340	14.16667	25.6	26.2	16.51613	16.90323
343	14.29167	25.6	26.1	16.51613	16.83871
346	14.41667	25.6	26.2	16.51613	16.90323
349	14.54167	25.7	26.2	16.58065	16.90323
352	14.66667	25.6	26.2	16.51613	16.90323
355	14.79167	25.6	26.1	16.51613	16.83871
358	14.91667	25.6	25.9	16.51613	16.70968
361	15.04167	25.4	25.9	16.3871	16.70968
385	16.04167	25.4	25.8	16.3871	16.64516
388	16.16667	25.3	25.8	16.32258	16.64516
391	16.29167	25.4	25.8	16.3871	16.64516
394	16.41667	25.6	25.8	16.51613	16.64516
397	16.54167	25.4	25.8	16.3871	16.64516
400	16.66667	25.3	25.8	16.32258	16.64516
403	16.79167	25.3	25.7	16.32258	16.58065
406	16.91667	25.2	25.7	16.25806	16.58065
409	17.04167	25.2	25.7	16.25806	16.58065
412	17.16667	25.2	25.7	16.25806	16.58065
415	17.29167	25.2	25.7	16.25806	16.58065
418	17.41667	25.2	25.5	16.25806	16.45161
421	17.54167	25.2	25.5	16.25806	16.45161
424	17.66667	25	25.5	16.12903	16.45161
427	17.79167	25	25.4	16.12903	16.3871
430	17.91667	24.9	25.4	16.06452	16.3871
433	18.04167	24.9	25.4	16.06452	16.3871
436	18.16667	24.9	25.4	16.06452	16.3871
439	18.29167	24.9	25.4	16.06452	16.3871
442	18.41667	24.9	25.4	16.06452	16.3871
445	18.54167	24.9	25.4	16.06452	16.3871
448	18.66667	24.8	25.3	16	16.32258
451	18.79167	24.8	25.3	16	16.32258
454	18.91667	24.6	25.3	15.87097	16.32258
457	19.04167	24.8	25	16	16.12903
460	19.16667	24.6	25	15.87097	16.12903
463	19.29167	24.6	25	15.87097	16.12903
466	19.41667	24.6	25	15.87097	16.12903
469	19.54167	24.6	25	15.87097	16.12903

472	19.66667	24.5	25	15.80645	16.12903
475	19.79167	24.5	24.9	15.80645	16.06452
478	19.91667	24.4	24.9	15.74194	16.06452
481	20.04167	24.4	24.7	15.74194	15.93548
484	20.16667	24.5	24.9	15.80645	16.06452
487	20.29167	24.5	24.7	15.80645	15.93548
490	20.41667	24.5	24.7	15.80645	15.93548
493	20.54167	24.5	24.7	15.80645	15.93548
496	20.66667	24.4	24.7	15.74194	15.93548
499	20.79167	24.2	24.7	15.6129	15.93548
502	20.91667	24.1	24.6	15.54839	15.87097
505	21.04167	24.1	24.6	15.54839	15.87097
508	21.16667	24.2	24.6	15.6129	15.87097
511	21.29167	24.2	24.6	15.6129	15.87097
514	21.41667	24.2	24.7	15.6129	15.93548
517	21.54167	24.2	24.6	15.6129	15.87097
520	21.66667	24.1	24.6	15.54839	15.87097
523	21.79167	24.1	24.6	15.54839	15.87097
526	21.91667	24.1	24.5	15.54839	15.80645
529	22.04167	24	24.3	15.48387	15.67742
532	22.16667	24.1	24.3	15.54839	15.67742
535	22.29167	24.1	24.3	15.54839	15.67742
538	22.41667	24.2	24.3	15.6129	15.67742
541	22.54167	24.2	24.5	15.6129	15.80645
544	22.66667	24.2	24.5	15.6129	15.80645
547	22.79167	24.1	24.3	15.54839	15.67742
550	22.91667	24.1	24.3	15.54839	15.67742
553	23.04167	24	24.3	15.48387	15.67742
556	23.16667	24.1	24.2	15.54839	15.6129
559	23.29167	24.1	24.3	15.54839	15.67742
562	23.41667	24.1	24.3	15.54839	15.67742
565	23.54167	24	24.2	15.48387	15.6129
568	23.66667	24	24.2	15.48387	15.6129
571	23.79167	24	24.3	15.48387	15.67742
574	23.91667	23.8	24.3	15.35484	15.67742
577	24.04167	24.1	24.2	15.54839	15.6129
580	24.16667	24	24.2	15.48387	15.6129
583	24.29167	24	24.2	15.48387	15.6129
586	24.41667	24	24.2	15.48387	15.6129
589	24.54167	24	24.3	15.48387	15.67742
592	24.66667	24.1	24.2	15.54839	15.6129
595	24.79167	23.8	24.2	15.35484	15.6129
598	24.91667	23.7	24.2	15.29032	15.6129
601	25.04167	23.7	23.9	15.29032	15.41935
604	25.16667	23.7	24	15.29032	15.48387

607	25.29167	23.7	23.9	15.29032	15.41935
610	25.41667	23.7	24	15.29032	15.48387
613	25.54167	23.7	24	15.29032	15.48387
616	25.66667	23.3	23.9	15.03226	15.41935
619	25.79167	23.3	23.9	15.03226	15.41935
622	25.91667	23.1	23.9	14.90323	15.41935
625	26.04167	23.3	23.9	15.03226	15.41935
649	27.04167	23	23.4	14.83871	15.09677
652	27.16667	23.1	23.4	14.90323	15.09677
655	27.29167	23.3	23.8	15.03226	15.35484
658	27.41667	23.1	23.8	14.90323	15.35484
661	27.54167	23.1	23.5	14.90323	15.16129
664	27.66667	23.1	23.5	14.90323	15.16129
667	27.79167	23	23.8	14.83871	15.35484
670	27.91667	23	23.4	14.83871	15.09677
673	28.04167	23.1	23.2	14.90323	14.96774
676	28.16667	23.1	23.2	14.90323	14.96774
679	28.29167	23.1	23.2	14.90323	14.96774
682	28.41667	23.3	23.2	15.03226	14.96774
685	28.54167	23.1	23.2	14.90323	14.96774
688	28.66667	23.1	23.2	14.90323	14.96774
691	28.79167	23.1	23.2	14.90323	14.96774
694	28.91667	23	23.1	14.83871	14.90323
697	29.04167	23	23.2	14.83871	14.96774
700	29.16667	23	23.1	14.83871	14.90323
703	29.29167	23	23.1	14.83871	14.90323
706	29.41667	23	23.1	14.83871	14.90323
709	29.54167	22.9	23.1	14.77419	14.90323
712	29.66667	22.7	22.8	14.64516	14.70968
715	29.79167	22.6	22.7	14.58065	14.64516
718	29.91667	22.5	22.7	14.51613	14.64516
721	30.04167	22.5	22.7	14.51613	14.64516
724	30.16667	22.6	22.7	14.58065	14.64516

B.3: Delhi-300-80kg – Operating Conditions

Table B-5: Off gases for Delhi-300-80kg experiments

Extraction Date	Isooctane	Toluene	m-xylene	Mesitylene	Naphthalene	Total off gases (mg/kg carbon)	Total synthetic gasoline (mg)
2017-06-17	8361.65	1577.96	124215.3	212473	63.96897	346691.9	34.66919
2017-06-18	48431.07	3028.502	83794.22	148160.3	305.0377	283719.2	28.37192
2017-06-19	1001.871	0	758.0823	2206.217	0	3966.17	0.396617
2017-06-21	33707.18	26.00025	5182.276	101010.7	131.6704	140057.8	14.00578
2017-06-19	3545.822	753.1095	30057.36	89597.86	137.9688	124092.1	12.40921
2017-06-20	36860.15	113.4111	13336.63	105958.8	234.9937	156504	15.6504
2017-06-21	30008.97	23.84669	4635.955	89972.15	116.4665	124757.4	12.47574
2017-06-22	16534.65	0	1269.044	44412.69	43.0384	62259.42	6.225942
2017-06-24	14733.06	0	712.2868	36669.59	51.58037	52166.52	5.216652
2017-06-25	11539.77	0	329.2155	25384.86	25.57116	37279.41	3.727941
2017-06-26	13881.18	0	376.9435	25426.73	51.55108	39736.41	3.973641
2017-06-27	14651.56	0	230.155	15889.74	18.5222	30789.97	3.078997
2017-06-28	9789.814	0	175.17	10605.41	23.96617	20594.36	2.059436
2017-06-29	11880.88	0	164.3249	8965.661	21.29974	21032.16	2.103216
2017-06-30	7445.715	114.5082	170.1757	4858.094	14.12576	12602.62	1.260262
2017-07-01	9979.259	0	129.456	4104.336	21.20506	14234.26	1.423426
2017-07-02	3552.607	0	38.03685	986.0898	0	4576.734	0.457673
2017-07-03	2538.867	0	38.05029	782.8725	0	3359.79	0.335979
2017-07-04	5558.144	0	54.88539	1129.493	10.21634	6752.739	0.675274
2017-07-06	2748.47	0	16.33798	346.2868	0	3111.094	0.311109
2017-07-07	5479.042	0	49.39013	1043.62	16.63283	6588.685	0.658869
2017-07-08	4757.632	0	23.0962	505.1245	0	5285.852	0.528585
2017-07-09	1270.397	0	0	198.4702	0	1468.867	0.146887
2017-07-10	3510.088	0	16.76792	436.714	0	3963.57	0.396357
2017-07-11	0	0	0	0	0	0	0
2017-07-12	3007.326	11.7653	16.26718	397.2237	0	3432.582	0.343258
2017-07-13	3295.111	0	14.13658	376.8013	0	3686.049	0.368605

2017-07-14	2515.857	0	0	228.2103	0	2744.067	0.274407
2017-07-15	2915.688	0	10.0153 6	254.6366	0	3180.34	0.318034
2017-07-16	2215.067	0	0	189.1105	0	2404.178	0.240418

Table B-6: Oxygen levels during the Delhi-300-80kg experiment

DATE	DAY	O2 (%)
16-Jun	0	20.7
17-Jun	1	20.5
18-Jun	2	20.3
19-Jun	3	20.5
20-Jun	4	20.6
21-Jun	5	20.5
22-Jun	6	20.6
23-Jun	7	20.3
24-Jun	8	20.5
25-Jun	9	20.6
26-Jun	10	20.6
27-Jun	11	20.6
28-Jun	12	20.7
29-Jun	13	20.5
30-Jun	14	20.5
01-Jul	15	20.6
02-Jul	16	20.7
03-Jul	17	20.8
04-Jul	18	20.9
05-Jul	19	21
06-Jul	20	20.7
07-Jul	21	20.6
08-Jul	22	20.6
09-Jul	23	20.9
10-Jul	24	20.7
11-Jul	25	20.6
12-Jul	26	20.9
13-Jul	27	20.8
14-Jul	28	20.7
15-Jul	29	20.7
16-Jul	30	20.6

Table B-6: Volumetric Water Content and Gravimetric Water Content during the Delhi-300-80kg experiment

DELHI 300 RUN TIME		VOLUMETRIC WATER CONTENT (%)		GRAVIMETRIC WATER CONTENT (%)	
Hours	Days	Interior	Exterior	Interior	Exterior
0	0	24.6	25	15.87097	16.12903
12	0.5	28.8	24.5	18.58065	15.80645
24	1	28.1	23.8	18.12903	15.35484
36	1.5	26.9	23.2	17.35484	14.96774
48	2	26.1	23.2	16.83871	14.96774
60	2.5	25.4	22.8	16.3871	14.70968
72	3	25	22.8	16.12903	14.70968
84	3.5	24.6	22.7	15.87097	14.64516
96	4	24.5	22.6	15.80645	14.58065
108	4.5	24.1	22.6	15.54839	14.58065
114	4.75	24.1	22.4	15.54839	14.45161
126	5.25	24.1	22.4	15.54839	14.45161
138	5.75	23.7	22.2	15.29032	14.32258
150	6.25	23.8	22.3	15.35484	14.3871
162	6.75	23.8	22.4	15.35484	14.45161
174	7.25	24	22.4	15.48387	14.45161
186	7.75	23.8	22.4	15.35484	14.45161
198	8.25	23.8	22.4	15.35484	14.45161
210	8.75	23.7	22.3	15.29032	14.3871
222	9.25	23.3	22.4	15.03226	14.45161
234	9.75	23.1	22.3	14.90323	14.3871
258	10.75	23	22.2	14.83871	14.32258
270	11.25	23.1	22.2	14.90323	14.32258
282	11.75	23	22	14.83871	14.19355
294	12.25	23	22.2	14.83871	14.32258
306	12.75	23	22.2	14.83871	14.32258
318	13.25	23	22.2	14.83871	14.32258
330	13.75	23.1	22.2	14.90323	14.32258
342	14.25	23	22.2	14.83871	14.32258
354	14.75	23	22	14.83871	14.19355
355	14.79167	23	22	14.83871	14.19355
367	15.29167	23	22	14.83871	14.19355
379	15.79167	23	22	14.83871	14.19355
391	16.29167	23	22	14.83871	14.19355
403	16.79167	22.7	21.9	14.64516	14.12903
415	17.29167	22.6	21.8	14.58065	14.06452
427	17.79167	22.5	21.6	14.51613	13.93548
439	18.29167	22.6	21.6	14.58065	13.93548
451	18.79167	22.5	21.6	14.51613	13.93548
463	19.29167	22.3	21.6	14.3871	13.93548
475	19.79167	22.2	21.6	14.32258	13.93548

500	20.83333	22.3	21.5	14.3871	13.87097
512	21.33333	22.5	21.6	14.51613	13.93548
524	21.83333	22.3	21.6	14.3871	13.93548
536	22.33333	22.1	21.5	14.25806	13.87097
548	22.83333	22.1	21.4	14.25806	13.80645
560	23.33333	22.2	21.4	14.32258	13.80645
572	23.83333	22.3	21.5	14.3871	13.87097
584	24.33333	22.5	21.5	14.51613	13.87097
596	24.83333	22.5	21.5	14.51613	13.87097
608	25.33333	22.6	21.5	14.58065	13.87097
620	25.83333	22.6	21.6	14.58065	13.93548
629	26.20833	22.6	21.4	14.58065	13.80645
641	26.70833	22.3	21.4	14.3871	13.80645
653	27.20833	22.5	21.2	14.51613	13.67742
665	27.70833	22.3	21.1	14.3871	13.6129
677	28.20833	22.3	21.2	14.3871	13.67742
689	28.70833	22.3	21.1	14.3871	13.6129
701	29.20833	22.3	21.2	14.3871	13.67742
713	29.70833	22.2	21.1	14.32258	13.6129
725	30.20833	22.1	21.1	14.25806	13.6129
737	30.70833	22.1	21.1	14.25806	13.6129
749	31.20833	21.9	21	14.12903	13.54839

B.4: 150g Experiments – Operating Conditions

B.4-1 Delhi-270-150g and Delhi-300-150g

Table B-7: Operating conditions for the Delhi-270-150g and Delhi-300-150g experiment, detailing the soil pH, KOH pH, and Water Content

Delhi-270-150g			
Day	pH	KOH	WC (%)
0	7.32	13.57	40.91273
0	7.32		43.26502
0			41.08856
0			45.64819
3	6.51	13.58	12.57355
3	6.62	13.55	12.55107
3			12.23187
3			12.11164
8	6.54	13.4	12.66329
8	6.64	13.36	12.43984
8			12.69894
8			12.48108
14	7.12	13.43	12.47881
14	7	13.41	13.15829
18	7.12	13.43	11.5825
18	7.08	13.41	11.6286
18			11.90825
18			12.07278
21	6.5	13.9	14.17184
21	6.75	13.92	11.96928
21			12.81117
21			12.79928
30	6.82	13.9	12.73649
30			12.45929
30	6.75	13.92	10.96879
30			13.71857

Delhi-300-150g			
Day	pH	KOH	WC (%)
0	7.39	14.03	13.84218
0	7.1	14.04	15.05034
1	7.15	14.02	13.47615
1	7.08	14.01	13.4348
3	6.53	14.01	
3	6.21	14.03	
5	6.95	14.02	13.15789
5	7	14.03	13.21344
7	6.67	14.07	13.54607
7	6.56	14.08	13.60932
11	7.27	14.1	12.43875
11	7.23		14.47062
15	6.25	13.6	
15	6.1	13.61	
20	6.79	13.54	12.5454
20	6.82	13.54	12.47874
30	7.45	13.51	13.08183
30	7.46	13.49	12.11724

B.4-2 Long-Term Aging

Table B-8: Operating conditions for the Delhi-LT-150g experiments, detailing the soil pH, KOH pH, and Water Content. (*) Biotic Control

Nov 2016 – 0 Days Aging			
Day	pH	KOH	MC (%)
0	6.23		16.25128
3	5.99		16.36709
8	6.22		15.76266
17	NA		16.28857
30	6.3		15.78327
30*	5.01		17.75544
Jan 2017 – 0 Days Aging			
Day	pH	KOH	MC (%)
0	6.5	13.67	15.0702
3		13.7	15.49953
9	5.88	13.56	15.37502
14	6.43	13.38	15.55382
30*	6.4	13.56	19.30992
30	5.22	13.41	15.57714
Jan 2017 – 64 Days Aging			
Day	pH	KOH	MC (%)
0	6.38		16.44241
3		13.67	16.02263
9	6.09	13.56	15.81012
14	6.34	13.42	15.48469
30	6.26	13.48	15.32237
30*	5.03	13.28	16.64228
Mar 2017 – 132 Days Aging			
Day	pH	KOH	MC (%)
0	6.98	13.46	16.4156
3	6.74	13.47	14.38513
9	6.77	13.59	15.80617
15	7.07	13.52	14.6656
33			16.28938
33*			16.41793

May 2017 – 177 Days Aging			
Day	pH	KOH	MC (%)
0	7.09	13.61	15.8262
0			15.95324
2	6.55	13.38	16.01486
2			15.73593
7	7.06	13.36	15.34696
7			15.61562
14	7.24	10.58	15.31084
14			15.62732
33	6.32	10.16	17.24277
33	6.51	9.29	14.59709
Jun 2017 – 217 Days Aging			
Day	pH	KOH	MC (%)
0	NA	14	15.49435
3	7.34	13.9	15.26803
8	6.41	13.79	15.24965
15	7	12.94	15.07234
30	7.46	9.78	15.14184
30*	7.6	12.88	11.93237
Jul 2017 – 245 Days Aging			
Day	pH	KOH	MC (%)
0		13.63	30.01229
3	7.22	13.58	
8	7.29	13.63	
14	7.28	13.44	5.998255
30	7.77	10.42	14.99788

Sept 2017 – 305 Days Aging			
Day	pH	KOH	MC (%)
0	7.89	14.04	14.40601
0	8	14.07	14.51508
2	7.92	12	13.97252
2	9.87	12.01	14.0995
5	7.85	13.9	16.79455
5	7.52	13.92	15.93001
8	7.99	13.81	
8	7.93		
12	8.04	13.66	
12	7.96	13.5	
15	8.12	13.49	13.43605
15	8.27	12.03	14.069
31	8.3	12.93	
31	8.35	10.63	
31*	8.25	13.77	
31*	8.27	13.76	

B.4-3 Short-Term Aging

Table B-9: Operating conditions for the Delhi-150g short term experiments, detailing the soil pH, KOH pH, and Water Content.

Delhi - 0 Day Aging			
Day	pH	KOH	MC (%)
0	6.9	14.04	14.3899
0	6.88	14.04	14.6063
1	6.44	14.04	
1	6.47	14.02	
3	6.89	13.93	14.14869
3	6.83	13.92	13.85236
5		13.96	
5		13.94	
7	6.96	13.59	13.82762
7	7.02	13.71	13.99132
9	7.05	14.04	29.56782
9	6.98	14.08	13.64404
15	6.64	13.37	14.27204
15	6.61	13.41	13.43821
20	6.47	13.54	
20	6.52	13.56	
30	7.53	13.35	13.59186
30	7.4	13.37	13.61366
Delhi - 15 Day Aging			
Day	pH	KOH	MC (%)
0			14.27695
1	7.93	14.01	
1	8.08	14.01	
3	7.79	13.87	
3	7.76	13.86	
5	7.66	13.89	14.18958
5	7.74	13.88	14.53855
7	8.06	13.71	
7	8.09	13.75	
10	7.91	13.79	14.02059
10	7.95	13.78	14.10988
15	8.22	13.12	13.98053
15	8.22	13.33	13.80925
20	8.34	11.9	
20	8.43	12.95	
32	8.38	11.35	12.46147

32	8.31	11.18	13.82936
----	------	-------	----------

Delhi - 30 Day Aging			
Day	pH	KOH	MC (%)
0	8.1	14.04	15.07173
0	8.08	14.01	14.94556
1	7.91	13.99	
1	7.89	13.99	
3	8.05	13.81	
3	8.12	13.2	
5	8.04	13.9	14.80812
5	7.97	13.87	14.76229
7	7.97	13.9	
7	8.21	13.93	
15	8.16	13.55	16.02041
15	8.1	13.44	14.11476

Table B-10: Operating conditions for the Elora-150g short term experiments, detailing the soil pH, KOH pH, and Water Content.

Elora - 0 Day Aging			
Day	pH	KOH	MC (%)
0	8.19	13.67	14.30605
0	8.23		14.77398
1	8.44	13.77	
1	8.5	13.69	
3	8.15	13.81	
3	8.15	13.78	
7	7.63	13.68	14.50384
7		13.57	13.97469
9	8.22	13.62	
9	8.17	13.47	
11	8.26	13.31	15.64427
11	8.22	13.52	16.07214
15	8.62	11.04	
15	8.77	10.86	
20			19.78897
20			12.69691
Elora - 15 Day Aging			
Day	pH	KOH	MC (%)
0	8.11	13.79	14.01785
0	8.03	13.78	13.76733
1	8.16	13.69	
1	8.16	13.69	
3	8.19	13.72	14.03982
3	8.2	13.71	13.70749
5	8.53	13.71	
5	8.61	13.72	
7	8.73	13.81	14.61514
7	8.91	13.75	16.40097
10			14.95042
10			16.51966
15	8.74	10.17	
15	8.83	13.57	
23	8.74	10.06	13.25587
23	8.73	9.79	13.94205
30			14.68248
30			13.75335

Elora - 30 Day Aging			
Day	pH	KOH	MC (%)
0	7.6	13.92	16.2842
0	7.69	13.91	16.23317
1	7.88	13.78	16.33981
1	8.13	13.79	16.1627
3	8.3	13.58	17.6231
3	8.19	13.59	16.41825
5	8.07	13.64	
5	8.11	13.65	
7	8.01	12.71	15.44797
7	8.1	13.24	14.7379
11	8.03	10.46	
11	8.05	10.42	
20	8.03	9.41	
20			
30	8.55	9.8	16.32077

Table B-11: Operating conditions for the Elora-A-150g short term experiments, detailing the soil pH, KOH pH, and Water Content.

Elora-A - 0 Day Aging			
Day	pH	KOH	MC (%)
0	8.16	13.63	15.10836
0	8.33	13.63	14.90441
1	8.42	13.67	
1	8.31	13.64	
3	8.45	13.73	
3	8.06	13.71	
7	8.36	13.71	14.79907
7	7.89	13.71	14.43077
9	8.13	13.47	
9	8.11	13.12	
11	8.2	13.61	15.91783
11	8.24	13.24	15.36997
15	8.5	10.82	
15	8.55	12.35	
20			15.91354
20			15.77439
Elora-A - 15 Day Aging			
Day	pH	KOH	MC (%)
0	8.08	13.8	15.26677
0	8	13.81	15.07531
1	8.41	13.69	
1	8.24	13.69	
3	8.09	13.69	15.43109
3	8.07	13.7	15.31658
5	8.47	13.67	
5	8.48	13.61	
7	8.71	13.52	16.70238
7	8.66	13.55	15.84964
10			17.00879
10			16.70054
15	8.65	11.4	
15	8.67	13.2	
23	8.76	10.62	15.58933
23	8.73	10.51	13.40267
30			15.84148
30			19.1815

Elora-A - 30 Day Aging			
Day	pH	KOH	MC (%)
0	7.64	13.98	15.99641
0	7.73	13.95	15.85119
1	7.98	13.75	15.934
1	7.94	13.74	15.81202
3	8.2	13.32	16.0605
3	8.11	13.32	15.88917
5	8.09	12.73	
5	8.17	12.34	
7	8.15	10.51	15.13418
7	8.16	10.5	15.37729
11	8.14	9.67	
11	8.05	10.33	
16	8.22	9.88	15.24156
16	8.29	9.98	16.53934
20	8.13	9.68	
20	8.15	9.73	
30	8.74	10.01	16.19654
30	8.5	9.91	

B4-4: Microbial Data

Table B-12: Microbial Plate Counting Data

	Delhi-270 After	Delhi-300 Before	Delhi-300 After	Elora-270 After	Elora-A Before
48 Hrs Incubation	0	9	0	1	1
	0	6	8	10	0
	8	3	10	0	3
	3	5	0	1	2
	1	0	6	0	7
	7	5	1	5	8
48 Hrs Blank	0	0	0	0	0
	0	0	0	0	1
	0	0	0	0	0
72 Hrs Incubation	2	11	2	3	1
	1	8	8	8	1
	12	4	11	0	4
	5	6	1	2	2
	3	0	6	1	7
	9	9	3	7	10
B72 Hrs Blank	0	0	0	0	0
	0	0	0	0	1
	0	0	0	0	0

APPENDIX C: BIODEGRADATION RATE – DATA

Full degradation rate coefficient table with statistical analysis

	DEGRADATION RATE COEFFICIENT					
	Isooctane	Toluene	m-Xylene	Mesitylene	Naphthalene	TOTAL
DELHI-15-150G	0.0718	0.1972	0.2318	0.1016	0.2103	0.1114
DELHI-30-150G	0.1859	0.2464	0.2519	0.1284	0.2556	0.1771
DELHI-0-150G	0.0423	0.0265	0.0302	0.0245	0.0023	0.0337
DELHI-270-150G	0.0217	0.0000	0.0603	0.1070	0.0825	0.1206
DELHI-270-80KG	0.0867	0.0368	0.1594	0.0949	0.1897	0.1242
DELHI-300-150G	0.0944	0.0000	0.0417	0.1703	0.1177	0.1709
DELHI-300-80KG	0.0848	0.0000	0.0485	0.1249	0.1173	0.1327
ELORA-15-150G	0.2629	0.1327	0.1417	0.0438	0.0248	0.0633
ELORA -30-150G	0.1035	0.1634	0.2365	0.0753	0.2382	0.1138
ELORA -0-150G	0.2014	0.3296	0.3399	0.1548	0.3505	0.2050
ELORAA-15-150G	0.1816	0.0892	0.0619	-0.0067	0.0034	0.0110
ELORAA -30-150G	0.1711	0.1018	0.1361	0.0563	0.2047	0.0966
ELORAA-0-150G	0.1896	0.3593	0.3686	0.1385	0.3937	0.2002
DELHI-LT-JAN0	0.0663	0.0928	0.0790	0.0659	0.0389	0.0723
DELHI-LT-JAN2	0.1222	0.0789	0.0704	0.0005	0.0327	0.0510
DELHI-LT-JUL-8	0.1507	0.1715	0.2093	0.0714	0.2430	0.1362
DELHI-LT-JUN-7	0.1312	0.1231	0.2225	0.1184	0.2271	0.1898
DELHI-LT-MAR-4	0.1890	0.1951	0.0799	0.0489	0.2011	0.0942
DELHI-LT-MAY-6	0.1166	0.1102	0.1925	0.0377	0.2045	0.0978
DELHI-LT-NOV0	0.1282	0.1075	0.0886	0.0672	0.0323	0.0851
DELHI-LT-SEP-10	0.0924	0.1224	0.1941	0.1861	0.2012	0.1855
DELHI-LT-SEPB-10	0.1642	0.1887	0.2284	0.1965	0.2281	0.2266

	P-VALUE					
	Isooctane	Toluene	m-Xylene	Mesitylene	Naphthalene	TOTAL
DELHI-15-150G	1.03E-02	7.82E-08	1.53E-12	6.07E-09	2.07E-10	2.64E-07
DELHI-30-150G	3.52E-12	1.88E-10	4.95E-15	3.47E-11	5.11E-15	5.55E-13
DELHI-0-150G	1.19E-06	4.10E-01	2.64E-02	1.37E-02	8.69E-01	2.32E-03
DELHI-270-150G	1.48E-01	1.58E-01	3.85E-04	1.34E-13	3.74E-04	3.37E-12
DELHI-270-80KG	7.49E-04	1.59E-04	4.81E-15	1.51E-11	6.24E-14	6.11E-14
DELHI-300-150G	2.11E-04	2.79E-01	2.72E-02	1.70E-11	3.79E-05	2.19E-08
DELHI-300-80KG	4.26E-10	1.13E-01	1.07E-09	3.25E-41	2.12E-21	3.06E-29
ELORA-15-150G	7.76E-15	1.70E-07	4.03E-05	4.44E-05	4.77E-01	4.89E-05
ELORA -30-150G	9.55E-03	4.28E-07	1.31E-07	5.01E-02	1.48E-06	9.69E-03
ELORA -0-150G	1.13E-19	2.20E-16	7.01E-15	1.91E-14	9.41E-19	1.05E-19
ELORAA-15-150G	1.71E-15	1.13E-04	1.32E-03	3.42E-01	9.16E-01	2.80E-01
ELORAA -30-150G	4.40E-18	2.71E-06	1.20E-06	7.23E-07	2.96E-11	1.21E-13
ELORAA-0-150G	2.28E-11	1.91E-14	1.83E-18	1.39E-11	4.15E-14	3.33E-15
DELHI-LT-JAN0	3.88E-06	1.63E-05	4.56E-05	9.18E-05	4.62E-04	1.76E-05
DELHI-LT-JAN2	1.06E-10	7.49E-06	1.03E-05	9.84E-01	9.83E-04	1.45E-03
DELHI-LT-JUL-8	1.30E-06	9.07E-07	6.81E-09	4.87E-04	4.24E-08	1.50E-09
DELHI-LT-JUN-7	4.83E-05	1.93E-07	1.47E-11	1.80E-09	1.05E-06	1.55E-16
DELHI-LT-MAR-4	1.59E-04	4.87E-08	1.84E-05	6.51E-04	2.22E-05	1.89E-06
DELHI-LT-MAY-6	7.98E-03	9.76E-03	4.77E-11	2.31E-04	1.08E-04	6.13E-08
DELHI-LT-NOV0	1.46E-08	9.46E-08	3.16E-07	9.81E-07	7.44E-05	8.82E-07
DELHI-LT-SEP-10	6.93E-02	3.57E-04	7.33E-07	2.21E-06	1.00E-05	1.35E-05
DELHI-LT-SEPB-10	2.64E-05	2.56E-05	1.44E-10	3.73E-06	2.73E-08	3.13E-10

	ADJUSTED R-SQUARED VALUE					
	Isooctane	Toluene	m-Xylene	Mesitylene	Naphthalene	TOTAL
DELHI-15-150G	0.1234	0.4807	0.6841	0.5379	0.6041	0.4512
DELHI-30-150G	0.7564	0.6930	0.8340	0.7217	0.8337	0.7813
DELHI-0-150G	0.3395	-0.0056	0.0699	0.0893	-0.0177	0.1412
DELHI-270-150G	0.0287	0.5028	0.2606	0.7524	0.2617	0.7082
DELHI-270-80KG	0.1530	0.1914	0.6190	0.5095	0.5870	0.5873
DELHI-300-150G	0.2192	0.4932	0.0729	0.5767	0.2669	0.4450
DELHI-300-80KG	0.1775	0.4981	0.1698	0.6032	0.3679	0.4741
ELORA-15-150G	0.7209	0.4326	0.2892	0.2864	-0.0102	0.2835
ELORA -30-150G	0.1385	0.4718	0.5022	0.0717	0.4379	0.1379
ELORA -0-150G	0.8522	0.7900	0.7536	0.7419	0.8369	0.8526
ELORAA-15-150G	0.7233	0.2494	0.1749	-0.0016	-0.0202	0.0039
ELORAA -30-150G	0.7305	0.3107	0.3296	0.3410	0.5344	0.6152
ELORAA-0-150G	0.6510	0.7502	0.8388	0.6591	0.7408	0.7700
DELHI-LT-JAN0	0.8543	0.8114	0.7735	0.7434	0.6585	0.8089
DELHI-LT-JAN2	0.9498	0.7558	0.7446	-0.0714	0.5195	0.4934
DELHI-LT-JUL-8	0.8326	0.8415	0.9249	0.5914	0.9006	0.9404
DELHI-LT-JUN-7	0.6326	0.8134	0.9425	0.8955	0.7701	0.9863
DELHI-LT-MAR-4	0.7171	0.9339	0.8074	0.6372	0.8007	0.8719
DELHI-LT-MAY-6	0.4114	0.3928	0.9736	0.6647	0.7036	0.9133
DELHI-LT-NOV0	0.9317	0.9069	0.8863	0.8629	0.7211	0.8653
DELHI-LT-SEP-10	0.1257	0.4897	0.7388	0.7053	0.6526	0.6411
DELHI-LT-SEPB-10	0.6829	0.6841	0.9360	0.7545	0.8716	0.9290

Delhi-270-150g

File Name	Vial Number	Vial Name	Extraction Date	Soil (g)	MeCl (mL)	Isooctane	Toluene	m-Xylene	Mesitylene	Naphthalene	Total
mx170523	013F0101	Delhi1-150-2	2017-05-15	3.1486	10	0.0000	0.0000	5.3413	18.1180	14.3132	37.7725
mx170523	014F0101	Delhi1-150-3	2017-05-15	2.9929	10	0.0000	0.0000	4.3945	16.0263	12.9587	33.3795
mx170523	015F0101	Delhi1-150-4	2017-05-15	2.9647	10	0.0000	0.0000	4.0448	14.8621	15.2553	34.1622
mx170523	016F0101	Delhi1-150-5	2017-05-15	3.0358	10	4.6398	0.0000	3.0408	13.3847	13.1062	34.1715
mx170523	017F0101	Delhi1-150-6	2017-05-15	3.1911	10	4.7817	0.0000	3.3325	13.6434	12.5810	34.3385
mx170523	018F0101	Delhi1-150-7	2017-05-18	3.0584	10	0.0000	0.0000	0.0000	3.7171	0.0000	3.7171
mx170523	019F0101	Delhi1-150-8	2017-05-18	3.1323	10	0.0000	0.0000	0.0000	3.2920	0.0000	3.2920
mx170523	020F0101	Delhi1-150-9	2017-05-18	2.8884	10	0.0000	0.0000	0.0000	3.8729	0.0000	3.8729
mx170523	021F0101	Delhi1-150-10	2017-05-18	2.9502	10	0.0000	0.0000	0.0000	3.5614	0.0000	3.5614
mx170523	022F0101	Delhi1-150-11	2017-05-18	3.01	10	0.0000	0.0000	0.0000	3.6692	0.0000	3.6692
mx170523	023F0101	Delhi1-150-12	2017-05-18	3.1332	10	0.0000	0.0000	0.0000	3.4285	0.0000	3.4285
mx170529	028F0401	Delhi1-150-14	2017-05-23	2.9225	10	0.0000	0.0000	0.0000	3.4407	0.0000	3.4407
mx170529	029F0401	Delhi1-150-15	2017-05-23	2.9458	10	0.0000	0.0000	0.0000	3.6235	0.0000	3.6235
mx170529	030F0401	Delhi1-150-16	2017-05-23	3.1141	10	0.0000	0.0000	0.0000	5.0672	0.0000	5.0672
mx170529	031F0401	Delhi1-150-17	2017-05-23	2.9344	10	0.0000	0.0000	0.0000	4.4324	0.0000	4.4324
mx170529	032F0401	Delhi1-150-18	2017-05-23	3.0666	10	0.0000	0.0000	0.0000	4.8932	0.0000	4.8932
mx170605	009F0201	Delhi1-150-13	2017-05-23	3.2	10	0.0000	0.0000	0.0000	3.2625	0.0000	3.2625
mx170605	010F0201	Delhi1-150-19	2017-05-29	2.9937	5	0.0000	0.0000	0.0000	1.2186	0.0000	1.2186
mx170605	011F0201	Delhi1-150-20	2017-05-29	3.0168	5	0.0000	0.0000	0.0000	1.3211	0.0000	1.3211
mx170605	012F0201	Delhi1-150-21	2017-05-29	3.0944	5	0.0000	0.0000	0.0000	1.2880	0.0000	1.2880
mx170605	013F0201	Delhi1-150-22	2017-05-29	2.9737	5	0.0000	0.0000	0.0000	1.6867	0.0000	1.6867
mx170605	014F0201	Delhi1-150-23	2017-05-29	2.9465	5	0.0000	0.0000	0.0000	1.6390	0.0000	1.6390
mx170605	015F0201	Delhi1-150-24	2017-05-29	3.0534	5	0.0000	0.0000	0.0000	1.7837	0.0000	1.7837
mx170605	016F0201	Delhi1-150-25	2017-06-02	3.1409	5	0.0000	0.0000	0.0000	1.7892	0.0000	1.7892
mx170605	017F0201	Delhi1-150-26	2017-06-02	3	5	0.0000	0.0000	0.0000	1.5061	0.0000	1.5061
mx170605	018F0201	Delhi1-150-27	2017-06-02	3.053	5	0.0000	0.0000	0.0000	1.6749	0.0000	1.6749
mx170605	019F0201	Delhi1-150-28	2017-06-02	2.9394	5	0.0000	0.0000	0.0000	2.1694	0.0000	2.1694
mx170605	020F0201	Delhi1-150-29	2017-06-02	3.0427	5	4.0182	0.0000	0.0000	1.9549	0.0000	5.9731
mx170605	021F0201	Delhi1-150-30	2017-06-02	3.1015	5	0.0000	0.0000	0.0000	2.2572	0.0000	2.2572

mx170619	025F0401	Delhi1-150-37	2017-06-14	2.9131	5	0.0000	0.0000	0.0000	1.4635	0.0000	1.4635
mx170619	026F0401	Delhi1-150-38	2017-06-14	2.9737	5	0.0000	0.0000	0.0000	0.5947	0.0000	0.5947
mx170619	027F0401	Delhi1-150-39	2017-06-14	3.0587	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170619	028F0401	Delhi1-150-40	2017-06-14	2.9650	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170619	029F0401	Delhi1-150-41	2017-06-14	3.0021	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170619	030F0401	Delhi1-150-42	2017-06-14	3.1088	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170712	007F0201	Delhi1-150-31	2017-06-05	3.0985	5	0.0000	0.0000	0.0000	2.3265	0.0000	2.3265
mx170712	008F0201	Delhi1-150-32	2017-06-05	3.0623	5	0.0000	0.0000	0.0000	2.5126	0.0000	2.5126
mx170712	009F0201	Delhi1-150-33	2017-06-05	3.1631	5	0.0000	0.0000	0.0000	2.2082	0.0000	2.2082
mx170712	010F0201	Delhi1-150-34	2017-06-05	3.0006	5	0.0000	0.0000	0.0000	1.1808	0.0000	1.1808
mx170712	011F0201	Delhi1-150-35	2017-06-05	2.9682	5	0.0000	0.0000	0.0000	1.1421	0.0000	1.1421
mx170712	012F0201	Delhi1-150-36	2017-06-05	3.0029	5	0.0000	0.0000	0.0000	1.1587	0.0000	1.1587

Delhi-270-80kg

File Name	Vial Number	Vial Name	Extraction Date	Soil (g)	MeCl (mL)	Isooctane	Toluene	m-Xylene	Mesitylene	Naphthalene	Total
mx170523	032F0301	Delhi1-80-1	2017-05-13	3.1655	10	11.2288	3.0061	17.1495	35.0536	52.0044	118.4423
mx170523	033F0301	Delhi1-80-2	2017-05-13	2.9612	10	15.8320	1.7871	11.5515	29.1204	47.1968	105.4878
mx170523	034F0301	Delhi1-80-3	2017-05-13	3.1844	10	21.3433	1.4956	13.9148	32.0648	37.5007	106.3192
mx170523	035F0301	Delhi1-80-4	2017-05-13	3.3976	10	16.5659	2.5693	15.9887	32.3257	35.7869	103.2364
mx170523	036F0301	Delhi1-80-5	2017-05-14	3.0057	10	10.4707	0.0000	9.4571	21.4187	29.0350	70.3815
mx170523	037F0301	Delhi1-80-6	2017-05-14	2.917	10	0.0000	2.2816	11.6920	24.8194	44.3027	83.0957
mx170523	040F0301	Delhi1-80-9	2017-05-15	2.9534	10	14.4401	0.0000	9.6029	23.0565	30.1114	77.2108
mx170523	041F0301	Delhi1-80-10	2017-05-15	3.2754	10	0.0000	0.0000	5.3284	15.2948	36.1234	56.7466
mx170523	044F0301	Delhi1-80-13	2017-05-16	2.9283	10	7.1145	0.0000	10.4265	22.1987	19.4860	59.2257
mx170523	045F0301	Delhi1-80-14	2017-05-16	3.0439	10	6.3766	0.0000	9.7828	27.2044	48.7044	92.0682
mx170523	048F0501	Delhi1-80-17	2017-05-17	3.1189	10	10.7311	0.0000	6.3753	20.5545	12.1253	49.7861
mx170523	049F0501	Delhi1-80-18	2017-05-17	3.1677	10	0.0000	0.0000	8.9028	25.3533	53.8576	88.1137
mx170523	052F0501	Delhi1-80-21	2017-05-18	3.1846	10	6.8154	0.0000	6.0615	21.0452	16.8504	50.7725
mx170523	053F0501	Delhi1-80-22	2017-05-18	3.0607	10	4.5270	0.0000	2.5950	16.7043	5.7542	29.5806
mx170523	056F0501	Delhi1-80-25	2017-05-19	3.0774	10	18.8165	0.0000	1.8637	21.2833	4.3915	46.3551

mx170523	057F0501	Delhi1-80-26	2017-05-19	2.9509	10	0.0000	0.0000	5.3181	16.6637	29.6246	51.6064
mx170523	060F0501	Delhi1-80-29	2017-05-20	3.0397	10	14.9085	0.0000	1.3576	22.0250	2.9255	41.2166
mx170523	061F0501	Delhi1-80-30	2017-05-20	2.9888	10	7.0368	0.0000	4.0076	18.4642	31.7613	61.2699
mx170523	064F0501	Delhi1-80-33	2017-05-21	3.0587	10	0.0000	0.0000	0.0000	10.0948	1.7474	11.8421
mx170523	065F0501	Delhi1-80-34	2017-05-21	3.0014	10	5.5043	0.0000	4.4064	19.3306	47.5720	76.8134
mx170523	068F0501	Delhi1-80-37	2017-05-22	3.0949	10	3.4475	0.0000	0.0000	14.0776	1.8964	19.4215
mx170523	069F0501	Delhi1-80-38	2017-05-22	2.9409	10	0.0000	0.0000	3.7854	19.4701	32.6466	55.9021
mx170529	007F0201	Delhi1-80-41	2017-05-23	3.0998	10	0.0000	0.0000	0.0000	16.1749	4.3504	20.5253
mx170529	008F0201	Delhi1-80-42	2017-05-23	3.08	10	4.5065	0.0000	3.6385	20.5200	29.2030	57.8680
mx170529	011F0201	Delhi1-80-45	2017-05-24	3.0696	5	2.3291	0.0000	0.0000	11.5380	0.6850	14.5520
mx170529	012F0201	Delhi1-80-46	2017-05-24	2.989	5	0.0000	0.0000	1.4826	13.6318	12.3153	27.4297
mx170529	015F0201	Delhi1-80-49	2017-05-25	2.9727	5	1.8437	0.0000	0.0000	7.5563	0.6986	10.0986
mx170529	016F0201	Delhi1-80-50	2017-05-25	3.156	5	10.3166	0.0000	2.4768	15.6867	17.5785	46.0586
mx170529	019F0201	Delhi1-80-53	2017-05-26	3.0807	5	1.6038	0.0000	0.0000	9.6151	0.6728	11.8918
mx170529	020F0201	Delhi1-80-54	2017-05-26	3.0225	5	3.7095	0.0000	1.9167	14.7004	10.3362	30.6628
mx170529	023F0401	Delhi1-80-57	2017-05-27	3.03	5	0.0000	0.0000	0.0000	4.4075	0.0000	4.4075
mx170529	024F0401	Delhi1-80-58	2017-05-27	3.0715	5	0.0000	0.0000	3.2191	21.7242	30.5469	55.4901
mx170605	007F0201	Delhi1-80-57	2017-05-27	3.03	5	2.2070	0.0000	0.0000	5.5457	0.0000	7.7527
mx170605	022F0401	Delhi1-80-61	2017-05-28	2.9674	5	3.3405	0.0000	0.0000	3.3873	0.0000	6.7277
mx170605	023F0401	Delhi1-80-62	2017-05-28	2.9463	5	3.1541	0.0000	0.0000	9.7244	0.7430	13.6215
mx170605	026F0401	Delhi1-80-65	2017-05-29	3.0269	5	0.0000	0.0000	0.0000	4.5222	0.0000	4.5222
mx170605	027F0401	Delhi1-80-66	2017-05-29	2.908	5	21.6617	0.0000	1.2176	16.7631	19.4379	59.0802
mx170605	030F0401	Delhi1-80-69	2017-05-30	3.0595	5	0.0000	0.0000	0.0000	2.7468	0.0000	2.7468
mx170605	031F0401	Delhi1-80-70	2017-05-30	3.0148	5	30.0739	0.0000	10.1192	48.0960	34.1029	122.3920
mx170605	034F0401	Delhi1-80-73	2017-05-31	3.1418	5	4.4621	0.0000	0.0000	1.7286	0.6373	6.8280
mx170605	035F0401	Delhi1-80-74	2017-05-31	3.0774	5	4.3013	0.0000	0.6008	8.8621	7.5596	21.3239
mx170605	038F0601	Delhi1-80-77	2017-06-01	3.0968	5	4.7111	0.0000	0.0000	1.8921	0.5823	7.1854
mx170605	039F0601	Delhi1-80-78	2017-06-01	3.0919	5	4.2500	0.0000	0.8570	12.8570	7.8523	25.8163
mx170605	042F0601	Delhi1-80-81	2017-06-02	3.0732	5	2.5336	0.0000	0.0000	1.7224	0.0000	4.2560
mx170605	043F0601	Delhi1-80-82	2017-06-02	3.0717	5	0.0000	0.0000	0.0000	5.8195	0.5489	6.3684
mx170605	046F0501	Delhi1-80-85	2017-06-03	2.9456	5	5.4840	0.0000	0.0000	1.0093	0.0000	6.4933
mx170605	047F0601	Delhi1-80-86	2017-06-03	2.9973	5	3.2833	0.0000	0.0000	7.8648	0.6838	11.8318

mx170605	050F0601	Delhi1-80-89	2017-06-04	3.0133	5	0.0000	0.0000	0.0000	1.4052	0.0000	1.4052
mx170605	051F0601	Delhi1-80-90	2017-06-04	3.0106	5	0.0000	0.0000	0.0000	8.2703	0.0000	8.2703
mx170612	017F0301	Delhi1-80-97	2017-06-06	3.0015	5	0.0000	0.0000	0.0000	1.1804	0.0000	1.1804
mx170612	018F0301	Delhi1-80-98	2017-06-06	3.155	5	4.6001	0.0000	0.0000	10.1489	0.5688	15.3177
mx170612	021F0301	Delhi1-80-101	2017-06-07	2.9911	5	0.0000	0.0000	0.0000	0.9946	0.0000	0.9946
mx170612	022F0301	Delhi1-80-102	2017-06-07	2.945	5	0.0000	0.0000	0.0000	7.9549	0.0000	7.9549
mx170612	025F0301	Delhi1-80-105	2017-06-08	2.9543	5	0.0000	0.0000	0.0000	0.9487	0.0000	0.9487
mx170612	026F0301	Delhi1-80-106	2017-06-08	3.102	5	0.0000	0.0000	1.0125	11.7548	2.9301	15.6974
mx170612	029F0301	Delhi1-80-109	2017-06-09	2.9213	5	3.9711	0.0000	0.0000	0.8723	0.0000	4.8434
mx170612	030F0301	Delhi1-80-110	2017-06-09	3.1366	5	0.0000	0.0000	0.0000	11.0509	0.7416	11.7925
mx170612	033F0501	Delhi1-80-113	2017-06-10	3.0496	5	0.0000	0.0000	0.0000	0.6972	0.0000	0.6972
mx170612	034F0501	Delhi1-80-114	2017-06-10	3.0317	5	3.9789	0.0000	0.0000	7.3596	0.8739	12.2124
mx170612	037F0501	Delhi1-80-117	2017-06-11	3.0196	5	4.3982	0.0000	0.0000	1.9291	0.7552	7.0825
mx170612	038F0501	Delhi1-80-118	2017-06-11	3.0676	5	0.0000	0.0000	0.0000	7.1836	0.7031	7.8867
mx170619	008F0201	Delhi1-80-121	2017-06-12	3.0114	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170619	009F0201	Delhi1-80-122	2017-06-12	3.0390	5	0.0000	0.0000	0.0000	7.2150	0.0000	7.2150
mx170712	013F0201	Delhi1-80-93	2017-06-05	3.0525	5	0.0000	0.0000	0.0000	1.0951	0.0000	1.0951
mx170712	014F0201	Delhi1-80-94	2017-06-05	3.0604	5	2.3283	0.0000	0.0000	11.4093	1.0465	14.7840

Delhi-300-150g

File Name	Vial Number	Vial Name	Extraction Date	Soil (g)	MeCl (mL)	Isooctane	Toluene	m-Xylene	Mesitylene	Naphthalene	Total
mx170702	007F0101	Delhi 2-150-1	2017-06-16	3.0383	5	22.6083	0.0000	10.5169	65.4082	82.1554	180.6887
mx170702	008F0101	Delhi 2-150-2	2017-06-16	2.9971	5	10.5581	0.0000	6.2309	49.2930	56.8589	122.9409
mx170702	009F0101	Delhi 2-150-3	2017-06-16	3.1717	5	7.3583	0.0000	3.5341	33.2883	54.9993	99.1801
mx170702	010F0101	Delhi 2-150-4	2017-06-16	3.106	5	12.4885	0.0000	6.9799	40.8941	58.4767	118.8393
mx170702	011F0101	Delhi 2-150-5	2017-06-16	3.0584	5	6.7090	0.0000	3.3348	38.5846	59.6385	108.2669
mx170702	012F0101	Delhi 2-150-6	2017-06-16	3.0191	5	9.3034	0.0000	4.9932	41.8699	52.2532	108.4197
mx170702	013F0101	Delhi 2-150-7	2017-06-17	2.9874	5	10.7732	0.0000	0.0000	15.9820	2.6740	29.4292
mx170702	014F0101	Delhi 2-150-8	2017-06-17	2.9857	5	5.5491	0.0000	0.0000	16.4831	3.6411	25.6733
mx170702	015F0101	Delhi 2-150-9	2017-06-17	3.0615	5	6.2259	0.0000	0.6720	23.0910	4.5156	34.5046

mx170702	016F0101	Delhi 2-150-10	2017-06-17	3.066	5	2.3918	0.0000	0.0000	17.1516	2.9334	22.4768
mx170702	017F0101	Delhi 2-150-11	2017-06-17	3.0995	5	5.7232	0.0000	0.0000	16.8721	2.4481	25.0433
mx170702	018F0101	Delhi 2-150-12	2017-06-17	3.0975	5	6.4215	0.0000	0.5622	21.3690	5.7742	34.1269
mx170702	019F0101	Delhi 2-150-13	2017-06-19	2.967	5	5.0706	0.0000	0.0000	7.6444	15.8580	28.5730
mx170702	020F0101	Delhi 2-150-14	2017-06-19	3.006	5	0.0000	0.0000	0.0000	6.7795	0.0000	6.7795
MX170707	007F0201	Delhi2-150-15	2017-06-19	3.0976	5	0.0000	0.0000	0.0000	3.5209	0.5122	4.0332
MX170707	008F0201	Delhi2-150-16	2017-06-19	3.0271	5	5.3546	0.0000	0.0000	4.8599	0.0000	10.2145
MX170707	009F0201	Delhi2-150-17	2017-06-19	2.9369	5	2.9160	0.0000	0.0000	4.6807	0.0000	7.5967
MX170707	010F0201	Delhi2-150-18	2017-06-19	2.9973	5	0.0000	0.0000	0.0000	2.8224	0.0000	2.8224
MX170707	011F0201	Delhi2-150-19	2017-06-21	2.9682	5	0.0000	0.0000	0.0000	1.9694	0.0000	1.9694
MX170707	012F0201	Delhi2-150-20	2017-06-21	3.0896	5	0.0000	0.0000	0.0000	1.6620	0.0000	1.6620
MX170707	013F0201	Delhi2-150-21	2017-06-21	2.9917	5	4.6131	0.0000	0.0000	2.0091	0.5407	7.1629
MX170707	014F0201	Delhi2-150-22	2017-06-21	2.9965	5	0.0000	0.0000	0.0000	1.9616	0.0000	1.9616
MX170707	015F0201	Delhi2-150-23	2017-06-21	3.0756	5	2.8702	0.0000	0.0000	2.0779	0.0000	4.9481
MX170707	016F0201	Delhi2-150-24	2017-06-21	2.9771	5	0.0000	0.0000	0.0000	1.5525	0.0000	1.5525
MX170707	017F0201	Delhi2-150-25	2017-06-23	3.0873	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	018F0201	Delhi2-150-26	2017-06-23	3.0584	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	019F0201	Delhi2-150-27	2017-06-23	2.9776	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	020F0201	Delhi2-150-28	2017-06-23	2.926	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	021F0201	Delhi2-150-29	2017-06-23	2.9939	5	0.0000	0.0000	0.0000	0.4653	0.0000	0.4653
MX170707	022F0201	Delhi2-150-30	2017-06-23	3.076	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	023F0201	Delhi2-150-31	2017-06-27	3.0726	5	0.0000	0.0000	0.0000	0.4986	0.0000	0.4986
MX170707	024F0201	Delhi2-150-32	2017-06-27	3.0678	5	4.4532	0.0000	0.0000	0.4909	0.0000	4.9441
MX170707	025F0401	Delhi2-150-33	2017-06-27	2.9871	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	026F0401	Delhi2-150-34	2017-06-27	3.055	5	0.0000	0.0000	0.0000	0.4609	0.0000	0.4609
MX170707	027F0401	Delhi2-150-35	2017-06-27	3.0526	5	0.0000	0.0000	0.0000	0.7660	0.0000	0.7660
MX170707	028F0401	Delhi2-150-36	2017-06-27	2.945	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	029F0401	Delhi2-150-37	2017-07-01	2.9582	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	030F0401	Delhi2-150-38	2017-07-01	3.0173	5	2.0439	0.0000	1.5435	1.3021	0.7538	5.6432
MX170707	031F0401	Delhi2-150-39	2017-07-01	2.9671	5	2.1574	0.0000	1.5414	1.7006	1.0440	6.4434
MX170707	032F0401	Delhi2-150-40	2017-07-01	2.9696	5	0.0000	0.0000	1.3064	1.0398	0.5643	2.9105
MX170707	033F0401	Delhi2-150-41	2017-07-01	2.9408	5	2.1597	0.0000	1.2308	1.3027	0.9941	5.6873

MX170707	034F0401	Delhi2-150-42	2017-07-01	3.0134	5	2.8324	0.0000	1.9776	1.6442	2.0231	8.4773
MX170707	035F0401	Delhi2-150-43	2017-07-06	3.0231	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	036F0401	Delhi2-150-44	2017-07-06	2.9579	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	037F0401	Delhi2-150-45	2017-07-06	3.03	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	038F0401	Delhi2-150-46	2017-07-06	3.0462	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	039F0401	Delhi2-150-47	2017-07-06	3.009	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170707	040F0401	Delhi2-150-48	2017-07-06	3.013	5	2.6527	0.0000	0.0000	0.0000	0.0000	2.6527
MX170716	067F0501	Delhi2-150-D30-1	2017-07-16	2.9643	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170716	068F0501	Delhi2-150-D30-2	2017-07-16	3.046	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170716	069F0501	Delhi2-150-D30-3	2017-07-16	2.9709	5	1.6798	0.0000	0.0000	0.0000	0.0000	1.6798
MX170716	070F0501	Delhi2-150-D30-4	2017-07-16	3.0228	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170716	071F0501	Delhi2-150-D30-5	2017-07-16	3.0362	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170716	072F0501	Delhi2-150-D30-6	2017-07-16	3.0556	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Delhi-300-80kg

File Name	Vial Number	Vial Name	Extraction Date	Soil (g)	MeCl (mL)	Isooctane	Toluene	m-Xylene	Mesitylene	Naphthalene	Total
mx170619	037F0601	Delhi2-80-D0-T1	2017-06-16	3.1958	5	13.9645	0.0000	11.2075	37.4660	51.1317	113.7696
mx170619	038F0601	Delhi2-80-D0-T2	2017-06-16	3.0161	5	18.1383	0.0000	10.3973	39.0214	61.6493	129.2064
mx170619	039F0601	Delhi2-80-D0-M1	2017-06-16	3.0643	5	3.2997	0.0000	1.2587	12.5434	15.8782	32.9800
mx170619	040F0601	Delhi2-80-D0-M2	2017-06-16	3.0072	5	36.7503	0.0000	2.8657	46.1490	23.8321	109.5970
mx170619	041F0601	Delhi2-80-D0-B1	2017-06-16	2.9608	5	0.0000	0.0000	0.0000	9.0440	3.5034	12.5474
mx170619	042F0601	Delhi2-80-D0-B2	2017-06-16	3.0844	5	0.0000	0.0000	0.0000	8.6122	1.7870	10.3992
mx170619	043F0601	Delhi2-80-D1-T1	2017-06-17	3.0412	5	12.5586	0.0000	8.7332	35.0118	50.9061	107.2097
mx170619	044F0601	Delhi2-80-D1-T2	2017-06-17	2.9323	5	23.5304	0.0000	21.6029	74.0211	71.3582	190.5126
mx170619	045F0601	Delhi2-80-D1-M1	2017-06-17	3.0542	5	2.9973	0.0000	1.3475	12.7304	7.8951	24.9704
mx170619	046F0601	Delhi2-80-D1-M2	2017-06-17	2.9318	5	0.0000	0.0000	0.0000	10.9928	3.6255	14.6182
mx170619	047F0601	Delhi2-80-D1-B1	2017-06-17	3.0589	5	2.8604	0.0000	0.0000	9.6150	2.4203	14.8958
mx170619	048F0601	Delhi2-80-D1-B2	2017-06-17	3.0272	5	0.0000	0.0000	0.0000	4.9064	0.5936	5.5000
mx170619	051F0601	Delhi2-80-D2-T1	2017-06-18	2.9907	5	7.4190	0.0000	2.2173	15.4980	31.7605	56.8948
mx170619	052F0601	Delhi2-80-D2-T2	2017-06-18	3.0725	5	9.8736	0.0000	2.3433	18.0413	31.8448	62.1029

mx170619	053F0601	Delhi2-80-D2-M1	2017-06-18	3.0432	5	4.1318	0.0000	0.0000	10.3817	2.6835	17.1970
mx170619	054F0601	Delhi2-80-D2-M2	2017-06-18	2.9945	5	0.0000	0.0000	0.0000	9.9365	3.5640	13.5004
mx170619	055F0601	Delhi2-80-D2-B1	2017-06-18	3.1074	5	0.0000	0.0000	0.0000	7.5700	3.0670	10.6369
mx170619	056F0601	Delhi2-80-D2-B2	2017-06-18	2.9928	5	0.0000	0.0000	0.0000	5.0948	0.7466	5.8414
MX170627	025F0401	Delhi2-80-D3-T1	2017-06-19	3.0995	5	15.5939	0.0000	4.6965	33.2744	58.4791	112.0439
MX170627	026F0401	Delhi2-80-D3-T2	2017-06-19	3.0352	5	51.3539	0.0000	17.4114	92.1893	65.3451	226.2998
MX170628	027F0201	Delhi2-80-D3-M1	2017-06-19	2.9505	5	0.0000	0.0000	0.0000	5.0836	1.2529	6.3365
MX170628	028F0201	Delhi2-80-D3-M2	2017-06-19	2.958	5	2.9677	0.0000	0.0000	5.7530	1.9141	10.6347
MX170628	029F0201	Delhi2-80-D3-B1	2017-06-19	2.9894	5	0.0000	0.0000	0.0000	1.8858	0.5093	2.3951
MX170628	030F0201	Delhi2-80-D3-B2	2017-06-19	3.0187	5	0.0000	0.0000	0.0000	2.3898	0.5030	2.8928
MX170628	045F0201	Delhi2-80-D5-B1	2017-06-21	3.0544	5	0.0000	0.0000	0.0000	1.1109	0.0000	1.1109
MX170628	046F0201	Delhi2-80-D5-B2	2017-06-21	2.9681	5	0.0000	0.0000	0.0000	1.1930	0.0000	1.1930
MX170628	049F0201	Delhi2-80-D6-T1	2017-06-22	2.9911	5	8.5721	0.0000	0.0000	11.0828	6.3466	26.0015
MX170628	050F0201	Delhi2-80-D6-T2	2017-06-22	3.0042	5	31.7394	0.0000	2.7647	29.5354	12.1338	76.1734
MX170628	051F0201	Delhi2-80-D6-M1	2017-06-22	3.0356	5	2.2478	0.0000	0.0000	3.0029	0.7317	5.9824
MX170628	052F0201	Delhi2-80-D6-M2	2017-06-22	2.9695	5	0.0000	0.0000	0.0000	3.5698	0.7874	4.3572
MX170629	007F0201	Delhi2-80-D3-T1	2017-06-19	3.0995	5	15.1841	0.0000	4.4066	31.1529	54.7633	105.5069
MX170629	008F0201	Delhi2-80-D3-T2	2017-06-19	3.0352	5	49.1542	0.0000	16.3043	86.2581	61.0780	212.7946
MX170629	009F0201	Delhi2-80-D3-M1	2017-06-19	2.9505	5	0.0000	0.0000	0.0000	5.1921	1.2433	6.4353
MX170629	010F0201	Delhi2-80-D3-M2	2017-06-19	2.958	5	3.0744	0.0000	0.0000	5.6482	1.8738	10.5965
MX170629	011F0201	Delhi2-80-D3-B1	2017-06-19	2.9894	5	0.0000	0.0000	0.0000	1.8608	0.5047	2.3656
MX170629	012F0201	Delhi2-80-D3-B2	2017-06-19	3.0187	5	0.0000	0.0000	0.0000	2.3650	0.0000	2.3650
MX170629	015F0201	Delhi2-80-D4-T1	2017-06-20	2.9985	5	12.1206	0.0000	1.1836	17.0927	35.2354	65.6323
MX170629	016F0201	Delhi2-80-D4-T2	2017-06-20	3.0482	5	10.0503	0.0000	0.8803	12.6770	29.3013	52.9089
MX170629	017F0201	Delhi2-80-D4-M1	2017-06-20	3.0202	5	8.1241	0.0000	0.0000	4.8260	1.4488	14.3989
MX170629	018F0201	Delhi2-80-D4-M2	2017-06-20	3.071	5	3.5718	0.0000	0.0000	5.4129	1.2408	10.2255
MX170629	019F0201	Delhi2-80-D4-B1	2017-06-20	3.0643	5	0.0000	0.0000	0.0000	1.4293	0.5153	1.9445
MX170629	020F0201	Delhi2-80-D4-B2	2017-06-20	3.096	5	0.0000	0.0000	0.0000	1.8529	0.5333	2.3862
MX170630	007F0101	Delhi2-80-D5-T1	2017-06-21	3.0711	5	11.8547	0.0000	2.2075	22.5735	24.6501	61.2858
MX170630	008F0101	Delhi2-80-D5-T2	2017-06-21	2.983	5	14.1779	0.0000	2.9999	26.0290	34.6915	77.8984
MX170630	009F0101	Delhi2-80-D5-M1	2017-06-21	2.9681	5	6.1599	0.0000	0.0000	4.9676	1.0761	12.2037
MX170630	010F0101	Delhi2-80-D5-M2	2017-06-21	3.0169	5	0.0000	0.0000	0.0000	5.0125	1.0686	6.0811

MX170630	011F0101	Delhi2-80-D5-B1	2017-06-21	3.0544	5	0.0000	0.0000	0.0000	1.0792	0.0000	1.0792
MX170630	012F0101	Delhi2-80-D5-B2	2017-06-21	2.9681	5	0.0000	0.0000	0.0000	1.2532	0.0000	1.2532
MX170630	015F0101	Delhi2-80-D6-T1	2017-06-22	2.9911	5	8.9399	0.0000	0.0000	1.1631	6.6399	16.7428
MX170630	016F0101	Delhi2-80-D6-T2	2017-06-22	3.0042	5	35.2639	0.0000	3.2792	34.7117	14.3208	87.5755
MX170630	017F0101	Delhi2-80-D6-M1	2017-06-22	3.0356	5	2.4209	0.0000	0.0000	3.2309	0.7854	6.4372
MX170630	018F0101	Delhi2-80-D6-M2	2017-06-22	2.9695	5	0.0000	0.0000	0.0000	3.6102	0.7990	4.4092
MX170630	019F0101	Delhi2-80-D6-B1	2017-06-22	3.0709	5	0.0000	0.0000	0.0000	1.1849	0.0000	1.1849
MX170630	020F0101	Delhi2-80-D6-B2	2017-06-22	2.9833	5	0.0000	0.0000	0.0000	0.7675	0.0000	0.7675
MX170630	023F0101	Delhi2-80-D7-T1	2017-06-23	3.0126	5	9.9913	0.0000	0.6500	13.6214	17.3192	41.5819
MX170630	024F0101	Delhi2-80-D7-T2	2017-06-23	3.0671	5	11.4403	0.0000	0.7847	10.3826	9.2336	31.8411
MX170630	025F0101	Delhi2-80-D7-M1	2017-06-23	2.9729	5	0.0000	0.0000	0.0000	2.7242	0.9516	3.6758
MX170630	026F0101	Delhi2-80-D7-M2	2017-06-23	3.0301	5	0.0000	0.0000	0.0000	2.9506	1.0617	4.0122
MX170630	027F0101	Delhi2-80-D7-B1	2017-06-23	3.1109	5	0.0000	0.0000	0.0000	1.0058	0.0000	1.0058
MX170630	028F0101	Delhi2-80-D7-B2	2017-06-23	2.9975	5	0.0000	0.0000	0.0000	0.8907	0.0000	0.8907
MX170630	029F0101	Delhi2-80-D8-T1	2017-06-24	3.0773	5	6.6007	0.0000	0.0000	8.3138	6.4746	21.3892
MX170630	030F0101	Delhi2-80-D8-T2	2017-06-24	3.0056	5	6.1542	0.0000	0.0000	7.3969	6.4082	19.9593
MX170630	031F0101	Delhi2-80-D8-M1	2017-06-24	2.979	5	0.0000	0.0000	0.0000	1.6385	0.6403	2.2787
MX170630	032F0101	Delhi2-80-D8-M2	2017-06-24	3.0352	5	0.0000	0.0000	0.0000	0.2063	0.9351	1.1414
MX170630	033F0101	Delhi2-80-D8-B1	2017-06-24	3.0601	5	0.0000	0.0000	0.0000	0.8112	0.0000	0.8112
MX170630	034F0101	Delhi2-80-D8-B2	2017-06-24	3.0546	5	0.0000	0.0000	0.0000	1.0716	0.5579	1.6296
MX170630	037F0101	Delhi2-80-D9-T1	2017-06-25	3.0404	5	5.9709	0.0000	0.0000	7.9126	3.4811	17.3646
MX170630	038F0101	Delhi2-80-D9-T2	2017-06-25	3.0186	5	5.1842	0.0000	0.0000	8.8938	2.7353	16.8133
MX170630	039F0101	Delhi2-80-D9-M1	2017-06-25	3.089	5	1.9697	0.0000	0.0000	2.1933	0.9720	5.1350
MX170630	040F0101	Delhi2-80-D9-M2	2017-06-25	3.0415	5	3.1249	0.0000	0.0000	1.7148	0.0000	4.8398
MX170630	041F0101	Delhi2-80-D9-B1	2017-06-25	3.0774	5	0.0000	0.0000	0.0000	0.7992	0.0000	0.7992
MX170630	042F0101	Delhi2-80-D9-B2	2017-06-25	3.0264	5	0.0000	0.0000	0.0000	0.6711	0.0000	0.6711
mx170701	007F0101	Delhi2-80-D10-T1	2017-06-26	2.9709	5	3.0222	0.0000	0.0000	6.0150	1.2221	10.2593
mx170701	008F0101	Delhi2-80-D10-T2	2017-06-26	3.038	5	7.3259	0.0000	0.0000	5.7628	2.8780	15.9666
mx170701	009F0101	Delhi2-80-D10-M1	2017-06-26	2.9904	5	0.0000	0.0000	0.0000	1.6373	0.5208	2.1581
mx170701	010F0101	Delhi2-80-D10-M2	2017-06-26	3.0756	5	0.0000	0.0000	0.0000	1.6713	0.5128	2.1841
mx170701	011F0101	Delhi2-80-D10-B1	2017-06-26	3.0116	5	0.0000	0.0000	0.0000	0.5561	0.0000	0.5561
mx170701	012F0101	Delhi2-80-D10-B2	2017-06-26	3.0836	5	0.0000	0.0000	0.0000	0.5118	0.0000	0.5118

mx170701	015F0201	Delhi2-80-D11-T1	2017-06-27	3.0341	5	5.6591	0.0000	0.4961	7.9240	5.5665	19.6458
mx170701	017F0301	Delhi2-80-D11-M1	2017-06-27	3.0078	5	0.0000	0.0000	0.0000	1.5564	0.0000	1.5564
mx170701	018F0301	Delhi2-80-D11-M2	2017-06-27	2.9939	5	2.7518	0.0000	0.0000	1.0918	0.4831	4.3267
mx170701	019F0301	Delhi2-80-D11-B1	2017-06-27	3.0477	5	0.0000	0.0000	0.0000	0.9505	0.0000	0.9505
mx170701	020F0301	Delhi2-80-D11-B2	2017-06-27	3.0162	5	0.0000	0.0000	0.0000	1.1215	0.0000	1.1215
mx170701	023F0501	Delhi2-80-D12-T1	2017-06-28	3.0606	5	2.6693	0.0000	0.0000	4.6903	1.6134	8.9730
mx170701	024F0501	Delhi2-80-D12-T2	2017-06-28	3.044	5	0.0000	0.0000	0.0000	3.4972	1.9364	5.4335
mx170701	025F0501	Delhi2-80-D12-M1	2017-06-28	2.963	5	0.0000	0.0000	0.0000	0.8568	0.5678	1.4246
mx170701	026F0501	Delhi2-80-D12-M2	2017-06-28	2.9783	5	0.0000	0.0000	0.0000	0.7645	0.5003	1.2647
mx170701	027F0501	Delhi2-80-D12-B1	2017-06-28	3.059	5	0.0000	0.0000	0.0000	0.7546	0.0000	0.7546
mx170701	028F0501	Delhi2-80-D12-B2	2017-06-28	2.9987	5	0.0000	0.0000	0.0000	0.6488	0.0000	0.6488
mx170701	031F0501	Delhi2-80-D13-T1	2017-06-29	2.936	5	0.0000	0.0000	0.0000	2.7825	0.7886	3.5710
mx170701	032F0501	Delhi2-80-D13-T2	2017-06-29	2.9722	5	3.5466	0.0000	0.0000	6.4470	1.6821	11.6757
mx170701	033F0501	Delhi2-80-D13-M1	2017-06-29	3.0117	5	3.3718	0.0000	0.0000	0.7404	0.0000	4.1122
mx170701	034F0501	Delhi2-80-D13-M2	2017-06-29	3.0845	5	0.0000	0.0000	0.0000	0.8536	0.4560	1.3096
mx170701	035F0501	Delhi2-80-D13-B1	2017-06-29	3.0497	5	0.0000	0.0000	0.0000	0.5366	0.0000	0.5366
mx170701	036F0501	Delhi2-80-D13-B2	2017-06-29	2.9791	5	0.0000	0.0000	0.0000	0.4652	0.0000	0.4652
mx170701	039F0501	Delhi2-80-D14-T1	2017-06-30	3.032	5	0.0000	0.0000	0.0000	2.7077	0.7996	3.5073
mx170701	040F0501	Delhi2-80-D14-T2	2017-06-30	3.0258	5	0.0000	0.0000	0.0000	2.0399	0.6360	2.6759
mx170701	041F0501	Delhi2-80-D14-M1	2017-06-30	3.0327	5	0.0000	0.0000	0.0000	0.7884	0.0000	0.7884
mx170701	042F0501	Delhi2-80-D14-M2	2017-06-30	3.0612	5	0.0000	0.0000	0.0000	0.7635	0.4738	1.2373
mx170701	043F0501	Delhi2-80-D14-B1	2017-06-30	3.0224	5	0.0000	0.0000	0.0000	0.5059	0.0000	0.5059
mx170701	044F0501	Delhi2-80-D14-B2	2017-06-30	2.9266	5	0.0000	0.0000	0.0000	0.5707	0.0000	0.5707
mx170710	031F0401	Delhi2-80-D15-T1	2017-07-01	3.0505	5	3.4408	0.0000	0.0000	1.8715	0.8979	6.2102
mx170710	032F0401	Delhi2-80-D15-T2	2017-07-01	2.9447	5	0.0000	0.0000	0.0000	1.4248	0.5447	1.9695
mx170710	033F0401	Delhi2-80-D15-M1	2017-07-01	2.9807	5	0.0000	0.0000	0.5435	1.3557	0.5006	2.3998
mx170710	034F0401	Delhi2-80-D15-M2	2017-07-01	3.0008	5	0.0000	0.0000	0.0000	0.8791	0.4875	1.3665
mx170710	035F0401	Delhi2-80-D15-B1	2017-07-01	3.0193	5	0.0000	0.0000	0.0000	0.5473	0.0000	0.5473
mx170710	036F0401	Delhi2-80-D15-B2	2017-07-01	2.9914	5	0.0000	0.0000	0.0000	0.4830	0.0000	0.4830
MX170714	007F0201	Delhi2-80-D16-T1	2017-07-02	2.9984	5	5.2009	0.0000	0.0000	1.0494	0.4259	6.6763
MX170714	008F0201	Delhi2-80-D16-T2	2017-07-02	3.0909	5	1.4391	0.0000	0.0000	1.0979	0.4744	3.0114
MX170714	009F0201	Delhi2-80-D16-M1	2017-07-02	3.0121	5	0.0000	0.0000	0.0000	0.4510	0.0000	0.4510

MX170714	010F0201	Delhi2-80-D16-M2	2017-07-02	2.9458	5	0.0000	0.0000	0.0000	0.5629	2.4263	2.9893
MX170714	011F0201	Delhi2-80-D16-B1	2017-07-02	3.0327	5	0.0000	0.0000	0.0000	0.2660	0.0000	0.2660
MX170714	012F0201	Delhi2-80-D16-B2	2017-07-02	2.9476	5	0.0000	0.0000	0.0000	0.3183	0.0000	0.3183
MX170714	015F0201	Delhi2-80-D17-T1	2017-07-03	3.0002	5	0.0000	0.0000	0.0000	0.6399	0.3318	0.9717
MX170714	016F0201	Delhi2-80-D17-T2	2017-07-03	2.9399	5	3.4958	0.0000	0.0000	1.1069	0.5993	5.2020
MX170714	017F0201	Delhi2-80-D17-M1	2017-07-03	3.042	5	0.0000	0.0000	0.0000	0.4471	0.0000	0.4471
MX170714	018F0201	Delhi2-80-D17-M2	2017-07-03	3.0378	5	0.0000	0.0000	0.0000	0.5654	0.3371	0.9025
MX170714	019F0201	Delhi2-80-D17-B1	2017-07-03	3.0185	5	0.0000	0.0000	0.0000	0.2954	0.0000	0.2954
MX170714	020F0201	Delhi2-80-D17-B2	2017-07-03	3.059	5	0.0000	0.0000	0.0000	0.4813	0.0000	0.4813
MX170715	023F0101	Delhi2-80-D18-T1	2017-07-04	3.0011	5	1.4172	0.0000	0.0000	0.7407	0.3578	2.5157
MX170715	024F0101	Delhi2-80-D18-T2	2017-07-04	3.0613	5	0.0000	0.0000	0.0000	0.8419	1.3239	2.1658
MX170715	025F0101	Delhi2-80-D18-M1	2017-07-04	3.0006	5	0.0000	0.0000	0.0000	0.5126	0.3185	0.8311
MX170715	026F0101	Delhi2-80-D18-M2	2017-07-04	3.0415	5	0.0000	0.0000	0.0000	0.3902	0.0000	0.3902
MX170715	027F0101	Delhi2-80-D18-B1	2017-07-04	3.0687	5	0.0000	0.0000	0.0000	0.3392	0.0000	0.3392
MX170715	028F0101	Delhi2-80-D18-B2	2017-07-04	2.992	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170715	031F0101	Delhi2-80-D19-T1	2017-07-05	3.0469	5	2.9118	0.0000	0.0000	0.5869	0.3248	3.8236
MX170715	032F0101	Delhi2-80-D19-T2	2017-07-05	3.0156	5	0.0000	0.0000	0.0000	0.6143	0.7262	1.3405
MX170715	033F0101	Delhi2-80-D19-M1	2017-07-05	2.9925	5	0.0000	0.0000	0.0000	0.3575	0.0000	0.3575
MX170715	034F0101	Delhi2-80-D19-M2	2017-07-05	2.9992	5	0.0000	0.0000	0.0000	0.4342	0.2968	0.7310
MX170715	035F0101	Delhi2-80-D19-B1	2017-07-05	3.0121	5	0.0000	0.0000	0.0000	0.2891	0.0000	0.2891
MX170715	036F0101	Delhi2-80-D19-B2	2017-07-05	2.9846	5	0.0000	0.0000	0.0000	0.3278	0.0000	0.3278
MX170715	038F0401	Delhi2-80-D20-T1	2017-07-06	2.9849	5	0.0000	0.0000	0.0000	0.5969	0.3235	0.9204
MX170715	039F0401	Delhi2-80-D20-T2	2017-07-06	3.0111	5	8.0855	0.0000	0.0000	0.9321	0.3533	9.3708
MX170715	040F0401	Delhi2-80-D20-M1	2017-07-06	3.026	5	0.0000	0.0000	0.0000	0.4102	0.0000	0.4102
MX170715	041F0401	Delhi2-80-D20-M2	2017-07-06	2.9624	5	0.0000	0.0000	0.0000	0.4223	2.3551	2.7774
MX170715	042F0401	Delhi2-80-D20-B1	2017-07-06	3.0881	5	0.0000	0.0000	0.0000	0.4404	1.2309	1.6713
MX170715	043F0401	Delhi2-80-D20-B2	2017-07-06	2.9872	5	0.0000	0.0000	0.0000	0.3984	0.0000	0.3984
MX170715	046F0401	Delhi2-80-D21-T1	2017-07-07	3.0053	5	0.0000	0.0000	0.0000	0.7754	0.4538	1.2292
MX170715	047F0401	Delhi2-80-D21-T2	2017-07-07	3.0312	5	0.0000	0.0000	0.5136	1.8042	1.3751	3.6929
MX170715	048F0401	Delhi2-80-D21-M1	2017-07-07	2.9931	5	0.0000	0.0000	0.0000	0.4769	0.0000	0.4769
MX170715	049F0401	Delhi2-80-D21-M2	2017-07-07	3.0821	5	0.0000	0.0000	0.0000	0.6759	0.5075	1.1835
MX170715	050F0401	Delhi2-80-D21-B1	2017-07-07	2.9698	5	0.0000	0.0000	0.0000	0.3494	0.0000	0.3494

MX170715	051F0401	Delhi2-80-D21-B2	2017-07-07	3.0146	5	0.0000	0.0000	0.0000	0.3368	0.0000	0.3368
MX170715	054F0601	Delhi2-80-D22-T1	2017-07-08	3.0458	5	4.3517	0.0000	0.0000	0.6103	0.3026	5.2645
MX170715	055F0601	Delhi2-80-D22-T2	2017-07-08	3.0271	5	1.5887	0.0000	0.0000	0.6389	0.4162	2.6439
MX170715	056F0601	Delhi2-80-D22-M1	2017-07-08	2.9859	5	0.0000	0.0000	0.0000	0.3916	0.0000	0.3916
MX170715	057F0601	Delhi2-80-D22-M2	2017-07-08	3.0282	5	1.4009	0.0000	0.0000	0.4555	0.4367	2.2931
MX170715	058F0601	Delhi2-80-D22-B1	2017-07-08	3.0073	5	0.0000	0.0000	0.0000	0.2901	0.0000	0.2901
MX170715	059F0601	Delhi2-80-D22-B2	2017-07-08	3.0306	5	0.0000	0.0000	0.0000	0.3456	0.0000	0.3456
MX170715	062F0601	Delhi2-80-D23-T1	2017-07-09	2.9695	5	0.0000	0.0000	0.0000	0.4953	3.3796	3.8749
MX170715	063F0601	Delhi2-80-D23-T2	2017-07-09	2.9594	5	0.0000	0.0000	0.0000	0.5262	0.0000	0.5262
MX170715	064F0601	Delhi2-80-D23-M1	2017-07-09	3.0187	5	0.0000	0.0000	0.0000	0.4064	0.0000	0.4064
MX170715	065F0601	Delhi2-80-D23-M2	2017-07-09	2.9686	5	0.0000	0.0000	0.0000	0.4133	0.0000	0.4133
MX170715	066F0601	Delhi2-80-D23-B1	2017-07-09	2.9642	5	0.0000	0.0000	0.0000	0.2878	0.0000	0.2878
MX170715	067F0601	Delhi2-80-D23-B2	2017-07-09	3.01	5	0.0000	0.0000	0.0000	0.2946	0.0000	0.2946
MX170715	070F0601	Delhi2-80-D24-T1	2017-07-10	3.0178	5	0.0000	0.0000	0.0000	0.5968	0.3171	0.9139
MX170715	071F0601	Delhi2-80-D24-T2	2017-07-10	2.9935	5	0.0000	0.0000	0.0000	0.4656	0.2850	0.7506
MX170715	072F0601	Delhi2-80-D24-M1	2017-07-10	2.9812	5	0.0000	0.0000	0.0000	0.6100	0.0000	0.6100
MX170715	073F0601	Delhi2-80-D24-M2	2017-07-10	2.9863	5	0.0000	0.0000	0.0000	0.3963	0.0000	0.3963
MX170715	074F0601	Delhi2-80-D24-B1	2017-07-10	2.9692	5	0.0000	0.0000	0.0000	0.3063	0.0000	0.3063
MX170715	075F0601	Delhi2-80-D24-B2	2017-07-10	3.0203	5	0.0000	0.0000	0.0000	0.3420	0.0000	0.3420
MX170716	007F0101	Delhi2-80-D25-T1	2017-07-11	3.0775	5	0.0000	0.0000	0.0000	0.5898	0.3084	0.8982
MX170716	008F0101	Delhi2-80-D25-T2	2017-07-11	3.0221	5	1.3749	0.0000	0.0000	0.5211	0.0000	1.8961
MX170716	009F0101	Delhi2-80-D25-M1	2017-07-11	2.9715	5	2.2113	0.0000	0.0000	0.4485	0.0000	2.6599
MX170716	010F0101	Delhi2-80-D25-M2	2017-07-11	2.9448	5	0.0000	0.0000	0.0000	0.3879	0.5754	0.9633
MX170716	011F0101	Delhi2-80-D25-B1	2017-07-11	3.045	5	3.0152	0.0000	0.0000	0.4844	0.0000	3.4997
MX170716	012F0101	Delhi2-80-D25-B2	2017-07-11	2.9925	5	0.0000	0.0000	0.0000	0.3373	0.0000	0.3373
MX170716	015F0101	Delhi2-80-D26-T1	2017-07-12	3.0472	5	0.0000	0.0000	0.0000	0.5259	0.0000	0.5259
MX170716	016F0101	Delhi2-80-D26-T2	2017-07-12	3.0251	5	0.0000	0.0000	0.0000	0.4980	0.0000	0.4980
MX170716	017F0101	Delhi2-80-D26-M1	2017-07-12	2.9614	5	0.0000	0.0000	0.0000	0.3452	0.0000	0.3452
MX170716	018F0101	Delhi2-80-D26-M2	2017-07-12	2.9621	5	0.0000	0.0000	0.0000	0.3307	0.0000	0.3307
MX170716	019F0101	Delhi2-80-D26-B1	2017-07-12	3.0796	5	0.0000	0.0000	0.0000	0.3445	0.0000	0.3445
MX170716	020F0101	Delhi2-80-D26-B2	2017-07-12	2.9896	5	0.0000	0.0000	0.0000	0.3858	0.0000	0.3858
MX170716	023F0101	Delhi2-80-D27-T1	2017-07-13	2.9692	5	0.0000	0.0000	0.0000	0.5018	0.3422	0.8440

MX170716	024F0101	Delhi2-80-D27-T2	2017-07-13	3.0408	5	0.0000	0.0000	0.0000	0.4778	0.3674	0.8452
MX170716	025F0101	Delhi2-80-D27-M1	2017-07-13	3.0445	5	0.0000	0.0000	0.0000	0.4256	0.0000	0.4256
MX170716	026F0101	Delhi2-80-D27-M2	2017-07-13	2.9458	5	0.0000	0.0000	0.0000	0.3891	0.0000	0.3891
MX170716	027F0101	Delhi2-80-D27-B1	2017-07-13	3.0483	5	0.0000	0.0000	0.0000	0.3123	0.0000	0.3123
MX170716	028F0101	Delhi2-80-D27-B2	2017-07-13	2.9573	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170716	031F0101	Delhi2-80-D28-T1	2017-07-14	2.9965	5	2.8930	0.0000	0.0000	1.0290	0.6025	4.5244
MX170716	032F0101	Delhi2-80-D28-T2	2017-07-14	3.0009	5	0.0000	0.0000	0.0000	0.5384	0.3288	0.8671
MX170716	033F0101	Delhi2-80-D28-M1	2017-07-14	2.9585	5	0.0000	0.0000	0.0000	0.4774	0.0000	0.4774
MX170716	034F0101	Delhi2-80-D28-M2	2017-07-14	2.9632	5	0.0000	0.0000	0.0000	0.5652	0.0000	0.5652
MX170716	035F0101	Delhi2-80-D28-B1	2017-07-14	2.9472	5	0.0000	0.0000	0.0000	0.3236	0.0000	0.3236
MX170716	036F0101	Delhi2-80-D28-B2	2017-07-14	2.9691	5	0.0000	0.0000	0.0000	0.3281	0.0000	0.3281
MX170716	039F0301	Delhi2-80-D29-T1	2017-07-15	2.999	5	0.0000	0.0000	0.0000	0.4629	0.0000	0.4629
MX170716	040F0301	Delhi2-80-D29-T2	2017-07-15	3.087	5	0.0000	0.0000	0.0000	0.4868	0.0000	0.4868
MX170716	041F0301	Delhi2-80-D29-M1	2017-07-15	2.9289	5	0.0000	0.0000	0.0000	0.4096	0.0000	0.4096
MX170716	042F0301	Delhi2-80-D29-M2	2017-07-15	3.041	5	0.0000	0.0000	0.0000	0.3611	3.2648	3.6259
MX170716	043F0301	Delhi2-80-D29-B1	2017-07-15	3.0363	5	0.0000	0.0000	0.0000	0.5357	0.7718	1.3076
MX170716	044F0301	Delhi2-80-D29-B2	2017-07-15	3.0249	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170716	059F0501	Delhi2-80-D30-T1	2017-07-16	2.9355	5	4.9175	0.0000	0.0000	0.6587	0.0000	5.5762
MX170716	060F0501	Delhi2-80-D30-T2	2017-07-16	3.0546	5	0.0000	0.0000	0.0000	0.6832	0.3283	1.0116
MX170716	061F0501	Delhi2-80-D30-M1	2017-07-16	3.0262	5	0.0000	0.0000	0.0000	0.4007	0.0000	0.4007
MX170716	062F0501	Delhi2-80-D30-M2	2017-07-16	2.9926	5	0.0000	0.0000	0.0000	0.4108	0.0000	0.4108
MX170716	063F0501	Delhi2-80-D30-B1	2017-07-16	3.0858	5	0.0000	0.0000	0.0000	0.9189	0.0000	0.9189
MX170716	064F0501	Delhi2-80-D30-B2	2017-07-16	3.0304	5	0.0000	0.0000	0.0000	0.3166	0.0000	0.3166

Elora-270-80kg

File Name	Vial Number	Vial Name	Soil (g)	MeCl (mL)	Isooctane	Toluene	m-Xylene	Mesitylene	Naphthalene	Total
MX170322	017F0101	Elora-D1-Mid	3.2297	30	0.0000	0.0000	0.0000	0.0000	21.0086	21.0086
MX170322	018F0101	Elora-D1-Bot	2.782	30	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170322	019F0101	Elora-D1-150g	3.3389	30	0.0000	0.0000	0.0000	7.1796	66.0865	73.2661
MX170322	020F0101	Elora-D1-150g	2.9978	30	0.0000	0.0000	0.0000	13.1013	78.7647	91.8661
MX170322	021F0101	Elora-D1-150g	3.2697	30	0.0000	0.0000	0.0000	12.5364	93.2936	105.8300
MX170322	024F0101	Elora-D2-Top	3.2995	30	0.0000	0.0000	0.0000	13.3701	71.9142	85.2843
MX170322	025F0101	Elora-D2-Mid	3.1741	30	0.0000	0.0000	0.0000	22.9419	22.1115	45.0534
MX170322	026F0101	Elora-D2-Bot	3.2799	30	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170322	029F0101	Elora-D3-Top	2.5206	10	0.0000	0.0000	0.0000	4.4625	30.5131	34.9756
MX170322	030F0101	Elora-D3-Mid	2.7181	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170322	031F0101	Elora-D3-Bot	2.8137	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170323	010F0101	Elora-D4-Top	3.3429	10	0.0000	0.0000	0.0000	3.2546	30.4638	33.7184
MX170323	011F0101	Elora-D4-Mid	3.6398	10	0.0000	0.0000	0.0000	0.0000	2.0752	2.0752
MX170323	012F0101	Elora-D4-Bot	3.5394	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170323	014F0101	Elora-D5-Top	2.8368	10	0.0000	0.0000	0.0000	4.1516	3.5233	7.6749
MX170323	015F0101	Elora-D5-Mid	3.5661	10	0.0000	0.0000	0.0000	0.0000	2.0678	2.0678
MX170323	016F0101	Elora-D5-Bot	3.7014	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170323	019F0101	Elora-D6-Top	2.7475	10	0.0000	0.0000	0.0000	2.1184	2.2544	4.3728
MX170323	020F0101	Elora-D6-Mid	3.4261	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170323	021F0101	Elora-D6-Bot	3.2848	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170323	024F0201	Elora-D7-Top	2.9961	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170323	025F0201	Elora-D7-Mid	3.2965	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170323	026F0101	Elora-D7-Bot	3.5006	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Delhi-LT-150g

File Name	Vial Number	Vial Name	Extraction Date	Soil (g)	MeCl (mL)	Isooctane	Toluene	m-Xylene	Mesitylene	Naphthalene	Total
MX161111	010F0201	M0D0-01	2016-11-07	4.015	10	447.4247	363.2289	513.8872	94.1392	111.3399	1530.0199
MX161111	011F0201	M0D0-02	2016-11-07	3.8778	10	396.0393	315.2041	442.4435	82.4259	102.9430	1339.0557
MX161111	012F0201	M0D0-03	2016-11-07	3.2107	10	332.2592	249.1881	366.4850	70.2722	88.4524	1106.6570
MX161111	013F0201	M0D3-01	2016-11-10	3.3521	10	155.0962	117.4091	192.9087	42.5844	67.1379	575.1362
MX161111	014F0201	M0D3-02	2016-11-10	3.2618	10	183.1668	116.7676	211.5485	47.6623	75.9368	635.0819
MX161111	015F0201	M0D3-03	2016-11-10	3.1912	10	136.1563	85.0346	157.5257	36.7727	62.5544	478.0437
mx161116	011F0201	M0D8-01	2016-11-15	3.1455	10	56.2481	75.2618	133.2228	31.7019	54.5360	350.9706
mx161116	012F0201	M0D8-02	2016-11-15	3.0292	10	68.6504	77.1716	145.0308	34.3021	75.6911	400.8460
mx161116	013F0201	M0D8-03	2016-11-15	2.9743	10	62.1369	69.0675	129.7114	30.7358	57.9705	349.6220
mx161129	011F0201	M0D17-01	2016-11-24	3.0261	10	27.4013	24.9010	49.5118	15.2068	37.2310	154.2519
mx161129	012F0201	M0D17-02	2016-11-24	2.8924	10	19.2603	23.3008	47.8880	14.2741	38.4221	143.1452
mx161129	013F0201	M0D17-03	2016-11-24	3.0709	10	22.7067	21.9326	43.7478	13.0555	37.6217	139.0645
mx161212	011F0201	M0D30-02	2016-12-07	3.2028	10	7.6526	10.3514	29.1925	10.7472	37.5216	95.4654
mx161212	012F0201	M0D30-02	2016-12-07	3.2028	10	7.4416	11.0252	29.9322	10.7325	40.2368	99.3682
mx161212	013F0201	M0D30c-01	2016-12-07	3.2212	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx161212	014F0201	M0D30c-03	2016-12-07	3.0091	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170118	017F0201	M0D0-01	2017-01-10	3.0868	10	628.7334	622.8769	656.0715	107.4807	132.2432	2147.4056
mx170118	018F0201	M0D0-02	2017-01-10	3.0056	10	516.0201	504.8918	531.8525	88.4224	110.0175	1751.2043
mx170118	020F0201	M2D0-01	2017-01-10	3.0841	10	266.9372	213.8790	347.5045	69.6947	96.7121	994.7275
mx170118	021F0201	M2D0-02	2017-01-10	3.0705	10	275.2980	235.5754	343.9870	67.3113	127.7906	1049.9623
mx170118	022F0201	M2D0-03	2017-01-10	3.1372	10	274.7575	235.4397	355.7612	68.6870	91.6826	1026.3280
mx170201	007F0201	M0D3-01	2017-01-13	3.0312	10	402.6813	264.7576	305.8665	55.3407	71.0224	1099.6685
mx170201	008F0201	M0D3-02	2017-01-13	3.0827	10	351.4855	199.0135	243.8495	47.4487	61.9635	903.7607
mx170201	009F0201	M0D3-03	2017-01-13	2.9838	10	364.6726	216.8618	263.1296	50.8174	65.6874	961.1687
mx170201	010F0201	M2D3-01	2017-01-13	3.0703	10	92.7653	65.2635	113.3131	28.1091	50.0575	349.5086
mx170201	011F0201	M2D3-02	2017-01-13	2.9682	10	156.4245	94.2909	171.9640	40.9883	62.8668	526.5345
mx170201	012F0201	M2D3-03	2017-01-13	3.0774	10	106.0772	64.1194	117.1918	28.4302	50.8599	366.6785
mx170201	013F0201	M0D9-01	2017-01-19	3.1401	10	261.5183	285.0179	356.3404	65.5431	77.1919	1045.6115
mx170201	014F0201	M0D9-02	2017-01-19	3.1887	10	335.1946	335.4544	422.8439	76.0675	87.6062	1257.1666

mx170201	015F0301	M0D9-03	2017-01-19	2.9377	10	301.0605	317.5054	390.0824	69.6154	81.6954	1159.9590
mx170201	016F0301	M2D9-01	2017-01-19	3.1433	10	43.0685	32.6984	60.1358	15.1031	40.7891	191.7950
mx170201	017F0301	M2D9-02	2017-01-19	2.9458	10	69.6624	32.8272	63.2937	16.8601	39.7825	222.4260
mx170201	017F0201	M2D9-02	2017-01-19	2.9458	10	104.4516	43.4403	85.5105	21.8063	48.0848	303.2936
mx170201	018F0201	M2D9-03	2017-01-19	3.1412	10	52.3678	30.6917	54.9311	13.8309	35.1771	186.9985
mx170201	019F0201	M0D14-01	2017-01-24	3.0441	10	129.8135	60.5981	86.1443	19.4697	35.7035	331.7291
mx170201	020F0201	M0D14-02	2017-01-24	2.9382	10	188.7580	97.2646	125.9195	26.1241	43.0847	481.1509
mx170201	021F0201	M0D14-03	2017-01-24	3.0765	10	174.2042	88.9228	122.7089	25.5515	42.6461	454.0335
mx170201	022F0201	M2D14-01	2017-01-24	2.9586	10	43.8247	42.9374	87.7765	23.7917	53.9002	252.2305
mx170201	023F0201	M2D14-02	2017-01-24	3.1417	10	40.4075	36.5626	74.7799	20.6856	48.8575	221.2930
mx170201	024F0201	M2D14-03	2017-01-24	3.0172	10	43.8617	46.2969	94.7758	25.9694	65.2495	276.1533
mx170223	016F0201	M0D30-01	2017-02-09	3.0616	10	119.6018	38.7153	66.2257	18.0225	38.0766	280.6418
mx170223	017F0201	M0D30-02	2017-02-09	3.1583	10	45.4895	21.8702	35.1051	8.2622	27.5926	138.3196
mx170223	018F0201	M0D30-01C	2017-02-09	3.112	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170223	019F0201	M0D30-02C	2017-02-09	3.0482	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170223	020F0201	M0D30-03C	2017-02-09	3.1075	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170223	021F0201	M2D30-01	2017-02-09	2.994	10	7.3193	9.3459	19.1699	4.3959	18.1405	58.3715
mx170223	022F0201	M2D30-02	2017-02-09	2.9855	10	5.7498	17.6017	35.3208	190.0914	36.5385	285.3022
mx170223	023F0201	M2D30-03	2017-02-09	3.03	10	3.9326	14.8964	32.5036	124.4053	36.3477	212.0857
mx170223	024F0201	M2D30-01C	2017-02-09	3.0598	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170223	025F0201	M2D30-02C	2017-02-09	2.9474	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170223	026F0201	M2D30-03C	2017-02-09	3.1394	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170409	019F0201	M3D0-1	2017-03-19	3.1845	10	82.0537	133.4714	288.1372	64.9021	87.9700	656.5344
MX170409	020F0201	M3D0-2	2017-03-19	3.1771	10	89.4606	149.7481	322.4951	71.5015	105.6373	738.8426
MX170409	021F0201	M3D3-1	2017-03-22	2.9645	10	14.8232	25.2518	54.9669	15.0964	43.4425	153.5808
MX170409	022F0201	M3D3-2	2017-03-22	3.1095	10	31.4424	28.5851	71.0962	21.7742	50.1156	203.0135
MX170409	023F0201	M3D9-1	2017-03-28	2.9214	10	21.7792	24.9098	64.9410	20.5279	63.7227	195.8807
MX170409	024F0201	M3D9-2	2017-03-28	3.1492	10	8.8209	15.3691	44.3013	14.0908	52.1055	134.6876
MX170409	025F0201	M3D9-3	2017-03-28	3.3326	10	8.2316	15.4678	47.6372	14.5686	56.0225	141.9277
MX170409	026F0201	M3D15-1	2017-04-03	3.1975	10	0.0000	14.3584	53.4580	21.4442	69.6328	158.8935
MX170409	027F0201	M3D15-2	2017-04-03	2.9213	10	11.5671	15.9594	61.5091	24.2472	74.9747	188.2576
MX170409	028F0201	M3D15-3	2017-04-03	3.2129	10	0.0000	14.3634	54.1212	20.3873	70.2686	159.1405

mx170523	007F0101	M3D30-1A	2017-04-21	2.9284	10	0.0000	0.0000	10.7133	6.8013	0.0000	17.5146
mx170523	008F0101	M3D30-2A	2017-04-21	3.0294	10	0.0000	0.0000	11.2989	7.4350	0.0000	18.7340
mx170523	009F0101	M3D30-3A	2017-04-21	3.2228	10	0.0000	0.0000	10.2763	7.2631	0.0000	17.5394
mx170523	010F0101	M3D30-1	2017-04-21	2.9988	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170523	011F0101	M3D30-2	2017-04-21	3.2538	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170529	033F0401	May-D0-1	2017-05-03	3.002	10	8.8463	17.1498	105.6584	38.4454	79.4765	249.5763
mx170529	034F0401	May-D0-2	2017-05-03	3.0232	10	13.9342	26.2644	147.7282	49.1932	88.9239	326.0439
mx170529	035F0401	May-D2-1	2017-05-05	3.052	10	5.2960	3.6468	35.7722	15.7605	55.1543	115.6298
mx170529	036F0401	May-D2-2	2017-05-05	2.9708	10	8.7149	3.6454	38.6240	19.0969	55.3025	125.3836
mx170529	037F0401	May-D2-3	2017-05-05	3.0165	10	7.6188	3.6944	38.3857	17.0863	53.5892	120.3744
mx170529	038F0401	May-D7-1	2017-05-10	3.0589	10	0.0000	0.0000	25.1992	13.6966	20.8885	59.7843
mx170529	039F0401	May-D7-2	2017-05-10	3.1927	10	0.0000	0.0000	20.3180	12.6062	15.8864	48.8106
mx170529	040F0401	May-D7-3	2017-05-10	2.998	10	15.7485	0.0000	27.3236	23.6444	21.1102	87.8267
mx170529	041F0401	May-D15-1	2017-05-17	2.9639	10	5.5196	0.0000	9.9338	13.7356	0.0000	29.1890
mx170529	042F0401	May-D15-2	2017-05-17	2.987	10	6.4938	0.0000	10.1699	14.0103	0.0000	30.6740
mx170529	043F0401	May-D15-3	2017-05-17	3.0177	10	0.0000	0.0000	9.9701	13.0519	0.0000	23.0221
mx170605	054F0801	May-D30-1	2017-06-05	3.0656	5	0.0000	0.0000	0.0000	6.9465	0.0000	6.9465
mx170605	055F0801	May-D30-2	2017-06-05	3.1123	5	0.0000	0.0000	0.0000	7.8781	0.0000	7.8781
mx170605	056F0801	May-D30-3	2017-06-05	2.93	5	0.0000	0.0000	0.0000	7.5483	0.0000	7.5483
mx170605	057F0801	May-D30-4	2017-06-05	3.0059	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170605	058F0801	May-D30-5	2017-06-05	2.9304	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170605	059F0801	May-D30-6	2017-06-05	3.0473	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170619	031F0401	June-150-1	2017-06-12	2.9198	5	3.0858	3.4478	37.7189	20.9056	71.9345	137.0927
mx170619	032F0401	June-150-2	2017-06-12	3.0570	5	4.0026	3.8461	45.7818	24.2983	77.1776	155.1063
mx170619	033F0401	June-150-3	2017-06-12	3.0707	5	7.3961	5.8594	58.7695	28.7151	79.1398	179.8799
mx170619	034F0401	June-150-4	2017-06-15	3.0166	5	5.5251	2.6247	32.2246	18.1207	62.0698	120.5650
mx170619	035F0401	June-150-5	2017-06-15	2.9909	5	2.2045	2.2898	27.3414	14.0047	63.6262	109.4665
mx170619	036F0401	June-150-6	2017-06-15	2.9945	5	8.4512	2.6275	34.1845	21.9854	66.0415	133.2901
MX170709	013F0201	June-150-7	2017-06-20	2.9784	5	8.7235	0.8305	20.9959	14.3053	1.1077	45.9628
MX170709	014F0201	June-150-8	2017-06-20	3.058	5	0.0000	0.8057	20.3858	12.5117	1.0561	34.7592
MX170709	015F0201	June-150-9	2017-06-20	2.9995	5	1.8022	0.8943	20.1570	12.4435	1.2181	36.5151
MX170709	016F0201	June-150-10	2017-06-27	3.0904	5	2.6919	0.0000	2.9737	14.1827	0.5974	20.4457

MX170709	017F0201	June-150-11	2017-06-27	2.9774	5	0.0000	0.0000	1.8937	10.5463	0.0000	12.4399
MX170709	018F0201	June-150-12	2017-06-27	2.993	5	2.9028	0.0000	2.6105	11.2282	0.0000	16.7414
mx170712	007F0201	June-150-31	2005-06-01	3.0985	5	0.0000	0.0000	0.0000	2.1805	0.0000	2.1805
mx170712	008F0201	June-150-32	2005-06-01	3.0623	5	0.0000	0.0000	0.0000	2.3549	0.0000	2.3549
mx170712	009F0201	June-150-33	2005-06-01	3.1631	5	0.0000	0.0000	0.0000	2.0696	0.0000	2.0696
MX170716	047F0301	June-150-D30-1	2017-07-12	2.9704	5	0.0000	0.0000	0.0000	0.7057	0.0000	0.7057
MX170716	048F0301	June-150-D30-2	2017-07-12	3.0592	5	0.0000	0.0000	0.0000	0.5885	0.0000	0.5885
MX170716	049F0301	June-150-D30-3	2017-07-12	2.9418	5	0.0000	0.0000	0.0000	0.4801	0.0000	0.4801
MX170716	050F0301	June-150-D30-B1	2017-07-12	2.9811	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170716	051F0301	June-150-D30-B2	2017-07-12	2.9634	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MX170716	052F0301	June-150-D30-B3	2017-07-12	3.0376	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
mx170731	007F0201	July-D0-1	2017-07-10	2.99	5	8.0984	15.9920	104.7655	39.8683	92.0427	260.7669
mx170731	008F0201	July-D0-2	2017-07-10	3.0095	5	7.7625	12.7164	83.3106	32.4469	76.5786	212.8150
mx170731	009F0201	July-D0-3	2017-07-10	2.9935	5	8.3667	13.8928	89.4509	36.5537	82.9124	231.1765
mx170731	010F0201	July-D3-1	2017-07-13	2.9659	5	7.7333	6.8401	55.6068	25.4730	71.7240	167.3772
mx170731	011F0201	July-D3-2	2017-07-13	3.0757	5	7.2700	5.6016	42.4752	20.4312	65.9781	141.7560
mx170731	012F0201	July-D3-3	2017-07-13	3.0332	5	4.8458	6.0606	45.7734	20.0528	65.6343	142.3668
mx170731	013F0201	July-D8-1	2017-07-18	2.948	5	2.9443	5.5519	39.3321	17.1230	67.1357	132.0870
mx170731	014F0201	July-D8-2	2017-07-18	2.9506	5	3.0049	5.1683	37.4056	16.6309	63.6082	125.8179
mx170731	015F0201	July-D8-3	2017-07-18	3.042	5	9.9227	8.8561	67.3124	32.0435	97.5662	215.7010
mx170731	016F0201	July-D15-1	2017-07-28	3.0349	5	0.0000	0.0000	7.8972	9.1880	0.5062	17.5913
mx170731	017F0201	July-D15-2	2017-07-28	3.0326	5	1.5371	0.0000	7.8360	0.9576	0.6163	10.9470
mx170731	018F0201	July-D15-3	2017-07-28	2.9937	5	0.0000	0.0000	7.2478	8.8721	0.4840	16.6039
MX170821	007F0201	July-150-D30-1	2017-08-09	3.0157	5	0.0000	0.0000	0.0000	4.7928	0.0000	4.7928
MX170821	008F0201	July-150-D30-2	2017-08-09	3.0122	5	0.0000	0.0000	0.0000	5.0736	0.0000	5.0736
MX170821	009F0201	July-150-D30-3	2017-08-09	2.9694	5	0.0000	0.0000	0.0000	4.9808	0.0000	4.9808
mx170926	007F0201	Sept-D0-1	2017-09-08	2.9939	5	6.9882	13.0993	91.2920	406.2827	92.6942	610.3565
mx170926	008F0201	Sept-D0-2	2017-09-08	3.0479	5	3.8778	10.4429	73.4579	325.8251	80.8672	494.4709
mx170926	009F0201	Sept-D0-3	2017-09-08	2.9898	5	4.2754	8.8922	69.7566	325.8734	83.3048	492.1024
mx170926	010F0201	Sept-D0-B-1	2017-09-08	2.9902	5	27.5876	64.4547	192.6975	529.6754	92.8404	907.2556
mx170926	011F0201	Sept-D0-B-2	2017-09-08	3.0203	5	24.7298	64.9554	203.5515	587.5573	113.4568	994.2508
mx170926	012F0201	Sept-D0-B-3	2017-09-08	3.0925	5	24.1821	57.1262	173.8358	489.4734	93.3597	837.9771

mx170926	013F0201	Sept-D1-1	2017-09-09	3.0023	5	8.9633	3.6623	30.7455	193.7790	66.5800	303.7301
mx170926	014F0201	Sept-D1-2	2017-09-09	3.0517	5	4.5524	2.7436	21.3265	119.4833	49.6534	197.7592
mx170926	015F0201	Sept-D1-3	2017-09-09	2.9984	5	4.0996	2.2664	16.8466	105.3621	49.7123	178.2869
mx170926	016F0201	Sept-D1-B-1	2017-09-09	3.014	5	20.9829	16.3206	72.6841	241.7040	72.3379	424.0294
mx170926	017F0201	Sept-D1-B-2	2017-09-09	3.034	5	22.1490	13.3281	63.9011	235.0401	64.1288	398.5472
mx170926	018F0201	Sept-D1-B-3	2017-09-09	3.0529	5	20.7568	16.4446	78.3286	265.8998	77.9460	459.3758
mx170927	007F0201	Sept-D4-1	2017-09-12	2.9624	5	5.9274	1.7505	18.8685	15.9000	7.5540	50.0004
mx170927	008F0201	Sept-D4-2	2017-09-12	3.0062	5	1.9939	1.3269	16.1372	12.9286	5.3819	37.7684
mx170927	009F0201	Sept-D4-3	2017-09-12	2.9878	5	5.1117	1.1537	15.1885	13.7503	5.4257	40.6298
mx170927	010F0201	Sept-D4-B-1	2017-09-12	2.9603	5	6.1609	6.2732	22.5865	8.6016	31.5021	75.1243
mx170927	011F0201	Sept-D4-B-2	2017-09-12	2.9894	5	12.2733	6.0253	25.2327	10.8577	32.7702	87.1591
mx170927	012F0201	Sept-D7-1	2017-09-15	3.0348	5	0.0000	0.0000	0.6094	4.8350	0.6110	6.0554
mx170927	013F0201	Sept-D7-2	2017-09-15	2.9852	5	7.3885	0.0000	3.9728	10.1825	2.0195	23.5633
mx170927	014F0201	Sept-D7-B-1	2017-09-15	3.0238	5	4.4998	2.1934	15.3822	7.4023	26.6112	56.0889
mx170927	015F0201	Sept-D7-B-3	2017-09-15	3.0388	5	6.3641	2.3485	13.7207	6.2105	23.1487	51.7925
mx170927	016F0201	Sept-D11-1	2017-09-19	2.9948	5	93.0544	2.2437	17.2384	36.2590	24.7952	173.5907
mx170927	017F0201	Sept-D11-2	2017-09-19	3.0219	5	115.2434	4.3224	33.5832	54.2021	34.8436	242.1949
mx170927	018F0201	Sept-D11-3	2017-09-19	3.028	5	61.3404	1.8028	19.0553	40.3844	24.3065	146.8894
mx170927	019F0201	Sept-D11-B-1	2017-09-19	3.021	5	60.3296	0.0000	6.7283	21.6424	2.0934	90.7937
mx170927	020F0201	Sept-D11-B-2	2017-09-19	2.9679	5	50.4489	0.0000	6.7871	22.5195	2.9050	82.6606
mx170927	021F0201	Sept-D11-B-3	2017-09-19	3.0002	5	73.4963	1.8313	20.0081	39.8949	7.1563	142.3869
mx170927	022F0201	Sept-D14-1	2017-09-22	2.9787	5	0.0000	0.0000	0.6733	2.0123	0.5785	3.2641
mx171002	007F0201	Sept-D14-2	2017-09-22	3.0033	5	0.0000	0.0000	1.0891	2.0232	0.8097	3.9220
mx171002	008F0201	Sept-D14-3	2017-09-22	2.9751	5	0.0000	0.0000	0.4831	1.3531	0.0000	1.8363
mx171002	009F0201	Sept-D14-B-1	2017-09-22	2.9906	5	2.6691	0.0000	0.7137	7.1129	0.0000	10.4958
mx171025	013F0201	Sept-D30-1	2017-10-08	2.9534	5	0.0000	0.0000	0.0000	0.6149	0.0000	0.6149
mx171027	007F0201	Sept-D30-2	2017-10-08	3	5	0.0000	0.0000	0.0000	0.6393	0.0000	0.6393
mx171027	008F0201	Sept-D30-3	2017-10-08	3.0027	5	3.6558	0.0000	0.0000	0.7558	0.0000	4.4116
mx171027	009F0201	Sept-D30-B-1	2017-10-08	2.9785	5	0.0000	0.0000	0.0000	0.5181	0.0000	0.5181
mx171027	010F0201	Sept-D30-B-2	2017-10-08	3.0029	5	0.0000	0.0000	0.0000	0.5454	0.0000	0.5454
mx171027	011F0201	Sept-D30-B-3	2017-10-08	2.9999	5	0.0000	0.0000	0.0000	0.7719	0.0000	0.7719