UNIVERSITY OF CINCINNATI

Date: 12-Aug-2010

1, Dounia El Khatib

hereby submit this original work as part of the requirements for the degree of:

Master of Science

in Environmental Engineering

It is entitled:

Municipal Solid Waste in Bioreactor Landfills: A Large Scale Study

Student Signature: Dounia El Khatib

This work and its defense approved by:

Committee Chair: Makram Suidan, PhD

Makram Suidan, PhD
Municipal Solid Waste Decomposition in Bioreactor Landfills: A Large Scale Study

A thesis proposal

In partial fulfillment of the requirement

for the degree of

MASTER OF SCIENCE

In the department of Civil and Environmental Engineering

College of Engineering at the University of Cincinnati

2010

Prepared by

Dounia El Khatib

BS.Civil Engineering, Lebanese University, 2007

Committee members

Dr. Makram Suidan UC
Dr. Thabet Tolaymat EPA
Dr. Georges Sorial UC
Abstract

Bioreactor landfills allow a more active landfill management that recognizes the biological, chemical and physical processes involved in a landfill environment. The bioreactor landfill provides control and process optimization, primarily through the addition of leachate or other liquid amendments. This research presents an analysis of leachate, gas and solid parameters data collected during the Acid Formation Phase of anaerobic solid waste decomposition in simulated bioreactor landfills. The main focus of the study is the analysis of the effect of temperature on solid waste decomposition in bioreactor landfills.

In accordance with this objective, three simulated landfill bioreactors were designed and constructed at the EPA Center Hill Facility. Two of the lysimeters were operating at a normal temperature of 37°C and the third was operating at high temperature (60°C). The lysimeters were filled with synthetic municipal solid waste (MSW) material prepared at the site, typical to the landfill composition waste generated in the USA, and reported by U.S. EPA 2008.

In the first part of this study, the results of the indicator parameters are analyzed to quantify the effect of temperature on the waste degradation in bioreactor landfills. Tables and graphical representation of the data are provided for each of the three lysimeters, and compared in order to study the variation of biodegradation of MSW according to the temperature.

In the second part of the study, landfill settlement has been studied in order to predict the settlement in bioreactor landfills. Prediction of landfill settlement is one of the important parameters that affect the design and maintenance of bioreactor landfills. Settlement is known to be a function of many factors (i.e. moisture, density, type of waste etc.); therefore, large number of variables is involved in the settlement mechanism. In this work, a biodegradation settlement model incorporating two parameters (A and B) was developed. In addition, an empirical check of the settlement model was studied, using an exponential function to fit the settlement.
Acknowledgments

First and foremost I owe my deepest gratitude to my supervisor, Dr Makram Suidan, who has given me the opportunity to get into the MS program of environmental engineering, and for his guidance and mentoring throughout the course of this work.

I am heartily thankful to my co-advisor, Dr Thabet Tolaymat, whose knowledge, guidance and support from the initial to the final level enabled me to develop an understanding of the subject. One simply could not wish for a better or friendlier advisor.

I would like also to thank Dr Georges Sorial for being a committee member and for his valuable advices.

In my daily work at EPA Center Hill, I have been blessed with a friendly and cheerful group of people: Dr Gune Silva who has provided good arguments about my thesis work; and my friends with whom I had the pleasure to work. Special thanks to my friend, Darine, for her valuable advices and encouragement.

Most of all, I would like to dedicate this work to my lovely mother Bushra, and my beloved father Mohiedin, and also my sisters for their encouragement, support and endless love all through my life.

Finally, my greatest thanks to my beloved husband, Mohamad, who has been by my side all the time and has been a wonderful support as we journey together throughout life.
Table of Contents

Abstract ................................................................................................................................. 1

Acknowledgments .................................................................................................................. 3

Table of Contents ................................................................................................................. 4

List of Tables ....................................................................................................................... Error! Bookmark not defined.

List of Figures ................................................................................................................. Error! Bookmark not defined.

Chapter 1 ............................................................................................................................... 13

1 Introduction ....................................................................................................................... 13
  1.1 Landfill Bioreactor Technology .................................................................................. 13
  1.2 Purpose of Study ........................................................................................................ 13
  1.3 Report Organization ................................................................................................. 14

Chapter 2 ............................................................................................................................... 16

2 Overview of Bioreactor Landfills .................................................................................. 16
  2.1 Anaerobic Decomposition Fundamentals ................................................................ 16
  2.2 Bioreactor Landfills ................................................................................................. 18
  2.3 Bioreactor Landfill: Benefits and Concerns ............................................................ 19
  2.4 Landfill Gas ............................................................................................................... 21
  2.5 Leachate ..................................................................................................................... 22
    2.5.1 Leachate formation mechanisms ......................................................................... 22
    2.5.2 Characteristics of Leachate ................................................................................ 23
  2.6 Settlement: ................................................................................................................... 23
  2.7 Solid Waste Composition .......................................................................................... 25
  2.8 Factors controlling the degradation process in bioreactor landfills ......................... 27
    2.8.1 Leachate Monitoring Parameters ....................................................................... 27
    2.8.2 Solids Monitoring Parameters ............................................................................ 29
    2.8.3 Gas Monitoring Parameters ................................................................................ 30
Methodology ................................................................................................................................. 31
3.1 Experimental Design .................................................................................................................. 31
3.2 Lysimeter Stack .......................................................................................................................... 32
   3.2.1 Heating System ..................................................................................................................... 34
   3.2.2 Instrumentation .................................................................................................................... 34
Materials and Methods .................................................................................................................... 36
4.1 Sampling Strategy ....................................................................................................................... 36
4.2 Testing and Measurement Protocols .......................................................................................... 37
   4.2.1 Measurement Methods ......................................................................................................... 37
4.3 QA/QC Checks ........................................................................................................................... 37
   4.3.1 Definitions ............................................................................................................................ Error! Bookmark not defined.
   4.3.2 Types of QC Samples ........................................................................................................... 39
   4.3.3 Statistical Evaluation .......................................................................................................... 40
4.4 Data Reporting ........................................................................................................................... 40
4.5 Statistical Analysis ..................................................................................................................... 40
   4.5.1 Normal distribution: ............................................................................................................ 41
   4.5.2 Two-Sample t-Test: ............................................................................................................. 42
Results and Discussions .................................................................................................................. 45
5.1 Leachate Analyses: ..................................................................................................................... 45
   5.1.1 pH: ....................................................................................................................................... 45
   5.1.2 Oxidation-Reduction Potential: ......................................................................................... 47
   5.1.3 Conductivity: ....................................................................................................................... 47
6.4.1 Settlement Data: ................................................................................................................. 87
6.4.2 Settlement Model: .................................................................................................................. 90
6.4.3 Empirical Check of the settlement Model: ............................................................................ 93
6.5 Conclusions: ............................................................................................................................... 96

Appendix A .................................................................................................................................... 98
A. Method for Volatile Fatty Acids Measurement ........................................................................... 98
   1. References: ......................................................................................................................... 98
   2. Apparatus & Reagents: ....................................................................................................... 98
   3. Procedure .......................................................................................................................... 98
B. Method for Gas Analysis using Gas Chromatography (GC) .......................................................... 99
   1. Scope and Application ........................................................................................................ 99
   2. Method Summary ............................................................................................................. 99
   3. Sample Preservation, Containers, Handling, and Storage .................................................. 99
   4. Apparatus ........................................................................................................................ 100
   5. Method ............................................................................................................................ 100
   6. Procedure for Gas Analysis .............................................................................................. 101
   7. Quality control ................................................................................................................ 102
   8. References ...................................................................................................................... 102

Appendix B .................................................................................................................................... 103
Statistical Analysis Results ............................................................................................................ 103
A. Normal distribution: ................................................................................................................ 103
B. Two-Sample t-Test: ............................................................................................................... 106
   1. ORP t-test: .................................................................................................................. 106
   2. Phosphorus t-test: ......................................................................................................... 107
   3. COD t-test: ................................................................................................................ 108
4. Ammonia t-test: ........................................................................................................ 109
5. Alkalinity t-test: .................................................................................................... 110
6. BOD t-test: ............................................................................................................ 111
7. CO2 t-test: ............................................................................................................. 112
8. N2 t-test: ............................................................................................................... 113
9. H2 t-test: ............................................................................................................... 114
10. Acetic Acid t-test: ................................................................................................ 115
11. Propionic t-test: .................................................................................................. 116

Appendix C .................................................................................................................. 118

Settlement Data .......................................................................................................... 118

A. Measured settlement rates in lysimeters B, C, and D ............................................. 118
B. Predicted settlement rates by biodegradation in lysimeters C, and D ................. 121
C. Relative percent Errors calculated in lysimeters C, and D .................................. 123
D. Reports for linear regression in lysimeters C and D ............................................. 124
E. Reports for the fit curves in lysimeters B, C, and D ............................................. 126

References: .................................................................................................................. 130
List of Tables
Table 2-1 Potential Advantages and Disadvantages of Bioreactor Landfills (*) ........................................ 21
Table 2-2 Concentration Ranges in Terms of Waste Stabilization (*) ......................................................... 24
Table 3-1 Municipal Solid Waste Composition for each lysimeter ............................................................... 32
Table 4-1 Leachate Sampling Schedule ........................................................................................................ 36
Table 4-2 Solids Sampling Schedule ............................................................................................................ 37
Table 4-3 Gas Sampling Schedule ................................................................................................................ 37
Table 4-4 Outline of Analysis Methods ......................................................................................................... 38
Table 4-5 Reporting Units ............................................................................................................................... 41
Table 5.5-1 Variation of BOD5/COD Ratio during time ................................................................................. 61
Table 6-1 Long-term settlement mechanisms ............................................................................................... 83
Table 6-2 Initial conditions in lysimeters B, C, and D .................................................................................. 87
Table 6-3 Values obtained for parameters A and B ....................................................................................... 94
Table 6-4 Comparison between parameters A and B obtained by the model and the literature ............. 96
Table C-1 Settlement rate in lysimeter C ........................................................................................................ 118
Table C-2 Settlement Rate in Lysimeter B ..................................................................................................... 119
Table C-3 Settlement Rate in Lysimeter D ..................................................................................................... 120
Table C-4 Predicted Settlement in Lysimeter C ............................................................................................. 121
Table C-5 Predicted Settlement in Lysimeter D ............................................................................................. 122
Table C-6 Relative percent error for predicted and measured settlement in Lysimeter C ..................... 123
Table C-7 Relative percent error for predicted and measured settlement in Lysimeter D ................. 124
List of Figures

Figure 2-1 Phases of degradation in a typical landfill (source: Pohland et al. 1993) .............................................. 17
Figure 2-2 Total MSW Generation- 254 Million tons in 2007(6) ................................................................................. 27
Figure 3-1 Schematic Diagram for Lysimeter System .............................................................................................. 33
Figure 4-1 Probability Plot of ORP data ..................................................................................................................... 42
Figure 4-2 Two-sample t-test for ORP ...................................................................................................................... 43
Figure 5-1 Variation of pH during time in lysimeters B, C and D .................................................................................. 46
Figure 5-2 Solubility of Gases vs Temperature (Ophardt, C. 2003) ........................................................................... 47
Figure 5-3 Variation of Leachate ORP in Lysimeters B, C and D ................................................................................ 48
Figure 5-4 Variation of Leachate Conductivity in Lysimeters B, C and D ................................................................. 48
Figure 5-5 Variation of Dissolved Oxygen in lysimeters B, C and D .......................................................................... 49
Figure 5-6 Alkalinity Variation over time in Stacks B, C and D .................................................................................. 50
Figure 5-7 VFA Concentrations in lysimeter D during time ....................................................................................... 52
Figure 5-8 VFA Concentrations in Lysimeter C during time ....................................................................................... 53
Figure 5-9 VFA Concentrations in Lysimeter B during time ....................................................................................... 53
Figure 5-10 Total VFA calculated as Acetic Acid ......................................................................................................... 54
Figure 5-11 Total VFA as Acetic Acid vs pH in Lysimeter B ....................................................................................... 55
Figure 5-12 Total VFA as Acetic Acid vs pH in Lysimeter C ....................................................................................... 55
Figure 5-13 Total VFA as Acetic Acid vs pH in Lysimeter ......................................................................................... 56
Figure 5-14 COD Concentrations in Lysimeters B, C, and D .................................................................................... 57
Figure 5-15 BOD Concentrations in Lysimeters B, C, and D .................................................................................... 58
Figure 5-16 TOC Concentrations in Lysimeters B, C, and D .................................................................................... 59
Figure 5-17 Evolution of BOD5/COD in stacks B, C, and D .................................................................................... 60
Figure 5-18 Variation of Ammonia Leachate Concentrations in Lysimeters B, C, and D ........................................... 62
Figure 5-19 Dominant form of ammoniacal nitrogen in solution at 25C at various pH levels (Berge et al, 2005) ................................................................................................................................. 62
Figure 5-20 Variation of phosphorous concentrations during time ............................................................... 64
Figure 5-21 Sulfide Concentrations in Lysimeters B, C, and D ................................................................. 64
Figure 5-22 Variation of Total Dissolved Solids during time ................................................................. 65
Figure 5-23 Variation of Total Solids during time ....................................................................................... 66
Figure 5-24 Variation of Calcium concentration during time ................................................................. 67
Figure 5-25 Variation of iron Concentration during time ........................................................................ 68
Figure 5-26 Variation of Potassium concentration during time ................................................................. 68
Figure 5-27 variation of Magnesium concentration during time ............................................................. 69
Figure 5-28 Variation of Manganese concentration during time .............................................................. 69
Figure 5-29 Variation of Sodium Concentration during time ................................................................. 70
Figure 5-30 Variation of Sulfur concentration during time ...................................................................... 70
Figure 5-31 Variation of Strontium concentration during time ............................................................... 71
Figure 5-32 variation of Temperature in Lysimeter B ................................................................................ 72
Figure 5-33 Variation of Temperature in Lysimeter C ............................................................................... 72
Figure 5-34 Variation of Temperature in Lysimeter D ............................................................................. 73
Figure 5-35 Moisture variation in Lysimeter B ....................................................................................... 74
Figure 5-36 Variation of Moisture in Lysimeter C .................................................................................. 74
Figure 5-37 Variation of moisture in Lysimeter D ................................................................................... 75
Figure 5-38 Settlement variation in Lysimeters B, C, and D ................................................................. 76
Figure 5-39 Cumulative Gas production in Lysimeters B, C, and D ........................................................ 77
Figure 5-40 Evolution of gas composition in lysimeter D ....................................................................... 79
Figure 5-41 Evolution of Gas composition in lysimeter C ..................................................................... 79
Figure 5-42 Evolution of gas composition in lysimeter B ..................................................................... 80
Figure 6-1 Settlement data during time in Lysimeter B .......................................................................... 88
Figure 6-2 Settlemet data during time in Lysimeter C ............................................................................ 89
Figure 6-3 Settlement rate during time in Lysimeter D

Figure 6-4 Measured Settlement vs. settlement estimate by biodegradation in lysimeter C

Figure 6-5 Measured Settlement vs settlement estimate by biodegradation in lysimeter D

Figure 6-6 Global fit curve for settlement during time in lysimeter B

Figure 6-7 Global fit curve for settlement during time in Lysimeter D

Figure 6-8 Global fit curve for settlement during time in lysimeter C

Figure A.1- Probability Plot of ORP data 0-1

Figure A.2- Probability Plot of Ammonia data 0-2

Figure A.3- Probability Plot for Alkalinity data0-3

Figure A.4- Probability Plot for BOD data0-4
Chapter 1

1 Introduction

1.1 Landfill Bioreactor Technology

The traditional routes for solid waste disposal are recycling, composting, landfilling, and combustion. Currently, the municipal solid waste industry is undergoing transformation in the manners solid waste is managed to confront the increasing rates of municipal solid waste (MSW) generation and reducing the associated adverse health and environmental impacts. The total annual MSW generation has increased more than 58% between 1980 and 2005 to approximately 245.5 million tons of MSW in the United States (Tolaymat et al., 2004; Townsend, T. and Tolaymat, T., 2003).

A new promising method of solid waste management is the operation of traditional MSW landfills as bioreactors instead of being merely dry waste isolation cells in which the solid waste is entombed. Operating a landfill as a bioreactor is accomplished through moisture addition, to enhance the degradation and stabilization of the organic waste materials.

A bioreactor landfill is a sanitary landfill that uses enhanced microbiological processes to transform and stabilize the readily and moderately decomposable organic waste constituents within 5 to 10 years of bioreactor process implementation. Landfill bioreactors significantly increase the extent of organic waste decomposition, enhance the potential for gas recovery and utilization, diminish management time, and reduce the adverse environmental impacts. Leachate alone is usually not available in sufficient quantities to sustain the bioreactor process, therefore liquid addition could be necessary to reach and maintain optimal conditions for biological activity (Munoz, M.L. et al. 2003). The rationale behind deliberate moisture management is to provide the suitable environment for microorganisms to initiate and regulate the sequential anaerobic phases of acid and methane formation.

1.2 Purpose of Study

Based on the above discussion, the bioreactor landfill is the state of the art technology for solid waste disposal and more research has to be conducted in this area to improve our current understanding of this process in depth and to make it a fully proven technology in order to broaden its full scale application.

The core objective of this project is to study the data collected during Acid Formation Phase of anaerobic solid waste decomposition in simulated bioreactor landfills. Special attention will be directed toward studying the effect of temperature on solid waste decomposition in bioreactor landfills. Therefore, three simulated landfill bioreactors were designed and constructed at the EPA Center Hill Facility. Two of the lysimeters are operating at a normal temperature of 37°C and the third is operating at high temperature (60°C).
The unique design of those Lysimeters opens the doors for a variety of research ideas. This work, however, will focus on:

- The effect of temperature on the waste degradation in bioreactor landfills during Acid Formation Phase.
- Numerical modeling to predict settlements in bioreactor landfills.

The methodology and results are summarized to quantify the effect of temperature on the waste degradation in bioreactor landfills, which is the main objective of this study. Tables including summary statistics are provided including number of samples analyzed, mean, maximum, and minimum and standard deviations. Graphical representation of the data are introduced using multiple straight line and spline curves plots which give an indication of frequency distribution of the data, also plots for the mean values with standard error bars around the means are provided in order to evaluate the trends and determine correlations. Data from the three lysimeters are compared in order to study the effect of the temperature on the biodegradation of waste.

The second main objective is the prediction of landfill settlement, which is one of the important parameters that affects the design and maintenance of bioreactor landfills. Due to the large number of variables involved in the settlement mechanism, accurate prediction of landfill settlement is a challenge. The operational protocol of a landfill and the fraction of organic matter in the municipal solid waste (MSW) have to be reflected in the parameters of the model that will be used to predict the settlement of MSW. In this work, a biodegradation settlement model is developed.

1.3 Report Organization
This report will discuss and study the anaerobic decomposition of municipal solid waste in bioreactor landfills, while focusing on the effect of temperature on the biodegradation and settlement. The dissertation is organized into a series of five chapters followed by three appendices.

The first part of the work involved a literature review including an overview of the anaerobic decomposition phases and the stabilization processes occurring within a Municipal solid waste landfill. It includes also, a summary of the status of bioreactor landfills, their advantages and disadvantages, and the recirculation management strategy used in bioreactor landfills. The literature goes also over the landfill gas generation and the leachate quality. It sums up the characteristics of the leachate produced with an understanding of the leachate formation mechanisms and the importance of leachate quality to ensure proper landfill management.

Another factor included in the literature is the Settlement. The causes of settlement are discussed in this part, as well as the importance of prediction of settlement in the design and maintenance of bioreactor landfills. Moreover, a brief discussion of the solid waste composition is involved in this part, and also the factors that influence the composition and the nature of the municipal solid waste placed in landfills.
The second part of this work includes the methodology and procedure of the project. This section includes the experimental design of the lysimeter, a simulated small scale bioreactor landfill; and it shows also the instrumentation used to measure the parameters. The sampling strategy applied to monitor the parameters is presented in this section. It also presents the measurement methods used to analyze the leachate, solid and gas parameters. Moreover, this part gives an idea of how the data is reported and the way the results are analyzed.

The third part discusses in details the results obtained from the analysis of the leachate, gas, and solid data. The results are divided into three major sections: leachate, solid and gas; in which the corresponding data are displayed. The parameters are analyzed and interpreted in order to give an insight regarding the extent of biological waste conversion. A special focus on the effect of temperature on each parameter is also discussed. In addition, a graphical representation of each parameter is presented in this part. The graphs reflect the evolution of this parameter during the time of experiment. It also includes the statistical analysis of each parameter showing the significance of temperature on the parameter.

The last part of this work concentrates on the second main objective, the prediction of landfill settlement by developing a mathematical model reflecting the biodegradation settlement. Based on this objective, a small introduction about settlement in municipal solid waste landfills is presented. A literature review about the MSW settlement theories is then reported. The MSW settlement mechanisms are then described. Finally, a mathematical model representing the settlement in municipal solid waste bioreactor landfill is developed. This model is later validated on the real data obtained through the experiment.

The appendices include raw data and statistical analysis data from laboratory lysimeter experiments and instrumented data.
Chapter 2
2 Overview of Bioreactor Landfills

2.1 Anaerobic Decomposition Fundamentals

Stabilization processes occurring within a municipal solid waste (MSW) landfill normally proceed through a series of physical, chemical and biological transformations. These changes include: biological decay of putrescible material, either aerobically or anaerobically, with the evolution of gases and liquids; chemical oxidation of waste constituents; dissolution and transport of organic and inorganic liquid transport; movement of dissolved constituents as a result of concentration gradients and osmosis; and uneven settlement caused by waste degradation and consolidation of material into void spaces (Pohland et al. 1992).

A MSW landfill does not have a single waste age, but rather different ages associated with the various cells within the landfill and their respective stabilization stages. As a result, the different landfill stabilization phases often overlap. MSW landfills have been shown to evolve through five relatively discrete and sequential phases of stabilization, starting with an initial lag or adjustment phase which is prolonged until sufficient moisture develops to stimulate an active microbiological community and produce leachate. Operating a MSW landfill as a bioreactor has an effect only on the rates and not the sequence of the degradation phases (Kim and Pohland 2003; Pohland and Al-Yousfi 1994; Reinhart and Townsend 1998). Understanding each of these events is important for landfill management. A brief discussion of the stabilization phases (presented graphically in Figure 1) is presented below.

• Phase I and II (Initial Adjustment and Transition Phase)

Initially, waste decomposition within the landfill proceeds aerobically, primarily utilizing the oxygen contained within the void spaces of the MSW during placement. After available free oxygen is depleted, stabilization continues anaerobically during the remaining life of the landfill. After the initial placement of the waste, a short-lived transition from an oxic to an anoxic microbial stabilization processes, takes place. During that phase, the primary electron acceptors shift from oxygen to nitrates and sulfates with the disappearance of oxygen and production of carbon dioxide in the gas phase. Additionally, intermediates such as volatile organic fatty acids, appear and increase in the leachate.

• Phase III (Acid Formation Phase)

With the hydrolysis of the biodegradable fraction of the solid waste, the volatile organic acids become dominant. Consequently, a decrease in pH occurs with concomitant mobilization and possible complexation of metal species. Nutrients, such as nitrogen and phosphorous, are
released and utilized in support of microbial biomass growth. Hydrogen gas may be detected and affect the nature and type of intermediary metabolism and product formation.

- **Phase IV (Methane Formation Phase)**

  Intermediary products, primarily volatile organic acids formed during the acid formation phase, are converted principally into methane and carbon dioxide. As a result of VFA consumption by mehanogens, the pH drifts to neutrality (approximately 7). Oxidation Reduction Potentials (ORP) are at their lowest reducing levels with the accumulation of reduced sulfur and nitrogen species. The leachate organic strength (characterized by low biochemical oxygen demand) is dramatically decreased in correspondence with increase in gas production. Also, complexation and precipitation of metals proceed.

- **Phase V (Final Maturation Phase)**

  The final stage of solid waste decomposition is characterized by a lower rate of biological activity. During this stage landfill methane production is almost negligible. Oxygen and oxidized species may slowly be converted, with the possible production of humic-like substances.

![Figure 2-1 Phases of degradation in a typical landfill (source: Pohland et al. 1993)](image1)

During anaerobic stabilization, complex organic materials are converted to methane and carbon dioxide by a variety of microorganisms. The four steps of anaerobic digestion include
hydrolysis, fermentation, acidogenesis, and methanogenesis. Each of these steps is performed by a separate and distinct microbial population.

The first step, hydrolysis, involves the transformation of complex insoluble organic material to less complex soluble material, a form and size that can permeate into bacterial cells and be used as energy or nutrient sources.

During the second step, fermentation, organic monomers are converted into simpler intermediates, such as medium- and long-chain volatile organic acids and the short chain acetic, propionic, butyric and valeric acids as well as hydrogen and carbon dioxide.

During the third step, Acidogenesis, the higher volatile organic acids are converted to acetic acid, carbon dioxide and hydrogen. For all longer volatile organic acids, the conversion to acetic acid occurs via –oxidation; whereas the conversion of propionic acid to acetic acid occurs via –carboxylation.

The final step, Methanogenesis, consists of the conversion of acetic acid, carbon dioxide and hydrogen to methane. It is during the methane formation phase that the majority of waste stabilization takes place.

### 2.2 Bioreactor Landfills

The recirculation management strategy used in bioreactor landfills includes leachate containment, collection, and recirculation. During leachate recycling, the leachate produced as moisture percolates through the landfill, is mixed with waste materials and redistributed back over the landfill. There have been numerous studies which have proven the effectiveness of bioreactors (Reinhart, 1998). The increase in the moisture content by using leachate recycling results in accelerated biodegradation, more efficient methane production, enhanced stabilization and even faster decrease in leachate strength than occurs in conventional landfills (Lee, Pohland, Harper, Otiento).

Over the last two decades ago, the idea of applying enhanced leachate recycling appeared (Townsend et al., 1996, Reinhart and Townsend, 1997; Pohland and Kim, 1999; Knox et al., 1999; El-Fadel et al., 1999; Metha et al., 2002). Recycling or recirculation of the leachate back to the landfill creates the perfect environment for rapid microbial decomposition of the biodegradable waste products by providing better contact between insoluble substrates, soluble nutrients and microorganisms (Barlaz et al., 1990). Not only does the system remain a storage facility for the solid waste; it also becomes a treatment system. In the last two decades, several studies were conducted on testing and evaluating the effects of leachate recycling and a number of full-scale bioreactor and leachate recirculation operations have been implemented in the US (Reinhart et al., 2002), in part due to greater recognition of the potential advantages of bioreactor landfills as well as more frequent regulatory acceptance. Studies showed that the benefits of the leachate recirculation are reasonably good.
A report by Townsend et al. (1996) indicated that a landfill in Florida, where leachate recycling was applied, had a lower Biochemical Methane Potential (BMP) than the control areas, where it was not applied. Metha’s and Barlaz’s (2002) research on a Californian landfill was consistent with Townsend’s. It also indicated that by producing an environment with a higher amount of moisture content the pH is more likely to be in the optimal range pH 6.8-7.4 for methanogenesis decomposition. A study by Benson and Barlaz (2006) on five landfills in North America, showed that leachate recirculation accelerated waste decomposition, and settlements of MSW are larger and occur much faster in landfills operated as bioreactors or with leachate recirculation. This was also proven by Edil et al., 1990; El-Fadel et al., 1999 and Hossain et al., 2003. This rapid settlement provides the landfill owner with additional airspace prior to closure (i.e., a greater mass of waste can be buried per unit volume of landfill) and limits the potential for settlement-induced damage of the final cover (Benson, 2000). Appropriate management can enhance fast landfill stabilization, and a high rate of methane production.

Recirculating leachate can also reduce leachate treatment costs (Pohland, 1975, 1980; Reinhart et al., 2002). Berge (2009) developed an economic model to evaluate the costs and benefits associated with bioreactor landfills. Effective operation of bioreactor landfills involves careful operation and construction of infrastructure beyond that necessary in traditional landfills. Thus upfront capital and operating costs of such systems are greater than those associated with traditional landfills. These additional costs, however, may be off-set by numerous economic advantages resulting from bioreactor landfill operation.

Researchers have postulated financial benefits of bioreactor landfills to include extension of the active life of the landfill through additional waste placement, more efficient utilization of airspace (Hater et al., 2001), reduced leachate treatment/disposal costs, deferred new cell and cap construction, earlier beneficial reuse of land, post-closure savings from fewer monitoring and financial assurance requirements, and more efficient gas collection resulting in larger revenues from energy production (SAIC, 2000). These economic benefits, however, may be diminished by costs associated with increased operating requirements.

The disadvantage of using leachate recycle landfills is the increased potential for groundwater pollution associated with the increased hydraulic load and the concerns regarding the effectiveness of landfill lining systems (Benson, 2007). Modern composite liners, however, used for landfills limit leakage to miniscule amounts when properly installed (Foose et al., 2001; Bonaparte et al., 2002). Therefore, highly reliable liner leak detection systems double-composite-liner has to be installed at new, leachate recycling landfills, where the lower composite liner serves as a leak detector for the upper liner.

2.3 Bioreactor Landfill: Benefits and Concerns

Operating a landfill as a bioreactor offers several potential benefits over a conventional landfill.
- **Waste Stabilization**: The primary advantage of operating a bioreactor landfill is fast waste stabilization, making bioreactor operation a more sustainable waste management option. This in turn relates to several other advantages.

- **Leachate Treatment, Capital, and Operating Costs**: Using leachate recirculation for moisture addition may offer considerable costs savings on leachate treatment. At sites where leachate treatment is not expensive, this advantage may not be significant. At sites with limited leachate managements options, saving could be substantial.

- **Air Space Recovery**: It has been demonstrated that a 15 to 30 percent gain in landfill space, due to an increase in density of waste mass, can be achieved when a landfill becomes stabilized. If the landfill operator structures their sequence to utilize this air space gain, savings can be substantial.

- **Landfill Gas Generation Rates**: In bioreactor landfills, gas generation rates are much higher than conventional landfills; therefore landfill gas can potentially be recovered and used economically.

- **Environmental Impacts**: A bioreactor offers considerable reduction in environmental impacts as the waste gets stabilized in a short span of time, when the landfill is still being monitored and when the landfill infrastructure is in top condition.

- **Post Closure Care, Maintenance and Risks**: Bioreactors have the potential to save on post closure care, maintenance and risk management costs. The landfill is stabilized in a short span of time, therefore the final cover settles and repairs needed reduce maintenance and monitoring costs in comparison to the conventional dry tomb landfills. To date, the regulatory authorities have not reduced the long term monitoring frequency and duration for bioreactors.

Bioreactor landfills offer several potential benefits, but they can be a cause of concern if bioreactor operations such as leachate recirculation are not performed correctly. A few of the more common concerns are described here. Possible methods of preventing and mitigating these concerns are also described here in brief.

- **Leachate Seeps**: When the liquids are added at a high pressure or at a flow rate higher than the local infiltration rate or absorption capacity of the waste mass, there is a possibility of seeps. Seeps may be observed along the slopes of the landfills where leachate front meets the daily cover due to preferential flow paths and channeling.

- **Landfill Slope Stability**: Since liquids are added in the bioreactor, internal pore water pressures have the potential to increase and thus decrease the shear strength of the waste. Excessive pore water pressures can cause slope failures.

- **Gas and Odor Control**: Gas production is enhanced at bioreactors. If the gas is not controlled, odors and other environmental problems with gas can result.

Table 2.1 summarizes the advantages and disadvantages of the bioreactor landfills.
Table 2-1 Potential Advantages and Disadvantages of Bioreactor Landfills (*)

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• More rapid waste stabilization.</td>
<td>• Potential for increased odors.</td>
</tr>
<tr>
<td>• Minimize long-term environmental liability.</td>
<td>• Higher capital and operating costs than sanitary landfills.</td>
</tr>
<tr>
<td>• Potential reduced post-closure time period.</td>
<td>• Not fully proven technology as of yet.</td>
</tr>
<tr>
<td>• Increased airspace caused by settlement that may minimize need for</td>
<td>• Slope stability problems.</td>
</tr>
<tr>
<td>siting new landfills.</td>
<td>• Increased generation of methane, a green house gas leading to environmental problems.</td>
</tr>
<tr>
<td>• Enhanced gas production with potential energy recovery revenues.</td>
<td>• Landfill fires</td>
</tr>
<tr>
<td>• Improved leachate storage and treatment at lower costs.</td>
<td></td>
</tr>
<tr>
<td>• Reduced leachate toxicity.</td>
<td></td>
</tr>
<tr>
<td>• Doesn’t compete with recycling and composting programs.</td>
<td></td>
</tr>
</tbody>
</table>


2.4 Landfill Gas

One of the advantages of bioreactor landfills is the increased methane production that results when biological reactions in the landfill are accelerated. Methane is a very valuable energy source and bioreactors have the potential to produce high amounts of the gas in a very short period of time, which could possibly be collected.

Results indicate that the rate of landfill gas generation and recovery in the bioreactor landfill under controlled conditions improves the quality of the landfill gas, potentially providing a greater rate of energy production that can be recovered for electricity generation, if collection occurred early and consistently (Tolaymat et al., 2006; Warith, 2001).

Engineered bioreactor landfills reduce environmental impacts by controlling the LFG emissions; they will have minimum impact on groundwater, surface water, and the neighboring environment. Another major benefit of bioreactor landfills is the reduction of greenhouse gas emissions to the environment.

Landfill Gas emissions are, however, a concern that must be addressed in the design and operation of landfills. The amount and composition of gas emissions expected from MSW landfills are well documented, and the U.S. Environmental Protection Agency (EPA) has developed regulations regarding management of these systems (Powell, 2006). Operating a landfill as an anaerobic bioreactor increases gas production relative to that of conventional MSW landfills, and the EPA has recently promulgated regulations to address this concern.
Landfill gas is produced during the microbially mediated degradation of the organic portion of waste. Decomposition under aerobic conditions occurs immediately after waste disposal due to the entrapped atmospheric air (Nastev, 2001). Mostly carbon dioxide is produced during this stage and heat is generated. Since oxygen is rapidly depleted, the long-term degradation continues under anaerobic conditions. The gas mixture primarily contains methane (CH₄), usually between 50 and 60% by volume, and carbon dioxide (CO₂), 40–50%, with other minor constituents having molar fractions less than 1%. Heat is also generated during the anaerobic degradation, but at a smaller rate than during the initial aerobic phase. The gas pressure and composition vary during the active life of the landfill. The constant generation of landfill gas creates excess pressure within the landfill that provokes its exit into the atmosphere.

When released to the atmosphere, landfill gas represents a threat to the environment, because both methane and carbon dioxide are greenhouse gases. Also, several of the produced organic compounds present health hazards. Furthermore, methane is explosive when its volumetric concentration attains 5% to 15% in an air mixture. Those safety and environmental concerns therefore require that gas emissions be controlled at landfills. Another incentive for controlling gas migration is that, when rich in methane, landfill gas is a valuable energy source.

Usually, landfill gas migrates preferentially through the surface of the landfill because this is more permeable. However, lateral migration of landfill gas is also possible and this must be taken into consideration due to the risk factor. In this case, landfill gas may surface hundreds of meters from the landfill, with its consequent risk. Therefore, sanitary landfills should be equipped with a system of controlled recovery of landfill gas (Fernández et al. 1995; Martín et al. 2000).

2.5 Leachate

Leachate in landfills is considered to be a factor of environmental risk and represents a key consideration during the design and operation of a landfill. In order to design and implement appropriate treatment and disposal actions in the landfill, it is necessary to know the quantitative and qualitative characteristics of the leachate produced as accurately as possible. The factors affecting the chemical composition and the production rate of leachate include the characteristics of the waste (initial composition, particle size, density and soon), the interaction between the percolating landfill moisture and the waste, the hydrology and climate of the site, the landfill design and the operational variables, microbial processes taking place during the stabilization of the waste, and the stage of the landfill stabilization (Yildiz et al. 2004). Most of these factors change during the operational period of the landfill as the landfill is developed causing significant changes in leachate quality and quantity. Therefore, a better understanding of leachate formation mechanisms and leachate quality is necessary to ensure proper leachate management.

2.5.1 Leachate formation mechanisms
Leachate is formed when the refuse moisture content exceeds its field capacity. Moisture retention is attributed primarily to the holding forces of surface tension and capillary pressure. Percolation occurs when the magnitude of the gravitational forces exceed the holding forces. This process is influenced by many factors which can be divided into those that contribute directly to landfill moisture (rainfall, snowmelt, ground water intrusion, initial moisture content, recirculation) and those that affect leachate or moisture distribution within the landfill (compaction, permeability, particle size, density, settlement, cover, sidewall and liner material, gas and heat generation and transport). While increased moisture content is the major contributor to leachate formation, it is also commonly associated with enhancing biodegradation processes in landfills (El Fadel et al. 2002).

2.5.2 Characteristics of Leachate

Soluble organic and inorganic compounds are encountered in the refuse at emplacement or are formed as a result of chemical and biological processes within the landfill. Leachate formation creates a non-uniform and intermittent percolation of moisture through the refuse mass, which results in the removal of these soluble compounds from the refuse and their dissolution and suspension in the leachate. In addition, leachate formation is indicative of increased moisture content, which is associated with enhancing biochemical processes in landfills. The by-products of these processes contribute significantly to the concentration of organics in leachate particularly in the early stages of organic matter decomposition. The composition of landfill leachate can vary depending upon site operations and management practices, refuse characteristics, and internal landfill processes. Many chemical compounds have been detected in landfill leachate. Table 2.2 summarizes the compositional range for a variety of landfill leachates reported in the literature. The intensity of these parameters can vary according to the prevailing phase of landfill stabilization and the manifestation of waste conversion.

2.6 Settlement:

Landfills are very complex systems in which various interactive processes proceed simultaneously. Gas and liquid pressures in landfills change as a result of the gas generated from waste decomposition. These temporary changes in liquid and gas pressures may affect some parameters such as porosity, total stress, degree of gas and liquid saturations, and consequently cause deformations, i.e., settlements.

Settlement is a very significant problem during practical landfill development (Wall and Zeiss 1995) since it is important in the design and maintenance of bioreactor landfills such as designing the piping systems used for the delivery of re-circulated leachate and recovery of landfill gas. Therefore, understanding the patterns of settlement of municipal solid waste (MSW) is critical for the design of a good landfill system, to maintain the various engineered components of an existing landfill facility and to consider the space that could be recovered for further filling of MSW. Prediction of landfill waste settlement is difficult since it is known to be a function of many factors such as the waste type, moisture content, depth, density achieved after
compaction of the landfill, self-weight, overburden, climate, method of filling, mode of operation, etc. (Youcai et al. 2002; Swati. 2007; Hettiarachchi. 2006).

Table 2-2 Concentration Ranges in Terms of Waste Stabilization (*)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Transition Phase (II)</th>
<th>Acid Formation Phase (III)</th>
<th>Methane Formation Phase (IV)</th>
<th>Final Maturation Phase (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.7</td>
<td>4.7-7.7</td>
<td>6.3-8.8</td>
<td>7.1-8.8</td>
</tr>
<tr>
<td>ORP (mV)</td>
<td>+40 to +80</td>
<td>+80 to -240</td>
<td>-70 to -240</td>
<td>+97 to +163</td>
</tr>
<tr>
<td>Conductivity (µhmhos/cm)</td>
<td>2450-3310</td>
<td>1600-17100</td>
<td>2900-7700</td>
<td>1400-4500</td>
</tr>
<tr>
<td>BOD₅ (mg/l)</td>
<td>100-1000</td>
<td>1000-57000</td>
<td>600-3400</td>
<td>4-120</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>480-18000</td>
<td>1500-71000</td>
<td>580-9760</td>
<td>31-900</td>
</tr>
<tr>
<td>TOC (mg/l)</td>
<td>100-3000</td>
<td>500-27700</td>
<td>300-2230</td>
<td>70-260</td>
</tr>
<tr>
<td>Ammonia Nitrogen (NH₃-N)</td>
<td>120-125</td>
<td>2-1030</td>
<td>6-430</td>
<td>6-430</td>
</tr>
<tr>
<td>Total (VFA) mg/l as Acetic Acid</td>
<td>100-3000</td>
<td>3000-18800</td>
<td>250-4000</td>
<td>0</td>
</tr>
<tr>
<td>Total Alkalinity (mg/l as CaCO₃)</td>
<td>200-2500</td>
<td>140-9650</td>
<td>760-5050</td>
<td>200-3520</td>
</tr>
<tr>
<td>Sulfide (S²⁻ mg/l)</td>
<td>Essentially absent</td>
<td>0-818</td>
<td>0.9</td>
<td>Absent</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻ mg/l)</td>
<td>10-458</td>
<td>10-3240</td>
<td>Absent</td>
<td>5-40</td>
</tr>
<tr>
<td>Chloride (Cl⁻ mg/l)</td>
<td>30-5000</td>
<td>30-5000</td>
<td>30-5000</td>
<td>30-5000</td>
</tr>
</tbody>
</table>


Edil et al. (1990) indicated four main mechanisms involved in settlement. They are mechanical (distortion, bending, crunching and reorientation), ravelling (movement of fine particles into large voids), physical-chemical change (corrosion, oxidation, and combustion) and bio-chemical decomposition (fermentation and decay).

Municipal solid waste (MSW) typically shows an immediate settlement upon placement followed by a time dependent settlement (Edil et al., 1990). The settlement that takes place immediately is believed to be due to rearrangement of the MSW skeleton caused by the self-weight and/or other applied loads. In the literature this is defined as the initial settlement and it is mechanical or structural in nature (El-Fadel and Khoury, 2000). However, the considerable portion of settlement occurs due to biodegradation of MSW.

Bioreactor landfills use enhanced microbiological activities to transform and stabilize the biodegradable fractions of MSW at a faster rate (Hettiarachchi, 2008). Enhancement in biodegradation is usually achieved by recirculating the leachate collected from the bottom of the landfill. Recirculation of leachate helps the landfill to maintain a wet environment, in addition to
supplying nutrients required for the biodegradation. Increased moisture content and enhanced biodegradation normally lead to high rates of settlement in bioreactor landfills.

According to Park et al. (2002), the settlement with the four main mechanisms mentioned earlier, occurs in three distinguishable stages. The first one is initial compression, the second is primary compression and the third is secondary compression. Initial compression occurs immediately after the external load is applied in the landfill, and the main mechanism is mechanical. Primary compression occurs quickly, usually within a month of load application. Primary compression is due to the dissipation of gas and pour water from void spaces. The magnitude of primary compression during the first month is higher than the secondary compression, but eventually both of them cause almost the same order of magnitude of compression. Secondary compression takes place over a longer period of time (years) and it is due to creep of the refuse skeleton and biological decay (Leonard and Floom). It is proposed that landfill settlement should be considered to have stabilized when the percentage of settlement during the past year is less than 5% of the total settlement recorded since cessation of all waste placement activities (Morris et al. 2003).

For proper construction and maintenance planning of a bioreactor landfill, it is essential to know how the MSW in a bioreactor landfill behaves and settles during construction and subsequent operation. Based on the regulations, when the final grade is reached at a certain segment of a landfill, it is required to close immediately that particular segment with a temporary or final cover. Also, additional filling is not allowed, even if the top surface settles below the permitted final grade (Hettiarachchi, 2008). It has also been proposed that the final cover of a bioreactor landfill should not be placed until the majority of settlement occurs (Hettiarachchi, 2008). This is to avoid the possible damage to the final cover by the large settlement in a bioreactor landfill.

2.7 Solid Waste Composition

The composition, and therefore, the nature of the MSW placed into landfills depend on several factors. These factors are location, season, cultural practices, extent of leachate recycling, climate, collection frequency, and technology changes. The waste generation varies geographically, both between and within counties. Each region and area has its own waste characteristics; therefore the landfills are not homogenous, but very much heterogeneous. Over the years, this composition has changed dramatically. Surveys from the early 1900s show that a city's waste typically included thousands of horse carcasses along with huge amounts of coal and wood ash, food and yard waste, street sweepings and other debris. Not surprisingly, the vast cultural and technological changes of the past century have transformed the contents of municipal waste.

There are many regional variations that require each community to examine its own waste management needs. Such factors as local and regional availability of suitable landfill space, proximity of markets for recovered materials, population density, commercial and industrial
activity, and climatic and groundwater variations all may motivate each community to make its own plans. Specific reasons for regional differences may include:

- Variations in climate and local waste management practices, which greatly influence generation of yard trimmings. For instance, yard trimmings exhibit strong seasonal variations in most regions of the country. Also, the level of backyard composting in a region will affect generation of yard trimmings.

- Variance in the per capita generation of some products, such as newspapers and telephone directories, depending upon the average size of the publications. Typically, rural areas will generate less of these products on a per person basis than urban areas.

- Level of commercial activity in a community. This will influence the generation rate of some products, such as office paper, corrugated boxes, wood pallets, and food scraps from restaurants.

- Variations in economic activity, which affect waste generation in both the residential and the commercial sectors.

Over the last few decades, the generation, recycling, and disposal of MSW have changed substantially. Annual MSW generation has continued to increase from 1960, when it was 88 million tons (EPA, 2007). The generation rate in 1960 was just 2.68 pounds per person per day; it grew to 3.66 pounds per person per day in 1980, reached 4.50 pounds per person per day in 1990, and increased to 4.65 pounds per person per day in 2000. Since 2000, MSW generation has remained fairly steady. The generation rate was 4.62 pounds per person per day in 2007. This MSW rates include waste from residential, commercial, and institutional sources.

The breakdown, by weight, of product categories generated in MSW in 2007 is shown in Figure 1.2. Containers and packaging comprised the largest portion of products generated in MSW, at about 31 percent (78.4 million tons). Nondurable goods were the second-largest fraction, at 24.5 percent (62.2 million tons). The third-largest category of products is durable goods, which made up 17.9 percent (45.4 million tons) of total MSW generation (EPA, 2007). U.S. EPA 2008 issued a recent report that stated the composition of MSW generated in the USA in 2007 and the results are summarized in Figure (2.2).
2.8 Factors controlling the degradation process in bioreactor landfills

As briefly discussed earlier, the anaerobic refuse degradation process requires at least two different groups of microorganisms (acidogenic and methanogenic). These microorganisms occur naturally in MSW but require different conditions to achieve optimal performance. There are key parameters, if examined closely, that will collectively ensure the optimal operation of bioreactor landfills and minimize risk to human health and the environment. The parameters to be monitored are divided into three main categories, leachate, solid and gas monitoring parameters. The following section discusses those parameters in details.

2.8.1 Leachate Monitoring Parameters

Leachate monitoring is of a great importance to be followed in that, it gives a neat idea regarding what is happening exactly within the landfill and reflects the progression of solid waste conversion and the extent of stabilization.

2.8.1.1 pH

The optimum pH for the anaerobic environment ranges between 6.5 and 7.6 (Tolaymat, 2004). The interaction between volatile organic acids, alkalinity and partial pressure of evolving carbon dioxide determine the prevailing pH. The pH is expected to be low during the acid phase due to the formation of volatile Fatty acids (VFA); also a measurable amount of ionized species will
appear in the leachate. As the degradation go further, the VFAs will be utilized by the methanogenic bacteria and converted to biogas, therefore the pH will start to rise again to values characteristic of bicarbonate buffering systems (Pohland, 1992). pH will be measured automatically by using pH probes penetrated in the leachate collection sump.

2.8.1.2 Volatile Fatty Acids (VFA)

The type and degree of waste conversion, as well as the amount of CH$_4$ and CO$_2$ that could be produced, could be indicated by the amount of VFA present in the leachate (Pohland, 1992). The leachate becomes acidic when an accumulation of VFAs occurs and the excess of VFAs causes inhibition to the activity of methanogenic bacteria. Consequently, low methane production and prolonged time for methane appearance could be expected (Tolaymat, 2004).

2.8.1.3 Total Alkalinity

Total alkalinity of leachate is considered reflective of the buffering capacity. Measuring the leachate alkalinity is important in determining its ability to resist changes in pH. According to the alkalinity, the buffer to be added to the leachate to bring to neutral pH could be determined.

2.8.1.4 Organic Strength Indicators (COD and TOC)

The measurement of the oxygen demand of a leachate can give an estimate of its organic content. It could be chemical oxygen demand (COD) if a chemical oxidizing agent is used or biochemical oxygen demand (BOD$_5$) if the bacteria are used to oxidize the organic matter. The COD value is normally higher than the BOD$_5$ value because more organic matter can be oxidized by using the chemical oxidant than are biodegradable. TOC is also used as an indicator of the organic strength of leachate. It is expected that COD and TOC concentrations will be high during the acid formation phase due to the high VFA concentration and adversely their values will decrease after the onset of the methane formation phase (Tolaymat, 2004).

2.8.1.5 Oxidation - Reduction Potential (ORP)

The availability of electrons within the leachate is determined by the ORP. Therefore, it is used as an indicator for the intensity of oxidation and reduction in the system (Townsend, 2003). Reduction/oxidation (Redox) reactions chemically convert hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. Reducing conditions (typically ORP less than -200 mV) could be created by biological activity and results in reducing the mobility of heavy metals through precipitation with sulfides and complexation with organic acids (Townsend, 2003).

2.8.1.6 Conductivity

Conductivity is considered to be an indicator of the ionic strength of leachate and consequently, the activity. The activity of ions is a function of their concentrations. Conductivity is expected to increase during the acid formation phase due to mobilization of metals and decreases in the methane formation phase due to the complexation of metals with sulfides (Pohland, 1992).
2.8.1.7 **Leachate Nitrogen Content**

Total Kjeldahl Nitrogen (TKN), ammonia and nitrate are the main forms of nitrogen in leachate, but ammonia is considered the most important because it could be inhibitory for the methanogenic activity if it is found in high concentrations. Ammonia tends to accumulate in the leachate under anaerobic conditions especially with recirculation. Despite the adverse effect of increasing ammonia concentration, it could be considered an indicator for advanced waste decomposition while at the same time it could be used as an alarm to stop recirculation at very high concentration (Tolayamat, 2004). Ammonia concentration of 1500-3000 mg/l could be inhibitory of methanogenic activity, while concentration more than 3000 mg/l has a toxic effect (Pohland, 1992).

2.8.1.8 **Sulfate and Sulfide**

Clogging could be formed due to sulfured forms, so it has to be measured. Reduction of sulfate could occur and lead to an inhibition of methanogenic activity and the presence of HS reveals this phenomenon (Munoz, 2003). Sulfate starts decreasing as the anaerobic conditions are established until it nearly becomes absent due to complete conversion to sulfides during the methanogenic phase. On the other hand, sulfide begins to appear and increase due to sulfate reduction under acidic conditions and starts to be lower at the methanogenic phase due to heavy metal precipitation (Pohland, 1992).

2.8.1.9 **Phosphorous**

One of the main nutrients for microbial growth is phosphorous; accordingly low quantities of it will slow down the biological activity and waste conversion. Thus leachate analysis will be performed for total phosphorous to give indication of the availability of nutrients.

2.8.1.10 **Metals**

Metal toxicity depends on both the speciation and the metals partitioning in the anaerobic environment. Toxicity causes inhibition to the biological activity. pH, ORP, presence of complexing ligands, and the presence of precipitants such as sulfide and hydroxide, are some of the numerous factors that affects metals solubility. The highest metals concentration should be observed during the acid formation phase because the metals solubility in leachate increases as pH decreases (Pohland, 1992). On the other hand, metal concentration should decrease after the onset of the methane forming phase. Metals do not degrade but are transformed from one chemical state to another. Under anaerobic conditions, metals could precipitate, bind to organic waste ligands, chelates or being subjected to ion exchange within the landfill.

2.8.2 **Solids Monitoring Parameters**

2.8.2.1 **Temperature**

Temperature within the anaerobic environment affects the biological activity. The optimum temperature range for the anaerobic processes is to occur within either mesophilic (30-38 °C) or thermophilic (50 to 60 °C) ranges (Tolayamat, 2004). Thermocouples will be used to measure the temperature at four intervals on the lysimeter stacks using ports on the short segments.
2.8.2.2  Moisture Content

The biodegradation of solid waste increases with the increase in moisture content and the optimum should be greater than 40% (Pohland, 1992). Therefore, leachate will be recirculated to the solid waste to increase the water content of the waste in order to maintain the optimal conditions for biological activity. The volumetric moisture content will be measured using a Time Domain Reflectometry system as mentioned earlier.

2.8.2.3  Volatile Solids

Operating the landfill as a bioreactor increases the degradation of solid waste which means an increase in the degradation of cellulose and hemicellulose and an increase in the settlement rate. The cellulose, hemicellulose and lignin content are strongly correlated to the volatile solids (VS) content of MSW. Therefore, the analysis of volatile solids will be used as an indicator of the degradability. The decrease in volatile solids indicates the decomposition of solid waste due to the cellulose and hemicellulose content loss (Tolaymat, 2004).

2.8.3  Gas Monitoring Parameters

The gas volume and composition are indicators for the refuse stabilization progression. The primary end products of the anaerobic stabilization are methane and carbon dioxide. Generally, the generated gas consists mainly of 15-60% methane and 5-40% carbon dioxide and oxygen should be lower than 5 % and Nitrogen is the balance gas (Tolaymat, 2004). The oxygen and nitrogen that will be introduced during waste loading and contained within the refuse void spaces are expected to be removed and nitrogen will be displaced by gas production (Pohland, 1992). Gas composition/concentration will be verified using a gas chromatography equipped with a thermal conductivity detector (GC/TCD; Agilent 6980N).
Chapter 3
3 Methodology

3.1 Experimental Design

Based on the advantages of bioreactor landfill discussed earlier, three small scale bioreactor landfills, referred to as Lysimeters, were designed and constructed at the EPA Center Hill Facility to simulate real bioreactor landfills. The lysimeter stacks were constructed at the high bay area at Center Hill Facility. The lysimeter is a freestanding vessel that was filled with synthetic MSW material prepared at the site (typical to the landfill composition waste in the USA) with recirculation of leachate and water. Prior to filling the lysimeter, MSW was thoroughly saturated with tap water. To achieve homogeneity and uniform compaction across the lysimeter, filling was done in 6 inches layers. One of lysimeters is operating at 37°C as the control (D). A layer of MSW in the second (C) and third (B) lysimeters was replaced with a layer of drinking water treatment arsenic containing sludge (obtained from a drinking water treatment plant) and course sand (1:1 ratio). Lysimeter C is also operating at 37°C. Lysimeter B is operating at 60°C.

The lysimeters are equipped with instrumentation to log near real-time values for the main parameters that indicates the performance of a bioreactor landfill. They are equipped with Time-Domain Reflectometry (TDR) probes, electrodes, thermocouples, gauges, and sensors connected to a data acquisition system to automatically monitor the pH, Oxidation Reduction Potential (ORP), conductivity, Dissolved Oxygen (DO), moisture content, gas flow rate, gas composition and settlement of contents.

Each lysimeter consists of a set of modular rings 2 feet in diameter stacked to a height of approximately 10 feet. A portable press applies pressure to compact the waste media using compressed air from the laboratory supply. The press adds 40 inches to the height of each lysimeter stack. A hydronic heating system wrapped around the modular rings keeps them at the desired temperature within the range of 35°C to 60°C. Ports are provided for extracting gas, liquid and solid samples for analysis in the laboratory. A compactor press operated by air pressure from the laboratory air supply will be used to compress the waste after filling the lysimeters by applying a force of 6014 lbs using air pressure of 70 P.S.I. Leachate is collected in a closed stainless steel sump that contains a level controller to start a small air- driven pump, and a batch of 4.2 L of leachate is recirculated to the top of the stack through a spray nozzle, Figure 3.1. Sensors for measuring pH, ORP, D.O and conductivity are attached to the sump as shown in Figure 3.1. A computer based data acquisition system provides near real-time display and logging of the instrumentations.

Based on the municipal solid waste composition reported in section 2.1.7, 1590 kilogram of synthetic solid waste that is representative of the typical landfill waste in the USA was used to fill the three lysimeters (530 kg/lysimeter) as shown in Table 3.1. The synthetic MSW was
prepared at the site and compacted to mimic landfill bulk density (about 0.5 g.cm$^{-3}$) reported in the literature.

Table 3-1- Municipal Solid Waste Composition for each lysimeter

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage % (by mass)</th>
<th>Weight (Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper (34.2%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Office Paper</td>
<td>17.0</td>
<td>89.74</td>
</tr>
<tr>
<td>Magazine &amp; Newspaper</td>
<td>9.8</td>
<td>51.74</td>
</tr>
<tr>
<td>Cardboard</td>
<td>7.4</td>
<td>39.07</td>
</tr>
<tr>
<td>Glass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magazine &amp; Newspaper</td>
<td>5.3</td>
<td>27.45</td>
</tr>
<tr>
<td>Metals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magazine &amp; Newspaper</td>
<td>8.2</td>
<td>40.12</td>
</tr>
<tr>
<td>Plastic (12.10%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Garbage Bags</td>
<td>6.05</td>
<td>31.15</td>
</tr>
<tr>
<td>Plastic Bottles</td>
<td>6.05</td>
<td>31.15</td>
</tr>
<tr>
<td>Leather and Textiles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leather</td>
<td>3.0</td>
<td>15.84</td>
</tr>
<tr>
<td>Textiles</td>
<td>4.3</td>
<td>22.7</td>
</tr>
<tr>
<td>Wood (5.60%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treated</td>
<td>2.8</td>
<td>15.05</td>
</tr>
<tr>
<td>Untreated</td>
<td>2.8</td>
<td>15.05</td>
</tr>
<tr>
<td>Yard Trimmings</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yard Trimmings</td>
<td>12.8</td>
<td>69.16</td>
</tr>
<tr>
<td>Food Scraps</td>
<td>12.5</td>
<td>62.82</td>
</tr>
<tr>
<td>Other (Soil)</td>
<td>3.20</td>
<td>16.89</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>527.906</td>
</tr>
</tbody>
</table>

- Assume Solid Waste Density = 1000 lb.yd$^{-3}$ = 593.82 Kg.m$^{-3}$
- Volume of one Lysimeter = 0.889 m$^3$
- Total Mass of Solid Waste per Lysimeter = 530 Kg

3.2 Lysimeter Stack

Two sizes of segments were used to construct the stack, short segment and long segment. The short segment is intended for instrumentation, and includes several ports for access through the side. The lysimeter stack is mounted on a base that is 48” square, made from carbon steel bars welded into a grid. In the center of the base is welded the bottom cover, to which the stacked rings are bolted. Drain ports are included in the bottom cover. The base includes leveling screws so that the stacks adjusted to be exactly vertical. Core-Tex TM joint sealant cord is used to seal the rings together. Each ring has twenty 0.5” diameter grade 8 bolts, which are tightened to a final torque of 76 ft-lbs by using an air ratchet.

The choice of material for the lysimeter vessel was determined by the requirements to resist degradation from the acidic leachate, be physically strong enough to withstand the forces exerted by the compaction press, and be inert so as not to contaminate the sample analysis. The strength of materials used in the lysimeter system depends on the expected load. Assumptions include: the stack is half full of water, and the trash is compacted to 44.4 lbs/cu.ft. The compaction press force corresponds to 14.17 lb/sq.in to simulate an overburden depth of 40 ft.
Figure 3-1 Schematic Diagram for Lysimeter System

1- Leachate Collection Sump.  
2- Level Probes.  
3- Dissolved Oxygen Sensor.  
4- Conductivity Sensor.  
5- pH Electrode.  
6- ORP Electrode.  
7- Leachate Recirculation Pump.  
8- Leachate Flow Meter.  
9- Sump Cleanout Plug.  
10- Leachate sampling Port.  
11- In-Line pH Buffer.  
12- Sump Venting Path.  
13- Thermocouples.  
14- Gas Sampling Port.  
15- Solid Waste Sampling Port.  
16- TDM for Measuring Moisture Content.  
17- Leachate Recirculation Line.  
18- Leachate Spray Nozzles.  
19- Depth Measuring  
20- Gas Flow Meter.  
21- Gas Composition Detectors
3.2.1 Heating System

The lysimeter stacks were heated hydraulically. That is, hot water was circulated in tubes that wrap around the stack. An insulation blanket of 1 inch thick Rubatex™ was wrapped around the stack to conserve energy. The heat source is a water heater with a 40 gallon tank and power vent to allow the tank to be located conveniently since only a PVC pipe is required to vent.

The tubing was wrapped around the stack in a double helix, with return line adjacent to the supply line, to even out the temperature.

3.2.2 Instrumentation

The lysimeters were instrumented to measure temperature, moisture content, pH, ORP, D.O, conductivity, gas flow rate, gas composition and settlement of the contents.

3.2.2.1 Temperature Measurement

Thermocouples were used to measure the temperature at four intervals on the lysimeter stacks, using ports on the short segments. The type-T thermocouples were sheathed in 316 SS and mounted in a fitting that allows insertion at up to 12” depth. A four channel DGH™ transmitter module was connected to a set of thermocouples, and transmitted the data using RS-485 protocol.

3.2.2.2 Moisture Content Measurement

The volumetric moisture content measuring system had 16 channels for monitoring the four lysimeter stacks. It communicated using RS-232 protocol with a computer running the WinTrase™ software package. The moisture content was measured using a Time Domain Reflectometry (TDM) system. The trase™ system (made by Solimoisture Equipment Corp.) sends an electromagnetic pulse from a waveguide mounted in the lysimeter. Up to four waveguides may be placed at intervals in the lysimeter stack short segment.

3.2.2.3 pH, ORP, D.O and Conductivity Measurement

A sump was constructed from 13 gauge stainless steel measures 16” x 8” x 8” deep, with an acrylic plastic cover that was sealed to the top lip. An air-driven diaphragm pump moved the accumulated leachate from the sump to the top of the lysimeter stack, where it is sprayed through a set of two nozzles, at a rate of about three L/min. A controller monitors the level of the leachate in the sump and activates the pump as needed. A level drawdown of 2” in the sump produces about 4 L.

The pH and ORP probes are mounted in 1” Tee stainless steel fittings, and the D.O and conductivity probes are mounted in 2” Tee unions. A controller periodically starts the sampling pump and opens the valves to a particular sump, so that at least two pipe volumes of fluid are passed through, and then the data acquisition system reads the sensors. A digital input module flags the data to indicate which lysimeter sump is being sampled.
The pH Electrode: is a differential type with replaceable salt bridge, temperature compensation and preamplifier. The body material is PEEK with glass process electrode and titanium ground electrode.

The ORP electrode: is the same construction as pH electrode but with platinum bands.

The Dissolved Oxygen sensor: is a Clark Cell type polarigraphic probe, with three electrodes.

The conductivity sensor: is an electrodeless toroidal type. This type of sensor avoids problems of fouling, and is encapsulated with inert PFA TeflonTM.

Front panel mounted displays show pH, ORP, D.O, and conductivity. All the sensor transmitters interface with a 4-20 mA current-loop signal to four-channel DGH TM modules. The modules connect to a remote computer using RS-485 protocol and a USB interface. The computer runs a software package called WinWedgePro TM that logs and displays the data directly in an Excel TM spreadsheet.
Chapter 4
4 Materials and Methods

4.1 Sampling Strategy

The monitoring parameters for leachate, solids and gas were measured for the first year according to the schedule presented in Tables 4.1, 4.2 and 4.3. This schedule will continue for the remaining years of the project unless some changes are recommended to obtain better representative data.

Table 4-1- Leachate Sampling Schedule

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Frequency</th>
<th>No. of Samples/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Continuously</td>
<td></td>
</tr>
<tr>
<td>Oxidation Reduction Potential (ORP)</td>
<td>Continuously</td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>Continuously</td>
<td></td>
</tr>
<tr>
<td>Dissolved Oxygen (D.O)</td>
<td>Continuously</td>
<td></td>
</tr>
<tr>
<td>Chemical Oxygen Demand (COD)</td>
<td>Biweekly</td>
<td>24</td>
</tr>
<tr>
<td>Biological Oxygen Demand (BOD)</td>
<td>Biweekly</td>
<td>24</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>Biweekly</td>
<td>24</td>
</tr>
<tr>
<td>Total Organic Carbon (TOC)</td>
<td>Biweekly</td>
<td>24</td>
</tr>
<tr>
<td>Ammonia Nitrogen (NH₃-N)</td>
<td>Biweekly</td>
<td>24</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>Biweekly</td>
<td>24</td>
</tr>
<tr>
<td>Volatile Fatty Acids (VFA)</td>
<td>Biweekly</td>
<td>24</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>Biweekly</td>
<td>24</td>
</tr>
<tr>
<td>Anions (SO₄²⁻, NO₃⁻, NO₂⁻ and Cl⁻)</td>
<td>Monthly</td>
<td>12</td>
</tr>
<tr>
<td>Sulfide</td>
<td>Monthly</td>
<td>12</td>
</tr>
<tr>
<td>RCRA Metals and Ca, Cu, Fe, Mg, Al, Ni &amp;Zn</td>
<td>Biweekly</td>
<td>24</td>
</tr>
<tr>
<td>Voltage</td>
<td>Continuously</td>
<td></td>
</tr>
</tbody>
</table>

Samples will be collected and analyzed on-site at the Center Hill Facility labs, therefore no shipping is required. Samples will be collected from the lysimeters using different techniques according to the matrix to be analyzed. The matrices of interest in this study are leachate, solid waste and the gas.

**Leachate Sampling:** Leachate will be sampled from a tap on the leachate collection sump. However, part of the leachate monitoring parameters (i.e., Conductivity, D.O, pH and ORP) will be analyzed automatically using sensors and electrodes without the need for manual sampling except for calibration checks.
Table 4-2: Solids Sampling Schedule

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Frequency</th>
<th>No. of Samples/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Continuously</td>
<td></td>
</tr>
<tr>
<td>Moisture Content</td>
<td>Biweekly</td>
<td>24</td>
</tr>
<tr>
<td>Settlement</td>
<td>Continuously</td>
<td></td>
</tr>
<tr>
<td>Biochemical Methane Potential (BMP)</td>
<td>Quarterly</td>
<td>4</td>
</tr>
<tr>
<td>Volatile Solids</td>
<td>Quarterly</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 4-3: Gas Sampling Schedule

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Frequency</th>
<th>No. of Samples/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Flow Rate</td>
<td>Continuously</td>
<td></td>
</tr>
<tr>
<td>Gas Composition % (CH₄, CO₂, H₂, O₂, H₂S, N₂)</td>
<td>Daily</td>
<td></td>
</tr>
</tbody>
</table>

Gas Sampling: The generated gas volume was measured using a gas flow meter, while the gas composition was measured using the Gas Chromatography (i.e., the percentage of CH₄, CO₂, N₂, O₂, and H₂). The Gas Chromatography was calibrated once per month using standard gases bottles for CH₄, CO₂, N₂, O₂, and H₂. The calibration curve consisted of 8 points and the correlation coefficient, R², should have at least 3 nines, ex. 0.999…

All the instrumentations were calibrated prior to use according to the manufacturer’s guidelines. Samples were collected at regular time intervals.

4.2 Testing and Measurement Protocols

4.2.1 Measurement Methods

The methods for matrices analysis are summarized in Table 4.4. Most of the critical measurements were analyzed automatically and the results were sent directly through the data acquisition system and logged using WinWedgePro™ software onto Excel spreadsheets every data acquisition cycle.

4.3 QA/QC Checks

A quality control plan must be established and followed to ensure optimum generation of data with acceptable quality. The accuracy checks, precision, the estimated detection limits and the calibration issues, are all parameters to be used to ensure the quality control and the confidence level of the obtained results.

4.3.1 Definitions

Accuracy is the nearness of a test result to the true value (recovery). Both, standard addition (spiking) and standard checks are common techniques for checking the accuracy.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Instrument</th>
<th>Analytical Method/SOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leachate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>Automatic Temperature and Compensation electrode</td>
<td>EPA Method 150.1</td>
</tr>
<tr>
<td>Oxidation Reduction Potential (ORP)</td>
<td>ORP Electrode</td>
<td>Manufacturer manual</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Electrodless Toroidal Conductivity Sensor</td>
<td>Manufacturer manual</td>
</tr>
<tr>
<td>Dissolved Oxygen (D.O)</td>
<td>Clark Cell Type sensor with three electrodes</td>
<td>EPA Method 410.4</td>
</tr>
<tr>
<td>Chemical Oxygen Demand</td>
<td>HACH DR890 Colorimeter</td>
<td>Standard Methods for the examination of Water and Wastewater/ 2510 B</td>
</tr>
<tr>
<td>Biological Oxygen Demand (BOD₅)</td>
<td>Dissolved Oxygen Probe</td>
<td></td>
</tr>
<tr>
<td>Total Organic Carbon (TOC)</td>
<td>Shimadzu TOC-V SSM analyzer</td>
<td>SW 846 Method 9060A /SOP #2</td>
</tr>
<tr>
<td>Ammonia Nitrogen (NH₃-N)</td>
<td>HACH DR890 Colorimeter</td>
<td>EPA Method 350.1</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>HACH DR890 Colorimeter</td>
<td>Appendix A</td>
</tr>
<tr>
<td>Volatile Fatty Acids (VFA)</td>
<td>Gas Chromatograph (GC) Agilent 6890 N Series</td>
<td>EPA Method 365.2</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>Titration</td>
<td>EPA Method 310.1</td>
</tr>
<tr>
<td>Anions (SO₄²⁻, NO₃⁻, NO₂⁻ and Cl⁻)</td>
<td>Ion Chromatograph (IC), using AS-18 Dionex chromatography column.</td>
<td>EPA Method 300</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>---</td>
<td>Standard Methods for the examination of Water and Wastewater/ 2540 C</td>
</tr>
<tr>
<td>Sulfide</td>
<td>HACH DR890 Colorimeter</td>
<td>SW-846 Method 6010B</td>
</tr>
<tr>
<td>RCRA Metals and Ca, Cu, Fe, Mg, Al, Ni &amp;Zn</td>
<td>Thermo Elemental 61 E trace analyzer ICP-AES</td>
<td>EPA Method 376.2</td>
</tr>
<tr>
<td>Solids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Type T Thermocouple</td>
<td>Standard Methods for the examination of Water and Wastewater 2550 A-B</td>
</tr>
<tr>
<td>Moisture Content</td>
<td>Time Domain Reflectometry (TDM) system</td>
<td></td>
</tr>
<tr>
<td>Volatile Solids</td>
<td>---</td>
<td>Standard Method 2540E</td>
</tr>
<tr>
<td>Gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Flow Rate</td>
<td>Omega⁸ FVL-1619A volumetric flowmeter</td>
<td>Manufacturer manual</td>
</tr>
<tr>
<td>Gas Composition</td>
<td>Gas Chromatograph (GC/TCD) Agilent 6890 N Series</td>
<td>Appendix A</td>
</tr>
</tbody>
</table>

For matrix spikes, the percent recovery could be calculated as follows:

\[
\% R = \left( \frac{C_s - C_u}{C_a} \right) \times 100
\]

Where:  
\( C_s \) = Concentration in spiked aliquot
\[ C_u = \text{Concentration in unspiked aliquot} \]
\[ C_a = \text{Actual concentration of spike added} \]

For standard checks, the percent recovery will be calculated as follows:

\[ \% R = \frac{C_m}{C_a} \times 100 \]

Where: \( C_m \) = measured concentration of the check standard.
\( C_a \) = actual concentration of the check standard.

**Precision** is how repeated measurements closely agree with each other. Laboratory duplicates and triplicates will be used to ensure precision; the relative percent difference (RPD) between duplicates will be calculated as follows:

\[ \% RPD = \frac{|C_1 - C_2|}{0.5(C_1 + C_2)} \times 100 \]

Where: \( C_1 \) = Concentration of the analyte in the sample
\( C_2 \) = Concentration of the analyte in the matrix duplicate

The relative standard deviation between replicates will be calculated as follows:

\[ \% RSD = \left( \frac{S}{\bar{y}'} \right) \times 100 \]

Where: \( S \) = Standard deviation
\( \bar{y}' \) = Mean of the replicates

**Method Detection Limit (MDL)** is the lowest concentration that is different from zero with a 99% level of confidence. To determine the MDL, the lowest standard concentration used for the calibration will be injected number of times and the MDL will be calculated using the following equation:

\[ \text{MDL} = t(n-1, 1-\alpha = 0.99) \times S \]

Where: \( n \) = the number of replicates
\( S \) = Standard deviation of the replicates

### 4.3.2 Types of QC Samples

**Method Blank** is a generated sample prepared from a clean matrix (generally deionized water and it could be gas or solid according to the type of matrix), and it is treated exactly as a sample. It is prepared to check for contamination.

**Calibration Blank** is a volume of reagent water without the analyte. The concentration of the analyte should be less than three times the instrument detection limit
Matrix Spike is a sample with a known concentration of the analyte added to original sample and is used to assure that the recovery of the target compounds is acceptable for the matrix involved.

Standard Check is a sample with a known concentration of the analyte is used to assure that the recovery of the target compounds is acceptable for the matrix involved.

4.3.3 Statistical Evaluation
Tables including summary statistics will be provided including number of samples analyzed, mean, maximum, and minimum and standard deviations. Graphical representation of the data will be introduced using box plots which give an indication of frequency distribution of the data, also plots for the mean values with standard error bars around the means will be provided in order to evaluate the trends and determine correlations. Non parametric tests will be conducted using the relationship between time-adjacent results to detect if there is any increasing or decreasing trend.

4.4 Data Reporting
Table 4.5 summarizes the reporting units for each monitoring parameter. The analyst will reduce the results to the appropriate reporting units. A computer running a software package called WinWedgeProTM logs and displays the analysis data (the automatically measured parameters only) directly in Excel TM spreadsheets. The remaining analysis results will be recorded in a laboratory notebook and each page will be dated and signed by the person who performs the analysis, then, those data will be fed manually to Excel spreadsheets for statistical analysis.

4.5 Statistical Analysis
A statistical hypothesis test, applied on the landfill parameters, would be useful to study the effect of temperature on each of these parameters in bioreactor landfills. A detailed t-test was applied on each parameter to assess whether this parameter and the temperature are statistically different from each other. This analysis is appropriate to compare the means of two parameters, one of them is temperature. It is applied to compare whether the average difference between these two groups is really significant or if it is due instead to random chance. The t-test is most commonly applied when the test statistic follows a normal distribution.

This section will summarize the correlations that fit the experimental data for each monitoring parameter. Statistical analysis software, SYSTAT was used to perform the statistical analysis.

The data collected during the experimental process for each of the parameters, were first tested for the normal distribution, and then we performed the two-sample t-test to compare the mean effect of the temperature on the parameters. Therefore, the independent variable was the temperature and the dependant variable was each of the parameters.
Table 4-5- Reporting Units

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>pH Units</td>
</tr>
<tr>
<td>Oxidation Reduction Potential (ORP)</td>
<td>mV</td>
</tr>
<tr>
<td>Conductivity</td>
<td>µS/cm</td>
</tr>
<tr>
<td>Dissolved Oxygen (D.O)</td>
<td>mg/L</td>
</tr>
<tr>
<td>Chemical Oxygen Demand (COD)</td>
<td>mg/L</td>
</tr>
<tr>
<td>Biological Oxygen Demand (BOD₅)</td>
<td>mg/L</td>
</tr>
<tr>
<td>Total Organic Carbon (TOC)</td>
<td>mg/L</td>
</tr>
<tr>
<td>Ammonia Nitrogen (NH₃-N)</td>
<td>mg/L</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>mg/L</td>
</tr>
<tr>
<td>Volatile Fatty Acids (VFA)</td>
<td>mg/L</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mg/L as CaCO₃</td>
</tr>
<tr>
<td>Sulfate</td>
<td>mg/L</td>
</tr>
<tr>
<td>Sulfide</td>
<td>mg/L</td>
</tr>
<tr>
<td>Total Dissolved solids</td>
<td>mg/L</td>
</tr>
<tr>
<td>Metals</td>
<td>mg/L</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
</tr>
<tr>
<td>Moisture Content</td>
<td>% M/M</td>
</tr>
<tr>
<td>Biochemical Methane Potential (BMP)</td>
<td>ml/g</td>
</tr>
<tr>
<td>Volatile Solids</td>
<td>µg/L</td>
</tr>
<tr>
<td>Gas Flow Rate</td>
<td>Cm³/min</td>
</tr>
<tr>
<td>Gas Composition</td>
<td>% V/V or ppm</td>
</tr>
<tr>
<td>Electric Potential</td>
<td>V</td>
</tr>
</tbody>
</table>

4.5.1 Normal distribution:

The normal distribution was tested for all the following parameters: pH, ORP, Conductivity, DO, Volatile fatty acids, Alkalinity, COD, BOD, TOC, Ammonia, Sulfate, Phosphorus, Total dissolved solids, Methane, Carbon dioxide, Hydrogen, Oxygen and Nitrogen. Figures illustrating the normal distribution of some of these parameters are displayed in Appendix B. For all the factors, the data was normally distributed except for conductivity, DO, and Phosphorus. A log transformation was necessary for these factors to obtain the normal distribution.

Figure 4.1, for example, shows the data distribution for ORP. Since the p-value (p= 0.3716) is above 0.05 (or 5 percent), it can be concluded that ORP data are normally distributed. The test for normality is performed for which the null hypothesis is “Data are normally distributed” and the alternative hypothesis is “Data are not normally distributed.”
Variable Name: ORP
Distribution: Normal
Estimated: Location or mean (\( \mu \)) = -182.362731   Scale or SD (\( \sigma \)) = 89.957815
Estimation of parameter(s): Maximum likelihood method.
Test Results: Chi-square test statistic = 9.256563 df = 3
Kolmogorov-Smirnov test statistic = 0.099733 Lilliefors Probability (2-tail) = 0.209248
Shapiro-Wilk test statistic for normality = 0.975972 p-value = 0.371677

4.5.2 Two-Sample t-Test:
The purpose of running the “two-sample t-test” is to compare responses from each monitoring parameter and the temperature, and study the effect of temperature on each of these parameters.

The main assumptions done in this test are:
- Each group is considered to be a sample from a distinct parameter;
- The responses in each group are independent of those in the other group;
- The distributions of the variable of interest are normal.
The hypotheses we need to establish in this test are the null hypothesis and the alternative hypothesis to be evaluated with data. The null hypothesis is that the two group means are equal to each other.

The following is an example of the results obtained from the two-sample t-test applied on the data, using the SYSTAT program. Group 1 refers to the data collected at high temperature (60°C) and group 2 refers to the lowest temperature (37°C).

**ORP t-test:**

Two-sample t-test on ORP grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>-223.790</td>
<td>84.356</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>-140.936</td>
<td>78.401</td>
</tr>
</tbody>
</table>

Separate variance:

Difference in means = -82.854
95.00% CI = -128.224 to -37.484
\( t \) = -3.668
df = 49.7
p-value = 0.001

Pooled variance:

Difference in means = -82.854
95.00% CI = -128.218 to -37.490
\( t \) = -3.668
df = 50
p-value = 0.001

Figure 4-2 Two-sample t-test for ORP
This result is interpreted as significant at the 5% level since p-value (p=0.001) is less than 0.05, and because $t = 3.668 > t^* = 2.101$, where $t^*$ is the critical t-value. Therefore, the temperature has a significant effect on the oxidation-reduction potential parameter.
Chapter 5
5 Results and Discussions

During the simulated landfill studies, leachate, solid and gas produced by the three lysimeters were analyzed for the parameters reflective of the phases of landfill stabilization as well as the behavior of the anaerobic decomposition of the solid waste. The total gas volume produced was measured, and gas composition was determined to reflect the progression of stabilization events within the lysimeters. Leachate quantity and quality, which vary with time and extent of waste conversion, were evaluated as characteristic of the nature and extent of waste conversion.

The collected data has been studied until project day 500, when the lysimeters were operating during the Acid Formation Phase. Therefore, the following discussion concentrates on the Acid Formation of landfill stabilization within the three stacks B, C and D.

Leachate and gas data were obtained approximately once every two weeks. For purpose of consistent data presentation and interpretation, a sampling time period of every 14 days was developed, and missing sample values were determined using linear interpolation. In the event of more than one sample being obtained during a 14-day period, and average of the sample results was considered representative of that time period.

5.1 Leachate Analyses:

Leachate, which provides moisture, nutrients and a principal substrate for biological activity and serves as a transport medium, reflects the progression of landfill waste degradation. Therefore, through the analysis and interpretation of certain leachate parameters, an insight could be gained regarding the extent of biological waste conversion.

5.1.1 pH:

The variation of pH profile over time in the simulated landfill columns is provided in the Figure 5.1. pH trends in lysimeters B, C, and D follow the same behavior.

The pH of an anaerobic system such as landfill is an indication of the intensity of the prevailing buffer system, and also affects species ionization. The prevailing pH is dependent upon interactions between volatile organic acids (VOA), alkalinity and partial pressure of evolving carbon dioxide gas. The leachate pH ranges between 5.4 and 8.6 for bioreactor landfills (EPA 2003; Pohland and Harper 1986). During the Acid formation phase of landfill stabilization, pH values are generally low due to the presence of volatile organic acids (VOA) and their effect on system pH. During periods of low pH, an abundance of mobilized ions may appear in the leachate along with volatile organic acids. The pH, however will tend to move to neutrality as methanogens consume these acids.

A statistical analysis, two-sample t-test, was applied on the pH data to study them according to the temperature. The test showed a p-value equal to 0.229 which is higher than 0.05 and t =
$1.218 < t^* = 2.101$; where $t^*$ is the critical t-value. Therefore, the temperature hasn’t any significance on the pH parameter according to the t-test. This result is in accordance with the data shown in the graph.

The variation of solubility for a gas with temperature can be determined by examining the graphic in figure 5.2. As the temperature increases, the solubility of a gas decreases as shown by the downward trend in the graph. More gas is present in a solution with a lower temperature compared to a solution with a higher temperature. The reason for this gas solubility relationship with temperature is very similar to the reason that vapor pressure increases with temperature. Increased temperature causes an increase in kinetic energy. The higher kinetic energy causes more motion in molecules which break intermolecular bonds and escape from solution.

Based on the discussion above, the solubility of CO$_2$ in stack C and D is higher than in stack B, since lysimeter B is operating at a higher temperature than lysimeters C and D. Thus, pH values should be lower in lysimeters C and D compared to lysimeter B. However, we cannot notice this difference in our data (Figure 5.1).
5.1.2 Oxidation-Reduction Potential:

Oxidation-reduction potential (ORP) is a quantitative measure of electron availability and is used as a means of indicating the oxidizing or reducing conditions present in the simulated landfills columns. Measured leachate ORP values for the lysimeters are presented in Figure 5.3.

As indicated in Figure 5.3, leachate ORP values for all stacks B, C and D remained characteristic of a reducing environment. ORP values followed a similar pattern in all the lysimeters. At the beginning of the experiment, ORP values were high reflecting the initial phase, when Oxygen was still available. But as soon as the oxygen was depleted, the ORP values went down from 100 mV to negative values around -150 mV. Lysimeter B, however, showed some fluctuations during the Acid phase indicating lower values than C and D, around -250 mV and reached – 380 mV around day 100. These lower values in lysimeter B could be explained by the faster degradation occurring in stack B because it is operating at higher temperature than C and D.

The two-sample t-test applied on ORP data indicated compatible results with the one showed in the graph. This result is significant at the 5 % level since p-value (p=0.001) is less than 0.05, and because $t = 3.668 > t^* = 2.101$, where $t^*$ is the critical t-value. Therefore, the temperature has a significant effect on the oxidation-reduction potential parameter according to the statistical analysis.

5.1.3 Conductivity:

Figure 5.4 shows the variation of conductivity over the time in lysimeters B, C and D. Conductivity values follow the same trend in all the lysimeters. Conductivity is expected to increase during the acid formation phase due to mobilization of metals and decreases in the methane formation phase due to the complexation of metals with sulfides (Pohland, 1992). As shown in Figure 5.4, conductivity values had increased dramatically around day 50, from 1 ms to 18 ms for lysimeter D, 22 ms in lysimeter C, and 26 ms in lysimeter B. After that, values were constant in all the stacks. It is noted, however, that lysimeter B shows higher conductivity values than C and D.
Conductivity is considered to be an indicator of the ionic strength of leachate and consequently, the activity. The activity of ions is a function of their concentrations.

5.1.4 Dissolved Oxygen:
Dissolved Oxygen reflects the amount of oxygen dissolved in leachate. DO concentrations for lysimeters B, C and D are represented in Figure 5.5. Initially, waste decomposition within the landfill proceeded aerobically, utilizing the oxygen contained within the void.
spaces of the MSW. Therefore, the graph shows initially a DO concentration around 2 mgL\(^{-1}\) then decreased on day 30 to near zero after the oxygen had depleted and the stabilization continued anaerobically.

5.1.5 Total Alkalinity:

Total alkalinity is a measure of system buffer capacity. The measured leachate alkalinity concentrations for the lysimeters B, C, and D are provided in Figure 5.6. Alkalinity concentrations were around 6000 eqL\(^{-1}\) at the beginning of the experiment in all three stacks then they increased with time until they reached a value of 10000 eqL\(^{-1}\) on day 200. After 200 days, during the Acid Formation Phase, leachate alkalinity remained relatively constant around this value along with low pH (5.0 to 6.0). These values are in accordance with the literature (see Table 2.2).

Based on the statistical two-sample t-test applied for alkalinity data, the result is not considered significant because p-value (p = 0.214) is higher than 0.05 and \(t = 1.257 < t^* = 2.101\). Therefore, the temperature hasn’t any significance on Alkalinity parameter as stated by the statistics.

5.1.6 Volatile Organic Acids:

Volatile organic acids are produced during degradation of organic material and provide substrate for the methanogens. Total volatile acids (TVA) represent the combination of individual volatile acids, usually expressed as an equivalent amount of acetic acid. Volatile organic acids measured in the leachate included: acetic acid, butyric acid, propionic acid, and valeric acid. Leachate VFA concentrations for the lysimeters B, C and D are shown respectively in figures 5.7, 5.8 and 5.9. The graphs show the variation of acetic, propionic, N-butyric and valeric acids along with
time. For all three lysimeters, Acetic and Butyric acid were the major acids present in leachate. Acetic Acid concentrations behaved similarly in stacks C and D; their values increased from 5000 to 11000 mgL$^{-1}$, while Butyric acid concentrations went from 1500 to 11000 mgL$^{-1}$ in both stacks. However, in stack B, acetic and butyric values were higher. Acetic concentrations started around 7000 mgL$^{-1}$ then increased to 13000 mgL$^{-1}$, butyric values went from 7000 to 11000 mgL$^{-1}$. We can notice a decrease in lysimeter B, in the acetic and butyric concentrations around day 200.

For the propionic and valeric acids, the concentrations were nearly constant in all stacks with different values. In lysimeter D, the values were around 2000 mgL$^{-1}$; in lysimeter C, values were around 1000 mgL$^{-1}$ and in lysimeter B, the concentrations alter around 700 mgL$^{-1}$.

Propanol concentrations were very low compared to the other acids. At the beginning, propanol concentrations, in lysimeters C and D, were zero until day 150 when the values became around 70 mgL$^{-1}$. In lysimeter B, values increased from zero to 90 mgL$^{-1}$ around day 80 then decreased again to 50 mgL$^{-1}$.

The two-sample t-test revealed a considerable result for the acetic acid. The answer was significant at the 5 % level since p-value ($p=0.000$) is less than 0.05, and because $t = 5.831 > t^* = 2.101$, where $t^*$ is the critical t-value. Therefore, the temperature has a significant effect on the Acetic Acid parameter.

The propionic acid t-test, however, didn’t indicate any effect versus the temperature. The p-value ($p=0.932$) was higher than 0.05 and $t = 0.086 < t^* = 2.101$. Therefore, the temperature hasn’t any significance on Propionic Acid parameter.
For the N-butyric and I-butyric acid, the t-test showed p-values of 0.011 and 3.242 respectively, and t values of 2.69 and 3.242 respectively; indicating the significance of temperature on N-butyric and I-butyric acid.

The t-test for valeric acid however revealed that temperature has considerable effect on it, with p-value = 0.00 and t = 4.417.

During anaerobic stabilization, acetic and propionic acids are the most important volatile organic acids frequently occurring (Parawira et al, 2004). Acetic acid, the most prevalent acid occurring during anaerobic digestion, is formed directly from fermentation of proteins, carbohydrates and fats, and also as an intermediate in the fermentation of longer-chained volatile organic acids (Wang et al. 2006). Propionic acid is formed primarily from carbohydrates, but is also produced from proteins containing odd-numbered-carbon amino acids and butyric acid is formed during the degradation of proteins and fats. Propionic acid is an inferior substrate for the methanogenic phase, and the accumulation of propionic acid should be avoided in the anaerobic process.

Volatile fatty acids are among the main products of the acidogenesis of organic matter). The appearance of VFAs in the leachate indicated the initiation of acidogenesis. Medium- and long-chain volatile organic acids, such as propionic, butyric and valeric acids, are formed from the hydrolysis products. In addition, acetic acid, carbon dioxide and methane are also formed during this step. During the final step, methanogenesis, acetic acid, carbon dioxide and hydrogen are converted to methane. Accumulation of organic acids and lowering of pH are known to lead to suppression of methanogenic activity.

Acetic and propionic acids are the most important volatile organic acids frequently occurring under unbalanced digested conditions; acetic acid, the most prevalent acid occurring during anaerobic digestion, is formed directly from fermentation of proteins, carbohydrates and fats, and also as an intermediate in the fermentation of longer-chained volatile organic acids (Wang et al. 2006). Propionic acid is formed primarily from carbohydrates, but is also produced from proteins containing odd-numbered-carbon amino acids and butyric acid is formed during the degradation of proteins and fats. Propionic acid is an inferior substrate for the methanogenic phase, and the accumulation of propionic acid should be avoided in the anaerobic process.

Aceticogenic bacteria are responsible for the conversion of longer-chained volatile organic acids to acetic acid, carbon dioxide and hydrogen. β-oxidation, consisting of the separation of two-carbon groups from an even-numbered-carbon volatile organic acid until acetic acid remains, has been shown to be the major mechanism of degradation of medium- and long-chain even-numbered-carbon volatile organic acids. If the medium- or long-chain VOA is comprised of an odd number of carbon atoms, β-oxidation will proceed until propionic acid remains, which then is converted to acetic acid by α-carboxylation.

Research has also suggested that the oxidation-reduction potential of an anaerobic system affects the type of volatile organic acids present (Pohland, 1993). At an ORP of +300mV Eh,
acetic acid is the only acid detected. As the oxidation-reduction potential is lowered to -100mV, acetic acid concentrations increase and propionic acid is detected followed by iso-butyric acid. When the redox potential reaches -200 mV, butyric acid is detected and acetic, propionic, butyric and iso-butyric acids accumulate in that order, respectively. Decreasing the oxidation-reduction potential to around -300 mV will promote the conversion of volatile organic acids to methane and carbon dioxide.

Figure 5-7 VFA Concentrations in lysimeter D during time
Figure 5-8 VFA Concentrations in Lysimeter C during time

Figure 5-9 VFA Concentrations in Lysimeter B during time
The total volatile acids were calculated as acetic acid and are plotted for lysimeters B, C and D. The calculation was done using the following equation:

$$[\text{Total VOAs}] = [\text{Acetic Acid}] + 60 \times ([\text{Butyric}] / 88 + [\text{Propionic}] / 74 + [\text{Valeric}] / 102)$$

Where:
- Numerals indicate the molecular weight of each compound in grams;
- Brackets indicate concentration in mg/L; and
- Total VOAs are expressed in mg/L as acetic acid.

Figure 5.10 shows the evolution of VFA as Acetic acid during the time in all three lysimeters. Figures 5.11, 5.12 and 5.13 present the variation of VFA as Acetic Acid with the variation of pH in each lysimeter.

---

Figure 5-10 Total VFA calculated as Acetic Acid
Figure 5-11 Total VFA as Acetic Acid vs pH in Lysimeter B

Figure 5-12 Total VFA as Acetic Acid vs pH in Lysimeter C
5.1.7 Leachate Biochemical (BOD) and Chemical Oxygen Demand (COD):

Leachate chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are measured as indicators of organic strength and the potential pollutional impact that may result if leachate is released. Leachate COD concentrations for the stacks B, C, and D are presented in Figure 5.14 and BOD concentrations are presented in Figure 5.15.

BOD values reported in the literature for bioreactor landfills ranged from 20 to 28,000 mg/L (EPA 2003; Reinhart and Townsend 1998; Miller et al. 1994; Pohland et al. 1993); while COD values ranged from 500 to 60,000 mg/L. These values are in accordance with the BOD and COD concentrations observed in lysimeters B, C and D.

According to figure 5.14, COD concentrations were consistent in all three lysimeters, and varied constantly around 60,000 mgL\(^{-1}\). In figure 5.15, however, BOD concentrations showed dramatic fluctuations but all the values fall in the range between 15,000 and 35,000 mgL\(^{-1}\), as reported in the literature.

According to the graphs, there was no difference in BOD concentrations between lysimeters B, C and D. This statement is consistent with the result obtained from the two-sample t-test. This result is not considered significant regarding the temperature, because p-value (p = 0.956) is higher than 0.05 and \(t = 0.0557 < t^* = 2.101\). Therefore, the temperature hasn’t any significance on BOD parameter.

The statistical analysis for COD, using the two-sample t-test, showed a similar result of the BOD. This result is not considered significant because p-value (p = 0.164) is higher than 0.05.
and $t = 1.411 < t^* = 2.101$. Therefore, the temperature hasn’t any significance on BOD parameter as stated by the t-test.

BOD mainly consists of the biologically degradable dissolved organics in the landfill leachate. COD is a measure of chemically oxidizable organics in leachate. Variations in these two parameters may be closely related to those observed with VFAs production and their ratio can act as an indicator of the biodegradability of organics present in MSW (refer to 5.1.8).

Immediately after waste placement, the BOD and COD concentrations are relatively low. This may be caused by the initial stabilization of the MSW or by a delay in the hydrolysis of the waste. During the Acid formation phase, the majority of the oxygen demand (both COD and BOD) is caused by the presence of high concentration of VFAs. BOD and COD concentrations may decrease after the onset of the methane fermentation phase and the conversion of VFAs.

![COD Concentrations in Lysimeters B, C, and D](chart.png)

*Figure 5-14 COD Concentrations in Lysimeters B, C, and D*
5.1.8 Total Organic Carbon (TOC):

In general, like COD and BOD (§ 5.1.7), after the initial placement of the waste, TOC begins to appear as a result of microbial stabilization of the organics. During the acid formation phase, TOC increases rapidly. An increase in TOC may also be observed soon after the introduction of highly organic liquid waste. Because of the conversion of the VFAs to methane, TOC concentration tends to decrease during the fermentation phase.

TOC values of landfills leachate, reported in the literature, range between 30 and 30,000 mg/L (EPA 2003; Pohland 1992). Figure 4.16 shows the variation of TOC concentrations in lysimeters B, C and D. The TOC concentrations remained relatively constant at a range of 20000 mg/L during the Acid Formation Phase, with slight fluctuations around this value. These concentrations fall in the same range reported in the literature. Moreover, there is no significant difference observed in the graph, between the 3 lysimeters B, C and D.

This result, however, is not in agreement with the two-sample t-test applied on TOC. The p-value was found to be equal to 0.013 which is less than 0.05 and $t = 2.575$ is higher than $t^* = 2.101$, the temperature has therefore a considerable effect on TOC, as stated by the statistical analysis.
5.1.9 Measurements of BOD$_5$/COD ratio:

BOD$_5$/COD ratio of the lysimeter leachate (Table 5.1), which is also represented in Figure 5.17, varied constantly in the acidic phase passing from 0.3 to 0.6 in stacks B, C and D. We can see, however, some fluctuations in stacks B and C. These fluctuations could be the result of experimental errors during analyses. BOD$_5$/COD values obtained, correspond to a very biodegradable leachate (Warith, 2002). In fact, the organic content of leachate affects the degree of biological treatability (El-Fadel et al., 2002).

In general, the ratio of BOD to COD can potentially be used to assess the relative biodegradability of the leachate substrate. Relative to conventional landfills, bioreactor landfills may have a higher BOD$_5$/COD ratio during the acid formation phase (Tolaymat et al, 2006; Reinhart and Townsend 1998). However, research suggests this ratio may decrease during the methane fermentation phase. After waste stabilization, both BOD and COD may be influenced by high molecular weight organics present in the leachate (e.g. humic and fulvics) (Pohland et al. 1993). These residuals tend to elevate COD to a higher level than BOD and possibly reduce the BOD$_5$/COD ratio. For instance, leachate BOD$_5$/COD ratios are usually higher than 0.5 for acid formation phases of decomposition but may decline to less than 0.1 for heavily decomposed waste (Barlaz et al., 2002). It is noted that COD is also influenced by the increase in ammonia concentration.

Leachate with higher BOD$_5$/COD ratios or higher organic contents should be more treatable. Landfill leachate from a young landfill usually has a higher BOD$_5$/COD ratio and a leachate
from an older or stable one has a lower BOD$_5$/COD ratio. Morris et al. (2003) has reported that the BOD$_5$/COD ratio of landfill leachates varies from 0.6 to 0.2. El-Fadel’s (2002) study of leachate quality indicated an average BOD$_5$/COD ratio of 0.3. According to Benson (2007), the BOD$_5$/COD ratio, which is indicative of the fraction of the organics that are degradable, varied from 0.5 to 0.7 initially then decreased slightly to 0.1, which is characteristic of leachate from well decomposed refuse.

Recycling of leachate or nutrient addition should improve BOD$_5$/COD ratio and thus, leachate biodegradability prospects.

![Figure 5-17 Evolution of BOD5/COD in stacks B, C, and D](image)

5.1.10 Ammonia:

Ammonia concentrations in stack B are generally higher than stacks D and C after the initial phase. After about one year, ammonia concentration in lysimeter B was about 1700 mgL$^{-1}$. The corresponding values for lower temperature lysimeter D and C were 1400 and 1200 mgL$^{-1}$ respectively (Figure 5.18). The relatively higher ammonium concentration could be due to the greater degradation at high temperature in stack B than the lower temperature. Even though all three lysimeters had a general trend, the rate of concentration change was slightly higher in lysimeter B than the others. Additionally, ammonia concentrations in lysimeters C and D started to flatten after 250 days while lysimeter B has an upward trend.

The high concentrations of Ammonia in lysimeter B compared to lysimeters C and D show that the temperature has an important effect on the rates of ammonia. This is also proved by the two-sample t-test. The result was found significant at the 5 % level since p-value (p=0.000) is less than 0.05, and because $t = 4.140 > t^* = 2.101$, where $t^*$ is the critical t-value.
### Table 5.5-1: Variation of BOD\textsubscript{5}/COD Ratio during time

<table>
<thead>
<tr>
<th>Days since Filling</th>
<th>BOD/COD ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>0.691</td>
</tr>
<tr>
<td>27</td>
<td>0.573</td>
</tr>
<tr>
<td>41</td>
<td>0.447</td>
</tr>
<tr>
<td>56</td>
<td>0.582</td>
</tr>
<tr>
<td>69</td>
<td>0.446</td>
</tr>
<tr>
<td>83</td>
<td>0.473</td>
</tr>
<tr>
<td>98</td>
<td>0.487</td>
</tr>
<tr>
<td>111</td>
<td>0.446</td>
</tr>
<tr>
<td>127</td>
<td>0.497</td>
</tr>
<tr>
<td>140</td>
<td>0.642</td>
</tr>
<tr>
<td>153</td>
<td>0.804</td>
</tr>
<tr>
<td>167</td>
<td>0.627</td>
</tr>
<tr>
<td>181</td>
<td>0.280</td>
</tr>
<tr>
<td>196</td>
<td>0.440</td>
</tr>
<tr>
<td>210</td>
<td>0.457</td>
</tr>
<tr>
<td>224</td>
<td>0.665</td>
</tr>
<tr>
<td>238</td>
<td>0.382</td>
</tr>
<tr>
<td>253</td>
<td>0.419</td>
</tr>
<tr>
<td>266</td>
<td>0.393</td>
</tr>
<tr>
<td>284</td>
<td>0.557</td>
</tr>
<tr>
<td>294</td>
<td>0.706</td>
</tr>
<tr>
<td>308</td>
<td>0.777</td>
</tr>
<tr>
<td>322</td>
<td>1.118</td>
</tr>
<tr>
<td>336</td>
<td>0.494</td>
</tr>
</tbody>
</table>

Within the existing pH range in the columns, the main form of N is in ammonium ion (see Figure 5.19). Thus, the vast majority of the ammonia-nitrogen in the landfill leachate will be in the form of the ammonium ion (NH\textsubscript{4}	extsuperscript{+}) during the acidogenic phase as pH levels are generally less than 8.0 (Berge and Reinhart, 2005). The Ammonium concentration was attributed to be related to the nature of the leachate recirculation management strategy, whereby available nutrients are contained and recirculated within the column, providing an increased opportunity to their accumulation or used by microbial community. However, the use of ammonium by microbes is not only a function of its concentration but also other factors including the available energy.

Proteins present in the waste are the major source of ammonia-nitrogen. This conversion of organic nitrogen to ammonia-nitrogen by heterotrophic bacteria is termed ammonification. Ammonification is a two-step process consisting of the enzymatic hydrolysis of proteins by aerobic and anaerobic microorganisms releasing amino acids and the subsequent deamination or fermentation (depending on aerobic vs. anaerobic conditions) of the acids to carbon dioxide, ammonia-nitrogen, and volatile fatty acids (Burton, 1998). During deamination, amine groups
are liberated to form ammonia or ammonium, depending on the pH, and alkalinity is slightly elevated.

![Graph showing the variation of ammonia leachate concentrations in Lysimeters B, C, and D over time.](image)

**Figure 5-18 Variation of Ammonia Leachate Concentrations in Lysimeters B, C, and D**

![Graph showing the dominant form of ammoniacal nitrogen in solution at 25°C at various pH levels.](image)

**Figure 5-19 Dominant form of ammoniacal nitrogen in solution at 25°C at various pH levels (Berge et al, 2005)**

Although the organic strength of the leachate is significantly reduced in bioreactor landfills, ammonia-nitrogen remains an issue. The ammonia-nitrogen concentrations found in leachate from bioreactor landfills are greater than those found in leachate from conventional landfills. Ammonia-nitrogen tends to accumulate in both systems because there is no degradation pathway for ammonia-nitrogen in anaerobic systems (Barlaz, 2002). However, in bioreactor landfills, moisture addition and/or recirculating leachate increases the rate of ammonification, resulting in accumulation of higher levels of ammonia-nitrogen, even after the organic fraction of the waste
is degraded. The increased ammonia-nitrogen concentrations intensify the toxicity of the leachate to aquatic species, potentially inhibiting the degradation process and necessitating leachate treatment before ultimate disposal to protect receiving waters. It has been suggested that ammonia-nitrogen is one of the most significant long-term pollution problem in landfills, and it is likely that the presence of ammonia-nitrogen will determine when the landfill is biologically stable and when postclosure monitoring may end (Berge and Reinhart, 2005).

5.1.11 Phosphorus:
Total Phosphorus concentrations are presented in Figure 5.20. Lysimeters B, C and D showed similar behavior regarding Phosphorous concentrations. At the beginning, the values were high around 400 mgL⁻¹, and then they decreased gradually to 100 mgL⁻¹ around day 100. After day 100, during Acid formation phase, concentrations of phosphorus range between 80 and 120 mgL⁻¹ which are in the same range found by Pohland (1993) and Swati (2005).

Since all the lysimeters showed similar behavior during time, the temperature doesn’t influence the phosphorous concentrations. This result is compatible with the t-test, where p-value (p=0.297) is higher than 0.05 and t = 1.057 < t* = 2.101. Thus, the temperature hasn’t any significance on phosphorus parameter.

Nutrients, such as nitrogen and phosphorous, are released and utilized in support of microbial biomass growth commensurate with prevailing substrate conversion rates. Phosphorus is one of the main nutrients for microbial growth; accordingly low quantities of it will slow down the biological activity and waste conversion.

Phosphorus compounds in the water environment undergo complex physical, chemical and microbiological transformations. The solubility of phosphate in leachate depends upon pH and alkalinity.

5.1.12 Sulfide:
The following graph, presented in Figure 5.21, shows the variation of sulfide concentrations during the acid formation phase in lysimeters B, C and D. In all three lysimeters, sulfide values follow the same trend over the time. Sulfide concentrations are changing constantly between 0.2 and 1 mgL⁻¹. Actually, the appearance of sulfide becomes possible at low ORP values (below -200 mV).

The two-sample t-test indicated a p-value of 0.862 which is higher than 0.05; and t = 0.174 is less than t* = 2.101. Consequently, the temperature didn’t affect the sulfide concentrations based on the t-test.
Figure 5-20 Variation of phosphorous concentrations during time

Figure 5-21 Sulfide Concentrations in Lysimeters B, C, and D
5.1.13 Total Dissolved Solids:

Figure 5.22 gives the Total Dissolved Solids measurement results of the lysimeters B, C and D; and Figure 5.23 shows the variation of Total Solids during the time. TDS concentrations varied between 20 and 35 mgL\(^{-1}\) and TS concentrations varied between 25 and 40 mgL\(^{-1}\) in all the lysimeters.

According to the t-test, temperature has significant effect on total dissolved solids and total solids since \(p\) for TDS parameter is 0.003 and 0.001 for TS, which are less than 0.05; and \(t\) is equal to 3.198 for TDS and 3.546 for TS, which are higher than \(t^* = 2.101\). Thus, the temperature has an important influence on TDS and TS parameters.

Based on a statistical evaluation, total solids (TS) concentrations increase during Acid Formation phase due to solubilization of organics/inorganics and mobilization of metals. As the leachate moves from acidogenic to methanogenic phase, total solids concentration is expected to decrease, reported by Kylefors and Lagerkvist (1997). Yuen (1999), reported the same results for total solids, but indicated that the dissolved solids concentrations do not change in large quantities as total solids.

![Figure 5-22 Variation of Total Dissolved Solids during time](#)
Metal solubility is a function of numerous factors, including pH, ORP, dilution, presence of complexing ligands, and the presence of precipitants such as sulfide and hydroxide. Analyses for leachate metals included sodium, potassium, magnesium, calcium, iron, manganese, sulfur, and strontium.

The alkali metals include sodium (Na) and potassium (K). Leachate sodium concentrations are presented in Figure 5.28, and leachate potassium concentrations are illustrated in Figure 5.26. Sodium concentrations varied constantly around the value 900 mgL$^{-1}$ for all the stacks B, C, and D during time. Similarly, the potassium concentrations were constant around 700 mgL$^{-1}$ during time, in all the stacks B, C, and D.

The alkali-earth metals include calcium (Ca), magnesium (Mg) and strontium (Sr). Leachate calcium and magnesium concentrations are presented in figures 5.24, 5.27 and 5.30 respectively. Both calcium and magnesium had relatively conservative concentrations, which were reflected in their behavior within the simulated landfills columns. The calcium concentrations varied within a narrow range around the value 3000 mgL$^{-1}$ in all the three stacks B, C, and D. Magnesium concentrations were also constant around the value 350 mgL$^{-1}$ during the time in both stacks C and D. In stack B, however, magnesium concentrations increased from 300 to 600 mgL$^{-1}$ during the time. The strontium concentrations were very low and varied constantly around 4 mgL$^{-1}$ in lysimeters B, C, and D.
The heavy metals include iron (Fe) and manganese (Mn); leachate iron and manganese concentrations are presented in figures 5.25 and 5.28. Iron concentrations were increasing during time from 1000 to 3000 mgL⁻¹ for stack B, 3500 mgL⁻¹ for stack C, and 4500 mgL⁻¹ for stack D. Likewise, manganese concentrations increased in all the stacks from 30 to 50 mgL⁻¹.

Leachate sulfur is illustrated in figure 5.29. Sulfur concentrations were constant during time around the value 300 mgL⁻¹.

![Figure 5-24 Variation of Calcium concentration during time](image_url)
Figure 5-25 Variation of iron Concentration during time

Figure 5-26 Variation of Potassium concentration during time
Figure 5-27 variation of Magnesium concentration during time

Figure 5-28 Variation of Manganese concentration during time
Figure 5-29 Variation of Sodium Concentration during time

Figure 5-30 Variation of Sulfur concentration during time
**5.2 Solid Analyses**

**5.2.1 Temperature**

Internal lysimeter temperature, which is determined by thermocouples, is presented in figures 4.24, 4.25 and 4.26 in lysimeters B, C and D. Each figure shows the temperature in the three levels in the lysimeters; TC 1 refers to the bottom level, TC 2 for the middle and TC 3 for the top level. Lysimeter B is operating at a temperature of 60°C, and this can be verified in the graph in figure 4.24. The graph shows that, until day 100, the temperature didn’t reach the 60°C yet. This was caused by a leak in the lysimeter at the beginning of the experiment.

Lysimeters C and D are running at a temperature of 37°C, which is verified and represented in figures 4.25 and 4.26. We can also notice, in the 3 graphs below, that the bottom level has lower temperature (around 55°C for B, and 32°C for C and D) than the other sections; the reason is that the bottom level is not covered at the end by an insulation blanket.

Temperature within the anaerobic environment affects the biological activity. The optimum temperature range for the anaerobic processes is to occur within either mesophilic (30-38 °C) or thermophilic (50 to 60 °C) ranges (Tolaymat, 2004).
Figure 5-32 Variation of Temperature in Lysimeter B

Figure 5-33 Variation of Temperature in Lysimeter C
5.2.2 Moisture Content

The volumetric moisture content, which is measured using a Time Domain Reflectometry system as mentioned in section (3.2), is represented in figures 4.27, 4.28, and 4.29. Lysimeters B, C, and D show an average of moisture around 55%. In lysimeter B, however, channel 1 showed lower moisture around 45%.

The biodegradation of solid waste increases with the increase in moisture content and the optimum should be greater than 40% (Pohland, 1992). Therefore, leachate was recirculated to the solid waste to increase the water content of the waste in order to maintain the optimal conditions for biological activity.
Figure 5-35 Moisture variation in Lysimeter B

Figure 5-36 Variation of Moisture in Lysimeter C
5.2.3 Settlement

Decomposition settlement in lysimeters B, C and D are represented in figure 4.30. As shown in the figure, the settlement in lysimeters C and D, increased in a linear pattern from 15 cm at the beginning of the experiment to 35 cm on day 100; after that, settlement was maintained constant during the acid formation phase. In lysimeter B, however, the settlement increased from 15 cm at the beginning, and kept increasing to around 45 cm on day 350. We can notice that settlement in stack B is higher than stacks C and D, which reflects that the decomposition in B is faster than C and D. And this can be explained by the higher temperature in stack B than C and D.

Decomposition of organic material in the landfill causes a considerable amount of settlement as the organic material is converted into intermediate decomposition products as liquid forms and the final products of methane and related gases (Elagroudy, 2008).
5.3 Gas Analyses:

Gas volume and composition were determined as indications of the progression of landfill stabilization processes. Methane and carbon dioxide are the primary end products of anaerobic biological waste stabilization and reflect the rate of biological activity and organic material conversion within the landfill environment. The data collected, however, doesn’t reflect the end products of the waste degradation; it reflects the degradation of waste during Acid formation phase.

5.3.1 Gas Production

Cumulative gas volumes produced in lysimeters B, C, and D are shown in figure 4.31. The overall volume of gas produced during the acid formation phase is very low. The values fluctuate at the beginning around 20000 m$^3$ until day 100, and then the values became around 200 m$^3$ in stacks C and D. In stack B, the values were higher; at the beginning, values were around 30000 m$^3$ and then they became around 1000 m$^3$ during acid phase. Thermophilic condition in lysimeter B shows higher gas productivity indicating greater degradation of solid waste in stack B than stacks C and D. This result is in accordance with Pohland’s (1992) study, where the gas production rates were relatively low during acid formation phase, but increased during methane formation phase when methanogenesis are promoted.
5.3.2 Gas Composition:

The gas compositions for the stacks D, C, and B are given in the figures 1, 2, and 3 respectively.

Oxygen, probably originated from within the refuse void spaces, is present in all columns at the beginning in amounts ranging from 1 to 5% of the total gas volume. The initial presence and subsequent disappearance of oxygen is indicative of the transition from an initial aerobic to anaerobic environment within the columns.

Hydrogen is present in all columns, in amounts of 0.05 to 1%, but for stack B where the hydrogen amounts are of 14 to 47% of the total gas volume. The main reason is that, at high temperature, fermenters bacteria produce high hydrogen amounts, and thermophilic condition causes inhibitory effect on methanogenesis production which are hydrogen consumers. Shin et al. (2004) showed in his study about hydrogen production, that total hydrogen production from the thermophilic test is greater than that from the mesophilic test. This was also proved by Liu (2006) in his study about hydrogen and methane production in the fermentation process.

Nitrogen is present in the air entrained in the refuse void spaces during column loading operations. All the simulated landfill columns contain nitrogen until gas volumes produced will be large enough to displace the nitrogen. Nitrogen amounts increased from 5 to 75% in lysimeter D, and from 2 to 65% in lysimeters B and C.
Methane gas is present in very low amounts in the acid formation phase (around 15% in all stacks). Methane will be produced in the columns at later stages in high percentages.

The gases have been tested statistically using the two-sample t-test. The analysis showed that temperature had significant effect on methane and hydrogen concentrations, but not an important effect on carbon dioxide, nitrogen and Oxygen.

Gases arising from biodegradation landfills consist of mainly hydrogen and carbon dioxide in the early stages followed by mainly methane and carbon dioxide in the later stages; however, a wide range of other gases can be potentially formed and the gas is also saturated with moisture. By volume, final landfill gas typically contains 45% to 60% methane and 40% to 60% carbon dioxide. Landfill gas also includes small amounts of nitrogen, oxygen, ammonia, sulfides, hydrogen, carbon monoxide, and nonmethane organic compounds (NMOCs) such as trichloroethylene, benzene, and vinyl chloride.

The degradation processes inside the landfill are the key to understanding and controlling the environmental impacts. The microbial processes in most landfills are dominating the stabilization of the waste and hence govern the generation of landfill gas.

The most important interactions between the involved bacterial groups, the involved substrates and intermediate products can be explained by the anaerobic fermentation. The anaerobic degradation can be viewed as consisting of three stages. In the first stage solid and complex, dissolved organic compounds are hydrolysed and fermented by fermenters to primarily volatile fatty acids, alcohols, hydrogen and carbon dioxide. In the second stage, an acetogenic group of bacteria converts the products from the first stage to acetic acid, hydrogen and carbon dioxide. In the final stage, methane is produced by the methanogenic bacteria. This may be done by acetophilic bacteria converting acetic acid to methane and carbon dioxide or by hydrogenophilic bacteria converting hydrogen and carbon dioxide to methane.

The amount and composition of the generated gas can be predicted for different substrates using the equation below presented by Tchobanoglous et al. (1997):

\[ C_aH_bO_cN_d + \left( \frac{4a - b - 2c + 3d}{4} \right) H_2O \rightarrow \left( \frac{4a + b - 2c - 3d}{8} \right) CH_4 + \left( \frac{4a - b + 2c + 3d}{8} \right) CO_2 + d NH_3 \]
Figure 5-40 Evolution of gas composition in lysimeter D

Figure 5-41 Evolution of gas composition in lysimeter C
Figure 5-42 Evolution of gas composition in lysimeter B

5.4 Summary and Conclusions

The purpose of this research was to compare and evaluate the degradation of municipal solid waste in bioreactor landfill in thermophilic and mesophilic conditions during Acid Formation Phase. In accordance with this objective, the experimental results can be summarized as follows:

1. In general, simulated bioreactor landfill columns operating at high temperature achieve waste stabilization more quickly and completely than simulated bioreactor landfill columns operating at normal temperature. This is reflected by the trends shown in the leachate, solids and gas parameters. The ORP graph showed lower values in lysimeter B than lysimeters C and D, reflecting faster degradation in B at high temperature. Conductivity, on the other hand, showed higher values in stack B than C and D indicating more rapid degradation at high temperature. The plot of Ammonia concentrations indicated as well higher values in lysimeter B compared to C and D because of the greater degradation in B at thermophilic condition. Moreover, settlement graph expressed the faster decomposition in lysimeter B by showing high settlement values in stack B than stacks C and D. This more complete and rapid waste degradation in lysimeter B is attributed to the more favorable environment that is developed because of the higher temperature.

2. Based on the statistic tests applied on each monitoring parameter, it has been shown that the temperature has significant effect on ORP, Ammonia, TDS and TS. For the gases, results showed that temperature has some influence on Methane and Hydrogen production, but not a significant effect on carbon dioxide, oxygen and nitrogen. As for the volatile fatty acids, the
two-sample t-test indicated a significant effect on Acetic acid, I-butyric acid, and valeric acid. No significant effect of temperature, however, was found on propionic acid and N-butyric acid.
Chapter 6
6 Evaluation of Settlement in MSW landfills

6.1 Introduction
Municipal solid waste (MSW) disposal in landfills requires estimation of refuse degradation and settlement behavior in order to utilize the available volume to its maximum capacity.

The settlement in landfills is a response to biochemical degradation and compaction including creep in the refuse. It is advantageous to estimate the settlement as it provides additional storage volume for MSW. The problems associated with settlement are rupture and failure of liners with leachate contaminating the ground water, disruption of leachate and gas conduits and control equipment and possible vermin nuisance due to exposure of refuse to atmosphere.

Understanding the patterns of settlement of municipal solid waste (MSW) is critical for designing a good landfill system, maintaining the various engineered components of an existing landfill facility and predicting the space that could be recovered for further filling of MSW. Settlement of MSW is known to be a function of many factors such as the type of waste, organic and moisture contents, thickness compaction density, self-weight, overburden, porosity, compressibility, biodegradation rate (level of nutrients available for biological activities, presence of enzymes, sludge addition, pH, temperature), climate, method of filling and mode of landfill operation are some of them (Wall and Zeiss, 1995; Ling et al., 1998; Youcai et al., 2002; Durmusoglu et al., 2005).

Only few case studies of modeling settlement behavior of bioreactor landfills are found in the literature. Some of these cases are actually adapted from the versions of the traditional models that have been originally proposed for dry landfills. Accurate prediction of landfill settlement is a challenge due to the large number of variables involved in the settlement process, as mentioned previously. Moreover, none of the studies have studied the effect of temperature on the settlement. The objective of the present chapter is to examine the effect of some of these variables, specifically the temperature on the settlement using a mathematical model.

6.2 MSW Settlement Mechanisms
The rate of landfill settlement depends primarily on the refuse composition, operational practices and factors affecting biodegradation of landfill waste particularly moisture content (El Fadel et al., 1999). The mechanisms of refuse settlement are (Edil et al, 1990; Reinhart and Townsend, 1998):

1. Mechanical: Distortion, bending, crushing and reorientation; similar to consolidation of organic soils, due to the refuse thickness and own weight, or the load exerted by construction material and structures erected on the landfill.

2. Raveling: Movement of smaller particles into larger voids.


Settlement of waste is characteristically irregular. MSW settlement is observed in 3 distinct stages as identified in the literature, these are initial compression, primary compression and secondary compression (El Fadel and Khoury, 2000). Initial compression occurs on application of a direct load or overburden in a landfill. This results in an immediate compaction of void space and particles due to superimposed loads, and causes particle deformation to some extent; analogous to the instantaneous elastic compression in soils. This settlement is estimated to be completed in one month.

Primary settlement may occur as quickly as 4-5 weeks (Edil et. al. 1990). This is the settlement associated with the dissipation of pore water and gas from the void spaces as a result of compaction load. It occurs rather quickly after load application. Operational and load-related settlements typically constitute 5 to 30% of total settlement and occur during landfill operations.

The secondary compression is caused by decaying mass within the landfill as a result of the physicochemical and biochemical decomposition, which continue until the waste is fully stabilized. The secondary compression is independent of the stress on the waste and can theoretically reach 40% of the original waste thickness and can occur gradually for several years at a continually decreasing rate depending on stabilization processes within the landfill.

The settlement of landfills can be summarized in the short- and long-term. Mechanical/primary compression is the predominant short-term settlement mechanism. The long-term settlement mechanisms that are likely at a landfill and their relative contribution to total settlement can be summarized as follows:

Table 6-1 Long-term settlement mechanisms

<table>
<thead>
<tr>
<th>LONG-TERM SETTLEMENT MECHANISM</th>
<th>RELATIVE CONTRIBUTION TO LONG-TERM SETTLEMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodegradation</td>
<td>High</td>
</tr>
<tr>
<td>Physical Creep Compression</td>
<td>Moderate</td>
</tr>
<tr>
<td>Physical-Chemical/Corrosion</td>
<td>Low</td>
</tr>
<tr>
<td>Interaction</td>
<td>Generally Low; Potentially High in Localized Areas</td>
</tr>
<tr>
<td>Consolidation</td>
<td>None to Low</td>
</tr>
</tbody>
</table>

Two long-term settlement mechanisms, the biodegradation and the physical creep compression, are of primary importance at landfills. Settlement due to biodegradation is the result of biological activity which transforms cellulose and water in the MSW into primarily methane and carbon dioxide; which then migrates from the landfill. This solid mass transformation to gas results in vertical downward movements (settlement). Some long-term
physical settlement may also occur at a landfill as a secondary effect of biodegradation. This settlement mechanism is associated with an elastic deformation of the structure of inert material remaining as biodegradation occurs. This component of settlement is termed physical creep compression.

Many researchers modeled the secondary settlement of bioreactor landfills. El-Fadel and Al-Rashed (1998) used Terzaghi’s one-dimensional consolidation model to model the secondary settlement. Wall and Zeiss (1995), who used a reactor volume of the order of 0.4 m$^3$, applied the secondary compression model. They studied the effect of biodegradation on settlement for 250 days and concluded that decomposition did not significantly affect the rate of secondary settlement during the test period.

Gabr et al. (2000) identified two stages of decomposition and proposed a conceptual two-stage model to describe the settlement behavior of a biocell landfill. During the early stage of biological decomposition, compressibility of the waste is governed by an increase in voids ratio due to solids loss, and the material physical size and stiffness. Thus, during this stage, the compressibility of solids is governed by the matrix stiffness changes under its own weight and external loads. As decomposition takes place, the material breakdown may lead to increase in the surface area, and with the leachate recirculation, Terzaghi’s model with primary and secondary settlement may then be applied.

### 6.3 Settlement Mathematical Model

There are a number of interactive processes proceeding simultaneously in landfills. It is not always practical or even feasible to carry out sufficient field or laboratory experiments to understand the relative importance of these processes. In such cases, mathematical modeling can be an important tool in understanding and predicting the landfill processes for future scenarios. These predictions are based on the solutions of the governing equations developed.

The change in volume of waste is mainly due to the load (or stress) acting on it and the mass loss due to decay. According to the settlement mechanisms, the total settlement has to be modeled as a combination of mechanical compression and biodegradation-induced settlements.

Movement of gas and moisture is assumed to occur in the vertical direction. Due to the recirculation of leachate the waste is assumed to be always at its field capacity. Gas is expected to reach the top surface where it is mixed with atmospheric air at zero excess pressure. The waste settlement is caused by compression of voids and solids due to the weight of the overlying waste. Since the strain is a function of stress, mechanical compression at a given depth is a function of stress.

Boni et al. (2006) identified a strong correlation between mechanical behaviour of biostabilised waste and biochemical characteristics of the leachate produced from it. They have emphasized that such observations will help to predict settlement from laboratory analysis of leachates. Estimation of compression indices using simple equations, application of empirical
functions to experimental data and modeling can be of help to forecast settlement of MSW in landfills.

El-Fadel and Khoury (2000) classified existing settlement models into four broad categories: soil mechanics based models; rheological models; empirical models; and the models accounting for the biodegradation of MSW. Most of the existing settlement models were originally developed to analyze dry landfills. However, in recent years, these models have been adopted to predict settlement due to enhanced biodegradation. Wall and Zeiss (1995) and El-Fadel and Al-Rashed (1998) used a one-dimensional consolidation equation (i.e., a soil mechanics based model) to model settlements in bioreactor landfill test cells. Park et al. (2002) attempted to evaluate the effects of biodegradation on long-term settlements using a rheological model, as well as empirical models such as power creep law, logarithmic model, and hyperbolic function. Edgers et al. (1992), Kang et al. (1997), and Hettiarachchi et al. (2007a, 2007b) have proposed models accounting for the biodegradation of MSW.

A conceptual model was also proposed by Hettiarachchi et al. (2005) in which settlement due to mechanical compression was separated from that of biodegradation. They suggested that modeling mechanical compression could be achieved with the help of laboratory simulations. To model the settlement due to biodegradation, waste was assumed to follow the first order reaction kinetics. Therefore, this procedure allowed settlement due to mechanical reasons to be separated from that of biodegradation.

The basic equations to calculate mechanical compression ($\varepsilon_m$) and biodegradation induced-settlements ($\varepsilon_b$), as reported by Hettiarachchi (2005), were defined as:

$$\varepsilon_m = C^* \log \left[ \frac{(\sigma' + \delta \sigma')}{\sigma'} \right] \quad \text{(Eq. 1)}$$

$$\varepsilon_b = (1-n_i) \sum f_{sj} (G_{si}/G_{sj})(1+w_j(t)G_{sj}[1-\exp(-\lambda_j t)]) \quad \text{(Eq. 2)}$$

where $C^*$ is the compressibility parameter, $\sigma'$ (N/m$^2$) is the effective stress and $\delta \sigma'$ (N/m$^2$) is the difference in effective stress. $n_i, w_j,$ and $\rho_w$ are the initial landfill porosity, gravimetric water content, and the density of water, respectively, $G_{si}$ and $G_{sj}$ are the initial overall specific gravity of waste solids and specific gravity of the jth group of the waste solids, respectively, $\lambda_j$ (day$^{-1}$) is the first order kinetic constant for the jth group, and $f_{sj}$ is the initial solids fraction for each waste group.

There are four main settlement prediction models for MSW reported by Park (2002) for trying to provide a single equation for both primary and secondary compression. The compression was modeled assuming that the settlement is linear with respect to logarithm of time.

a) **Logarithmic function** (Yen and Scanlon, 1975) expressed the strain rate (m) in terms of strain rate parameters.

$$m = \frac{1}{H_o} \frac{dS}{dt} = c - d \log t \quad \text{(Eq. 3)}$$
m is the strain rate (T⁻¹), S is the settlement (L), Ho is the initial height of the landfill, c and d are strain rate parameters (T⁻¹).

Sohn and Lee integrated this strain rate to give the settlement over time as:

\[ S = Ho \int_0^m m \, dt = Ho \left( \frac{ct - \frac{d}{\ln 10}}{t \ln t - t} \right)^a \]

(Eq. 4)

t₀ is the age of fill at beginning of settlement computation period and t₁ the age at end of this period. Limits for obtaining a positive settlement give \( t₁ \leq 10c / d \). The main limitation of this model is the model is an entirely empirical way to curve-fit observed data.

b) Rheological model (Edil, 1990) proposed the Rheological model of Gibson and Lo (1961) for secondary compression to predict long-term settlement as:

\[ \frac{S}{Ho} = \varepsilon(t) = \Delta \sigma(\alpha + b[1 - e^{-(\lambda/b)t}]) \]

(Eq. 5)

Where \( \varepsilon(t) \) is strain, \( \Delta \sigma = \) compressive stress (L²M⁻¹); \( \alpha \) is primary compressibility parameter (L²M⁻¹); \( \lambda / b \) is the rate of secondary compression (T⁻¹). Plotting log10(\( \Delta \varepsilon(t) / \Delta t \)) versus log10t we get slope of line = -0.434(\( \lambda / b \)) and intercept as log10(\( \Delta \sigma \lambda / b \)). Denoting \( t_k \) as the time to complete primary compression we get:

\[ a = \frac{\varepsilon(t_k)}{\Delta \sigma} - b[1 - e^{-(\lambda/b)t_k}] \]

(Eq. 6)

The model assumes that secondary settlement is linear with respect to the logarithm of time. Estimation of the time to complete primary compression (\( t_k \)) is difficult as primary and secondary compression occur simultaneously. The model also needs to be verified for its sensitivity to \( t_k \).

c) Power Creep Law (Edil, 1990) applied the power creep law as:

\[ \frac{S}{Ho} = \varepsilon(t) = \Delta \sigma m(t/t_r)^n \]

(Eq. 7)

Where \( m \) is a reference compressibility (L²M⁻¹), \( n \) is rate of compression. The power creep function has been found (Gibbons, 2002) to fit the observed data across 7 landfills comprising of 35 individual locations. The study also combined data across the sites to develop a time series model to fit all observations, and indicated that this model can be used to predict settlement at a location using settlement data from sites having similar settling characteristics.

d) Hyperbolic function has been used first by Ling et al. (1998) as

\[ \frac{S}{Ho} = \varepsilon(t) = \frac{t}{Ho} \frac{Ho}{\rho o + Ho t} \]

(Eq. 8)
Thus:

\[
\frac{t}{e(t)} = \frac{H_o}{\rho_o} S_{ult} t
\]  \hspace{1cm} \text{(Eq. 9)}

\(S_{ult}\) is the ultimate settlement of the fill at \(t(\infty)\).

The major limitation of this model is that it inherently predicts negative values for strain for short durations of time.

As a summary of the above settlement discussions, the mechanism of settlement can be divided into three major parts: the initial, primary and secondary settlement. In this study, only the secondary settlement, which is a result of the biodegradation process, is modeled. Two methods are used to model the settlement in this study: mathematical and empirical model.

In the mathematical model, equation 2 which was proposed by Hettiarachchi (2005), is applied to calculate the settlement in the lysimeters. This equation was generalized and modified to fit the conditions of the current study. The predicted settlement was then compared to the data measured during the experimental process, by using the relative error and the regression line.

The second method in modeling was the empirical check of the settlement. In this part, a fitting curve was used to find the best possible solution for the data. The obtained solution was then compared to the mathematical equation, which was used earlier. The differences/similarities were then discussed. The following section will discuss in details both of the models.

6.4 Results and discussion

6.4.1 Settlement Data:

The lysimeters are equipped with instrumentation to automatically measure some of the parameters, which settlement is one of them. The settlement values were measured over the experiment by using a depth sensor connected to a data acquisition system.

Table 6.1 shows the initial conditions related to settlement in lysimeters B, C and D.

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
 & Stack B & Stack C & Stack D \\
\hline
Initial moisture in the trash (L) & 18.99 & 18.99 & 18.99 \\
Initial Water added (L) & 111.55 & 111.55 & 111.55 \\
Total initial Water (L) & 130.54 & 130.54 & 130.54 \\
Initial Trash voulme (L) & 776.33 & 776.33 & 776.33 \\
Initial Trash Weight (lb) & 820.87 & 820.87 & 820.87 \\
Initial Trash Density (lb/yd3) & 808.39 & 808.39 & 808.39 \\
Initial net height of trash (m) & 2.7756 & 2.7756 & 2.7756 \\
Net lysimeter area (m2) & 0.2797 & 0.2797 & 0.2797 \\
\hline
\end{tabular}
\caption{Initial conditions in lysimeters B, C, and D}
\end{table}
Tables C.1, C.2, and C.3 (displayed in Appendix C) present the measured settlement (in meters) during the experimental process, as well as the percentage settlement that took place in the lysimeters B, C and D with respect to the initial height.

Graphical displays representing the changes in waste settlement with time have been plotted for each lysimeter using the data in the tables. Figures 6.1, 6.2 and 6.3 show the graphs for lysimeters B, C, and D respectively; where lysimeter B is operating at a high temperature of 60°C, while lysimeters C and D are operating at 37°C. The settlement rates rose exponentially during time in all the three lysimeters. In lysimeter C and D, settlement rates increased at the beginning of the experiment from 0 to 7% in C and 0 to 8% in D. Around day 100, however, the plots flattened and the rates had become nearly constant around the value of 8%. In lysimeter B, the settlement rates showed similar behavior, but the rates were higher and increased during the study time. The values rose from 0% at the beginning of the experiment to 10% at the current day.

![Figure 6-1 Settlement data during time in Lysimeter B](image)
Figure 6-2 Settlement data during time in Lysimeter C
It is obvious from the graphs that the settlement in bioreactor B operating at high temperature occurred rapidly than C and D where the temperature is lower. Moreover, a statistical analysis using the two-sample t-test (described in the methodology section) was applied on the settlement data to study the effect of temperature on settlement. The data was first checked for normal distribution then we applied the t-test. The results showed that all the settlement data were normally distributed and the two-sample t-test could be applied. The two-sample t-test was then checked by using two sets of data; the first represents the settlement occurring at high temperature (which is the settlement in lysimeter B), and the second set is the settlement measured at normal temperature (settlement in lysimeter C).

As a result of the t-test, we found p-value to be 0.003, which is less than 0.05 (or 5%). Therefore, the two sets of settlement data are significantly different and the temperature has a considerable effect on the settlement rate. The detailed results of the analysis are displayed in Appendix C.

6.4.2 Settlement Model:
As stated earlier, municipal solid waste was compacted uniformly during the filling of the lysimeters. A portable press was used applying a pressure to compact the waste media using compressed air from the laboratory supply. Therefore, the initial and primary settlement calculation associated with the operational and load applications are then neglected in this study.
And the secondary compression model that reflects the effect of biodegradation on settlement is studied in this section.

The settlement model, reported by Hettiarachchi, was used to calculate the predicted settlement. Predicted values were then compared with the data obtained from the real settlement measurements.

The data chosen for analysis in this work had considered only the biodegradation induced-settlement \((\varepsilon_b)\) defined by equation (2) and neglected the mechanical compression of MSW, as primary settlement was forced during the MSW filling stage. This equation is simplified to:

\[
\varepsilon_b = A \left[1 - \exp (-Bt)\right] \tag{Eq. 10}
\]

where \(A\) is a factor representing the final total settlement incorporated by the landfill bioreactor; and \(B\) is a factor representing the initial settlement rate.

Mathematically, the value of parameter \(A\) represents the maximum value on the curve obtained. Thus, it should be greater than the maximum value of the settlement occurring in each bioreactor. The value of \(B\) represents the initial slope of the curve.

The predicted settlement rates, according to equation 10, are presented in tables C.4 and C.5. Reported values for parameters \(A\) and \(B\) at normal temperature are: \(A\ (m) = 0.21\) and \(B\ (m\ day^{-1}) = 0.015\) (Elagroudy et al., 2008; Hettiarachchi et al., 2007). The settlement in lysimeter B, however, could not be predicted because no literature review had been found for settlement models in bioreactor landfills operating at high temperature. Therefore, there is no table summarizing the predicted settlement rates for lysimeter B.

The relative percent error which was calculated using the measured and the predicted data according to equation (11) is summarized in tables C.6 and C.7 for both lysimeters C and D operated at lower temperature.

\[
Relative\ Error(\%) = \frac{Measured\ Settlement - Predicted\ Settlement}{Measured\ Settlement} \times 100 \tag{Eq. 11}
\]

The comparison between measured and model predicted settlement revealed that the model estimated settlement in lysimeter C is slightly higher (5% higher); while in lysimeter D, it is slightly lower (around 3% lower) (Figures 6.4 and 6.5). A regression line was used to visualize and plot the curve that best describes the shape and behavior of the settlement data. The independent variable is the predicted settlement and the dependent is the measured variable. Regression had found the equation that most closely describes or fits the actual data, using the independent variables to predict the value of a dependent variable. The equation used is polynomial, linear in the form: \(f = y_0 + ax\).

The parameters \(y_0\) and \(a\) obtained in the resulting equation that fits the data in lysimeter C are: \(y_0 = -0.0144\) and \(a = 1.1277\), with standard errors of: 0.0147 and 0.0835. The most common measure of how well a regression model describes the data is to calculate the coefficient of
determination ($R^2$). $R^2$ is found to be 0.8546 in lysimeter C. The corresponding values in lysimeter D are: $y_0 = -0.0104$ and $a = 1.10182$ with standard errors for $y_0$ and $a$ respectively: 0.0149 and 0.0758. The coefficient of determination, $R^2$, is found to be 0.8493, very similar to lysimeter C.

Figure 6-4 Measured Settlement vs. settlement estimate by biodegradation in lysimeter C
6.4.3 Empirical Check of the settlement Model:

Another way to study the settlement model was to fit a curve for the measured settlement in lysimeters B, C, and D. The fit curve parameters are then compared to the parameters reported in the literature on one hand; and on the other hand, we compared the parameters found for the settlement in lysimeter B to the ones in lysimeters C and D in order to evaluate the effect of temperature on settlement.

A non-linear curve fitting is therefore used to find the best possible solution for the data. It is an iterative process that begins with a guess at the parameters, checks to see how well the equation fit, and then continues to make better guesses until the differences between the residual sum of squares no longer decreases significantly. Sigmaplot software was used to find the best fitting curve. The SigmaPlot curve fitter works by varying the parameters (coefficients) of an equation, finding the parameters which cause the equation to most closely fit your data. Both the equation and the initial parameter values must be provided. All built-in equations have the curve equation and the initial parameters predefined. The SigmaPlot curve fitter uses the Marquardt-Levenberg algorithm to find the coefficients (parameters) of the independent variable(s) that give the best fit between the equation and the data.

This algorithm seeks the values of the parameters that minimize the sum of the squared differences between the values of the observed and predicted values of the dependent variable.
The equation selected to fit the settlement curve is an exponential function, rise to maximum, similar to the one used in all the reported settlement models. The equation’s mathematical expression is: \( f = A \times (1 - \exp(-Bt)) \).

The resulting curves for lysimeters B, C and D were plotted on graphs shown in figures 5.6, 5.7, and 5.8. The statistical results and text reports of these graphs are provided in Appendix C.

According to these reports, the exponential curve was compatible with the settlement data for both lower and higher temperature; and the regression process was completed by converging. The parameters A and B obtained from the curves for each lysimeters are summarized in the table 6-3.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lysimeter B</th>
<th>Lysimeter C</th>
<th>Lysimeter D</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.2856</td>
<td>0.1882</td>
<td>0.2076</td>
</tr>
<tr>
<td>B</td>
<td>0.0097</td>
<td>0.02711</td>
<td>0.0235</td>
</tr>
</tbody>
</table>

Figure 6-6 Global fit curve for settlement during time in lysimeter B
Figure 6-7 Global fit curve for settlement during time in Lysimeter D

Figure 6-8 Global fit curve for settlement during time in lysimeter C
It was observed that the parameters A and B are different between the three lysimeters. Parameter “A” has a higher value for lysimeter B than C and D ($A_{(B)} = 0.2856; A_{(C)} = 0.1882; A_{(D)} = 0.2076$). If $A$ has a high value, then the settlement values will be higher over the time, and the faster the settlement will be. This is in accordance with the measured settlement values found in B, where values were higher than C and D. Parameter $B$, however, is lower in lysimeter B than the one found in lysimeters C and D ($B_{(B)} = 0.0097; B_{(C)} = 0.0271; B_{(D)} = 0.0235$). Since “$B$” reflects the initial slope of the curve, if $B$ is lower then initial settlement values will be lower as well. This is also verified in the measured settlement values (see tables C.1, C.2, and C.3). Initially, lysimeter B showed relatively less values than lysimeters C and D until around day 100; after that, settlement rates were higher in lysimeter B. Therefore, the parameters found in the empirical check reflect very well the behavior of settlement in bioreactor landfills.

On another hand, if we compare the parameters found in the empirical model with the ones reported in the literature, we found very compatible results. The table below summarizes the parameters in the lysimeters and show the difference between them.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lysimeter C (by the empirical model)</th>
<th>Lysimeter D (by the empirical model)</th>
<th>Literature data</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>0.1882</td>
<td>0.2076</td>
<td>0.21</td>
</tr>
<tr>
<td>$B$</td>
<td>0.0271</td>
<td>0.0235</td>
<td>0.015</td>
</tr>
</tbody>
</table>

It can be seen that the parameters $A$ and $B$ found in the empirical model have very similar values to the reported values in the literature.

### 6.5 Conclusions:

This chapter presents an analysis and evaluation of the settlement occurring in bioreactor landfills and moreover, the significance of temperature on settlement. A new methodology was proposed to predict bioreactor landfill settlement. The major mechanism of waste settlement was identified as due to biodegradation strains. The results obtained can be summarized as follows:

1-Based on the measured settlement data collected from the lysimeters, it was noticed that the settlement in lysimeter B was greater and faster than C and D. This can be attributed to the high temperature in lysimeter B (65°C) resulting in a faster microbial degradation and consequently an important effect on the settlement.

2-The influence of temperature on the settlement rate was also checked using a statistical analysis (two-sample t-test). The statistical comparison between settlement data reveals that higher temperature has a considerable impact on MSW settlement properties.
3-To model the settlement occurring in our simulated landfill bioreactors, a model based on previous studies reported in the literature was used. The analysis, however, had considered only the biodegradation induced-settlement and neglected the mechanical compression in MSW.

The simplified equation of biodegradation settlement reported by Hettiarachchi ($\varepsilon_b = A [1 - \exp (-Bt)]$) can be used to predict MSW settlement when parameters A and B are available. A and B were assumed based on previous studies ($A=0.21$ and $B=0.015$). The estimated settlement values of the biodegradation model and the measured settlement were calculate and plotted. To compare the two sets of settlement, a regression line was used in the form: $f = y_0 + ax$. This regression line had a coefficient of correlation $R^2$ equal to 0.8493. This indicates that the measured and the predicted data are not absolutely compatible but close to each other. The difference between the predicted and measured parameters could be due to initial compression that was applied initially. However, it is important to note that some mechanical compression could still occur during the biodegradation. This is due to recycling of water in the lysimeter, which can carry some of the waste leaving void spaces between the particles. The void spaces will cause some settlement not computed in the equation.

4- The predicted settlement using the empirical model reveals that predicted values for both low and high temperature were similar to the reported values in the literature. The fit curve used for the measured data in each lysimeter to find the best possible solution, had the same equation used in the previous model: $f = A(1-\exp(-Bt))$. Parameters A and B were obtained from the fit curves. The factors A and B were very similar in values in lysimeters C and D, and also similar to the one reported in the literature. In lysimeter B, however, the parameters had higher values. These values explain also the effect of temperature on settlement.
Appendix A

A. Method for Volatile Fatty Acids Measurement

1. References:

2. Apparatus & Reagents:
   Gas chromatography equipped with FID
   Column – Agilent (DB WAX ETR)
   4mL-capacity glass vials with rubber lined closure
   2mL-capacity auto-sampler GC vials and caps
   Pasteur pipettes
   20% H₂PO₄
   Sodium Chloride
   Ethyl Ether
   Volatile Fatty Acids Standard Mix (Supelco, USA)

3. Procedure

3.1 Sample extraction
   a- Place a small amount of sodium chloride into 4mL-glass vials
   b- Add 100 μL of 20% H₂PO₄ into each vial
   c- Add 900 μL of samples into each vial. Cap each vial right after mixing the sample with 20% H₂PO₄.
   d- Shake each vial to mix completely.
   e- Add 2mL of Ethyl Ether into each vial and cap it quickly.
   f- Shake it vigorously for at least 1 minute.
   g- Leave it for a while until two layers are completely separated
   h- Transfer only upper layer to prepared 2mL-autosample GC vials using a Pasteur pipette and seal it quickly.
i- Label each vial and store it at refrigerator.

3.2 Calibration

Prior to analysis, the gas chromatograph must be calibrated using VFA standard mix. Every 4mL of original VFA standard mix is stored in a glass vial with rubber closure without headspace. One of these standard vials is used for the calibration and the standard mix remained in the vial must be discarded after calibration. The compounds contained in VFA standard mix are as follows:

- Acetic acid
- Butyric acid
- Formic acid
- Heptanoic acid
- Hexanoic acid
- Isobutyric acid
- Isocaproic acid
- Isovaleric acid
- Propionic acid
- Valeric acid

The preparation of standard mix for calibration needs to follow the exact same procedure as sample extraction procedure. Generally, five to six standard mixes with different concentrations are used in the range of 1 to 500 mg/L as Acetic acid. One of the actual samples is chosen and spiked with a certain concentration of standard mix to check the reliability of whole procedures. Greater number of standard mix than any number required for the calibration needs to be prepared and used to check the reliability of GC condition every 10 samples.

B. Method for Gas Analysis using Gas Chromatography (GC)

1. Scope and Application

This standard operating procedure is for the measurement of the composition of the generated gas from the lysimeters. The main compounds to be investigated are CO₂, CH₄, H₂, O₂ and N₂.

2. Method Summary

Samples are collected in Tedlar bags from the gas sampling ports at the lysimeters then injected to the GC. The gas components will be separated using a packed column and a molecular sieve, then detected by a thermal conductivity detector. A calibration curve will be prepared in order to quantify the gas composition.

3. Sample Preservation, Containers, Handling, and Storage
Samples will be collected and injected to the GC directly for analysis, thus there is no preservation required.

4. **Apparatus**
- 1.0 L Tedlar Bags.
- 50 ml Gas tight syringe.
- 100 ul syringe
- Agilent 6890 N Gas Chromatograph equipped with Propack N column and a 13x molecular sieve.

5. **Method**
The analysis will be performed using the method called “Landfill Gas TCD “which could be loaded once the instrument started up. The details of the method are described below:-

5.1 **Oven**
Temperature: 80 °C
Duration: 7.5 min
Ramp: none
Maximum Temperature: 175 °C
Equilibration Time: 1 min

5.2 **Front Inlet**
Initial Temperature: 200 °C
Flow: 20.1 mL/min
Gas Type: Argon

5.3 **Column**
Packed Colum Porapak N with 13x molecular sieve
Maximum Temperature: 175 °C
Mode: Constant Flow
Nominal Initial Flow: 19.3 mL/min
Inlet: Front inlet
Outlet: Back Detector
Outlet Pressure: ambient

5.4 **Back Detector (TCD)**
Temperature: 250 °C
Reference Flow: 20.0 mL/min
Mode: Constant makeup flow
Makeup flow: 7.0 mL/min
Makeup gas type: Helium
Filament: on
Negative Polarity: on

**5.5 Valves**

*Valve1 Gas sampling*

Description: Back Inlet Sample Loop
Loop Volume: 1.0 ml
Load Time: 0.5 min
Inject Time: 0.5 min
Inlet: Back Inlet

*Valve2 Switching off*
Description: Molesieve

*Valve3 Gas Sampling*
Description: Front Inlet Sample Loop
Loop Volume: 1.0 mL
Load Time: 0.5 min
Inject Time: 0.5 min
Inlet: Front Inlet

**6. Procedure for Gas Analysis**

1. The instrument will be calibrated using gas mixtures prepared from standard gas cylinders.
2. Collect the sample to be analyzed in Tedlar Bag.
3. Open the “Chemstation” Software and choose the method “Landfill Gas TCD”.
4. From the “Run” menu click “Sample Info” and record the sample information.
5. Then, click “Run Method”.
6. The instrument will show “Waiting for injection”.
7. Pull a 100 ul of gas from the sample bag and inject it to the front inlet of the instrument.
8. After injection, press the “Start” button.
9. After 7.5 min the run will be complete and a data report could be printed.

7. **Quality control**
   - The GC will be calibrated on a weekly basis.
     - 6 calibration points will be performed.
     - A mid point standard will be run twice a week to ensure the performance of the GC. A recovery of 100 ± 20 % should be obtained.
     - Sample Duplicate will be run every 12 sample in order to check the precision and the relative standard deviation should be <20%.

8. **References**
Appendix B
Statistical Analysis Results

A. Normal distribution:

![Fitted Distribution](image)

**Figure A.1- Probability Plot of ORP data 0-1**

Variable Name: ORP  
Distribution: Normal  
Estimated: Location or mean (mu) = -182.362731   Scale or SD (sigma) = 89.957815  
Estimation of parameter(s): Maximum likelihood method.  
Test Results: Chi-square test statistic = 9.256563 df = 3  
Kolmogorov-Smirnov test statistic = 0.099733 Lilliefors Probability (2-tail) = 0.209248  
Shapiro-Wilk test statistic for normality = 0.975972 p-value = 0.371677
Figure A.2- Probability Plot of Ammonia data 0-2

Variable Name: AMMONIA
Distribution: Normal
Estimated: Location or mean (mu) = 1028.846154 Scale or SD (sigma) = 352.423772
Estimation of parameter(s): Maximum likelihood method.
Chi-square test statistic = 10.812407 df = 4
Kolmogorov-Smirnov test statistic = 0.128771 Lilliefors Probability (2-tail) = 0.031138
Shapiro-Wilk test statistic for normality = 0.955373 p-value = 0.049386.
Figure A.3 - Probability Plot for Alkalinity data

Variable Name: ALKALINITY
Distribution: Normal

Estimated: Location or mean (mu) = 8254.335827 Scale or SD (sigma) = 1564.249794
Estimation of parameter(s): Maximum likelihood method.
Chi-square test statistic = 3.745618 df = 3
Kolmogorov-Smirnov test statistic = 0.088008 Lilliefors Probability (2-tail) = 0.375843
Shapiro-Wilk test statistic for normality = 0.957483 p-value = 0.290275
Variable Name: BOD
Distribution: Normal
Estimated: Location or mean (mu) = 30351.445408 Scale or SD (sigma) = 6378.866542
Estimation of parameter(s): Maximum likelihood method.
Chi-square test statistic = 7.200833 df = 4
Kolmogorov-Smirnov test statistic = 0.100687 Lilliefors Probability (2-tail) = 0.232426
Shapiro-Wilk test statistic for normality = 0.977374 p-value = 0.460793

B. Two-Sample t-Test:

1. ORP t-test:
   Two-sample t-test on ORP grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>-223.790</td>
<td>84.356</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>-140.936</td>
<td>78.401</td>
</tr>
</tbody>
</table>

Separate variance:
Difference in means = -82.854
95.00% CI = -128.224 to -37.484
t = -3.668
This result is significant at the 5 % level since p-value (p=0.001) is less than 0.05, and because 
\[ t = 3.668 > t^* = 2.101, \] where \( t^* \) is the critical t-value. Therefore, the temperature has a 
significant effect on the oxidation-reduction potential parameter.

2. **Phosphorus t-test:**
Two-sample t-test on PO4 grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>134.417</td>
<td>100.514</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>110.635</td>
<td>55.291</td>
</tr>
</tbody>
</table>

Separate variance:

<table>
<thead>
<tr>
<th>Difference in means</th>
<th>= 23.782</th>
</tr>
</thead>
<tbody>
<tr>
<td>95.00% CI</td>
<td>= -21.729 to 69.294</td>
</tr>
<tr>
<td>t</td>
<td>= 1.057</td>
</tr>
<tr>
<td>df</td>
<td>= 38.9</td>
</tr>
<tr>
<td>p-value</td>
<td>= 0.297</td>
</tr>
</tbody>
</table>

Pooled variance:
This result is not considered significant because p-value (p=0.297) is higher than 0.05 and t = 1.057 < t* = 2.101. Therefore, the temperature hasn’t any significance on phosphorus parameter.

3. **COD t-test:**

Two-sample t-test on COD grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>61100.000</td>
<td>5470.430</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>58096.154</td>
<td>9375.563</td>
</tr>
</tbody>
</table>

Separate variance:

Difference in means = 3003.846
95.00% CI = -1297.778 to 7305.470
\( t = 1.411 \)
\( df = 40.3 \)
p-value = 0.166

Pooled variance:

Difference in means = 3003.846
95.00% CI = -1271.979 to 7279.672
\( t = 1.411 \)
\( df = 50 \)
p-value = 0.164

108
This result is not considered significant because p-value (p=0.164) is higher than 0.05 and t = 1.411 < t* = 2.101. Therefore, the temperature hasn’t any significance on COD parameter.

4. **Ammonia t-test:**

Two-sample t-test on AMMONIA grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>1206.923</td>
<td>377.590</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>850.769</td>
<td>223.176</td>
</tr>
</tbody>
</table>

Separate variance:

- Difference in means = 356.154
- 95.00% CI = 182.378 to 529.929
- t = 4.140
- df = 40.6
- p-value = 0.000

Pooled variance:

- Difference in means = 356.154
- 95.00% CI = 183.379 to 528.928
- t = 4.140
- df = 50
- p-value = 0.000
This result is significant at the 5 % level since p-value (p=0.000) is less than 0.05, and because \( t = 4.140 > t^* = 2.101 \), where \( t^* \) is the critical t-value. Therefore, the temperature has a significant effect on the Ammonia parameter.

5. **Alkalinity t-test:**

Two-sample t-test on ALKALINITY grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>8528.210</td>
<td>1505.970</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>7980.462</td>
<td>1632.649</td>
</tr>
</tbody>
</table>

Separate variance:

Difference in means = 547.748
95.00% CI = -327.326 to 1422.823
\( t \) = 1.257
df = 49.7
p-value = 0.214

Pooled variance:

Difference in means = 547.748
95.00% CI = -327.185 to 1422.682
\( t \) = 1.257
df = 50
p-value = 0.214
This result is not considered significant because p-value (p=0.214) is higher than 0.05 and t = 1.257 < t* = 2.101. Therefore, the temperature hasn’t any significance on Alkalinity parameter.

6. BOD t-test:
Two-sample t-test on BOD grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23</td>
<td>30296.956</td>
<td>7082.353</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>30399.648</td>
<td>5967.125</td>
</tr>
</tbody>
</table>

Separate variance:
Difference in means = -102.691
95.00% CI = -3901.890 to 3696.507
t = -0.055
df = 43.3
p-value = 0.957

Pooled variance:
Difference in means = -102.691
95.00% CI = -3853.268 to 3647.885
t = -0.055
df = 47
p-value = 0.956
This result is not considered significant because p-value (p=0.956) is higher than 0.05 and t = 0.0557 < t* = 2.101. Therefore, the temperature hasn’t any significance on BOD parameter.

7. CO2 t-test:
Two-sample t-test on CO2 grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>41.482</td>
<td>20.172</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>52.959</td>
<td>22.742</td>
</tr>
</tbody>
</table>

Separate variance:

Difference in means = -11.477
95.00% CI = -23.456 to 0.502
t = -1.925
df = 49.3
p-value = 0.060

Pooled variance:

Difference in means = -11.477
95.00% CI = -23.452 to 0.497
t = -1.925
df = 50
p-value = 0.060
This result is not considered significant because p-value (p=0.06) is higher than 0.05 and $t = 1.925 < t^* = 2.101$. Therefore, the temperature hasn’t any significance on CO$_2$ gas parameter.

8. **N2 t-test:**

Two-sample t-test on N2 grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>30.802</td>
<td>26.692</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>33.413</td>
<td>20.721</td>
</tr>
</tbody>
</table>

Separate variance:

- Difference in means = -2.611
- 95.00% CI = -15.941 to 10.720
- $t$ = -0.394
- df = 47.1
- p-value = 0.695

Pooled variance:

- Difference in means = -2.611
- 95.00% CI = -15.921 to 10.700
- $t$ = -0.394
- df = 50
- p-value = 0.695
This result is not considered significant because p-value (p=0.695) is higher than 0.05 and \( t = 0.394 < t^* = 2.101 \). Therefore, the temperature hasn’t any significance on \( N_2 \) gas parameter.

9. \( H_2 \) t-test:

Two-sample t-test on \( H_2 \) grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>26.654</td>
<td>10.504</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>3.016</td>
<td>7.192</td>
</tr>
</tbody>
</table>

Separate variance:

\[
\text{Difference in means} = 23.638 \\
\text{95.00\% CI} = 18.607 \text{ to } 28.669 \\
t = 9.468 \\
df = 44.2 \\
p-value = 0.000
\]

Pooled variance:

\[
\text{Difference in means} = 23.638 \\
\text{95.00\% CI} = 18.623 \text{ to } 28.653 \\
t = 9.468 \\
df = 50 \\
p-value = 0.000
\]
This result is significant at the 5 % level since p-value (p=0.000) is less than 0.05, and because $t = 9.468 > t^* = 2.101$, where $t^*$ is the critical t-value. Therefore, the temperature has a significant effect on the Hydrogen gas parameter.

10. **Acetic Acid t-test:**
Two-sample t-test on ACETIC grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14</td>
<td>11195.736</td>
<td>1857.816</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>6928.364</td>
<td>2251.169</td>
</tr>
</tbody>
</table>

Separate variance:

- Difference in means = 4267.371
- 95.00% CI = 2825.384 to 5709.359
- $t = 6.035$
- $df = 31.0$
- p-value = 0.000

Pooled variance:

- Difference in means = 4267.371
- 95.00% CI = 2776.593 to 5758.150
- $t = 5.831$
- $df = 32$
- p-value = 0.000
This result is significant at the 5 % level since p-value (p=0.000) is less than 0.05, and because t = 5.831 > t* = 2.101, where t* is the critical t-value. Therefore, the temperature has a significant effect on the Acetic Acid parameter.

11. Propionic t-test:
Two-sample t-test on PROPIONIC grouped by TEMPERATURE against Alternative = 'not equal'

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14</td>
<td>814.5</td>
<td>60.000</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>808.137</td>
<td>270.450</td>
</tr>
</tbody>
</table>

Separate variance:
Difference in means = 6.363
95.00% CI = -123.524 to 136.250
t = 0.102
df = 21.6
p-value = 0.920

Pooled variance:
Difference in means = 6.363
95.00% CI = -144.027 to 156.753
t = 0.086
df = 32
p-value = 0.932
This result is not considered significant because p-value (p=0.932) is higher than 0.05 and $t = 0.086 < t^* = 2.101$. Therefore, the temperature hasn’t any significance on Propionic Acid parameter.
Appendix C
Settlement Data

A. Measured settlement rates in lysimeters B, C, and D

Table C-1: Settlement rate in lysimeter C

<table>
<thead>
<tr>
<th>Stack C</th>
<th>Cumulative Days</th>
<th>Distance (cm)</th>
<th>Settlement (m)</th>
<th>% Settlement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>15.367175</td>
<td>0.00367175</td>
<td>0.132286713</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>20.15810127</td>
<td>0.051581013</td>
<td>1.858373423</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>26.49526492</td>
<td>0.114952649</td>
<td>4.141542341</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>28.81733868</td>
<td>0.138173387</td>
<td>4.97814479</td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>30.6535436</td>
<td>0.156535436</td>
<td>5.639697218</td>
</tr>
<tr>
<td></td>
<td>76</td>
<td>31.86603689</td>
<td>0.168660369</td>
<td>6.076537286</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>32.39363136</td>
<td>0.173936314</td>
<td>6.26662032</td>
</tr>
<tr>
<td></td>
<td>106</td>
<td>32.61474628</td>
<td>0.176147463</td>
<td>6.346284147</td>
</tr>
<tr>
<td></td>
<td>121</td>
<td>32.6842074</td>
<td>0.176842074</td>
<td>6.371309769</td>
</tr>
<tr>
<td></td>
<td>136</td>
<td>33.19430097</td>
<td>0.18194301</td>
<td>6.555087539</td>
</tr>
<tr>
<td></td>
<td>151</td>
<td>33.4255925</td>
<td>0.184255925</td>
<td>6.63841782</td>
</tr>
<tr>
<td></td>
<td>166</td>
<td>33.46104848</td>
<td>0.184610485</td>
<td>6.651191988</td>
</tr>
<tr>
<td></td>
<td>181</td>
<td>30.49248347</td>
<td>0.154924835</td>
<td>5.581670077</td>
</tr>
<tr>
<td></td>
<td>196</td>
<td>32.996009</td>
<td>0.17996009</td>
<td>6.483646419</td>
</tr>
<tr>
<td></td>
<td>211</td>
<td>29.3949133</td>
<td>0.14394913</td>
<td>5.185722486</td>
</tr>
<tr>
<td></td>
<td>226</td>
<td>34.12855642</td>
<td>0.191285564</td>
<td>6.891683389</td>
</tr>
<tr>
<td></td>
<td>241</td>
<td>34.07913523</td>
<td>0.190791352</td>
<td>6.873877802</td>
</tr>
<tr>
<td></td>
<td>256</td>
<td>33.69708811</td>
<td>0.186970881</td>
<td>6.736232926</td>
</tr>
<tr>
<td></td>
<td>271</td>
<td>33.32087543</td>
<td>0.183208754</td>
<td>6.600690097</td>
</tr>
<tr>
<td></td>
<td>286</td>
<td>33.30038962</td>
<td>0.183003896</td>
<td>6.593309418</td>
</tr>
<tr>
<td></td>
<td>301</td>
<td>33.67682881</td>
<td>0.186768288</td>
<td>6.728933857</td>
</tr>
<tr>
<td></td>
<td>316</td>
<td>33.56495669</td>
<td>0.185649657</td>
<td>6.688628295</td>
</tr>
<tr>
<td></td>
<td>331</td>
<td>33.61107653</td>
<td>0.186110765</td>
<td>6.705244462</td>
</tr>
<tr>
<td></td>
<td>346</td>
<td>33.66749373</td>
<td>0.186674937</td>
<td>6.72557059</td>
</tr>
<tr>
<td></td>
<td>361</td>
<td>33.7484911</td>
<td>0.187484911</td>
<td>6.754752522</td>
</tr>
<tr>
<td></td>
<td>376</td>
<td>33.93538751</td>
<td>0.189353875</td>
<td>6.822088022</td>
</tr>
<tr>
<td></td>
<td>391</td>
<td>34.35757214</td>
<td>0.193575721</td>
<td>6.974193737</td>
</tr>
<tr>
<td></td>
<td>406</td>
<td>34.45130723</td>
<td>0.194513072</td>
<td>7.007964846</td>
</tr>
<tr>
<td></td>
<td>421</td>
<td>34.56713854</td>
<td>0.195671385</td>
<td>7.049696835</td>
</tr>
<tr>
<td></td>
<td>436</td>
<td>36.43201406</td>
<td>0.214320141</td>
<td>7.72157878</td>
</tr>
<tr>
<td></td>
<td>451</td>
<td>35.12139822</td>
<td>0.201213982</td>
<td>7.249386879</td>
</tr>
<tr>
<td></td>
<td>466</td>
<td>35.65452615</td>
<td>0.206545262</td>
<td>7.441463522</td>
</tr>
<tr>
<td></td>
<td>481</td>
<td>35.2494993</td>
<td>0.202494993</td>
<td>7.29553945</td>
</tr>
</tbody>
</table>
Table C-2- Settlement Rate in Lysimeter B

<table>
<thead>
<tr>
<th>Cumulative Days</th>
<th>Distance (cm)</th>
<th>Settlement (m)</th>
<th>% Settlement</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>16.98087869</td>
<td>0.019808787</td>
<td>0.713675852</td>
</tr>
<tr>
<td>22</td>
<td>22.29663732</td>
<td>0.072966373</td>
<td>2.628850454</td>
</tr>
<tr>
<td>37</td>
<td>26.581075</td>
<td>0.11581075</td>
<td>4.172458207</td>
</tr>
<tr>
<td>52</td>
<td>28.94221388</td>
<td>0.139422139</td>
<td>5.023135133</td>
</tr>
<tr>
<td>67</td>
<td>28.3854036</td>
<td>0.13854036</td>
<td>4.822526157</td>
</tr>
<tr>
<td>82</td>
<td>29.9826154</td>
<td>0.149826154</td>
<td>5.397973555</td>
</tr>
<tr>
<td>97</td>
<td>31.06053445</td>
<td>0.160605344</td>
<td>5.786328884</td>
</tr>
<tr>
<td>112</td>
<td>31.0348373</td>
<td>0.160348373</td>
<td>5.77707065</td>
</tr>
<tr>
<td>127</td>
<td>32.0034752</td>
<td>0.170034752</td>
<td>6.126053898</td>
</tr>
<tr>
<td>142</td>
<td>36.0266602</td>
<td>0.210266602</td>
<td>7.575536893</td>
</tr>
<tr>
<td>157</td>
<td>38.49276797</td>
<td>0.23492768</td>
<td>8.464032272</td>
</tr>
<tr>
<td>172</td>
<td>39.5945749</td>
<td>0.245945749</td>
<td>8.860993984</td>
</tr>
<tr>
<td>187</td>
<td>39.52475012</td>
<td>0.245247501</td>
<td>8.835837339</td>
</tr>
<tr>
<td>202</td>
<td>39.82494769</td>
<td>0.248249477</td>
<td>8.943993258</td>
</tr>
<tr>
<td>217</td>
<td>40.63081944</td>
<td>0.256308194</td>
<td>9.234334718</td>
</tr>
<tr>
<td>232</td>
<td>40.33628285</td>
<td>0.253362828</td>
<td>9.128218348</td>
</tr>
<tr>
<td>247</td>
<td>41.34593984</td>
<td>0.263459398</td>
<td>9.491980056</td>
</tr>
<tr>
<td>262</td>
<td>41.34593984</td>
<td>0.263459398</td>
<td>9.491980056</td>
</tr>
<tr>
<td>277</td>
<td>41.95514378</td>
<td>0.269551438</td>
<td>9.71146555</td>
</tr>
<tr>
<td>292</td>
<td>42.06010101</td>
<td>0.27060101</td>
<td>9.749279798</td>
</tr>
<tr>
<td>307</td>
<td>43.09111768</td>
<td>0.280911177</td>
<td>10.12073702</td>
</tr>
<tr>
<td>322</td>
<td>43.24254037</td>
<td>0.282425404</td>
<td>10.17529196</td>
</tr>
<tr>
<td>337</td>
<td>40.72170341</td>
<td>0.257217034</td>
<td>9.267078618</td>
</tr>
<tr>
<td>352</td>
<td>42.31494123</td>
<td>0.273149412</td>
<td>9.84109426</td>
</tr>
<tr>
<td>367</td>
<td>42.04640991</td>
<td>0.270464099</td>
<td>9.744347137</td>
</tr>
<tr>
<td>382</td>
<td>42.69036375</td>
<td>0.276903638</td>
<td>9.97635241</td>
</tr>
<tr>
<td>397</td>
<td>43.23357182</td>
<td>0.282335718</td>
<td>10.17206075</td>
</tr>
<tr>
<td>412</td>
<td>43.40747625</td>
<td>0.284074762</td>
<td>10.23471547</td>
</tr>
<tr>
<td>Cumulative Days</td>
<td>Distance (cm)</td>
<td>Settlement (m)</td>
<td>% Settlement</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>15</td>
<td>17.61455771</td>
<td>0.026145577</td>
<td>0.941979289</td>
</tr>
<tr>
<td>30</td>
<td>25.42628783</td>
<td>0.104262878</td>
<td>3.756408644</td>
</tr>
<tr>
<td>45</td>
<td>27.0099446</td>
<td>0.120099446</td>
<td>4.326972402</td>
</tr>
<tr>
<td>60</td>
<td>30.7210582</td>
<td>0.157210582</td>
<td>5.664021545</td>
</tr>
<tr>
<td>75</td>
<td>33.92414059</td>
<td>0.189241406</td>
<td>6.818035951</td>
</tr>
<tr>
<td>90</td>
<td>35.29715418</td>
<td>0.202971542</td>
<td>7.312708669</td>
</tr>
<tr>
<td>105</td>
<td>35.62546963</td>
<td>0.206254696</td>
<td>7.430994967</td>
</tr>
<tr>
<td>120</td>
<td>34.88949525</td>
<td>0.198894952</td>
<td>7.165836304</td>
</tr>
<tr>
<td>135</td>
<td>35.04750399</td>
<td>0.20047504</td>
<td>7.22764083</td>
</tr>
<tr>
<td>150</td>
<td>35.03557178</td>
<td>0.200355718</td>
<td>7.218465118</td>
</tr>
<tr>
<td>165</td>
<td>35.559923</td>
<td>0.2055923</td>
<td>7.405938536</td>
</tr>
<tr>
<td>180</td>
<td>35.83388627</td>
<td>0.208338863</td>
<td>7.50608326</td>
</tr>
<tr>
<td>195</td>
<td>35.85222751</td>
<td>0.208522275</td>
<td>7.512691852</td>
</tr>
<tr>
<td>210</td>
<td>35.74166981</td>
<td>0.207416698</td>
<td>7.472859854</td>
</tr>
<tr>
<td>225</td>
<td>35.30835274</td>
<td>0.203083527</td>
<td>7.316743315</td>
</tr>
<tr>
<td>240</td>
<td>35.0433729</td>
<td>0.200433729</td>
<td>7.221275724</td>
</tr>
<tr>
<td>255</td>
<td>35.05202534</td>
<td>0.200520253</td>
<td>7.224393047</td>
</tr>
<tr>
<td>270</td>
<td>35.06165929</td>
<td>0.200616593</td>
<td>7.22786399</td>
</tr>
<tr>
<td>285</td>
<td>35.06562276</td>
<td>0.200656228</td>
<td>7.229291957</td>
</tr>
<tr>
<td>300</td>
<td>35.15646146</td>
<td>0.201564615</td>
<td>7.262019548</td>
</tr>
<tr>
<td>315</td>
<td>35.4809583</td>
<td>0.204809583</td>
<td>7.378930071</td>
</tr>
<tr>
<td>330</td>
<td>35.52834458</td>
<td>0.205283446</td>
<td>7.396002514</td>
</tr>
<tr>
<td>345</td>
<td>35.59988959</td>
<td>0.205998896</td>
<td>7.421778927</td>
</tr>
<tr>
<td>360</td>
<td>35.58220264</td>
<td>0.205822026</td>
<td>7.41540663</td>
</tr>
<tr>
<td>375</td>
<td>35.5253053</td>
<td>0.205253053</td>
<td>7.394907514</td>
</tr>
<tr>
<td>390</td>
<td>35.4974976</td>
<td>0.204974976</td>
<td>7.384888889</td>
</tr>
<tr>
<td>405</td>
<td>35.25311034</td>
<td>0.202531103</td>
<td>7.296840446</td>
</tr>
<tr>
<td>420</td>
<td>35.80627805</td>
<td>0.208062781</td>
<td>7.49613707</td>
</tr>
<tr>
<td>435</td>
<td>35.89789087</td>
<td>0.208978909</td>
<td>7.529143561</td>
</tr>
<tr>
<td>450</td>
<td>35.92085504</td>
<td>0.20920855</td>
<td>7.537417151</td>
</tr>
<tr>
<td>465</td>
<td>35.90673865</td>
<td>0.209067386</td>
<td>7.53231261</td>
</tr>
<tr>
<td>480</td>
<td>35.96396024</td>
<td>0.209639602</td>
<td>7.552947197</td>
</tr>
<tr>
<td>495</td>
<td>36.02648917</td>
<td>0.210264892</td>
<td>7.575475273</td>
</tr>
<tr>
<td>510</td>
<td>36.11555645</td>
<td>0.211155564</td>
<td>7.607564652</td>
</tr>
</tbody>
</table>
B. Predicted settlement rates by biodegradation in lysimeters C, and D

<table>
<thead>
<tr>
<th>Time (Days)</th>
<th>Predicted settlement in lysimeter C (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.003126493</td>
</tr>
<tr>
<td>16</td>
<td>0.044808149</td>
</tr>
<tr>
<td>31</td>
<td>0.078091628</td>
</tr>
<tr>
<td>46</td>
<td>0.104669025</td>
</tr>
<tr>
<td>61</td>
<td>0.125891509</td>
</tr>
<tr>
<td>76</td>
<td>0.142838005</td>
</tr>
<tr>
<td>91</td>
<td>0.156370058</td>
</tr>
<tr>
<td>106</td>
<td>0.167175622</td>
</tr>
<tr>
<td>121</td>
<td>0.175804039</td>
</tr>
<tr>
<td>136</td>
<td>0.182693971</td>
</tr>
<tr>
<td>151</td>
<td>0.188195693</td>
</tr>
<tr>
<td>166</td>
<td>0.192588907</td>
</tr>
<tr>
<td>181</td>
<td>0.19609696</td>
</tr>
<tr>
<td>196</td>
<td>0.198898197</td>
</tr>
<tr>
<td>211</td>
<td>0.20113503</td>
</tr>
<tr>
<td>226</td>
<td>0.202921178</td>
</tr>
<tr>
<td>241</td>
<td>0.204347446</td>
</tr>
<tr>
<td>256</td>
<td>0.205486344</td>
</tr>
<tr>
<td>271</td>
<td>0.206395772</td>
</tr>
<tr>
<td>286</td>
<td>0.207121966</td>
</tr>
<tr>
<td>301</td>
<td>0.207701843</td>
</tr>
<tr>
<td>316</td>
<td>0.208164884</td>
</tr>
<tr>
<td>331</td>
<td>0.20853463</td>
</tr>
<tr>
<td>346</td>
<td>0.208829879</td>
</tr>
<tr>
<td>361</td>
<td>0.209065639</td>
</tr>
<tr>
<td>376</td>
<td>0.209253898</td>
</tr>
<tr>
<td>391</td>
<td>0.209404225</td>
</tr>
<tr>
<td>406</td>
<td>0.209524264</td>
</tr>
<tr>
<td>421</td>
<td>0.209620117</td>
</tr>
<tr>
<td>436</td>
<td>0.209696657</td>
</tr>
<tr>
<td>451</td>
<td>0.209757776</td>
</tr>
<tr>
<td>466</td>
<td>0.20980658</td>
</tr>
<tr>
<td>481</td>
<td>0.209845551</td>
</tr>
</tbody>
</table>
Table C-5- Predicted Settlement in Lysimeter D

<table>
<thead>
<tr>
<th>Time (Days)</th>
<th>Settlement in lysimeter D (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.042311594</td>
</tr>
<tr>
<td>30</td>
<td>0.076098088</td>
</tr>
<tr>
<td>45</td>
<td>0.103077152</td>
</tr>
<tr>
<td>60</td>
<td>0.124620371</td>
</tr>
<tr>
<td>75</td>
<td>0.141822982</td>
</tr>
<tr>
<td>90</td>
<td>0.155559545</td>
</tr>
<tr>
<td>105</td>
<td>0.166528414</td>
</tr>
<tr>
<td>120</td>
<td>0.175287233</td>
</tr>
<tr>
<td>135</td>
<td>0.182281293</td>
</tr>
<tr>
<td>150</td>
<td>0.187866163</td>
</tr>
<tr>
<td>165</td>
<td>0.192325772</td>
</tr>
<tr>
<td>180</td>
<td>0.195886842</td>
</tr>
<tr>
<td>195</td>
<td>0.198730415</td>
</tr>
<tr>
<td>210</td>
<td>0.201001053</td>
</tr>
<tr>
<td>225</td>
<td>0.202814195</td>
</tr>
<tr>
<td>240</td>
<td>0.204262018</td>
</tr>
<tr>
<td>255</td>
<td>0.205418129</td>
</tr>
<tr>
<td>270</td>
<td>0.206341301</td>
</tr>
<tr>
<td>285</td>
<td>0.20707847</td>
</tr>
<tr>
<td>300</td>
<td>0.207667111</td>
</tr>
<tr>
<td>315</td>
<td>0.20813715</td>
</tr>
<tr>
<td>330</td>
<td>0.208512484</td>
</tr>
<tr>
<td>345</td>
<td>0.208812194</td>
</tr>
<tr>
<td>360</td>
<td>0.209051518</td>
</tr>
<tr>
<td>375</td>
<td>0.209242622</td>
</tr>
<tr>
<td>390</td>
<td>0.209395221</td>
</tr>
<tr>
<td>405</td>
<td>0.209517074</td>
</tr>
<tr>
<td>420</td>
<td>0.209614376</td>
</tr>
<tr>
<td>435</td>
<td>0.209692073</td>
</tr>
<tr>
<td>450</td>
<td>0.209754115</td>
</tr>
<tr>
<td>465</td>
<td>0.209803657</td>
</tr>
<tr>
<td>480</td>
<td>0.209843217</td>
</tr>
<tr>
<td>495</td>
<td>0.209874806</td>
</tr>
<tr>
<td>510</td>
<td>0.209900031</td>
</tr>
</tbody>
</table>
C. Relative percent Errors calculated in lysimeters C, and D

Table C-6: Relative percent error for predicted and measured settlement in Lysimeter C

<table>
<thead>
<tr>
<th>Time (Days)</th>
<th>Relative Error in lysimeter C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.8500665</td>
</tr>
<tr>
<td>16</td>
<td>13.13053623</td>
</tr>
<tr>
<td>31</td>
<td>32.06626515</td>
</tr>
<tr>
<td>46</td>
<td>24.24805678</td>
</tr>
<tr>
<td>61</td>
<td>19.57635168</td>
</tr>
<tr>
<td>76</td>
<td>15.31027334</td>
</tr>
<tr>
<td>91</td>
<td>10.09924564</td>
</tr>
<tr>
<td>106</td>
<td>5.093369556</td>
</tr>
<tr>
<td>121</td>
<td>0.586984023</td>
</tr>
<tr>
<td>136</td>
<td>0.412745175</td>
</tr>
<tr>
<td>151</td>
<td>2.138204102</td>
</tr>
<tr>
<td>166</td>
<td>4.321760053</td>
</tr>
<tr>
<td>181</td>
<td>26.5755489</td>
</tr>
<tr>
<td>196</td>
<td>10.52350383</td>
</tr>
<tr>
<td>211</td>
<td>39.74026564</td>
</tr>
<tr>
<td>226</td>
<td>6.082849875</td>
</tr>
<tr>
<td>241</td>
<td>7.105192796</td>
</tr>
<tr>
<td>256</td>
<td>9.902858944</td>
</tr>
<tr>
<td>271</td>
<td>12.65606439</td>
</tr>
<tr>
<td>286</td>
<td>13.17899235</td>
</tr>
<tr>
<td>301</td>
<td>11.20830254</td>
</tr>
<tr>
<td>316</td>
<td>12.12785881</td>
</tr>
<tr>
<td>331</td>
<td>12.04866631</td>
</tr>
<tr>
<td>346</td>
<td>1.86819269</td>
</tr>
<tr>
<td>361</td>
<td>11.51064794</td>
</tr>
<tr>
<td>376</td>
<td>10.50943503</td>
</tr>
<tr>
<td>391</td>
<td>8.1769055</td>
</tr>
<tr>
<td>406</td>
<td>7.717317753</td>
</tr>
<tr>
<td>421</td>
<td>7.128651846</td>
</tr>
<tr>
<td>436</td>
<td>2.157278918</td>
</tr>
<tr>
<td>451</td>
<td>4.246123314</td>
</tr>
<tr>
<td>466</td>
<td>1.578985007</td>
</tr>
<tr>
<td>481</td>
<td>3.629995043</td>
</tr>
</tbody>
</table>
### Table C-7: Relative percent error for predicted and measured settlement in Lysimeter D

<table>
<thead>
<tr>
<th>Time (Days)</th>
<th>Relative Error in Lysimeter D</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>61.83079008</td>
</tr>
<tr>
<td>30</td>
<td>27.01324825</td>
</tr>
<tr>
<td>45</td>
<td>14.17349945</td>
</tr>
<tr>
<td>60</td>
<td>20.73029063</td>
</tr>
<tr>
<td>75</td>
<td>25.0571083</td>
</tr>
<tr>
<td>90</td>
<td>23.35893798</td>
</tr>
<tr>
<td>105</td>
<td>19.26078925</td>
</tr>
<tr>
<td>120</td>
<td>11.86944098</td>
</tr>
<tr>
<td>135</td>
<td>9.075317789</td>
</tr>
<tr>
<td>150</td>
<td>6.233690312</td>
</tr>
<tr>
<td>165</td>
<td>6.437783384</td>
</tr>
<tr>
<td>180</td>
<td>5.97681135</td>
</tr>
<tr>
<td>195</td>
<td>4.695834225</td>
</tr>
<tr>
<td>210</td>
<td>3.093118736</td>
</tr>
<tr>
<td>225</td>
<td>0.132621436</td>
</tr>
<tr>
<td>240</td>
<td>1.910002526</td>
</tr>
<tr>
<td>255</td>
<td>2.442583747</td>
</tr>
<tr>
<td>270</td>
<td>2.853556791</td>
</tr>
<tr>
<td>285</td>
<td>3.20061943</td>
</tr>
<tr>
<td>300</td>
<td>3.027563224</td>
</tr>
<tr>
<td>315</td>
<td>1.62471257</td>
</tr>
<tr>
<td>330</td>
<td>1.572965781</td>
</tr>
<tr>
<td>345</td>
<td>1.365686232</td>
</tr>
<tr>
<td>360</td>
<td>1.569069956</td>
</tr>
<tr>
<td>375</td>
<td>1.943731758</td>
</tr>
<tr>
<td>390</td>
<td>2.156480397</td>
</tr>
<tr>
<td>405</td>
<td>3.44933235</td>
</tr>
<tr>
<td>420</td>
<td>0.745734279</td>
</tr>
<tr>
<td>435</td>
<td>0.341261374</td>
</tr>
<tr>
<td>450</td>
<td>0.260775594</td>
</tr>
<tr>
<td>465</td>
<td>0.352169032</td>
</tr>
<tr>
<td>480</td>
<td>0.097126012</td>
</tr>
<tr>
<td>495</td>
<td>0.185520971</td>
</tr>
<tr>
<td>510</td>
<td>0.594601307</td>
</tr>
</tbody>
</table>

### D. Reports for linear regression in lysimeters C and D

**Data Source:** Linear regression in Lysimeter C  
**Equation:** Polynomial, Linear

\[ f = y_0 + a \times x \]

<table>
<thead>
<tr>
<th>R</th>
<th>Rsqr</th>
<th>Adj Rsqr</th>
<th>Standard Error of Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9245</td>
<td>0.8546</td>
<td>0.8499</td>
<td>0.0201</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Std. Error</th>
<th>t</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>y0</td>
<td>-0.0144</td>
<td>-0.9751</td>
<td>0.3371</td>
</tr>
</tbody>
</table>
Analysis of Variance:

Analysis of Variance:
<table>
<thead>
<tr>
<th>DF</th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>2</td>
<td>1.1299</td>
</tr>
<tr>
<td>Residual</td>
<td>31</td>
<td>0.0125</td>
</tr>
<tr>
<td>Total</td>
<td>33</td>
<td>1.1424</td>
</tr>
</tbody>
</table>

Corrected for the mean of the observations:
<table>
<thead>
<tr>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>1</td>
<td>0.0737</td>
<td>0.0737</td>
<td>182.2458</td>
</tr>
<tr>
<td>Residual</td>
<td>31</td>
<td>0.0125</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>32</td>
<td>0.0862</td>
<td>0.0027</td>
<td></td>
</tr>
</tbody>
</table>

Statistical Tests:

Normality Test (Shapiro-Wilk) Failed (P = 0.0432)

W Statistic = 0.9332 Significance Level = 0.0500

Constant Variance Test Failed (P <0.0001)

Fit Equation Description:

[Variables]
x = col(3)
y = col(5)
reciprocal_y = 1/abs(y)
reciprocal_y^2 = 1/y^2

'Automatic Initial Parameter Estimate Functions
F(q) = ape(x,y,1,0,1)

[Parameters]
y0 = F(0)[1] "Auto {[previous: -0.0143713]} {[MinRange: -12.3]} {[MaxRange: 36.9]}
a = F(0)[2] "Auto {[previous: 1.12772]} {[MinRange: -4.5]} {[MaxRange: 1.5]}

[Equation]
f = y0+a*x

'fit f to y
"fit f to y with weight reciprocal_y
"fit f to y with weight reciprocal_y^2

[Constraints]

Data Source: Linear Regression in Lysimeter D
Equation: Polynomial, Linear
f = y0+a*x

R   Rsqr   Adj Rsqr   Standard Error of Estimate
0.9216  0.8493   0.8446   0.0164

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Std. Error</th>
<th>t</th>
<th>P</th>
</tr>
</thead>
</table>
y0           | -0.0104    | 0.0149| -0.7023 | 0.4876 |
a            | 1.0182     | 0.0758| 13.4310| <0.0001|

125
Analysis of Variance:

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>2</td>
<td>1.2190</td>
<td>0.6095</td>
</tr>
<tr>
<td>Residual</td>
<td>32</td>
<td>0.0086</td>
<td>0.0003</td>
</tr>
<tr>
<td>Total</td>
<td>34</td>
<td>1.2276</td>
<td>0.0361</td>
</tr>
</tbody>
</table>

Corrected for the mean of the observations:

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>1</td>
<td>0.0486</td>
<td>0.0486</td>
<td>180.3918</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>32</td>
<td>0.0086</td>
<td>0.0003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>33</td>
<td>0.0572</td>
<td>0.0017</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Statistical Tests:

Normality Test (Shapiro-Wilk) Failed (P = 0.0003)

W Statistic 0.8488 Significance Level 0.0500

Constant Variance Test Failed (P = <0.0001)

Fit Equation Description:

Variables:
x = col(9)
y = col(11)
reciprocal_y = 1/abs(y)
reciprocal_ysquare = 1/y^2

'Automatic Initial Parameter Estimate Functions
F(q) = ape(x,y,1,0,1)

Parameters:
y0 = F(0)[1] "Auto [{previous: -0.0104355}] [{MinRange: -12.3}] [{MaxRange: 36.9}]
a = F(0)[2] "Auto [{previous: 1.01823}] [{MinRange: -4.5}] [{MaxRange: 1.5}]

Equation:
f = y0+a*x
fit f to y
"fit f to y with weight reciprocal_y
"fit f to y with weight reciprocal_ysquare

Constraints:

E. Reports for the fit curves in lysimeters B, C, and D

Data Source: Fit Curve in lysimeter D

Equation: Exponential Rise to Maximum, Single, 2 Parameter
f=a^b*(1-exp(-b*x))

<table>
<thead>
<tr>
<th>R</th>
<th>Rsqr</th>
<th>Adj Rsqr</th>
<th>Standard Error of Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9693</td>
<td>0.9396</td>
<td>0.9377</td>
<td>0.0094</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Std. Error</th>
<th>t</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.2076</td>
<td>0.0019</td>
<td>107.7967</td>
</tr>
<tr>
<td>b</td>
<td>0.0235</td>
<td>0.0014</td>
<td>16.4987</td>
</tr>
</tbody>
</table>
Analysis of Variance:

Analysis of Variance:

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>2</td>
<td>1.3035</td>
<td>0.6517</td>
</tr>
<tr>
<td>Residual</td>
<td>32</td>
<td>0.0028</td>
<td>8.8493E-005</td>
</tr>
<tr>
<td>Total</td>
<td>34</td>
<td>1.3063</td>
<td>0.0384</td>
</tr>
</tbody>
</table>

Corrected for the mean of the observations:

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>1</td>
<td>0.0441</td>
<td>0.0441</td>
<td>497.9308</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>32</td>
<td>0.0028</td>
<td>8.8493E-005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>33</td>
<td>0.0469</td>
<td>0.0014</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Statistical Tests:

Normality Test (Shapiro-Wilk) Failed (P = <0.0001)

W Statistic= 0.8203 Significance Level = 0.0500

Constant Variance Test Passed (P = 0.0914)

Fit Equation Description:

[Variables]

x = col(6)
y = col(8)
reciprocal_y = 1/abs(y)
reciprocal_ysquare = 1/y^2

'Automatic Initial Parameter Estimate Functions
first(q)=if(size(q)<10,size(q)-1,int(0.9*size(q)))
ylast(q)=mean(q[data(first(q),size(q))])

[Parameters]
a = ylast(y) "Auto {{previous: 0.2076}} {{MinRange: 6}} {{MaxRange: 18}}
b = -ln(.5)/(x50(x,y,.5)-min(x)) "Auto {{previous: 0.0235009}} {{MinRange: 0}} {{MaxRange: 0.12}}

[Equation]
f=a^(1-exp(-b*x))
fit f to y
"fit f to y with weight reciprocal_y
"fit f to y with weight reciprocal_ysquare

Data Source: Fit curve in lysimeter B
Equation: Exponential Rise to Maximum, Single, 2 Parameter
f=a^(1-exp(-b*x))

R Rsqr Adj Rsqr Standard Error of Estimate
0.9818 0.9640 0.9626 0.0139

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Std. Error</th>
<th>t</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.2856</td>
<td>0.0059</td>
<td>48.6534</td>
</tr>
<tr>
<td>b</td>
<td>0.0097</td>
<td>0.0006</td>
<td>14.9711</td>
</tr>
</tbody>
</table>

Analysis of Variance:
Analysis of Variance:

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>2</td>
<td>1.4602</td>
<td>0.7301</td>
</tr>
<tr>
<td>Residual</td>
<td>26</td>
<td>0.0050</td>
<td>0.0002</td>
</tr>
<tr>
<td>Total</td>
<td>28</td>
<td>1.4653</td>
<td>0.0523</td>
</tr>
</tbody>
</table>

Corrected for the mean of the observations:

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>1</td>
<td>0.1350</td>
<td>0.1350</td>
<td>695.7082</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>26</td>
<td>0.0050</td>
<td>0.0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>27</td>
<td>0.1400</td>
<td>0.0052</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Statistical Tests:

**Normality Test (Shapiro-Wilk)**
Passed (P = 0.1829)

W Statistic= 0.9486 Significance Level = 0.0500

**Constant Variance Test**
Passed (P = 0.0606)

**Fit Equation Description:**

[Variables]
x = col(11)
y = col(13)
reciprocal_y = 1/abs(y)
reciprocal_ysquare = 1/y^2

'Automatic Initial Parameter Estimate Functions
first(q)=if(size(q)<10,size(q)-1,int(0.9*size(q)))
ylast(q)=mean(q[data(first(q),size(q))])

[Parameters]
a = ylast(y) "Auto {[previous: 0.285599]} {[MinRange: 6]} {[MaxRange: 18]}
b = -ln(.5)/(x50(x,y,.5)-min(x)) "Auto {[previous: 0.00971208]} {[MinRange: 0]} {[MaxRange: 0.12]}

[Equation]
f=a*(1-exp(-b*x))
fit f to y
"fit f to y with weight reciprocal_y
"fit f to y with weight reciprocal_ysquare

**Data Source:** Fit curve in lysimeter C

**Equation:** Exponential Rise to Maximum, Single, 2 Parameter
f=a*(1-exp(-b*x))

**R Rsqr Adj Rsqr Standard Error of Estimate**
0.9564 0.9146 0.9119 0.0126

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Std. Error</th>
<th>t</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.1882</td>
<td>71.9715</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>b</td>
<td>0.0271</td>
<td>10.4826</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>

Analysis of Variance:
Analysis of Variance:

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>2</td>
<td>1.0223</td>
<td>0.5112</td>
</tr>
<tr>
<td>Residual</td>
<td>31</td>
<td>0.0049</td>
<td>0.0002</td>
</tr>
<tr>
<td>Total</td>
<td>33</td>
<td>1.0272</td>
<td>0.0311</td>
</tr>
</tbody>
</table>

Corrected for the mean of the observations:

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>1</td>
<td>0.0530</td>
<td>0.0530</td>
<td>332.1876</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>31</td>
<td>0.0049</td>
<td>0.0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>32</td>
<td>0.0579</td>
<td>0.0018</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Statistical Tests:

Normality Test (Shapiro-Wilk) Failed (P = 0.0002)

W Statistic = 0.8342 Significance Level = 0.0500

Constant Variance Test Passed (P = 0.2757)

Fit Equation Description:

[Variables]
x = col(1)
y = col(3)
reciprocal_y = 1/abs(y)
reciprocal_ysquare = 1/y^2

'Automatic Initial Parameter Estimate Functions
first(q)=if(size(q)<10,size(q)-1,int(0.9*size(q)))
ystart(q)=mean(q[data(first(q),size(q))])

[Parameters]
a = ylast(y) "Auto {[previous: 0.188159]} {[MinRange: 6]} {[MaxRange: 18]}
b = -ln(.5)/(x50(x,y,.5)-min(x)) "Auto {[previous: 0.0271062]} {[MinRange: 0]} {[MaxRange: 0.12]}

[Equation]
f=a*(1-exp(-b*x))
fit f to y
"fit f to y with weight reciprocal_y
"fit f to y with weight reciprocal_ysquare
References:


5- S.T.S. Yuen, Bioreactor landfills promoted by leachate recirculation: a full-scale study, Ph.D. Thesis, Department of Civil & Environmental Engineering, University of Melbourne, Australia, 1999.


