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Methane Oxidation in Landfill Cover Soil

by

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A thesis

submitted under the supervision of

Dr. Leta Fernandes

in partial fulfillment of the
requirements for the degree of
Master of Applied Science
in
Civil Engineering

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ABSTRACT

Methane, one of the primary greenhouse gases, negatively affects climate change. Its atmospheric concentration has increased dramatically over the last century and is expected to continue rising due to human activities. Oxidation of methane by methanotrophic bacteria provides a sink for methane. The rate at which methane is biologically oxidized depends on different parameters. This study aims to better understand methane oxidation in landfill cover soils. This was done through laboratory batch reactor experiments, under two levels of moisture content, two soil layer thicknesses and with and without nutrient additions.

Adding nutrients to the 200 mm layer of landfill cover soil that contained 30% moisture content (by weight), increased the CH₄ oxidation efficiency from 38% to 81% and the CH₄ substrate utilization from 2750 μmoles/L to 5540 μmoles/L.

The kinetic constants were studied in the landfill cover soil. The maximum CH₄ utilization rate for different experimental runs and under different levels of the three specified parameters were between 31 and 699 μmoles/ day×kg of dry soil weight.

A statistical design model was developed to describe the expected methane oxidation efficiencies under different levels of moisture content and nutrient addition that can occur in a typical landfill cover soil.

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GLOSSARY

Abbreviations and Acronyms

atm	atmosphere
cc	cubic centimeter
CEC	Commissions of European Communities
ε	error
EPS	Exopolymeric Substances
FID	flame ionization
GC	gas chromatograph
GWP	global warming potential
HP	Hewlett Packard
IPCC	Intergovernmental Panel on Climate Change
K_{CH_4}	half saturation constant ($\mu\text{moles CH}_4$)
LFG	landfill gas
mc /MC	moisture content
MSW	municipal solid waste
MMO	monooxygenases enzyme
ppm	parts per million
R^2	coefficient of determination value (a regression statistic)
T	temperature

TCD	thermal conductivity
Tg	teragrams
TOC	total organic carbon
USEPA	United States Environmental Protection Agency
USDA	United States Department of Agriculture
v, vol	volume
V_{\max}	maximum CH_4 reaction rate ($\mu\text{moles/ day} \times \text{kg of dry soil weight}$)

CHAPTER 1 - INTRODUCTION

Methane (CH_4) is an important radiatively active organic gas and one of the principal greenhouse gases. Its atmospheric concentration levels have significantly increased during the past few hundred years, and sharply increased after the industrial revolution. The effects of CH_4 on climate and atmospheric chemistry are the reason for concern over its high growth rates. CH_4 and Carbon Dioxide (CO_2) are released into the atmosphere by a wide variety of sources, both natural and anthropogenic. Natural CH_4 emissions arise from wetlands, termites and oceans. Typically, anthropogenic emissions are generated from sources related to agriculture, waste disposal and extraction of fossil fuels. Concerns over the potentially negative impact of climate change have resulted in a search for different techniques to reduce and/or utilize anthropogenic emissions of CH_4 (Knaebel and Reinhold, 2002; Hilger et al., 1999; Czepiel et al., 1996a).

Landfills are estimated to be one of the largest sources of anthropogenic CH_4 emissions (Masters, 1996). In the last several decades, solid waste management options have expanded, but landfilling remains the dominant practice in many parts of the world. Dependency on landfills for the ultimate disposal of treated or untreated waste will unavoidably remain for a considerable number of years. Design improvements have reduced the environmental impacts of new landfills, but landfills continue to require technical and regulatory attention (Hilger and Humer, 2003). Despite the evolution of

landfills into properly engineered facilities, the generation of leachate and biogas from landfill sites is unavoidable. Both migration of leachate away from the boundaries of the site, and gases to the atmosphere, can present a threat to the environment (Westlake, 1996; El_Fadel et al., 1995). On the other hand, the collection and utilization of the biogas can serve as a potential renewable energy source (Zacharof and Butler, 2003).

To manage the biogas production from a landfill, more detailed knowledge of the fundamental processes taking place within the landfill is needed, particularly with respect to waste characterization and operation of sites. As mathematical modeling is a well-established tool for understanding and analyzing complex natural systems, numerous models simulating the processes taking place within landfills have been developed, each successful to a greater or lesser extent (Zacharof and Butler, 2003).

Solid waste is delivered to landfills, then the waste is generally spread out, compacted, and covered with a fresh layer of soil each day. Waste deposited in landfills decomposes by microbial action to form mainly CH_4 , CO_2 and water. This biogas product is called landfill gas (LFG); it is a flammable and potentially harmful mixture. The LFG generally consists of 50-65% by volume CH_4 and 35-50% by volume CO_2 plus trace amounts of numerous chemical compounds (Shin et al., 2001). Knaebel and Reinhold (2002) called LFG a biofuel, since plant material (biomass) is a significant component of solid waste. These researchers indicated that in this vein, LFG is viewed as a renewable resource.

CH₄ is the most valuable component of LFG, but it is also potentially harmful. Combustion without prior enrichment is the simplest disposal option and this will diminish the potential greenhouse gas effect of CH₄ in the LFG. Alternatively, CH₄ in LFG can be extracted and utilized as a form of energy and potential fuel. LFG extraction techniques are well developed, but are mainly feasible for large landfills sites and the costs involved are high.

Another important and effective method to reduce fugitive CH₄ emissions from landfills is the use of reactive biological covers for CH₄ oxidation. There are many advantages for this method; it can complement the efficiency of gas collection systems and also it can be an alternative option to remediate small landfills, open dumps and older landfills after closure of the sites. In addition to all of this, the cost of this method is low (Gebert et al., 2003).

In the greenhouse gas budget, biological CH₄ oxidation in landfill cover soil is an important process for mitigating CH₄ fluxes into the atmosphere (Borjesson et al., 1998). Landfill cover soils can contain various groups of microorganisms that are capable of oxidizing CH₄, such as methanotrophic bacteria (Hilger and Humer, 2003). These authors have reported that methanotrophic bacteria possess the CH₄ monooxygenase enzyme, which enables them to consume CH₄ and oxidize it to CO₂ and water for energy yield, while another fraction is incorporated to biomass. However, methanotrophic bacteria are present in small numbers in most soils.

1.1 RESEARCH OBJECTIVES

The general purpose of this experimental study is to gain better quantitative understanding of the physical and biochemical processes that affect CH₄ oxidation efficiency in landfill cover soils. This research aims also to clarify the importance of using biologically active landfill cover soils by determining the maximum efficiency of biological CH₄ oxidation that can occur in typical landfill soils, under varying operating conditions, in order to optimize the design of landfill cover soils.

The specific objectives of this research are:

- 1) To investigate the individual and combined effects of different parameters affecting CH₄ oxidation, in laboratory scale heterogeneous batch reactors, specifically:
 - Moisture content: is a critical physical constraint affecting CH₄ oxidation capacity. It is necessary to investigate this parameter since a large range of optimum values are reported in the literature.
 - Nutrient addition: To examine the effect of adding nutrients to the landfill cover soil, such as soil fertilizer, on the CH₄ oxidation efficiency.
 - Soil layer thickness: To investigate the CH₄ oxidation efficiency that can occur in different soil layer thicknesses.

- 2) To develop a statistical model that can describe CH₄ oxidation efficiencies based on the experimental results, obtained from a 2³ factorial design, where the three parameters are: two levels of moisture content, addition and no nutrient addition and two soil layer thicknesses;
- 3) To determine the kinetic constants for CH₄ oxidation using the heterogeneous batch reactor experiments;
- 4) To quantify the maximum biological CH₄ oxidation efficiency that can occur in a permeable landfill cover soil.
- 5) To apply a mathematical description of the CH₄ oxidation processes that occur in landfill cover soil continued in a heterogeneous closed batch reactor system.

1.2 THESIS OUTLINE

The thesis is divided into seven chapters. The first chapter gives an introduction and objectives of this research. *Chapter 2* presents literature review. *Chapter 3* discusses the materials, as well as the experimental and analytical procedures that were used during the course of this research. *Chapter 4* presents statistical analyzes of the results obtained and discusses kinetic parameters. *Chapter 5* presents the mathematical description of the CH₄ oxidation process in heterogeneous batch reactor system. Finally, conclusions and recommendations are presented in *Chapter 6* and *7*, respectively. The *Appendices* present supplementary facts and figures that include much of the observed data, analyses and calculations.

CHAPTER 2 – LITERATURE REVIEW

2.1 GLOBAL WARMING AND GREENHOUSE GASES

The scientific agreement on global warming is becoming clearer and more compelling everyday; changes in our climate are real and underway. Global warming is defined according to Intergovernmental Panel on Climate Change (IPCC, 1995) as the increase in the Earth's average temperature mainly as a result of greenhouse gas effect. According to Meyerson (1998), IPCC has projected an increase of 2°C in the global mean surface temperature between 1990 and 2100; meanwhile, the global temperature has already increased by 0.5° C since the late nineteenth century. Meyerson (1998) stressed that in all IPCC scenarios, the rate of warming over the 21st century will likely be greater than any rate increase seen in the last 10,000 years.

The atmosphere is made up almost entirely of nitrogen (N₂) and oxygen (O₂), plus some other gases and particles that exist in very small concentrations. Table 2-1 shows the composition of the earth's atmosphere. The values given are for "clean", dry air.

Table 2-1 Composition of Clean, Dry Air (Fraction by Volume in Troposphere, 1994), (Masters, 1996)

Constituent	Formula	Percent by volume	Parts per million
Nitrogen	N ₂	78.08	780,800
Oxygen	O ₂	20.95	209,500
Argon	Ar	0.93	9,300
Carbon dioxide	CO ₂	0.035	358
Neon	Ne	0.0018	18
Helium	He	0.0005	5.2
Methane	CH ₄	0.00017	1.7
Krypton	Kr	0.00011	1.1
Nitrous oxide	N ₂ O	0.00003	0.3
Hydrogen	H ₂	0.00005	0.5
Ozone	O ₃	0.000004	0.04

While most of the values in the table are essentially unchanging, that is not the case for the principle greenhouse gases, being (CO₂), (CH₄) and nitrous oxide (N₂O), which are rising.

Climate Change Journal (2002), in one of the editorial essays, stated that the increased fossil fuel emissions for example caused an increase in the atmospheric CO₂ concentration by 16 ppmv for the decade spanning 1980 – 1990. Furthermore, if the fossil fuel emissions continue to increase at this rate to the year 2100, the rate of CO₂ increase

will reach a maximum of > 40 ppmv/decade, and the global warming will accelerate toward $+0.3^{\circ}\text{C}/\text{decade}$.

At the beginning, the concern that human activities may be affecting global climate was largely centered on CO_2 , because of its importance as a greenhouse gas, as well as the rapid rate at which its atmospheric concentration was increasing. Masters (1996) indicated that Arrhenius (1896) is usually credited with the first calculations on global temperature as a function of atmospheric CO_2 content. However, it is clear now that the other principal greenhouse gas (CH_4) has significantly affected climate over the past few centuries. Wuebbles and Hayhoe (2001) have explained that both greenhouse gases CO_2 and CH_4 absorb infrared radiations emitted by the relatively warm planetary surface and emit radiation into space at the colder atmospheric temperature, leading to a net trapping of infrared radiation in the atmosphere. These authors indicated that this is called the “greenhouse effect”. Moreover, the balance between the absorbed solar radiation and the emitted infrared radiation determine the net radiative forcing on climate. The radiative forcing of the main greenhouse gases are listed in Table 2-2.

Table 2-2 Globally Average Radiative Forcing due to Changes in Greenhouse Gases, Aerosols and Solar Intensity from 1850 to 1996 (Masters, 1996)

Direct Greenhouse Gas	Radiative forcing ΔF (W/m^2)
Carbon dioxide, CO_2	1.56
Methane, CH_4	0.47
Halocarbons	0.28
Nitrous oxide, N_2O	0.14

One of the tools developed to assist policy makers to implement the commitment to prevent dangerous anthropogenic interference with the climate system is the use of an index called the Global Warming Potential (GWP). The GWP is a weighting factor that enables comparisons to be made between the GWP of one kilogram release of CO₂ and other greenhouse gases (Wuebbles and Hayhoe, 2001; Masters, 1996). It is a dimensionless quantity and includes a time horizon during which the impact will be felt. When the GWP for each greenhouse gas is multiplied by the year's emission rate, a true measure of the impact of each of these gases can be found.

Figure 2-1 shows the relative influences of the three main greenhouse gases over different time horizons based on the products of GWP and one year emissions. According to this figure and over the course of 100 years for example, the cumulative direct effect on the atmosphere's energy budget resulting from one kilogram release of CH₄ is 23 times the direct effect of one kilogram release of CO₂.

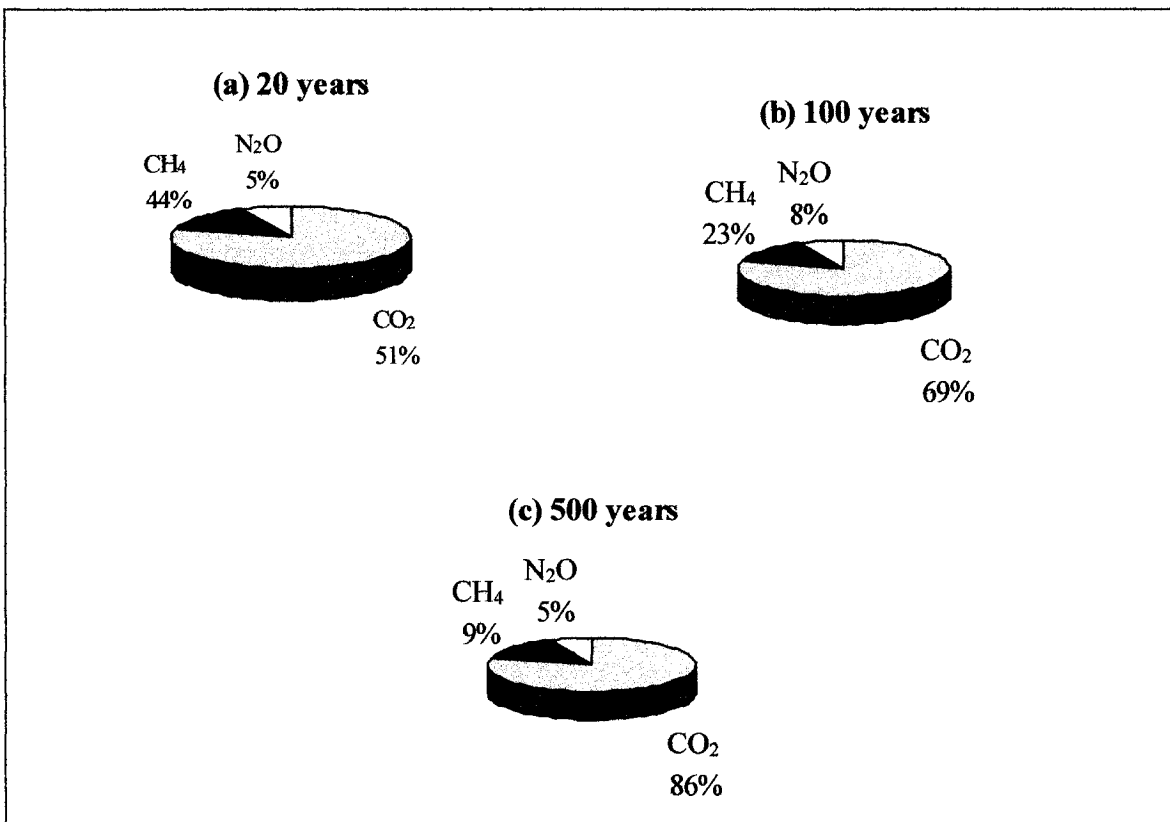


Figure 2-1 Relative Influences of the Three Main Greenhouse Gases Over Different Time Horizons Based on GWP (Masters, 1996)

The atmospheric lifetime of CH₄ is shorter than CO₂; the atmospheric life time of CH₄ is about 9 years compared with 120 years for CO₂ (Czepiel et al., 2003). This fact means that CH₄ global warming potential is higher for shorter time horizons.

Global warming is a universal problem. It affects sea level rise, and can cause flooding (Meyerson, 1998). As a result many countries will suffer sever losses of agricultural and residential lands. It can also increase the net global forest losses because of temperature and precipitation changes. Different measures should be taken universally to reduce emissions of the two principal greenhouse gases CO₂ and CH₄, slow the rate of global warming, and minimize future increase in the Earth's surface temperature.

2.2 METHANE

Many researchers (De Visscher and Schippers, 2000; Ridgwell et al., 1999; Boeckx and Van Cleemput, 1996a; Masters, 1996) have indicated that the accumulation of CH₄ in the atmosphere accounts for 15 to 20% of total direct greenhouse forcing effect. Besides, the atmospheric CH₄ concentration is on the rise. As shown in Figure 2-2, the concentration of CH₄ in the atmosphere was approximately 700 ppb for hundreds of years; afterwards, it began its rapid climb starting from the 1800s. In 1992 it reached 1714 ppb, which is an increase of almost 250% over the pre-industrial levels, and second only to the increase of CO₂.

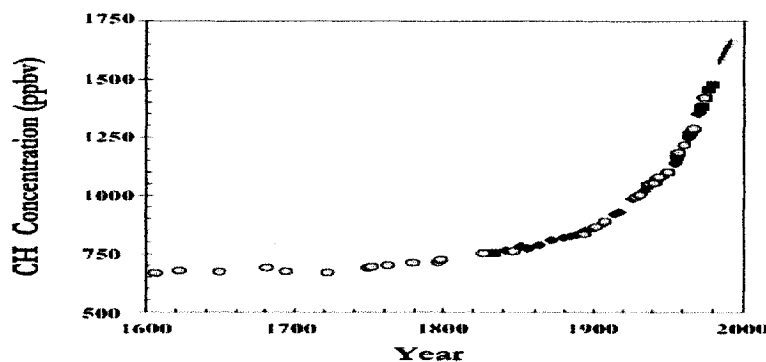


FIGURE 2-2 Atmospheric Records of the Increase in Atmospheric CH₄ from Pre-industrial Times to the Present (Wuebbles and Hayhoe, 2001)

As mentioned in *Chapter 1*, CH₄ emissions arise from both natural and anthropogenic sources. Natural CH₄ emissions arise from wetlands, termites and other wild ruminants, oceans and hydrates. Figure 2-3 shows the contributions of individual sources to total natural CH₄ emissions.

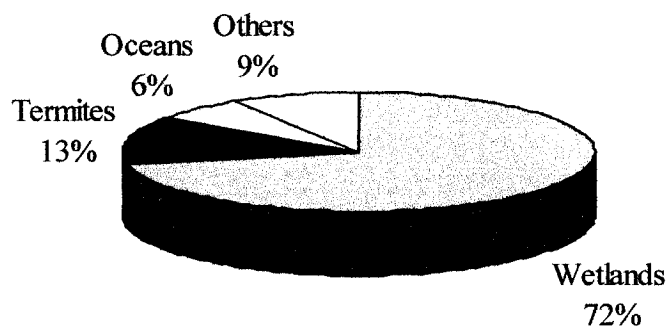


FIGURE 2-3 Contribution of Individual Sources to Total Natural CH₄ Emissions (Wuebbles and Hayhoe, 2001)

On the other hand, many researchers (Czepiel et al., 2003; Wuebbles and Hayhoe, 2001; Boeckx and Van Cleemput, 1996a; Masters, 1996) have identified different sources of anthropogenic CH₄ emissions, as follows:

- 1- CH₄ emissions from energy sources (coal mining, natural gas systems, petroleum systems, stationary combustion, and mobile source combustion).
- 2- CH₄ emissions from agricultural sources are dominated by emissions from domestic livestock, including the animals themselves (enteric fermentation) and the anaerobic decomposition of the manure and other organic waste.
- 3- CH₄ emissions from waste management sources include two subcategories: emissions from the anaerobic decomposition of municipal solid waste in landfills and emissions

from wastewater treatment facilities. Figure 2-4 indicates the contribution of individual sources to total anthropogenic CH₄ emissions.

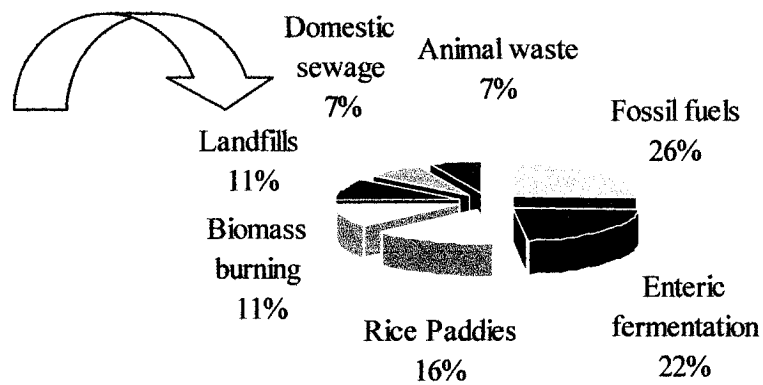


FIGURE 2-4 Anthropogenic Sources of CH₄ Emissions (Masters, 1996)

2.3 LANDFILLS

Landfills are used for the disposal of municipal solid wastes (MSW), non-hazardous industrial wastes, water and wastewater treatment sludge as well as agricultural residues. Since there is a limit to the types of waste that can be recycled or composted, landfills continue to be an important repository of MSW for the predictable future (Knaebel and Reinhold, 2002).

Many researches (Czepiel et al., 2003; Hilger and Barlaz, 2002; Anex, 1996; Boeckx and Van Cleemput, 1996b; Borjesson and Svensson, 1996; Czepiel et al., 1996a; Bogner et al., 1995; El-Fadel et al., 1995) have stated that a complex series of biological

and chemical reactions begin with the burial of refuse in landfills, where an active anaerobic ecosystem generates CH_4 and CO_2 as major end components. These researchers also confirmed that a period ranging from months to years is necessary for proper growth conditions of anaerobes and the required microbiological system to establish and decompose the waste. Hilger and Barlaz (2002) conducted laboratory simulations in order to define the microbiology of refuse decomposition. Based on their research, it was concluded that solid waste microbial decomposition goes through four phases as follows:

- Aerobic phase.
- Anaerobic acid phase.
- Accelerated CH_4 production phase.
- Decelerated CH_4 production phase.

In the first phase of the decomposition (aerobic), oxygen and ammonia are consumed with soluble sugars, and this acts as a carbon source for the microbial activities. All of the trophic groups required for the waste methanogenesis are present in the fresh solid waste. During the second phase (anaerobic acid phase) carboxylic acids accumulate, which decreases the pH because of the imbalance between fermentative, acetogenic, and methanogenic activity. Also, there is some cellulose and hemicellulose decomposition. In this phase CH_4 is first detected as the methanogen population starts to increase. Throughout the third phase (the accelerated CH_4 production phase), the maximum value of CH_4 is produced, while the concentration of carboxylic acid

decreases, the pH increases and the population of methanogenesis bacteria increases. At this phase the main substrate supporting CH₄ production is the accumulated carboxylic acid. CH₄ production rates decrease during the fourth phase (the decelerated CH₄ production phase) and the carboxylic acids are depleted.

The gaseous product resulting from the biodegradation of wastes is LFG. LFG can migrate to the surface and enter the atmosphere. According to (Hilger and Humer, 2003), the biochemical reactions that produce LFG typically continue long after a landfill is capped. So, even after the closure of the landfill, LFG emissions into the atmosphere will continue. Landfills are estimated to be one of the largest sources of anthropogenic CH₄ emissions, contributing to almost 11% of total global emissions (Figure 2.4), and 26% of Canada's anthropogenic CH₄ emissions, as reported by Environment Canada (1995).

2.3.1 REGULATIONS TO REDUCE CH₄ EMISSIONS FROM LANDFILLS

In some countries where solid waste landfilling is highly regulated, several initiatives and steps have been undertaken to reduce landfill CH₄ emissions. In the United States, landfills are recognized as one of the major CH₄ emission sources. The Clean Air Act has recently been amended to include requirements for gas collection at new and existing landfill sites, based on its size and emission test results. This regulation is expected to result in a decline of LFG emissions from their 1997 level of 11.6 Tg (teragrams) to 9.1 Tg by 2010 according to (USEPA, 1999). The collected biogas can be used directly as fuel or converted to electricity and the remainder can be flared.

Similar measures are being undertaken in Europe. In the United Kingdom, landfills are the largest source of anthropogenic CH₄ (Meadows, 1996). In the European Union, landfills are the second largest anthropogenic source as indicated by CEC (1996). Both entities have applied approaches to increase landfill gas collection systems and make systematic reductions in the quantity of biodegradable wastes that are buried in the landfill sites. Some countries, such as Germany and Austria have placed quantitative limits on the allowable total organic carbon (TOC) of landfilled wastes in order to minimize the CH₄ generation potential. For these steps to be effective, time to plan, apply and gain public support is required. Furthermore, the efficiency of these plans will depend on economy, proper management and public compliance.

While tighter landfill regulations are applied in developed countries, many urban centers in the developing world still rely on open dumps for solid waste disposal. This practice presents health and safety problems. It is expected that the total global methane emissions from landfills are to increase by 2025, with the contributions from Asia and Eastern Europe rising to equal those of the United States and Western Europe (Hilger and Humer, 2003).

2.3.2 UTILIZATION AND/OR MITIGATION OF CH₄ FROM LANDFILLS

In a sense, CH₄ produced from landfills is renewable, since it is a byproduct of civilization. Thus, it is important not to allow CH₄ to escape into the atmosphere, but rather capture it for proper utilization. There are new technologies that can extract, recover and utilize CH₄ from the collected LFG, using appropriate collection and

separation systems (Knaebel and Reinhold, 2002). After this step, CH₄ can be converted to a useful form of energy. Knaebel and Reinhold (2002), Riemer (1996) and Westlake (1996) described some of these technologies, which are costly and generally suited for large landfill operations. Stein et al. (2001) reported that USEPA considers only landfills containing more than 900,000 tonnes of waste to be capable of generating enough energy to support CH₄ recovery projects. For this reason, gas recovery will only be feasible at landfills in large urban cores.

At older landfill sites, the CH₄ concentrations are generally lower and hence landfill gas collection systems may not be economically feasible. If not collected, LFG will migrate through landfill covers and disperse into the atmosphere. Biological CH₄ oxidation within the landfill cover soil is one of the few biogeochemical sinks for removing CH₄ and reducing emissions to the atmosphere.

2.4 BIOLOGICAL CH₄ OXIDATION IN LANDFILL COVER SOIL

In the greenhouse gas budget, biological CH₄ oxidation mediated by methanotrophic bacteria is an important process for mitigating CH₄ fluxes to the atmosphere. Biological CH₄ oxidation was found to restrict the fluxes of CH₄ produced in lakes and rice paddies by up to almost 100% (Borjesson et al., 1998). Several investigations of microbial landfill CH₄ uptake were conducted to document its occurrence and explore the conditions and factors that enhanced it. Microbial CH₄

consumption generally occurs at the interface of aerobic and anaerobic zones. CH₄ is generated in the anaerobic regions and most of its uptake is performed by aerobes (Horz et al., 2002; Hilger et al., 1999; Hanson and Hanson, 1996). Oxidation rates of CH₄ differ within and between landfill sites, due to seasonal climate changes, physical heterogeneities in the cover and CH₄ concentrations (Brojesson et al., 2004; Bogner et al., 1997; Whalen and Reeburgh, 1996).

2.4.1 MICROBIOLOGY OF CH₄ OXIDATION

Most microbial CH₄ oxidation is accomplished by methanotrophs. Methanotrophic bacteria seem to oxidize CH₄ most efficiently when they occur in consortia amongst other bacteria, however, they may constitute 90% of the microbial population (Borjesson et al., 1998). Methanotrophs are defined as gram-negative aerobic bacteria with the ability to grow on CH₄ as its sole carbon and energy source (Borjesson et al., 2004). Hanson and Hanson (1996) stated that Sohngen in 1906 isolated the first CH₄ oxidizing bacterium and named it *Bacillus methanicus*. Hilger and Humer (2003) reported that methanotrophs (a subset of a highly diverse group of bacteria named methylotrophs) can metabolize C-1 compounds such as CH₄, methanol and methylamines.

Methanotrophs are found in different types of soils and in a variety of ecosystems. They can consume CH₄ and oxidize it to CO₂ and water for energy yield, while another fraction is incorporated into biomass. Long-term exposure to high levels of CH₄

encourages the growth of populations of methanotrophs with a high capacity for CH₄ oxidation.

Borjesson et al. (2004) stated that there are two main groups of methanotrophic bacteria, which are designated Type I and Type II. Also, they observed that shifts in the methanotroph populations in soils can occur in response to environmental stimulus such as change in concentrations of CH₄ and O₂, temperature, pH and N₂ sources.

Hanson and Hanson (1996) explained that the oxidation of CH₄ by aerobic methanotrophs is initiated by CH₄ monooxygenases (MMOs), which are classical monooxygenases that utilize two reducing equivalents to split the O-O bonds of dioxygen. One of the oxygen atoms is reduced to form water (H₂O) and the other is incorporated into CH₄ to form methyl alcohol (CH₃OH). For the methanotrophic conversion of CH₄, two pathways were recognized. These two paths are: the ribulose monophosphate path and the serine path (Anthony, 1982). Figure 2-5 illustrates the two pathways for the oxidation of CH₄ as reported by (Hanson and Hanson, 1996).

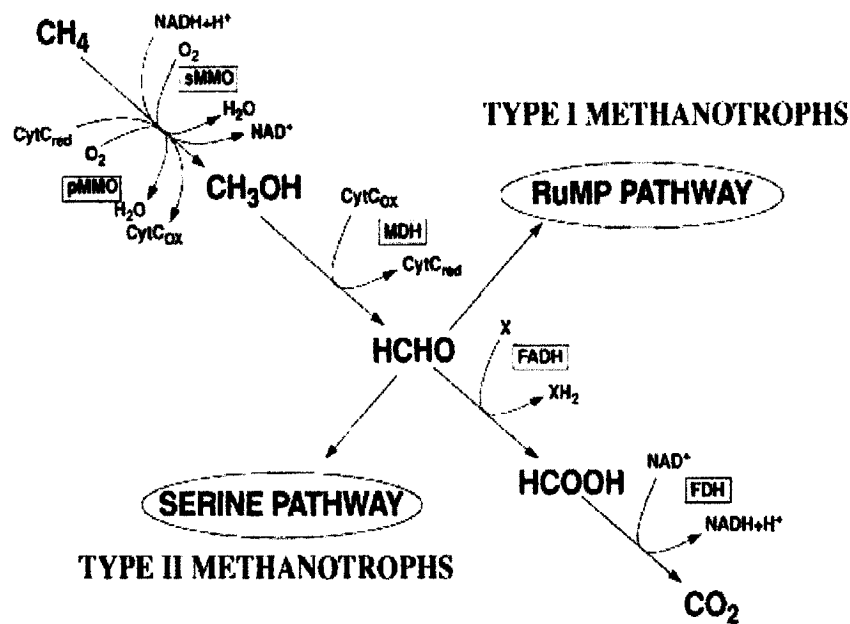
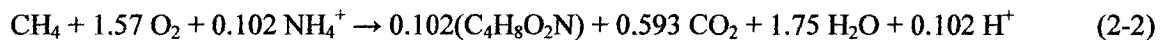
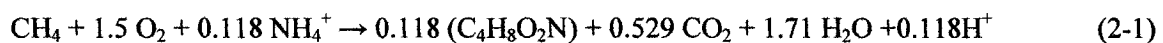


Figure 2-5 Pathways for the Oxidation of CH₄ and Assimilation of Formaldehyde. Abbreviations: CytC, rtochrome c; FADH, Formaldehyde Dehydrogenase; FDH, Formate Dehydrogenase (Hanson and Hanson, 1996)

Hilger and Humer (2003) showed the following two equations that summarize O₂ and N₂ demands for those two pathways, noting that C₄H₈O₂N is the microbial biomass. These two pathways start with the conversion of methane to methanol (CH₃OH). This reaction is mediated by the CH₄ monooxygenase enzyme, which is responsible for oxidation of CH₄.



Hilger and Barlaz (2002) indicated that kinetic properties for methanotrophs vary. When pure methanotroph cultures and methanotrophs in soil are enriched with CH₄, reaction rates are high, but methane affinity is very low to support uptake of atmospheric methane.

2.4.2 FACTORS AFFECTING CH₄ OXIDATION IN LANDFILL COVER SOIL

The rate at which CH₄ is biologically oxidized depends on several environmental conditions, such as moisture content, temperature, soil characteristics and composition, pH, nutrients and O₂ concentrations. Some studies have been conducted previously to test single or combined influences of these factors on CH₄ oxidation in soils. Some of these results are described below.

2.4.2.1 Moisture Content

Moisture content is one of the most important parameters affecting CH₄ oxidation in landfill cover soil. The moisture strongly affects the capacity for CH₄ consumption by determining the extent of CH₄ diffusion between the soil gas phase and the atmosphere (Schnell and King, 1995). Soil pore volume available for gas exchange seems to be the critical factor at different moisture contents (Hilger and Humer, 2003). Under higher moisture conditions, CH₄ must reach the microbes by aqueous diffusion, which is much slower than gas diffusion. Gas diffusion in saturated soils is limited by the diffusion coefficient of CH₄ in water, which is four orders of magnitude lower than in air. On the other hand, some researchers (Czepiel et al., 1996b; Whalen et al., 1990) observed a

decrease in the soil oxidizing capacity at lower moisture content (e.g. 5% by weight), presumably due to the response to water stress, which result in a lower microbial activities.

Borjesson et al. (1998); Boeckx et al. (1996b); Whalen and Reeburgh (1996) recorded the optimum moisture content for CH₄ uptake in landfill cover soils to be in the range of 10-20% (by weight). At this range of moisture content, Borjesson et al. (1998) recorded CH₄ maximum oxidation rate of 2 μmoles of CH₄/ h×g of dry soil weight, Boeckx et al. (1996b) reported a maximum rate of 10.86 ng of CH₄/ h×g of dry soil weight (7×10^{-4} μmoles/h×g of dry soil weight) and Whalen and Reeburgh (1996) reported an oxidation rate of 706 ng of CH₄/ h×g dry soil weight (4.4×10^{-2} μmoles /h×g dry soil weight). Bender and Conrad (1995) reported maximum CH₄ oxidation rate of 31.1 μmoles/d×g dry soil weight (1.3 μmoles/ h×g dry soil weight) at the optimum moisture content in the range of 20% to 35% (by weight). Hilger and Barlaz (2002) reported that results from recent experiments conducted using landfill covers composed of composted MSW with a moisture content as high as 45% exceeded the results for soil covers with less moisture content, this suggested that high performance can be maintained at high moisture levels, as long as soil pores volumes are not water saturated. The results from the last two studies showed that CH₄ oxidation rates revealed an upward trend with the increased moisture content.

It is obvious that there is variability in the range of optimum moisture content reported in the literature, for maximum oxidation of CH₄ in landfill cover soils.

2.4.2.2 Temperature

Microbial CH₄ uptake shows seasonal temperature dependence, with an optimum temperature in the range of 30-36°C. Czepiel et al. (1996b) found 36°C as the optimum temperature, while Whalen et al. (1990) found the optimum temperature ranged between 31 to 36°C. Boeckx and Van Cleemput (1996b); Bender and Conrad (1995) reported the range to be between 25-30°C. Kjeldsen et al (1997) stated that high CH₄ oxidation potentials of 150 – 250 µmoles CH₄/h×g of dry soil weight (0.4 – 0.7 µmoles/h ×g of dry soil weight) were observed in the laboratory at 25° C, and was 3-4 times slower at 10° C. It is obvious from these results that there is no significant variability in the range of the optimum temperature reported in the literature.

Stein (2001) reported that the temperature effect can be described by the Arrhenius equation. The Arrhenius equation is shown in equation (2-3):

$$k = A * \exp^{(-E_a / R * T)} \quad (2-3)$$

where, k is the specific rate constant (sec⁻¹), A is a constant with the same k units (sec⁻¹), E_a is the activation energy (kJ/mol), R is the universal gas constant (kJ/mol×K), and T is the temperature in degrees Kelvin.

Garzon (2003) stated that although the activation energy is poorly defined, the Arrhenius equation was widely used, not only to fit the empirical data, but to develop

models for the extrapolation of the results obtained for a given range of temperature to other temperatures.

Equation 2-3 is based on the concept that at higher temperatures the probability that two molecules will collide is higher. The higher collision rate results in a higher kinetic energy, which has an effect on the activation energy of the reaction.

There is also evidence that the sensitivity to temperature change may be muted when the soil is at optimum moisture content (Boeckx and Van Cleemput, 1996b). When discussing the effect of temperature on different CH₄ oxidation rates, it is important to remember that effective management of CH₄ in nature depends on considerations regarding how much CH₄ can be oxidized by the cover soils throughout the four seasons of the year.

2.4.2.3 Nutrients

In addition to a carbon source, bacteria need other elements as nutrients for their cellular metabolism. The effects of nutrients were studied by some researchers; these studies have shown that nitrate and lime (Hilger and Barlaz, 2002), sewage sludge (DeVisscher and Schippers, 2000), ground wheat and sugar beet leaf amendment (Boeckx et al., 1997) added to fresh soil enhanced CH₄ uptake. Lime tends to increase the soil pH from 6.3 to 7.4, which is close to optimum pH for the CH₄ oxidizers. Sewage sludge provides additional nutrients and additional microorganisms. A study conducted by Gebert et al. (2003) indicated that the activity of the dense methanotrophic population,

which had developed under conditions of high CH₄ fluxes, was limited by other factors such as nutrient availability. It is important to mention that usually in other types of engineered biological treatment systems and in order to enhance the microbial activities, nitrogen and phosphorous are usually added, in many forms, mainly ammonia and orthophosphate (Stein, 2001).

2.4.2.4 Soil Properties

Soil properties such as soil texture, particle size and soil gas concentrations affect CH₄ uptake. The more porous compost media has better gas penetration. Boeckx et al. (1997) reported that higher oxidation rates (61%) occurred in coarse sand than in fine sand or clay (40-41%), and in smaller sized particles diameters of mineral soils such as clay, silt and fine sands (0.5-2 mm). Finer particles result in decreased gas permeability, which inhibits O₂ penetration. CH₄ oxidation rates are sensitive to CH₄ concentration but not to O₂ concentration until the latter falls to about 3% by volume in gas concentration, which is the minimum O₂ concentration needed for the bacteria to grow. A porous medium allows O₂ penetration almost throughout the full cover depth to support the methane oxidizers.

Boeckx et al. (1997) reported that soil texture, land use and drying have an influence on CH₄ oxidizing capacity of cover soils. Coarse textured soils in this experiment showed higher oxidizing capacity (16.38 μg CH₄/m² ×h) than fine textured soils (9.3 μg CH₄/m²×h). These authors affirm that soil texture influences gas transport and therefore controls CH₄ emissions and oxidation rates. The influence of landuse on

CH₄ oxidation according to their experiment showed the following rates proportions: forests soil > arable land > grassland. The same study confirmed that the reduced CH₄ oxidation in some soils after drying could be related to a stratification and starvation of CH₄ oxidizing bacteria.

2.4.2.5 Oxygen Concentration

Oxygen concentration plays an important role in the control of CH₄ oxidation and the microbial ecology of methanotrophs (Wilshusen et al., 2004). Equations 2-1 and 2-2 show that proper oxygen concentrations are essential for CH₄ to be microbially oxidized. Czepiel et al. (1996b) have stated that CH₄ oxidation activities are slightly sensitive to O₂ gas concentrations above 3%, but these activities dropped off at O₂ gas concentrations of less than 3%.

2.4.2.6 Exopolymer Accumulations

Many bacteria including CH₄ oxidizers produce exopolymeric substances (EPS) that can serve as means of anchorage. EPS production may also offer resistance to desiccation and a mechanism to keep certain populations in close proximity. The nature and degree of polymer formation varies widely between both microbial species and environmental conditions, and EPS production was linked to both nutrient imbalance and oxygen deficiency. Hilger et al. (1999) conducted experiments to evaluate whether CH₄ oxidation in landfill cover soil promoted EPS production, examined the nature and quantity of EPS produced during CH₄ oxidation and evaluated whether this EPS could

cause short circuiting of the gas fed to soil columns. According to the experimental results, the phenomenon of EPS production in landfill gas-sparged laboratory soil columns filled with fresh landfill soil cores was confirmed. It was shown that a substantial quantity of highly viscous polymeric substance was produced in response to CH₄ exposure. Although the presence of viscous polymer was confirmed, there was no evidence that it caused short circuiting and reduced CH₄ retention times in the columns.

Wilshusen et al. (2003), as a result from their experiment to study the relation between the formation of EPS in compost and the effect of O₂ concentration, stated that at a higher O₂ concentration higher EPS formation is observed, while only limited EPS formation is observed when O₂ concentrations were lower.

2.5 MODELING OF BIOLOGICAL CH₄ OXIDATION

Past modeling efforts for the biological, biochemical, physical and hydrological processes in landfills have been influential to a certain degree in highlighting the issues that need to be addressed, if the landfill environment is to be modeled successfully. In general, some mathematical models have focused on the liquid phase to predict the quality and quantity of leachate generated in landfill sites and attempted to capture the linkages between waste degradation, and gas and liquid transport processes. Other models described the generation and transport of gases through the landfills. The general approach for these models is to treat the landfill as an anaerobic reactor, and use basic

principals governing microbiological processes to develop a simplified model of time dependant anaerobic waste degradation, and include a part in the model for the analysis of gas transport and biological reactions. Zacharof and Butler (2003) have developed a model representing stochastic modeling of landfill leachate and biogas production, while White et al. (2003) developed a model for the biochemical degradation of solid waste in landfills. Salvage and Yeh (1997) presented a numerical model of kinetic and equilibrium microbiological and geochemical reactions. El-Fadel et al. (1995) developed a numerical model for the generation and transport of gas and heat in landfills. In this model, mass balance coupled with the Monod Model for microbial growth was used to relate the various components of the modeled ecosystem. The model approached gas transport based on describing the time development of the pressure and gas concentration profiles, and the time variations of the total gas production from the landfill cell. The gas transport module in porous media was presented as follows:

$$\phi \frac{\partial C_i}{\partial t} = -\frac{\partial(U_k C_i)}{\partial X_k} + \frac{\partial}{\partial X_k} \left(D_{ik} \frac{\partial C_i}{\partial X_j} \right) + G_i \quad (2-4)$$

where: ϕ is Porosity, C_i is the concentration of the i^{th} component of the gas mixture (kg/m^3), U_k is the advective velocity in the k^{th} direction (m/day), D_{ik} is the diffusion coefficient of gas i in the k^{th} direction (m^2/day). X_k is the k^{th} direction (m), and G_i is the generation or reduction of the i^{th} component of the gas (kg/day).

This model incorporated the theory and the derivation of the equations of gas flow in porous media. The viscosity of the gas mixture in this model was expressed as a

function of the viscosities of the individual gases, the diffusion coefficient of each gas in the three-gas mixture was estimated as a function of the diffusion coefficient of the individual gases in a binary mixture with each of the other two gases.

Czepiel et al. (1996b) developed a model to quantify the effect of oxidation rate on landfill CH₄ emissions. The model assumed the zone of maximum CH₄ oxidation is constant, and V_{\max} is proportional to concentration of CH₄. Seasonal variability was calculated using BROOK90 to determine the environmental factors affecting oxidation in the soil.

In general, some modeling efforts reported in the literature have resulted in complex model formulation requiring unrealistic amounts of data input; others used simplified formulations to eventually determine that the key processes in the system are not well presented.

CH₄ oxidation in landfill cover soil was modeled by transport-reactive numerical and simulation models. Modeling CH₄ oxidation processes can aid in developing the design of CH₄ oxidative soil cover systems, by reducing the number of laboratory experiments required to select the optimal soil type and by establishing the thickness of landfill cover. These models can impart quantitative perceptions of biological and physical processes, with reference to CH₄ transport, oxidation and reaction rates. In this review, some of the previous modeling efforts are illustrated below.

- De Visscher and Cleemput (2003) have presented a simulation model for gas diffusion and CH₄ oxidation in landfill cover soils. This model incorporated Stefan-Maxwell diffusion, CH₄ oxidation and methanotrophic growth. The model was dynamic in order to allow predictions of the methanotrophic activity profile. De Visscher and Cleemput have emphasized the difference between the steady-state solution of a dynamic model and a static model, as dynamic models produce a methanotrophic activity profile that depends on the landfill gas flux and other factors. According to De Visscher and Cleemput model (2003), the difference between the steady-state solution of a dynamic model and static model is that the dynamic model yields a methanotrophic activity profile that depends on the landfill gas flux and other factors, whereas the static model yields a constant methanotrophic activity profile. The model was based on transient mass balance across an infinitesimal soil layer, which led to the following equation:

$$\varepsilon \frac{\partial y_i}{\partial t} \frac{P}{RT} = \rho_{DB} r_i - \frac{\partial N_i}{\partial z} \quad (2-5)$$

where, ε the air filled pore space ($\text{m}^3_{\text{gas}} / \text{m}^3_{\text{soil}}$), ρ_{DB} the dry bulk density of the soil ($\text{kg}_{\text{soil dry weight}} / \text{m}^3_{\text{soil}}$), r_i the reaction rate of compound i ($\text{mol} / \text{kg}_{\text{soil dry weight}} \times \text{s}$).

For the multicomponent gas mixture the Stefan-Maxwell equation was used, as follows:

$$-\frac{P}{RT} \frac{\partial y_i}{\partial z} = \sum_{j=1, j \neq i}^n \frac{N_j y_i - N_i y_j}{D_{ij}} \quad (2-6)$$

where, y_i the mole fraction of component i , P the absolute pressure (Pa), R the universal gas constant (8.31 J/mol×K), and T the absolute temperature (degrees K), D_{ij} the diffusion coefficient of component i in component j , N_i the flux of component i using a fixed frame of reference, z is the depth.

In this model, the Stefan-Maxwell equations were applied to a soil matrix, and the diffusion coefficient used was $D_{\text{soil},ij}$ ($\text{m}^3_{\text{gas}}/\text{m}_{\text{soil}} \times \text{s}$) which is the binary diffusion coefficient of a mixture of gases i and j in a soil matrix. This binary diffusion coefficient was calculated from the molecular diffusion coefficient in the free gas ($\text{m}^2_{\text{gas}}/\text{s}$) multiplied by a factor incorporating the effects of limiting pore space, constrictivity and tortuosity ($\text{m}_{\text{gas}}/\text{m}_{\text{soil}}$).

The biological reaction rate was described by Michaelis-Menton model.

According to De Visscher and Cleemput, there was an excellent agreement between the model and previously reported experimental data, but the model was not validated with field data. The sensitivity analysis of the model showed that the model was mostly sensitive to $V_{\text{max,max}}$ (which is the maximum CH_4 reaction rate that can be obtained), therefore, the researchers have concluded that future work should investigate the factors that determine the maximum methanotrophic activity that can be reached in the soil.

- Stein et al. (2001) has developed a numerical model for biological oxidation and migration of CH₄ in soils. The model indicated that the oxidative reactions by methanotrophs rule the stoichiometry of biological CH₄ oxidation. A Monod equation was used to model the biological oxidation rate of methane. In the gas transport phase, the model employed the theory of physical transport of gases by diffusion and advection. The general flux equation for gas components was used to describe the gas transport, as follows:

$$J_i = -D_i \Delta C_i + vC_i \quad (2-7)$$

where, J_i the molar flux of gas component i , D_i the diffusion coefficient of component i in soil, ΔC_i the concentration gradient, v the flow velocity of the gas mixture through the soil, C_i the concentration of component i .

The final model equation was:

$$\phi \frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} - \frac{\partial(vC_i)}{\partial x} \pm R_i \quad (2-8)$$

where, ϕ the soil porosity, C_i the concentration of component i , v the flow velocity of gas mixture through soil, D the diffusion coefficient of gas mixture, R the rate of biological reaction of component i .

De Visscher and Cleemput (2003) compared their simulation model to this model developed by Stein (2001), and stated that the latter model incorporated flow and Fickian diffusion with concentration- dependent diffusion coefficient. This model

according to (De Visscher and Cleemput) was dynamic in gas concentrations but static in the methanotrophic activity. According to De Visscher and Cleemput model, the difference between the steady-state solution of a dynamic model and static model is that the dynamic model yields a methanotrophic activity profile that depends on the landfill gas flux and other factors, whereas the static model yields a constant methanotrophic activity profile.

- Bogner et al. (1997) developed a three dimensional finite difference model for landfill gas transport and oxidation of CH_4 in landfill cover soils. This model simulated mass movement of CH_4 in terms of molecule collisions with soil matrices. The soil matrix was modeled in each node. The model calculated the probability of collisions between gas molecules and solid sphere. The transport of CH_4 was described as pressure driven gas flow. De Visscher and Cleemput (2003) stated that this model is attractive from a computational point of view, but assumptions are unconventional.

The models listed above are some of the models in this field, and they simulate different parameters as bases for the physical transport of gas and CH_4 oxidation processes. Many models had limitations and many of them concluded with a discussion that further research is needed. There is definitely a need to develop more comprehensive landfill gas transport models that realistically simulate the landfill cover system and can be validated with field data successfully.

2.6 SUMMARY

LFG can escape from a landfill site through the soil surrounding the site and through the soil cover on the surface of a landfill. Methanotrophs are the bacteria that can oxidize CH_4 into CO_2 and water. They have been found to be environmentally abundant and are present in soils where CH_4 can be found, such as landfill cover soils. The potential to mitigate LFG emissions by methanotrophs in landfill cover soils has sparked intense interest and is currently considered as promising technology. Due to the interest in the potential benefits of CH_4 oxidation in landfill cover soils, research studies have been carried out to understand the preferential parameters for this process, in order to optimize CH_4 oxidation rates and provide the most suitable environment for the methanotrophic bacteria to thrive.

Although landfill cover soils have demonstrated the higher rates of CH_4 oxidation than any natural soil, the rates of CH_4 oxidation in landfill cover soils was found to vary from one research study to another. In laboratory studies, Czepiel et al. (1996a) reported a range from 10% to 20% oxidation rate of CH_4 migrating through landfill cover soil, while others reported higher rates. Whalen et al. (1996) reported a range from 19% to 69% CH_4 oxidation rates. De Visscher and Schippers (2000) reported maximum a oxidation rate of 87%. Field studies have shown that there are wide variations in CH_4 consumption rates both within and between landfill sites, and the variability has been attributed to seasonal climate change, physical heterogeneity in the cover and other environmental parameters, such as nutrient availability.

Field and laboratory studies also have been used to investigate the role of different parameters affecting the CH₄ oxidation processes. The effect of temperature is very well established and there are many studies indicating that the optimum temperature for the CH₄ oxidation process is between 20° C – 35° C. Moisture content is an important parameter affecting the oxidation process. Contradicting values of optimum moisture content have been reported in the literature, as mentioned in section (2.4.2.1) from this chapter. The addition of nutrients has been found to enhance the CH₄ oxidation rates. Nutrients added in some previous experiments were phosphate, lime, sewage sludge and ammonium. There is not much information about adding soil fertilizer as the nutrient agent. Although it will be more practical in field application to add the fertilizer, it was found to increase the oxidation rate and enhance the process.

It is noted that there is not much information available in the literature regarding the minimum thickness of the landfill cover soil, and the effect of the amount of soil on oxidation rates. This information is important and can reflect on the total cost of applying the landfill cover soil and the maintenance of this soil after that.

There is still a need to develop a model and/or models that can realistically simulate the landfill cover soil system and the processes that occur in this system. A comprehensive model can provide information on the CH₄ transport and oxidation processes under different environmental conditions, at much less time and cost, when the physical and biochemical processes are defined and well evaluated.

CHAPTER 3 – METHODS AND MATERIALS

To accomplish the objectives outlined in the first chapter of this thesis, and to analyze the interaction between different parameters (moisture content, nutrient additions and thickness of soil layer) affecting CH₄ oxidation, laboratory experiments were designed for this study, using batch reactors.

3.1 EXPERIMENTAL DESIGN

There are two aspects to any experimental study: the design of the experiment and the statistical analysis of the data. Experimental design is the process of planning an experiment so that data to be analyzed by statistical methods will be collected, resulting in valid and objective conclusions.

Factorial design was defined by Montgomery (1997) as an experimental strategy in which factors are varied *together* instead of one at a time. Factorial design is necessary when interaction may be present in order to avoid misleading conclusions. The guidelines for designing the experiment were:

- 1- Selection of the variables.
- 2- Choice of factors, levels, and ranges.
- 3- Statistical analysis of the data.

This experiment was set up to investigate and explore the interaction effects between three factors, namely moisture content (MC), nutrient addition and soil layer thickness. The experimental runs were designed as a three-factor two-level factorial (2^3). The result is eight combinations of these three factors across the two levels of each, and these eight combinations can be represented geometrically as the corners of a cube, as indicated in figure 3-1.

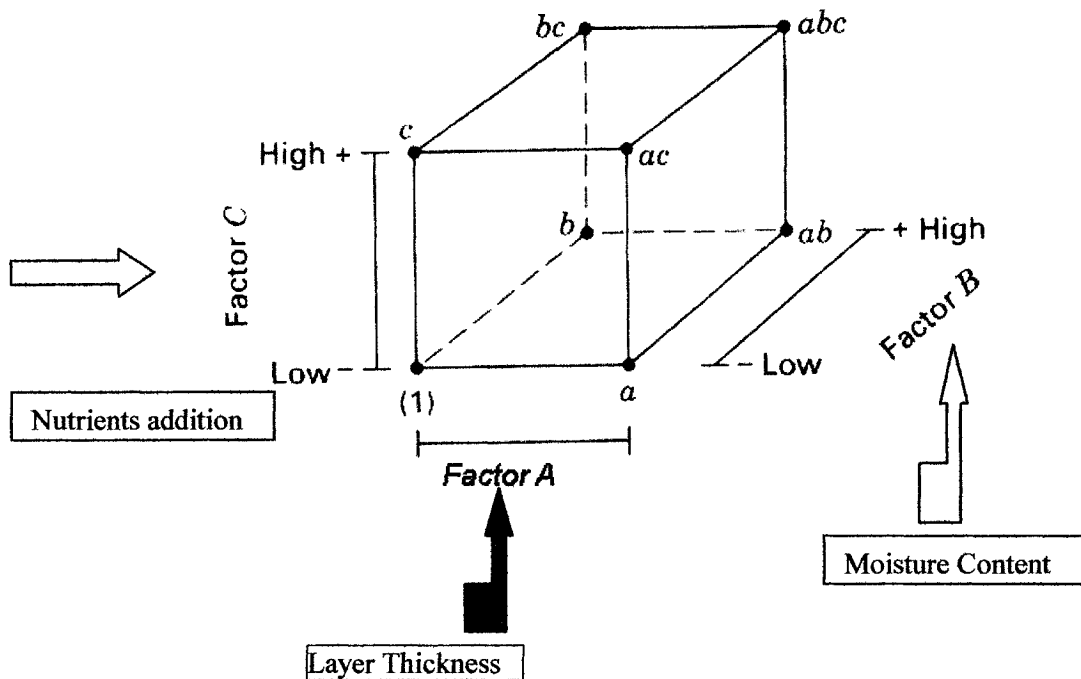


Figure 3-1 The 2^3 Factorial Design (Montgomery, 1997)

All three parameters chosen were tested at two levels, low and high. The moisture content was studied at the levels of *15% MC* and *30% MC*. The nutrients were studied also at two levels: low- *no nutrients added* and high- *added nutrients*. The nutrients source used was all purpose fertilizer, named *Plant-Prod 20-20-20*. The amounts of

added nutrients as (*high*) level were 1.5 g of fertilizer/kg of soil. For the last factor scrutinized, the soil layer thicknesses were: low- 150 mm thickness and high- 200 mm. The experimental variables and their layout are shown in Table 3-1 below. All experiments were carried out in duplicate, namely A and B.

Table 3-1 Experimental Variables Layout

Run #	Duplicate	Layer Thickness (mm)	Moisture Content (%)	Nutrients
1	A	150	15%	No nutrients
	B	150	15%	No nutrients
2	A	200	15%	No nutrients
	B	200	15%	No nutrients
3	A	150	30%	No nutrients
	B	150	30%	No nutrients
4	A	200	30%	No nutrients
	B	200	30%	No nutrients
5	A	175	22.5%	Medium Nutrients
	B	175	22.5%	Medium Nutrients
6	A	150	15%	Nutrients
	B	150	15%	Nutrients
7	A	200	15%	Nutrients
	B	200	15%	Nutrients
8	A	150	30%	Nutrients
	B	150	30%	Nutrients
9	A	200	30%	Nutrients
	B	200	30%	Nutrients

In total nine experimental sets were tested. The middle point experiment (experiment No. 5 – Table 3.1) was run with medium (22.5%) moisture content, medium layer thickness (175 mm) and with medium amount of nutrients (0.75 g of fertilizer/kg of soil) to fulfill the requirements of factorial design.

For each experimental set, there was a control reactor. The controls were filled with Ottawa sand, and were run in parallel at different experimental levels of varying moisture content, nutrients addition and soil layer thickness.

3.2 EXPERIMENTAL SETUP

Batch reactors were used for this experimental work. Each reactor was made of plexiglas and the dimensions were 320 mm in length and 100 mm in diameter. Figure 3-2 shows a schematic diagram for the reactor used in the experiment.

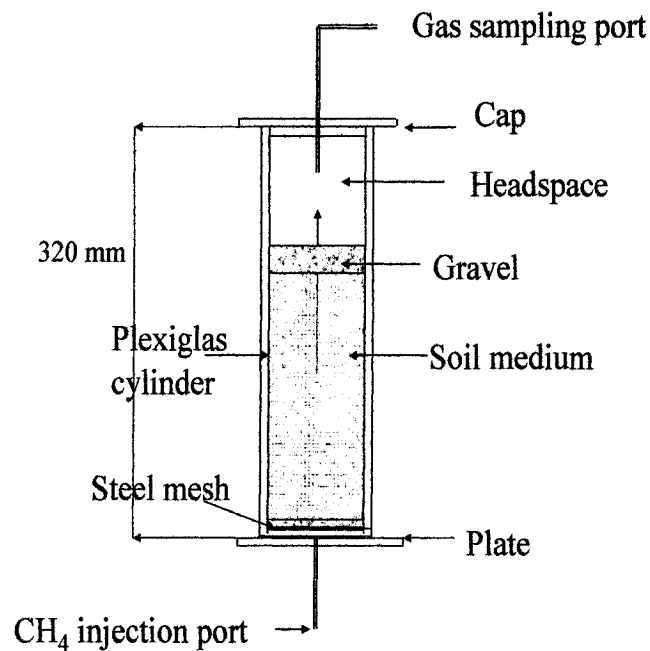


Figure 3-2 Schematic of the Experimental Set-up

The reactor parts were as follows:

- Reactor inlet for gas injection port.
- Bottom plate made of plexiglas and fitted tightly with rubber 100 mm O-rings. Different sealants were used to prevent any possible leaks.
- Steel mesh was placed at the base of the reactor to support the soil and gravel.
- Thin layer of gravel around 20 mm, was placed at the bottom of the reactor and above the steel mesh, to distribute the gas from the inlet into the soil matrix.
- According to the experimental design and as indicated in Table 3-1, 150, 175 or 200 mm of landfill cover soil or sand layer was placed above the lower layer of gravel.
- Another layer of gravel was placed above the soil. The objective of this layer was to have an equal headspace gas volume above the soil in every reactor. The thickness of the top gravel layer varied to maintain constant headspace gas volume. The headspace gas volume was 785 cm^3 . The volume of soil and gravel was 1727 cm^3 . Total volume of the reactor equal to 2512 cm^3 .
- Each reactor was closed with plexiglas cap, fitted tightly with rubber 100 mm diameter O- rings. The bottom and top end caps were fastened tightly to the reactor with threaded rods. These rods ran through the length of the reactor and were tightened carefully. Different sealants were used to prevent any possible leaks.
- A gas sampling port was connected to each reactor's outlet.

3.3 EXPERIMENTAL METHODS

At the beginning of each experimental set, the soil or sand was packed in each batch reactor after flushing it with air for 4 minutes at a rate of 70 ml/min. Then, CH₄ gas was injected in each batch reactor through the inlet port at a rate of 70 ml/min for 2 min, and the reactor's inlet was tightly closed. The total amount of CH₄ gas injected was 140 ml; this amount of injected CH₄ provided a mixing ratio in the headspace of around 18% CH₄ of the total headspace gas volume. Inlet CH₄ flow was controlled with flow meters. The pressure inside each reactor was almost equal to atmospheric pressure.

The concentration of headspace gas was monitored by taking samples from the sampling port connected to the outlet, using a gas tight 1.0 cc syringe. A volume of 0.5cc of the collected sample was injected in the Gas Chromatograph, and analyzed. The concentration of gases in the headspace was monitored over time.

The end of each experiment was determined when the concentration of CH₄ in the reactor's headspace did not change significantly over time.

The O₂ concentrations in the headspace were measured using Alltech GC – TCD model at the beginning and the end of each experiment, to determine the aerobic conditions.

Soil and sand initial moisture contents (%w/w basis) were tested, and determined gravimetrically by oven drying samples at 105°C for 24 hours. Initial moisture content was expressed as the mass ratio of water to dry soil or sand.

The moisture of each soil sample was adjusted from the initial moisture content according to the experimental design before each experiment. Prior to placing each soil sample in the reactor, the moisture content was tested again to insure the right required percentage (%by weight).

After the end of each experiment, moisture content was tested to check if there was change in the soil moisture content resulting from the oxidation process.

Soil porosity (field value) was determined from the laboratory tested bulk density (Compaction was done according to ASTM D 698-64T, in a 1/30 ft³ mold, 3 layers, 25 blows per layer) and particle density. Field soil porosity value is less than the values for the soil during the experiments, due to the compaction inside the plexiglas reactors and therefore the bulk density of soil samples. The differences between the field and the experiments values of the soil bulk density and porosity are within an acceptable range and in agreement with the literature. During the experiments it was important to keep values of soil porosity consistent for all the experimental runs, using the laboratory bulk density to estimate the soil porosity for each experimental run. Bulk Density and soil porosity calculations for all the experiments are presented in *Appendix A*.

All the experiments were conducted in the laboratory at the temperature of 22° C ± 2° C.

Figure 3-3 shows the laboratory experimental set up simulating the landfill cover soil.

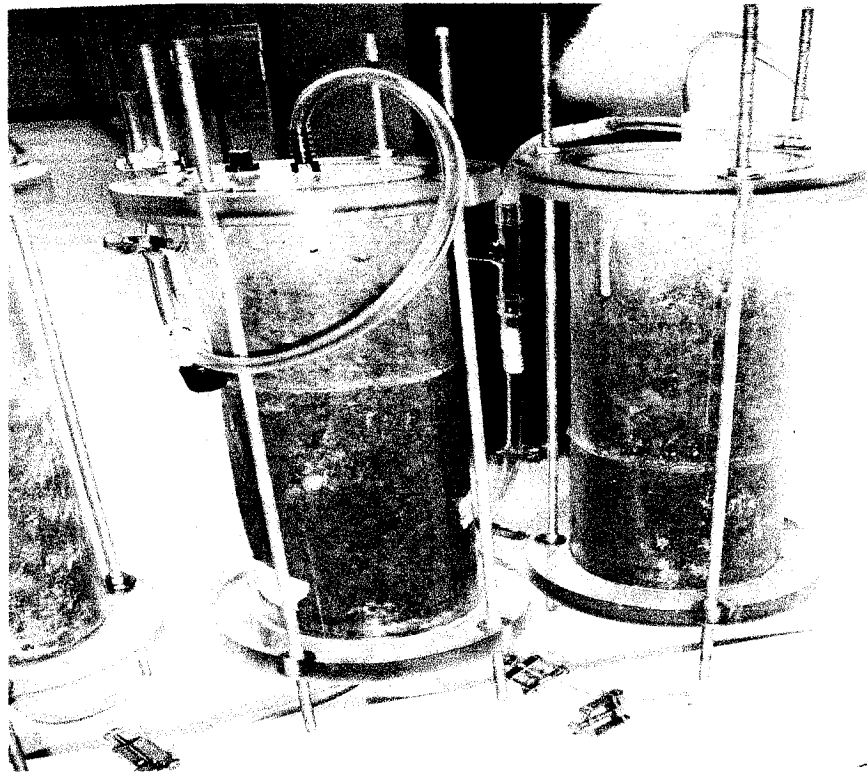


Figure 3-3 Landfill Cover Soil Batch Reactor Laboratory Experiment.

Three months of pre-experimental trials were conducted to optimize the operating parameters and ensure quality control of the experiments. One of the pre-experimental trials was conducted with a reactor without soil; this was used to check the CH_4 mass balance in the system. Another reactor, filled with soil, was run without injecting the CH_4 , this was to evaluate if there was any CH_4 produced anaerobically from the degradation of organics in the soil itself.

It is very important to emphasize the fact that after injecting the required amount of CH_4 in the reactor, the inlet was closed and never opened again throughout the entire experimental period. The reactor was left for one day to allow the gas to diffuse through the soil. From the pre-experimental trials, it was noticed that the highest GC reading was

after one day from injecting the CH₄ into the reactor. After this point, headspace gas samples were collected regularly from the sampling port and analyzed with the gas chromatograph. To evaluate the experiments, changes of CH₄ and CO₂ concentrations in the reactor headspace were monitored.

3.4 MATERIALS

SOIL

The soil used in this experiment was collected from the top (250 mm) of the final cover soil at Trail Road Landfill in Ottawa, Canada. This soil was exposed to CH₄, since it was taken from an area in the landfill cover located near the CH₄ vents. These conditions presumably should contribute to a large number of methanotrophs being present in the collected soil sample, and therefore serve as seed organisms for the proposed batch experiments.

The soil sample was collected from the landfill site and transported immediately to the laboratory, where it was stored in the cold room at a temperature of 3° C until needed for the experiments.

The most important characteristics of the soil are presented in table 3-2.

Table 3-2 Characteristics of Trail Road landfill cover soil and Ottawa sand

	Trail Road Landfill Cover Soil	Ottawa Sand
Moisture Content	30 %	1 %
Organic Content	3.9 %	0
pH	6.37	7.85
Specific Gravity	2710 kg/m ³	2670 kg/m ³
Bulk Density	1126 kg/m ³	1603 kg/m ³
Porosity	58.45	39.97
Hydraulic Conductivity	6 * 10 ⁻⁸ m/sec	8.63 * 10 ⁻⁶ m/sec
Textural Classification	25% Clay – 75% Silt Loam	75% retained on 20 mesh – Medium Sand

SAND

Ottawa sand was chosen to be used as the control. The sand was supplied by Unimin Canada, LTD as pure silica, free of organic matter including any bacterial cells. Therefore, this sand was assumed to be free of methanotrophic bacteria. The characteristics of dense Ottawa sand are presented also in Table 3-2.

GAS

Pure CH₄ gas (>=99% purity) and pure air were obtained from commercial supplier –PraxAir-.

NUTRIENTS

The source of nutrients used was soil fertilizer called *Plant-Prod 20-20-20, All Purpose Fertilizer*. The amounts of fertilizer used in the experiments were: (1.5 g of fertilizer/ kg of soil), this amount of added fertilizer gave the ratio of 0.3 g N₂: 0.13 g P: 0.249 g K for each kilogram of soil. The C-N-P ratio (based on CH₄-C only) after adding nutrients to the soil was 100: 4.8: 2, this is a good C-N-P ratio for aerobic bacteria. Table 3-3 shows the chemical composition of the fertilizer used.

Table 3-3 Fertilizer Composition

Component	Symbol	Percentage
Total Nitrogen	(N ₂)	20% (5.9% Nitrate Nitrogen, 3.85% Ammoniacal Nitrogen, 10.25% Urea Nitrogen)
Available Phosphoric Acid	(P ₂ O ₅)	20% (8.7% is soluble Phosphorous P)
Soluble Potash	(K ₂ O)	20%(16.6% is soluble Potassium K)
Boron	(B)	0.02%
Chelated Copper (actual)	(Cu)	0.05%
Chelated Iron (actual)	(Fe)	0.10%
Chelated Manganese	(Mn)	0.05%
Molybdenum (actual)	(Mo)	0.0005%
Chelated zinc (actual)	(Zn)	0.05%
EDTA (Ethylene Diamine Tetraacetate) (Chelating Agent)		1.00%

3.5 ANALYTICAL PROCEDURE AND INSTRUMENTS

3.5.1 ANALYSIS OF THE HEADSPACE GAS

The gas samples from the reactor's headspace were analyzed for CH₄, CO₂ and N₂ using a Hewlett Packard Gas Chromatograph (HP 5710 A), FID model 1976. The operating parameters of this HP gas chromatograph are as follows:

- Meter Selector = FID Detector
- Detector temperature = 150° C
- Injection port temperature = 100° C
- Packing = PoraPak T, 50/80
- Column = 10 ft × 0.25" O.D.

All peaks were quantified using LabView integration software on the laboratory computer.

The headspace gas samples were also analyzed for O₂ using an Alltech Gas Chromatograph, TCD model 1989. The operating parameters of this gas chromatograph are:

- Meter Selector = TCD Detector
- Detector temperature = 150° C
- Injection port temperature = 80° C
- Packing = Molecular Sieve 5 A, 80/100
- Column = 6 ft × 1/8" O.D., SS

3.5.2 SOIL AND SAND ANALYSES

MOISTURE CONTENT

Moisture content was determined by oven-drying soil at 105° C for 24 hours and expressed as the mass ratio of water to dry soil. The procedure followed to determine the moisture content was ASTM D2974-87.

ORGANIC CONTENT

The organic content was also tested as per ASTM D 2974-87, by placing the oven-dried test specimen from the moisture determination, in a muffle furnace, and held until the specimen was completely ashed, and then the loss of weight on ignition at 550±50° C of the oven dried samples was determined.

pH

pH of the soil or sand was determined by preparing a known soil or sand – water mixture ratio (1:2.5), and testing the mixture using a digital pH meter, 530 pH meter by Corning Pinnacle.

TEXTURE CLASSIFICATIONS

Trail Road landfill cover soil and Ottawa sand textural classification were determined by grain size sieve analyses –Hydrometer method, ASTM D421 and D422, AASHTO T 87 and T-88 - and classified in accordance with (USDA) textural classes.

Soil structure was determined by the arrangement of soil particles relative to each other. The dispersing agent added was Calgon.

BULK DENSITY

Field bulk density of the soil and the bulk density of the sand were determined by weighting soil or sand- filled steel cylinders and subtracting the cylinder weight, then dividing by cylinder volume (Das, 2002).

PERMEABILITY AND HYDRAULIC CONDUCTIVITY

The permeability test was conducted using the falling head method (Das, 2002). The following empirical relation to determine the hydraulic conductivity was used,

$$K = \frac{Q * L}{A * h * t} \quad (3-1)$$

where, Q the volume of water collected (m^3), A the area of cross section of the soil specimen (m^2), t the duration of water collection (sec), L the distance between two points or the length of flow over which the loss of head occurred (m), h the total head at the beginning of the experiment (m).

POROSITY

Soil and sand porosity was determined by applying the following equation (Ley, 2004):

$$Porosity(\%) = \left(1 - \frac{BulkDensity}{ParticleDensity}\right) * 100 \quad (3-2)$$

CHAPTER 4 – CH₄ OXIDATION RESULTS AND DISCUSSION

The results of CH₄ oxidation batch experiments described in *Chapter 3* are reported and discussed in this chapter. The CH₄ oxidation kinetics constants were determined. Finally, a CH₄ oxidation statistical model was developed and used to describe the CH₄ oxidation efficiency in the landfill cover soil.

4.1 CH₄ OXIDATION EFFICIENCY IN THE LANDFILL COVER SOIL

The headspace gas in each batch reactor was monitored and the results were used to calculate CH₄ draw-down as well as the increase in CO₂ production for the same period of time.

Figure 4-1 shows the decrease in CH₄ concentration (%v/v) and the increase in CO₂ concentration (%v/v) with time in the headspace gas for the nine experimental runs tested in this study using Trail Road landfill cover soil. Data represent the average reading of the duplicate reactors.

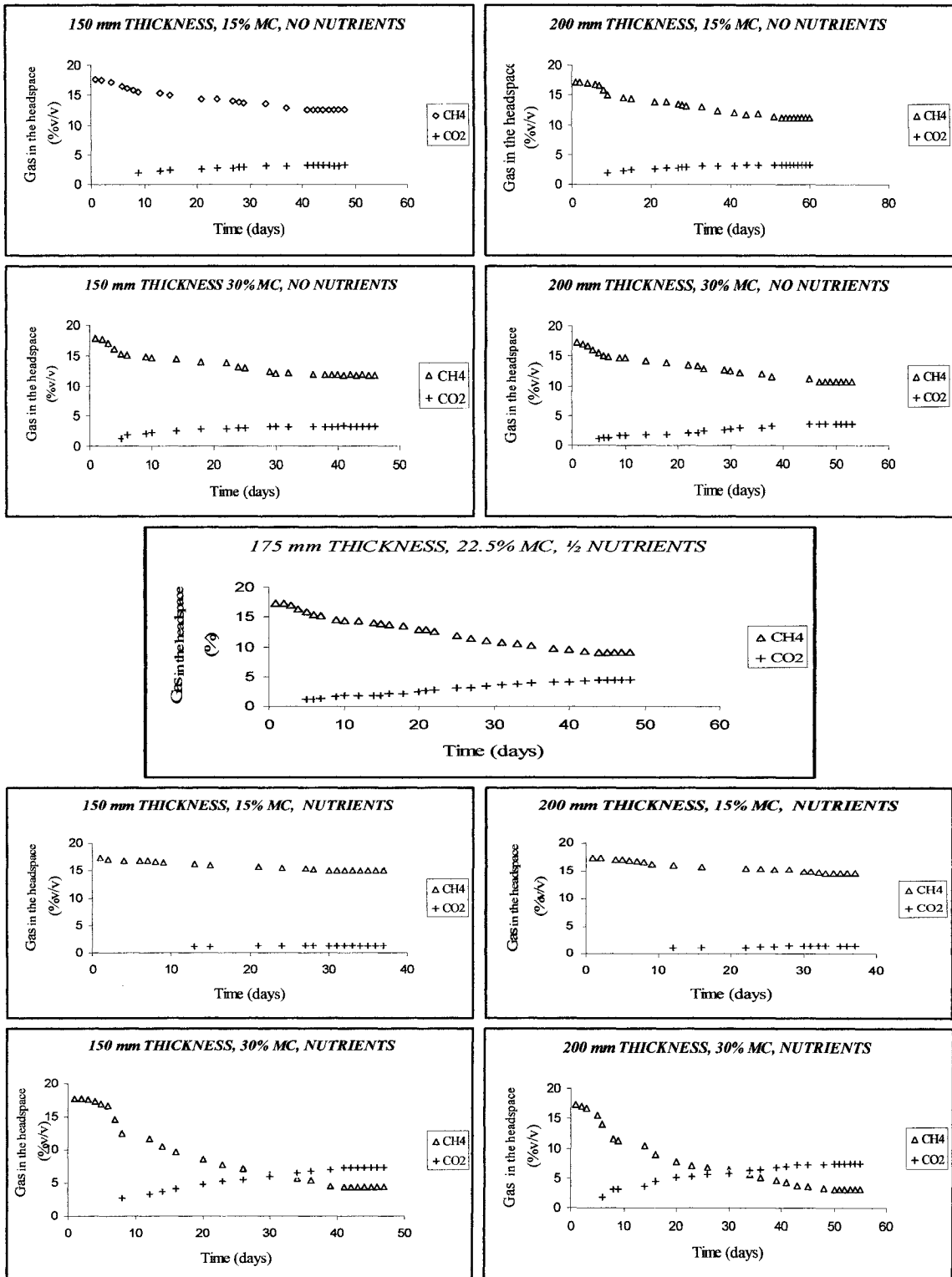


Figure 4-1 Decrease in CH₄ (%v/v) and Increase in CO₂ (%v/v) with Time for the Experimental Runs

Results plotted in Figure 4-1 illustrate that the largest CH₄ consumption occurred in experimental runs 8 and 9, where nutrients were added to 150 mm and 200 mm thickness landfill cover soil layers that contained 30% moisture, respectively. In experimental run 9, the CH₄ concentration (%v/v) in the headspace gas dropped from about 17% to about 3%. In comparison with experimental run 4, conducted under the same operational variables but without adding additional nutrients, the CH₄ concentration (%v/v) in the headspace gas dropped from around 17% to 11%.

The increase in CO₂ concentration (%v/v) in the headspace gas as a result of CH₄ oxidation process was gradual over time. The maximum increase observed in CO₂ concentration (%v/v) was about 7.5% of the headspace gas for experimental runs nos. 8 and 9 where nutrients were added to the 150 mm and 200 mm soil layer thicknesses with 30% moisture content. The CO₂ concentration monitored in experimental runs nos. 6 and 7 was about 1.5% of the headspace gas, where nutrients were added to the soil contained 15% moisture and for the two layer thicknesses. In these two experiments CH₄ consumptions were the least monitored. CH₄ concentration in the headspace dropped from 17.4% to 14.7% for 200 mm soil layer thickness, and from 17.3% to 15.1% for 150 mm layer thickness.

Details of the headspace gas change with time are provided in Table 4-1 for experimental run no. (1), as an example. Data are the average reading of the duplicate reactors. Details for all other experimental runs including detailed calculations are provided in *Appendix A*. Mass balances were conducted for all experiments on the rates

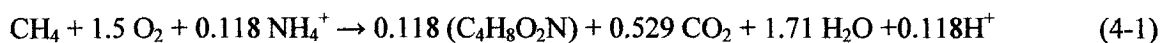
of substrate removal with time, assuming that the headspace gas is representative of the gas space.

Table 4-1 Gases in the Reactor Headspace, with Time, for Experimental Run No. 1 (15% MC, 150 mm Layer Thickness and No Nutrients Added).

No. of Days	CH ₄ Concentration in the headspace (1) (%v/v)	CO ₂ Concentration in the headspace (2) (%v/v)	CH ₄ Oxidized (3) (%)	CH ₄ in the Headspace (4) (μmoles/L)	Substrate (5) (μmoles)	Reaction Rate (6) (μmoles/d× kg of dry.s.w)
1	17.7		0.0	7311	0	0
2	17.6		0.7	7260	40	48
4	17.1		3.1	7086	177	70
6	16.6		6.4	6844	367	87
7	16.2		8.3	6702	478	95
8	15.8		10.5	6543	604	102
9	15.5	1.3	12.6	6393	721	107
13	15.3	1.4	13.4	6331	770	76
15	15.0	1.6	15.0	6215	861	73
21	14.4	1.9	18.4	5969	1054	63
24	14.4	2.0	18.6	5933	1082	56
27	14.1	2.1	20.1	5840	1155	53
28	13.9	2.1	21.7	5725	1245	55
29	13.7	2.4	22.8	5644	1309	55
33	13.5	2.7	23.5	5591	1350	50
37	12.9	2.9	27.0	5338	1549	51
41	12.6	2.9	28.7	5213	1647	49
42	12.6	2.9	28.7	5215	1646	48
43	12.6	2.9	28.8	5209	1651	47
44	12.6	2.9	28.7	5215	1646	45
45	12.6	2.9	28.7	5211	1649	44
46	12.6	2.9	28.7	5213	1647	43
47	12.6	2.9	28.7	5213	1647	42
48	12.6	2.9	28.7	5215	1646	42

The data shown in Table 4-1 were used to calculate CH₄ concentration, the maximum CH₄ oxidation efficiency, substrate and the reaction rate, and will be discussed in the next sections.

The decrease in the CH₄ concentration (%v/v) and the increase in the CO₂ concentration (%v/v) in the headspace gas were clear indications that there was biological activity taking place and varied in efficiency under different operating parameters. As mentioned in *Chapter 2*, there is evidence that most of the biological oxidation of CH₄ is accomplished by methanotrophs. Borjesson et al. (1998) had reported that methanotrophic bacteria appear to oxidize most efficiently when they occur in consortium with other bacteria, but the former may constitute 90% of the microbial population. Hilger and Humer (2003) reported that methanotrophs consume CH₄ and oxidize it to CO₂ and water for energy yield, while another fraction is incorporated into biomass (C₄H₈O₂N) according to the following equation:



Methanotrophs are found in different types of soils and in a variety of ecosystems. In these experiments, the presence of methanotrophic bacteria can be traced to the source of the soil, which was taken from an existing and operating landfill cover soil. Therefore, the CH₄ reductions in the headspace gas, as seen in Figure 4-1, confirm the biological reaction in the landfill cover soil described in Equation 4-1. Changing levels of soil moisture content and layers thickness with and without nutrient additions, showed different percentages of CH₄ reductions in the headspace gas, which indicate that these

parameters affected the bacterial growth and consequently bacterial activities, which led to different levels of CH₄ oxidation efficiencies.

As mentioned in *Chapter 3*, and during the pre-experimental trials, a batch reactor was filled with landfill cover soil and was operated without injecting CH₄. This trial was performed to validate whether there was any CH₄ produced anaerobically from the degradation of the organics in the soil. In addition, and despite that the reactor was monitored for 45 days, there was no CH₄ generation detected in the reactor headspace. This indicates that there was no methanogenesis activity taking place and, therefore, no biological production of CH₄ from the soil itself took place.

The concentration of O₂ plays an important role in the CH₄ oxidation process. Equation 4-1 shows that proper O₂ concentrations are essential for the CH₄ to be microbially oxidized (each mole of CH₄ needs 1.5 moles of O₂) and the lack of oxygen can limit CH₄ degradation. The O₂ concentration (%v/v) in the headspace gas was tested at the beginning and at the end of each experiment using the Gas Chromatograph, to verify if there was an O₂ limitation affecting the oxidation process. At the beginning of the experiments, the O₂ concentration in the headspace gas varied between 19.5 %v/v and 20.5 %v/v of the air composition, which was equal to 18% of the headspace gas after injecting the CH₄. At the end of the experiments, the O₂ concentration varied between 5.6 %v/v and 13.7 %v/v of the headspace gas volume. Except for experimental runs 8 and 9, where the soil in these two experiments contained nutrients and 30% moisture, the concentration of O₂ in the headspace gas was 2.9 and 2.6 %v/v, respectively. It is

possible that O₂ availability in these two experiments (8 and 9) was the limiting factor for CH₄ biological oxidation process, while sufficient nutrients availability was the limiting factor in experiments 1 through 4. Czepiel et al. (1996b) have stated that CH₄ biological oxidation process is insensitive to O₂ concentrations if this concentration is above 3%, but these activities dropped significantly at O₂ concentration less than 3%. In this study, the O₂ concentration was just below 3% only for experimental runs 8 and 9, where the observed CH₄ concentrations in the headspace gas dropped from 18% to about 4% for experimental run 8 and from about 17.3% to about 3% for experimental run 9.

The Ottawa sand, mainly industrial quartz and free from any organic matters, was used in the experiments as the control. The Ottawa sand was tested in the laboratory according to the analytical procedure in Section 3.5.2, and no organic matter was detected, thus confirming that the sand did not contain any bacterial cells nor seeds, including methanotrophs. The objective of running the controls under the same environmental operating parameters as the experimental runs for the landfill cover soil was to confirm the role of methanotrophic bacteria in the oxidation process. The CH₄ concentration changes in the headspace gas of all reactors filled with sand was monitored over a period of 40 to 50 days. The maximum changes calculated between the initial and final CH₄ concentration values divided by the initial concentration in these reactors varied in the range of 4% to 5%. It was assumed that this range is within the acceptable error for any blank or control experiments (5%). Also, there was no increase in CO₂ in the headspace gas in any of the control reactors. These results further support that there was no biological oxidation of CH₄ occurring in the reactors packed with sand.

The CH₄ oxidation efficiency was calculated for each experiment from the CH₄ consumption results, as shown in column (3) – Table 4-1, as an example, and as follows:

$$\text{CH}_4 \text{ oxidation efficiency} = \frac{(C_{\text{CH}_4})_{t,0} - (C_{\text{CH}_4})_{t,i}}{(C_{\text{CH}_4})_{t,0}} \times 100\% \quad (4-2)$$

where, (CH₄)_{t,0} is the CH₄ concentration (%v/v) at the beginning of the experiment, (CH₄)_{t,i} is the CH₄ concentration (%v/v) at time = i days.

In calculating the maximum CH₄ oxidation efficiency, the variable (CH₄)_{t,i} is the CH₄ concentration (%v/v) at the end of the experiment. The end of the experiment was assumed when there were no significant changes of CH₄ concentration in the headspace gas. Table 4-2 shows the maximum CH₄ oxidation efficiencies of the landfill cover soil studied here under different environmental parameters and calculated using Equation 4-2.

Table 4-2 Maximum CH₄ Oxidation Efficiencies of the Nine Experimental Runs

Run No.	Layer Thickness (mm)	Moisture Content (%)	Nutrients Addition	Maximum CH ₄ Oxidation Efficiency (%)
1	150	15	Not added	29 ± 0.2
2	200	15	Not added	35 ± 0.4
3	150	30	Not added	34 ± 0.2
4	200	30	Not added	38 ± 0.2
5	175	22.5	Medium addition	47 ± 0.5
6	150	15	Added	13 ± 0.8
7	200	15	Added	16 ± 2
8	150	30	Added	75 ± 1
9	200	30	Added	81 ± 0.5

The maximum CH₄ oxidation efficiency found was in the range of 75% to 81% for experimental runs 8 and 9, where nutrients were added to 150 mm and 200mm thickness landfill cover soil that contained 30% moisture, as indicated in Table 4 -2.

For the four experimental runs without nutrient additions, experimental run no. 1 through 4, table 4-2 shows that the CH₄ oxidation efficiency of the Trail Road Landfill cover soil was in the range of 29% to 38%.

The addition of nutrients to the landfill cover soil that had 15% moisture content, showed lower CH₄ oxidation efficiency; 13% and 16% for both 150 mm and 200mm layer thickness, respectively. The impact of adding nutrients to soils with different levels of moisture content is discussed in Section 4.2.

The individual effects of increasing the moisture content and the layer thickness without adding nutrients showed modest increase in the maximum CH₄ oxidation efficiency. However, the effect of nutrient additions to the two layer thicknesses combined with the higher level of moisture content (30% MC) was evident on the CH₄ maximum oxidation efficiency.

4.2 THE EFFECT OF NUTRIENT ADDITIONS

In addition to the carbon substrate (CH₄), the bacteria in the soil need other nutrients for their cellular metabolism. A commercial fertilizer was used as the source of

nutrients. The amount of this fertilizer added to the soil for the different experimental runs was 1.5 g of fertilizer/ kg of soil. The chemical components of the fertilizer are listed in Table 3-3. In analyzing the chemical components, the amount of added fertilizer gave a ratio of 0.3 g Nitrogen: 0.13 g Phosphorous: 0.249 g Potassium for each kilogram of soil. Adding nutrients positively affected the microbial activity, and consequently the CH₄ oxidation efficiency. Figure 4-2 shows the CH₄ oxidation efficiency as calculated using Equation 4-1 and over a period of time for the experimental runs that had soil with 30% moisture and two levels of thicknesses, with and without nutrient additions.

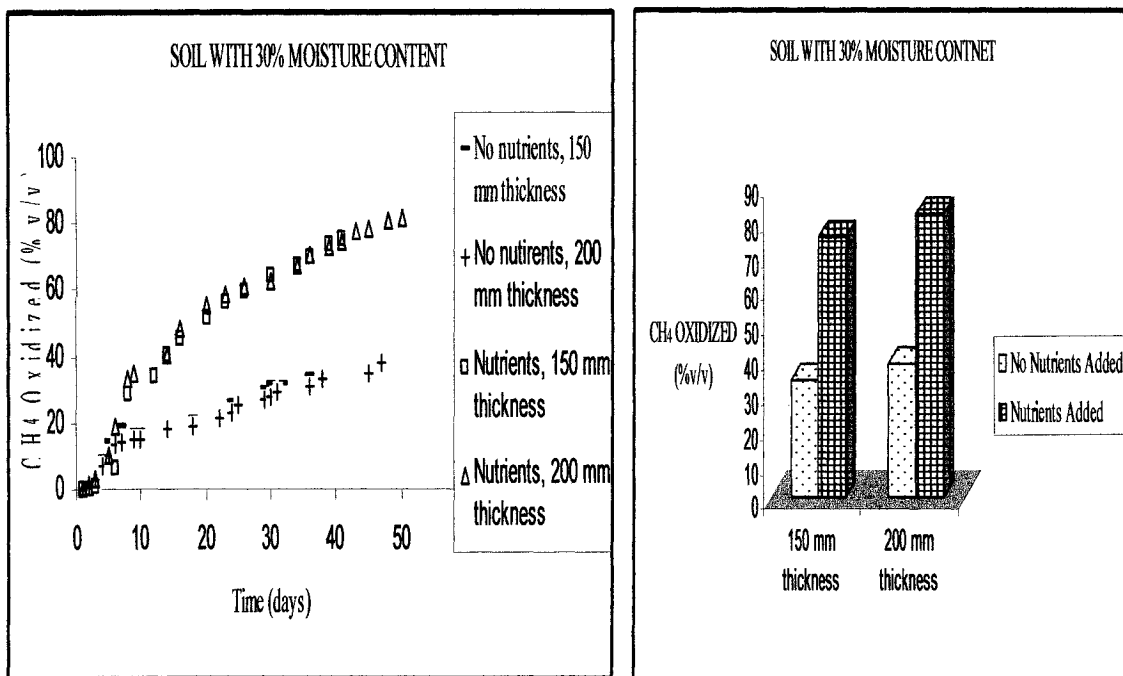


Figure 4-2 Effect of Nutrient Additions on CH₄ Oxidation Efficiencies

The effect of nutrient additions on the CH₄ oxidation efficiency is obvious, as illustrated in Figure 4-2. Adding nutrients to the soil that contained higher level of moisture (30% MC) increased the maximum oxidation efficiency from 38% to 81% for

the 200 mm soil layer thickness, and from 34% to 75% for the 150 mm soil layer thickness. The percentage increase in the maximum CH₄ oxidation efficiency due to the nutrient additions was in the range of 113% to 120%. In these experimental runs moisture content did not change (30% MC), and the layer thickness had no apparent significance on the process performance. The maximum CH₄ oxidation efficiency of the middle point was 47%, which is almost in the middle between the results with and without adding the nutrients.

The CH₄ oxidation efficiency results for the soil containing 30% moisture content, with and without nutrient additions, and for the 150 mm and 200 mm soil layer thickness, were compared statistically by conducting a t-test with 95% level of confidence ($\alpha = 0.05$). The t-test assesses whether the means of two groups are statistically different from each other. The results of paired t-test are shown in tables 4-3 and 4-4.

Table 4-3 Results of Paired t-test ($\alpha=0.05$) of the Effect of Nutrients on the Maximum CH₄ Oxidation Efficiency (%) for Soil with 30% MC and 200 mm Layer Thickness

	Nutrients Added	No Nutrients
Mean	81.4	38.4
Variance	0.5	0.2
Observations	2.0	2.0
df	2.0	
t Stat	73.7	
P(T<=t) one-tail	0.000092	
t Critical one-tail	2.9	
P(T<=t) two-tail	0.000184	
t Critical two-tail	4.3	

Table 4-4 Results of Paired t-test ($\alpha=0.05$) of the Effect of Nutrients on the Maximum CH₄ Oxidation Efficiency (%) for Soil with 30% MC and 150 mm Layer Thickness

	Nutrients Added	No Nutrients
Mean	75.2	33.9
Variance	1.3	0.2
Observations	2.0	2.0
df	1.0	
t Stat	47.4	
P(T<=t) one-tail	0.0067	
t Critical one-tail	6.3	
P(T<=t) two-tail	0.0134	
t Critical two-tail	12.7	

The results of the paired t-tests shown in Tables 4-3 and 4-4 indicate that there were significant differences between the experiments with and without adding nutrients to the landfill cover soil. For the 200 mm soil layer thickness with 30% moisture content, the maximum CH₄ oxidation efficiency increased from 38% for the experiment with no nutrients to 81% when the nutrients were added to the soil. Due to the nutrient additions the percentage increase in the mean of the maximum CH₄ oxidation efficiency was 113% for the 200 mm layer thickness. Almost the same result was obtained for the 150 mm soil layer thickness, and the percentage increase in the mean of the maximum CH₄ oxidation efficiency was 120% due to nutrient additions to soil.

In Table 4-3, the t-Stat value calculated from the data was 73.7. The P (T<=t) two-tail was 0.000184. This probability was extremely low, which indicates that the means of the maximum CH₄ oxidation efficiency are significantly different between the experiments when nutrients were added to soil with 30% moisture content, and the experiments without adding the nutrients and for the 200 mm layer thickness.

In Table 4-4, for the soil layer 150 mm thickness with 30% moisture, the t-Stat value was 47.4 and the P ($T \leq t$) two-tail was 0.0134. Although these values were different from the statistical values obtained for the 200 mm soil layer thickness (t-Stat is less and P ($T \leq t$) is larger), still these values indicate that the mean of the maximum CH₄ oxidation efficiency when nutrients were added to the soil is significantly different from the mean of the maximum oxidation efficiency when no nutrients were added to the 150 mm soil layer thickness.

Statistical t-test analyses are useful in comparing the actual differences between two means in relation to the variation in the data. When the calculated t value exceeds the tabulated value, then the means are significantly different, and this can be seen in Tables 4-3 and 4-4, where the calculated t values were 73.7 and 47.4, respectively, while the tabulated values were 4.3 and 12.7. The 95% level of confidence ($\alpha=0.05$) denotes that there is 95% probability of the mean being significantly different and the data are good enough to support a conclusion with 95% confidence.

It is worth mentioning that in experimental runs nos. 3 and 4, no nutrients were added to the soil with 30% moisture content and for 150 mm and 200 mm soil layer thicknesses, the maximum CH₄ oxidation efficiencies were 34% and 38%. Although the oxygen percentages in the headspace gas at the end of these two experiments were 9% and 7.8% respectively, which means oxygen availability for the reactions to continue, but the reactions stopped as result of lack of nutrients in the soil. As a conclusion, nutrients availability is essential to increase CH₄ oxidation capacity of the landfill cover soil.

Adding the nutrient source to the soil with 15% moisture content had negative effect on CH₄ oxidation efficiency. Actually, as seen from experimental run 1 and 6 results in Table 4-2, CH₄ maximum oxidation efficiency dropped from 29% for the experiments without nutrients to 13% for experiments with added nutrients, for the 150 mm layer thickness. Also, for experimental runs 2 and 7, the maximum CH₄ oxidation efficiency for the 200 mm layer thickness was reduced from 35% for experiments without nutrients to 16% for experiments with added nutrients.

Tables 4-5 and 4-6 summarize the t-Stat analysis of CH₄ oxidation efficiency for the soil with lower level of moisture content (15%) and soil layer thicknesses of 150 mm and 200 mm, respectively, when the nutrients were added to the soil.

Table 4-5 Results of Paired t-test ($\alpha=0.05$) of the Effect of Nutrients on the Maximum CH₄ Oxidation Efficiency (%) for Soil with 15% MC and 200 mm Layer Thickness

	Nutrients Added	No Nutrients
Mean	15.6	34.9
Variance	1.6	0.5
Observations	2.0	2.0
df	2.0	
t Stat	-18.7	
P(T<=t) one-tail	0.001	
t Critical one-tail	2.9	
P(T<=t) two-tail	0.003	
t Critical two-tail	4.3	

Table 4-6 Results of Paired t-test ($\alpha=0.05$) of the Effect of Nutrients on the maximum CH₄ Oxidation Efficiency (%) for Soil with 15% MC and 150 mm Layer Thickness

	Nutrients Added	No Nutrients
Mean	12.8	28.7
Variance	0.7	0.2
Observations	2.0	2.0
df	1.0	
t Stat	-23.7	
P(T<=t) one-tail	0.001	
t Critical one-tail	6.3	
P(T<=t) two-tail	0.003	
t Critical two-tail	12.7	

It can be seen from the mean values of the maximum CH₄ oxidation efficiency presented in Tables 4-5 and 4-6 that they were reduced by almost 50% for the experiments with added nutrients to the soil with 15% moisture content. Adding the nutrients to the soil with less moisture affected negatively the bacterial performance, possibly as a result of toxicity.

Furthermore, the value of the P(T<=t) two-tail was low (0.003), so the means of the maximum CH₄ oxidation efficiency were significantly different for the experiments with and without nutrient additions to the 200 mm and 150 mm soil layer thickness that contained 15% moisture content. The mean value of the maximum CH₄ oxidation efficiency for soil with 15% moisture content and 200 mm layer thickness dropped from 34.9% to 15.6% after adding the nutrients, and the mean value dropped from 28.7% to 12.8% after adding nutrients to the 150 mm soil layer with 15% moisture content. It was hypothesized that microbial water stress could prevent the development of a larger

methanotrophic community. It is concluded that the bacteria need moisture also in order for nutrients to increase CH₄ oxidation capacity. It appears that the lower level of soil moisture content could not provide adequate support to the bacterial activities when nutrients were added to this soil, resulting in a lower CH₄ oxidation efficiency.

4.3 THE EFFECT OF MOISTURE CONTENT

The results of the maximum CH₄ oxidation efficiency for different experimental runs shown in Table 4-2 illustrate that the second environmental parameter that has an important effect on the CH₄ oxidation process is the soil moisture content. Soil moisture is an important physical parameter, since it affects the diffusion of the gas within the soil pores. To investigate the effect of moisture content on the CH₄ oxidation efficiency, Figure 4-3 was generated to illustrate the CH₄ oxidation efficiency with time for the landfill cover soil experiments without nutrients addition, and for the two soil layer thicknesses.

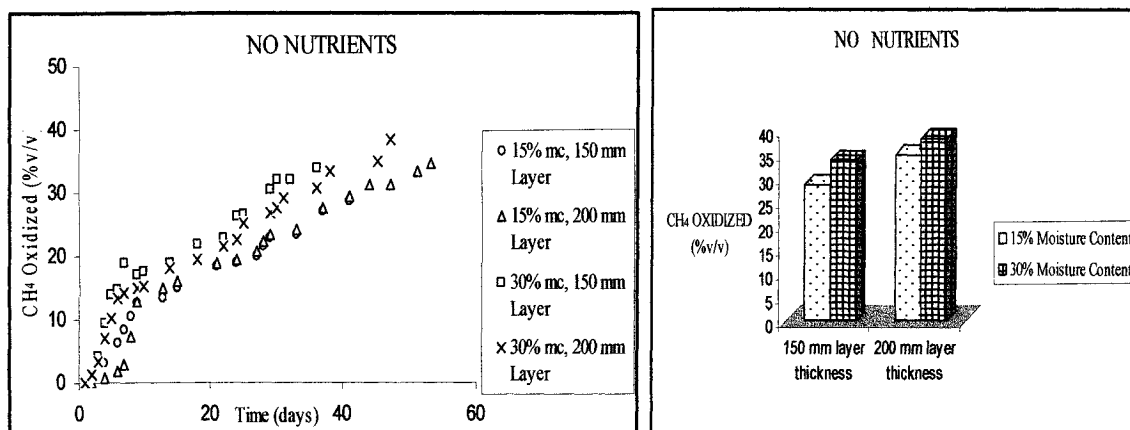


Figure 4-3 Moisture Content Effect on CH₄ Oxidation Efficiency with Time for Experimental Runs without Nutrients

Figure 4-3 indicates that higher CH₄ oxidation efficiencies were obtained in soils with higher moisture content. The maximum CH₄ oxidation efficiency, for the 150 mm soil layer thickness but without nutrients increased from 29% for the soil with 15% moisture content to 34% for the soil with 30% moisture content; this comprise an 17% increase in CH₄ oxidation efficiency due to the increase in soil moisture content. The same type of result was obtained for the 200 mm soil layer experiments without nutrients. The maximum CH₄ oxidation efficiency increased from 35% for the soil with 15% moisture content to 38% for the soil with 30% moisture content. The percentage increase due to the increase in moisture content for the 200 mm soil layer thickness was 9%.

The moisture content is a critical physical parameter affecting the CH₄ oxidation efficiency. Higher moisture affects the movement of gas through the soil pores and consequently, the microbial activity and growth. Increasing the moisture content levels from 15% to 30% in this study increased the CH₄ oxidation efficiency. These results are in agreement with other results reported in the literature by Bender and Conrad (1995), where the optimum moisture content was in the range of 20% to 35%. Hilger and Barlaz (2002) reported that CH₄ oxidation results from soil with moisture content as high as 45% exceeded the oxidation results for the soil with less moisture content, as long as soil pores volume are not water saturated.

Two t-tests were conducted to investigate the effect of moisture content on the 150 mm and 200 mm soil layer thicknesses. Tables 4-7 and 4-8 show the results of t-tests

for the maximum CH₄ oxidation efficiency in the landfill cover soil at two different moisture content levels.

Table 4-7 Results of Paired t-test ($\alpha=0.05$) of the Effect of Moisture Content on the Maximum CH₄ Oxidation Efficiency (%) for **200 mm Soil Layer Thickness without Nutrients**

	30% MC	15% MC
Mean	38.4	34.9
Variance	0.2	0.5
Observations	2.0	2.0
df	2.0	
t Stat	10.5	
P(T<=t) one-tail	0.01	
t Critical one-tail	2.9	
P(T<=t) two-tail	0.027	
t Critical two-tail	4.3	

Table 4-8 Results of Paired t-test ($\alpha=0.05$) of the Effect of Moisture Content on the Maximum CH₄ Oxidation Efficiency (%) for **150 mm Soil Layer Thickness without Nutrients**

	30% MC	15% MC
Mean	33.9	28.7
Variance	0.2	0.2
Observations	2.0	2.0
df	2.0	
t Stat	11.2	
P(T<=t) one-tail	0.004	
t Critical one-tail	2.9	
P(T<=t) two-tail	0.008	
t Critical two-tail	4.3	

By increasing the moisture content from 15% to 30%, the mean of the maximum CH₄ oxidation efficiency has increased from 35% to 38% for the 200 mm soil layer thickness. This is 10% increase. The mean of the maximum CH₄ oxidation efficiency increased from 29% to 34% for the 150 mm soil layer thickness which is 18% increase. However, and as it is reflected in the t-Stat results, the calculated t-Stat values were 10.5 (Table 4-7) and 11.2 (Table 4-8). In both tables the value of the calculated t Stat was higher than the t Critical two tail, this statistically indicate that the means are different to a certain level between the two levels of the moisture content (15% and 30%). Comparing statistically the effects of nutrients and the moisture content, the t Stat value for the combined effect of nutrients and 30% moisture content for the 200 mm soil layer thickness was 73.7 (Table 4-3), while t Stat for the effect of moisture content alone without nutrient addition was 10.5 (Table 4-7) for the same soil layer thickness (200 mm). Also, the P (T<=t) two-tail for the combined effect of nutrients and higher moisture content was 0.000184, the probability was extremely small so the means between levels of nutrients combined with 30% moisture content were significantly different, while the P(T<=t) two-tail for the moisture content effect alone was 0.027, indicating that the means were less significantly different between the different levels of moisture content without nutrient additions. The combined effect of increased moisture content with nutrients was reflected on the middle point experiment, where the CH₄ oxidation efficiency increased to 47% when the moisture content increased to 22.5% and the layer thickness increased to 175 mm with half level of nutrient additions.

4.4 THE EFFECT OF LANDFILL COVER SOIL THICKNESS

The third parameter investigated in this study was the effect of soil layer thickness on the CH_4 oxidation process. Figures 4-4 and 4-5 illustrate the CH_4 oxidation efficiency with time for the two soil layer thicknesses with 15% and 30% moisture content, without and with added nutrients, respectively.

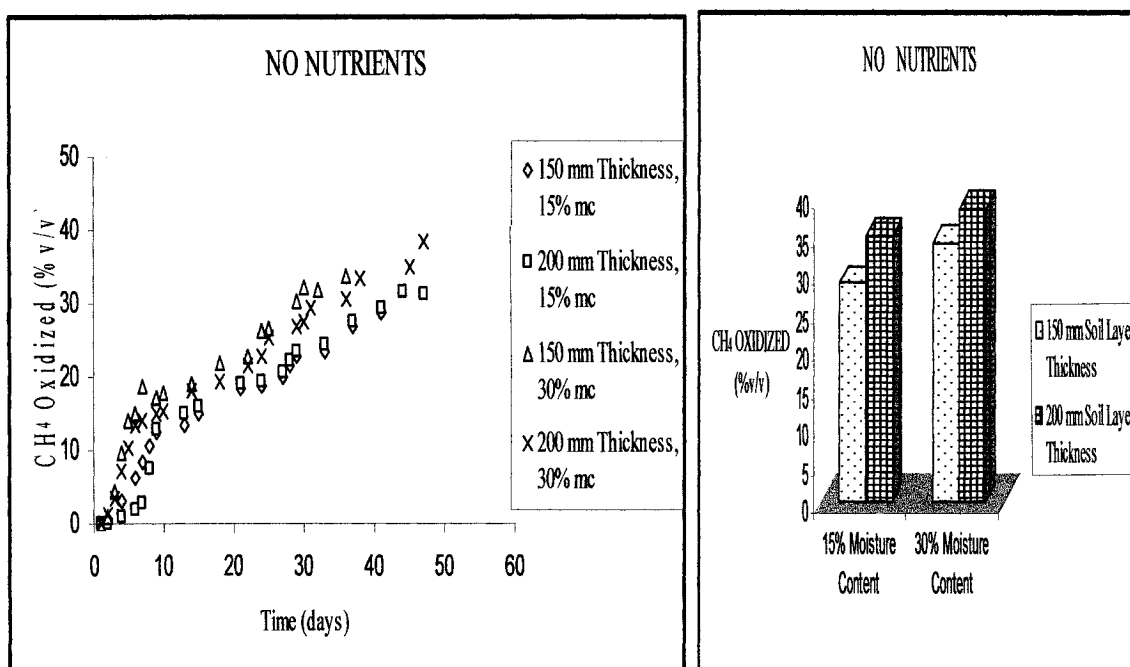


Figure 4-4 Soil Layer Thickness Effect on CH_4 Oxidation Efficiency with Time for Experimental Runs without Nutrients

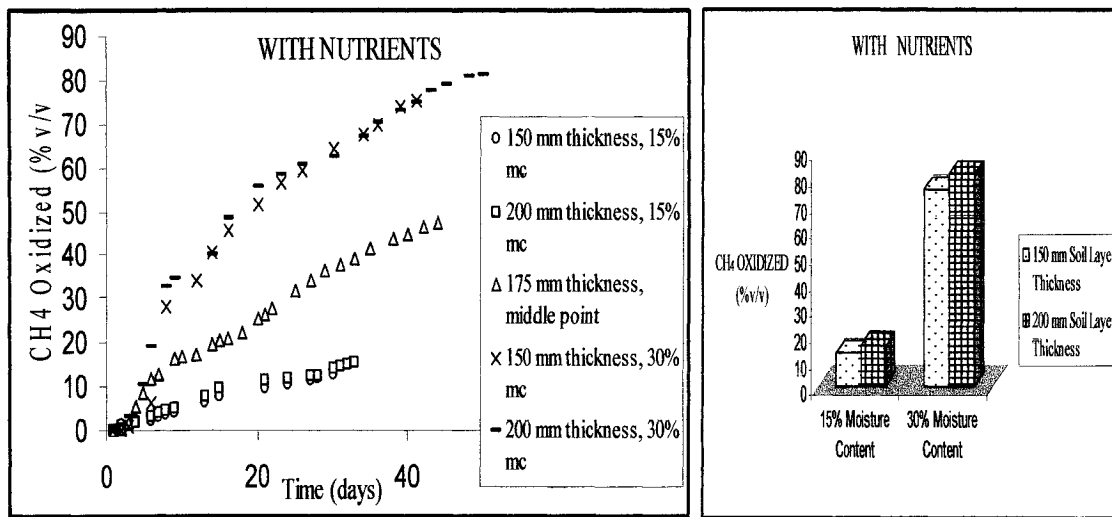


Figure 4-5 Soil Layer Thickness Effect on CH₄ Oxidation Efficiency with Time for Experimental Runs with Nutrients

From the Figures 4-4 and 4-5 illustrated above, it is obvious that CH₄ oxidation processes in the two soil layer thicknesses followed almost the same general trend, except for the value of the maximum oxidation efficiency. The 200 mm soil layer thickness had higher maximum oxidation efficiency than the 150 mm layer thickness; this can be explained in that the former case there was bigger volume of soil, larger population of methanotrophic bacteria and thus greater bacterial activities, resulting in higher CH₄ maximum oxidation efficiency values. Soil layer thickness has hardly any difference on maximum CH₄ oxidation efficiency, as can be seen in Figure 4-4. The differences in the maximum oxidation efficiencies are mainly due to the increase in the moisture content. From Figure 5-4 it can be seen that the differences in the maximum oxidation efficiencies are mainly due to the combined effect of moisture content and nutrients. Tables 4-9 and 4-10 show the t-tests conducted to study the outcome for different layer thicknesses and 30% moisture content, without and with adding nutrients respectively.

Table 4-9 Results of Paired t-test ($\alpha=0.05$) of the Effect of Soil Layer Thickness on the Maximum CH₄ Oxidation Efficiency (%) for Soil with **30% Moisture Content without Nutrients**

	200 mm Layer Thickness	150 mm Layer Thickness
Mean	38.4	33.9
Variance	0.2	0.2
Observations	2.0	2.0
df	2.0	
t Stat	9.9	
P(T<=t) one-tail	0.005	
t Critical one-tail	2.9	
P(T<=t) two-tail	0.01	
t Critical two-tail	4.3	

Table 4-10 Results of Paired t-test ($\alpha=0.05$) of the effect of Soil Layer Thickness on the Maximum CH₄ Oxidation Efficiency (%) for Soil with **30% Moisture Content and Added Nutrients**

	200 mm Layer Thickness	150 mm Layer Thickness
Mean	81.4	75.2
Variance	0.5	1.3
Observations	2.0	2.0
df	2.0	
t Stat	6.6	
P(T<=t) one-tail	0.01	
t Critical one-tail	2.9	
P(T<=t) two-tail	0.02	
t Critical two-tail	4.3	

The results presented in Tables 4-9 and 4-10 show that the maximum CH₄ oxidation efficiency has increased from mean value 33.9% for the 150 mm layer thickness to 38.4% for the 200 mm layer thickness, where soil contained 30% moisture

and no additional nutrients. Also, maximum CH₄ oxidation efficiency for 150 mm soil layer thickness increased from 75.2% to 81.4% when the soil layer thickness increased from 150 mm to 200 mm for the soil with 30% moisture content and added nutrients. The t-Stat values for the 200 mm and 150 mm soil layer thicknesses with 30% moisture content with and without nutrients were 9.9 and 6.6 (Tables 4-9 and 4-10). These are low value compared to the t-Stat value for the nutrient addition effect with 30% moisture content which was 73.7 (Table 4-3).

Analyzing the t-Stat values for the effect of the three operating parameters in these experiments, the highest values were for the combined effect of adding nutrients to the soil with 30% moisture content (73.7 for 200 mm layer thickness and 47.4 for 150 mm layer thickness). The t-Stat values for the effect of moisture content were 10.5 for 200 mm soil layer thickness without nutrients addition and 11.2 for the 150 mm soil layer thickness without nutrients addition. The t-Stat values for the effect of soil layer thickness were the lowest (9.9 and 6.6 as shown in Tables 4-9 and 4-10). The higher the t-Stat values the more significant is the mean differences. These results confirm that the most significant experimental parameter in this study was adding nutrients to the soil that contained 30% moisture. The statistical analysis reflected the importance of the combined effect of the nutrients addition and the higher level of moisture content on the maximum CH₄ oxidation efficiency in the landfill cover soil. Adding nutrients to landfill cover soil with 30% moisture content doubled the maximum CH₄ oxidation capacity of this soil.

In addition to the statistical analysis presented above, *Appendix B* includes the hypothesis testing for variance and the analysis of variance, 3-way between groups factorial ANOVA, between the maximum CH₄ oxidation efficiency of the different experimental runs using SYSTAT 11. The statistical analysis presented in *Appendix B* reflected the importance of the combined effect of the nutrients addition and the higher levels of moisture content and layer thickness on the maximum CH₄ oxidation efficiency in the landfill cover soil. Statistical design model is presented in Section 4.7.

4.5 CH₄ OXIDATION KINETIC CONSTANTS

The apparent half saturation constant (K_{CH_4}) and maximum reaction rate (V_{max}) of CH₄ are characteristic parameters, which determine the ability of bacteria to grow on CH₄. The observed CH₄ draw down rates were used to calculate the maximum reaction rate of CH₄ oxidation, and the apparent half saturation constant according to Monod equation (Equation 4-3).

$$V_{CH_4} = \frac{V_{max} \times C_{CH_4}}{K_{CH_4} + C_{CH_4}} \quad (4-3)$$

where, V_{CH_4} is the CH₄ reaction rate ($\mu\text{moles/ day} \times \text{kg}$ of dry soil weight), V_{max} is the maximum CH₄ reaction rate ($\mu\text{moles/ day} \times \text{kg}$ of dry soil weight), C_{CH_4} is the CH₄ concentration (μmoles), K_{CH_4} is the CH₄ apparent half saturation constant (μmoles).

The difference between CH₄ uptake rates on consecutive days represented the substrate utilization and it is an indication of the bacterial growth. Figures 4-6 and 4-7

show the relation between the CH₄ reaction rate ($\mu\text{mole}/\text{day} \times \text{kg soil dry weight}$) and CH₄ substrate utilization (μmole) with time for experimental runs Nos. 3 and 8, without adding nutrients and with added nutrients, respectively to the 150 mm soil layer thickness with 30% moisture content.

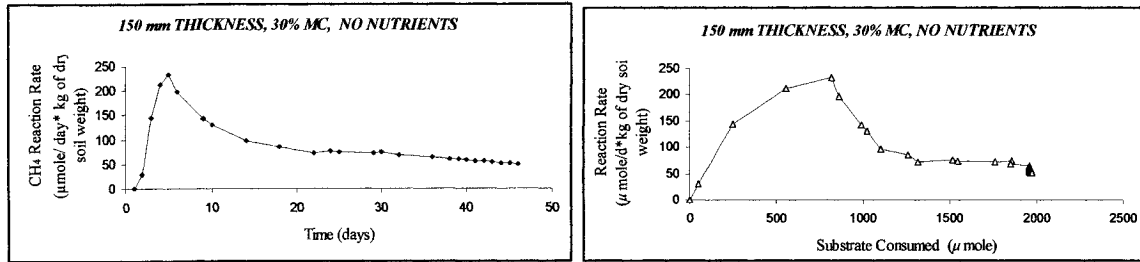


Figure 4-6 CH₄ Reaction Rate and Substrate Utilization with Time for Experimental Run 3

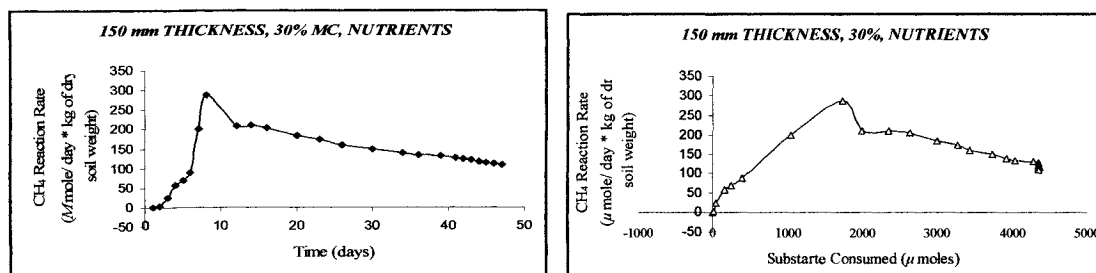


Figure 4-7 CH₄ Reaction Rate and Substrate Utilization with Time for Experimental Run 8

Figures 4-6 and 4-7 show that adding nutrient to the 150 mm soil layer thickness that contained 30% moisture content, affected the CH₄ substrate utilization and the CH₄ reaction rate. Adding nutrients to this soil increased the CH₄ substrate utilization from 1972 μmole to 4350 μmole and from 2157 μmole to 4571 μmole for the 200 mm soil layer thickness. The highest CH₄ reaction rate was found when nutrients were added to the soil with 30% moisture content (287 $\mu\text{mole}/\text{day} \times \text{kg soil dry weight}$ for the 150 mm soil layer thickness, and 236 $\mu\text{mole}/\text{day} \times \text{kg soil dry weight}$ for the 200 mm soil layer

thickness). Monod model is the most commonly applied model of microbial growth, it is a semi empirical equation that relates growth rate to substrate concentration. Figure 4-8 shows the relationships between the CH₄ reaction rate ($\mu\text{moles/day} \cdot \text{kg}$ of dry soil weight) and the CH₄ substrate (μmoles) for all the experimental runs.

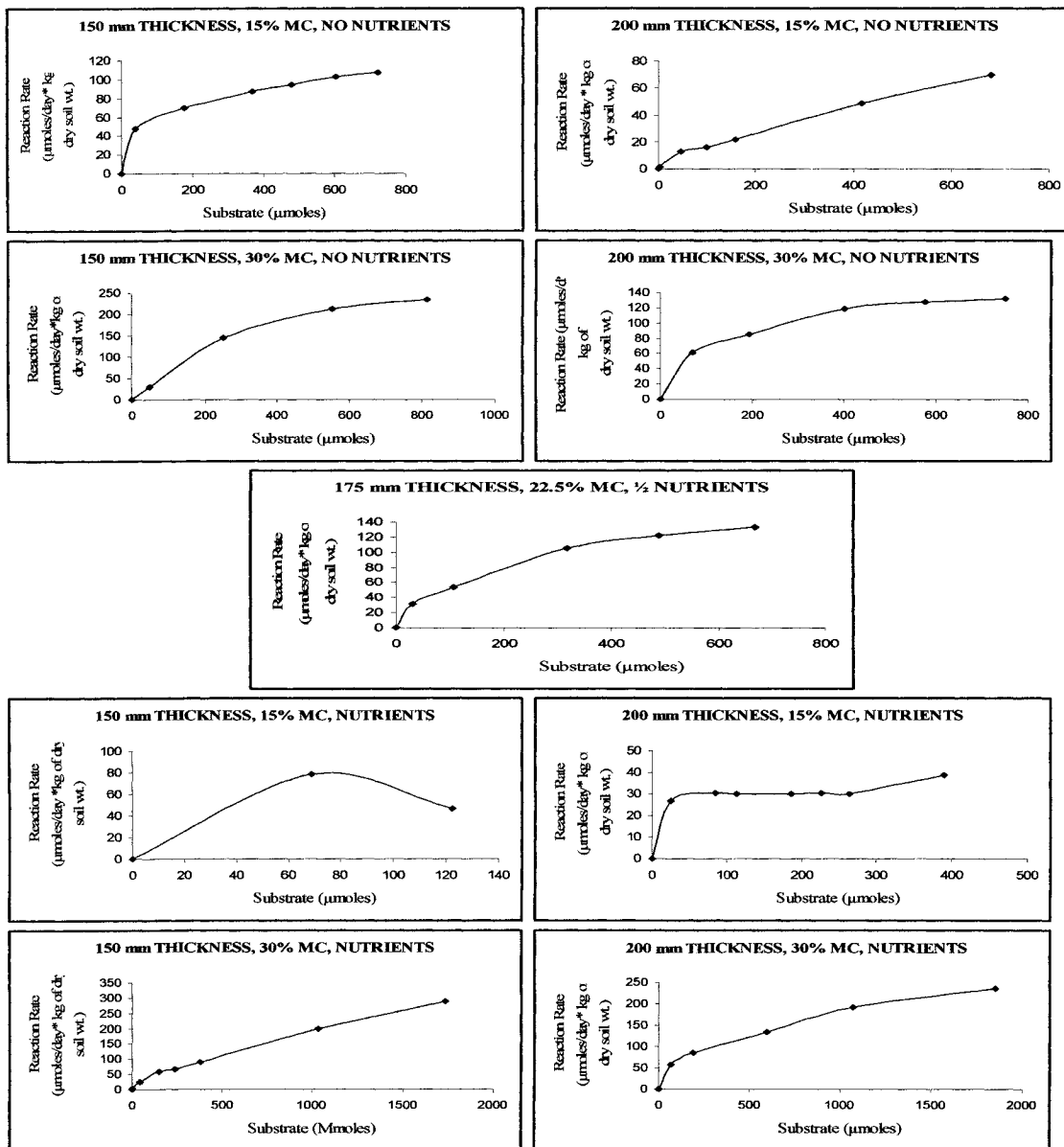


Figure 4-8 Relationship between the CH₄ Reaction Rate and Substrate for all Experimental Runs

The kinetic constants were calculated from the relation between CH₄ reaction rate and CH₄ substrate using *SYSTAT 11* (2005). SYSTAT 11 is statistical software used to calculate the values of V_{max} and K_{CH₄} and is built on the Monod equation. It basically contains files that describe reaction which occur in many biochemical processes and is capable of calculating the kinetic constants accordingly.

Figure 4-9 shows a typical example for the determination of the kinetic constants using SYSTAT 11, for the experimental run No. 1, where the soil moisture content was 15%, the soil layer thickness was 150 mm and no nutrients were added. Detailed calculations for the kinetic constants for all experimental runs using SYSTAT 11 are included in *Appendix A*.

Using the experimental data of CH₄ reaction rate and CH₄ substrate values, the software presented the regression analyses, the calculations of residuals sum of squares, degree of freedom and mean square values. Finally the values of V_{max} and K_{CH₄} were estimated. After that, the software performed a comparison between some values of experimental CH₄ reaction rate and the predicted reaction rate and calculated the residuals. The calculated residuals are the least possible. In Figure 4-9 the V_{max} was 110 (μmoles/ day × kg of dry soil weight) and K_{CH₄} was 71 μmoles.

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME1.SYD,
created Wed May 11, 2005 at 16:29:25, contains variables:

V
S

Iteration No.	Loss	VMAX	KM
0	0.118545D+04	0.101000D+03	0.102000D+03
1	0.228960D+03	0.111261D+03	0.698634D+02
2	0.222949D+03	0.110233D+03	0.707539D+02
3	0.222942D+03	0.110286D+03	0.709787D+02
4	0.222941D+03	0.110299D+03	0.710317D+02
5	0.222941D+03	0.110303D+03	0.710441D+02
6	0.222941D+03	0.110303D+03	0.710471D+02

Dependent variable is V

Zero weights, missing data or estimates reduced degrees of freedom

Source	Sum-of-Squares	df	Mean-Square
Regression	45367.340	2	22683.670
Residual	222.941	5	44.588
Total	45590.281	7	
Mean corrected	8651.969	6	

Raw R-square (1-Residual/Total) = 0.995

Mean corrected R-square (1-Residual/Corrected) = 0.974

R(observed vs predicted) square = 0.975

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval	
				Lower < 95%>	Upper
VMAX	110.303	6.119	18.027	94.574	126.032
KCH4	71.047	20.217	3.514	19.076	123.018

Case	V Observed	V Predicted	Residual
1	0.000	0.000	0.000
2	47.651	39.840	7.811
3	69.964	78.702	-8.738
4	87.133	92.424	-5.291
5	94.546	96.035	-1.489
6	102.271	98.686	3.585
7	106.931	100.411	6.520

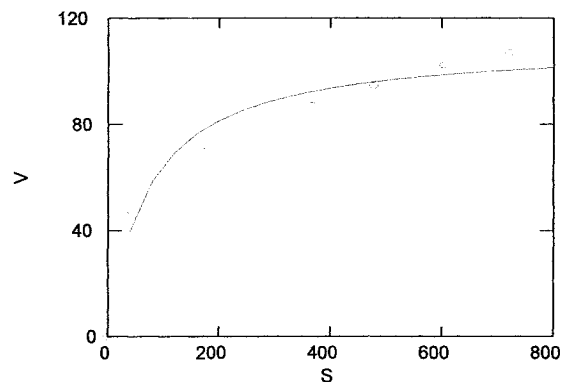


Figure 4-9

SYSTAT Determination of V_{max} and K_{CH4} for Experimental Run 1

Table 4-11 shows the values for CH₄ oxidation kinetic constants for all the experiments, carried out in this study.

Table 4-11 Kinetic Constants for all Experimental Runs

Run No.	Layer Thickness (cm)	Moisture Content (%)	Nutrients Addition	V _{max} (μmole/ day × kg of dry soil weight)	K _{CH₄} (μmoles)
1	15	15	Not added	110 ± 1	71 ± 0.5
2	20	15	Not added	170 ± 2	992 ± 17
3	15	30	Not added	351 ± 3	382 ± 5
4	20	30	Not added	153 ± 1	123 ± 0.7
5	17.5	22.5	Medium addition	175 ± 2	211 ± 2
6	15	15	Added	63 ± 4	-
7	20	15	Added	33 ± 3	7 ± 0.5
8	15	30	Added	619 ± 12	2056 ± 118
9	20	30	Added	290 ± 2	523 ± 10

The kinetics constants values in this study illustrated in Table 4-11, show that the highest values of V_{max} and K_{CH₄} were determined for experimental run when nutrients were added to the soil containing the higher level of moisture (30% MC), and the lowest values of V_{max} and K_{CH₄} determined were for the experimental runs when nutrients were added to the soil with the lowest moisture content (15% MC). The range of V_{max} values was between 33 and 619 μmoles CH₄/ day×kg of dry soil weight. Although the kinetics constants in this study were determined from the experimental results using heterogeneous batch reactor of a size (32x10) cm, and different from other batch

mixed small batch system, the kinetics constants determined in this study are in agreement with the values reported in recent years by Dubey (2003) where the values of V_{\max} were in the range of 105 – 615 $\mu\text{moles CH}_4/\text{day}\times\text{kg}$ of dry soil weight, and Horz et al. (2002) who reported V_{\max} values in the range from 21 to 88 $\mu\text{moles CH}_4/\text{day}\times\text{kg}$ of dry soil weight. In the study conducted by Dubey (2003) to determine the biological kinetics constants, chemical fertilizers in the form of NH_4Cl , NH_4NO_3 and urea were applied to the tested soil that contained 43% moisture content (% by weight); also some soil samples were not fertilized and served as the control. Horz et al. (2002) performed their field study using non-grazed, managed (fertilized with 50-80 $\text{kg N Ha}^{-1} \text{ year}^{-1}$) meadow.

Values for kinetic constants certainly reflect complex interaction between the environment and the bacterial enzyme systems. Also, many elements influence the reported kinetic constants values like experimental design and curve fitting. The values of V_{\max} depend on microbial energy and size. In this study, the high K_{CH_4} values in this study could be attributed to the experimental operating conditions, where the experiments were conducted in heterogeneous batch reactor systems.

There is a wide range of V_{\max} and K_{CH_4} values reported previously by other researchers. Table 4-12 illustrates a comparison between kinetic constants values obtained in this study and those previously reported in the literature.

Table 4-12 Kinetic Constants Reported in the Literature

Researchers	V_{\max} Reported	V_{\max} ($\mu\text{moles/ day}$ $\times \text{kg of dry}$ soil weight)	K_{CH_4} Reported	K_{CH_4} (μmoles)
Results from this study	33 – 619 $\mu\text{moles/ day} \times \text{kg of d.s.w}$	33 – 619	7 – 2056 μmoles	7 – 2056 μmoles
Dubey, (2003)	0.07 – 0.41 $\mu\text{g/ h} \times \text{g of d.s.w}$	105 - 615	26 – 133 $\mu\text{g/g}$	*
Horz et al., (2002)	0.88 -3.65 $\text{nmol/h} \times \text{g of d.s.w}$	21 - 88	137 – 1206 nmoles	0.14 – 1.2
Whalen and Reeburgh,(1996)	12 – 3570 $\text{ng / h} \times \text{g of d.s.w.}$	18 - 5355	37 – 1090 nmoles	0.037 – 1.1
Whalen et al., (1990)	60 - 96 $\mu\text{g/ d} \times \text{g}$	3750 - 6000	3 – 10 μmoles	3 – 10
De Visscher and Schippers, (2001)	0.068 – 0.73 $\mu\text{mol/ s} \times \text{kg of d.s.w.}$	5875 - 63072	4 – 15 μmoles	4 – 15
Borjesson et al. (1998)	2 $\mu\text{mol/ h} \times \text{g of d.s.w.}$	48000	**	**
Kjeldsen et al. (1997)	150 – 250 $\mu\text{g/d} \times \text{g of d.s.w.}$	9375 - 15625	**	**
Czepiel et al., (1996)	40 – 2594 $\text{nmol/ h} \times \text{g of d.s.w.}$	984 - 62256	195 – 5847 ppm	*

* K_{CH_4} constant value could not be converted to μmoles due to lack of information in the literature

** No Information in the literature
d.s.w. is dry soil weight

The range of the values of the biological kinetics constants reported previously in the literature was extremely broad. In Table 4-12, it is noticed that, for example, in the study by Czepiel et al. (1996) the range of V_{\max} was between 40 to 2594 $\text{nmole/ h} \times \text{g}$ of dry soil weight. Another wide range of V_{\max} values between 12 to 3570 $\text{ng/ h} \times \text{g}$ of dry soil weight was reported by Whalen and Reeburgh (1996). Hilger et al. (2002) stated

that the cause of such variability was not fully understood, and some of the reasons could be attributed to either procedural issues or degree of exopolymer accumulations which can limit the rate of diffusion, also other climatic and environmental factors.

4.6 DECAY RATE CONSTANT (K_d)

Decay or death rate follows first order kinetics. In order to determine the decay constant for each experimental run, a plot of $\ln C_{CH_4}$ versus t yields a line of slope, and this slope represents the value of $-K_d$. The values of C_{CH_4} are the experimental CH_4 substrate concentrations (μ moles) found in the reactor in each experimental run. These values are included in Appendix A.

Table 4-13 summarizes the (K_d) values for all the experimental run. Also, Figure 4-10 shows the obtained values of decay constants (K_d) for all experimental runs.

Table 4-13 Decay Rate Constant K_d (day^{-1}) for all the Experiments

Run No.	Layer Thickness (mm)	Moisture Content (%)	Nutrients Addition	K_d (day^{-1})
1	150	15	Not added	0.0068
2	200	15	Not added	0.0068
3	150	30	Not added	0.0088
4	200	30	Not added	0.0081
5	175	22.5	Medium addition	0.0115
6	150	15	Added	0.0045
7	200	15	Added	0.0032
8	150	30	Added	0.0317
9	200	30	Added	0.0308

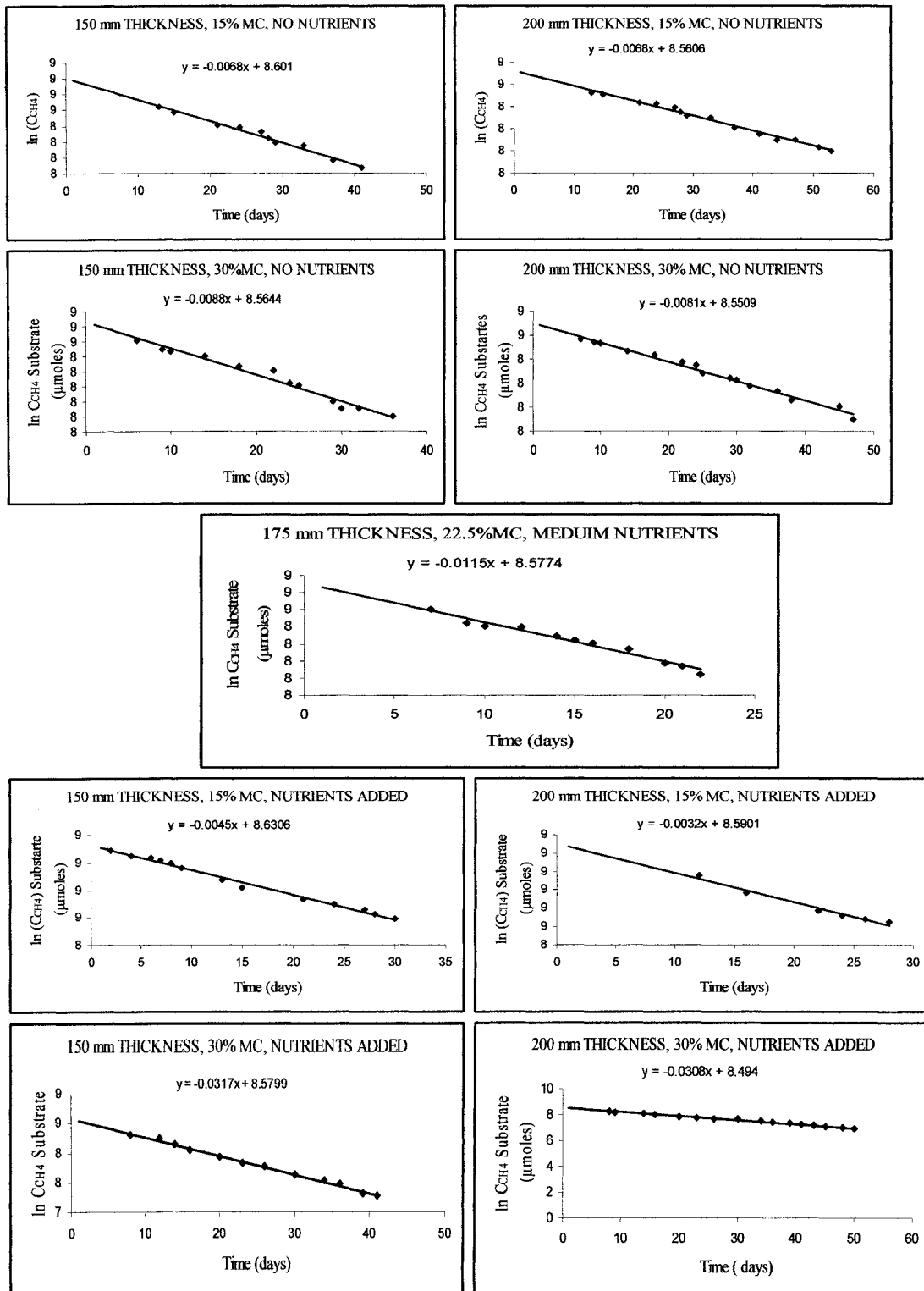


Figure 4-10

Plot of $\ln C_{CH_4}$ versus Time to Obtain the Decay Rate Constant for the Experimental Runs

4.7 STATISTICAL DESIGN MODEL

As mentioned in *Chapter 3*, to assess the effect of soil layer thickness, moisture content and the addition of nutrients on the biological CH₄ oxidation process, a two level factorial design experiment was conducted. In addition to its use as a screening tool, two-level factorial design can provide information on the relative importance of each parameter with respect to others and show interactions between parameters of concern. To simplify the calculation and comparison of the individual or combined influence of the parameters, the lower and upper values were coded and these are shown in Table 4-14.

Table 4-14 Two-Level Factorial Design

Parameter	Level	Coded level
Soil Layer Thickness	15 cm	-1
	20 cm	1
Moisture Content	15%	-1
	30%	1
Nutrients Addition	No added nutrients	-1
	Added nutrients	1

The two-level full factorial design model has the following form, shown in Equation 4-4.

$$\begin{aligned}
 E(q) = & \beta_0 + \beta_1 \textit{Thickness} + \beta_2 \textit{MC} + \beta_3 \textit{Nutrients} + \beta_{12} \textit{Thickness} * \textit{MC} \\
 & + \beta_{13} \textit{Thickness} * \textit{Nutrients} + \beta_{23} \textit{MC} * \textit{Nutrients} + \beta_{123} \textit{Thickness} * \textit{MC} * \textit{Nutrients} + \varepsilon
 \end{aligned}
 \tag{4-4}$$

where, $E(q)$ is the expected value of response, oxidation efficiency in the case of this study, *Soil Layer Thickness*, *MC* and *Nutrients* represent independent variables being tested, β_0 represents the overall mean, $\beta_{1,2,3}$ are the principal effects, $\beta_{12,13,23}$ are the 2-way interactions between parameters, β_{123} is the 3-way interaction, and ε is the random error.

To obtain the confidence of intervals and test the adequacy of the model, one needs to estimate the variance of error. The variance of error can be obtained from the replicates. Each operating condition was replicated twice. The results are presented in Table 4-15.

Table 4-15 Maximum CH₄ Oxidation Efficiency Experimental Results for Two-Level Full Factorial Design

Replicate	Thick	MC	Nutrient	Thick × MC	Thick × Nutrient	MC × Nutrient	Thick × MC × Nutrient	Oxidation Efficiency (%)	Standard Deviation σ^2
1-A	-1	-1	-1	1	1	1	-1	29.0	0.18
1-B	-1	-1	-1	1	1	1	-1	28.4	
2-A	1	-1	-1	-1	-1	1	1	35.4	0.43
2-B	1	-1	-1	-1	-1	1	1	34.4	
3-A	-1	1	-1	-1	1	-1	1	33.5	0.24
3-B	-1	1	-1	-1	1	-1	1	34.2	
4-A	1	1	-1	1	-1	-1	-1	38.7	0.20
4-B	1	1	-1	1	-1	-1	-1	38.1	
5-A	0	0	0	0	0	0	0	47.2	0.46
5-B	0	0	0	0	0	0	0	48.1	
6-A	-1	-1	1	1	-1	-1	1	13.4	0.84
6-B	-1	-1	1	1	-1	-1	1	12.2	
7-A	1	-1	1	-1	1	-1	-1	16.5	1.66
7-B	1	-1	1	-1	1	-1	-1	14.7	
8-A	-1	1	1	-1	-1	1	-1	74.4	1.38
8-B	-1	1	1	-1	-1	1	-1	76.0	
9-A	1	1	1	1	1	1	1	81.9	0.48
9-B	1	1	1	1	1	1	1	80.9	

The outcome of the regression analysis is presented in Table 4-16.

Tables 4-16 Parameters Estimate for Two-Level Full Factorial Design

	Effect	Lower 95%	Upper 95%
β_0	40.95	35.64	46.27
β_1	4.92	-6.15	15.99
β_2	34.19	23.13	45.26
β_3	12.28	1.22	23.35
β_{12}	0.41	-10.66	11.48
β_{13}	-0.45	-11.52	10.62
β_{23}	29.88	13.81	40.94
β_{123}	1.24	-9.83	12.31

The confidence intervals for all interaction terms that contain zero or less may be deleted from the model. After deleting these terms, the regression analysis was repeated with the remaining parameters.

The final statistical model is shown in Equation 4-5.

$$E(q) = 40.08 + 17.38 MC + 5.8 Nutrient + 15.23 MC \times Nutrient \quad (4-5)$$

where $E(q)$ is the expected CH_4 oxidation efficiency, 40.08 is β_0 or the overall mean, 17.38 is β_2 or the value of main effect of moisture content, 5.8 is β_3 or the value

of main effect of nutrients and 15.23 is β_{23} or the value of two ways interaction between moisture content and nutrients.

According to the experimental results and the statistical model of this study, the effects of nutrient additions according to the statistical model (5.8) and moisture content (17.38) on the CH_4 oxidation process were important; the interaction between these two parameters (15.23) on the oxidation process was very important.

The significance of the model inadequacy was tested by comparing the value of R^2 ratio, as illustrated in Figure 4-11. This figure compares the experimental oxidation rates with the rates calculated using the model in Equation 4-5.

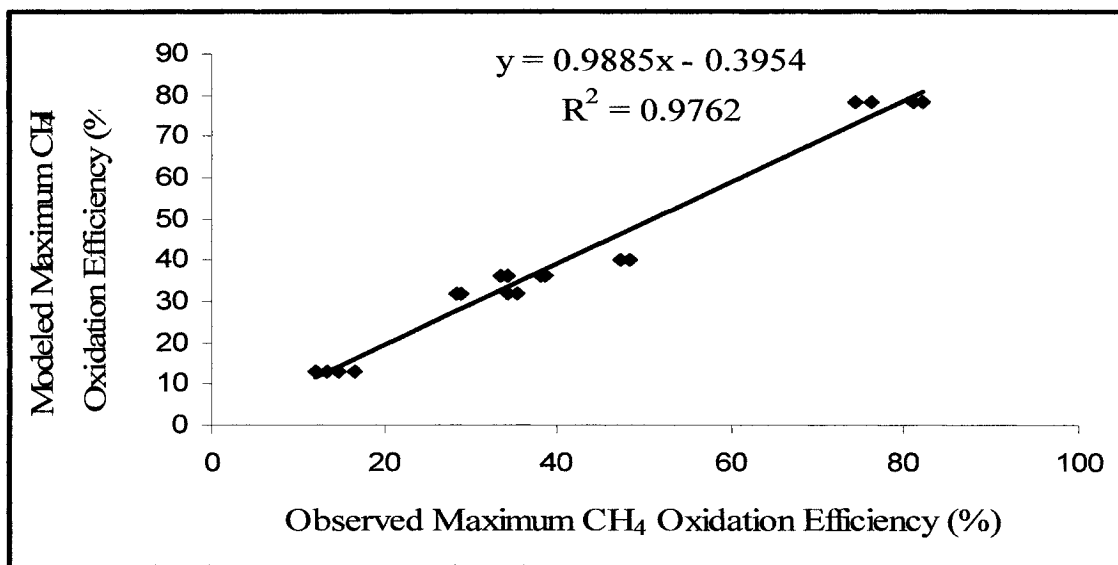


Figure 4-11 Comparison between the Experimental versus Modeled Maximum CH_4 Oxidation Efficiencies

The model demonstrates very good fit and representation of the data, where the coefficient of determination value (R^2) was 0.9762. This model describes the oxidation

process very well and has the advantage of incorporating main effect of moisture content and nutrient additions, which is in agreement with the experimental results. This was reflected when the nutrients were added to 30% soil moisture content, the highest values of CH₄ oxidation efficiencies (75% and 81%) were obtained. On the other hand, when the nutrients were added to soil with 15% moisture content, the lowest CH₄ oxidation efficiencies (13% and 16%) were attained.

Figure 4-12 and Table 4-17 illustrate the model's trend with various moisture contents and nutrient addition amongst the coded levels and within the experiment limits.

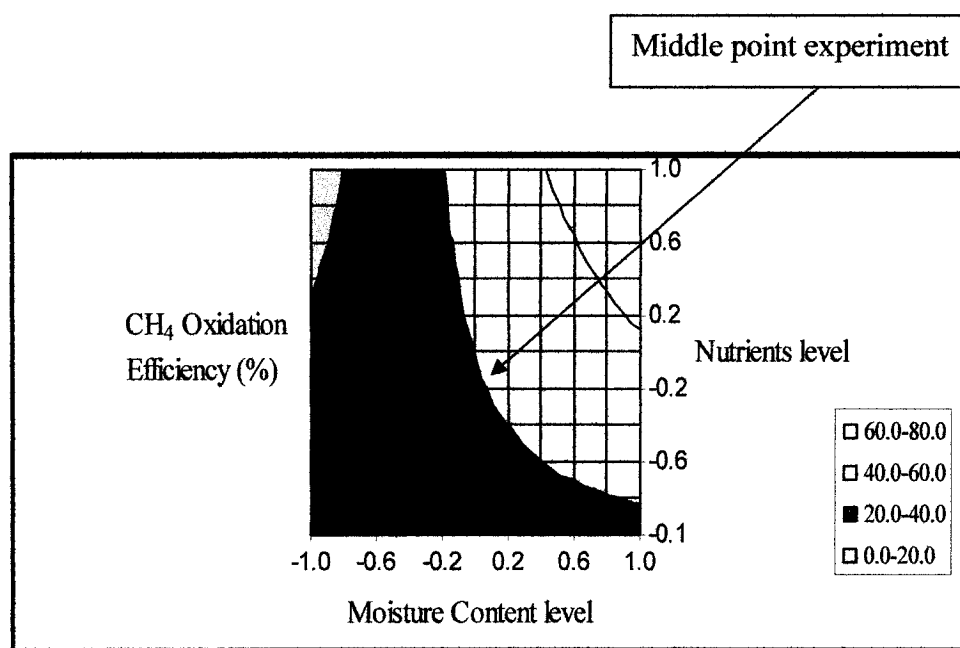


Figure 4-12 Plot of the Modeled Maximum CH₄ Oxidation Efficiency (%) at Different Coded Levels of Moisture Content and Nutrient Additions

Table 4-17 Modeled Values of Maximum CH₄ Oxidation Efficiencies (%) with Different Levels of Application of Moisture Content and Nutrients

<i>Levels</i>	mc 15 %	16.5 %	18 %	19.5 %	21 %	22.5 %	24 %	25.5 %	27 %	28.5 %	30 %
Nutrients 0	23.6	26.8	30.0	33.2	33.9	34.2	34.8	35.1	35.5	36.0	36.4
10%	30.2	31.3	32.3	33.3	34.4	35.4	36.5	37.5	38.5	39.6	40.6
20%	28.3	30.0	31.6	33.3	34.9	36.6	38.2	39.9	41.5	43.2	44.8
30%	26.5	28.7	31.0	33.2	35.5	37.8	40.0	42.3	44.5	46.8	49.0
40%	24.6	27.4	30.3	33.2	36.0	38.9	41.8	44.7	47.5	50.4	53.3
50%	22.7	26.2	29.7	33.1	36.6	40.1	43.6	47.0	50.5	54.0	57.5
60%	20.8	24.9	29.0	33.1	37.2	41.2	45.3	49.4	53.5	57.6	61.7
70%	18.9	23.6	28.3	33.0	37.7	42.4	47.1	51.8	56.5	61.2	65.9
80%	17.1	22.4	27.7	33.0	38.3	43.6	48.9	54.2	59.5	64.8	70.1
90%	15.2	21.1	27.0	32.9	38.8	44.7	50.6	56.6	62.5	68.4	74.3
100%	13.3	19.8	26.3	32.9	39.4	45.9	52.4	58.9	65.5	72.0	78.5

In Figure 4-12, the coded x-axis represents the levels of soil moisture content. The coded level is between (-1) which represents 15% soil moisture and (+1) which represents 30% soil moisture content. In between these coded levels, moisture content changes in equal levels, for example the code (-0.8) represents 16.5% moisture content, (-0.4) represents 19.5% soil moisture content, (0) represents 22.5% soil moisture content and (0.6) represents 27% moisture content. The same can be said about nutrients coded level, where (-1) represents no nutrients added and (+1) represents nutrient additions (1.5 g of fertilizer/kg of soil). The codes in between represents the added percentage, for

example (-0.8) represents 10% of (1.5 g of fertilizer/kg of soil) added nutrients. (-0.4) represents 30% of added nutrients, (0) represents 50% of added nutrients and (0.6) represents 80% of added nutrients.

It can be noticed from this Figure 4-10 and Table 4-17 that the modeled maximum CH₄ efficiency for the middle point (where moisture content is 22.5% and 50% nutrients added) is 40%. The experimental value of maximum CH₄ oxidation efficiency of the middle point was 46%. As for the experiment where the nutrients were added to the soil contained 30% moisture, the modeled maximum CH₄ oxidation efficiency is 79%, while the experimental maximum CH₄ oxidation efficiency was 81%. The model showed that the combination of higher levels of moisture content and nutrient additions is more desirable, and higher CH₄ oxidation efficiencies can be obtained from the interaction between these two parameters. The model results showed very good agreement with the experimental results.

The model was verified using all the experimental CH₄ maximum oxidation efficiency results. Table 4-18 shows the comparison between the experimental CH₄ oxidation efficiency results and the modeled results.

Table 4-18 Comparison between the Experimental and the Modeled Maximum CH₄ Oxidation Efficiencies

Run No.	Moisture Content (mc) (%)	Nutrients Addition	Maximum Experimental CH ₄ Oxidation Efficiency (%)	Maximum Modeled CH ₄ Oxidation Efficiency (%)
1 and 2	15	Not added	Average = 32	24
3 and 4	30	Not added	Average = 36	36
5	22.5	50% addition	46	40
6 and 7	15	Added	Average = 14	13
8 and 9	30	Added	Average = 78	79

Table 4-18 shows that the model described the experimental results very well. Furthermore, model results of maximum CH₄ oxidation efficiency (Table 4-17) were compared with Stein et al. (2001) study, which indicated that maximum experimental CH₄ oxidation rate obtained was 26% with 15% soil moisture content and without adding nutrients to the landfill cover soil. According to the statistical model results it is expected to get 24% maximum oxidation efficiency with such moisture content level. These experimental results are also in agreement with the statistical model in this study.

Such a model can simulate the CH₄ oxidation efficiency of landfill cover soil by applying knowledge about the factors that influence this process. Also, the model can assist in the design of biological cover soil and evaluate a candidate landfill cover soil, using similar batch experiments with the suggested factorial design, and then the generated statistical model can be used to reduce the number of laboratory experiments required to select the recommended operational parameters in such a landfill cover soil.

CHAPTER 5 –MATHEMATICAL DESCRIPTION of CH₄ OXIDATION PROCESS IN HETEROGENEOUS BATCH

This chapter deals with the application of a mathematical description of CH₄ oxidation process, to provide a quantitative understanding of the biological and physical processes related to the CH₄ oxidation process in landfill cover soils in such a heterogeneous closed batch system.

5.1 THE CONCEPTUAL MODEL

CH₄ reaction rate with time and CH₄ reaction rate with substrate utilization shown in Figures 4-6 and 4-7, provided in *Chapter 4*, illustrate that CH₄ oxidation process has two reaction phases in the heterogeneous batch experiments, namely:

- CH₄ oxidation during the bacterial growth phase: in this phase the CH₄ oxidation reaction can be described by the physical transport of CH₄ from the higher concentrations in the headspace to the lower concentrations in the soil pores by diffusion, and the biological reaction resulting from the microbial activities in the soil.

- CH₄ oxidation during the bacterial decay phase: In this phase CH₄ oxidation reaction can be described by a declining first order reaction, due to the decay of bacteria as a result of oxygen or essential nutrients limitations in the closed reactor.

5.1.1 CH₄ OXIDATION DURING BACTERIAL GROWTH PHASE

In this phase, CH₄ was transported physically from the headspace gas to the bacteria in the soil, through the soil pore voids, by diffusion, as a result of a gradient from the higher concentrations in the headspace to the lower concentrations in the soil voids. The solubility of CH₄ in the water in the soil pores was calculated and was found to be low, in comparison to the CH₄ concentration in the headspace gas. Calculation of CH₄ solubility in the water is included in *Appendix A, section A.13*. Initially, an equal concentration of CH₄ in the headspace gas and the soil pores was assumed. Since there was a biological CH₄ oxidation reaction resulting from the microbial growth and activities in the soil, and the bacteria consumed CH₄ and oxidized it to CO₂ and water for energy yield while another fraction was incorporated into biomass, therefore, the biological oxidation of CH₄ by the bacteria resulted in CH₄ depletion in the soil pores, which resulted in lower concentrations of CH₄ in the soil pores. A gradient was produced from the higher concentration of CH₄ in the headspace gas to the lower concentration of CH₄ in the soil pores. Diffusion was the responsible mechanism for the movement of CH₄ from the headspace gas to the soil pores. The biological CH₄ oxidation reaction continued in the soil. The CH₄ concentration in the headspace gas was adjusted by conducting mass

balances repeatedly, which were linked to the concentration gradient of CH_4 at the soil interface. In the experiments, the change in the headspace gas concentration was measured with time. This change in CH_4 concentration was assumed to be a result of the biological oxidation of CH_4 by methanotrophs in the soil pores.

Figure 5-1 illustrates the system boundaries and the relation between the CH_4 in the headspace gas and the soil.

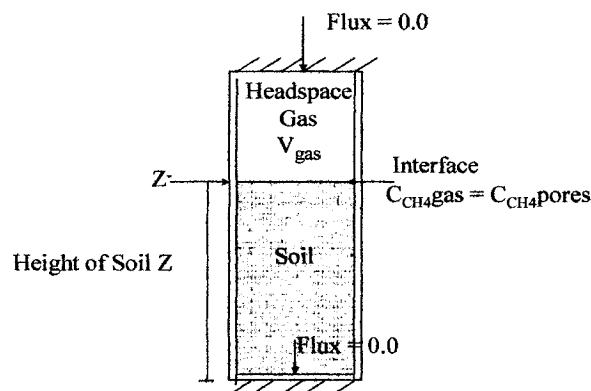


Figure 5-1 System Boundaries of the Batch Reactor

Since there was no continuous flow into the system as indicated in Figure 5-1, the system boundaries were no flow boundaries. Therefore, it was assumed that diffusion was the primary mechanism for CH_4 to move between the gas phase and the soil pores. In the soil, microbial reactions generated CH_4 reductions, as a consequence CH_4 diffused from the headspace gas where it was at a higher concentration into the soil pores. At the

interface of the gas and soil phases the concentration of CH_4 was assumed to be the same. It was assumed also that the CH_4 in the headspace was well mixed.

The reduction in CH_4 concentrations in the batch reactor was caused by the bacterial reaction, and since this reaction occurred in the soil, Figure 5-2 illustrates a control volume that represents the soil, and mass balance around the soil control volume. At the gas-soil interface, and at time=0.0, the CH_4 concentration in the soil was assumed to be equal to the CH_4 concentration in the headspace gas.

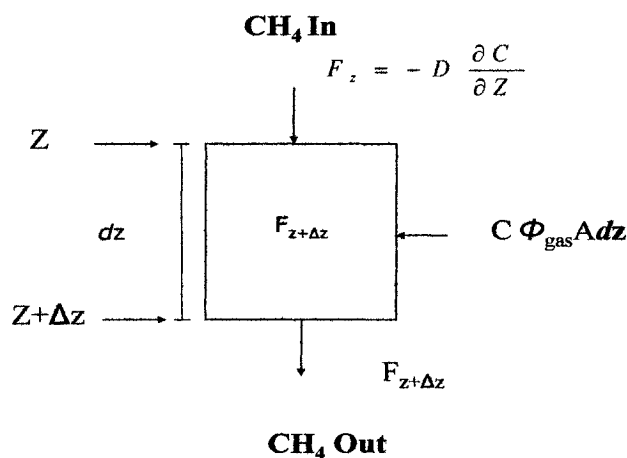


Figure 5-2 Control Volume Representing soil

where, C is the CH_4 concentration, $\phi_{\text{gas}} A dz$ is the volume occupied by gas, A is the control volume area, ϕ_{gas} is the gas filled soil porosity, R is the biological reaction, Z is the height of soil.

The general mass balance equation within the system boundary around the soil control volume, is shown in equation (5-1),

$$\begin{aligned} \text{Rate of accumulations of CH}_4 \text{ within the system control volume} &= (\text{Rate of flow of CH}_4 \\ \text{into the system control volume}) &- (\text{Rate of flow of CH}_4 \text{ out of the system control volume}) - \\ (\text{Rate of CH}_4 \text{ consumed within the system control volume}) &\quad (5-1) \end{aligned}$$

The rate of change of CH₄ in the differential volume is given by:

$$\phi_{gas} A dz \cdot \frac{\partial C}{\partial t} \quad (5-2)$$

This is equal to the net rate of CH₄ transported into the reactor, less the amount consumed by the reaction:

$$\left[F_z - F_{(z+\Delta z)} \right] A - R A dz \quad (5-3)$$

giving,

$$\phi_{gas} A dz \cdot \frac{\partial C}{\partial t} = \left[F_z - F_{(z+\Delta z)} \right] A - R A dz \quad (5-4)$$

we have:

$$F_z = -D \left. \frac{\partial C}{\partial z} \right|_z$$

$$F_{z+\Delta z} = -D \left. \frac{\partial C}{\partial z} \right|_{z+\Delta z}$$

Substituting these flux expressions into the balance equation and dividing by Adz gives:

$$\phi_{gas} \frac{\partial C}{\partial t} = \frac{\left[D \frac{\partial C}{\partial z} \Big|_{z+\Delta z} - D \frac{\partial C}{\partial z} \Big|_z \right]}{dz} - R \quad (5-5)$$

In the limit as dz approaches 0, we have:

$$\phi_{gas} \frac{\partial}{\partial t} = \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right) - R, \text{ which can be rewritten as:}$$

$$\phi_{gas} \frac{\partial C_{CH_4}}{\partial t} = D \frac{\partial^2 C_{CH_4}}{\partial z^2} - R_{CH_4} \quad (5-6)$$

$$\text{where } R_{CH_4} = V \max \left(\frac{C_{CH_4}}{C_{CH_4} + K_{CH_4}} \right)$$

Then, the CH_4 concentration in the headspace is decreased with each time step, by conducting mass balances which are linked to the CH_4 concentration at the soil interface, to reflect the amount of CH_4 transported across the interface.

Equation 5-6 describing the CH_4 transport and biological reaction is similar to other models in the literature except that Equation 5-6 is more simplified, since there is no velocity gradient in the heterogeneous batch system in this experiment.

5.1.2 CH₄ OXIDATION DURING THE DECAY PHASE

Because oxygen and essential nutrients are required for biological CH₄ oxidation process and bacterial growth, lack of sufficient oxygen or essential nutrients can be limiting factors for the CH₄ oxidation process. In the decay phase and due to oxygen limitations inside the closed reactor, the decay rate usually follows first-order kinetics (Metcalf & Eddy, 1991; Droste, 1997). The first order decay model in this phase is described as,

$$\frac{dC_{CH_4}}{dt} = -K_d * C_{CH_4} \quad (5-7)$$

where, dC/dt is the rate of change of CH₄ concentration with time in the decay phase (μmoles), K_d is the first order decay rate constant (day^{-1}), t is the time (day), C_{CH_4} is the concentration of CH₄ substrate (μmoles), the negative sign indicates an initial concentration decrease.

A plot of $\ln C_{CH_4}$ versus time yields a straight line of negative slope equals to $-K_d$.

5.2 NUMERICAL METHODS

The two main equations that represent the phases of CH₄ oxidation process, Equations (5-6) and (5-7), were solved numerically.

As for Equation (5-6), a finite volume approach was chosen to approximate the differential equation. Patankar (1980) assigned steps that were followed to discretize and

solve this partial differential equation, using the mentioned Finite Control Volume Method. The method outlined in Patankar (1980) was followed to solve the partial differential equation (5-6). Detailed numerical solution is included in *Appendix C*, following the details outlined by Patankar (1980) and following the implicit scheme. The solution of the discretized equation for the one-dimensional situation was obtained by the standard Gaussian elimination method and the algebraic equations indicated in *Appendix C*.

As for the decay phase, Equation (5-7) demonstrates the reaction during the decay phase. First order reaction occurs at a rate that is proportional to the concentration of CH₄ in the substrate. The numerical solution of Equation (5-7) is shown in *Appendix C*.

5.3 BOUNDARY CONDITIONS

The boundary conditions were defined for the system as follows:

- At the interface between the soil surface and headspace gas, CH₄ concentrations were equal.

$C_{CH_4}^*(t) = C_{CH_4}(t)$ at $Z = Z^-$ at the interface between headspace gas and soil.

- $(-D \frac{\partial C_{CH_4}}{\partial z} = 0)$ at $Z = 0$ (5-8)

- The initial concentration of CH₄ in the headspace gas was assumed to be the injected CH₄ which was equal to 18% v/v or around 7311 μmoles/L.
- The CH₄ concentration in the headspace was decreased with each time step to reflect the amount of CH₄ transported across the interface.

From the initial conditions, the CH₄ gas concentration at the boundary was known, then the concentration at each node was calculated using the algorithm described by Patankar (1980), as detailed in *Appendix C* from and to the soil interface.

5.4 INPUT PARAMETERS

DIFFUSION COEFFICIENT

As for diffusion coefficient, since the system was stagnant, and CH₄ concentration was fairly diluted in the gas headspace, because of this fact, the diffusion coefficient between CH₄ and air was calculated using the Equation (5-9), which was presented by Welty, Wicks, Wilson and Rorrer (2001) as follows:

$$D_{CH_4, Air} = \frac{0.001858 T^{2/3} \left(\frac{1}{M_{CH_4}} + \frac{1}{M_{Air}} \right)^{1/2}}{P \sigma_{CH_4 Air}^2 \Omega_D} \quad (5-9)$$

where,

$D_{CH_4, Air}$ the Mass diffusivity of CH₄ through Air in (m)²/sec,

T the absolute temperature = 295 K

M_{CH_4}	Molecular weight of $CH_4 = 16$ g/mole
M_{Air}	Molecular weight of Air = 29 g/mole
P	Absolute pressure, in atmospheres
$\sigma_{CH_4,air}$	Lennard-Jones parameter = 3.495 Å (Welty, Wicks, Wilson and Rorrer, 2001)
Ω_D	Collision integral for molecular diffusion = 0.992 (Welty, Wicks, Wilson and Rorrer, 2001)

The same equation was employed by Bird, Stewart and Lightfoot (2002) to calculate the binary diffusion coefficient between CH_4 and air. The diffusion coefficient calculated was equal to $D_{CH_4/Air} = (0.176 \text{ cm}^2/\text{s})$ or $(1.76 \times 10^{-5} \text{ m}^2/\text{s})$ or $(1.52 \text{ m}^2/\text{day})$. The value of calculated diffusion coefficient was compared with the diffusion coefficient value reported by Stein et al. (2001), who calculated the diffusion coefficient between O_2 and CH_4 and the value of $D_{O_2-CH_4} = 1.11 \times 10^{-5} \text{ m}^2/\text{s}$.

SOIL BULK DENSITY

Field soil bulk density was measured for the landfill cover soil as indicated in *Chapter 3* and it was found to be 1.126 g/cm^3 or 1126 kg/m^3 . The field dry bulk density value was the one used.

GAS FILLED SOIL POROSITY

Total soil porosity was around 58.45 %. The soil voids contained water and gas, since the soil tested in the experimental runs had two levels of moisture content, 15% and 30% (by weight). The calculations of gas filled porosity were based on the data from the

laboratory test according to ASTM D 698-64 T, where the total volume of the mold was $1/30 \text{ ft}^3$ which equals to 944 cm^3 . The gas filled porosity was calculated based on the volume of gas. The volume of gas was calculated from the following equations:

$$\text{Total volume} = \text{Volume of Solids} + \text{Volume of Water} + \text{Volume of gas} \quad (5-10)$$

where, the volume of the solids (cm^3) = dry soil weight / particle density (g/cm^3), and the volume of water (cm^3) = weight of water (g)/ water density (g/cm^3), so, the gas filled soil porosity (ϕ_{gas}) was calculated as follows,

$$\phi_{\text{gas}} = \frac{\text{GasVolume}(V_g)}{\text{TotalVolume}(V_T)} \times 100\% \quad (5-11)$$

From the equations (5-10) and (5-11),

- ϕ_{gas} for the soil that contained 15% moisture content = 42 % ($\text{m}^3 \text{gas}/\text{m}^3 \text{soil}$),

- ϕ_{gas} for the soil that contained 30% moisture content = 27% ($\text{m}^3 \text{gas}/\text{m}^3 \text{soil}$).

KINETIC CONSTANTS V_{max} and K_{CH_4}

From the range of kinetics obtained in *Chapter 4*, the chosen V_{max} value was 350 $\mu\text{moles}/\text{day} \times \text{kg}$ of dry soil weight and the chosen value K_{CH_4} was 382 μmoles .

DECAY RATE CONSTANT (K_d)

As mentioned in *Chapter 4*, decay rate follows first order kinetics. Since the effect of nutrient additions was evident on the decay rate constants determined, the chosen decay rate constant value was $k_d = 0.0308 \text{ day}^{-1}$ for full amount of added nutrients. For medium amount of added nutrients, the chosen decay rate constant k_d value was $= (1/2 \times 0.0308) \text{ day}^{-1}$. While, for no added nutrients, $k_d = (1/4 \times 0.0308) \text{ day}^{-1}$. For added nutrients with 15% soil moisture content, $k_d = (1/8 \times 0.0308) \text{ day}^{-1}$.

5.5 MATHEMATICAL DESCRIPTION

This mathematical description included the two phases mentioned in this chapter, and was used to calculate the headspace gas concentration profiles that can be expected during the incubation of Trail Road Landfill cover soil at the different environmental conditions specified according to this study in the closed reactors.

The mathematical description generated similar results or trends as the experimental data and appears to be working properly, and agrees conceptually with what happened in the experiments. Using the batch oxidation efficiencies as the CH_4 oxidation efficiencies in the soil gave a reasonable match indicating the diffusion wasn't a limiting process, except for experimental runs 8 and 9, where nutrients were added to soil with

30% moisture content.. Figures 5-3 and 5-4 show the mathematical description results for each experimental run compared to the experimental results.

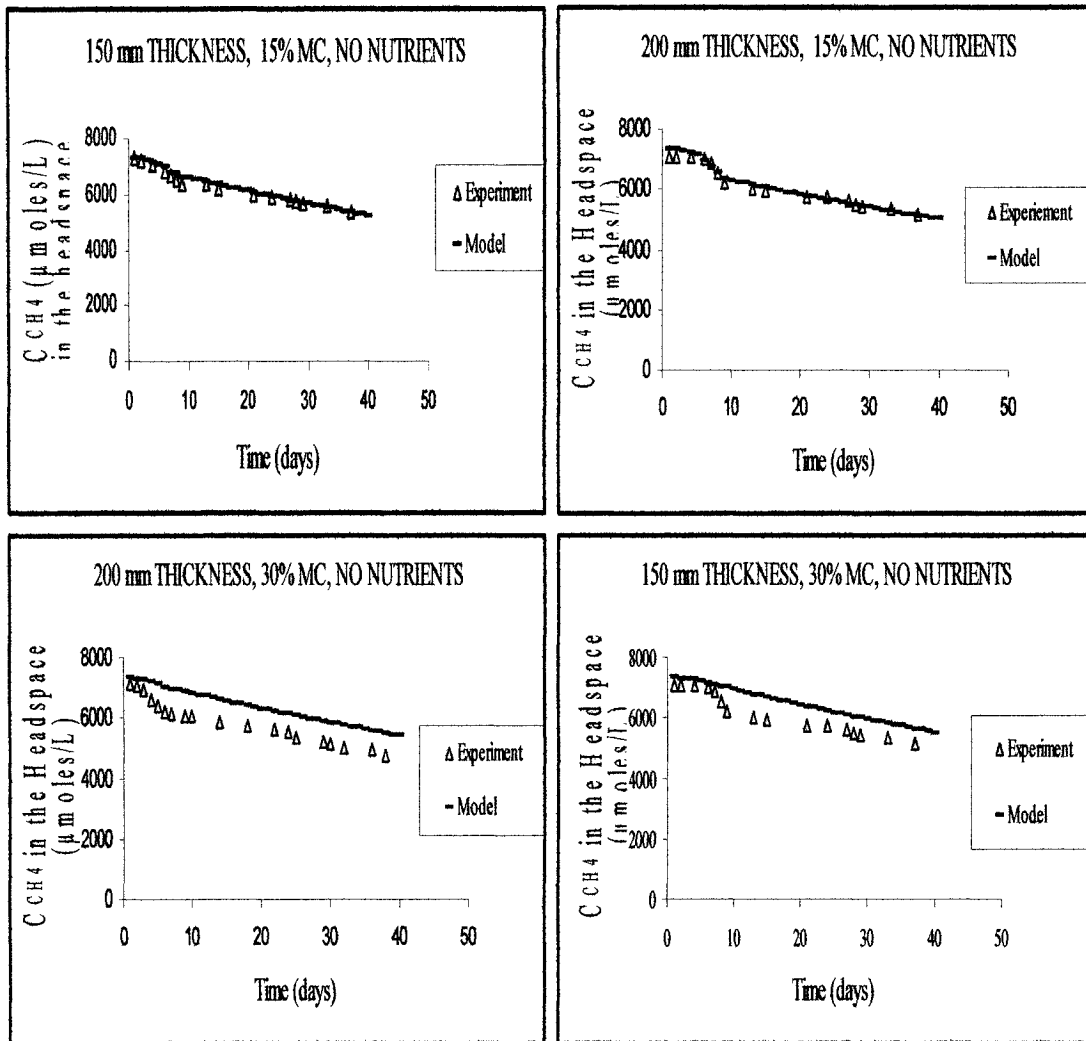


Figure 5-3

Mathematical Description of CH_4 Concentrations in the Headspace with Time, Compared to Experimental Runs with Different Layer Thicknesses, Moisture Content and Without Adding Nutrients

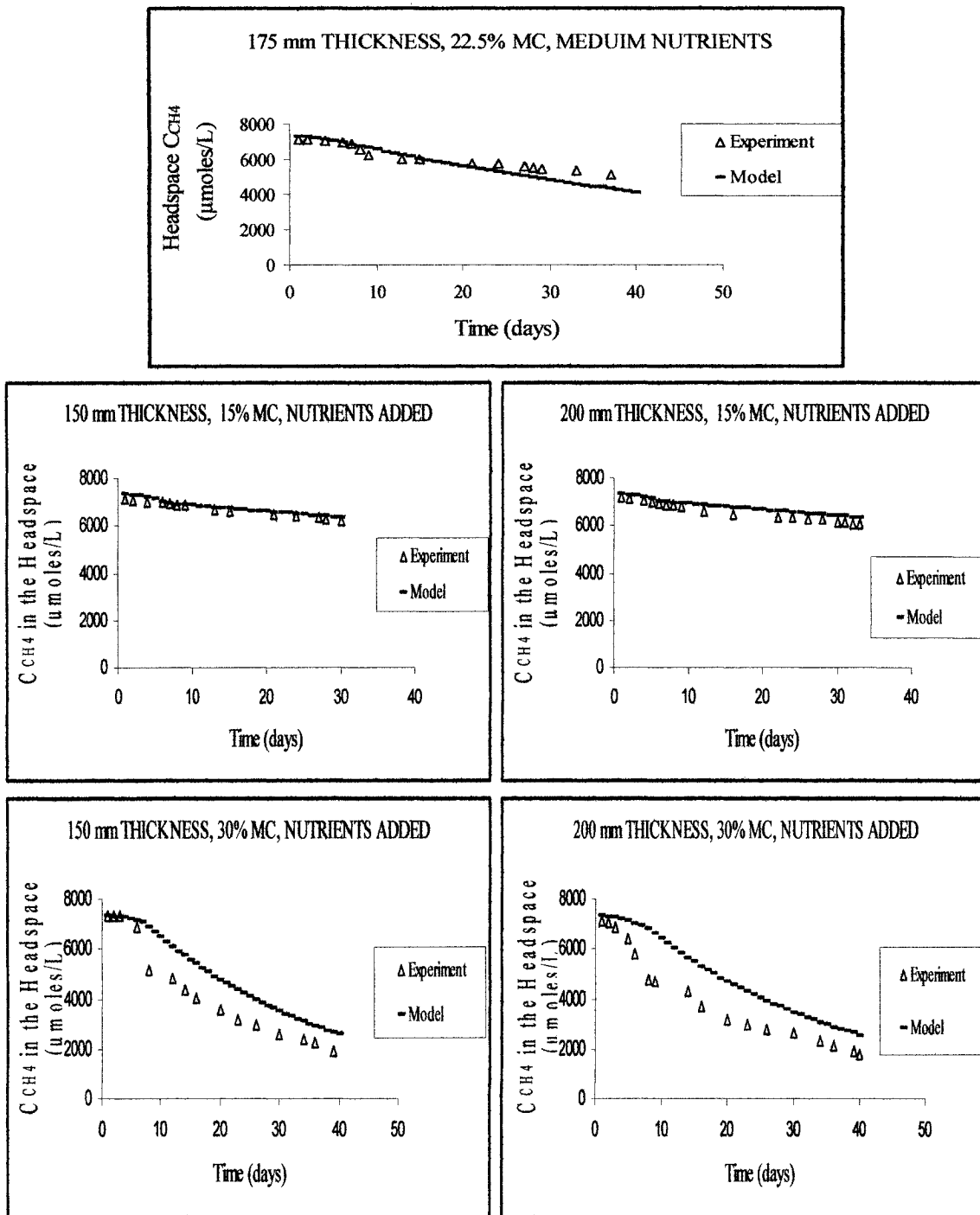


Figure 5-4

Mathematical Description of CH_4 Concentrations in the Headspace with Time, Compared to Experimental Runs with Different Layer Thicknesses, Different Moisture Content and With Nutrients

The mathematical description illustrated the experimental results closely, except for experimental runs nos. 8 and 9 where nutrients were added to the soil with higher level of moisture content and for the two layer thicknesses. This can be attributed to the limitation of diffusion in the first phase of the mathematical description in these two experiments, and therefore the value of decay constant used for the description of these two experiments. Changing the decay constant and increase it to the value of 0.04 day^{-1} instead 0.0308 day^{-1} reduced the differences between the mathematical description and the experimental results. Since the decay phase description fit all other experiments, this indicate that the process description is right, but there could be some incorrect experimental data in these two runs, which affected the calculation of decay constant and therefore the mathematical description results. Also, it can be noticed that the soil porosity values in the experiments were higher than the laboratory tested soil porosity value (the field value which was used as one of the model's input parameters), due to the compaction inside the plexiglass reactors, as discussed in *Chapter 3*, therefore, higher soil porosity in the experimental runs resulted in higher gas filled porosity (the moisture content was monitored and controlled in all the experimental runs), and this can explain the difference between the experiments and the mathematical description results.

5.6 SENSITIVITY ANALYSIS

The objective of the above mathematical description was to describe the batch reactor system and the processes in this system. The decay phase depended on the decay constant that was calculated from the experimental data. This part could not be verified with other data in the literature and the mathematical description for this phase depended on the decay constants that were calculated from the experimental results in this study. Therefore, the sensitivity analyses were only performed for the gas transport and biological reaction phase (the first phase of the mathematical description). Repeated forward runs were performed to determine the sensitivity of a certain input parameter. The following parameters were studied:

- Diffusion coefficient.
- Gas filled soil porosity (ϕ_{gas}).
- Kinetic constant (V_{max})

The following input parameters were used, unless otherwise stated:

- Diffusion Coefficient = 1.52 m²/day
- Initial CH₄ concentration in the headspace = 7300 μmoles/L
- V_{max} = 350 μmoles/day × kg of dry soil weight)
- K_{CH_4} = 382 μmoles
- Gas filled soil porosity $\phi_{gas} = 42\%$ (m³_{gas}/m³_{soil})
- Layer thickness = 150 mm

The results of the sensitivity analysis are presented in Figure 5-5 through 5-7.

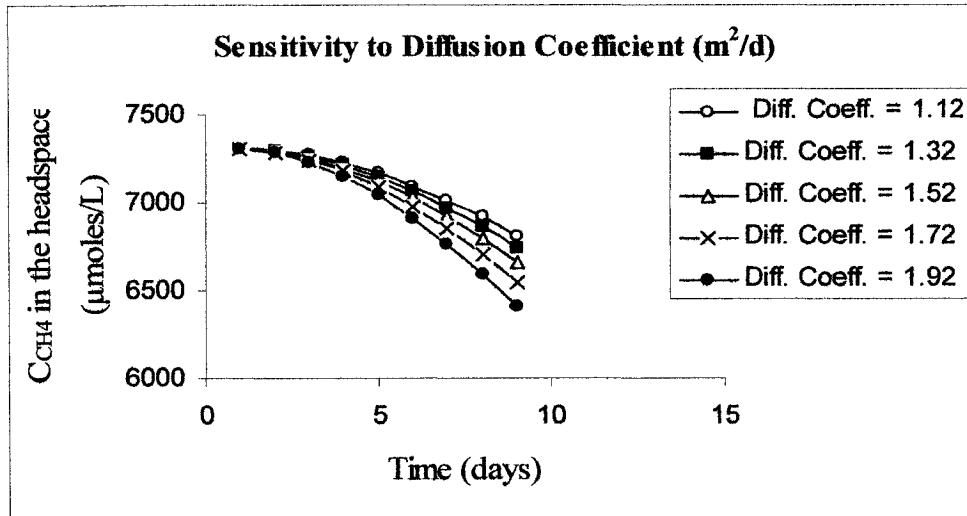


Figure 5-5 Sensitivity to Diffusion Coefficient, Performed on the Gas Physical Transport and Bacterial Growth Phase. (Diffusion coefficient = $1.52 \text{ m}^2/\text{d}$ is the calculated $D_{\text{CH}_4\text{-Air}}$ in this study, Diffusion coefficient = $1.12 \text{ m}^2/\text{d}$ is a reported $D_{\text{CH}_4\text{-soil}}$ in the literature)

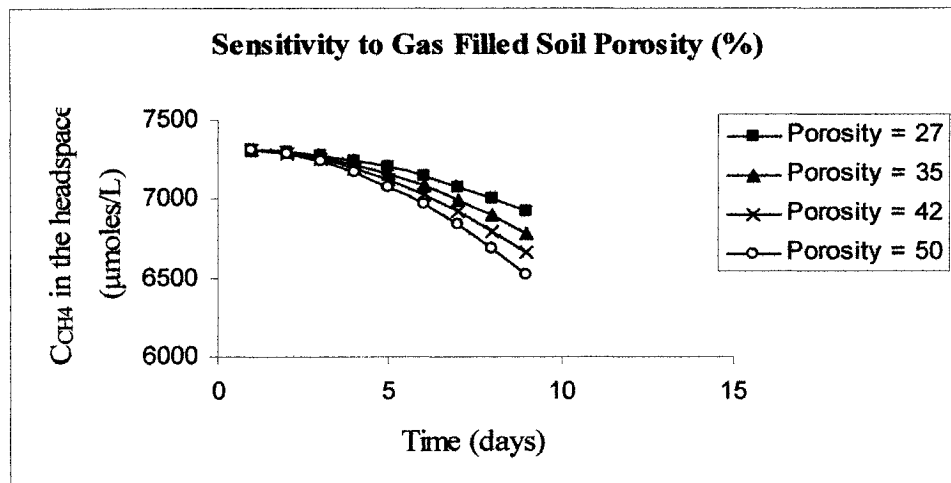


Figure 5-6 Sensitivity to Gas Filled Soil Porosity, Performed on the Gas Physical Transport and Bacterial Growth Phase. ($\phi_{\text{gas}} = 27\%$ for soil with 30% m/c, $\phi_{\text{gas}} = 35\%$ for soil with 22.5% m/c –middle point experiment–, $\phi_{\text{gas}} = 42\%$ for soil with 15% m/c).

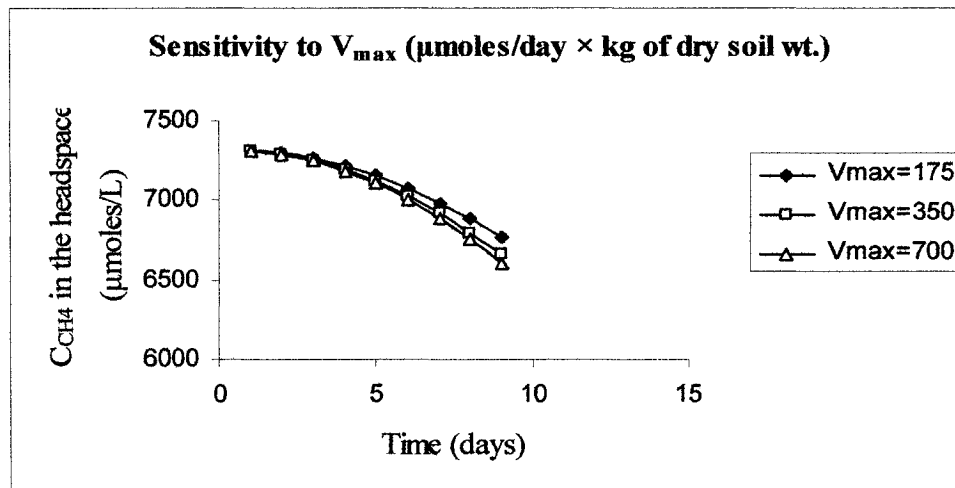


Figure 5-7 Sensitivity to V_{max} , Performed on the Gas Physical Transport and Bacterial Growth Phase (V_{max} = 350 $\mu\text{moles/day} \times \text{kg}$ of dry soil weight is the determined kinetic constant in this study)

As can be seen in Figure 5-5 to 5-7, the growth phase was sensitive mostly to diffusion coefficient and gas filled soil porosity. This result was in agreement with observation in literature and the model sensitivity analysis presented by Stein et al. (2001). According to the sensitivity analysis reported by Stein et al. (2001), the CH_4 oxidation rates increased when the diffusion coefficient values were increased and when the soil porosity values were increased. Also, the model was sensitive to the maximum CH_4 oxidation reaction rate (V_{max}), which was in agreement with DeVisscher and Cleemput (2003) sensitivity analysis. According to the sensitivity analysis presented by these authors, the CH_4 oxidation rates increased with increase of V_{max} values.

5.7 LIMITATIONS

The mathematical description of the processes in the heterogeneous batch system in this study had the following limitations:

- ❖ The diffusion coefficient used was the diffusion coefficient of CH₄ and air ($D_{\text{CH}_4\text{-Air}}$). This was assumed because the system in this study was stagnant and closed. The value of the diffusion coefficient was calculated using the empirical equation (5-9). The value determined was $D_{\text{CH}_4\text{-Air}} = 1.76 \times 10^{-5} \text{ m}^2/\text{s}$ (1.52 m²/day). This value of $D_{\text{CH}_4\text{-Air}}$ is definitely higher than the diffusion coefficient between CH₄ and soil. In fact, diffusion coefficient of CH₄ in soil ($D_{\text{CH}_4\text{-soil}}$) will be affected by soil porosity and tortuosity. These factors were not considered in calculating the diffusion coefficient in this study. The mathematical description presented neglected the effects of limiting pore space, constrictivity and tortuosity of the soil on diffusion through it. The soil tortuosity was not measured due to laboratory limitations; however, the value of diffusion coefficient used was compared with other values of diffusion coefficient in the literature. Stein et al. (2001) used the diffusion coefficient of CH₄ and O₂, and the value reported was $1.11 \times 10^{-5} \text{ m}^2/\text{s}$ (0.96 m²/day). MIT joint program on the Science and Policy of Global Warming (2004) reported diffusion coefficient of CH₄ throughout soil profile to be $1.32 \times 10^{-5} \text{ m}^2/\text{s}$ (1.14 m²/day), which is close to the value assumed in this study.

Using the $D_{\text{CH}_4\text{,Air}}$ was therefore considered adequate for describing the processes in the heterogeneous batch system. On the other hand, a more accurate equation for the calculation of $D_{\text{CH}_4\text{,soil}}$ is recommended for reliable model predictions in the future.

- ❖ O_2 concentrations and O_2 kinetic constant (K_{O_2}) were not considered when calculating the reaction rates. The O_2 concentration profiles were not determined due to equipment limitations. In these experiments, the concentrations of O_2 at the beginning and the end of the experiments were measured for the purpose of confirming that the level of O_2 was sufficient to meet reaction demands.

As a summary, the objective of the mathematical description efforts presented in this study was to illustrate the heterogeneous batch reactor and the processes in such a system. As shown in Figures (5-4) and (5-5), this mathematical description presented served as a useful tool to verify the reaction processes in the landfill cover soils that could occur in a heterogeneous batch system. The mathematical description had two phases: The first part was the gas transport and bacterial reaction phase, which was similar to models in the literature simulating the physical and biological processes occurring in the landfill cover soil.

The second part is the bacterial decay phase. This part has not been reported in the literature and it described the reaction in the decay phase that occurred in heterogeneous batch system.

The application of the mathematical description presented had limitations. It had succeeded in describing the CH_4 oxidation processes in a heterogeneous batch system, but did not simulate comprehensively the landfill cover soil and its continuous processes, where all the physical and biological processes are well evaluated and defined.

CHAPTER 6 – CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

To maintain adequate CH₄ oxidation efficiencies in the landfill cover soil, proper environmental requirements should be provided. A quantitative study of three factors influencing the microbial oxidation of CH₄ is presented in this thesis. These factors are: the effect of moisture content, the effect of soil layer thickness, and the effect of nutrient additions. To investigate statistically the individual and combined effect of these three factors on the CH₄ oxidation process, a full factorial 2³ experimental design using heterogeneous batch reactors was conducted. Soil used in the experiment was obtained from an active landfill cover soil that contained cells of the methanotrophic bacteria. The design of this batch experiment was different than other batch experiments in literature in this field. The size of each batch reactor was 320 mm in length and 100 mm in diameter. These soil batch reactor experiments afforded the opportunity to evaluate whether the use of heterogeneous batch experiments is a valid technique for estimating the maximum CH₄ oxidation capacity of landfill cover soil. Encouraging results were obtained from this study, and heterogeneous batch experiments reflected CH₄ oxidation capacity of the soil under different environmental conditions, in a shorter period of time compared to continuous columns.

In all experimental runs the CH₄ oxidation efficiency increased with time indicating the growth of a microbial community capable of oxidizing CH₄. Maximum CH₄ oxidation efficiencies were different under different experimental operating conditions.

Another important finding in this study is the combined effect of nutrient addition to the soil with higher level of moisture content. Adding nutrient source increased the CH₄ oxidation efficiencies for the soil with 30% moisture content and 200 mm layer thickness from 38% to 81% and from 35% to 75% for the 150 mm layer thickness. The percentage increase in the maximum CH₄ oxidation efficiency due to the nutrient addition combined with higher level of moisture content (30%) was in the range of 112% to 122%. Commercial fertilizer that contains the essential nutrients of nitrogen, phosphorus and potassium can be source of nutrients for methanotrophs in the landfill cover soil when the moisture is adequate. The C-N-P ratio (based on CH₄-C only) should be studied for the nutrient source to meet the demand of the methanotrophs, which are aerobic bacteria. On the other hand, adding nutrient to the soil with low level of moisture content decreased the CH₄ maximum oxidation efficiency. This is an important experimental result. It is concluded that the bacteria need moisture in order for nutrients to increase the CH₄ oxidation capacity of the soil.

Increasing the moisture content from 15% to 30% increased the CH₄ oxidation efficiencies by 11% to 18%. Soil moisture content is a critical physical constraint and it affects the movement of gas through the soil pores. With higher moisture the microbes

can rapidly consume CH_4 and this consequently increases the microbial activities. It was also hypothesized that microbial water stress was preventing the development of a larger methanotrophic community.

Increasing the soil layer thickness from 150 mm to 200 mm increased the CH_4 oxidation efficiencies by a range from 7% to 12%. Decision makers should consider this increase in the CH_4 oxidation efficiency in comparison with the cost incurred by increasing the soil thickness and the cost of maintenance for this layer.

A statistical model was developed that has the capability of predicting CH_4 oxidation efficiencies with changing levels of soil moisture content and nutrient additions. This model was competent and can reduce the laboratory efforts of experimentally obtaining the CH_4 oxidation efficiencies in such landfill cover soil.

This study evaluated the kinetic constants from a heterogeneous batch system, where CH_4 reached the bacteria by diffusion. Kinetic constants were calculated using SYSTAT 11. The values of V_{\max} were between 31 and 699 $\mu\text{moles/d} \times \text{kg}$ of dry soil weight. The K_{CH_4} values were between 4 and 2025 μmoles . Although the batch design is different than others in the literature, the range of the kinetics constant (V_{\max}) in this experiment was in agreement with the biological kinetics constant (V_{\max}) values documented in literature, especially with previous studies that used the fertilizers as nutrient sources.

6.2 RECOMMENDATIONS

- The kinetic constants in this study were calculated based on heterogeneous batch system results. It is acknowledged that these constants should be compared with biological kinetic constants for the same soil and the same environmental conditions in a well mixed batch system.
- When a type of soil is selected for an oxidative cover, it is fundamental to study the moisture content within the soil. This is a site specific parameter, and depends on climate variability and type of vegetation prevalent in that environment. Higher moisture content levels can decrease the oxidizing capacity of the landfill cover soil, presumably due to the decrease in the gas diffusion between the soil and the gas phase. Gas diffusion is limited when the soil pores are water saturated. Also, lower levels of moisture content can decrease the oxidation capacity of the soil due to the response to water stress, which will decrease microbial activities.
- Encouraging results were obtained from this study. It is recommended to use samples of soil from other environments, taken at different seasons. This will increase our knowledge and complement this research about the microbial CH_4 consumptions in landfill cover soils.
- In this study, the additions of nutrient source, and the soil moisture content were very important parameters affecting the CH_4 oxidation process. It is recommended to study vegetation effect on this system. Vegetation could compete with CH_4 consuming microbes for nutrients and water. This may decrease the overall CH_4 consumption.

REFERENCES

- Akesson, M. and Nilsson, P. (1998), "Material Dependence of Methane Production Rates in Landfills," *Waste Management Resources*, 16: 2, pp. 108- 118.
- Al-Jayyousi, O., Kattan, P. (1998), *Scientific Research for Engineers*, Dar Al-Manahej, Amman, Jordan.
- American Water Works Association (1999), *Water Quality and Treatment*, McGraw-Hill, INC, New York.
- Anex, R. (1996), "Optimal Waste Decomposition- Landfill as Treatment Process," *Journal of Environmental Engineering*, 122, pp. 964- 974.
- Anthony, C. (1982), *The Biochemistry of Methylootrophs*, Academic Press, London, Toronto, Canada.
- ASTM (1993), *Annual Book for ASTM Standards- Soil and Rock; Dimension Stone; Geosynthetics*, Volume 04.08
- Bender, M. and Conrad, R. (1995a), "Flux Estimates from Soil Methanogenesis and Methanotrophy: Landfills, Rice Paddies, Natural Wetlands and Aerobic Soils," *Environmental Monitoring and Assessment*, 42, pp. 189-207.
- Bender, M. and Conrad, R. (1995b), "Effect of CH₄ Concentrations and Soil Conditions on the Induction of CH₄ Oxidation Activity," *Pergamon- Soil Biol. Biochem.*, 27, pp. 1517- 1527.
- Bendtsen, A.B., Glarborg, P., and Dam-Johansen, K. (2001), "Visualization Methods in Analysis of Detailed Chemical Kinetics Modeling," *Computers and Chemistry*, 25, pp. 161- 170.
- Berthouex, Paul Mac and Brown, Linfield C. (1994), *Statistics for Environmental Engineers*, Lewis Publishers, Boca Raton, Florida 33431, U.S.A.
- Bird, B., Stewart, W. and Lightfoot E. (2002), *Transport Phenomena*, John Wiley & Sons, New York, U.S.A.

- Boeckx, P. and Van Cleemput, O. (1996a), "Methane Emission From a Landfill and the Methane Oxidizing Capacity of its Covering Soil," *Soil Biol. Biochem.*, 28, pp. 1397-1405.
- Boeckx, P. and Van Cleemput, O. (1996b), "Methane Oxidation in a Neutral Landfill Cover Soil: Influence of Moisture Content, Temperature, and Nitrogen Turnover," *Environmental Qual.*, 25 (1996), pp. 178- 183.
- Boeckx, P. and Van Cleemput, O. (1996c), "Flux Estimates from Soil Methanogenesis and Methanotrophy: Landfills, Rice Paddies, Natural Wetlands and Aerobic Soils," *Environmental Monitoring and Assessment*, 42 (1996), pp. 189- 207.
- Boeckx, P., Van Cleemput, O., Villaralvo I. (1997), "Methane Oxidation in Soils With Different Textures and Land Use," *Nutrient Cycling in Ecosystems*, 49, pp. 91-95.
- Bogner, J., Spokas, K., Burton, E., Sweeney, R., Corona, V., (1995), "Landfill As Atmospheric Methane Source and Sinks," *Chemosphere*, 31, pp. 4119-4130.
- Bogner, J., Spokas, K., Burton, E.A. (1997), "Kinetics of Methane Oxidation in a Landfill Cover Soil: Temporal Variations, a Whole-Landfill Oxidation Experiment and Modeling of Net CH₄ Emissions," *Environmental Science Technology*, 31, pp. 2504-2514.
- Borjesson, G. and Svensson, B.H. (1996), "Seasonal and Diurnal Methane Emissions From a Landfill and Their Regulation by Methane Oxidation," *Waste Management & Research*, 15 (1997), pp. 33-54.
- Borjesson, G., Sundh, I., Tunlid, A., Frostegard, A., Svensson, B.H. (1998), "Microbial Oxidation of CH₄ at High Partial Pressures in an Organic Landfill Cover Soil under Different Moisture Regimes," *FEMS Microbiology Ecology*, 26, pp. 207-217.
- Borjesson, G., Sundh, I., Svensson, B.H. (2004), "Microbial Oxidation of CH₄ at Different Temperatures in Landfill Cover Soils," *FEMS Microbiology Ecology*, 48, pp. 305-312.
- Brun, A. and Engesgaard, P. (2001), "Modelling of Transport and Biogeochemical Processes in Pollution Plumes: Literature Review and Model Development," *Journal of Hydrology*, 256 (2002), pp. 211-227.

- CEC- Commissions of the European Communities (1996),” Strategy Paper for Reducing Methane Emissions”: 15.11.1996 COM (96) 557, Belgian Federal Department for the Environment.
- Chan, A.S.K and Parkin, T.B. (2000), “Evaluation of Potential Inhibitors of Methanogenesis and Methane Oxidation in a Landfill Cover Soil,” *Soil Biology & Biochemistry*, 32, pp. 1581-1590.
- Climate Change Journal, An Editorial Essay (2002) , “Mitigating the Rate and Extent of Global Warming,” *Climate Change*, 52, 255 – 262.
- Czepiel, P.M., Mosher, B., Crill, P.M., Harris R.C. (1996a), “Quantifying the Effect of Oxidation on Landfill Methane Emissions,” *Journal of Geophysical Research*, 101, pp. 16.721-16.729.
- Czepiel, P.M., Mosher, B. and Harris, R.C. (1996b), “Landfill Methane Emissions Measured by Enclosure and Atmospheric Tracer Method,” *Journal of Geophysical Research*, 101, pp. 16.711-16.719.
- Czepiel, P.M., Shorter, J.H., Mosher, B., Allwine, E., McManus, J.B., Harris, R.C., Kolb, C.E., Lamb, B.K. (2003), “The Influence of Atmospheric Pressure on Landfill Methane Emissions,” *Waste Management*, 23, pp. 593-598.
- Das, B. M. (2001), *Principles of Geotechnical Engineering*, Brooks/Cole- Thomson Learning, U.S.A.
- De Visscher, A. and Van Cleemput, O. (2003), “Simulation Model for Gas Diffusion and Methane Oxidation in Landfill Cover Soils,” *Waste Management*, 23, pp. 581-591.
- De Visscher, A. and Schippers, M. (2000), “Short-Term Kinetic Response of Enhanced Methane Oxidation in Landfill Cover Soils to Environmental Factors,” *Biol. Fertile Soils*, 33 (2001), pp. 231-237.
- Droste, R.L. (1997), *Theory and Practice of Water and Wastewater Treatment*, John Wiley & Sons, Inc., New York, U.S.A.
- Dote, Y. (2002), “Kinetics of CH₄ Oxidation in Mixed Cultures,” *Waste Management and Research*, 20, pp. 494- 500.

- Dubey, S.K. and Singh, J.S. (2001), "Plant-Induced Spatial Variations in the Size of Methanotrophic Population in Dry land and Flooded rice Agroecosystems," *Nutrient Cycling in Agroecosystems*, 59, 161- 167.
- Dubey, S.K. (2003), "Spatio-Kinetic Variation of Methane Oxidizing Bacteria in Paddy Soil at Mid-tillering: Effect of N-Fertilizers," *Nutrient Cycling in Agroecosystems*, 65, pp. 53- 59.
- El-Fadel, M., Findikakis, A.N., Leckie, J.O. (1995), "Environmental Impacts of Solid Waste Landfilling," *Journal of Environmental Management*, 50 (1997), pp. 1-25.
- El-Fadel, M., Findikakis, A.N., Leckie, J.O. (1995), "Numerical Modelling of Generation and Transport of Gas and Heat in Landfills: I. Model Formulation," *Waste Management and Research*, 14 (1996), pp. 483-504.
- El-Fadel, M., Findikakis, A.N., Leckie, J.O. (1995), "Numerical Modelling of Generation and Transport of Gas and Heat in Landfills: II. Model Application," *Waste Management and Research*, 14 (1996), pp. 537-551.
- El-Fadel, M., Findikakis, A.N., Leckie, J.O. (1995), "Numerical Modelling of Generation and Transport of Gas and Heat in Landfills: III. Sensitivity Analysis," *Waste Management and Research*, 15 (1997), pp. 87-102.
- El-Fadel, M., Findikakis, A.N., Leckie, J.O. (1995), "Migration and Atmospheric Emissions of Landfill Gas," *Hazardous Waste & Hazardous Materials*, 12, pp. 309-327.
- El-Fadel, M., Findikakis, A.N., Leckie, J.O. (1996), "Estimating and Enhancing Methane Yield from Municipal Solid Waste," *Hazardous Waste & Hazardous Materials*, 13, pp. 309-331.
- Environment Canada (March 1995), Pollution Data Presentation.
- Fernandes, L., Warith, M.A. and La Forge, F. (1996), "Modelling of Contaminant Transport within a Marshland Environment," *Waste Management*, 16, pp. 649- 661.
- Garzon, L. (2004), "Microbial and Temperature: A Semi Empirical Approach," *Origins of Life and Evolution of the Biosphere*, 34, pp. 421-438.
- Gebert, J., Groengroeft, A., Miehlich, G. (2003), "Kinetics of Microbial Landfill Methane Oxidation in Biofilters," *Waste Management*, 23, pp. 609-619.

- Gowing, A.L.(2001), *Measuring and Modelling of Landfill Gas Emissions*, PhD Thesis, University of Waterloo, Waterloo, Ontario, Canada.
- Hanson, R. and Hanson, T.E. (1996), "Methanotrophic Bacteria," *Microbiological Reviews*, 60, pp. 439- 471.
- Hilger, H., Cranford, D., Barlaz, M. (1999), "Methane Oxidation and Microbial Exopolymer Production in Landfill Cover Soil," *Soil Biology and Biochemistry*, 32 (2000), pp. 457-467.
- Hilger, H. and Barlaz, M. (2002), "Anaerobic Decomposition of Refuse in Landfills and Methane Oxidation in Landfill Cover Soils," In *Manual of Environment Microbiology*. Hurst C.J., Crawford R.L., Knudsen G.R., McInernery M.C., and Stezenback L.D.(Eds.), ASM Press, Washington, D.C., 696-717.
- Hilger, H. and Humer, M. (2003), "Biotic Landfill Cover Treatments for Mitigating Methane Emissions," *Environmental Monitoring and Assessment*, 84, pp. 71-84.
- Horz, H.P., Raghubanshi, A.S., Heyer, J., Kammann, C., Conrad, R., Dunfield, P.F. (2002), "Activity and Community Structure of Methane-Oxidising Bacteria in a Wet Meadow Soil," *FEMS Microbiology Ecology*, 41 (2002), pp. 247- 257.
- Inubushi, K., Sugii, H., Watanabe, I and Wassmann, R. (2002), "Evaluation of Methane Oxidation in Rice Plant-Soil System," *Nutrient Cycling in Agroecosystems*, 64, pp. 71- 77.
- Intergovernmental Panel on Climate Change, (1995), *IPCC Working Group I Summary for Policymakers*, Cambridge, UK: Cambridge University Press.
- Islam, J. and Singhal N. (2001), "A One-Dimensional Reactive Multi-Component Landfill Leachate Transport Model," *Environmental Modeling & Software*, 17 (2002), pp. 531-543.
- Jeongdae, I., Jae Young K., Kyoungphile N. (2003), "Methane Oxidation in Landfill Cover Soil; Mathematical Simulation of Influence of Soil Porosity on Methane Oxidation," School of Civil, Urban and Geosystem Engineering, Seoul National University, San 56-1, Shilim-dong, Gwanak-ku, 151-742, Seoul, Korea.
- Kightley, D., Nedwell, D.B., Cooper, M. (1995), "Capacity for Methane Oxidation in Landfill Cover Soils Measured in Laboratory-Scale Soil Microcosms," *Appl. Environ. Microbiol.*, 61, pp. 592-601.

- Kjeldsen, P., Dalager, A. and Broholm, K. (1997), "Attenuation of Methane and Nonmethane Organic Compounds in Landfill Gas Affected Soils," *Air & Waste Management*, 47, pp. 1268- 1275.
- Knaebel, K.S. and Reinhold, H. (2002), "Landfill Gas: From Rubbish to Resource," *Adsorption*, 9, pp. 87- 94.
- Ley, T., Stevens, R., Topielec, R., Neibling, T. (2004), "*Soil Water Monitoring and Measurements*," Washington State University, CEPublications, Washington, U.S.A.
- Liu, Ch. and Evett, J. (1997), "*Soil Properties- Testing, Measurement and Evaluation*," Prentice Hall , Upper Saddle River, NJ, U.S.A.
- Masters, G.M. (1996), *Introduction to Environmental Engineering and Science*, Prentice Hall, Upper Saddle River, New Jersey, U.S.A.
- Matthews, R.B., Wassmann, R., Buendia, L.V. and Knox, J.W. (2000), "Using a Crop/Soil Simulation Model and GIS Techniques to Assess Methane Emissions from Rice Fields in Asia," *Nutrient Cycling in Agroecosystems*, 58, pp. 161-177.
- McDougall, J.R. and Pyrah, I.C. (1999), "Moisture Effects in a Biodegradation Model for Waste Refuse", Proceedings Sardinia 99, Seventh International Waste Management and landfill Symposium, Cagliari, Italy.
- Meadows, M. (1996), "Estimating Landfill Methane Emissions," *Pergamon - Energy Convers. Mgmt*, 37, pp. 1099-1104.
- Meadows, G. and Wiesenmayer, R. (1999), "Identifying and Addressing Students' Alternative Conceptions of the Cause of Global Warming: The Need for Cognitive Conflict," *Journal of Science and Technology*, 8, pp. 235 -239.
- Metcalf and Eddy (1991), *Wastewater Engineering: Treatment, Disposal, and Reuse*, McGraw-Hill, New York, U.S.A.
- Meyerson, F. (1998), "Population, Development and Global Warming: Averting the Tragedy of the Climate Commons," *Population and Environment: A Journal of Interdisciplinary Studies*, 19, 443- 463.

- MIT Joint Program on the Science and Policy of Global Change (2004), "Methane Fluxes Between Terrestrial Ecosystems and the Atmosphere at Northern High Latitudes During the Past Century: A Retrospective Analysis with a Process-Based Biochemistry Model", Cambridge, MA.
- Montgomery, Douglas (1997), *Design and Analysis of Experiment*, John Wiley & Sons, Inc., New York, U.S.A.
- Park, S.Y., Brown, K.W. and Thomas, J.C. (2003), "The use of Biofilters to Reduce Atmospheric Methane Emissions from Landfills," *Water, Air, and Soil Pollution*, 155, pp. 63- 85.
- Patankar, Suhas V. (1980), *Numerical Heat Transfer and Fluid Flow*, Hemisphere Publishing Corporation, New York, U.S.A.
- Pfiffner, S.M., Palumbo, A.V., Phelps, T.J. and Hazen, T.C. (1997), "Effects of Nutrient dosing on Subsurface Methanotrophic Populations and Trichloroethylene Degradation," *Journal of Industrial Microbiology and Biotechnology*, 18, pp. 204 -212
- Postma, D. and Jakobsen, R. (1996), "Redox Zonation: Equilibrium Constraints on the Fe(III)/SO₄⁻ Reduction Interface," *Geochimica et Cosmochimica Acta.*, 60, pp. 3169-3175.
- Powrie, W. and White, J. (2004), "Landfill Process Modeling," *Waste Management*, 24, pp.225-226.
- Prommer, H., Barry, D.A., Davis, G.B. (1999), "A One Dimensional Reactive Multi-Component Transport Model for Biodegradation of Petroleum Hydrocarbons in Groundwater," *Environmental Modelling & Software*, 14, pp. 213-223.
- Reid, R.C., Prausnitz, J.M., Sherwood, T.K. (1996), *The Properties of Gases and Liquids*, McGraw-Hill Book Co., Inc., New York, NY, U.S.A.
- Reynolds, T. and Richards, P. (1996), *Unit Operations and Processes in Environmental Engineering*, PWS Publishing Company, Boston, MA., U.S.A.
- Ridgwell, A. J., Marshall, S.J., Gregson, K. (1999), "Consumption of Atmospheric Methane by Soils: A Process-based Model," *Global Biogeochemical Cycles*, 13, pp. 59- 70.

- Riemer, P. (1996), "Greenhouse Gas Mitigation Technologies, an Overview of the CO₂ Capture, Storage and Future activities of the IEA Greenhouse Gas R&D Program," *Pergamon – Energy Convers. Mgmt*, 37, pp. 665- 670.
- Salvage, K., Yeh, G.T. (1998), "Development and Application of a Numerical Model of Kinetic and Equilibrium Microbiological and Geochemical Reactions (BIOKEMOD)," *Journal of Hydrology*, 209, pp. 27-52.
- Savvichev, A.S., Rusanov, I.I., Yusupov, S.K., Pimenov, N.V., Lein, A. Yu., and Ivanov, M.V. (2004), "The Biogeochemical Cycle of Methane in the Coastal Zone and Littoral of the Kandalaksha Bay of the White Sea," *Microbiology*, 73, pp. 457- 468.
- Scheutz, C., Mosbaek, H., Kjeldsen, P. (2004), "Attenuation of Methane and Volatile Organic Compounds in Landfill Soil Covers," *Environmental Quality*, 33, pp. 61-71.
- Schnell, S. and King, G.M. (1995), "Stability of Methane Oxidation Capacity to Variations in Methane and Nutrient concentrations," *FEMS Microbiology Ecology*, 17, pp. 285-294.
- Shin, H.C., Park, J.W., Park, K., Song, H.C., (2001), "Removal Characteristics of Trace Compounds of Landfill Gas by Activated Carbon Adsorption," *Environmental Pollution*, 119(2002), pp. 227 – 236.
- Stein, V.B. (2001), *A Numerical Model for Biological Oxidation and Migration of Methane in Soils*, M.A.Sc. Thesis, University of Calgary, Alberta, Canada.
- Tebes-Stevens, G., Valocchi, A.J., VanBriesen, J.M, Rittmann, B.E. (1998), "Multicomponent Transport with Coupled Geochemical and Microbiological Reactions: Model Description and Example Simulations," *Journal of Hydrology*, 209, pp. 8-26.
- USEPA: 1999a, "Inventory of Greenhouse Gas Emissions and Sinks 1990-1997, Office of Policy and Planning and Evaluation, U.S. Environmental Protection Agency, Washington, DC; EPA 236-R-99-003, <http://www.epa.gov/globalwarming/inventory/1999-inv.html>.
- Van Breukelen, B.M., Griffioen, J., Roling, W.F.M., Van Verseveld, H.W. (2003), "Reactive Transport Modeling of Biogeochemical Processes and Carbon Isotope Geochemistry Inside a Landfill Leachate Plume," *Journal of Contaminant Hydrology*, 70 (2004), pp. 249-269.

- Wang, B. and Adachi, K. (2000), "Differences Among Rice Cultivars in Root Exudation, Methane Oxidation, and Populations of Methanogenic and Methanotrophic Bacteria in Relation to Methane Emissions," *Nutrient Cycling in Agroecosystems*, 58, pp. 349-356.
- Warith, M. (2001), "Bioreactor Landfills: Experimental and Field Results," *Waste Management*, 22 (2002), pp. 7-17.
- Welty, J., Wicks, C., Wilson, R., Rorrer, G. (2001), *Fundamentals of Momentum, Heat, and Mass Transfer*, John Wiley & Sons, Inc., New York, U.S.A.
- Westlake, K. (1997), "Sustainable landfill- possibility or pipe-dream?" *Waste Management and Research*, 15, pp. 453-461.
- Whalen, S.C., Reeburgh, W.S. and Sandeck, K.A. (1990), "Rapid Methane Oxidation in a Landfill Cover Soil," *Applied and Environmental Microbiology*, 56, pp. 3405- 3411.
- Whalen, S.C. and Reeburgh, W.S. (1996), "Moisture and Temperature Sensitivity of CH₄ Oxidation in Boreal Soils," *Soil Biol. Biochem.*, 28, pp.1271-1281.
- White, J., Robeinson, J., Ren, Q. (2004), "Modelling the Biochemical Degradation of Solid Waste in Landfills," *Waste Management*, 24, pp. 227-240.
- Willison, T.W., O'Flaherty, M.S., Tlustos, P., Goulding, K.W.T. and Powelson, D.S. (1997), "Variations in Microbial Populations in Soils with Different Methane Uptake Rates," *Nutrients Cycling in Agroecosystems*, 49, pp. 85- 90.
- Wilshusen, J.H., Hettiaratchi, J.P.A., De Visscher, A., Saint-Fort, R. (2004), "Methane Oxidation and Formation of EPS in Compost: Effect of Oxygen Concentration", *Environmental Pollution*, 129, pp. 305-314.
- Wilshusen, J.H., Hettiaratchi, J.P.A., Stein, V.B. (2004), "Long-Term Behavior of Passively Aerated Compost Methanotrophic Biofilters Columns," *Waste Management*, 24, pp. 643-653.
- Wuebbles, D.J. and Hayoe, K. (2002), "Atmospheric Methane and Global Change," *Earth-Science Review*, 57, pp. 177-210.
- Zacharof, A.I. and Butler, A.P. (2004), "Stochastic Modeling of Landfill Leachate and Biogas Production Incorporating Waste Heterogeneity. Model Formulation and Uncertainty Analysis," *Waste Management*, 24, pp. 453-462.

APPENDIX A – EXPERIMENTAL DATA & CALCULATIONS

A.1. EXPERIMENTAL RUN No. 1

A.1.1. Gases in the Reactor Headspace, with Time, for Experimental Run No. 1 (15% MC, 150 mm Layer Thickness and No Nutrients Added).

No. of Days	CH ₄ Concentration in the headspace (1) (%v/v)	CO ₂ Concentration in the headspace (2) (%v/v)	CH ₄ Oxidized (3) (%)	CH ₄ in the Headspace (4) (μmoles/L)	Substrate (5) (μmoles)	Reaction Rate (6) (μmoles/d × kg of dry.s.w)
1	17.7		0.0	7311	0	0
2	17.6		0.7	7260	40	48
4	17.1		3.1	7086	177	70
6	16.6		6.4	6844	367	87
7	16.2		8.3	6702	478	95
8	15.8		10.5	6543	604	102
9	15.5	1.3	12.6	6393	721	107
13	15.3	1.4	13.4	6331	770	76
15	15.0	1.6	15.0	6215	861	73
21	14.4	1.9	18.4	5969	1054	63
24	14.4	2.0	18.6	5933	1082	56
27	14.1	2.1	20.1	5840	1155	53
28	13.9	2.1	21.7	5725	1245	55
29	13.7	2.4	22.8	5644	1309	55
33	13.5	2.7	23.5	5591	1350	50
37	12.9	2.9	27.0	5338	1549	51
41	12.6	2.9	28.7	5213	1647	49
42	12.6	2.9	28.7	5215	1646	48
43	12.5	2.9	28.8	5209	1651	47
44	12.6	2.9	28.7	5215	1646	45
45	12.6	2.9	28.7	5211	1649	44
46	12.7	2.9	28.7	5213	1647	43
47	12.7	2.9	28.7	5213	1647	42
48	12.6	2.9	28.7	5215	1646	42

A.1.2. DATA ANALYSIS USING SYSTAT SOFTWARE-
EXPERIMENTAL RUN No. 1

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME1.SYD,
 created Wed May 11, 2005 at 16:29:25, contains variables:
 V S

Iteration No.	Loss	VMAX	KCH4
0	0.118545D+04	0.101000D+03	0.102000D+03
1	0.228960D+03	0.111261D+03	0.698634D+02
2	0.222949D+03	0.110233D+03	0.707539D+02
3	0.222942D+03	0.110286D+03	0.709787D+02
4	0.222941D+03	0.110299D+03	0.710317D+02
5	0.222941D+03	0.110303D+03	0.710441D+02
6	0.222941D+03	0.110303D+03	0.710471D+02

Dependent variable is V

Zero weights, missing data or estimates reduced degrees of freedom

Source	Sum-of-Squares	df	Mean-Square
Regression	45367.340	2	22683.670
Residual	222.941	5	44.588
Total	45590.281	7	
Mean corrected	8651.969	6	

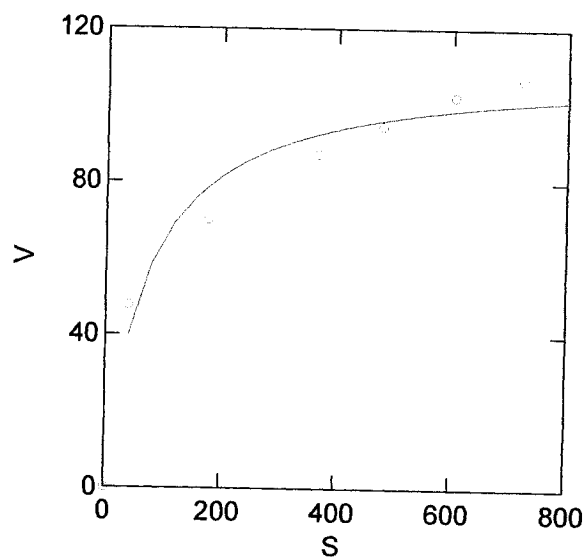
Raw R-square (1-Residual/Total)	=	0.995
Mean corrected R-square (1-Residual/Corrected)	=	0.974
R(observed vs predicted) square	=	0.975

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval	
				Lower < 95%>	Upper
VMAX	110.303	6.119	18.027	94.574	126.032
KCH4	71.047	20.217	3.514	19.076	123.018

Case	V Observed	V Predicted	Residual
1	0.000	0.000	0.000
2	47.651	39.840	7.811
3	69.964	78.702	-8.738
4	87.133	92.424	-5.291
5	94.546	96.035	-1.489
6	102.271	98.686	3.585
7	106.931	100.411	6.520

Asymptotic Correlation Matrix of Parameters

	VMAX	KCH4
VMAX	1.000	
KCH4	0.825	1.000



A.2. EXPERIMENTAL RUN No. 2

A.2.1. Gases in the Reactor Headspace, with Time, for Experimental Run No. 2 (15% MC, 200 mm Layer Thickness and No Nutrients Added).

No. of Days	CH ₄ Concentration in the headspace (%v/v)	CO ₂ Concentration in the headspace (%v/v)	CH ₄ Oxidized (%)	CH ₄ in the Headspace (μmoles/L)	Substrate (μmoles)	Reaction Rate (μmoles/day ×kg of dry.soil.wt)
1	17.2		0.0	7105	0	0
2	17.2		0.0	7102	2	2
4	17.0		0.8	7046	46	13
6	16.9		1.7	6980	98	16
7	16.7		2.8	6903	158	22
8	15.9		7.5	6573	417	49
9	15.1	1.4	12.2	6238	680	70
13	14.6	1.5	15.0	6038	837	57
15	14.4	1.6	15.9	5971	889	52
21	13.9	1.8	19.0	5756	1059	43
24	13.9	1.9	19.4	5726	1082	39
27	13.6	2.1	20.7	5633	1155	37
28	13.4	2.3	22.3	5518	1245	38
29	13.2	2.5	23.5	5436	1309	38
33	13.0	2.5	24.3	5380	1353	35
37	12.5	2.7	27.6	5146	1537	35
41	12.1	2.8	29.5	5009	1645	34
44	11.8	3.0	31.4	4872	1752	33
47	11.8	3.0	31.2	4886	1762	31
51	11.4	3.2	33.5	4725	1868	31
53	11.2	3.3	34.8	4629	1943	31
54	11.2	3.3	34.9	4624	1947	30
55	11.2	3.3	34.8	4630	1942	30
56	11.2	3.3	34.9	4627	1944	29
57	11.2	3.3	35.0	4618	1952	29
58	11.2	3.3	35.0	4624	1947	28
59	11.2	3.3	34.8	4630	1942	28
60	11.2	3.3	34.8	4629	1943	27

**A.2.2. DATA ANALYSIS USING SYSTAT SOFTWARE -
EXPERIMENTAL RUN No. 2**

SYSTAT Rectangular file C:\Documents and Settings\muna\Desktop\Thesis
final\Batch2\ENZYME2.syd,
created Wed May 11, 2005 at 16:40:38, contains variables:
V S

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME2.SYD,
created Wed May 11, 2005 at 16:38:47, contains variables:
V S

Iteration No.	Loss	VMAX	KCH4
0	0.440343D+04	0.101000D+03	0.102000D+03
1	0.499530D+03	0.867238D+02	0.206202D+03
2	0.122256D+03	0.106881D+03	0.411845D+03
3	0.455165D+02	0.135495D+03	0.676247D+03
4	0.338958D+02	0.158625D+03	0.889411D+03
5	0.330777D+02	0.167995D+03	0.975555D+03
6	0.330608D+02	0.169593D+03	0.990067D+03
7	0.330607D+02	0.169742D+03	0.991391D+03
8	0.330607D+02	0.169753D+03	0.991496D+03
9	0.330607D+02	0.169754D+03	0.991504D+03

Dependent variable is V

Zero weights, missing data or estimates reduced degrees of freedom

Source	Sum-of-Squares	df	Mean-Square
Regression	8126.186	2	4063.093
Residual	33.061	5	6.612
Total	8159.246	7	
Mean corrected	4002.163	6	

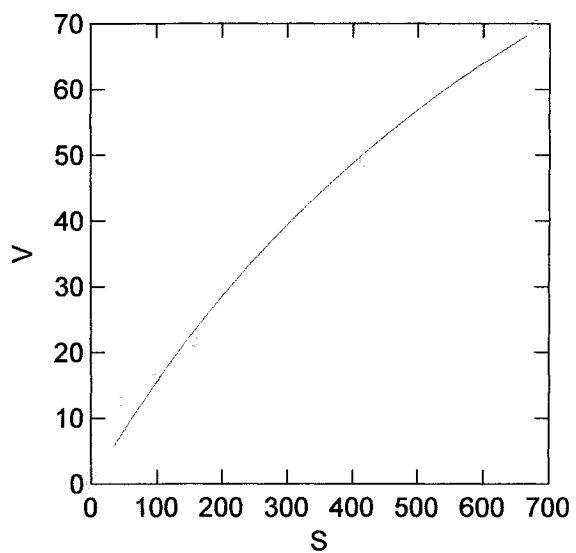
Raw R-square (1-Residual/Total)	=	0.996
Mean corrected R-square (1-Residual/Corrected)	=	0.992
R(observed vs predicted) square	=	0.993

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval	
				Lower < 95%>	Upper
VMAX	169.754	35.153	4.829	79.390	260.118
KCH4	991.504	309.455	3.204	196.023	1786.985

Case	V		Residual
	Observed	Predicted	
1	0.000	0.000	0.000
2	1.572	0.327	1.245
3	12.574	7.512	5.062
4	16.032	15.206	0.826
5	21.612	23.309	-1.697
6	48.950	50.257	-1.307
7	69.846	69.060	0.786

Asymptotic Correlation Matrix of Parameters

	VMAX	KCH4
VMAX	1.000	
KCH4	0.990	1.000



A.3. EXPERIMENTAL RUN No. 3

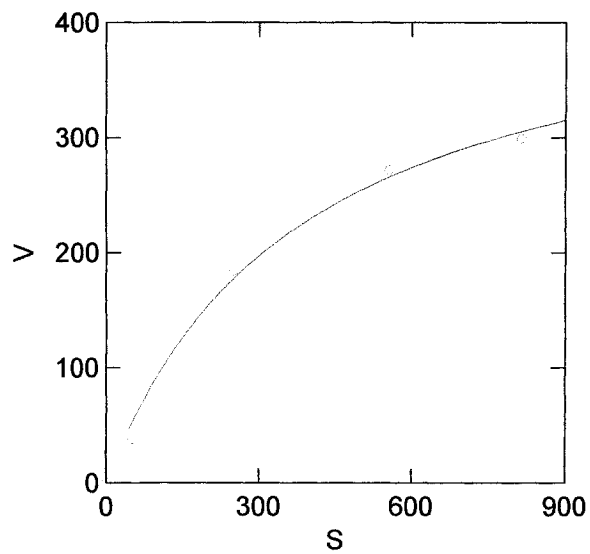
A.3.1. Gases in the Reactor Headspace, with Time, for Experimental Run No. 3 (30% MC, 150 mm Layer Thickness and No Nutrients Added).

No. of Days	CH ₄ Concentration in the headspace (%v/v)	CO ₂ Concentration in the headspace (%v/v)	CH ₄ Oxidized (%)	CH ₄ in the Headspace (μmoles/L)	Substrate (μmoles)	Reaction Rate (μmoles/day × kg of dry.soil.wt.)
1	17.8		0.0	7368	0	0
2	17.7		0.9	7302	52	30
3	17.1		4.3	7048	251	144
4	16.1		9.6	6661	554	212
5	15.3	1.4	14.1	6331	814	234
6	15.2	1.5	14.9	6273	859	197
9	14.8	1.7	17.1	6104	992	143
10	14.7	1.8	17.7	6065	1022	131
14	14.4	1.9	19.1	5964	1102	97
18	13.9	2.0	21.8	5760	1262	85
22	13.8	2.2	22.8	5690	1317	72
24	13.1	2.5	26.2	5434	1518	76
25	13.1	2.6	26.7	5402	1543	74
29	12.4	2.9	30.4	5126	1760	72
30	12.1	3.1	32.1	5004	1855	74
32	12.1	3.3	32.0	5009	1852	69
36	11.8	3.3	33.8	4874	1958	64
38	11.8	3.3	33.9	4873	1958	61
39	11.8	3.3	33.9	4873	1958	59
40	11.8	3.3	33.9	4873	1958	58
41	11.8	3.4	34.0	4860	1968	57
42	11.8	3.3	33.8	4874	1958	55
43	11.8	3.3	34.0	4864	1965	54
44	11.8	3.3	33.9	4873	1958	52
45	11.8	3.3	34.0	4866	1964	51

Case	V		Residual
	Observed	Predicted	
1	0.000	0.000	0.000
2	29.682	41.801	-12.119
3	144.013	139.002	5.011
4	212.429	207.730	4.699
5	233.884	238.768	-4.884

Asymptotic Correlation Matrix of Parameters

	VMAX	KCH4
VMAX	1.000	
KCH4	0.962	1.000



A.4. EXPERIMENTAL RUN No. 4

A.4.1. Gases in the Reactor Headspace, with Time, for Experimental Run No. 4 (30% MC, 200 mm Layer Thickness and No Nutrients Added).

No. of Days	CH ₄ Concentration in the headspace (%v/v)	CO ₂ Concentration in the headspace (%v/v)	CH ₄ Oxidized (%)	CH ₄ in the Headspace (μmoles/L)	Substrate (μmoles)	Reaction Rate (μmoles/day × kg of dry.soil.wt.)
1	17.3		0.0	7157	0	0
2	17.1		1.2	7068	70	62
3	16.7		3.4	6911	193	85
4	16.1		7.2	6644	403	119
5	15.5		10.3	6422	577	128
6	15.0		13.3	6202	750	133
7	14.9	1.3	14.1	6147	793	117
9	14.7	1.5	15.1	6077	847	94
10	14.7	1.6	15.4	6055	865	85
14	14.2	1.8	18.1	5862	1017	69
18	14.0	1.9	19.4	5771	1087	57
22	13.6	2.1	21.7	5606	1218	51
24	13.4	2.2	22.8	5528	1279	49
25	12.9	2.5	25.2	5350	1418	52
29	12.7	2.7	26.8	5240	1504	48
30	12.6	2.8	27.5	5188	1546	47
32	12.2	2.9	29.3	5057	1648	47
36	12.0	3.0	30.7	4962	1723	44
38	11.5	3.6	33.4	4767	1876	45
45	11.3	3.6	34.9	4660	1960	39
47	10.7	3.7	38.4	4409	2157	41
48	10.7	3.7	38.4	4411	2156	41
49	10.7	3.7	38.4	4409	2157	40
51	10.7	3.7	38.3	4413	2154	39
52	10.7	3.7	38.4	4411	2156	38
53	10.7	3.6	38.4	4411	2156	37

A.4.2. DATA ANALYSIS USING SYSTAT SOFTWARE- EXPERIMENTAL RUN 4

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME4.SYD,
created Wed May 11, 2005 at 12:47:18, contains variables:

V S

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME4.SYD,
created Tue Jun 14, 2005 at 06:22:39, contains variables:

V S

Iteration No.	Loss	VMAX	KCH4
0	0.380728D+04	0.101000D+03	0.102000D-02
1	0.379425D+04	0.101060D+03	0.103020D+00
2	0.268870D+04	0.107113D+03	0.104050D+02
3	0.450674D+03	0.135367D+03	0.634447D+02
4	0.134693D+03	0.148206D+03	0.103985D+03
5	0.111229D+03	0.152549D+03	0.119960D+03
6	0.110716D+03	0.153283D+03	0.122659D+03
7	0.110712D+03	0.153359D+03	0.122924D+03
8	0.110712D+03	0.153366D+03	0.122947D+03
9	0.110712D+03	0.153367D+03	0.122949D+03

Dependent variable is V

Zero weights, missing data or estimates reduced degrees of freedom

Source	Sum-of-Squares	df	Mean-Square
Regression	59015.988	2	29507.994
Residual	110.712	4	27.678
Total	59126.700	6	
Mean corrected	12951.243	5	

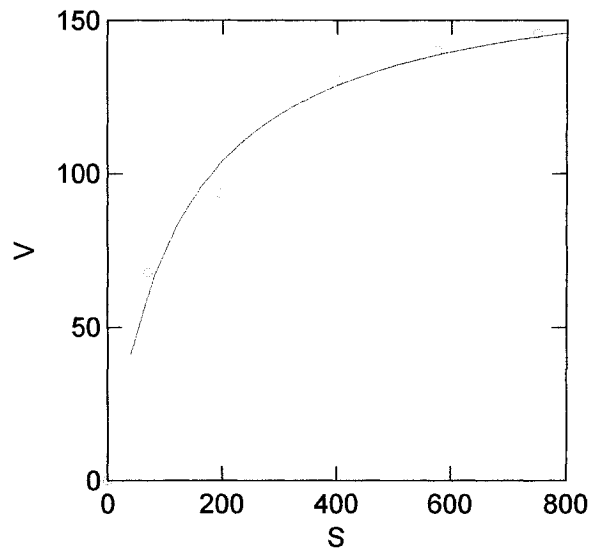
Raw R-square (1-Residual/Total)	=	0.998
Mean corrected R-square (1-Residual/Corrected)	=	0.991
R(observed vs predicted) square	=	0.992

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval	
				Lower < 95%>	Upper
VMAX	153.367	7.082	21.655	133.704	173.030
KCH4	122.949	21.341	5.761	63.698	182.200

Case	V Observed	V Predicted	Residual
1	0.000	0.000	0.000
2	61.787	55.548	6.239
3	85.486	93.723	-8.237
4	118.777	117.491	1.286
5	127.594	126.416	1.178
6	132.714	131.762	0.952

Asymptotic Correlation Matrix of Parameters

	VMAX	KCH4
VMAX	1.000	
KCH4	0.883	1.000



A.5. EXPERIMENTAL RUN No. 5 – MIDDLE POINT

A.5.1. Gases in the Reactor Headspace, with Time, for Experimental Run No. 5 (22.5% MC, 175 mm Layer Thickness and ½ Nutrients Added).

No. of Days	CH ₄ Concentration in the headspace (%v/v)	CO ₂ Concentration in the headspace (%v/v)	CH ₄ Oxidized (%)	CH ₄ in the Headspace (μmoles/L)	Substrate (μmoles)	Reaction Rate (μmoles/day × kg of dry.soil.wt.)
1	17.4		0.0	7202	0	0
2	17.3		0.6	7162	32	31
3	17.1		1.9	7064	108	54
4	16.4		5.6	6797	318	106
5	15.9		8.7	6578	490	122
6	15.4		11.8	6350	669	133
7	15.2	1.4	13.0	6269	733	122
9	14.6	1.6	16.5	6014	933	116
10	14.4	1.8	17.1	5971	966	107
12	14.4	1.8	17.5	5938	992	90
14	14.0	1.9	19.6	5793	1106	85
15	13.9	1.9	20.4	5730	1155	82
16	13.7	2.1	21.2	5675	1198	80
18	13.5	2.2	22.5	5581	1272	75
20	13.0	2.5	25.6	5355	1450	76
21	12.8	2.6	26.3	5310	1485	74
22	12.5	2.8	28.0	5185	1583	75
25	11.8	3.1	32.1	4887	1817	75
27	11.5	3.2	34.1	4743	1930	74
29	11.1	3.5	36.5	4574	2063	73
31	10.8	3.7	38.1	4458	2154	72
33	10.5	3.8	39.5	4358	2232	70
35	10.2	4.0	41.4	4222	2339	69
38	9.8	4.1	43.9	4043	2480	67
40	9.6	4.1	44.9	3967	2539	65
42	9.3	4.3	46.7	3842	2638	64
44	9.1	4.4	47.7	3768	2695	62
45	9.1	4.4	47.6	3771	2693	61
46	9.1	4.4	47.8	3760	2702	60
47	9.1	4.4	47.9	3749	2711	59
48	9.1	4.4	47.9	3754	2707	57

A.5.2. DATA ANALYSIS USING SYSTAT SOFTWARE - EXPERIMENTAL RUN 5

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME5.SYD,
created Tue Jun 14, 2005 at 10:10:04, contains variables:
V S

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME5.SYD,
created Tue Jun 14, 2005 at 10:10:04, contains variables:
V S

Iteration	No.	Loss	VMAX	KCH4
	0	0.447350D+04	0.101000D+03	0.102000D+03
	1	0.191697D+03	0.162845D+03	0.193600D+03
	2	0.105044D+03	0.174106D+03	0.209328D+03
	3	0.104977D+03	0.174594D+03	0.210490D+03
	4	0.104977D+03	0.174615D+03	0.210568D+03
	5	0.104977D+03	0.174617D+03	0.210573D+03
	6	0.104977D+03	0.174617D+03	0.210574D+03

Dependent variable is V

Source	Sum-of-Squares	df	Mean-Square
Regression	47592.730	2	23796.365
Residual	104.977	4	26.244
Total	47697.707	6	
Mean corrected	14509.946	5	

Raw R-square (1-Residual/Total)	=	0.998
Mean corrected R-square (1-Residual/Corrected)	=	0.993
R(observed vs predicted) square	=	0.993

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval	
				Lower < 95%>	Upper
VMAX	174.617	11.684	14.945	142.176	207.058
KCH4	210.574	39.565	5.322	100.724	320.423

Case	V		Residual
	Observed	Predicted	
1	0.000	0.000	0.000
2	31.468	22.761	8.707
3	53.876	59.225	-5.349
4	105.528	104.991	0.537
5	122.056	122.108	-0.052
6	133.308	132.791	0.517

Asymptotic Correlation Matrix of Parameters

	VMAX	KCH4
VMAX	1.000	
KCH4	0.936	1.000

A.6. EXPERIMENTAL RUN No. 6

A.6.1. Gases in the Reactor Headspace, with Time, for Experimental Run No. 6 (15% MC, 150 mm Layer Thickness and Nutrients Added).

No. of Days	CH ₄ Concentration in the headspace (%v/v)	CO ₂ Concentration in the headspace (%v/v)	CH ₄ Oxidized (%)	CH ₄ in the Headspace (μmoles/L)	Substrate (μmoles)	Reaction Rate (μmoles/day × kg of dry.soil.wt.)
1	17.3		0.0	7156	0	0
2	17.1		1.2	7068	69	79
4	16.9		2.2	7000	122	47
6	16.9		2.5	6980	138	31
7	16.8		3.1	6936	172	33
8	16.7		3.5	6905	197	33
9	16.6		4.3	6848	241	34
13	16.2	1.2	6.3	6702	356	34
15	16.0	1.2	7.7	6606	431	35
21	15.6	1.3	9.6	6466	541	31
24	15.5	1.3	10.5	6407	587	29
27	15.4	1.3	11.3	6349	633	28
28	15.2	1.4	12.0	6299	672	28
30	15.1	1.4	12.8	6239	719	28
31	15.1	1.4	12.8	6242	717	27
32	15.1	1.4	12.7	6244	715	26
33	15.1	1.4	12.8	6238	720	26
34	15.1	1.4	12.7	6249	712	25
35	15.1	1.4	12.9	6234	723	24

A.6.2. DATA ANALYSIS USING SYSTAT SOFTWARE - EXPERIMENTAL RUN 6

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME6.syd,
created Tue Jun 14, 2005 at 12:30:10, contains variables:

V S

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME6.SYD,
created Tue Jun 14, 2005 at 12:30:10, contains variables:

V S

Iteration

No.	Loss	VAMX	KCH4
0	0.151508D+04	0.101000D+03	0.102000D+03
1	0.698552D+03	0.530629D+02	0.102000D-04
2	0.514018D+03	0.626685D+02	0.102000D-04
3	0.514018D+03	0.626685D+02	0.102000D-04
4	0.514018D+03	0.626685D+02	0.102000D-04

Dependent variable is V

Zero weights, missing data or estimates reduced degrees of freedom

Source	Sum-of-Squares	df	Mean-Square
Regression	7854.682	1	7854.682
Residual	514.018	2	257.009
Total	8368.700	3	
Mean corrected	3132.245	2	

Raw R-square (1-Residual/Total)	=	0.939
Mean corrected R-square (1-Residual/Corrected)	=	0.836
R(observed vs predicted) square	=	0.836

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval	
				Lower < 95%>	Upper
VMAX	62.669	42.043	1.491	-118.229	243.566
KCH4	0.000	56.945	0.000	-245.013	245.013

Case	V		Residual
	Observed	Predicted	
1	0.000	0.000	0.000
2	78.700	62.668	16.032
3	46.637	62.669	-16.032

Asymptotic Correlation Matrix of Parameters

	VMAX	KCH4
VMAX	1.000	
KCH4	0.963	1.000

A.7. EXPERIMENTAL RUN No. 7

A.7.1. Gases in the Reactor Headspace, with Time, for Experimental Run No. 7 (15% MC, 200 mm Layer Thickness and Nutrients Added).

No. of Days	CH ₄ Concentration in the headspace (%v/v)	CO ₂ Concentration in the headspace (%v/v)	CH ₄ Oxidized (%)	CH ₄ in the Headspace (μmoles/L)	Substrate (μmoles)	Reaction Rate (μmoles/day × kg of dry.soil.wt.)
1	17.4		0.0	7184	0	0
2	17.3		0.6	7152	25	27
4	17.1		2.0	7078	84	30
5	17.0		2.4	7039	114	30
6	16.8		3.3	6946	187	30
7	16.7		4.0	6895	227	30
8	16.6		4.7	6848	263	30
9	16.2		5.2	6688	389	39
12	16.0		7.8	6622	441	32
16	15.7		9.6	6494	541	29
21	15.4	1.2	11.3	6370	639	26
24	15.3	1.2	11.8	6337	665	23
26	15.3	1.3	12.1	6312	684	22
28	15.2	1.3	12.3	6297	696	21
30	15.0	1.4	14.0	6180	788	22
31	14.8	1.4	14.6	6136	823	22
32	14.7	1.5	15.2	6091	858	22
33	14.7	1.5	15.6	6061	881	22
34	14.7	1.5	15.7	6059	883	21
35	14.7	1.5	15.6	6061	881	21
36	14.7	1.5	15.7	6057	885	20
37	14.7	1.5	15.7	6058	884	20

A.7.2. DATA ANALYSIS USING SYSTAT SOFTWARE - EXPERIMENTAL RUN 7

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME7.SYD,
created Thu Jun 16, 2005 at 19:04:06, contains variables:

V S

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME7.SYD,
created Thu Jun 16, 2005 at 19:04:06, contains variables:

V S

Iteration

No.	Loss	VMAX	K
0	0.274869D+04	0.101000D+02	-.102000D+02
1	0.129789D+03	0.310827D+02	0.122914D+02
2	0.588086D+02	0.328758D+02	0.556350D+01
3	0.580429D+02	0.328685D+02	0.639999D+01
4	0.580391D+02	0.328888D+02	0.648595D+01
5	0.580391D+02	0.328906D+02	0.649237D+01
6	0.580391D+02	0.328907D+02	0.649284D+01

Dependent variable is V

Zero weights, missing data or estimates reduced degrees of freedom

Source	Sum-of-Squares	df	Mean-Square
Regression	6691.961	2	3345.980
Residual	58.039	6	9.673
Total	6750.000	8	
Mean corrected	918.000	7	

Raw R-square (1-Residual/Total)	=	0.991
Mean corrected R-square (1-Residual/Corrected)	=	0.937
R(observed vs predicted) square	=	0.937

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval	
				Lower < 95%>	Upper
VMAX	32.891	1.773	18.553	28.553	37.229
K	6.493	4.561	1.424	-4.668	17.654

Case	V		Residual
	Observed	Predicted	
1	0.000	0.000	0.000
2	27.000	26.110	0.890
3	30.000	30.531	-0.531
4	30.000	31.118	-1.118
5	30.000	31.787	-1.787
6	30.000	31.976	-1.976
7	30.000	32.098	-2.098
8	39.000	32.351	6.649

Asymptotic Correlation Matrix of Parameters

	VMAX	K
VMAX	1.000	
K	0.709	1.000

A.8. EXPERIMENTAL RUN No. 8**A.8.1. Gases in the Reactor Headspace, with Time, for Experimental Run No. 8 (30% MC, 150 mm Layer Thickness and Nutrients Added).**

No. of Days	CH ₄ Concentration in the headspace (%v/v)	CO ₂ Concentration in the headspace (%v/v)	CH ₄ Oxidized (%)	CH ₄ in the Headspace (μmoles/L)	Substrate (μmoles)	Reaction Rate (μmoles/day × kg of dry.soil.wt.)
1	17.8		0.0	7368	0	0
2	17.8		0.0	7364	3	2
3	17.7		0.7	7315	41	24
4	17.4		2.5	7177	149	58
5	17.0		4.5	7068	235	68
6	16.7		6.6	6882	381	88
7	14.6	1.8	18.0	6052	1033	200
8	12.5	2.8	30.0	5161	1732	287
12	11.7	3.3	34.3	4841	1984	209
14	10.6	3.8	40.6	4374	2350	210
16	9.7	4.2	45.6	4010	2636	204
20	8.6	4.9	51.8	3551	2996	183
23	7.7	5.3	56.6	3195	3275	173
26	7.3	5.6	59.3	2999	3429	159
30	6.3	6.0	64.6	2607	3737	149
34	5.7	6.5	67.8	2370	3923	138
36	5.4	6.8	69.7	2233	4030	134
39	4.6	7.1	73.9	1920	4276	131
41	4.4	7.3	75.2	1825	4351	126
42	4.4	7.3	75.2	1827	4350	123
43	4.4	7.3	75.3	1821	4354	120
44	4.4	7.3	75.4	1816	4358	118
45	4.4	7.3	75.2	1827	4350	115
46	4.4	7.3	75.3	1821	4354	112
47	4.4	7.3	75.2	1827	4350	110

**A.8.2. DATA ANALYSIS USING SYSTAT SOFTWARE -
EXPERIMENTAL RUN No. 8**

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME8.syd,
created Tue Jun 14, 2005 at 07:04:47, contains variables:

V S

Iteration

No.	Loss	VMAX	K
0	0.485022D+05	0.101000D+03	0.102000D+03
1	0.763131D+04	0.276806D+03	0.589650D+03
2	0.122498D+04	0.446534D+03	0.124199D+04
3	0.604389D+03	0.562165D+03	0.176964D+04
4	0.567310D+03	0.608758D+03	0.200323D+04
5	0.566355D+03	0.617658D+03	0.205037D+04
6	0.566344D+03	0.618616D+03	0.205554D+04
7	0.566344D+03	0.618704D+03	0.205601D+04
8	0.566344D+03	0.618712D+03	0.205606D+04

Dependent variable is V

Zero weights, missing data or estimates reduced degrees of freedom

Source	Sum-of-Squares	df	Mean-Square
Regression	138114.656	2	69057.328
Residual	566.344	6	94.391

Total	138681.000	8
Mean corrected	72614.875	7

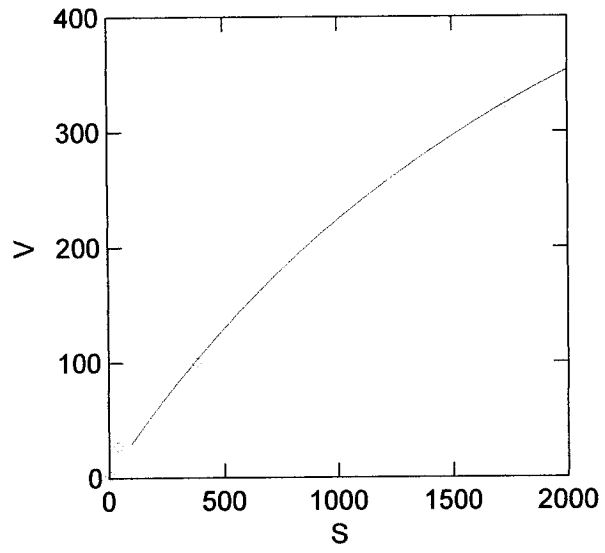
Raw R-square (1-Residual/Total)	=	0.996
Mean corrected R-square (1-Residual/Corrected)	=	0.992
R(observed vs predicted) square	=	0.994

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval	
				Lower < 95% >	Upper
VMAX	618.712	96.098	6.438	383.568	853.857
K	2056.055	510.226	4.030	807.578	3304.533

Case	V		Residual
	Observed	Predicted	
1	0.000	0.000	0.000
2	2.000	0.901	1.099
3	24.000	12.097	11.903
4	58.000	41.808	16.192
5	68.000	63.463	4.537
6	88.000	96.727	-8.727
7	200.000	206.901	-6.901
8	287.000	282.892	4.108

Asymptotic Correlation Matrix of Parameters

	VMAX	K
VMAX	1.000	
K	0.986	1.000



A.9. EXPERIMENTAL RUN No. 9**A.9.1. Gases in the Reactor Headspace, with Time, for Experimental Run No. 8 (30% MC, 200 mm Layer Thickness and Nutrients Added).**

No. of Days	CH ₄ Concentration in the headspace (%v/v)	CO ₂ Concentration in the headspace (%v/v)	CH ₄ Oxidized (%)	CH ₄ in the Headspace (μmoles/L)	Substrate (μmoles)	Reaction Rate (μmoles/day × kg of dry.soil.wt.)
1	17.3		0.0	7151	0	0
2	17.1		1.2	7068	65	58
3	16.7		3.4	6908	190	85
5	15.5		10.6	6389	598	134
6	14.0	1.8	19.1	5786	1071	192
8	11.6	3.1	33.0	4791	1853	237
9	11.3	3.2	34.7	4669	1948	218
14	10.3	3.7	40.2	4276	2256	155
16	8.9	4.5	48.6	3678	2726	163
20	7.7	5.1	55.6	3178	3119	147
23	7.2	5.3	58.6	2961	3289	134
26	6.8	5.6	60.7	2808	3409	122
30	6.4	5.8	62.8	2662	3523	109
34	5.7	6.2	67.3	2340	3776	102
36	5.1	6.5	70.5	2110	3957	101
39	4.6	6.8	73.1	1921	4105	97
41	4.4	6.9	74.8	1803	4198	94
43	3.8	7.2	77.8	1585	4369	93
45	3.6	7.3	79.0	1505	4432	90
48	3.3	7.3	80.7	1377	4532	86
50	3.2	7.5	81.4	1328	4571	84
51	3.2	7.5	81.4	1330	4569	82
52	3.2	7.5	81.4	1328	4571	80
53	3.2	7.5	81.5	1326	4573	79
54	3.2	7.5	81.4	1330	4569	77
55	3.2	7.5	81.4	1328	4571	76

**A.9.2. DATA ANALYSIS USING SYSTAT SOFTWARE -
EXPERIMENTAL RUN No. 9**

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ENZYME9.SYD,
created Wed May 18, 2005 at 15:33:44, contains variables:

Iteration No.	Loss	VMAX	K
0	0.299709D+05	0.101000D+03	0.102000D-02
1	0.299229D+05	0.101092D+03	0.103020D+00
2	0.254380D+05	0.110391D+03	0.104050D+02
3	0.560244D+04	0.193138D+03	0.112657D+03
4	0.237151D+04	0.233864D+03	0.240840D+03
5	0.149909D+04	0.261560D+03	0.369848D+03
6	0.131531D+04	0.278660D+03	0.459829D+03
7	0.128936D+04	0.286449D+03	0.502164D+03
8	0.128676D+04	0.289161D+03	0.516895D+03
9	0.128654D+04	0.289975D+03	0.521289D+03
10	0.128653D+04	0.290205D+03	0.522529D+03
11	0.128652D+04	0.290269D+03	0.522873D+03
12	0.128652D+04	0.290286D+03	0.522968D+03
13	0.128652D+04	0.290291D+03	0.522995D+03
14	0.128652D+04	0.290292D+03	0.523002D+03

Dependent variable is V

Zero weights, missing data or estimates reduced degrees of freedom

Source	Sum-of-Squares	df	Mean-Square
Regression	120291.476	2	60145.738
Residual	1286.524	4	321.631
Total	121578.000	6	
Mean corrected	38505.333	5	

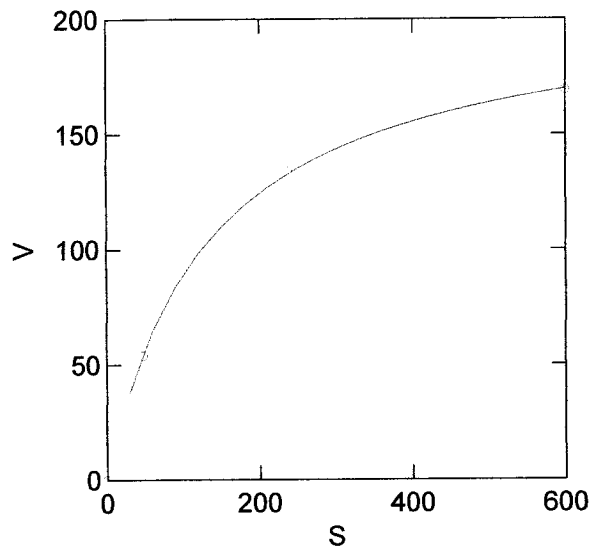
Raw R-square (1-Residual/Total)	=	0.989
Mean corrected R-square (1-Residual/Corrected)	=	0.967
R(observed vs predicted) square	=	0.972

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval	
				Lower < 95%	Upper
VMAX	290.292	38.878	7.467	182.349	398.236
K	523.002	193.068	2.709	-13.042	1059.046

Case	V Observed	V Predicted	Residual
1	0.000	0.000	0.000
2	58.000	32.090	25.910
3	85.000	77.357	7.643
4	134.000	154.857	-20.857
5	192.000	195.046	-3.046
6	237.000	226.394	10.606

Asymptotic Correlation Matrix of Parameters

	VMAX	K
VMAX	1.000	
K	0.922	1.000



A.10. CH₄ in the Headspace Gas of the Control for all Experiments

Day	Cont. 1 CH ₄ (%v/v)	Cont.2 CH ₄ (%v/v)	Cont.3 CH ₄ (%v/v)	Cont.4 CH ₄ (%v/v)	Cont.5 CH ₄ (%v/v)	Cont.6 CH ₄ (%v/v)	Cont.7 CH ₄ (%v/v)	Cont.8 CH ₄ (%v/v)	Cont.9 CH ₄ (%v/v)
1	58.76	59.16	60.05	59.94	59.11	58.76	59.73	58.76	59.35
3	58.72	59.29	60.05	59.80	59.18	58.72	59.72	58.93	59.07
5	58.24	59.77	60.01	59.79	59.20	58.24	59.24	58.51	58.94
7	58.11	59.23	60.07	59.31	59.15	58.11	59.19	58.23	58.89
9	58.49	59.29	60.04	59.35	59.08	58.09	59.12	57.75	58.77
11	58.21	59.32	60.01	59.55	59.04	57.95	59.08	57.62	58.68
13	58.13	59.01	60.07	59.14	59.07	57.98	58.96	57.71	58.59
15	57.89	58.79	59.99	59.15	58.72	57.76	58.89	57.33	58.24
17	57.35	58.56	59.55	58.98	58.31	57.65	58.63	57.39	57.99
19	57.45	58.41	59.45	58.91	58.45	57.44	58.47	56.87	57.97
21	57.35	58.15	59.50	58.65	58.01	57.19	58.29	56.72	57.88
23	57.27	58.24	59.10	58.75	58.05	56.98	58.12	56.68	57.84
25	57.14	58.04	58.75	58.61	57.69	56.91	58.09	56.20	57.79
27	56.94	57.81	58.70	58.04	57.51	56.94	57.93	56.05	57.74
31	56.88	57.73	58.01	58.31	57.24	56.87	57.87	55.99	57.63
33	56.63	57.23	57.83	58.01	56.98	56.68	57.31	55.97	57.64
35	56.57	56.66	57.68	57.84	56.73	56.71	56.94	55.89	57.28
37	56.41	56.81	57.50	57.64	56.77	56.65	56.91	55.86	56.98
39	56.29	56.53	57.39	57.70	56.62	56.53	56.93	55.83	56.87
41	55.96	56.50	57.20	57.55	56.33	56.58	56.86	55.84	56.66
43	55.98	56.39	57.05	57.01	56.09	56.47	56.83	55.78	56.61
45	55.91	56.42	56.95	57.09	55.93	56.43	56.72	55.75	
47	55.86	56.33		56.96	55.93	56.02	56.70		
49				56.98	55.95				
51				56.75	55.91				
53				56.73	55.90				

A.11 EXPERIMENTAL SOIL BULK DENSITY AND POROSITY

The soil bulk density and porosity values in all the experiments were calculated for consistency. These experimental values are higher than the soil field bulk density and porosity, and this is due to the compaction inside the plexiglas reactors and therefore the bulk density of soil samples.

Experimental Run	Weight of dry soil (g)	Volume (cm ³)	Experiment Bulk Density (dry) (g/cm ³)	Experiment Soil Porosity
1-A	958	1099	0.87	0.680
1-B	930	1099	0.84	0.689
2-A	1237	1500	0.83	0.69
2-B	1251	1500	0.84	0.688
3-A	967	1099	0.88	0.675
3-B	975	1099	0.887	0.673
4-A	1245	1500	0.83	0.69
4-B	1220	1500	0.81	0.698
5-A	1090	1295	0.84	0.688
5-B	1120	1295	0.865	0.679
6-A	980	1099	0.89	0.67
6-B	970	1099	0.88	0.674
7-A	1253	1500	0.84	0.688
7-B	1247	1500	0.83	0.69
8-A	948	1099	0.86	0.683
8-B	982	1099	0.891	0.67
9-A	1300	1500	0.86	0.68
9-B	1240	1500	0.84	0.687

A.12. MASS BALANCE SAMPLE CALCULATION

(This sample calculation is for experimental run no. 1, where no nutrients were added to 150 mm soil layer thickness that contained 15% moisture).

- Base line GC reading where 140 ml of CH₄ is assumed is 60.47%. A GC reading at the beginning of this experimental run was 60.01%. Calculate corrected volume of CH₄ =
 $0.14 \times (60.01/60.47) = 0.139 \text{ L or } 139 \text{ ml or } 1.39 \times 10^{-4} \text{ m}^3$.
- Calculate headspace volume = $3.14 \times r^2 \times L =$
 $= 3.14 \times (0.05)^2 \times (0.1) = 7.85 \times 10^{-4} \text{ m}^3$.
- Calculate number of CH₄ moles in the headspace gas at the beginning of the experiment using ideal gas law:
 $P V = n R T$
 and using correction for temperature. $R = 8.2057 \times 10^{-2}$. Pressure = 1 atm. Temp. = 295 K.
 The number of CH₄ moles in the headspace = 5.73×10^{-3} moles in the beginning of the experiment.
- Percentage concentration of CH₄ in the beginning of the experiment =
 $1.39 \times 10^{-4} \text{ m}^3 / 7.85 \times 10^{-4} \text{ m}^3 = 17.7\%$ Actual concentration of CH₄
- Headspace gas in the reactor had the atmospheric air, so the volume of air in the headspace = $7.85 \times 10^{-4} \text{ m}^3$.
- Percentage of O₂ in the air = 20%. Therefore, the volume of O₂ in the beginning of the experiment = $7.85 \times 10^{-4} \text{ m}^3 \times 20\% = 1.57 \times 10^{-4} \text{ m}^3$.
- Number of O₂ moles calculated at the beginning of the experiment using ideal gas law and corrected for temperature = 6.085×10^{-3} moles.
- According to the reaction equation: each 1 mole of CH₄ will consume 1.5 moles of O₂.

 Number of CH₄ moles consumed in the experiment = 5730.516 μmoles – 4084.35 μmoles (according to the experiment results) = 1646.962 μmoles.
- Therefore, number of O₂ moles consumed in the experiment = 1646.962 μmoles × 1.5 = 2470.443 μmoles.
- O₂ moles remaining in the headspace = 6085 μmoles – 2470.443 μmoles = 3615 μmoles of O₂ available in the headspace gas at the end of the experiment.

- Calculate the volume of O₂ remaining in the headspace gas (using ideal gas law and corrections) = 0.081206 Liters = $8.12 \times 10^{-5} \text{ m}^3$.
- Percentage of O₂ remaining in the headspace gas = $(8.12 \times 10^{-5} / 7.85 \times 10^{-4}) \times 100\% = 10.3\%$.
- The GC reading for O₂ concentration at the end of the experiment was 9.8%.
- Carbon Dioxide (CO₂) :

According to the reaction equation, each mole of consumed CH₄ will produce 0.529 moles of CO₂

- Amount of CH₄ consumed in this experiment was = 5730 – 4084 = 1646 μmoles
- Amount of CO₂ produced = 1646 × 0.529 = 871 μmoles at the end of the experiment.
- Convert CO₂ moles to volume using ideal gas law and corrections = 0.023 Liters = $2.3 \times 10^{-5} \text{ m}^3$.
- Percentage of CO₂ in the headspace gas at the end of the experiment = $(2.3 \times 10^{-5} \text{ m}^3 / 7.85 \times 10^{-4} \text{ m}^3) \times 100 = 2.93\%$.
Compare to GC reading = 3.2%.

A.13. METHANE SOLUBLE IN THE SOIL PORES

- o Mass of CH₄ in the gas = Volume of gas × concentration of CH₄ =
 = 0.785 L × 7311 μmoles/L = **5740 μmoles in the headspace gas**
 Mass of CH₄ = (5740/1000,000) mole × 16 g/mole = 0.092 g the mass of CH₄ in
 the headspace gas.
- o The volume of the water in the soil = 302 cm³ (0.3 L) for the soil that contained
 30% moisture, and 157 cm³ (0.157 L) for the soil that contained 15% moisture
 content. These data were obtained from the laboratory tests and for a sample in
 the volume of 1/30ft³.
- o Henry's Law Constant of CH₄ = 28.7 (L_{H₂O}/L_{air}) – (American Water Works
 Association, 1999)
 Convert to H (L.atm/mole):
 $H (L_{H_2O}/L_{air}) = H (L.atm/mol) / R T$
 Where R = 0.08205 (atm.L /mol K)
 So, Henry's Law Constant = 694.7 L.atm/mole
- o Molecular mass of CH₄ soluble in 30% moisture content= (Volume of Liquid ×
 Partial Pressure)/K_H of CH₄
 = 4.35 × 10⁻⁴ moles is the mass of CH₄ in the liquid.
 = **435 μmoles of CH₄ in the water**
 So, the mass of CH₄ in the water = 7 × 10⁻³ g.
- o Molecular mass of CH₄ soluble in 15% moisture content= (Volume of Liquid ×
 Partial Pressure)/K_H of CH₄
 = 2.26 × 10⁻⁴ moles is the mass of CH₄ in the liquid.
 = **226 μmoles of CH₄ in the water**
 So, the mass of CH₄ in the water = 3.6 × 10⁻³ g.

Result: Mass of CH₄ in the water is much less than the mass of CH₄ in the headspace
 gas

APPENDIX B – ADDITIONAL STATISTICAL ANALYSIS

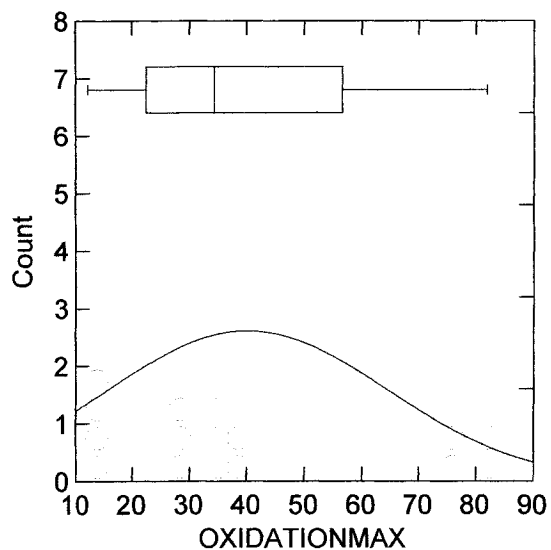
B.1 HYPOTHESIS TESTING FOR VARIANCE USING SYSTAT 11

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\ANOVAEXP.syd, contains variables:

EXPERIMENT	THICKNESS	MC	NUTRIENTS	MAX OXIDATION
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One-sample variance test of MAX OXIDATION EFFICIENCY with 16 cases
Ho: Variance = 0.950 against Alternative = 'not equal'

Mean	=	40.106
Variance	=	597.974
95.00% CI	=	326.305 to 1432.356
Chi_Sq	=	9441.694
df	=	15
p-value	=	0.000



The following effects have lost degrees of freedom.

Effect	Initial df	Lost df	Final df
NUTRIENTS*MC*THICKNESS	1	1	0

Dep Var: OXIDATIONMAX N: 16 Multiple R: 0.998 Squared multiple R: 0.995

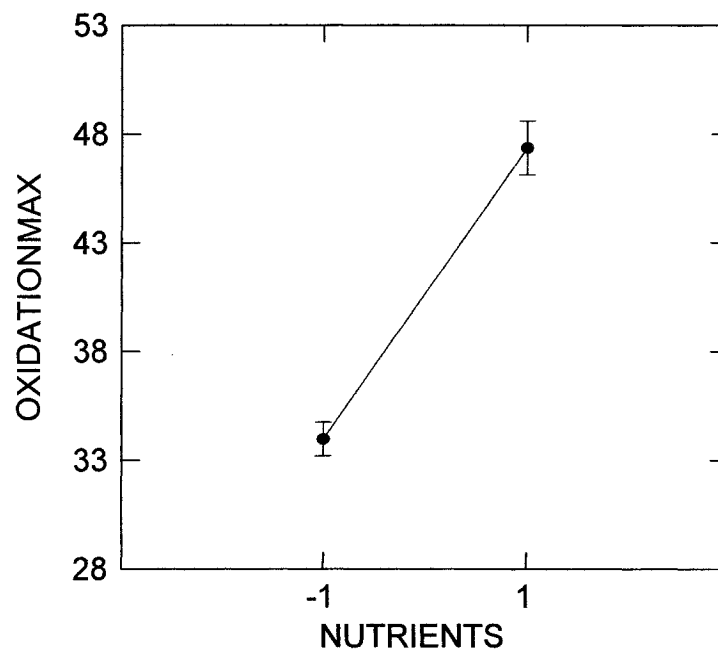
Analysis of Variance

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Model	8925.944	6	1487.657	306.628	0.000
Error	43.665	9	4.852		

Least squares means

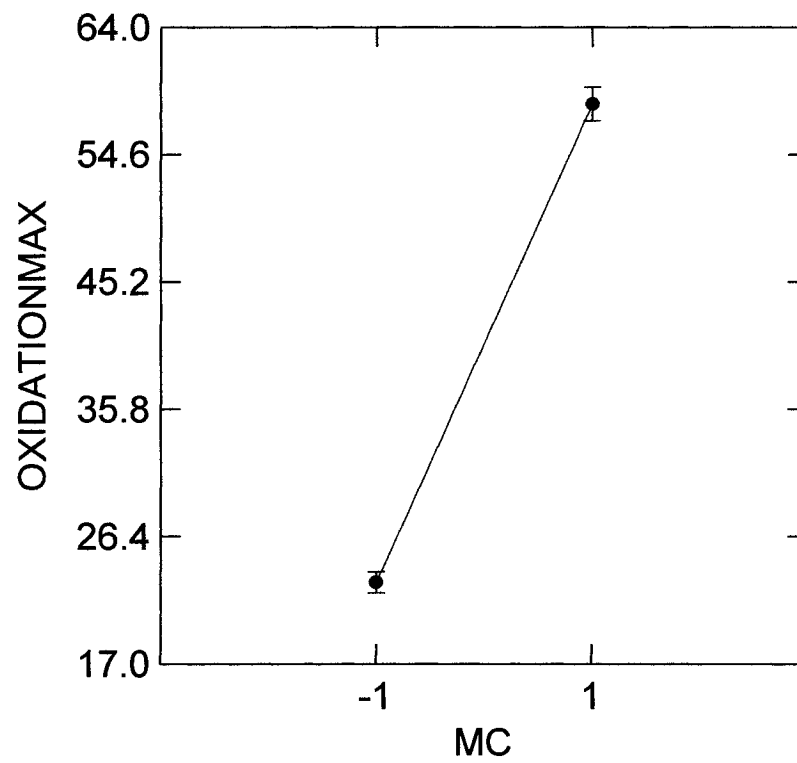
		LS Mean	SE	N
NUTRIENTS	-1	33.963	0.779	8
NUTRIENTS	1	47.363	1.231	8

Least Squares Means



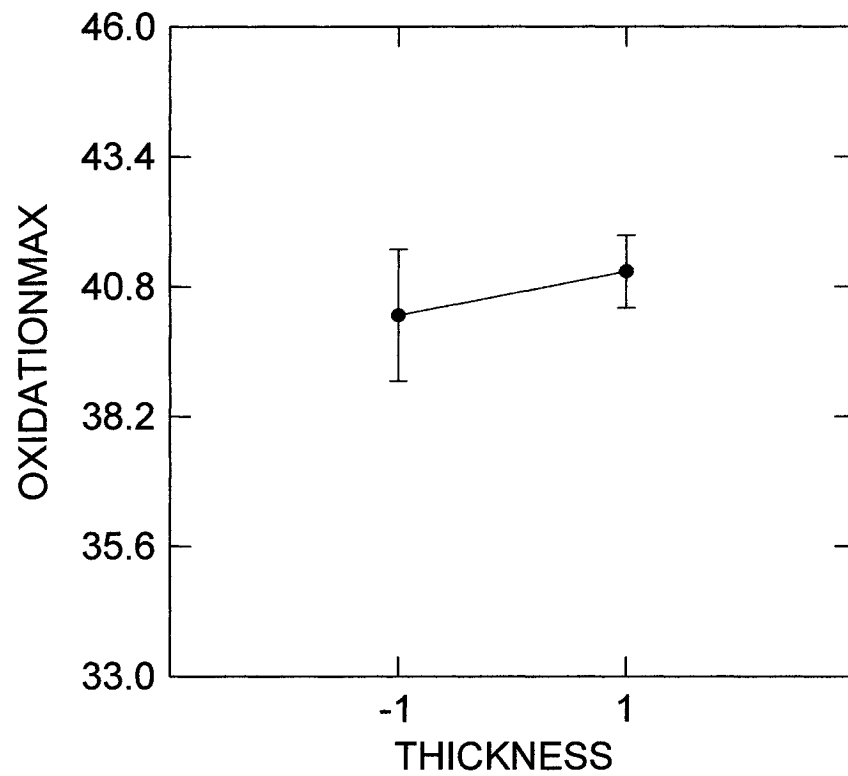
MC	-1	23.000	0.779	8
MC	1	58.325	1.231	8

Least Squares Means



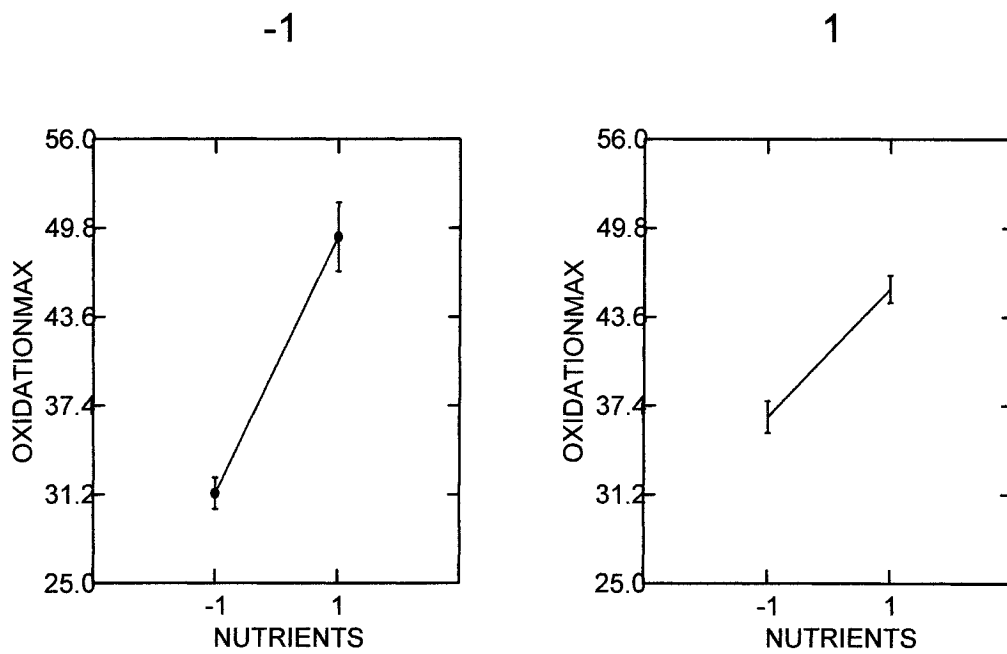
THICKNESS	-1	40.225	1.320	6
THICKNESS	1	41.100	0.728	10

Least Squares Means



NUTRIENTS	-1			
THICKNESS	-1	31.275	1.101	4
NUTRIENTS	-1			
THICKNESS	1	36.650	1.101	4
NUTRIENTS	1			
THICKNESS	-1	49.175	2.400	2
NUTRIENTS	1			
THICKNESS	1	45.550	1.101	4

Least Squares Means

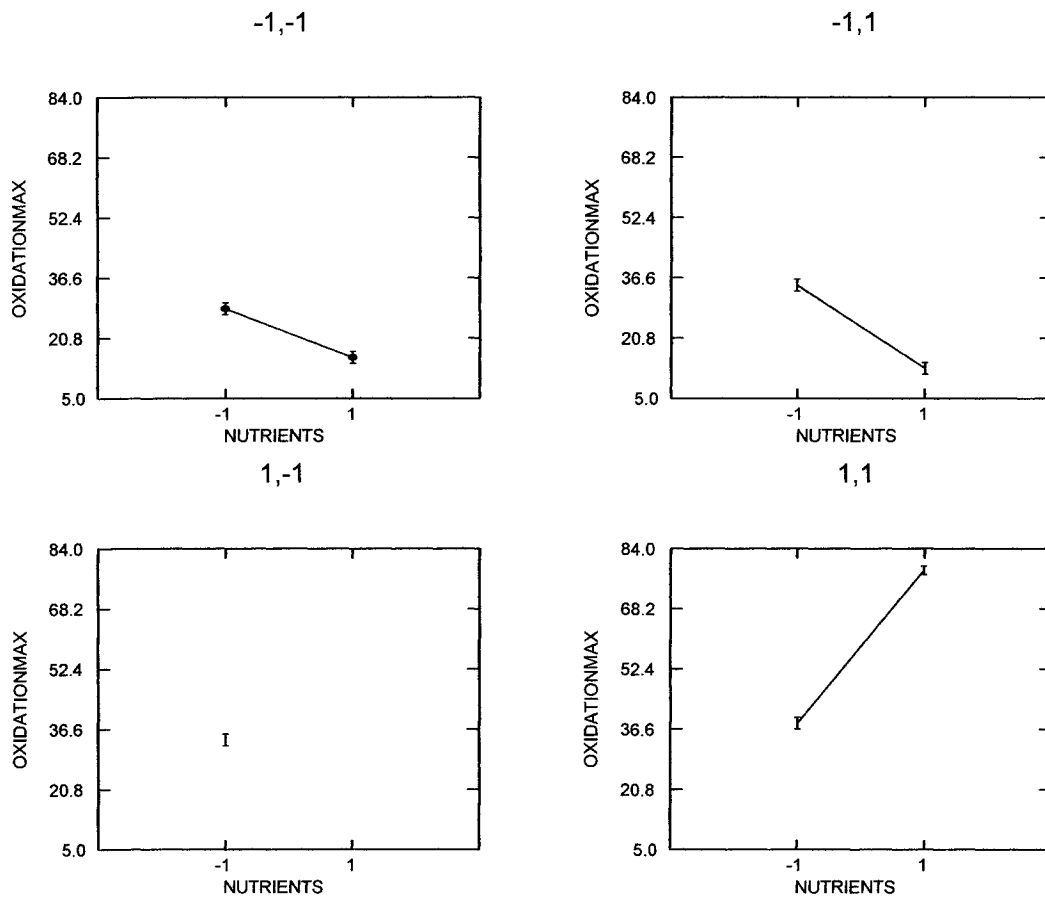


NUTRIENTS	-1			
MC	-1			
THICKNESS	-1	28.700	1.558	2
NUTRIENTS	-1			
MC	-1			
THICKNESS	1	34.900	1.558	2
NUTRIENTS	-1			
MC	1			
THICKNESS	-1	33.850	1.558	2
NUTRIENTS	-1			
MC	1			
THICKNESS	1	38.400	1.558	2
NUTRIENTS	1			
MC	-1			
THICKNESS	-1	15.600	1.558	2
NUTRIENTS	1			
MC	-1			
THICKNESS	1	12.800	1.558	2
NUTRIENTS	1			
MC	1			
THICKNESS	1	78.300	1.101	4

Studentized Residual = -2.634)

Durbin-Watson D Statistic 1.328
 First Order Autocorrelation 0.258

Least Squares Means



From the analysis presented above – 3way interaction-, the highest interaction is between the nutrients addition and the higher level of moisture content and soil layer thickness.

For the 2-way interaction, the interaction between nutrients addition and moisture content is important, which was discussed earlier in *Chapter 4*.

APPENDIX C – NUMERICAL METHODS

C.1 EQUATION (5-6) – GAS TRANSPORT AND BIOLOGICAL REACTION PHASE-

$$\phi \frac{\partial C_{CH_4}}{\partial t} = D \frac{\partial^2 C_{CH_4}}{\partial z^2} - R_{CH_4} \quad (5-6)$$

$$\text{where } R_{CH_4} = V \max \left(\frac{C_{CH_4}}{C_{CH_4} + K_{CH_4}} \right)$$

Equation (5-6) is a finite volume approach was chosen to approximate the differential equation (5-6). Integrating Equation (5-6) over the control volume and with respect to time, this will result the following equation,

$$\phi \int_{CV} \int_t^{t+\Delta t} \frac{\partial C}{\partial t} dv = \int_{CV} \int_t^{t+\Delta t} \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right) dv - \int_{CV} \int_t^{t+\Delta t} R dv \quad (C-1)$$

where, CV is the control volume.

Patankar (1980) assigned steps that were followed to discretize and solve this partial differential equation, using the mentioned Finite Control Volume Method. The method outlined in Patankar (1980) was followed to solve the partial differential equation (5-6). As was detailed by Patankar (1980), since time is a one way coordinate, the solution was obtained by marching in time from a given initial distribution of C_{CH_4} . Thus in a typical “time step” the task is to give the grid point values of C_{CH_4} at time equals (t),

then to find the values of C_{CH_4} at time $(t+\Delta t)$. The “old” given values of C_{CH_4} at the grid points will be denoted by C_i^0 , C_{i+1}^0 , C_{i-1}^0 , and the new (unknown) values at time $(t+\Delta t)$ by C_i^1 , C_{i+1}^1 and C_{i-1}^1 . The batch modeled system is one dimensional and has unsteady state conditions.

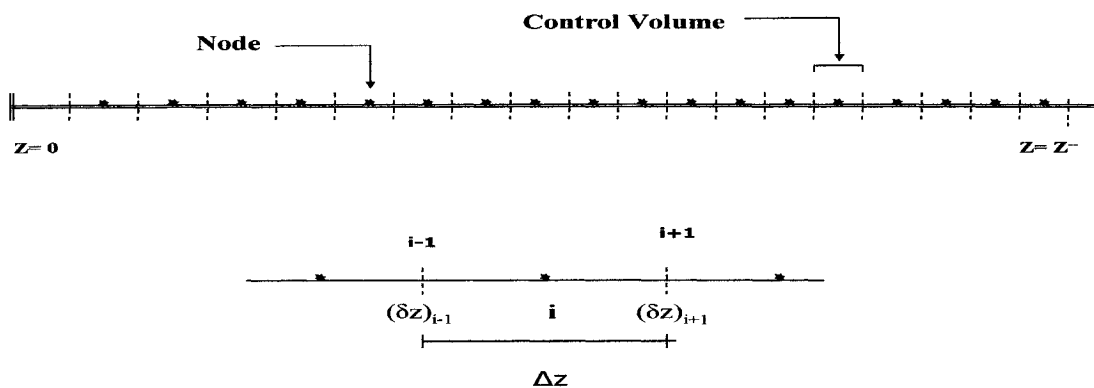


Figure C-1 Grid point cluster for one-dimensional system (Patankar, 1980)

Carrying out the integration, assuming the concentration of CH_4 prevails throughout the control volume:

$$\begin{aligned} \phi \Delta z [C_i^1 - C_i^0] &= f \left[D_{i+1} \frac{(C_{i+1} - C_i)}{(\partial z)_{i+1}} - D_{i-1} \left(\frac{C_i - C_{i-1}}{(\partial z)_{i-1}} \right) \right]^1 \Delta t \\ &+ (1-f) \left[D_{i+1} \frac{(C_{i+1} - C_i)}{(\partial z)_{i+1}} - D_{i-1} \frac{(C_i - C_{i-1})}{(\partial z)_{i-1}} \right]^0 \Delta t - R \Delta z \Delta t \end{aligned} \quad (C-2)$$

where, θ is the old time, l is the new time, f is the weighting factor for time 1, $(1-f)$ is weighting factor for time 0, R is the average value of biological reaction over the control volume

Rearrange the above equation,

$$\begin{aligned} \phi_{gas} \Delta z C_i^1 - \phi \Delta z C_i^0 &= f D_{i+1} \left(\frac{C_{i+1} - C_i}{(\partial z)_{i+1}} \right)^1 \Delta t - f D_{i-1} \frac{(C_i - C_{i-1})^1}{(\partial z)_{i-1}} \Delta t + \\ (1-f) D_{i+1} \frac{(C_{i+1} - C_i)^0}{(\partial z)_{i+1}} \Delta t &- (1-f) D_{i-1} \frac{(C_i - C_{i-1})^0}{(\partial z)_{i-1}} \Delta t - R \Delta z \Delta t \end{aligned} \quad (C-3)$$

Rearrange again,

$$\begin{aligned} \phi_{gas} \Delta z C_i^1 + f \frac{D_{i+1} C_i^1}{(\partial z)_{i+1}} \Delta t + f \frac{D_{i-1} C_i^1}{(\partial z)_{i-1}} \Delta t &= \phi \Delta z C_i^0 + f \frac{D_{i+1} C_{i+1}^1}{(\partial z)_{i+1}} \Delta t + \\ f \frac{D_{i-1} C_{i-1}^1}{(\partial z)_{i-1}} \Delta t + (1-f) \frac{D_{i+1} C_{i+1}^0}{(\partial z)_{i+1}} \Delta t &- (1-f) \frac{D_{i+1} C_i^0}{(\partial z)_{i+1}} \Delta t - \\ (1-f) \frac{D_{i-1} C_i^0}{(\partial z)_{i-1}} \Delta t + (1-f) \frac{D_{i-1} C_{i-1}^0}{(\partial z)_{i-1}} \Delta t &- R \Delta z \Delta t \end{aligned} \quad (C-4)$$

Define the following coefficients:

$$\begin{aligned} a_i^0 &= \phi_{gas} \Delta z \\ a_{i+1} &= \frac{D_{i+1}}{(\partial z)_{i+1}} \\ a_{i-1} &= \frac{D_{i-1}}{(\partial z)_{i-1}} \\ a_i &= a_i^0 + a_{i+1} + a_{i-1} \end{aligned} \quad (C-5)$$

Substitute the above coefficients into Equation (C-4), then rearrange and divide by Δt , which will yield to:

$$a_i C_i^1 = a_{i+1} [f C_{i+1}^1 + (1-f) C_{i+1}^0] + a_{i-1} [f C_{i-1}^1 + (1-f) C_{i-1}^0] + [a_i^0 - (1-f) a_{i+1} - (1-f) a_{i-1}] C_i^0 - R \Delta z \quad (C-6)$$

Patankar (1980) has defined three specific values of the weighting factor f . If $f=0$, this leads to the explicit scheme. If $f=0.5$, this will lead to Crank-Nicolson scheme. And if $f=1$, this will lead to fully implicit scheme. Patankar (1980) indicated clearly that the preference is for the implicit, therefore, the implicit scheme is used in this study.

As for the reaction rate, Patankar (1980) indicated that if the reaction rate (R_{CH_4}) is nonlinear function of the concentration (C_{CH_4}), this reaction rate must be linearized.

The biological reaction term linearization was done using *Quotient rule*, the biological reaction term, which is basically described by the Monod model, will lead to the final linear equation as follows,

$$V_{CH_4} = V_{\max} \frac{C_i^0}{C_i^0 + K_{CH_4}} + V_{\max} \frac{K_{CH_4} \times (C_i^1 - C_i^0)}{(C_i^0 + K_{CH_4})^2} \quad (C-7)$$

Equation (C-7) can be simplified to express a linear equation of the type $y = mx+n$, as follows:

$$V_{CH_4} = n + m(C_i^1 - C_i^0) \quad (C-8)$$

From Equations (C-7) and (C-8), the biological reaction term can be divided to two functions that are defined as follows:

$$R_p = V_{\max} \left[\frac{C_i^0}{C_i^0 + K_{CH_4}} - \frac{K_{CH_4} \times C_i^0}{(C_i^0 + K_{CH_4})^2} \right] \quad (C-9)$$

and $R_C = V_{\max} \left(\frac{C_i^0}{C_i^0 + K_{CH_4}} \right)$

where, R_C is the constant part of the biological reaction R, R_p is the coefficient of CH_4 concentration .

Going back to equation (C-6) after linearizing the reaction rate, the implicit scheme was applied to Equation (C-6), where f is considered to equal 1, and the biological reaction rate was linearized according to Equation (C-9). The following coefficients (a , b , c , d) are defined and in relation to Equation (C-5). Equation (C-5) can be rewritten to include the reaction rate terms as follows:

$$a_i = a_i^0 + a_{i+1} + a_{i-1} - R_p \Delta z, \text{ or } a_i = a_i^0 + b_i + c_i - R_p \Delta z$$

$$a_i^0 = \phi_{gas} \Delta z$$

$$b_i = \frac{D_{i+1}}{\Delta z_{i+1}} \text{ and is related to } a_{i+1}$$

$$c_i = \frac{D_{i-1}}{\Delta z_{i-1}} \text{ and is related to } a_{i-1} \quad (C-10)$$

$$d_i = a_i^0 C_i^0 - R_c \Delta z$$

If Equation (C-6) is written for C_i^1 it will have the following form:

$$a_i C_i^1 = b_i C_{i+1}^1 + c_i C_{i-1}^1 + d_i \quad (C-11)$$

C_i is known at the boundary. Following the steps assigned by Patankar (1980), the solution of the discretization equations for one dimensional situation can be obtained by the standard Gaussian-elimination method. Because of the simple form of the equations, the elimination process turns into a convenient algorithm. This is also called TDMA (Tri-diagonal Matrix Algorithm). For the convenience in presenting the algorithm, it is necessary as recommended by Patankar to use different nomenclature. It is assumed now that the grid point is numbered $1,2,3,\dots,N$, with points 1 and N denoting the boundary points. The discretization equation can be written now as:

$$a_i C_i = b_i C_{i+1} + c_i C_{i-1} + d_i \quad (\text{C-12})$$

for $i = 1,2,3,\dots,N$. Thus the concentration of CH_4 at point i is related to the neighboring concentrations of C_{i+1} and C_{i-1} . This Equation (C-12) is the same as Equation (C-11), but written with $i=1,2,3..N$ in order to solve this linear algebraic equation.

To start the TDMA, and as outlined by Patankar, suppose, in the forward- substitution process, we seek a relation,

$$C_i = P_i C_{i+1} + Q_i \quad (\text{C-13})$$

after we have just obtained:

$$C_{i-1} = P_{i-1} C_i + Q_{i-1} \quad (\text{C-14})$$

Now substituting Equation (C-14) in Equation (C-12) leads to:

$$a_i C_i = b_i C_{i+1} + c_i (P_{i-1} C_i + Q_{i-1}) + d_i \quad (\text{C-15})$$

which can be rearranged to look like equation (C-13). In other words, the coefficients P_i and Q_i will be obtained as:

$$P_i = \frac{b_i}{a_i - c_i P_{i-1}}, \quad \text{and} \quad Q_i = \frac{d_i + c_i Q_{i-1}}{a_i - c_i P_{i-1}} \quad (\text{C-16})$$

These equations are recurrence relations, since they give P_i and Q_i in terms of P_{i-1} and Q_{i-1} . To start the recurrence process, Equation (C-12) for $i=1$ is almost of the form of equation (C-13). Thus, the values of P_1 and Q_1 are given by:

$$P_1 = \frac{b_1}{a_1} \quad \text{and} \quad Q_1 = \frac{d_1}{a_1} \quad (\text{C-17})$$

The solution of the discretization equation for one-dimensional situation was obtained by the standard Gaussian elimination method and the algebraic equations indicated above and the detailed steps assigned by Patankar (1980) were followed as mentioned earlier.

C.2 EQUATION (5-7) – DECAY PHASE -

$$\frac{dC_{CH_4}}{dt} = -K_d * C_{CH_4} \quad (5-7)$$

As for the decay phase, Equation (5-7) demonstrates the reaction during the decay phase. First order reaction occurs at a rate that is proportional to the concentration of CH_4 in the substrate. To solve Equation (5-7) numerically, the equation was integrated as follows,

$$\int_{C_0}^C \frac{dC}{C} = -K_d \int_0^t dt \quad (\text{C-18})$$

where C_0 is the concentration of CH_4 at the end of growth phase, and this gives,

$$\ln \frac{C}{C_0} = -K_d * t \quad (\text{C-19})$$

or,

$$\ln C - \ln C_0 = -K_d * t \quad (\text{C-20})$$

which may be rearranged to ,

$$\ln C = \ln C_0 - K_d * t \quad (\text{C-21})$$

This is a linear equation, so,

$$\frac{C}{C_0} = e^{-K_d * t} \quad \text{or} \quad C = C_0 * e^{-K_d * t} \quad (\text{C-22})$$