uOttawa

L'Université canadienne
Canada's university

FACULTÉ DES ÉTUDES SUPÉRIEURES ET POSTDOCTORALES

uOttawa

L'Université canadienne
Canada's university

FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

Muna Albanna

AUTEUR DE LA THÈSE / AUTHOR OF THESIS

Ph.D. (Environmental Engineering)

GRADE / DEGREE

Department of Civil Engineering

FACULTÉ, ÉCOLE, DÉPARTEMENT / FACULTY, SCHOOL, DEPARTMENT

Methane and Non-methane Organic Compounds Oxidation in Landfill Bio-covers

TITRE DE LA THÈSE / TITLE OF THESIS

M. Warith

DIRECTEUR (DIRECTRICE) DE LA THÈSE / THESIS SUPERVISOR

CO-DIRECTEUR (CO-DIRECTRICE) DE LA THÈSE / THESIS CO-SUPERVISOR

EXAMINATEURS (EXAMINATRICES) DE LA THÈSE / THESIS EXAMINERS

M. Fall

R. Narbaitz

R. Galvez

P. Simms

P. Mehrani

Gary W. Slater

Le Doyen de la Faculté des études supérieures et postdoctorales / Dean of the Faculty of Graduate and Postdoctoral Studies

METHANE AND NON-METHANE ORGANIC COMPOUNDS OXIDATION IN LANDFILL BIO-COVERS

by

Muna Albanna

Ph.D. Thesis

Submitted to the School of Graduate Studies and Research

Under the supervision of

Prof. Mostafa Warith

Prof. Leta Fernandes

In partial fulfillment of the requirements for the degree of

Ph.D. in Environmental Engineering

The Ottawa-Carleton Institute for Environmental Engineering

Department of Civil Engineering

University of Ottawa, Ottawa, ON

Canada, K1N 6N5

Your file Votre référence
ISBN: 978-0-494-59509-1
Our file Notre référence
ISBN: 978-0-494-59509-1

To

Wael, Mohammad and Motaz

ABSTRACT

One critical source, which adds to the anthropogenic methane (CH_4) emissions, is solid waste disposal. The biogas generated from biodegradation of solid waste in landfills, known as landfill gas (LFG), consists of CH_4, carbon dioxide (CO_2), plus trace amounts of non-methane organic compounds (NMOCs). Most of the existing landfills around the world do not have LFG collection setups, and the emissions are just released into the atmosphere. Oxidation of CH_4 and NMOCs by methanotrophic bacteria within the landfill cover (LFC) provides a sink for these harmful fugitive emissions.

The scope of this research was to carry out a comprehensive study on the biological oxidation of CH_4 and NMOCs in the LFC, under diverse operating conditions. To achieve this goal, various parameters affecting the oxidation process, including cover medium, temperature, saturation limit and nutrients addition, were studied. Statistical analysis and modeling were carried out to estimate the interactions between several parameters under investigation, and to draw conclusions about the combined effects of these parameters on the LFC system. The effects of NMOCs on CH_4 oxidation capacity of the LFC were examined in batch scale and continuous flow column experiments. Additionally, the co-metabolic abilities of methanotrophs were explored and the biological bio-degradation rates on NMOCs were estimated under different temperature and moisture content levels. Artificial neural networks (ANN) modeling technique was used to describe the complex input/output relationships and to simulate the CH_4 oxidation rates in the presence of NMOCs under diverse conditions that are representative of LFC system.

ACKNOWLEDGMENTS

The end of what seemed a never ending journey has almost been reached, but sadly without my dear and beloved supervisor; late Dr. Leta Fernandes, whom we lost September 6th, 2008. She meant a lot to me and to all her students; besides being an outstanding professor, educator, researcher and supervisor, she was a great human being, role model, and friend. Her professionalism, experience, knowledge, and passion had changed my life. I am forever indebted to her and I will honor her memory in all my future's professional and personal endeavors. She will always remain in my heart, thoughts, and prayers for the rest of my life.

I would like to express my sincere gratitude and deepest appreciation to my supervisor Dr. Mostafa Warith for the support, assistance and help I have received from him throughout my studies. I am sincerely grateful to him for believing in me and giving me the opportunity to work and continue in this project.

I would like to express my gratitude to Ms. Balinder Rai and Ontario centers of Excellence, for their support, believe and recognition of our project. My sincere thanks and appreciation to the two industrial partners that supported and believed in this project; Lafleche environmental Inc. and Versus Goliath Project Solutions Inc..

I would like to extend my sincere appreciation to Dr. Roberto Narbaitz; I have learnt a lot from him, he is an outstanding professor and human being. I am deeply indebted to my other research proposal committee members, Dr. Poupak Mehrani, Dr. Mamadou Fall and Dr. Paul Simms, for the valuable discussion throughout this research.

The assist I have received from Mr. Francisco Aposaga in the laboratory is acknowledged and highly appreciated. I would like also to express deep gratitude to Dr. Nimal De Silva (Department of Earth Sciences), Dr. John Basso (Biology Department), Paul Middlestead and Wendy Abdi (G.G. Hatch Stable Isotope Laboratory). Thanks to our department staff Lise Rousseau, Manon Racine and Yolande Hogan for their continuous support.

Special thanks and wishes of success go to my colleagues and research team members; Haleh, Mohamed, Elias, Andrew, Yannick, Jordan, Rania, Gina and Yamara. I am forever indebted to my special friends Jill Hass, Cidgem, Vienna and Omar for their friendship and encouragement.

Finally, I express my gratitude to my mother, father, and brothers Issam, Saeed and Basem who are far away but their souls and prayers are always with me. For my boys; Mohammad and Motaz I am so grateful and thankful for being with me, so patient and supportive in the good as well as the bad times, you never complained and your were always encouraging. For my husband Wael, words can never state how much I appreciate your love, support, encouragement and trust. Without Wael's unconditional love and support I could never proceed.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

ANN	Artificial Neural Networks
ANOVA	Analysis of variance
ASTM	American Society for Testing and Material
CH_4	Methane
CO_2	Carbon dioxide
DCM	Dichloromethane
ECD	Electron Capture Detector
eCO_2	Carbon dioxide equivalent
GHG	Greenhouse gas
IPCC	Intergovernmental Panel on Climate Change
ICP	Inductively Coupled Plasma
LFC	Landfill cover
LFG	Landfill gas
LMEM	Landfill Methane Emissions Model
MMO	Monooxygenase
MOE	Ontario Ministry of Environment
MSW	Municipal solid waste
Mt	Million metric tonnes
NMOCs	Non-methane organic compound
NSPS	New Source Performance Standards
O_2	Oxygen
pMMO	Membrane-bound form of monooxygenase
RuMP	Ribulose monophosphate pathway
S.L.	Saturation limit
sMMO	Soluble form of monooxygenase
SW	Solid waste
TCA	Trichloroethane
TCE	Trichloroethylene
TCD	Thermal Conductivity Detector
USEPA	United States Environmental Protection Agency
USDA	United States Department of Agriculture
VOC	Volatile organic compound

CHAPTER 1

INTRODUCTION

The scientific consensus on global warming has promoted many research projects to focus on the attenuation of factors contributing to the climate change. The recent increase in global average temperatures is believed to be the result of growing anthropogenic greenhouse gases (GHGs); mainly carbon dioxide (CO_2) and methane (CH_4). Different measures should be taken universally to reduce emissions of the principal GHGs, slow the rate of global warming, and minimize future increase in the Earth's surface temperature.

Methane is an important GHG, its accumulation in the atmosphere accounts for 22.9% of total direct greenhouse forcing effect (USEPA 2006a). The Intergovernmental Panel on Climate Change (IPCC 2001) reported that the CH_4 atmospheric life time (9-15 years) is shorter than CO_2 (200- 450 years); this means that the global warming potential of CH_4 is higher for shorter time horizons. In addition, CH_4 is 23 times more effective in trapping heat in the atmosphere than CO_2 over a 100-year period (IPCC 2001).

Methane emissions arise from both natural and anthropogenic sources. The anthropogenic CH_4 emissions are rising due to increased industrial activities over the years. One of the main sources that add to the anthropogenic CH_4 in the atmosphere is solid waste (SW) disposal. In Canada, SW disposal is responsible for 23% of total anthropogenic CH_4 emissions (Environment Canada 2005). In the United States, landfills

are the largest human-related source of CH_4, accounting for 34% of all CH_4 emissions (USEPA 2006b).

A complex series of biological and chemical reactions begin with the burial of refuse in landfills, where an active anaerobic ecosystem generates landfill gas (LFG) as a major end product (Czepiel et al. 2003; Hilger and Barlaz 2002). Landfill gas is a flammable and potentially harmful mixture; it consists by volume of 50-65% CH_4, 35-50% CO_2 and around 1% non-methane organic compounds (NMOCs) (USEPA 2006c). The biochemical reactions that produce LFG will continue long after a landfill is capped and therefore, LFG emissions will continue even after landfill closure (Environment Canada 2006). If not collected, LFG can migrate to the surface and enter the atmosphere, consequently increasing the GHGs emissions.

Newly constructed landfills can be engineered with a vacuum system for commercial recovery of CH_4 which can be used as an energy source. The Ontario Ministry of Environment (MOE) has regulations requiring mandatory LFG collection and control set ups in all new or expanding landfill sites with capacity larger than 3 million m^3 of waste (Environmental Registry 2007). Landfill gas extraction techniques are well developed but costly, hence they are mainly feasible for large landfills sites. Nevertheless, LFG collection systems are not 100% efficient; thus fugitive emissions of CH_4 and NMOCs from landfills with gas recovery systems will continue to occur. Reported collection efficiencies typically range from 60 to 80%, with an average of 75% most commonly cited (USEPA 1999).

The vast majority of existing landfills sites around the world do not have biogas capturing setups. Methane emissions from these sites are entirely released to the environment; in addition, they also emit millions of tonnes of volatile organic compounds. Figure 1.1 shows CH_4 generation, capture and net emission trends from Canadian municipal solid waste (MSW) landfills.

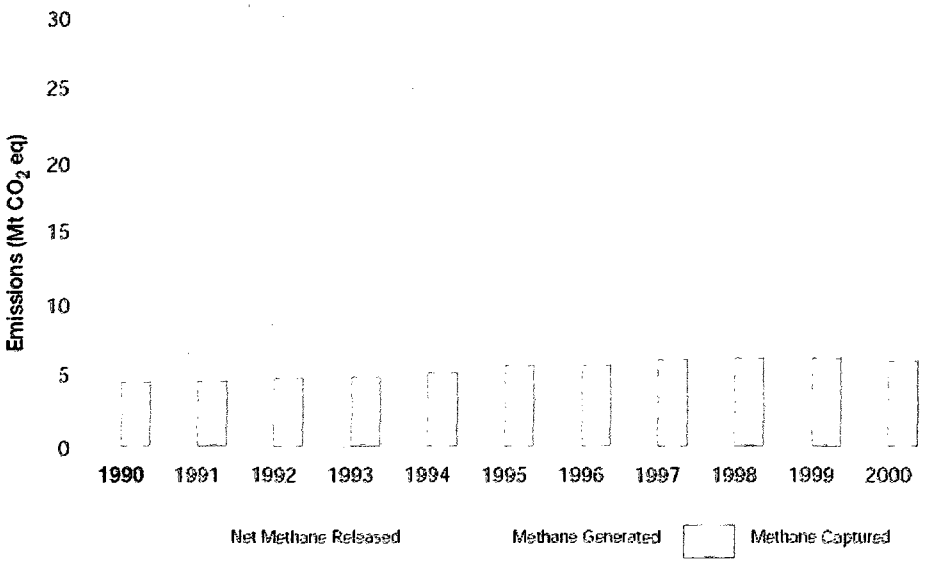


Figure 1.1 Methane generation, capture and net emission trends from Canadian municipal solid waste landfills (adapted from Environment Canada 2006).

As illustrated in Figure 1.1, the majority of landfill gases are released into the atmosphere. The net CH_4 emissions from Canadian landfills in 2002 were estimated to be 22 million metric tonnes (Mt) of carbon dioxide equivalent (eCO_2) and only 6.6 Mt eCO_2 were captured (Environment Canada, 2005). Moreover, the average emission rate of hazardous volatile substances from landfills was estimated to be 35 kg per million kg of refuse (Reinhart et al., 1992). Based on this estimation and Environment Canada (2005)

statistics, the amount of NMOCs emitted from Canadian landfills is estimated to be 1000 tonnes/year.

Hence, in the absence of biogas capturing systems or even as complementary to the collection techniques, CH_4 oxidation and NMOCs co-oxidation within a landfill cover (LFC) system is extremely important for the reduction of uncontrolled emissions of LFG.

Due to the interest in the potential benefits of CH_4 oxidation in LFC soils, some studies were carried out to understand the parameters affecting this process (Hilger and Barlaz 2002). Optimization of CH_4 oxidation rates and the most suitable environment for the methanotrophic bacteria to thrive have yet to be comprehensively researched. As for the oxidation of NMOCs present in the LFG by the methanotrophic bacteria, research has only recently been initiated.

1.1 THE HYPOTHESIS

The aim of this thesis was to investigate biological CH_4 oxidation and NMOCs co-oxidation in landfill bio-covers. It was hypothesized that the compost as landfill cover medium would promote conditions suitable for aerobic biological activity that would result in higher oxidation rates of CH_4 and NMOCs relative to the conventional soil covers. It was also hypothesized that the environmental conditions mainly temperature and cover's saturation level would affect the CH_4 oxidizing bacteria and consequently their oxidation capacity. In addition, it was hypothesized that NMOCs present in LFG negatively influence the bacterial CH_4 oxidation capacity due to inhibition effects.

1.2 RESEARCH OBJECTIVES

The specific objectives of this research can be summarized as follows:

- Determine and compare the extent of biological CH_4 oxidation within the LFC under various conditions, mainly type of cover medium, temperature, moisture level, and nutrients addition.
- Determine biological CH_4 oxidation kinetic parameters under different environmental conditions using compost as the LFC medium.
- Explore the effect of NMOCs on the biological CH_4 oxidation process in landfill bio-covers.
- Examine the co-metabolic abilities of methanotrophic bacteria in landfill bio-covers by estimating the biological degradation rates of the different NMOCs under various environmental conditions.
- Develop a model to estimate the biological CH_4 oxidation rates in the LFC when NMOCs are present as part of landfill gas, using artificial neural networks (ANNs) modeling technique.

1.3 THESIS ORGANIZATION

This thesis is arranged as a paper format thesis. Chapter 2 gives brief information on literature review of fundamentals of biological CH_4 oxidation. Results of this research are given as a journal manuscript format in Chapters 3-7. Conclusions and recommendations are presented in Chapter 8.

In Chapter 3, patterns of CH_4 oxidation were investigated and compared in two types of existing landfill cover soils, under various combinations of environmental factors including temperature, moisture content, and fertilizer addition (as an additional nutrient source). Some of the results were presented at the 60th Canadian Geotechnical Conference & 8th joint CGS/IAH-CNC Conference, October 21-24th 2007, Ottawa, Canada. This manuscript has been accepted by the American Society of Civil Engineers journal and is scheduled for publication in July 2009 issue of the Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management.

Chapter 4 presents the results of the CH_4 oxidation capacity of the compost as landfill bio-cover. These results were assessed with the CH_4 oxidation rates obtained using the conventional LFC soils. In this chapter, an empirical model was presented that describes the individual effects of the type of cover medium, temperature and moisture contents on the CH_4 oxidation rates, as well as the effects of the interactions between these variables. Some of these results were presented at the International Conference on Waste Engineering and Management in Hong Kong, China, 28 – 30 May 2008. This manuscript has been submitted to the Journal of Solid Waste Technology and Management.

In light of the experimental results in Chapter 4, it was decided to carry on the experiments using compost as landfill bio-cover. In Chapter 5, the kinetic parameters of CH_4 oxidation in the bio-cover were obtained under different temperatures and saturation levels. The effects of NMOCs present in LFG were studied and the biodegradation rates of CH_4 were examined and modeled using nonlinear regression analysis. Also, the degradation rates of the NMOCs and co-metabolic abilities of methanotrophic bacteria were estimated. Some of the results of these experiments were presented at The 23rd International Conference on Solid Waste Technology and Management, March 30 - April 2nd, 2008, Philadelphia, PA, U.S.A. The manuscript has been submitted to the Waste Management journal for publication.

In Chapter 6, the potential of CH_4 oxidation and NMOCs co-oxidation by methanotrophic bacteria was studied in depth using continuous flow column experiments that simulate landfill bio-cover environments. The manuscript has been submitted to the Journal of Environmental Engineering and Science for publication.

The final part of this research (Chapter 7) was on developing an Artificial Neural Network that was capable of estimating CH_4 oxidation rates in landfill bio-covers when NMOCs were present. The model was used to estimate the biological CH_4 oxidation rates under different sets of environmental conditions. The manuscript will be submitted to an accredited journal or conference for publication.

1.4 REFERENCES

Barlaz, M.A., Green, R.B., Chanton, J.P., Goldsmith, C.D., and Hater, G.R. (2004), "Evaluation of a Biologically Active Cover for Mitigation of Landfill Gas Emissions," *Environmental Science and Technology*, 38, pp. 4891-4899.

Czepiel, P.M., Shorter, J.H., Mosher, B., Allwine, E., McManus, J.B., Harris, R.C., Kolb, C.E., and Lamb, B.K. (2003), "The Influence of Atmospheric Pressure on Landfill Methane Emissions," *Waste Management*, 23, pp. 593-598.

Environment Canada (October, 2005), Landfill Gas Management in Canada Report, http://www.ec.gc.ca/pdb/ghg/inventory_report/2005_report/tdm-toc_eng.cfm.

Environment Canada (September, 2006), Greenhouse Gas Sources and Sinks, Fact sheet 8- Waste: 1990-2000, http://www.ec.gc.ca/pdb/ghg/inventory_report/1990_00_factsheet/fs8_e.cfm.

Environmental Registry (2007), Ontario Ministry of Environment, Landfill Gas Collection and Control Regulation, August 2007, http:// www.ebr.gov.on.ca/ERS-WEB External/displaynoticecontent.do?noticeId=MTAwOTc1&statusId=MTUwODE1

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., Mclnernery M.C., and Stezenback L.D.(Eds.), ASM Press, Washington, D.C., 696-717.

Intergovernmental Panel on Climate Change, (2001). IPCC Working Group I, The Scientific Basis, http://www.grida.no/climate/ipcc_tar/wg1/248.htm.

Reinhart, D.R., Cooper, D.C., and Walker, B.L., (1992), "Flux Chamber Design and Operation for the Measurement of Municipal Solid Waste Landfill Gas Emission Rates," *Journal of the Air and Waste Management Association*, 42, pp. 1067 – 1070.

Spokas, K., Bogner, J., Chanton, J.P., Morcet, M., Aran, C., Graff, C., Moreau-Le Golvan, Y., and Hebe, I., (2006). "Methane Mass Balance at Three Landfill Sites: What is the Efficiency of Capture by Gas Collection Systems?" *Waste Management*, 26, 516-525.

USEPA (1999), Municipal Solid Waste Landfills, Volume I: Summary of the Requirements for the New Performance Standards and Emissions Guidelines for Municipal Solid Waste Landfills. 453/R-96-004. Research Triangle Park, NC. USA.

USEPA (2006a), "Global Anthropogenic Non-CO_2 Greenhouse Gas Emissions: 1990-2020, U.S. Environmental Protection Agency, Office of Atmospheric Programs, Climate Change Division, U.S. Environmental Protection Agency, 1200 Pennsylvania Avenue, NW, Washington, DC 20460.

USEPA (2006b), Methane Sources and Emissions, October, 2006, http://www.epa.gov/methane/sources.html#anthropogenic.

USEPA (2006c), State of Knowledge, October, 2006, http://www.epa.gov/climatechange/science/stateofknowledge.html.

CHAPTER 2

LITERATURE REVIEW

2.1 EMISSIONS FROM LANDFILLS

Landfilling is the oldest and one of the most common methods of organized waste management globally. Landfills continue to be an important repository of municipal solid waste (MSW) for the predictable future since there is a limit to the types of waste that can be recycled or composted. The rate of MSW diversion through recycle and compost in Canada is only 22% of the total MSW generated (Environment Canada 2005).

The organic fraction of solid waste inside the landfills decomposes anaerobically by methanogenic bacteria. Landfill gas is the product resulting from the biodegradation of the waste and is composed of 50-65% CH_4, 35-50% carbon dioxide (CO_2), and approximately 1% non-methane organic compounds (NMOCs) (USEPA 2006). The high percentage of CH_4 contained in LFG is hazardous; in addition to being flammable and explosive, the uncontrolled CH_4 emissions which escape into the atmosphere may significantly contribute to the effects of global warming.

Solid waste disposal in landfill sites is considered one of the significant sources of anthropogenic CH_4 in the atmosphere (USEPA 2006). Furthermore, Methane's global warming potential is 23 times greater than CO_2 over a 100-year period (IPCC 2001).

Carbon dioxide, emitted as part of LFG and from the oxidation of CH_4, is not counted as anthropogenic GHG emission; these amount are harvested on sustainable basis (sustainable harvesting implies that photosynthesis which removes CO_2 from the atmosphere is equal to decomposition which adds CO_2 to the atmosphere) (EIIP 1999).

The sources of the NMOCs are the redundant substances such as household cleaning products, materials coated with or containing paints and adhesives, and such other items. The production of NMOCs and their movement within LFG can be attributed to the biological decomposition of heavier organic compounds into lighter and more volatile compounds, as well as the vaporization and chemical reactions of material present in the landfill (USEPA 1999). Their rate of emission is governed by LFG production and transport mechanisms. Trace components in LFG include hydrocarbons, aromatics, halogenated hydrocarbons and inorganic compounds. The concentrations of NMOCs can vary depending on several conditions such as the type of waste deposited in the landfill, the physical properties of each individual compound, and climatic conditions around the landfill site (USEPA 2003). USEPA (1999) proposed default values for NMOCs concentrations for regulatory compliance purposes, but site specific information should be taken into account when determining the total NMOCs concentrations for inventory purposes.

2.2 METHANOTROPHIC BACTERIA

Methane is produced in the anaerobic regions within the landfill by the methanogenic bacteria and the oxidation of CH_4 is performed by the methanotrophic bacteria within the LFC (Horz et al., 2002; Hilger et al., 1999; Hanson and Hanson, 1996). Figure 2.1 illustrates the production and the possible pathways of CH_4 release from a landfill cell.

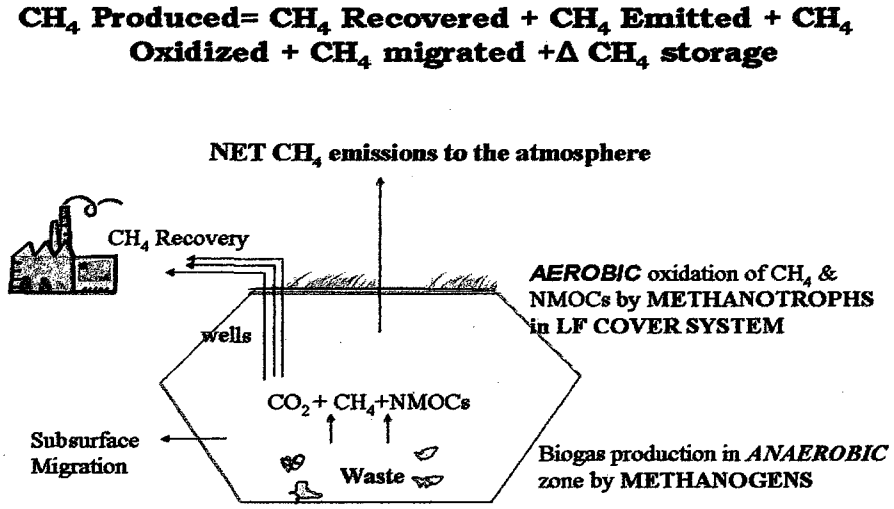


Figure 2.1 Methane Mass Balance in Landfills.

Landfill cover soils contain various groups of microorganisms, such as methanotrophic bacteria, that are capable of oxidizing CH_4 and co-oxidize NMOCs. There is an abundance of methanotrophs in the environment, where they can represent up to 8% of the total heterotrophic population (Bogner et al., 1997). Methanotrophs are also found in many environments where CH_4 diffuses into the aerobic zones, including wetlands, agricultural fields, forest soils and areas surrounding gas wells. Methanotrophic bacteria (or methanotrophs) are a subset of a physiological group of bacteria known as methylotrophs; they have a unique ability to utilize CH_4 as the carbon and energy source

(Borjesson et al. 2004). Methanotrophic bacteria possess the enzyme methane monooxygenases (MMO) which enable them to catalyze the oxidation of CH_4 to methanol (Hanson and Hanson 1996). The oxidation of CH_4 by methanotrophs is initiated by CH_4 monooxygenases (MMO) enzyme, which utilizes two reducing equivalents to split the O-O bonds of dioxygen; one of the oxygen (O_2) atoms is reduced to form water (H_2O) and the other is incorporated into CH_4 to form methanol (CH_3OH). The requirement for O_2 as a reactant in the initial oxidation process indicates that methanotrophs are obligate aerobes. The methanotrophic conversion of CH_4 has two pathways as shown in Figure 2.2; the ribulose monophosphate path and the serine path. These two pathways start with the conversion of CH_4 to methanol (CH_3OH). Hilger and Humer (2003) affirmed that the following two equations summarize O_2 and nitrogen (N_2) demands for those two pathways. This reaction is mediated by the CH_4 monooxygenase enzyme, which is responsible for oxidation of CH_4. The $C_4H_8O_2N$ is the formula of the microbial biomass.

$$CH_4 + 1.5\ O_2 + 0.118\ NH_4^+ \rightarrow 0.118\ (C_4H_8O_2N) + 0.529\ CO_2 + 1.71\ H_2O + 0.118H^+ \quad [2.1]$$

$$CH_4 + 1.57\ O_2 + 0.102\ NH_4^+ \rightarrow 0.102\ (C_4H_8O_2N) + 0.593\ CO_2 + 1.75\ H_2O + 0.102\ H^+ \quad [2.2]$$

Borjesson et al. (1998) stated that the biological oxidation proceeds according to the following general equation reported:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \qquad \Delta G^o = -780\ \text{kJ/mol}CH_4 \quad [2.3]$$

There are two main groups of methanotrophic bacteria, which are designated Type I and Type II (Borjesson et al. 2004; Hanson and Hanson 1996). Type I methanotrophs assimilate formaldehyde through the ribulose monophosphate pathway (RuMP); most of them form cysts and are incapable of fixing N_2. Type II methanotrophs include the genera Methylocystis and Methylosinus, which assimilate formaldehyde via the serine pathway. Methylosinus form exospores and Methylocystis form cysts, and both can fix N_2 (Hanson and Hanson, 1996). Shifts in the methanotrophic populations in soils can occur as a response to environmental stimulus, such as change in concentrations of CH_4 and O_2, temperature, pH and N_2.

All methanotrophs can synthesize a membrane-bound form of the enzyme (pMMO) and produce a soluble form (sMMO). The soluble form sMMO can rapidly co-metabolize a variety of aliphatic compounds, including halogenated hydrocarbons (Scheutz et al. 2004a; Hanson and Hanson 1996). Figure 2.2 illustrates the pathways of CH4 oxidation by methanotrophs.

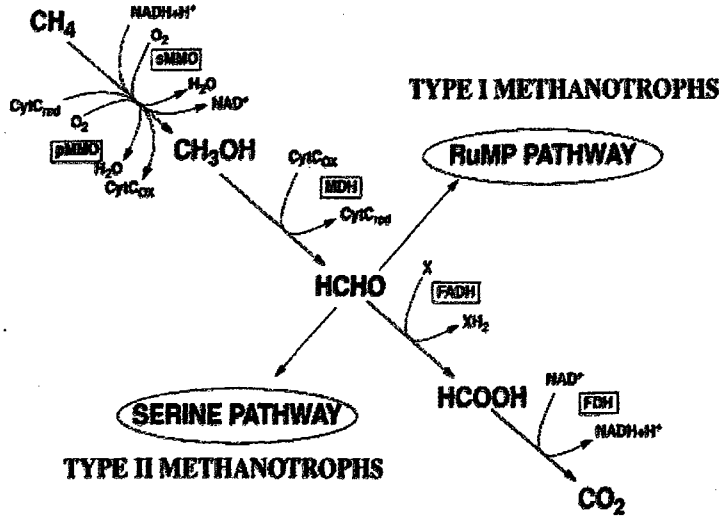


Figure 2.2 Pathways for the oxidation of CH_4 (Adapted from Hanson and Hanson 1996).

It was reported in the literature that methanotrophs are also capable of performing oxidative conversions of a number of chemical compounds (Scheutz et al. 2003; Kjeldsen et al. 1997). The conversion of halogenated hydrocarbons is the result of a process referred to as co-metabolism; co-metabolism is the transformation of a compound by organisms that do not obtain their energy or carbon for cell growth from the transformation and hence require an alternative source of carbon and energy (Scheutz et al. 2004a).

2.3 METHANE OXIDATION IN THE LANDFILL COVER SYSTEM

Microbial oxidation of CH_4 in landfill cover (LFC) system plays an important role in reducing CH_4 emissions into the atmosphere. Oxidation rates of CH_4 differ within and between landfill sites due to seasonal climate changes, physical heterogeneities in the cover medium and CH_4 concentrations (Kallistova et al. 2005, Borjesson et al. 2004; Bogner et al. 1997; Whalen and Reeburgh 1996).

Previous studies investigated some individual effects of environmental variables on the rate at which CH_4 is biologically oxidized. The rate of CH_4 oxidation in LFC depends on temperature, moisture content, medium physical characteristics and chemical composition, pH, nutrients and O_2 concentrations (Jugnia et al. 2008; Kettunen et al. 2006; Wilshusen et al. 2004b; Borjesson et al. 2004; Hilger and Barlaz 2002; Bogner et al. 1997; Whalen and Reeburgh 1996).

2.3.1 TEMPERATURE

Temperature conditions within the LFC can influence the growth of methanotrophic bacteria as well as the rate of O_2 diffusion in the soil pores. Microbial CH_4 uptake shows seasonal temperature dependence, with an optimum air temperature in the range of 25-36°C. Czepiel et al. (1996) found 36°C as the optimum temperature, and Whalen et al. (1990) recorded the optimum temperature ranged between 31 to 36°C. Boeckx and Van Cleemput (1996b) and Bender and Conrad (1995) reported the optimum to be between 25-30°C. On the other hand, Kettunen et al. (2006) stated that methanotrophs are still active at low temperatures (4-12°C). Einola et al. (2007) reported that CH_4 oxidation can occur at temperatures as low as 1°C. Kjeldsen et al. (1997) affirmed that high CH_4 oxidation potentials were observed in the laboratory at 25°C, but were 3-4 times slower at 10°C.

The temperature has a strong effect on which type of methanotrophs are active. Only Type I methanotrophic bacteria grow at temperatures between 3 and 10°C while both types grow at 20°C (Kallistova et al. 2005; Borjesson et al. 2004; Gebert et al. 2003; Horz et al. 2002). King and Adamsen (1992) concluded that the bacterial enzymatic processes at low temperature limit their performance more than any other environmental condition. Moreover, Kettunen et al. (2006) reported that lower temperatures affect negatively the O_2 diffusion within the cover, since the diffusion coefficient in the cover decreases with declining temperature, which in turn decrease the biological oxidation rates.

Studying the effect of temperature is important for the design and applications of biologically active LFC system. Effective CH_4 management plans depend on the

capacity of the LFC to biologically oxidize CH_4 throughout the four seasons, and for different climatic regions.

2.3.2 MOISTURE CONTENT

Moisture content is one of the most important parameters affecting CH_4 oxidation in the LFC. 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, CH_4 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 CH_4 in water, which is four orders of magnitude lower than in air (Borjesson et al. 1998). Moreover, some researchers (Czepiel et al. 1996; Whalen et al. 1990) observed a decrease in the soil oxidizing capacity at low moisture content, presumably due to physiological response to water stress, resulting in lower microbial activities.

Previous researchers (Borjesson et al. 1998; Boeckx et al. 1996b; Whalen and Reeburgh 1996) recorded the optimum moisture content for CH_4 uptake in LFC soils to be in the range of 10-20%. Bender and Conrad (1995) reported maximum CH_4 oxidation rate in LFC soil at the optimum moisture content in the range of 20 to 35%.

2.3.3 NUTRIENTS AND SOIL AMENDMENTS

Bacteria need other elements as nutrients for their cellular metabolism in addition to a carbon source. A study conducted by Gebert et al. (2003) indicated that the activity of a dense methanotrophic population, which had developed under conditions of high CH_4 fluxes, was limited by nutrient availability. Albanna et al. (2007) investigated the

combined effect of nutrient addition and soil moisture, and found that adding nutrients to the soil with 30% moisture content at 22°C enhanced the CH_4 oxidation efficiency from 38% to 81%, while adding nutrients to the soil with low moisture content (15% w/w) at 22°C resulted in decrease in CH_4 oxidation efficiency from 35% to 16%; it appears that the later conditions provided a stressful environment for bacterial activities due to the lower levels of moisture available. Kightley et al. (1995) stated that the amendment of coarse sand with sewage sludge was found to enhance CH_4 oxidation capacity by 26% compared to the un-amended control soil. De Visscher et al. (2001) reported that amending the LFC soil with nitrifying sludge or compost can enhance the CH_4 consumption after a brief inhibition period.

2.3.4 OXYGEN AND METHANE CONCENTRATIONS

The bacterial oxidation activities depend on the presence of sufficiently high concentrations of both CH_4 and O_2. Oxygen concentration plays an important role in the control of CH_4 oxidation and the microbial ecology of methanotrophs (Wilshusen et al. 2004b). Maximum CH_4 oxidation rates are obtained at cover depth from 0.1 to 0.2 m, where both CH_4 and O_2 are present (Scheutz et al. 2004b; De Visscher et al. 2001; Kightley et al., 1995). Proper O_2 concentrations are essential for CH_4 to be biologically oxidized. Czepiel et al. (1996) stated that CH_4 oxidation activities are slightly sensitive to O_2 concentrations above 3%, but these activities dropped off significantly at O_2 concentrations of less than 3%.

Methane concentration affects the biological oxidation rates in the LFC. The CH_4 oxidation rate is a function of the CH_4 concentration, and shows typical Michaelis-Menten characteristics (Stein 2001; Czepiel et al. 1996), as follows:

$$V_{CH\,4} = \frac{V_{\max} \times [CH_4]}{K_m + [CH_4]} \qquad [2.4]$$

where, V_{CH4} is the CH_4 reaction rate ($\mu gCH_4\ h^{-1}g^{-1}$), V_{max} is the maximum CH_4 reaction rate ($\mu gCH_4\ h^{-1}g^{-1}$), $[CH_4]$ is the CH_4 mixing ratio (ppm) in air, and K_m is the CH_4 half saturation constant (ppm).

Stein (2001) stated that the rate of oxidation is independent of the amount of CH_4 when CH_4 concentrations are high; in this case the bacterial oxidation occurs at maximum value (zero-order kinetics). Investigations by Czepiel et al. (1996) and Kightley et al. (1995) indicated that zero-order kinetics would be achieved when CH_4 headspace are greater than 2%.

2.3.5 EXOPOLYMERIC SUBSTANCES

Many bacteria including CH_4 oxidizers produce exopolymeric substances (EPS). The nature and degree of polymer formation varies widely between both: microbial species and environmental conditions. Wilshusen et al. (2004a) studied the CH_4 oxidation potential using several types of compost methanotrophic biofilters columns over a period of 220 days. They observed an increase in the methanotrophic activity over a period of 100 days (up to 400 $gCH_4 \times m^{-2} \times d^{-1}$), and then a gradual decrease within the next 120 days (up to 100 $gCH_4 \times m^{-2} \times d^{-1}$). These results were related to the formation of EPS in the

zones of maximum CH_4 oxidation. Hilger et al. (1999) found similar results and explained this phenomenon was due to the production of exopolymers, which clog the soil pores and hinder the gas diffusion to the microorganisms, which was reflected on the CH_4 oxidation capacity of the LFC. Wilshusen et al. (2004a) suggested that mixing the cover media may allow the breakage of EPS-induced clumps and distribution of EPS throughout the cover, and can have a significant stimulatory effect on CH_4 oxidation efficiency in the cover.

2.3.6 SOIL PROPERTIES

Soil properties such as texture, particle size and soil gas concentrations affect CH_4 uptake by methanotrophs. Boeckx et al. (1996a) reported that higher oxidation efficiencies (61%) occurred in coarse sand than in fine sand or clay (40-41%). Finer particles result in decreased gas permeability, which inhibits O_2 penetration. A porous medium allows O_2 penetration almost throughout the full cover depth to support the methane oxidizers. Boeckx et al. (1996b) reported that soil texture has an influence on CH_4 oxidizing capacity of cover soils; coarse textured soils in their experiment showed higher oxidizing rate (16.38 $\mu gCH_4 \times m^{-2} \times h^{-1}$) than fine textured soils (9.3 $\mu gCH_4 \times m^{-2} \times h^{-1}$). These authors affirm that soil texture influences gas transport and therefore controls CH_4 emissions and oxidation rates.

2.4 THE BIOLOGICAL CO-OXIDATION OF NMOCs IN LANDFILL COVER SYSTEM

The defining characteristic of methanotrophic bacteria is the enzyme monooxygenase (MMO). Monooxygenase is a broadly nonspecific enzyme by which methanotrophic bacteria derive both energy and carbon from the oxidation of CH_4. Monooxygenase can catalyze a wide range of oxidative reactions such as the co-metabolic transformation of chlorinated solvents (Alvarez-Cohen and McCarty 1991). Co-metabolic transformations are reactions that are catalyzed by existing microbial enzyme and that yield no carbon or energy benefits to the transforming cells (Alvarez-Cohen and Speitel Jr. 2001). Co-metabolism may occur relatively slowly in comparison to metabolism of the growth substrate (CH_4). It was demonstrated in literature that a wide range of chlorinated aliphatics can be biologically degraded by methanotrophs co-metabolic transformation reactions, but TCE was the most widely studied (Lontoh and Semrau 1998; McFarland et al. 1992; Oldenhuis et al. 1991; Alvarez-Cohen and McCarty 1991; Tsien et al 1989). Alvarez-Cohen and Speitel Jr. (2001) reported that the reaction of chlorinated solvents with the enzyme MMO generates chlorinated oxidation products that may react with cellular macromolecules or may be hydrolyzed spontaneously into CO_2, chloride or other non volatile products that are mineralized by the bacteria. These researchers demonstrated that there may be a competition between growth substrate and co-metabolic substrate on the enzyme active sites, and this competition can result in overall decreased transformation rates of each substrate.

All of the researches mentioned above were conducted using pure methanotrophic cultures. Very few studies have reported on the attenuation of CH_4 and NMOCs in LFC system, and all were based on laboratory scale batch experiments. Kjeldsen et al. (1997) conducted a batch incubation experiment to investigate the oxidation of CH_4, benzene, toluene, trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) in LFC soil. Their study showed that the LFC soil have potential for degrading CH_4, benzene and toluene only. Schutez et al. (2004a) also conducted batch experiments to investigate the potential for natural attenuation of CH_4 and VOCs in soil exposed to LFG, and to examine the degradation of 26 single trace components. These authors stated that lower level chlorinated compounds were shown to be degradable, and the degradation occurred in parallel with the oxidation of CH_4 (0.03-1.7 $\mu g \times g_{soil}^{-1} \times h^{-1}$). Aromatic hydrocarbons were rapidly degraded, giving high maximal oxidation rates (0.17-1.4 $\mu g \times g_{soil}^{-1} \times h^{-1}$). Fully halogenated hydrocarbons were not degraded under oxidative conditions.

The effect of volatile organic compounds (VOCs) on CH_4 oxidation in landfill cover soil was examined by Chiemchaisri et al. (2001), using a set of lab scale batch experiment. These authors stated that the presence of organic compounds affected the methanotrophic activities, and therefore a decrease in the CH_4 oxidation rates of the soil was monitored. Without VOCs, the oxidation rate observed was 0.302 $mg_{CH4} \times g_{soil}^{-1} \times d^{-1}$, but when benzene was injected with CH_4 into the batch reactors, the CH_4 oxidation rate dropped to 0.254 $mgCH_4 \times g_{soil}^{-1} \times d^{-1}$, and when dichloromethane (DCM) was injected in parallel with CH_4, the CH_4 oxidation rate dropped to 0.031 $mgCH_4 \times g_{soil}^{-1} \times d^{-1}$. These researchers concluded that VOC emissions are a significant variable to be considered in designing a

final cover to reduce CH_4 emissions since their presence can affect adversely the CH_4 oxidation rates.

2.5 THE OXIDATION CAPACITY OF METHANOTROPHS IN COMPOST LANDFILL COVER

As a LFC medium, compost offers a good mix of nutrient supply, porosity, water-holding capacity and pH buffer. Therefore, compost can be incorporated into the design of LFC system to enhance the biological attenuation of CH_4 and NMOCs in LFC. The biological oxidation capacity of compost was tested by few researchers. Barlaz et al. (2004) conducted field experiment to compare emissions of CH_4 and NMOCs from landfill cells covered with clay soil and another cell covered with a bio-cover consisting of yard waste compost. These researchers reported that the compost covered areas exhibited lower CH_4 and trace gas emissions relative to soil covered areas, and the biological cover offered advantages to traditional soil covers. Jugnia et al. (2008), Mor et al. (2006), Stern et al. (2007), and Hilger and Humer (2003), based on their experiments to examine CH_4 oxidation extent in compost as the LFC, concluded that compost promoted good microbial growth, enhanced CH_4 oxidation and appeared to be an effective medium for the LFC system.

However, subsequent investigations of bio-covers need to address the durability, active life of the cover material and its maintenance. Also physical and environmental variables affecting the process and the competition of other aerobic bacteria for nutrients and their

impact on the overall CH_4 consumption has to be addressed. Additionally, more research is still needed to tackle the biological oxidation of NMOCs throughout the compost layers under different environmental conditions.

2.6 SIMULATION OF BIOLOGICAL OXIDATION IN LANDFILL COVER SYSTEM

Modeling the biological oxidation processes that occur within the LFC can successfully lead to the optimization of design parameters such as cover type and thickness. All modeling efforts reported in literature focused on the biological oxidation of CH_4 particularly as the main component of LFG. In fact, these models disregarded the trace amounts of NMOCs, which can strongly affect the oxidation process and inhibit the activities of the bacterial consortiums. The previous mathematical models were developed based on transport-reactive simulation models, and imparted quantitative perceptions of biological and physical processes, with reference to CH_4 transport, oxidation and reaction rates. In this review, the key previous modeling efforts are presented below.

Hilger et al. (1999) and De Visscher and Cleemput (2003) described simulation models for gas diffusion and CH_4 oxidation in LFC soils, using Stefan-Maxwell model to represent CH_4 diffusion, and Michaelis-Menten model to describe CH_4 biological reaction rate. The Stefan-Maxwell equation applied to the soil matrix was:

$$-\frac{P}{RT}\frac{\partial y_i}{\partial z} = \sum_{j=1, j\neq i}^{n} \frac{N_i y_j - N_j y_i}{D_{soil,ij}} \qquad [2.5]$$

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 (K), D_{ij} the diffusion coefficient of component i in component j (m^3_{gas} m^{-1}_{soil} s^{-1}), Ni the flux of component i using a fixed frame of reference, z is the depth (m).

In the model presented by De Visscher and Cleemput (2003), Stefan-Maxwell equation was applied to a soil matrix, and the binary diffusion coefficient was calculated from the molecular diffusion coefficient in the free gas (m^2_{gas} s^{-1}) multiplied by a factor to incorporate the effects of limiting pore space, constrictivity and tortuosity (m_{gas}/m_{soil}). The sensitivity analysis of the model showed that it was mostly sensitive to the maximum CH_4 reaction rate that can be obtained. Therefore, these researchers concluded that future work should investigate the factors that determine the maximum methanotrophic activity that can be reached in the soil.

El-Fadel et al. (1995) and Stein (2001) used the general flux equation to describe CH_4 transport and Monod equation to model the biological oxidation rate of CH_4. Stein (2001) developed a numerical model for the biological oxidation and migration of CH_4 in soils. In the gas transport phase, their model employed the theory of physical transport of gases by diffusion and advection. The model was based on the following continuity equation:

$$a\frac{dC_i}{dt} = -\nabla J_i + R_i \qquad [2.6]$$

where, a is the air-filled porosity, C_i is the concentration of gas component i, ($mol \times m^{-3}$), J_i its flux ($mol \times m^{-2} \times s^{-1}$), and R_i its reaction rate.

The biological CH_4 oxidation was modeled with a two substrate Michaelis-Menten equation, as follows:

$$R_{CH4} = V_{max}\left(\frac{C_{CH4}}{K_{CH4}+C_{CH4}}\right)\left(\frac{C_{O2}}{K_{O2}+C_{O2}}\right) \qquad [2.7]$$

where, V_{max} is the maximum CH_4 consumption rate (nmol day^{-1} $g^{-1}_{soil\ dry\ weight}$), C_{CH4},C_{O2} are the average head space concentration for CH_4 and O_2, K_{CH4} and K_{O2} are the half-saturation constants for CH_4 and O_2, respectively.

The final model equation was:

$$\phi\frac{\partial C_i}{dt} = D\frac{\partial^2 C_i}{dx^2} - \frac{\partial(vC_i)}{dx} \pm R_i \qquad [2.8]$$

where, ϕ the soil porosity (dimensionless), v the flow velocity of gas mixture through soil ($m\ s^{-1}$), D the diffusion coefficient of gas mixture in soil ($m^2\ s^{-1}$).

Bogner et al. (1997) developed a three dimensional finite difference model (Landfill Methane Emissions Model) that described LFG transport and oxidation in LFC soils. In the LMEM, modified mass transfer coefficients were developed from field soil gas concentration profiles (CH_4, CO_2, and O_2) and physical properties (such as total porosity and volumetric moisture content) to calculate the net CH_4 flux at the soil atmosphere interface.

The models listed above are efforts to describe field conditions. All of the models presented in the literature were simulating CH_4 transport and biological oxidation only. There are limitations to the practical applications of these models and several researchers concluded with a discussion that further research is needed. There is definitely a need to develop a comprehensive landfill gas transport model that realistically simulates the LFC system, evaluates the physical and biochemical processes, and includes NMOCs transport and oxidation, as well as their effect on CH_4 oxidation rates.

The complexity and the multi-factorial interactions between the various factors affecting biological oxidation of CH_4 and NMOCs in LFC system impose a challenge for simulating this system using conventional mathematical methods. Recently, advanced methods, such as the artificial neural networks (ANN) analyses, established their reputation as alternative modeling techniques. An artificial neural network is a computational method that can be utilized to solve many complex and real-world problems (Basheer and Hajmeer 2000). The power of ANN lies in implementing the learning algorithms of neural networks to describe the behavior of the system without the need to know the exact interrelationships (Lu and Rosenbaum 2003). The ANN is constructed from interconnected processing elements called neurons or cells. The connections form circuits, allowing information supplied locally to be transferred. It is assumed that adapting ANN in this research will offer a computational mechanism that is able to acquire, represent and compute a mapping from one multivariate space of information to another, given a set of data representing the relationships of gas transport and biological oxidation. Artificial neural networks can be a powerful tool with ability to represent both linear and non-linear relationships and learn these relationships directly

from the data being modeled. This simulation method will identify connections, and focus on the parallel processing of numbers of simple parameters which together can represent a complex function.

The significant information processing capabilities of ANN approach, and the ability to learn from examples, make this method very efficient problem-solving tool (Lu and Rosenbaum 2003; Basheer and Hajmeer 2000; Yeh 1998), and thus can offer advantages in simulating the complex biological oxidation processes in the LFC system. Recently, applying ANN in modeling different complex engineering problems have received positive and wide attention, where dynamic characteristics and uncertainty may be important (Yeh 2007; Lu and Rosenbaum 2003; Lee 2003).

2.7 SUMMARY

The design of a new and innovative LFC system can provide practical solution to the control of CH_4 and NMOCs emissions, not only in North America but worldwide, where MSW is deposited in dumps or poorly designed landfills. Suthersan (2002) reported that there are 226,000 sanitary landfills in the U.S., that required evaluation for potential risks to human and environmental receptors, and almost all of them needed installation of a new cover as a final step in the closure process.

Optimizing the physical, chemical and biological LFC parameters can maximize the rate at which CH_4 and NMOCs are biologically oxidized; therefore, a clearer understanding of the pertinent controlling factors and mechanisms can help to achieve this goal. There are

very few results in the literature regarding NMOCs oxidation in the LFC, and mainly based on short-term incubation studies which may not represent long-term performance. Identifying and quantifying the effects of NMOCs present in the LFG is important, since these compounds might impact negatively on the oxidative capability of the bio-cover. Furthermore, the numerical methods available in the literature to model the biological CH_4 oxidation process have never incorporated the effect of NMOCs on this process. The use of ANN can provide a powerful tool to model the CH_4 oxidation rates when NMOCs are present, however, further studies are recommended to simulate the coupled processes of the LFC system using numerical modeling, and include NMOCs transport and oxidation, as well as their effect on CH_4 oxidation rates.

2.8 REFERENCES

Albanna, M., Fernandes, L., and Warith, M. (2007). "Methane Oxidation in Landfill Cover Soil; the Combined Effects of Moisture Content, Nutrient Addition, and Cover Thickness," *Journal of Environmental Engineering and Science*, 6, pp.191-200.

Alvarez-Cohen, L., and McCarty, P.L. (1991), "A Co-Metabolic Biotransformation Model For Halogenated Aliphatic Compounds Exhibiting Product Toxicity," *Environmental Science and Technology*, 25, pp. 1381-1387.

Alvarez-Cohen, L. and Speitel Jr. G.E. (2001), "Kinetics of Aerobic Cometabolism of Chlorinated Solvents," Biodegradation, 12: pp. 105–126.

Barlaz, M.A., Green, R.B., Chanton, J.P., Goldsmith, C.D., and Hater, G.R. (2004), "Evaluation of a Biologically Active Cover for Mitigation of Landfill Gas Emissions," *Environmental Science and Technology*, 38, pp. 4891-4899.

Basheer, I.A., and Hajmeer, M. (2000), "Artificial Neural Networks: Fundamentals, Computing, Design and Application," *Journal of Microbiological Methods*, 43, pp. 3-31.

Bender, M., and Conrad, R. (1995), "Effect of CH_4 Concentrations and Soil Conditions on the Induction of CH4 Oxidation Activity," *Soil Biology and Biochemistry*, 27, pp. 1517- 1527.

Boeckx, P. and Van Cleemput, O. (1996a), "Methane Emission From a Landfill and the Methane Oxidizing Capacity of its Covering Soil," *Soil Biology and Biochemistry*, 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 Quality*, 25 (1996), pp. 178- 183.

Bogner, J., Meadows, M., and Czepiel, P. (1997), "Fluxes of Methane between Landfills and the Atmosphere: Natural and Engineered Controls," *Soil Use and Management*, 13, pp. 268-277.

Borjesson, G., Sundh, I., Tunlid, A., Frostegard, A., and Svensson, B.H. (1998), "Microbial Oxidation of CH_4 at High Partial Pressures in an Organic Landfill Cover Soil under Different Moisture Regimes," *Microbiology Ecology*, 26, pp. 207-217.

Borjesson, G., Sundh, I., and Svensson, B.H. (2004), "Microbial Oxidation of CH_4 at Different Temperatures in Landfill Cover Soils," *Microbiology Ecology*, 48, pp. 305-312.

Chiemchaisri, W, Chettiyappan, V. and Shing Wu, J. (2001), "Effects of Trace Volatile Organic Compounds on Methane Oxidation," *Brazilian Archives of Biology and Technology*, 44, pp.135-140.

Czepiel, P.M., Mosher, B., Crill, P.M., and Harris R.C. (1996), "Quantifying the Effect of Oxidation on Landfill Methane Emissions," *Journal of Geophysical Research*, 101, pp. 16.721-16.729.

De Visscher, A. and Schippers, M. (2001), "Short-Term Kinetic Response of Enhanced Methane Oxidation in Landfill Cover Soils to Environmental Factors," *Biological Fertile Soils*, 33, pp. 231-237.

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.

El-Fadel, M., Findikakis, A.N., and Leckie, J.O. (1995), "Numerical Modelling of Generation and Transport of Gas and Heat in Landfills: I. Model Formulation," *Waste Management and Research*, 14, pp. 483-504.

Einola J-K.M., Kettunen, R.H., and Rintala, J.A. (2007), "Responses of Methane Oxidation to Temperature and Water Content in Cover Soil of a Boreal Landfill," *Soil Biology and Biochemistry*, 39, pp. 1156-1164.

Emission Inventory Improvement Program (EIIP)- (1999), "Methods for Estimating Greenhouse Gas Emissions from Municipal Waste Disposal". Volume 8, Chapter 5, EPA. http://www.arb.ca.gov/ei/areasrc/ccosmeth/att_b_waste_disposal.doc.

Environment Canada (October, 2005), Landfill Gas Management in Canada Report, http://www.ec.gc.ca/pdb/ghg/inventory_report/2005_report/tdm-toc_eng.cfm.

Gebert, J., Groengroeft, A., and Miehlich, G. (2003), "Kinetics of Microbial Landfill Methane Oxidation in Biofilters," *Waste Management*, 23, pp. 609-619.

Hanson, R. and Hanson, T.E. (1996), "Methanotrophic Bacteria," *Microbiological Reviews*, 60, pp. 439- 471.

Hilger, H., Cranford, D., and Barlaz, M. (1999), "Methane Oxidation and Microbial Exopolymer Production in Landfill Cover Soil," *Soil Biology and Biochemistry*, 32, 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., Mclnernery 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., and Dunfield, P.F. (2002), "Activity and Community Structure of Methane-Oxidising Bacteria in a Wet Meadow Soil," *Microbiology Ecology*, 41, pp. 247- 257.

Intergovernmental Panel on Climate Change, (2001). IPCC Working Group I, The Scientific Basis, http://www.grida.no/climate/ipcc_tar/wg1/248.htm.

Jugnia, L.B., Cabral, A. R., and Greer, C.W. (2008), "Biotic Methane Oxidation within an Instrumented Experimental Landfill Cover," *Ecological Engineering*, 33, pp. 102-109.

Kallistova, A. YU., Kevbrina, M.V., Nekrasova, V.K., Glagolev, M.V., Serebryanaya, M.I., and Nozhevnikova, A.N. (2005), "Methane Oxidation in Landfill Cover Soil," *Microbiology*, 74, pp. 608-614.

Kettunen, R., Einola, J-K.M. and Rintala, J.A. (2006), "Landfill Methane Oxidation in Engineered Columns at Low Temperature," *Water, Air and Soil*, 177, pp. 313-334.

Kightley, D., Nedwell, DB. and Cooper, M. (1995), "Capacity for Methane Oxidation in Landfill Cover Soils Measured in Laboratory-Scale Soil Microcosms," *Applied and Environmental Microbiology*, 61, pp. 592-601.

King, G.M., and Adamsen, P.S. (1992), "Effects of Temperature on Methane Consumption in a Forest Soil and in Pure Cultures of the Methanotroph Methylomonas Rubra." *Applied and Environmental Microbiology*, 58, pp. 2,758-2,763.

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.

Lee, Seung-Chang (2003), "Prediction of Concrete Strength Using Artificial Neural Networks," *Engineering Structures*, 25, pp. 849-857.

Lontoh, S., and Semrau, J. (1998), "Methane and Trichloroethylene Degradation by Methylosinus Trichosporium OB3b Expressing Particulate Methane Monooxygenase," *Applied and Environmental Microbiology*, 64, pp. 1106-1114.

Lu, P. and Rosenbaum, M.S., (2003), "Artificial Neural Networks and Grey Systems for the Prediction of Slope Stability," *Natural Hazards*, 30, pp. 383-398.

McFarland, M.J., Vogel, C.M. and Spain, J.C (1992), " Methanotrophic Cometabolism of Trichloroethylene (TCE) in a Two Stage Bioreactor System," *Water Resource,* 26, pp. 259-265.

Mor, S., De Visscher, A., Ravindra, K., Dahiya, R.P., Chandra, A., and Van Cleemput, O. (2006),"Induction of Enhanced Methane Oxidation in Compost: Temperature and Moisture Response," *Waste Management,* 26, pp. 381-388.

Oldenhuis, R., Oedzes, J.Y., Van Der Waarde, J.J., and Janssen, D.B. (1991), "Kinetics of Chlorinated Hydrocarbon Degradation by Methylosinus Trichosporium OB3b and Toxicity of Trichloroethylene", *Applied and Environmental Microbiology,* 57, pp. 7-14.

Scheutz, C., Bogner, J., Chanton, J., Blake, D., Morcet, M., and Kjeldsen, P. (2003),"Comparative Oxidation and Net Emissions of Methane and Selected Non-Methane Organic Compounds in Landfill Cover soils," *Environmental Science and Technology*, 37, pp. 5150-5158.

Scheutz, C., Mosbaek, H., and Kjeldsen, P. (2004a),"Attenuation of Methane and Volatile Organic Compounds in Landfill Soil Covers," *Environmental Quality*, 33, pp. 61-71.

Scheutz, C., and Kjeldsen, P. (2004b),"Environmental Factors Influencing Attenuation of Methane and Hydrochloroflorocarbons in Landfill Cover Soils," *Environmental Quality*, 33, pp. 72-79.

Stern, J.C., Chanton, J., Abichou, T., Powelson, D., Yuan, L., Escoriza, S., and Bogner, J., (2007), "Use of a Biologically Active Cover to Reduce Landfill Methane Emissions and Enhance Methane Oxidation", *Waste Management*, 27, pp. 1248-1258.

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.

Suthersan, S. (2002), "Natural and Enhanced Remediation Systems", Lewis Publishers, *Boca Raton*, Florida, U.S.A.

Tsien, H.C., Brusseau, G., Hanson, R., and Wackett, L.P. (1989),"Biodegradation of Trichloroethylene by Methylosinus trichosprium OB3b," *Applied and Environmental Microbiology,* 55, pp. 3155-3161.

USEPA (1999), Municipal Solid Waste Landfills, Volume I: Summary of the Requirements for the New Performance Standards and Emissions Guidelines for Municipal Solid Waste Landfills. 453/R-96-004. Research Triangle Park, NC. USA.

USEPA (2003), Landfill Gas and How It Affects Public Health, Safety and the Environment, http://www.epa.gov/lmop/docs/faqs_about_LFG.pdf.

USEPA (2006), "Global Anthropogenic Non-CO_2 Greenhouse Gas Emissions: 1990-2020, U.S. Environmental Protection Agency, Office of Atmospheric Programs, Climate Change Division, U.S. Environmental Protection Agency, 1200 Pennsylvania Avenue, NW, Washington, DC 20460.

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 CH_4 Oxidation in Boreal Soils," *Soil Biology and Biochemistry*, 28, pp.1271-1281.

Wilshusen, J.H., Hettiaratchi, J.P.A., and Stein, V.B. (2004a), "Long-Term Behavior of Passively Aerated Compost Methanotrophic Biofilters Columns," *Waste Management*, 24, pp. 643-653.

Wilshusen, J.H., Hettiaratchi, J.P.A., De Visscher, A., and Saint-Fort, R. (2004b), "Methane Oxidation and Formation of EPS in Compost: Effect of Oxygen Concentration", *Environmental Pollution*, 129, pp. 305-314.

Yeh, L.C. (1998), "Modeling of Strength of High-Performance Concrete Using Artificial Neural Networks," *Cement and Concrete Research*, 28(12), pp. 1797-1808.

Yeh, Cheng (2007), "Modeling Slump Flow of Concrete Using Second-Order Regressions and Artificial Neural Networks," *Cement & Concrete Composites*, 29, pp. 474-480.

CHAPTER 3

EFFECTS OF TEMPERATURE, MOISTURE CONTENT AND FERTILIZER ADDITION ON BIOLOGICAL METHANE OXIDATION IN LANDFILL COVER SOILS

Muna Albanna and Leta Fernandes

ABSTRACT

Patterns of methane (CH_4) oxidation were investigated under various combinations of environmental factors including temperature, moisture content, and fertilizer addition (as an additional nutrient source) in two types of existing landfill cover soils. In all the experimental runs, CH_4 and oxygen concentrations decreased with time, while carbon dioxide concentration increased suggesting that biological CH_4 oxidation was taking place. The highest CH_4 oxidation rates were achieved at 35°C (6.4- 12.3 $\mu gCH_4\ h^{-1}\ g^{-1}_{dry\ soil}$). The lowest oxidation rates were obtained for experiments conducted at 5°C without adding the fertilizer (3.3 to 4.7$\mu g\ CH_4\ h^{-1}\ g^{-1}_{dry\ soil}$). For both types of soil, without adding fertilizer, the soil with 20% moisture content (MC) showed consistently higher oxidation rates compared to soil samples containing 25 or 30% MC, for different operating temperatures. Adding the fertilizer as the nutrient source to the two soils samples with 30% moisture content resulted in enhanced CH_4 oxidation rates in a range of (44 - 145%) at tested temperatures (5 to 35°C).

3.1 INTRODUCTION

Many scientists agree that global warming is on the rise and highly correlated with human activities, not a natural occurrence (IPCC 2007). The atmospheric concentrations of the two principal greenhouse gases carbon dioxide (CO_2) and methane (CH_4) are mounting and have significantly affected climate over the past few centuries. Methane is emitted from a variety of natural and anthropogenic sources. Landfills are estimated to be one of the largest sources of anthropogenic CH_4 emissions; according to (Environment Canada 2005) this sector is responsible for 23% of CH_4 emissions in Canada. In the United States of America, landfills account for 34% of all CH_4 emissions (USEPA 2007). A series of complex biological and chemical reactions begin with the burial of refuse in landfills, where an active anaerobic ecosystem generates CH_4 and CO_2 as the major end products (Czepiel et al. 2003; Hilger and Barlaz 2002; Boeckx and Van Cleemput 1996a; Borjesson and Svensson 1996). The generated biogas, known as landfill gas (LFG), consists of 50-65% CH_4 and 35-50% CO_2, plus trace amounts of non-methane organic compounds (USEPA 2006). Landfill gas can migrate to the surface and enter the atmosphere. If collected appropriately, LFG can be used as a source of energy to generate electricity or can be used directly in some industrial processes to generate heat and steam (Spokas et al. 2006). Unfortunately, the vast majority of existing landfill sites around the world do not have biogas capturing or collection setups. In 2002, Canada's net greenhouse gas (GHG) emission from landfills was estimated to be 22Mt (million metric tonnes) carbon dioxide equivalent (eCO_2), however, only 6.6 Mt eCO_2 were captured (Environment Canada 2005).

In the absence of biogas extraction systems or even as complementary to an existing collection technology, CH_4 oxidation by methanotrophic bacteria in the landfill cover soil is extremely important for the reduction of CH_4 emissions from landfills (Barlaz et al. 2004; Borjesson et al. 1996). Methanotrophic bacteria possess the CH_4 monooxygenase enzyme, which enables them to consume CH_4 and oxidize it to CO_2 and water for energy yield, while another fraction is incorporated into biomass (Wilshusen et al. 2004a; Borjesson et al. 2004; Hilger and Humer 2003; Hanson and Hanson 1996). Previous studies investigated the individual effects of the environmental variables on the rate at which CH_4 is biologically oxidized. The rate of CH_4 oxidation in the landfill cover soil depends on several environmental conditions, such as moisture content (MC), temperature, soil characteristics and composition, pH, nutrients and oxygen (O_2) concentrations (Kettunen et al. 2006; Wilshusen et al. 2004b; Borjesson et al. 2004; Hilger and Barlaz 2002; Bogner et al. 1997; Whalen and Reeburgh 1996).

Microbial CH_4 uptake shows seasonal temperature dependence. Several researchers reported that the highest microbial CH_4 oxidation activity occurred at 30-36°C (De Visscher et al. 2001; Czepiel et al. 1996; Whalen et al. 1990). Kettunen et al. (2006) stated that several batch studies with various soils showed that methanotrophs were still active at low temperatures (4-12°C).

Moisture content is one of the most important parameters affecting CH_4 oxidation in landfill cover soil. Soil pore volume available for gas exchange seems to be the critical factor at different moisture contents (Hilger and Humer 2003). Some researchers (Czepiel et al. 1996; Boeckx and Van Cleemput 1996b) observed a decrease in the soil CH_4

oxidizing capacity at lower moisture content (5% w/w), presumably due to physiological response to water stress, hence resulting in lower microbial activity. Several researchers (Borjesson et al. 1998; Boeckx and Van Cleemput 1996b; Whalen and Reeburgh 1996) recorded the optimum moisture content for CH_4 uptake in landfill cover soils to be in the range of 10-20%. Bender and Conrad (1995) reported maximum CH_4 oxidation rate at the optimum moisture content to be in the range of 20% to 35%.

In addition to a carbon source, bacteria need other elements as nutrients for their cellular metabolism. A study conducted by Gebert et al. (2003) indicated that the activity of a dense methanotrophic population, which had developed under conditions of high CH_4 fluxes, was limited by nutrient availability. Albanna et al. (2007) investigated the combined effect of nutrient addition and soil MC, and found that adding nutrients to the soil with 30% MC at 22°C enhanced the CH_4 oxidation capacity from 38% to 81% in clayey silt soil, while adding nutrients to the same soil with 15% MC resulted in decrease in CH_4 oxidation capacity from 35% to 16%. It appears that the latter condition provided a stressful environment for bacterial activities.

This experimental study aims to elucidate the patterns of biological CH_4 oxidation under different levels of temperature and moisture content using two types of existing landfill cover soils in laboratory scale batch experiments and to draw conclusions about the expected oxidation rates. The two soils were extracted from existing landfill cover soils operating in the same region and under the same environmental conditions. Another objective of the laboratory study was to examine the effect of adding commercial fertilizer to the soil samples as an additional nutrient source. The main question

addressed was if the commercial fertilizer can enhance the biological oxidation in the landfill cover soil and to what extent. The results obtained were statistically compared to investigate the individual and combined effects of the three parameters (temperature, moisture content and fertilizer or nutrient addition) on the biological CH_4 oxidation capacity of the two types of soil.

3.2 MATERIALS AND METHODS

3.2.1 EXPERIMENTAL DESIGN AND SETUP

To analyze the interaction between three parameters affecting the CH_4 oxidation in the landfill cover soil, namely temperature, moisture content, and fertilizer or nutrient addition, a multilevel factorial type statistical design experiment was conducted. Figure 3.1 shows the multilevel factorial experimental design, where the soil samples were tested for three levels of temperature (5, 22 and 35°C) and moisture content (20, 25 and 30% w/w) as well as two levels of nutrients (without and with fertilizer addition), which resulted in 18 combinations of variables for each of the two types of soil being studied.

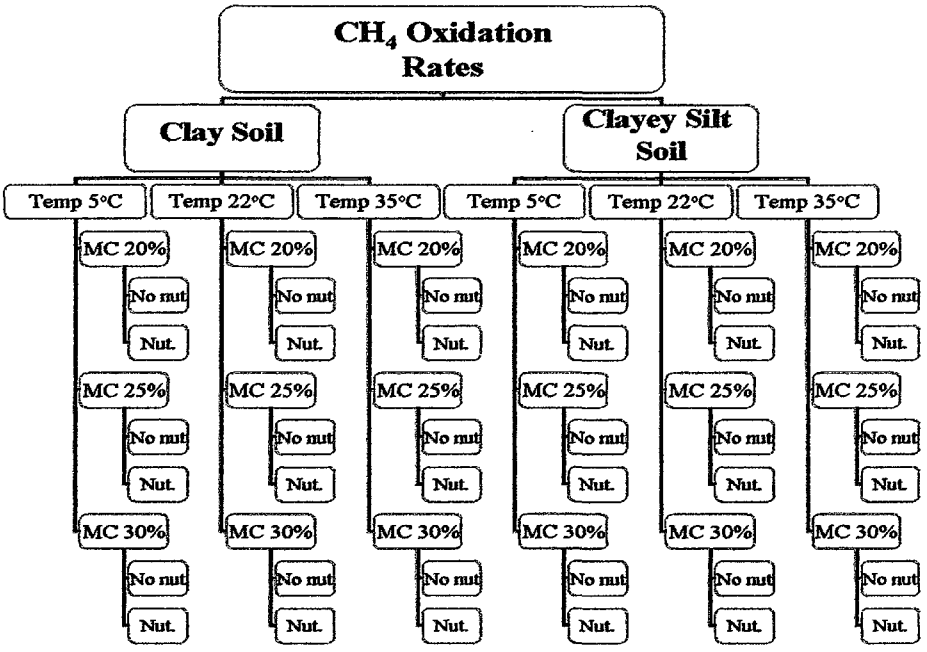


Figure 3.1 Multi-level factorial experimental design.

The chosen temperature levels were set to simulate various climatic conditions that might affect the capacity for biological CH_4 oxidation in the landfill cover soil. As for the moisture content levels it was reported in the literature that the optimum moisture levels were between 10 and 30% w/w, and that the effect of moisture content on CH_4 oxidation capacity of the soil usually follows a parabolic curve, with the reduced oxidation rates in conditions of low as well as high moisture content (Einola et al. 2007; Whalen and Reeburgh 1996; Boeckx and Van Cleemput 1996a).

3.2.2 MATERIALS

Soil samples were collected from the top (250 mm) of existing final cover soil at two landfill sites operating in the Ottawa (Ontario, Canada) region. The soil collected from Trail Road landfill was sampled from an area located near the biogas vents, and was characterized as being silt loam (this soil will be referred to as clayey silt soil). The soil

from Eastern Ontario landfill was collected from the slopes of the final cover and was characterized as clay (this soil will be referred to as clay soil). From these sites conditions, it was assumed that both types of soils were exposed to CH_4 and would contain adequate number of methanotrophs which would serve as seed for microbial activity in the proposed batch experiments. The soil samples were collected from the two landfill sites separately using shovels and transported to the laboratory. Individual samples from each site were sieved, homogenized and stored in closed containers in a dark and cold room at 3°C.

Soils Characteristics

The clayey silt soil sample had the following granulometric composition: 26% sand, 54% silt loam and 20% clay. This soil contained 3.9% organic matter and exhibited pH of 6.4. The field dry bulk density was 1626 kg/m^3. The soil texture was determined by sieve analyses and classified according to the United States Department of Agriculture (USDA) classification system.

The clay soil had the following composition: 1.6% sand, 18.4% silt and 80% clay. The dry bulk density was 1900 kg/m^3. The soil contained 2.4% organic matter, and pH of 8.7. For the grain size analysis, the hydrometer test was performed according to ASTM standard D 422. The grain size results were confirmed by conducting washing test. The coefficient of uniformity (C_u) was estimated to be 25, which indicates that the clay soil is non-uniform. The coefficient of curvature (C_c) was estimated to be 0.37, and therefore, the soil can be considered poorly graded. The soil liquid limit was 56%, the soil plastic limit was 25%. The plastic limit, liquid limit and plasticity index were determined

following ASTM D 4318. According to the soil plasticity characteristics (Day 2001), the clay soil was characterized as "Illites" clay. The clay soil is considered inactive clay, and the detailed calculations for the laboratory tests conducted (hydrometer, liquid and plastic limits, dry bulk density and porosity) are illustrated in Appendix III-5.

The initial MC of each soil (%w/w basis) was tested and determined gravimetrically by oven drying samples at 105°C for 24 hours, following the ASTM D2974-87 procedure. The bulk density was determined by weighing soil filled cylinders, subtracting the cylinder weight, and dividing by the cylinder volume. Organic content was determined by loss on ignition following ASTM D7348-08.

It was noticed during the pre-experimental works that the clay soil might contain higher levels of iron compared to the clayey silt soil. Therefore, to determine the mineral content of the two soils, samples were analyzed using Inductively Coupled Plasma (Varian Vista Pro ICP ES). The clay soil contained 479±37 ppm of iron while the clayey silt soil had an iron content of 308±52 ppm. Also, the clay soil samples contained 430±39 ppm aluminum, while the clayey silt contained 129±6 ppm aluminum. The phosphorus concentration was 7±0.3 ppm and 7±1.1 ppm in the clay soil and clayey silt soil, respectively. The mineral content tests were based on triplicate analysis.

3.2.3 EXPERIMENTAL METHODS

All 36 experimental runs were conducted using laboratory scale batch reactors in triplicates, in addition to controls and blanks. For each experimental set, there were two reactors: the control and the blank. For the control, autoclaved soil was incubated as a

sterile control to prove that the biological activity was the main process responsible for CH_4 decrease. The blanks did not contain soil, and only gases were injected according to the experimental design to account for losses due to leaks.

The CH_4 oxidation capacities of the two soils were tested in standard bottles (batch reactors), each of 160 ml total volume. Before each experimental run, the moisture content of each soil sample was adjusted from the initial moisture content to the required level according to the experimental design, either by drying the samples (air dry) to reduce the moisture or by adding small amounts of sterilized water to increase the moisture content. Soil samples were constantly consolidated and redistributed to obtain more homogenous experimental soils. Prior to placing each soil sample in the reactor, the moisture content was tested again to ensure the correct required percentage (%w/w). In each experiment, 30 g of sieved soil were added to the batch reactor. After placing the soil in each reactor, the glass bottle was sealed with gas tight aluminum seal with tan Teflon/silicone (PTFE) septum, which enabled gas sampling from the reactor's headspace with a gas tight needle and syringe. Afterwards, 40 ml of air from the headspace were withdrawn using a syringe and replaced with 16 ml of laboratory grade CH_4 gas (99% purity) and 24 ml of O_2 gas (100% purity). The injected amount of CH_4 and O_2 provided a mixing ratio of approximately 10% CH_4 and 30% O_2 (v/v) of the total headspace. The O_2 was added to ensure that aerobic conditions prevailed inside the reactor for the duration of the experiment. The concentrations of CH_4, O_2, N_2 and CO_2 were monitored periodically by withdrawing samples from the headspace using a 200 μL gas tight syringe, and injecting it into the inlet of a series 400 Gow-Mac Thermal Conductivity Gas Chromatograph. The first samples were taken immediately after the

addition of CH_4 and O_2 to the reactors, after which they were returned to the designated temperatures according to the experimental design. Between sampling and to ensure good mixing conditions, all batch reactors were rotated on an orbital shakers at a rotation speed of 50 rpm. The batch incubation was terminated when the CH_4 concentration is less than 0.5% of the total headspace; otherwise, the batch reactor was monitored for up to 10 days. The headspace gases in the batch reactors were analyzed and the results were used to calculate the decrease in CH_4 and O_2 concentrations as well as the increase in CO_2 with time. The CH_4 concentration in each batch reactor were plotted as a function of time and the CH_4 oxidation rates were determined from the linear regression of CH_4 concentration over time.

As for the nutrients source, soil fertilizer known as Plant-*Prod 20-20-20, All Purpose Fertilizer* was used. The fertilizer had 20% total nitrogen (5.9% nitrate nitrogen, 3.85% ammoniacal nitrogen, 10.25% urea nitrogen), 20% phosphoric acid (8.7% is soluble phosphorous) and 20% soluble potash (16.6% is soluble potassium). The amount of fertilizer used in the experiments was (0.15 g of fertilizer/ 100 g of soil). It was presumed that this amount would provide adequate C-N-P ratio for aerobic bacteria. The fertilizer was dissolved in sterilized water and added to the soil samples with simultaneous mixing. Then the soil samples were air dried, regularly consolidated and redistributed to promote even drying.

3.3 RESULTS AND DISCUSSION

3.3.1 METHANE OXIDATION CAPACITY OF THE TWO SOILS

In all the experimental runs, the CH_4 and O_2 concentrations decreased with time, suggesting that biological CH_4 oxidation was taking place. This was also supported by the increase in CO_2 concentration in the headspace gas. Hilger and Humer (2003) reported that most of the biological oxidation of CH_4 is accomplished by methanotrophs according to the following equation:

$$CH_4 + 1.5\ O_2 + 0.118\ NH_4^+ \rightarrow 0.118\ (C_4H_8O_2N) + 0.529\ CO_2 + 1.71\ H_2O + 0.118H^+ \quad [3.1]$$

It is worth mentioning that in all the batch experiments, the O_2 concentration was never below 10% v/v, which indicates that CH_4 oxidation was not limited in any of the experimental runs due to low O_2 concentrations. Czepiel et al. (1996) reported that CH_4 biological oxidation process is not affected adversely if O_2 concentration remains above 3%, but methanotrophic activities dropped significantly at O_2 concentration less than 3%.

For the control batch reactors containing sterilized soil samples, the maximum decrease observed in CH_4 concentration was 7% of the total CH_4 injected and there was no CO_2 increase in the headspace gas in any of the controls. These results support further that biological activity was the main mechanism responsible for CH_4 oxidation process.

Clayey Silt Soil

Figure 3.2 shows the results of CH_4 concentration (%v/v) in the headspace of the batch reactors versus time for different experimental runs using the clayey silt soil as a medium. The experimental data obtained represent the average value of the triplicate reactors.

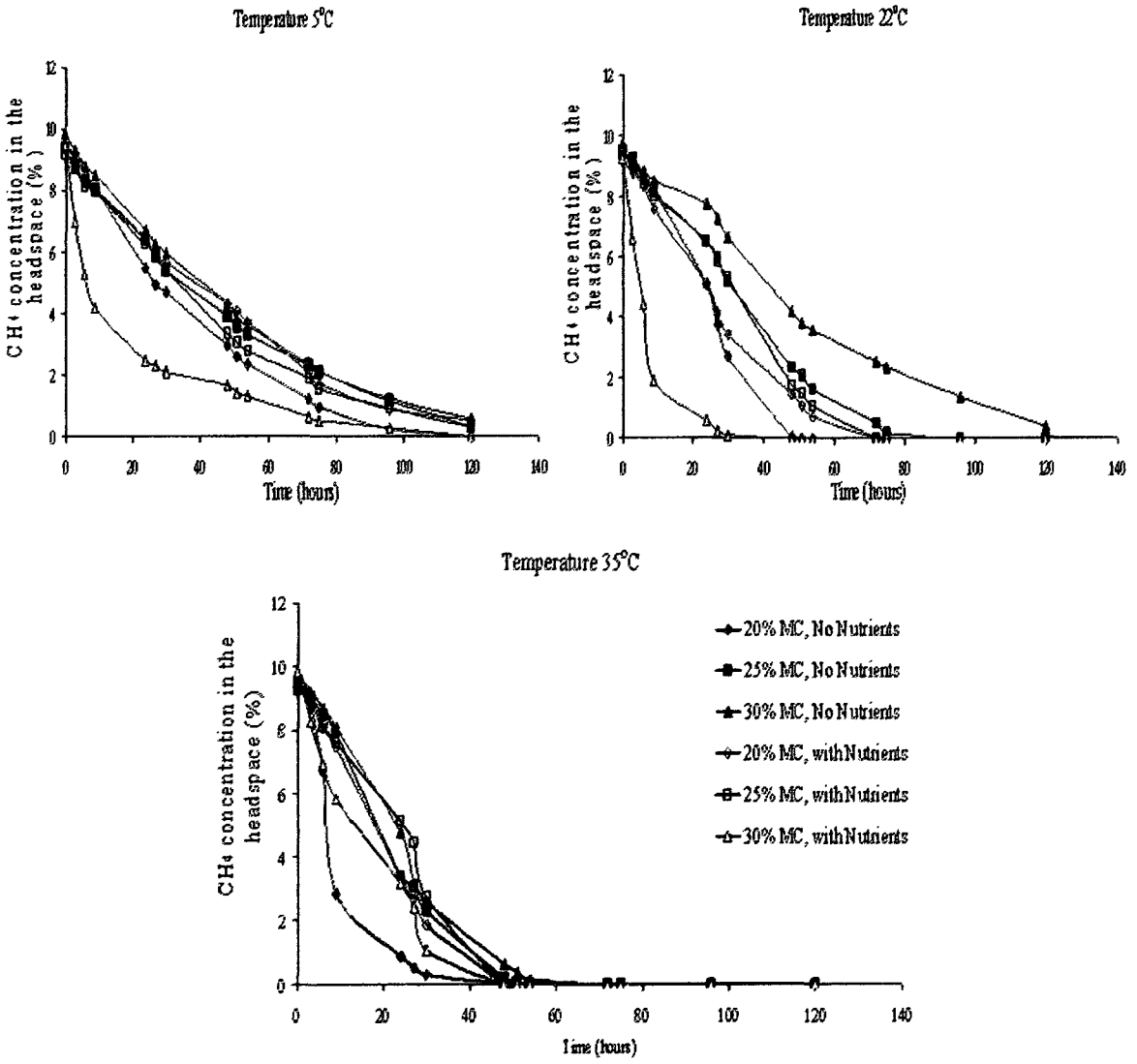


Figure 3.2 Methane concentration (%v/v) versus time in batch reactors using clayey silt soil samples under different operating conditions.

Results plotted in Figure 3.2 illustrate that the temperature effect on the CH_4 oxidation process was quite significant; it masked the effect of the other two variables: moisture content and nutrients. Complete oxidation occurred at 35°C within 48 to 55 hours, while more than 120 hours were necessary at 5°C. Excluding the nutrient addition effect and at all temperatures, the highest microbial CH_4 oxidation activity occurred in the soil with 20% MC. On the other hand, adding nutrients to the clayey silt soil overturned the outcome. The addition of fertilizer to the soil with 30% MC at the tested temperatures significantly improved the CH_4 oxidation performance when compared to the soil with 20% MC and fertilizer addition. At 22°C, fertilizer addition to the soil with 30% MC reduced the time needed for complete CH_4 oxidation from 120 hours to 48 hours. At 5°C, the highest microbial CH_4 oxidation activity occurred when fertilizer was added to the soil samples with 30% MC.

Methane oxidation rates in clayey silt soil under different conditions were calculated based on the linear section of the degradation curve for each experimental run. The zero-order rate constant was then normalized to the dry soil mass. For each experimental run, the average CH_4 oxidation rate was calculated based on triplicates. The determined CH_4 oxidation rates are presented in Figure 3.3.; these rates reflected the effect of the environmental conditions on the oxidation process.

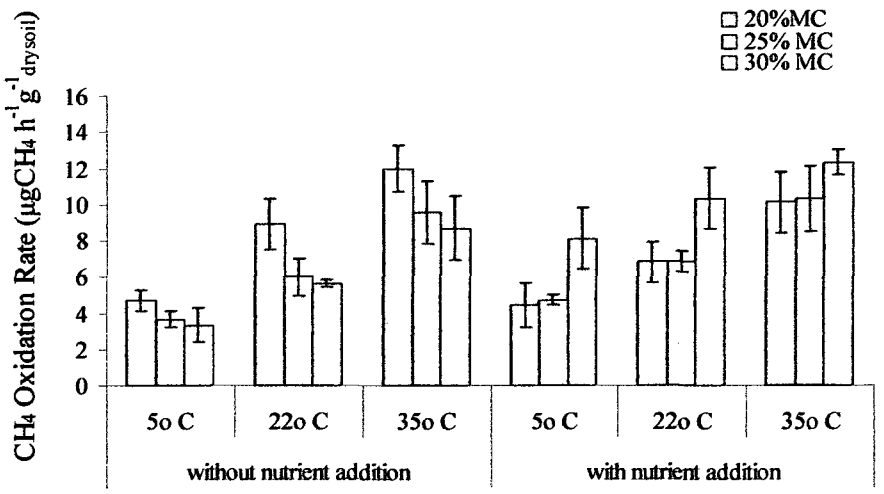


Figure 3.3 Methane oxidation rates with standard deviation using clayey silt soil samples.

Methane consumption rates increased with increasing temperature in all experimental runs. The highest CH_4 oxidation rates were achieved at 35°C (8.7±1.8 – 12.3±0.68 μgCH_4 h^{-1} g^{-1} $_{dry\ soil}$), which is in agreement with the findings by others (De Visscher et al. 2001; Czepiel et al. 1996; Whalen et al. 1990). The lowest oxidation rates were obtained for experiments conducted at 5°C without adding nutrients (3.3±0.96 – 4.7 ±0.26 μg CH_4 h^{-1} $g^{-1}$$_{dry\ soil}$). Figure 3.4 shows the CH_4 oxidation rates of the clayey silt soil samples with 20% MC and without nutrients addition.

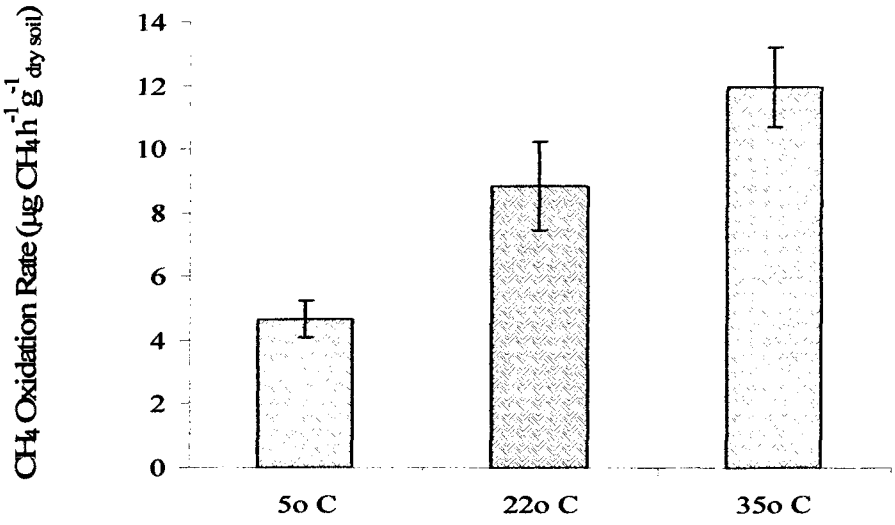


Figure 3.4 Effect of temperature on CH_4 oxidation rates with standard deviation using clayey silt soil samples with 20% MC and no nutrient addition.

Temperature has strong effect on which type of methanotrophs can be active and the changes in the methanotrophs population in the soil will occur in response to temperature. Many researchers reported that only Type I methanotrophic bacteria grow at low temperatures between 3 and 10°C while two types (Type I and Type II) grow at 20°C (Kallistova et al. 2005; Borjesson et al. 2004; Gebert et al. 2003; Horz et al. 2002). King and Adamsen (1992) confirmed that the bacterial enzymatic processes at low temperature restrict their performance more than any other environmental condition. Moreover, lower temperatures affect negatively the O_2 diffusion within the cover, where the diffusion coefficient in soil decreases with declining temperature, as was reported by (Kettunen at al. 2006).

Methane oxidation capacity of the clayey silt soil was also affected by the soil moisture level. Figure 3.5 illustrates the effect of soil moisture on CH_4 oxidation rates without adding nutrients to the clayey silt soil samples.

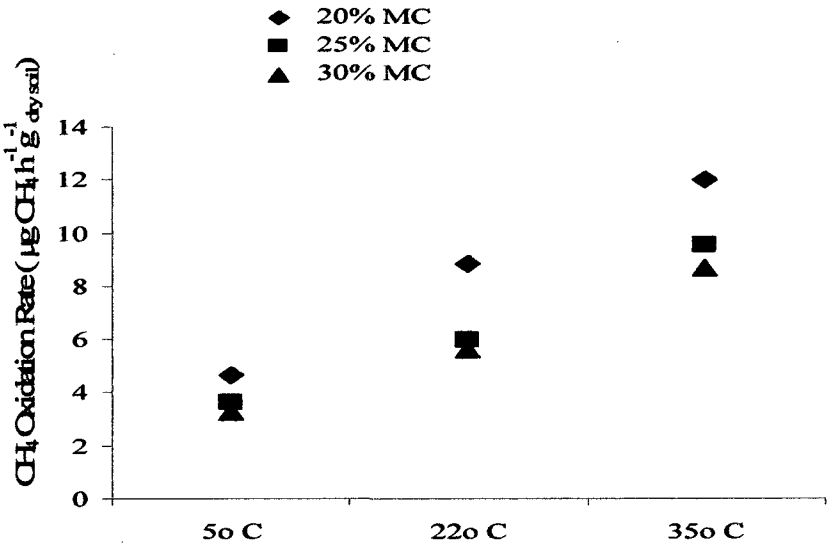


Figure 3.5 Effect of soil moisture on CH_4 oxidation rates using clayey silt soil without adding nutrients.

Without adding the fertilizer, the soil with 20% MC showed consistently higher oxidation rates compared to soil samples containing 25 or 30% MC for different operating temperatures. These results can be explained by the fact that higher moisture content restricts gas diffusion and CH_4 reaches the microbes by aqueous diffusion, which is much slower than gas diffusion. The observed decrease in the soil's oxidizing capacity at higher moisture content levels is presumably due to a decrease in gas diffusion. Previous researchers (Czepiel et al. 1996; Whalen et al. 1990) confirmed that gas diffusion at soil saturation is limited by the diffusion coefficient of CH_4 in water, which is four orders of magnitude lower than in air.

However, it appears that the effect of low temperature was diminished when the fertilizer was added to the soil with 30% MC. The CH_4 oxidation rate increased from 3.33±0.96 μg CH_4 h^{-1} g^{-1} $_{dry\ soil}$ without nutrients to 8.1±1.7 μgCH_4 h^{-1} g^{-1} $_{dry\ soil}$ when the fertilizer was added to the samples with 30% MC at 5°C. Figure 3.6 shows the effect of adding

fertilizer as an additional source of nutrients to the clayey silt soil samples under different levels of temperature and moisture content.

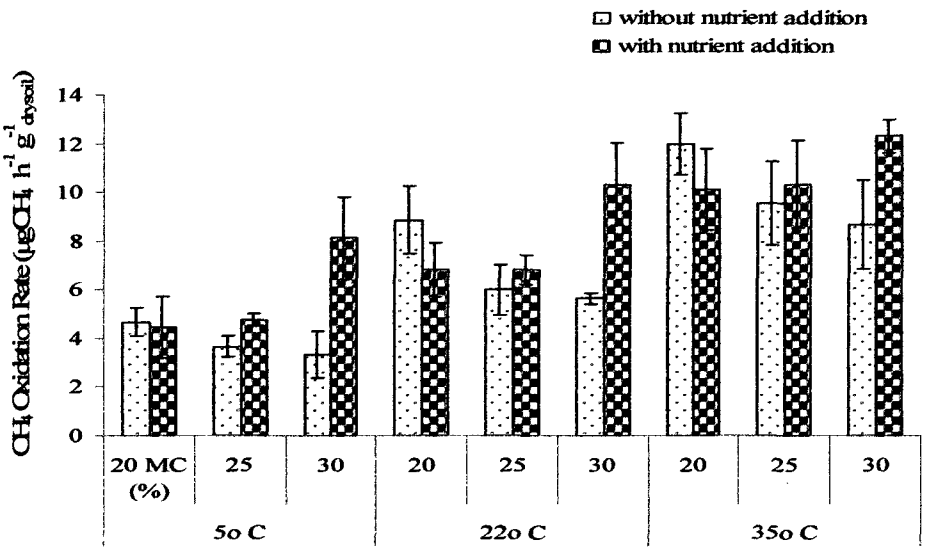


Figure 3.6 Effect of nutrient addition to clayey silt soil on the CH_4 oxidation rates under various temperature and moisture conditions.

The effect of adding nutrient source to the soil appears to be significant only at 30% moisture content. This observation can be explained by the fact that the methanotrophic bacteria need nutrients for their cellular metabolism and metabolic kinetics, in addition to the carbon substrate which is provided by CH_4. The synthesis of cellular tissue requires much more nitrogen and phosphorous than other nutrients. It seems that the commercial fertilizer which had nitrogen (5.9% nitrate nitrogen, 3.85% ammoniacal nitrogen, 10.25% urea nitrogen), phosphoric acid (8.7% is soluble phosphorous) in addition to soluble potash (16.6% is soluble potassium) supported the bacterial growth and activities at the higher levels of moisture content (30% w/w) and the biological oxidation rates increased consequently. At the lower level of moisture content (25% w/w) the fertilizer addition enhanced the oxidation rates, but to a lower extent compared when it was added to the

soil samples with 30% MC. When the fertilizer was added to the soil samples with 20% MC the oxidation rates were reduced due to a possible inhibition caused by the fertilizer.

Several researcher conducted experiments to determine the effect of nutrient amendments. Kightley et al. (1995) conducted experiments using several amendments (specifically, ammonia nitrate (NH_4NO_3), dipotassium hydrogen phosphate (K_2HPO_4), and anaerobically digested sewage sludge). These authors stated that only the amendment of coarse sand with sewage sludge was found to enhance CH_4 oxidation capacity by 26% compared to the un-amended control soil, while the NH_4NO_3 inhibited the CH_4 oxidation and K_2HPO_4 had no effect. DeVisscher et al. (2001) reported that amending the LFC soil with nitrifying sludge or compost can enhance the CH_4 consumption after a brief inhibition period. Hilger and Barlaz (2002) stated that short term incubations have shown that nitrate (NO_3) and lime amendments in fresh soil enhance CH_4 uptake, but when NO_3 was added to older landfill cover soils no stimulation was observed. The latter authors stated that ammonium addition enhanced CH_4 uptake in short term incubation but inhibited the CH_4 consumption in long time incubation. In general, all the reported information about nutrient amendments were based on experimental observations and the exact mechanism responsible for the amendments' enhancement effects or inhibition is controversial.

Clay Soil

Similar trends were observed for experimental runs conducted using the clay soil as the medium. Methane concentration decreased in the headspace of each batch reactor while CO_2 concentration increased as a result of microbial activity. Figure 3.7 shows CH_4

(%v/v) reduction for different experimental runs using clay soil. The experimental data represent the average value obtained from the triplicates batch reactors.

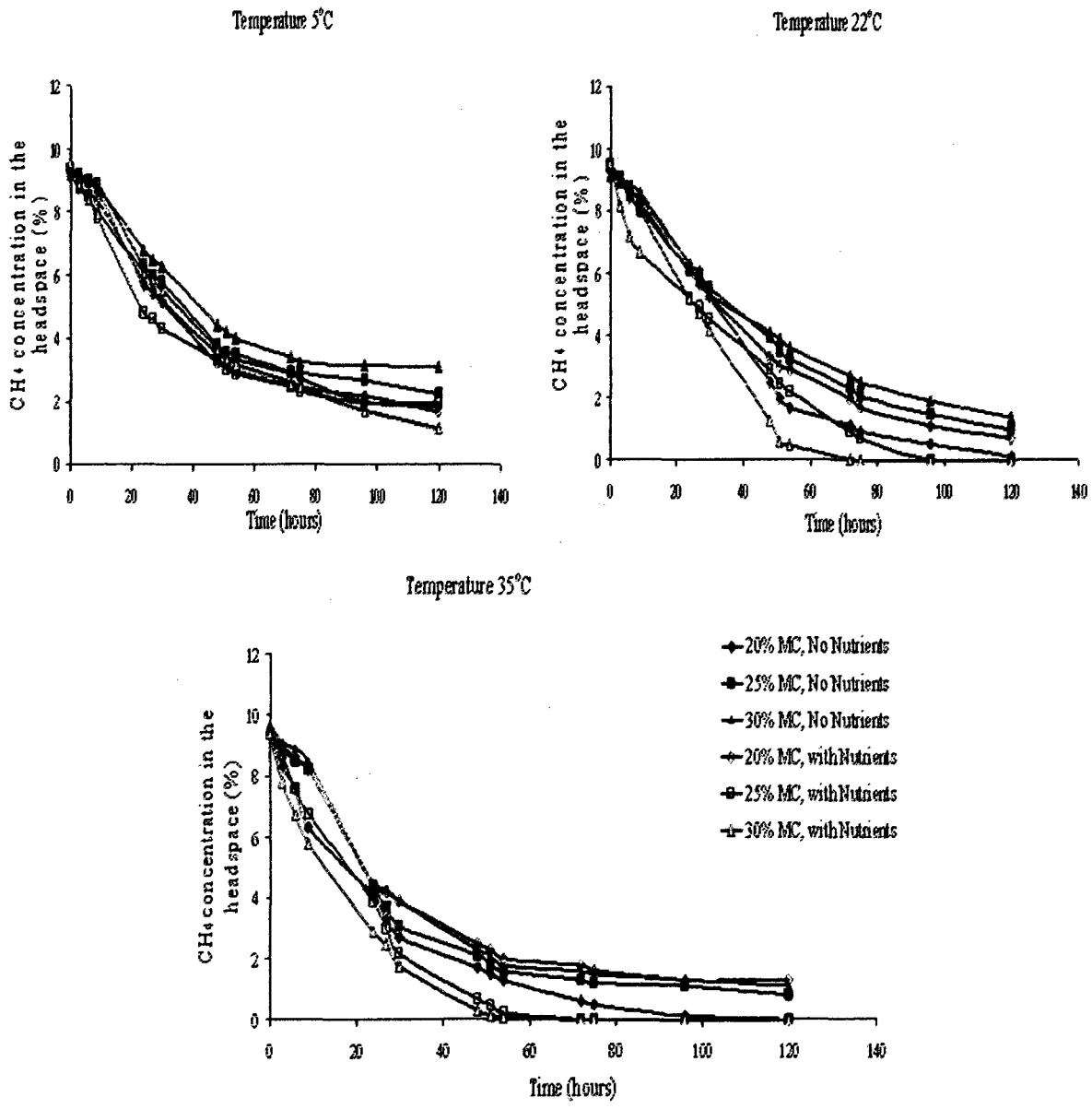


Figure 3.7 Methane concentration (%v/v) versus time in batch reactors using clay soil samples under different operating conditions.

Figure 3.7 illustrates that the clay soil showed lower CH_4 oxidation capacity compared to the clayey silt soil. It is worth mentioning that the reproducibility among the replicates in

all experimental runs using clay soil was low and affected the CH_4 oxidation trends. This may be attributed to the higher iron and aluminum contents of the clay soil. Several precautions during the preparation for the experiments were taken to obtain more homogenous experimental soils; nevertheless, the reproducibility was still lower than the clayey silt soil, which indicates the mineral content of the soil can affect negatively the biological CH_4 oxidation capacity.

The CH_4 oxidation rates were calculated based on the linear section of the CH_4 degradation curve with time for each experimental run and illustrated in Figure 3.8.

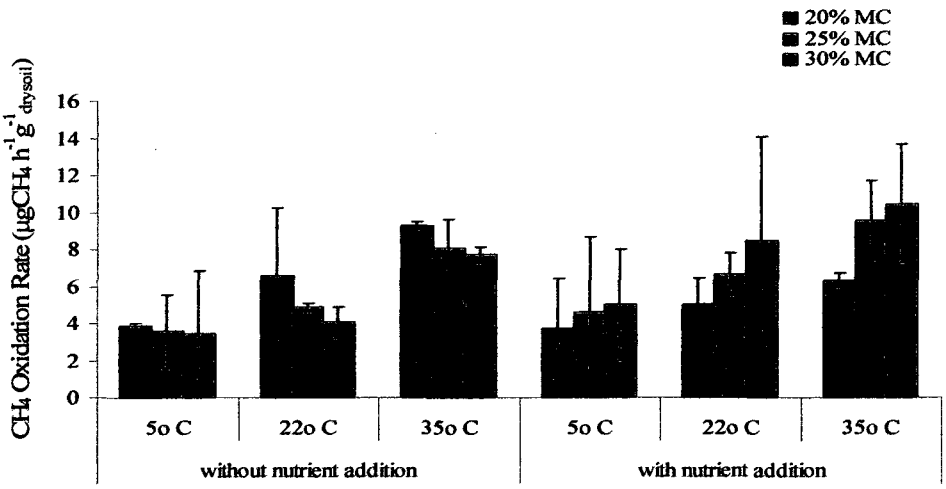


Figure 3.8 Methane oxidation rates with standard deviation using clay soil samples.

The lowest CH_4 oxidation rates were obtained using the clay soil samples without nutrients at 5°C (3.5±2.03 – 3.9±0.16 μg CH_4 h^{-1} $g^{-1}_{dry\ soil}$), while the highest oxidation rate was observed at 35°C (6.3±0.4 – 10.5±3.22 μg CH_4 h^{-1} $g^{-1}_{dry\ soil}$). The effects of temperature, water content and fertilizer addition on the oxidation capacity of the clay soil were the same effects monitored when the clayey silt soil samples were used.

However, the CH_4 oxidation rates obtained using the clay soil samples were lower than the oxidation rates obtained using the clayey silt soil under the same environmental conditions. This can be attributed to the soil structure and particle size distribution. Soil texture influences gas transport and therefore controls the CH_4 oxidation rates. Finer particles result in decreased gas permeability, which inhibits CH_4 and O_2 penetration. Borjesson et al. (2004) found similar results from their batch incubation experiments. They reported that soil samples with lower clay percentage and higher silt fraction had higher CH_4 consumption rates. Boeckx et al. (1997) reported that soil texture determines the tortuosity of the soil and influences the distribution of macro and micro-pores. The finer textured the soil the higher tortuosity it has, which will affect the gas diffusibility that will be slower in fine textured soils. The authors stated that in fine textured soils, the CH_4 transport to the methanotrophs will take longer which reduces its CH_4 uptake rate. Although the two soils used in this experiment were existing landfill cover soils and are considered fine textured, the clayey silt soil had larger content of sand and silt, which explains the higher oxidation capacity monitored from the experimental runs compared to the fine clay.

The CH_4 oxidation capacities of the two soils in this experimental study were in the range of rates previously reported in literature. Gebert et al. (2003) reported CH_4 oxidation rate of 6 $\mu gCH_4\ h^{-1}\ g^{-1}_{dry\ soil}$ when top soil samples were tested at 22°C. Borjesson et al. (2004) recorded CH_4 oxidation rates of 2.27 $\mu g\ CH_4\ h^{-1}\ g^{-1}_{dry\ soil}$ when soil samples with 40% MC (%ww) were tested at 3-5°C, the soil composition was 11.9% clay, 14.4 % silt and 48.8 % sand. The same researchers reported oxidation rate of 10.24 $\mu g\ CH_4\ h^{-1}\ g^{-1}_{dry\ soil}$ when the soil was tested at 20°C with 64% MC based on wet weight basis. Kjeldsen et al.

(1997) noted CH_4 oxidation rate of 6.25 – 10.5 μg CH_4 h^{-1} $g^{-1}_{dry\ soil}$ at 25°C using landfill cover soil of loamy sand with 15% MC.

3.3.2 INDIVIDUAL AND COMBINED ENVIRONMENTAL EFFECTS ON CH_4 OXIDATION CAPACITY IN CLAYEY SILT SOIL

In view of the fact that experimental results from clayey silt soil were more reproducible in terms of CH_4 oxidation efficiency between replicates, this soil was selected to statistically analyze the effects of the tested individual and combined environmental factors on the CH_4 oxidation process.

Statistical Analysis of the Individual Effects of Temperature, Moisture Content and Fertilizer Addition

The individual effect of temperature was statistically analyzed by conducting a t-test at 95% confidence level ($\alpha = 0.05$) between the oxidation rates at 5°C and 35°C. The *t stat* value calculated from the data was 13.9 and the P (T<=t) two-tail was 0.00035. The *t stat* value was large, and the probability P (T<=t) two-tail was low, which indicates that the means of the CH_4 oxidation rates were significantly different between the experiments conducted at 5°C and 35°C.

To investigate the individual effect of MC on the CH_4 oxidation rates, t-test was conducted on the soils with 20 and 30% MC at the 95% confidence level ($\alpha = 0.05$). The *t stat* value was 0.19 and the P (T<=t) two-tail was 0.86. These results designate that the means of CH_4 oxidation rates were not significantly different between soil samples containing 20 and 30% MC.

Analyzing statistically the main effect of fertilizer addition as a source of extra nutrients, a t-test with 95% confidence level was conducted on the results of CH_4 oxidation rates between the experimental runs without fertilizer addition and experimental runs with added fertilizer: the t-stat value was 1.8 and the P (T<=t) two-tail was 0.07. These numbers fall between the values obtained for the main effect of temperature and the main effect of MC, which confirms that the main effect of temperature was still the most significant.

The statistical results emphasized that the main effect of temperature on the soil oxidation rates was higher than the main effect of nutrient addition, followed by the main effect of MC. Lower temperatures affect the bacterial type, growth kinetics and reaction rate, while the methanotrophic bacteria in the landfill cover soil need nutrients for cellular metabolism in addition to the carbon substrate which is provided by CH_4. The moisture content is a physical parameter that affects the diffusion of gases (CH_4 and O_2) between the soil and gas phase; under higher moisture conditions, CH_4 must reach the methanotrophs by aqueous diffusion, which is much slower than gas diffusion; the diffusion coefficient of CH_4 in water (1.49×10^{-9} m^2 s^{-1} at 22°C) is four orders of magnitude lower than in air (2.12×10^{-5} m^2 s^{-1} at 22°C). It is also the same for O_2 diffusion; the diffusion coefficient of O_2 in water (1.97×10^{-9} m^2 s^{-1} at 22°C) is four orders of magnitude lower than in air (2.19×10^{-5} m^2 s^{-1} at 22°C) (Welty et al. 1984).

Statistical Analysis of the Combined Effects of Temperature, Moisture Content and Fertilizer Addition

As shown in Figure 3.1, this experiment was designed to allow the estimation of the interactions between the three variables under investigation namely temperature, MC and fertilizer or nutrient addition. The primary goal was to draw conclusions about the combined effects of these parameters on the landfill cover systems. Therefore, multifactor analyses of variance (ANOVA) was carried out using SYSTAT 11, which is a useful tool to detect significant factors in the multilevel factorial design indicated in Figure 3.1, for the CH_4 oxidation capacity of the clayey silt landfill cover soil. In the multifactor model, the response (dependent) variables are the CH_4 maximum oxidation rates. Independent variables were temperature (Temp.), moisture content (MC) and fertilizer addition (Nut.). The ANOVA results are shown in Table 3.1.

Table 3.1 Results of multifactor ANOVA for CH_4 oxidation rates in clayey silt landfill cover soil.

Source Value	Sum of Squares	Degree of freedom	Mean Squares	F-Ratio	p-value
Main Effects					
Temp.	290.133	2	145.067	54.625	**0.000**
MC	14.935	2	7.486	2.812	0.073
Nut.	22.532	1	22.532	8.485	0.006
Interactions					
Temp.* MC	5.442	4	1.360	0.512	0.727
Temp. * Nut.	2.521	2	1.260	0.475	0.626
MC* Nut.	75.378	2	37.869	14.192	**0.000**
Temp*MC*Nut	1.778	4	0.444	0.167	0.954
Error	95.604	36	2.656		

Table 3.1 illustrates that since the p-values of the main effect of temperature and the combined effect of nutrients addition and MC were equal to zero, these environmental variables have a statistically significant effect on CH_4 oxidation capacity of the soil at 95% confidence level. The results of the individual main effects from Table 3.1 are in agreement with the statistical analysis for the individual effect of tested parameters conducted, based on statistical t-stat, where the individual effect of temperature was found to be of a major significance followed by the nutrient addition effect, while the MC as an individual parameter was the least significant within the study range and conditions. In this type of experiment, special attention was paid to the interaction between the effects of the tested variables. Table 3.1 shows that p-value for the interaction between the effect of MC and nutrient addition on CH_4 oxidation was equal to zero. Among all possible interaction between the effect of temperature, MC and nutrient addition, these results imply that the interaction between the effect MC and the nutrient addition affected significantly the CH_4 oxidation capacity in landfill cover soil.

In order to learn statistically more about the pattern of the response behavior as changes are made in the variables affecting the process, a mathematical description was developed that best describe the CH_4 oxidation rates in the clayey silt soil and under the operating parameters in this study using SYSTAT 11.

The following mathematical description includes the individual parameters in this study and the interaction between their effect on CH_4 oxidation process had R^2 (1-resuidual/total) = 0.968,

$$E(q) = 4.353 + 4.829 \times Temp. - 2.966 \times MC - 2.939 \times Nutrient\ addition - 0.609 \times Temp. \times MC - 0.758 \times Temp. \times Nutrient\ addition + 2.633 \times MC \times Nutrient\ addition + 0.12\ Temp. \times MC \times Nutrient\ addition. \quad [3.2]$$

where *E(q)* is the expected CH_4 oxidation rate, *4.353* is β_0 or the overall mean, *4.829*is β_1 or the value of main effect of temperature, *-2.966* is β_2 or the value of main effect of moisture content, *-2.939* is β_3 or the value of the main effect of nutrient addition, *-0.609* is β_{12} or the value of the interaction between the effect of temperature and moisture content, *-0.758* is β_{13} or the value of the interaction between the effect of temperature and nutrient addition, 2.633 is β_{23} or the value of the interaction between the effect of MC and nutrient addition, and *0.12* is β_{123} or the value of three ways interaction between the effect of temperature, moisture content and nutrient addition.

The results obtained for the statistical analyses presented confirmed that the temperature is one of the main environmental parameters affecting the biological CH_4 oxidation process in the landfill cover soils. Lower temperature can affect the type of methanotrophic bacteria present, their growth and oxidation rate kinetics, as well as the CH_4 and O_2 diffusion within the cover. Also, the interaction between the effect of the soil moisture and fertilizer addition on the CH_4 oxidation capacity was statistically significant. From the experimental results, it was observed that adding nutrients to soil containing higher level of MC significantly increased the CH_4 oxidation rates at all temperatures. At 5°C, the CH_4 oxidation rates for the experimental runs using soil samples that contain 30% MC increased from 3.3±0.96 μg CH_4 $h^{-1}g^{-1}_{drysoil}$ without nutrients to 8.1±1.7 μgCH_4 $h^{-1}g^{-1}_{drysoil}$ when nutrients were added: this is 144% increase in

the soil oxidation capacity. At 22°C, CH_4 oxidation rate values for the soil samples with 30% moisture, increased from 5.6±0.21 $\mu gCH_4\ h^{-1}g^{-1}_{drysoil}$ without nutrients addition to 10.3±1.6 $\mu gCH_4\ h^{-1}g^{-1}_{drysoil}$ with nutrients: this is also 84% increase in the soil oxidation potential. The same trend can be seen at 35°C, where the values of CH_4 oxidation rate increased from 8.7±1.8 $\mu gCH_4\ h^{-1}g^{-1}_{drysoil}$ without nutrients to 12.3±0.68 $\mu g\ CH_4\ h^{-1}\ g^{-1}_{drysoil}$ with nutrients addition.

3.4 CONCLUSIONS

The CH_4 consumption rates in the two types of soil were clearly affected by temperatures, especially at 5°C. Although the methanotrophs are active over a wide temperature range, CH_4 oxidation rate values at 5°C were lower than the values obtained at 22 or 35°C. This was a physiological response to the temperature change. In the search of the interactions between the different variables in order to enhance the oxidation potential, it was found in this study that adding fertilizer as a source of nutrients to the higher level of MC (30%) increased the CH_4 oxidation rates observed at 5°C to the values of CH_4 oxidation rates obtained at 22°C. The same phenomenon was monitored at 22°C, where the values of CH_4 oxidation rates were increased to the level of CH_4 oxidation rates value at 35°C. The highest CH_4 oxidation rate value was obtained in this experiment when the fertilizer was added to the soil with 30% MC at 35°C.

Although this experimental study was conducted using existing landfill cover soils with potentially similar physical characteristics (silt and clay) in batch reactors that contained

disturbed samples and these can be limitations, it can be concluded that adding a commercial fertilizer as a source of nutrients to the cover soil with higher moisture content can enhance the capacity for CH_4 oxidation and moderate the slowdown of microbial activities at lower temperature. Also, it is recommended to study the effect of adding fertilizer as a nutrients source in longer time incubation in order to understand the mechanisms of the oxidation enhancement.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Lafleche Environmental Inc. for supplying funds for this study.

3.5 REFERENCES

Albanna, M., Fernandes, L., and Warith, M. (2007). "Methane Oxidation in Landfill Cover Soil; the Combined Effects of Moisture Content, Nutrient Addition, and Cover Thickness." Journal of Environmental Engineering and Science, 6, pp. 191-200.

ASTM D2974-87, American Society for Testing and Materials (2000), "Standard Test Method for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils". ASTM International, PA, USA.

ASTM D7348-08, American Society for Testing and Materials (2000), "Standard Test Methods for Loss on Ignition of Solid Combustion Residues". ASTM International, PA, USA.

ASTM D422, American Society for Testing and Materials (2002), "Standard Test Method for Particle Size Analysis of Soils". ASTM International, PA, USA.

ASTM D4318, American Society for Testing and Materials (2005), "Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils". ASTM International, PA, USA.

Barlaz, M.A., Green, R.B., Chanton, J.P., Goldsmith, C.D., and Hater, G.R. (2004), "Evaluation of a Biologically Active Cover for Mitigation of Landfill Gas Emissions," *Environmental Science and Technology*, 38, pp. 4891-4899.

Bender, M., and Conrad, R. (1995). "Effect of CH_4 Concentrations and Soil Conditions on the Induction of CH_4 Oxidation Activity." *Soil Biology and Biochemistry,* 27, pp. 1517- 1527.

Boeckx, P., and Van Cleemput, O. (1996a). "Methane Emission from a Landfill and the Methane Oxidizing Capacity of its Covering Soil." *Soil Biology and Biochemistry*, 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 Quality*, 25, pp. 178- 183.

Boeckx, P., Van Cleemput, O., and Villaralvo, I. (1997). "Methane Oxidation in Soils with Different Textures and Land Use." *Nutrient Cycling in Agroecosystems*, 49, pp. 91-95.

Bogner, J., Spokas, K., and Burton, E.A. (1997). "Kinetics of Methane Oxidation in a Landfill Cover Soil: Temporal Variations, a Whole-Landfill Oxidation Experiment and Modeling of Net CH_4 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, pp. 33-54.

Borjesson, G., Sundh, I., Tunlid, A., Frostegard, A., and Svensson, B.H. (1998). "Microbial Oxidation of CH_4 at High Partial Pressures in an Organic Landfill Cover Soil Under Different Moisture Regimes." *Microbiology Ecology*, 26, pp. 207-217.

Borjesson, G., Sundh, I., and Svensson, B.H. (2004). "Microbial Oxidation of CH_4 at Different Temperatures in Landfill Cover Soils." *Microbiology Ecology*, 48, pp. 305-312.

Czepiel, P.M., Mosher, B. and Harris, R.C. (1996). "Quantifying the Effect of Oxidation on Landfill Methane Emissions." *Journal of Geophysical Research*, 101, pp. 16,721-16,729.

Czepiel, P.M., Shorter, J.H., Mosher, B., Allwine, E., McManus, J.B., Harris, R.C., Kolb, C.E., and Lamb, B.K. (2003). "The Influence of Atmospheric Pressure on Landfill Methane Mmissions." *Waste Management*, 23, pp. 593-598.

Day, R. W., (2001), "Soil Testing Manual, Procedures, Classification Data, and Sampling Practices", McGraw-Hill, New York, USA.

De Visscher, A., Schippers M., and Van Cleemput O. (2001). "Short-Term Kinetic Response of Enhanced Methane Oxidation in Landfill Cover Soils to Environmental Factors." *Biology and Fertility of Soils*, 33, pp. 231-237.

Einola, J.K.M., Kettunen, R.H., and Rintala, J.A. (2007). "Responses of Methane Oxidation to Temperature and Water Content in Cover Soil of a Boreal Landfill." *Soil Biology and Biochemistry*, 39, pp. 1156-1164.

Environment Canada (October, 2005), Landfill Gas Management in Canada Report, http://www.ec.gc.ca/pdb/ghg/inventory_report/2005_report/tdm-toc_eng.cfm.

Gebert, J., Groengroeft, A., and Miehlich, G. (2003). "Kinetics of Microbial Landfill Methane Oxidation in Biofilters." *Waste Management*, 23, pp. 609-619.

Hanson, R. and Hanson, T.E. (1996). "Methanotrophic Bacteria." *Microbiological Reviews*, 60, pp. 439- 471.

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., Mclnernery M.C., and Stezenback L.D.(Eds.), ASM Press, Washington, D.C., pp. 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., and Dunfield, P.F. (2002). "Activity and Community Structure of Methane-Oxidising Bacteria in a Wet Meadow Soil." *Microbiology Ecology*, 41, pp. 247- 257.

Intergovernmental Panel on Climate Change, (2007). "IPCC Working Group I Summary for Policymakers". <http://www.ipcc.ch> (Feb., 2007).

Kallistova, A. YU., Kevbrina, M.V., Nekrasova, V.K., Glagolev, M.V., Serebryanaya, M.I., and Nozhevnikova, A.N. (2005). "Methane Oxidation in Landfill Cover Soil." *Microbiology*, 74, pp. 608-614.

Kettunen, R., Einola, J-K.M., and Rintala, J.A. (2006). "Landfill Methane Oxidation in Engineered Columns at Low Temperature." *Water, Air and Soil,* 177, pp. 313-334.

Kightley, D., Nedwell, DB. and Cooper, M. (1995), "Capacity for Methane Oxidation in Landfill Cover Soils Measured in Laboratory-Scale Soil Microcosms." *Applied and Environmental Microbiology,* 61, pp. 592-601.

King, G.M., and Adamsen, P.S. (1992), "Effects of Temperature on Methane Consumption in a Forest Soil and in Pure Cultures of the Methanotroph Methylomonas Rubra." *Applied and Environmental Microbiology*, 58, pp. 2,758-2,763.

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. 1,268- 1,275.

Spokas, K., Bogner, J., Chanton, J.P., Morcet, M., Aran, C., Graff, C., Moreau-Le Golvan, Y., and Hebe, I., (2006). "Methane Mass Balance at Three Landfill Sites: What is the Efficiency of Capture by Gas Collection Systems?" *Waste Management,* 26, pp. 516-525.

SYSTAT 11, (2004). Systat Software Inc., Chicago, USA.

United States Environmental Protection Agency-USEPA- (2006). "Global Anthropogenic Non-CO_2 greenhouse gas emissions: 1990-2020". U.S. Environmental Protection Agency, Office of Atmospheric Programs, Climate Change Division, U.S. Environmental Protection Agency, 1200 Pennsylvania Avenue, NW, Washington, DC 20460.

United States Environmental Protection Agency- USEPA- (2007). "Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2005, <http://epa.gov/climatechange/emissions/usinventoryreport.html> (April 2007).

Welty, J.R., C.E. Wicks, and R.E. Wilson. (1984), "Fundamentals of Momentum, Heat, and Mass Transfer", 3rd Ed. John Wiley & Sons, NY. 803.

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 CH_4 Oxidation in Boreal Soils." *Soil Biology and Biochemistry*, 28, pp. 1,271-1,281.

Wilshusen, J.H., Hettiaratchi, J.P.A., and Stein, V.B. (2004a). "Long-Term Behavior of Passively Aerated Compost Methanotrophic Biofilters Columns." *Waste Management*, 24, pp. 643-653.

Wilshusen, J.H., Hettiaratchi, J.P.A., De Visscher, A., and Saint-Fort, R. (2004b). "Methane Oxidation and Formation of EPS in Compost: Effect of Oxygen Concentration." *Environmental Pollution*, 129, pp. 305-314.

CHAPTER 4

CAPACITY FOR BIOLOGICAL METHANE OXIDATION IN DIFFERENT TYPES OF SOIL AND COMPOST

Muna Albanna and Leta Fernandes

ABSTRACT

In this study, patterns of methane (CH_4) oxidation under various environmental conditions were studied and compared in two types of landfill cover soils and compost. In all the experimental runs, CH_4 oxidation rates increased with time indicating the growth of well established microbial populations capable of utilizing CH_4 as substrate. It was found that CH_4 oxidation can be enhanced using compost as a landfill cover medium at higher temperature levels only. The highest CH_4 oxidation rates were observed when compost was tested under different moisture content levels at 35°C in the range of 27.3 to 35.5 $\mu gCH_4\ h^{-1}\ g^{-1}_{wet\ wt.}$. The lowest oxidation rate ranged between 2.5 – 3.9 $\mu gCH_4\ h^{-1}\ g^{-1}_{wet\ wt.}$ obtained for all the experiments conducted at 5°C using the three media: clay, clayey silt soils and compost.

The experimental results were analyzed statistically and used to develop an empirical model that showed the individual and combined effects of the tested environmental variables (cover medium, temperature, and moisture content) on the CH_4 oxidation process. The statistical model was validated using CH_4 oxidation rates in different types of landfill cover systems reported in the literature.

4.1 INTRODUCTION

The scientific consensus on global warming has promoted many research projects focusing on the attenuation of various causes of climate change. The recent increase in global average temperatures is believed to be the result of growing anthropogenic greenhouse gases (GHG) mainly: carbon dioxide (CO_2) and methane (CH_4). One critical source that adds to the anthropogenic CH_4 emissions is the disposal of solid waste. In Canada, this sector is responsible for 23% of total CH_4 emissions (Environment Canada 2005). The generated biogas from the biodegradation of solid waste in landfills, known as landfill gas (LFG), consists of 50-65% CH_4 and 35-50% CO_2, plus trace amounts of non-methane organic compounds. If collected, LFG can be utilized as an energy source. However, the reported efficiencies for gas collection systems range from 60 to 80% (USEPA 1999), and the remaining amounts of LFG simply escape to the environment. If LFG is not collected, as in the case of most existing landfill sites and open dumps, all the produced amounts of gas will be released to the atmosphere. Therefore, in the absence of biogas capturing systems or even as complementary to the existing setups, biological oxidation of CH_4 by methanotrophic bacteria within landfill cover layers is particularly important for the reduction of the harmful LFG emissions from landfills.

The defining characteristic of methanotrophic bacteria is the use of the enzyme methane monooxygenases (MMO) which enables the oxidation of CH_4 to CO_2, water and new bacterial cells (Hilger and Humer 2003; Hanson and Hanson 1996). There are two main groups of methanotrophic bacteria: Type I and Type II. Type I methanotrophs assimilate formaldehyde through the ribulose monophosphate pathway (RuMP); most of them form

cyst and are incapable of fixing nitrogen (N_2). Type II methanotrophs assimilate formaldehyde via the serine pathway; they form exospores and cysts and can fix N_2 (Borjesson et al. 2004; Wilshusen et al. 2004b; Hanson and Hanson 1996). The changes in the methanotrophs population in soils can occur in response to environmental conditions such as: change in concentrations of CH_4 and oxygen (O_2), temperature, pH and N_2 sources. It is very important to note that temperature has a strong effect on which type of methanotrophs are active. Only Type I methanotrophic bacteria grow at low temperatures between 3 and 10°C while both types grow at 20°C, as was reported by several researchers (Kallistova et al. 2005; Borjesson et al. 2004; Gebert et al. 2003; Horz et al. 2002). King and Adamsen (1992) concluded that the bacterial enzymatic processes at low temperature limit their performance more than any other environmental condition.

Microbial oxidation rates of CH_4 differ within and between landfill sites due to: seasonal climate changes, physical heterogeneities of the cover, CH_4 concentrations, temperature, moisture content and soil characteristics, and composition. Field studies have reported that high levels of CH_4 removal can be achieved by optimizing the environmental variables, and consequently the microbial activities in the cover soils. From this perspective, some researchers have conducted experiments to confirm the individual effects of different environmental conditions on CH_4 oxidation capability of different landfill cover soils (Albanna et al. 2007; Einola et al. 2007; Kettunen et al. 2006; Kallistova et al. 2005; Borjesson et al. 2004; Hilger and Barlaz 2002; Bogner et al. 1997; Whalen and Reeburgh 1996). Others have indicated that CH_4 oxidation can be optimized using compost as the final cover medium since compost can offer a good mix of nutrient supply, porosity, water-holding capacity and pH (Mor et al. 2006; Wilshusen et al. 2004a;

Barlaz et al. 2004; Hilger and Humer 2003). The main question addressed in this study was whether compost offers better landfill cover medium compared to traditional soils, and to what extent. Therefore, one of the main objectives of this study was to test and compare the patterns of CH_4 oxidation amongst the compost and two types of existing landfill cover (LFC) soils under various temperature and moisture content (MC) levels. The results obtained from this study were compared statistically to assess the performance of different LFC medium in terms of CH_4 oxidation rates. Another objective was to develop an empirical model that describe the individual effects of the type of cover medium, temperature and MC on the CH_4 oxidation rates, as well as the effects of the interactions between these variables.

4.2 MATERIALS AND METHODS

4.2.1 EXPERIMENTAL DESIGN

In order to assess the CH_4 oxidation capacity of different landfill cover media and to meet the objectives of this study, a multilevel factorial experimental design was conducted using compost and two types of soil. The experimental works focused on evaluating the individual and combined effects of the selected variables that would influence CH_4 oxidation in the LFC system, namely: cover medium, temperature and MC.

The compost and two types of soil were different in their physical characteristics, Therefore, the MC levels of the two types of soil were set as 20, 25, 30% w/w. While the

three levels of compost's MC were 57, 100, 142% w/w; the compost samples used in the experiments were acclimatized in laboratory scale columns that had 30, 50 and 75% saturation level (S.L.) respectively. The selected temperature and MC levels were chosen to simulate various climatic conditions that might affect microbial activities.

Figure 4.1 shows the multilevel factorial design of the experiment.

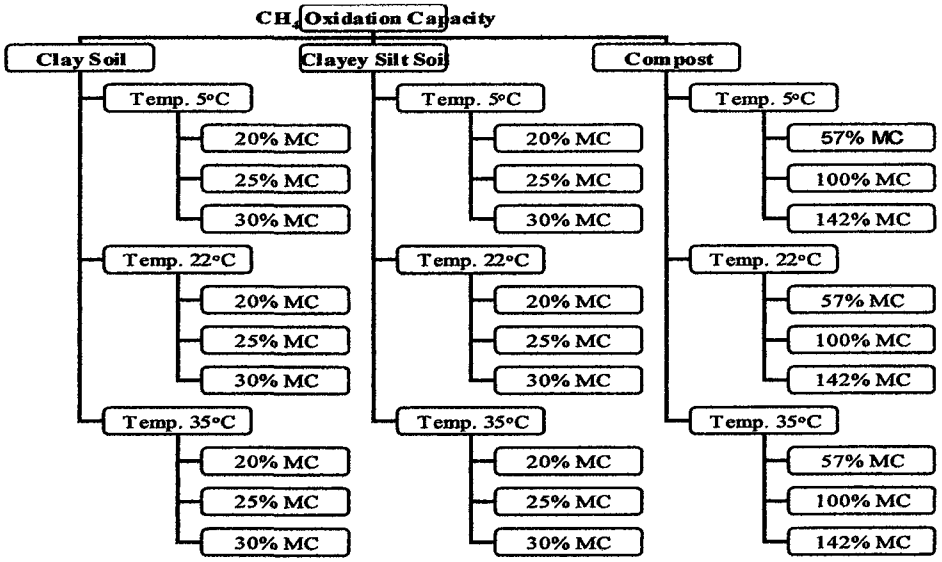


Figure 4.1 Multi-level experimental design.

The experimental design illustrated in Figure 4.1 resulted in 27 experimental runs in triplicates, in addition to blank and control reactors.

4.2.2 EXPERIMENTAL MATERIALS

The soil samples were collected from existing final cover at two landfill sites operating in the Ottawa, Canada. The soil collected from the slopes of the final cover of (Eastern Ontario landfill) was characterized as clay soil; while the soil collected from (Trail Road landfill) cover was characterized as being silt loam (this soil will be referred to as clayey silt soil). The samples were taken from areas located near the biogas vents in order to assure that both types of soils were exposed to CH_4 and should contain an adequate number of methanotrophs. The soil samples brought to the laboratory were sieved, homogenized, and stored in the cold room at 3°C temperature.

The compost used was mature and stabilized yard waste compost obtained from Trail Road composting facility. The stability of the compost was checked and the respiration rates were measured by incubating compost samples in batch reactors with air. The O_2 and CO_2 concentrations in the batch reactors were measured continuously to calculate the O_2 consumption and CO_2 production rates due to respiration. The O_2 consumption rate was 0.45 μmol O_2 h^{-1} $g^{-1}_{wet\ wt}$ and CO_2 evolution rate was 0.33 μmol CO_2 h^{-1} $g^{-1}_{wet\ wt.}$ at 22°C. The respiration rates were taken into consideration when calculating the mass balances in the reactors afterwards.

Since the compost had not been exposed to CH_4, and to ensure adequate population of methanotrophs, it was decided to acclimatize the compost by running a laboratory scale columns that contained the compost samples with three designated saturation levels (30, 50 and 75%). The columns had CH_4 inlet ports at the bottom and air inlet ports at the top to simulate the landfill cover system. Before filling the columns, the moisture content of

the compost was adjusted in each column, and then the samples were packed in the columns and compacted. Bulk density and specific gravity were measured, and void ratio and saturation level were calculated accordingly. The columns were run for 30 days before taking samples from the top 50 to 150 mm of the columns to conduct the batch experiments.

The compost and two types of soil were analyzed in the laboratory and the main physical and chemical characteristics in addition to the main minerals content are summarized in Table 4.1.

Table 4.1 Compost and soils main characteristics.

Characteristics	**Compost**	**Clayey Silt Soil**	**Clay Soil**
Initial moisture content (w%)	107	27	23[*a]
Bulk density (kg/cm^3)	890	1626	1900
Organic matter (w%)	31	3.9	2.4
pH	7.1	6.4	8.7
Specific gravity	2.17	2.68	2.62
Nitrogen (%N)	1.24	0.3	0.00
Carbon (%C)	14.81	7.16	0.66
Main mineral content (ppm)			
Aluminum	71	129	430
Calcium	361	1932	220
Iron	95	308	479
Phosphorus	22	7	7
Potassium	99	39	116

[*a] All weight fractions are on a dry weight basis.

The clayey silt soil had the following granulometric composition: 26% sand, 54% silt loam and 20% clay. The soil texture was determined by sieve analyses and classified according to the United States Department of Agriculture (USDA) classification system.

The clay soil had the following composition: 1.6% sand, 18.4% silt and 80% clay. The clay soil was characterized as uniform and poorly graded clay based on the coefficient of uniformity (C_u) which was 25 and the coefficient of curvature (C_c) which was 0.37. The hydrometer test was performed according to ASTM standard D 422 for the grain size analysis. Furthermore, the clay soil liquid limit was 56% and the plasticity limit was 25%. The plastic limit, liquid limit and plasticity index were determined following the ASTM D 4318. The clay soil was characterized as in active "Illites" clay.

The bulk density was determined by weighing soil or compost-filled cylinders, subtracting the cylinder weight, and dividing by the cylinder volume. Moisture content was determined gravimetrically by oven-drying soil or compost samples at 105°C for 24 hours and expressed as the mass ratio of water to dry soil or compost, following the ASTM D2974-87 procedure. Void ratio was calculated based on bulk density, specific gravity and moisture content. Saturation level was calculated based on the voids ratio, specific gravity and moisture content (Holtz and Kovacs, 1981). Organic content was determined by loss on ignition following ASTM D7348-08. Inductively Coupled Plasma (Varian Vista Pro ICP ES) was used to analyze the mineral content of the two soils and compost samples. The %N and %C were obtained by weighing soils and compost samples into tin capsules and loaded with standards into a Thermo-Finnigan Flash 1112 elemental analyzer. Each sample was flash combusted at about 1800°C and carried by helium through a column of reducing/oxidizing chemicals to get N_2, CO_2, H_2O and SO_2. The gases are separated as they pass through a gas chromatograph column so that the TCD (thermal conductivity detector) can detect each gas separately. The routine analytical precision (2sigma) is as follows: N, H & S = +/-0.1% C = +/-0.3%.

4.2.3 EXPERIMENTAL METHODS

The experimental runs were conducted using laboratory scale batch reactors in triplicates as well as controls and blanks. Glass bottles, of 160 mL total volume each, were used to conduct the laboratory scale batch experiments. 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 ensure the correct required percentage (%w/w). The compost samples were taken from the top 150 mm of the simulation columns prepared as described in section 4.2.2. After placing the soil or compost samples in each reactor, the glass bottle was sealed using a gas tight aluminum seal of a tan Teflon/silicone (PTFE) septum which enabled gas sampling from the reactor's headspace by a gas tight syringe. Thirty grams of soil or compost were added to each reactor which was subsequently tightly sealed. Afterwards, 40 ml of air from the headspace were withdrawn using a syringe and replaced with 16 ml of CH_4 gas (99% purity) and 24 ml of O_2 gas (100% purity). These amounts provided a mixing ratio of approximately 10% CH_4 (v/v) and 30% O_2 (v/v) of the total headspace. The O_2 was added to ensure that the aerobic conditions prevailed during the experiment. The concentrations of CH_4, O_2, N_2, and CO_2 in the headspace were measured regularly by withdrawing samples from the headspace using a 200 μL gas tight syringe. Then the samples were injected manually into the inlet of a series 400 Gow-Mac Thermal Conductivity Gas Chromatograph. The detector, injection port and column temperatures were 130, 130, and 120°C, respectively. The carrier gas was helium with a flow rate of 30 mL/min.

All reactors were rotated on orbital shakers at the designated temperatures. The headspace gases in the batch reactors were analyzed and the results were used to calculate the decrease in CH_4 and O_2 concentrations as well as the increase in CO_2 with time. The CH_4 concentration in each batch reactor were plotted as a function of time and the CH_4 oxidation rates were determined from the linear regression of CH_4 concentration over time or zero-order kinetics ($R^2 > 0.95$), then the zero-order rate constant was normalized to the dry soil mass. In the control reactors, and to confirm that the biological activity was the only reason for the CH_4 reductions, sodium azide was added to the soil and compost samples to inactivate all the viable microorganisms. In all control reactors, the maximum decrease in CH_4 and O_2 concentrations observed did not exceed 5%.

4.3 RESULTS AND DISCUSSION

In all the batch experimental runs, the headspace gases were analyzed and the data were used to calculate the rate of changes in CH_4 concentrations. Figure 4.2 shows as an example: (a) CH_4 headspace concentrations in the triplicates and controls versus time in batch reactors using clayey silt soil with 30% MC at 22°C, and (b) headspace gases concentrations (CH_4, O_2 and CO_2) in triplicates versus time in batch reactors using clayey silt soil with 20% MC at 22°C; the error bars are standard deviations from experiments on triplicate samples.

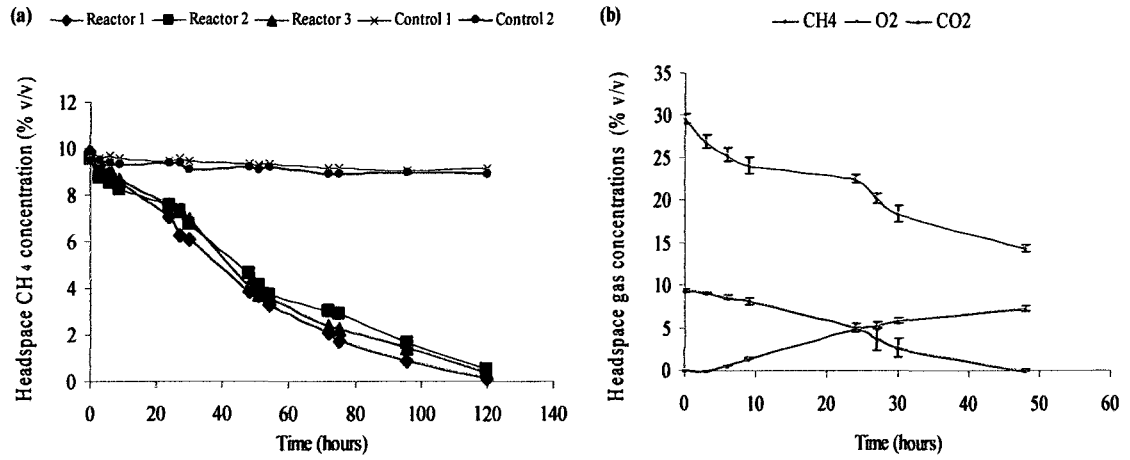


Figure 4.2 (a) Methane concentrations with time in triplicates and controls using clayey silt soil with 30% MC, (b) headspace gas concentrations versus time using clayey silt soil with 20% MC. These experiments were conducted at 22°C.

As demonstrated in Figure 4.2, the observed decrease in CH_4 and O_2 concentrations and the increase in CO_2 concentration in the reactors were clear confirmation of the methanotrophic activities. Moreover, there was no decrease of CH_4 or increase of CO_2 concentration in the headspace gas of the control reactors that contained the sodium azide- treated soil and compost samples. These results ensure that the main mechanism responsible for the CH_4 oxidation process was biological activity. In all the experimental runs, O_2 was not a limiting factor since its concentration was never below 10% v/v at the end of each experiment as shown in Figure 4.2(b). Czepiel et al. (1996) have stated that CH_4 biological oxidation process is insensitive to O_2 concentrations if this concentration is above 3%, but these activities dropped significantly at O_2 concentration less than 3%.

4.3.1 METHANE OXIDATION PERFORMANCE

At 22 and 35°C and at all moisture content levels, the compost showed higher CH_4 oxidation capacity than the clayey silt and clay soils. However, at 5°C, the three tested

cover media showed almost the same trends and oxidation performance. Figure 4.3 shows the results of CH_4 concentration (%v/v) in the headspace of the reactors versus time for different experimental runs conducted at 5 and 35°C using the three cover media containing the middle level of moisture content.

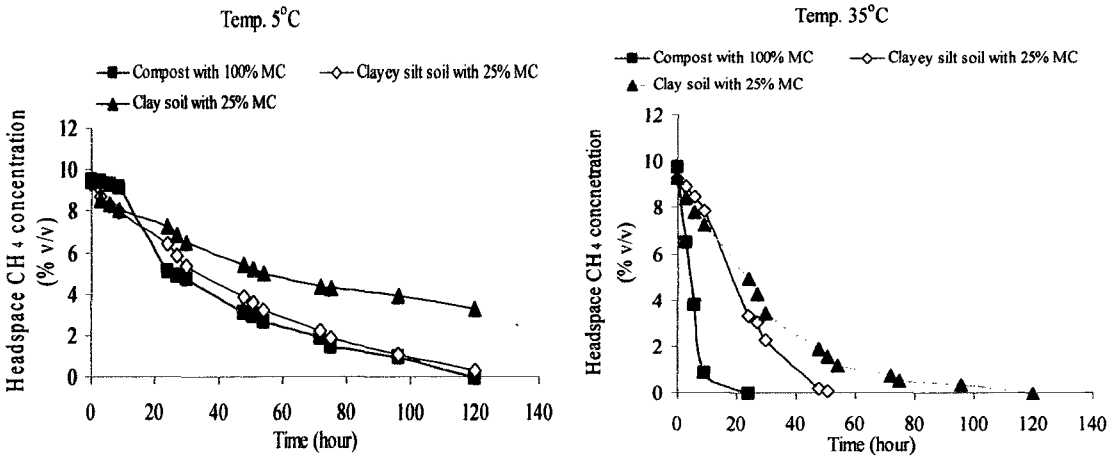


Figure 4.3 Methane concentrations (%v/v) versus time in batch reactors using the three types of cover media at 5 and 35°C. The readings are averages of triplicate runs.

As illustrated in Figure 4.3, at 35°C the compost showed high CH_4 oxidation capacity with time and complete CH_4 oxidation occurred almost within 12 hours; while approximately 48 and 120 hours were needed to complete the oxidation using the clayey silt and clay soils respectively. At 5°C, around 120 hours were needed to complete the CH_4 oxidation in the batch reactor that contained the compost. However, at 5°C, the compost's oxidation capacity was almost in the same range observed using the clayey silt soil, but still better than clay soil samples.

To further illustrate the CH_4 oxidation performance of the three cover media, the results of CH_4 concentration (%v/v) reductions in the headspace of the reactors versus time for different experimental runs were plotted and analyzed to calculate the biological

oxidation rates. The CH_4 oxidation rates were calculated based on the linear section of the degradation curve for each experimental run. The zero-order rate constant was then normalized to the wet soil or compost mass since the compost and the two types of soils had different MC and dry densities. For each experimental run, the average CH_4 oxidation rate was calculated based on triplicates. The determined CH_4 oxidation rates ($\mu gCH_4\ h^{-1}g^{-1}_{wet\ soil}$) are presented in Figure 4.4.

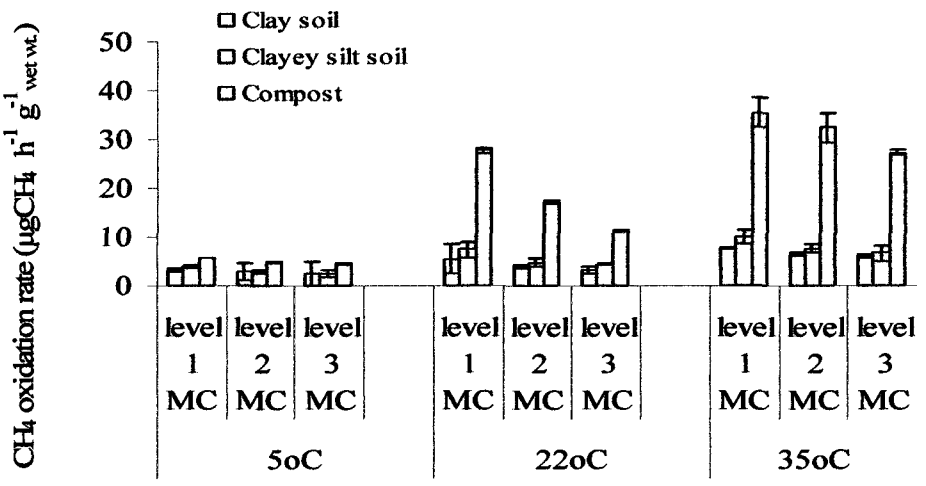


Figure 4.4 Methane oxidation rates with standard deviation using compost and two types of soil under different levels of temperature and moisture content.

The CH_4 oxidation rates reflected the effect of the tested environmental variables on the oxidation process. The lowest oxidation rates were obtained for all the experiments conducted at 5°C, they ranged between 2.6 – 5.7 $\mu g\ CH_4\ h^{-1}\ g^{-1}_{wet\ wt.}$ (3.3 – 9.8 $\mu gCH_4\ h^{-1}\ g^{-1}_{dry\ wt.}$). The highest CH_4 oxidation rates in the range of 27.3 – 35.5 $\mu gCH_4\ h^{-1}\ g^{-1}_{wet\ wt.}$ (56.0 – 66.9 $\mu gCH_4\ h^{-1}\ g^{-1}_{dry\ wt.}$) were achieved at 35°C using the compost samples, while the highest rates obtained using clayey silt and clay soil were at 35°C in the range of 5.9 to 10.0 $\mu gCH_4\ h^{-1}\ g^{-1}_{wet\ wt.}$ (7.7 – 12.0 $\mu gCH_4\ h^{-1}\ g^{-1}_{dry\ wt}$).

As shown in Figure 4.4, the experimental results confirmed that the compost offers better landfill cover medium for bacterial growth and CH_4 utilization than typical soils particularly when subjected to higher levels of temperature. At 35°C and in all the experimental runs using compost the CH_4 oxidation rates were 3 to 5 times higher than the oxidation rates obtained using clayey silt soil and 5 times higher than oxidation rates using clay soil samples. Compost has higher nitrogen and carbon content (as shown in Table 4.1) than clayey silt or clay soil, which may have affected the nutrient levels availabe for the bacteria. Compost has higher nutrients and greater CH_4 and O_2 penetration (due to bigger void ratio and therefore porosity) than the traditional soils, and this can result in better CH_4 oxidation capacity compared to the soil. Due to its chemical and physical characteristics, compost promotes good microbial growth and appears to make an effective cover medium at higher temperatures (22 and 35°C). However, at the low levels of temperature, the microbial growth is constrained by the temperature which affects the methanotrophic type. At 5°C, the compost and clayey silt had almost the same CH_4 oxidation rates as demonstrated in Figure 4.4; this can be explained by the fact that the methanotrophic bacteria population shifts due to temperature negatively affect the total oxidation performance regardless of the cover medium. At all temperature and MC levels, the clay soil showed the lowest oxidation rates. The performance of the clay soil was attributed to the soil structure and particle size distribution, where the finer particle size and thus smaller pores resulted in decreased gas transfer which reduced CH_4 and O_2 penetration (Albanna and Fernandes 2009). These results were in agreement with Boeckx et al. (1997); the researchers reported that soil that has finer texture generally has higher tortuosity, thus slower gas diffusibility is expected. The authors stated that in fine

textured soils the CH_4 transport to the methanotrophs will take longer which reduces its CH_4 uptake rate.

The temperature effect on the CH_4 oxidation rates in all LFC media was significant, as can be seen from the experimental results. Using the compost samples, CH_4 oxidation rates were 3-5 times higher when the temperature changed from 5 to 22°C and 6-7 times higher when the temperature changed from 5 to 35°C. The same trend was monitored when the clayey silt soil samples were used, yet to a lesser extent, where the oxidation rates were three times higher when the temperature increased from 5 to 35°C. Moreover, the clay soil samples showed better CH_4 oxidation when the temperature increased from 5 to 22 and 35°C. In general, the oxidation rates increased exponentially (R^2>0.92), which is in agreement with Arrhenius relationship. As discussed previously in section 4.1, the low temperature levels affect the methanotrophic bacteria type existing in the landfill cover system. Moreover, the O_2 diffusion within the cover at lower temperature cannot be neglected. Kettunen at al. (2006) reported that the diffusion coefficient in soil decreases with declining temperature: at 5°C the coefficient is roughly 0.9 times compared to that at 22°C, if the O_2 concentration gradient remains unchanged. Nevertheless, and regardless of the significant effect temperature has on the biological CH_4 oxidation, it is important to point out that the methanotrophic bacteria can still be active at low temperatures, as can be seen from the experimental results; their diversity indicate the adoption of the methanotrophic bacteria in the LFCs under different temperatures (Mor et al. 2006; Kallistova et al. 2005; Gebert et al. 2003), but at lower CH_4 oxidation kinetics values.

Soil or compost's MC is an important physical parameter since it affects the diffusion of the gas within the soil or compost pores. At all temperatures, the compost and two types of soil with the lower levels of MC consistently showed 20% higher oxidation rates than the soils samples containing the higher levels of MC based on the average values. These results can be explained by the fact that higher MC restricts gas diffusion. The decrease in CH_4 oxidation rates as soil moisture increases results from a change from the gas phase (CH_4 and O_2) to aqueous molecular diffusion (10^4 fold less rapid) for CH_4 transport to cells as reported previously by Whalen et al. (1990).

The results from this study indicate that using compost as a LFC medium can enhance the CH_4 oxidation capacity more than clayey silt and clay soils. Compost provides inexpensive cover material and offers a good mix of porosity, water-holding capacity, and nutrient supply, which is reflected positively by the higher CH_4 oxidation rates in this cover medium. Regardless of the cover medium, the CH_4 oxidation process was affected significantly at lower temperature due the methanotrophic strain prevailing at these conditions and their ability to synthesize CH_4, as well as the reduced O_2 diffusion coefficient at lower temperatures. Clay soil showed lower CH_4 oxidation rates than the clayey silt soil; this can be attributed to the soil texture, particle size distribution, mineral content levels, as well as the smaller voids ratio that affected the gas penetration and consequently the bacterial activities in the clay soil. Borjesson et al. (2004) had similar results from their batch incubation experiments, where they reported that soil samples with higher clay percentage and lower silt fraction showed lower CH_4 consumption rates.

4.3.2 STATISTICAL ANALYSIS

One of the main objectives of this study was to evaluate the individual and combined effects of the variables under investigation as well as the effects of their interactions on the CH_4 oxidation rates in the LFC systems. Hence, a multifactor ANOVA analysis was conducted using STATGRAPHICS Centurion XV software. The multifactor ANOVA procedure is designed to construct a statistical linear model describing the impact of two or more categorical independent factors, which in this study were cover medium, temperature and MC on a dependent variable (CH_4 oxidation rate). Statistical tests are run to determine whether or not there are significant differences between the means of CH_4 oxidation rates at the different levels of the factors and whether or not there are interactions between the factors. These statistical analyses are useful tools and can assist in the design of biological cover system to optimize CH_4 oxidation rates under variable environmental conditions.

The multilevel ANOVA table decomposes the variability of CH_4 oxidation rate into contributions due to various factors. The multifactor ANOVA results are shown in Table 4.2. From the analysis, the factors with P-values less than 0.05 have a statistically significant effect on CH_4 oxidation rate at the 95% confidence level.

Table 4.2 Results of multifactor ANOVA for CH_4 oxidation rates.

Source	Sum of Squares	Degree of Freedom	Mean Squares	F -Ratio	p-value
Main Effects					
Medium	3251.5	2	1625.8	62.1	**0.0000**
Temperature (Temp.)	1874.0	2	937.0	35.8	**0.0000**
Moisture content (MC)	244.8	2	122.4	4.7	0.13
Interactions					
Medium × Temp.	1508.0	4	377.0	6.6	**0.0000**
Medium × MC	131.9	4	33.0	5.4	**0.0003**
Temp. × MC	95.1	4	23.8	1.5	0.19
Medium × Temp.× MC	99.3	8	12.4	1.3	0.23
Total	4471.3				

The P-values of the main effects due to cover medium and temperature as well as the effects of the interaction between these two variables are equal to zero. This means that the type of medium and operating temperature have statistically significant effect on CH_4 oxidation rates in landfill cover system at 95% confidence level. The effect of the interaction between the cover medium and its MC level is also significant; the P-value obtained was equal to 0.0003.

4.3.3 EMPIRICAL MODELING

Box and Draper (1987) indicated that in any process (screening the variables) stage is important to determine which ones of all the suggested input variables have significant and important effect upon the response variable, moreover, (empirical model building) stage is important to learn more about the pattern of the response behavior as changes are made in the variables affecting the process. Therefore, the software package SYSTAT 11

was used to develop an empirical model that best describe the CH_4 oxidation rates in the compost and two types of soils under three levels of temperature and MC. To simplify the calculation and comparison of the individual or combined influence of the variables, the lower and upper values were coded according to the levels shown in Figure 4.1.

Models with different structures, from simple to complex, were tested. To evaluate the performance of these models, the following parameters were taken into consideration (Mac Berthouex and Brown 2002), and reported in Table 4.3. Detailed calculations are presented in Appendix III.

- Sum of squares:

$$S_r = \sum (Y - f(\theta, x)^2 \qquad [3.1]$$

- Residual Mean Square (MS):

$$MS = \sqrt{\frac{S_r}{DoF}} \qquad [3.2]$$

- Coefficient of determination (R^2):

$$R^2 = \frac{S_t - S_r}{S_t} \qquad \text{or } R^2 = 1 - \frac{S_r}{S_t} \qquad [3.3]$$

- Adjusted coefficient of determination (R^2_a)

$$R^2{}_a = 1 - \frac{S_r}{S_{tc}} \qquad [3.4]$$

where,

n = number of data points, m = number of parameters (coefficients) within the model, Y = observed values of the dependent variable, DoF = degree of freedom, S_r = Residual Sum of squares, S_t= Total sum of squares, S_{tc}= Mean corrected sum of squares.

Table 4.3 Empirical models tested to determine single and multi-parameter interactions of CH_4 oxidation in landfill cover system.

Model structure	Sum of Squares (S_r)	Degree of Freedom (DoF)	Regression Mean Square	Residual Mean Square	R^2	R^2_a
$E(R) = \beta_0+\beta_1\times Medium+\beta_2\times Temp.+\beta_3\times MC$	12087.2	4	54.97	5.80	0.823	0.645
$E(R)=\beta_0+\beta_1\times Medium+\beta_2\times Temp.+\beta_3\times MC+\beta_4\times Medium\times Temp.+ B_5\times Medium\times Temp.+\beta_6\times Temp.\times MC+\beta_7\times Medium\times Temp.\times MC$	13416.1	8	40.95	4.13	0.914	0.827
$E(R)=\beta_0+\beta_1\times Medium+\beta_2\times Temp.+\beta_3\times MC+\beta_4\times (Medium)^2+ \beta_5\times (Temp.)^2+ \beta_6\times (MC)^2$	12740.1	7	42.66	5.11	0.868	0.735
$E(R)=\beta_0+\beta_1\times Medium+\beta_2\times Temp.+\beta_3\times MC+\beta_4\times (Medium)^2 +\beta_5\times (Temp.)^2+\beta_6\times(MC)^2+\beta_7\times Medium\times Temp.+\beta_8\times Medium \times MC+ \beta_9\times Temp.\times MC+ \beta_{103}\times Medium\times Temp.\times MC$	14069.5	11	35.76	2.95	0.958	0.917
$E(R)=\beta_0+\beta_1*Medium+\beta_2*Temp.+\beta_3*MC+\beta_4*Medium*Temp.+\beta_5*Medium*MC+\beta_6*Temp.*MC+\beta_7*(Medium)^2+ \beta_8*(Temp.)^2+\beta_9*(MC)^2+\beta_{10}*Medium*Temp.*MC+\beta_{11}*(Medium)^2*Temp.+\beta_{12}*(Temp.)^2*Medium+ \beta_{13}*(MC)^2*Medium$	14396.5	**14**	**32.06**	**2.05**	**0.981**	**0.961**

Detailed statistical analyses of all the models are presented in Appendix IV-4.

Experimental results for the CH_4 oxidation rates were best represented with the model structures incorporating the terms for interaction among the variables (medium, temperature, and MC), second order for temperature, cover medium and MC. Among the different model structures tested, the last model shown in bold in Table 4.3 has the best fit based on the lowest value of regression and residual mean squares analyses and largest determination coefficients; R^2, R^2_a.

In Table 4.3: E(R) represents the expected values of the response (CH_4 oxidation rate), β_o, β_1, β_2,..., β_{13} are the model parameters or regression coefficients, Medium is the type of cover medium, Temp. is the temperature level, MC is the moisture content level. S_r is the sum of squares, DoF is the degree of freedom, R^2 is the determination coefficient, and R^2_a is the adjusted determination coefficient.

Table 4.4 illustrates parameter estimation results for the model selected to describe CH_4 oxidation rates in different cover media and under various conditions. The model's common parameters including regression coefficient estimated value and confidence intervals (95%).

Table 4.4 Parameter estimation results for the model selected to describe CH_4 oxidation rates in landfill cover system.

Regression Coefficient	Variable	Value	"Confidence lower	Interval" upper
β_0	**1**	**-3.8**	**-20.8**	**-3.2**
β_1	**Medium**	**12.5**	**0.2**	**24.7**
β_2	**Temp.**	**6.4**	**5.2**	**18.0**
β_3	MC	-0.9	-11.9	10.0
β_4	**Medium × Temp.**	**-11.8**	**-18.7**	**-4.8**
β_5	**Medium × MC**	**-0.7**	**-9.8**	**-1.4**
β_6	Temp. × MC	0.6	-1.2	2.4
β_7	**$(Medium)^2$**	**-4.4**	**-6.9**	**-1.8**
β_8	$(Temp.)^2$	1.0	-1.5	3.6
β_9	$(MC)^2$	0.3	-2.3	2.8
β_{10}	Medium × Temp× MC	-0.7	-1.6	0.1
β_{11}	**$(Medium)^2$× Temp.**	**5.2**	**4.0**	**6.4**
β_{12}	$(Temp.)^2$ × Medium	-0.5	-1.6	0.7
β_{13}	$(MC)^2$× Medium	0.1	-1.1	1.3

However, the confidence intervals for all interaction terms that contain zero may be deleted from the model. After deleting these terms, the regression analysis was repeated with the remaining parameters. The final statistical model is as follows:

$$E(R) = -3.8 + 12.5 \times Medium + 6.4 \times Temp - 11.8 \times Medium \times Temp \\ - 0.7 \times Medium \times MC - 4.4 \times (Medium)^2 + 5.2 \times (Medium)^2 \times Temp \quad [4.4]$$

The statistical model results correspond with the multifactor ANOVA analysis. Also, the model was verified using all the experimental CH_4 oxidation rates attained from this study. This model has the advantage of incorporating the main effects of cover medium, temperature, and MC on the CH_4 oxidation process, in addition to the effects of the

combined variables. Furthermore, the model was validated using some of the experimental CH_4 oxidation rates under various environmental conditions reported in the literature. Table 4.5 shows the comparison between the experimental CH_4 oxidation rates reported by different researchers and the model- based CH_4 oxidation rates.

Table 4.5 Comparison between some of the reported CH_4 oxidation rates and the modeled results.

Researchers	Reported environmental conditions	Reported CH_4 oxidation rate	Modeled CH_4 oxidation rate
Gebert et al. (2003)	Expanded clay in November	**3.1 – 6.1 μg_{CH4} $g^{-1}_{wet\ wt.}$ h^{-1}**	**3.3 μg_{CH4} $g^{-1}_{wet\ wt.}$ h^{-1}**, clay soil at 13°C, 20% MC.
Gebert et al. (2003)	Top soil in July (22°C)	**5.2 μg_{CH4} $g^{-1}_{wet\ wt.}$ h^{-1}**	**5.1 μg_{CH4} $g^{-1}_{wet\ wt.}$ h^{-1}** clayey silt soil, at 22°C, 25% MC.
Kallistova et al. (2005)	Clay and sand at 20°C	8.1 – 10.3 µmole CH_4 $g^{-1}_{dw}d^{-1}$ **(5.4 – 6.9 µg $_{CH4}$ $g^{-1}_{dry\ wt.}$ h^{-1})**	**4.1 µg $_{CH4}$ $g^{-1}_{dry\ wt.}$ h^{-1}** clay soil at 22°C, 20% MC. **7.5 µg $_{CH4}$ $g^{-1}_{dry\ wt.}$ h^{-1}**, clayey silt soil at 22°C, 20% MC.
Borjesson et al. (2004)	Clay, silt and sand at 5°C	0.026 – 0.14 µmole CH_4 $g^{-1}_{dw.}h^{-1}$ **(0.04 - 2.7 μg_{CH4} $g^{-1}_{dry\ wt.}$ h^{-1})**	**1.6 µg $_{CH4}$ $g^{-1}_{dry\ wt.}$ h^{-1}** for clayey silt soil at 5°C, 30% MC.

As shown in Table 4.5, the empirical model presented was able to validate successfully many of the CH_4 oxidation rates presented in the literature. By applying knowledge about the main factors that influence this process, the model can help in estimating the CH_4 oxidation rates in a landfill cover system. Although batch tests are considered a first step in understanding the biological CH_4 oxidation process, still the empirical modeling can estimate the expected oxidation rates under different environmental conditions, and can assist in the design of biological cover system to optimize the CH_4 oxidation rates and

consequently mitigate the harmful emissions from the existing landfill sites and open dumps.

4.4 CONCLUSIONS

The landfill cover medium affected the CH_4 oxidation process significantly. The results obtained in this study confirm that the compost offers a very good landfill cover medium. Compost showed the highest oxidation rates at 22 and 35°C, on the other hand the low temperature effect at 5°C prevailed over the cover medium effect, and the compost and two types of soil had low oxidation rates and almost in the same range. The results obtained confirmed that the temperature is one of the main environmental parameters affecting the biological CH_4 oxidation process in the landfill cover system. Lower temperature can affect the type of methanotrophic, their growth and oxidation kinetics, as well as the O_2 diffusion within the cover. The lowest oxidation rates were obtained at 5°C for all three tested cover medium, while the highest oxidation rates were achieved at 35°C. The differences between the oxidation rates at 5 and 35°C are statistically significant at 95% confidence level, especially for the compost samples. However, the CH_4 oxidation rates at 5°C were 2 to 3 times lower than at 22 and 35°C using clay and clayey silt soils. Using compost increased the gap between oxidation rates at 5°C and 35°C by almost 6 times.

In the tested range, the moisture content level is also considered an important physical parameter that affects the diffusion of gases (CH_4 and O_2) between the soil and gas phase, as well as restricts CH_4 solubility in water.

Statistical analysis and empirical modeling for the CH_4 oxidation in three types of landfill cover medium were presented under variable temperatures and moisture levels that reflect diverse climatic conditions. The empirical model could successfully predict the CH_4 oxidation rates obtained in this study, and furthermore it was validated with some other CH_4 oxidation rates reported in literature.

4.5 REFERENCES

Albanna, M., Fernandes, L., and Warith, M. (2007). "Methane Oxidation in Landfill Cover Soil; the Combined Effects of Moisture Content, Nutrient Addition, and Cover Thickness," *Journal of Environmental Engineering and Science*, 6, pp. 191-200.

Albanna, M., and Fernandes, L. (2009). "Effects of Temperature, Moisture Content and Fertilizer Addition on Biological Methane Oxidation in Landfill Cover Soils." *American Society of Civil Engineers*, in press.

ASTM D2974-87, American Society for Testing and Materials (2000), "Standard Test Method for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils". ASTM International, PA, USA.

ASTM D7348-08, American Society for Testing and Materials (2000), "Standard Test Methods for Loss on Ignition of Solid Combustion Residues". ASTM International, PA, USA.

ASTM D422, American Society for Testing and Materials (2002), "Standard Test Method for Particle Size Analysis of Soils". ASTM International, PA, USA.

ASTM D4318, American Society for Testing and Materials (2005), "Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils". ASTM International, PA, USA.

Barlaz, M.A., Green, R.B., Chanton, J.P., Goldsmith, C.D., and Hater, G.R. (2004), "Evaluation of a Biologically Active Cover for Mitigation of Landfill Gas Emissions," *Environmental Science and Technology*, 38, pp. 4891-4899.

Boeckx, P., Van Cleemput, O., and Villaralvo, I. (1997). "Methane Oxidation in Soils with Different Textures and Land Use." *Nutrient Cycling in Agroecosystems*, 49, pp. 91-95.

Bogner, J., Spokas, K., and Burton, E.A. (1997). "Kinetics of Methane Oxidation in a Landfill Cover Soil: Temporal Variations, a Whole-Landfill Oxidation Experiment and Modeling of Net CH_4 Emissions," *Environmental Science Technology*, 31, pp. 2504 - 2514.

Borjesson, G., Sundh, I., and Svensson, B.H. (2004), "Microbial Oxidation of CH_4 at Different Temperatures in Landfill Cover Soils," *FEMS Microbiology Ecology*, 48, pp. 305-312.

Box, G., and Draper, N. (1987), "Empirical Model-Building and Response Surfaces," Wiley Series in Probability and Mathematical Statistics, New York, USA.

Czepiel, P.M., Mosher, B. and Harris, R.C. (1996), "Landfill Methane Emissions Measured by Enclosure and Atmospheric Tracer Method," *Journal of Geophysical Research*, 101, pp. 16,711-16,719.

Einola J-K.M., Kettunen, R.H., and Rintala, J.A. (2007), "Responses of Methane Oxidation to Temperature and Water Content in Cover Soil of a Boreal Landfill," *Soil Biology and Biochemistry*, 39, pp. 1,156-1,164.

Environment Canada (October, 2005), Landfill Gas Management in Canada Report, http://www.ec.gc.ca/pdb/ghg/inventory_report/2005_report/tdm-toc_eng.cfm.

Gebert, J., Groengroeft, A., and Miehlich, G. (2003), "Kinetics of Microbial Landfill Methane Oxidation in Biofilters," *Waste Management*, 23, pp. 609-619.

Hanson, R. and Hanson, T.E. (1996). "Methanotrophic Bacteria," *Microbiological Reviews,* 60, pp. 439- 471.

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., Mclnernery M.C., and Stezenback L.D.(Eds.), ASM Press, Washington, D.C., pp. 696-717.

Hilger, H. and Humer, M. (2003). "Biotic Landfill Cover Treatments for Mitigating Methane Emissions," *Environmental Monitoring and Assessment*, 84, pp. 71-84.

Holtz, R., Kovacs, W. (1981), "An Introduction to Geotechnical Engineering," Prentice-Hall, Englewood Cliffs, New Jersey, USA.

Horz, H.P., Raghubanshi, A.S., Heyer, J., Kammann, C., Conrad, R., and Dunfield, P.F. (2002), "Activity and Community Structure of Methane-Oxidising Bacteria in a Wet Meadow Soil," *FEMS Microbiology Ecology*, 41, pp. 247- 257.

Kallistova, A. YU., Kevbrina, M.V., Nekrasova, V.K., Glagolev, M.V., Serebryanaya, M.I., and Nozhevnikova, A.N. (2005), "Methane Oxidation in Landfill Cover Soil," *Microbiology*, 74, pp. 608-614.

Kettunen, R., Einola, J-K.M. and Rintala, J.A. (2006). "Landfill Methane Oxidation in Engineered Columns at Low Temperature," *Water, Air and Soil*, 177, pp. 313-334.

King, G.M., and Adamsen, P.S. (1992), "Effects of Temperature on Methane Consumption in a Forest Soil and in Pure Cultures of the Methanotroph Methylomonas rubra", *Applied and Environmental Microbiology*, 58, pp. 2758-2763.

Mac Berthouex, P., and Brown, L. (2002), "Statistics for Environmental Engineers," Lewis Publishers, A CRC Press Company, Boca Raton, Florida.

Mor, S., De Visscher, A., Ravindra, K., Dahiya, R.P., Chandra, A., and Van Cleemput, O. (2006),"Induction of Enhanced Methane Oxidation in Compost: Temperature and Moisture Response," *Waste Management,* 26, pp. 381-388.

STATGRAPHICS Centurion XV, (2007), Statpoint Technologies, Inc., Virginia, USA.

SYSTAT 11, (2004). Systat Software Inc., Chicago, USA.

USEPA (1999), Municipal Solid Waste Landfills, Volume I: Summary of the Requirements for the New Performance Standards and Emissions Guidelines for Municipal Solid Waste Landfills. 453/R-96-004. Research Triangle Park, NC. USA.

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 Biology and Biochemistry*, 28, p. 1271-1281.

Wilshusen, J.H., Hettiaratchi, J.P.A., and Stein, V.B. (2004a), "Long-Term Behavior of Passively Aerated Compost Methanotrophic Biofilters Columns," *Waste Management*, 24, pp. 643-653.

Wilshusen, J.H., Hettiaratchi, J.P.A., De Visscher, A., and Saint-Fort, R. (2004b). "Methane Oxidation and Formation of EPS in Compost: Effect of Oxygen Concentration", *Environmental Pollution*, 129, pp. 305-314.

CHAPTER 5

KINETICS OF BIOLOGICAL METHANE OXIDATION IN THE PRESENCE OF NON-METHANE ORGANIC COMPOUNDS IN LANDFILL BIO-COVERS

Muna Albanna, Mostafa Warith, and Leta Fernandes

ABSTRACT

In this experimental program, the effects of non-methane organic compounds (NMOCs) on the biological methane (CH_4) oxidation process were examined. The investigation was performed on compost experiments incubated with CH_4 and selected NMOCs under different environmental conditions. The selected NMOCs had different concentrations and their effects were tested as single compounds and mixtures of compounds. The results from all experimental sets showed a decrease in CH_4 oxidation capacity of the landfill bio-cover with the increase in NMOCs concentrations. For example, in the experiment using compost with 100% moisture content at 35°C without any NMOCs the V_{max} value was 35.0 $\mu gCH_4\ h^{-1}\ g^{-1}_{wet\ wt}$. This value was reduced to 19.1 $\mu gCH_4\ h^{-1}\ g^{-1}_{wet\ wt}$ when mixed NMOCs were present in the batch reactors under the same environmental conditions. The experimental oxidation rates of CH_4 in the presence of single and mixed NMOCs were modeled using the uncompetitive inhibition model and kinetic parameters, including the dissociation constants, were obtained. Additionally, the degradation rates of the NMOCs and co-metabolic abilities of methanotrophic bacteria were estimated.

5.1 INTRODUCTION

Landfill gas (LFG) is generated from the biodegradation of wet organic waste under anaerobic conditions in landfills and open dumps; it comprises primarily 50-65% methane (CH_4), 35-50% carbon dioxide (CO_2), and approximately 1% non-methane organic compounds (NMOCs) (USEPA 2006). Landfill gas builds up and is slowly released into the atmosphere if the landfill site has not been engineered to capture the gas. Even if collection setups are placed in newly constructed landfills the reported collection efficiencies still range from 60 to 80% (USEPA 1999). The CH_4 contained in LFG is hazardous; in addition to being flammable and explosive, the uncontrolled CH_4 emissions which escape into the atmosphere may significantly contribute to the effects of global warming. Methane's global warming potential is 23 times than that of CO_2 over a 100-year period (IPCC 2001). Therefore, a landfill cover (LFC) system in which CH_4 oxidation is accomplished by methanotrophic bacteria can be a significant biological process for attenuating fluxes of CH_4 to the atmosphere. Additionally, methanotrophs are capable of performing oxidative conversions of a number of chemical compounds (Barlaz et al. 2004; Scheutz et al. 2004a; Kjeldsen et al. 1997), which suggest that a proper LFC that enhances CH_4 oxidation can also result in reduced emissions of trace constituents of NMOCs.

Methanotrophs are defined as gram-negative aerobic bacteria with the ability to grow using CH_4 as its sole carbon and energy source (Borjesson et al. 2004). The significant feature of methanotrophic bacteria is the enzyme methane monooxygenase (MMO), which facilitates the conversion of CH_4 to methanol as the first step of the pathway for

CH_4 consumption (Hanson and Hanson 1996). Methane monooxygenase (MMO) is a broadly nonspecific enzyme and can catalyze a wide range of oxidative reactions such as the co-metabolic transformation of chlorinated solvents. Co-metabolic transformation are defined as the reactions that are catalyzed by existing microbial enzyme and that yield no carbon or energy benefits to the transforming cells (Alvarez-Cohen and Speitel 2001). Co-metabolism may occur relatively slowly in comparison to metabolism of the growth substrate (CH_4). It was demonstrated in literature that chlorinated aliphatics can be biologically degraded by methanotrophs' (pure cultures) co-metabolic transformation reactions, but Trichloroethylene (TCE) was the most widely studied (Lontoh and Semrau 1998; McFarland et al. 1992; Oldenhuis et al. 1991; Alvarez-Cohen and McCarty1991a; Tsien et al 1989). Alvarez-Cohen and Speitel (2001) reported that the reaction of chlorinated solvents with the enzyme MMO generates chlorinated oxidation products that may react with cellular macromolecules or may be hydrolyzed spontaneously into CO_2, chloride or other non volatile products that are mineralized by the bacteria. These researchers demonstrated that there may be a competition between growth substrate and co-metabolic substrate on the enzyme active sites, and this competition can result in overall decreased transformation rates of each substrate, or enzyme inhibition. The binding of a chemical compound can stop the growth substrate from entering the enzyme's active site and hinder the enzyme from catalyzing its reaction. In the following general discussion, the co-metabolized NMOC represents the inhibitor (I); since it was hypothesized that its presence would cause an inhibition effect, and CH_4 represents the substrate (S). There are four main types of inhibition caused by the inhibitor present

along with the substrate as reported in literature (Jeremy et al. 2007; Leskovac 2003; Krogsgaard-Larsen and Liljefors 2002; LaGrega et al. 2001; Silverman 2000):

- Competitive Inhibition: The inhibitor (I) binds to the active site of the free enzyme (E) and prevent the substrate (S) from binding. Therefore, I and S compete for the active site. The term K_i is the dissociation constant for the E-I complex. The rate of reaction depends on I, K_i, S and K_m, and can be estimated as:

$$V = V_{max} \frac{[S]}{K_m\left(1+\frac{[I]}{K_i}\right)+[S]} \qquad [5.1]$$

where, V is the reaction rate, V_{max} is the maximum reaction rate, [S] is the substrate concentration, [I] is the concentration of the inhibitor, K_m is the half saturation constant and K_i is the dissociation constant for the E-I complex.

Equation [5.1] is identical to Michaelis-Menten equation except the presence of the inhibitor results in K_m being multiplied by the factor $(1+ (I/K_i))$.

- Uncompetitive Inhibition: When the inhibitor binds to the complex formed between the enzyme and the substrate (the E-S complex), producing an inactive E-S-I complex. Uncompetitive inhibition is most noticeable at high substrate (S) concentrations, the V_{max} and K_m are both reduced as a result of the inhibition effects and K_i is much greater than the total inhibitor concentration. The binding of the substrate modifies the structure of the enzyme making the inhibitor-binding

site available. The form of Michaelis-Menten equation that describes this behavior is:

$$V = V_{\max} \frac{[S]}{K_m + [S]\left(1 + \frac{[I]}{K_i}\right)} \qquad [5.2]$$

- Noncompetitive Inhibition: When the co-metabolized compound or inhibitor binds to both enzyme (E) and enzyme-substrate (E-S) complex. It is rare for single substrate reactions to exhibit this type of inhibition, but it is common in multiple-substrate system. The reaction rate derived from Michaelis-Menten equation is:

$$V = \frac{V_{\max}[S] \Big/ \left(1 + \frac{[I]}{K_i}\right)}{K_m + [S]} \qquad [5.3]$$

- Toxic Inhibition: The effect of toxic inhibition can be described Haldane equation, where the reaction rate can be estimated as follows:

$$V = V_{\max} \frac{[S]}{K_m + [S] + \frac{[S^2]}{K_i}} \qquad [5.4]$$

Previous researchers (McFarland et al. 1992; Alvarez-Cohen and McCarty1991b) recognized that the competition between CH_4 and chemical compound for the enzyme MMO caused competitive inhibition. However, these results were based on experiments using methanotrophic pure cultures and cell suspensions, and amounts of CH_4 and

chemical compounds that might not be descriptive of LFG, and therefore competitive inhibition may not be representative of the inhibition that occur in the LFC due to NMOCs present with CH_4. Enzyme kinetics are complex; mainly due to the many possible intermediates in the form of enzyme-substrate complexes and the inhibition that these intermediates may trigger. The type of inhibition caused by the presence of NMOCs in LFG and affecting the biological oxidation of CH_4 in the LFCs has not yet been thoroughly researched. The majority of researches presented in literature had studied the biological oxidation of CH_4 alone and did not include NMOCs. This study aims at a better understanding of methanotrophic CH_4 oxidation when the NMOCs are present as part of the LFG. The main objectives were: to identify and quantify the effects of NMOCs on CH_4 oxidation process in the LFC; to identify the enzyme inhibition type caused by concurrent degradation of growth substrate (CH_4) and co-metabolic substances (NMOCs) in LFC experiments; and, to examine the co-metabolic abilities of methanotrophic bacteria in the landfill cover system by estimating the degradation rates of the different NMOCs.

In order to accomplish the study's objectives, microbial CH_4 oxidation performance (without any NMOC) under different temperatures and moisture levels was studied in batch experiments, using compost as the LFC medium. Then, the effects of NMOCs present with CH_4 in different concentrations on the biological oxidation process in compost were studied by conducting another four sets of experiments: CH_4 combined with trichloroethane (TCA); trichloroethylene (TCE); dichloromethane (DCM); and, the mix of these compounds. Methane oxidation kinetic parameters in the presence of NMOCs were determined and compared with the kinetic parameters obtained for the

experiments performed with CH_4 alone. Furthermore, CH_4 oxidation rates (in the presence of mixed NMOCs) as a function of CH_4 concentrations were modeled and the kinetic parameters including the inhibition constants were obtained and used to describe the inhibition caused by the chemical compounds. Finally, the degradation rates of the NMOCs and co-metabolic abilities of methanotrophic bacteria were estimated. Compost was selected as the LFC medium, since it was confirmed by previous study (Albanna and Fernandes 2009) that oxidation rates in compost were 3-5 times higher than conventional LFC soils at 22 and 35°C.

5.2 MATERIALS AND METHODS

5.2.1 EXPERIMENTAL DESIGN

To analyze the effects of single and mixed NMOCs on CH_4 oxidation uptake of the compost, laboratory experiments were designed using batch reactors. The experimental runs were designed to test the CH_4 and NMOCs oxidation capacity of compost samples under three levels of temperature and moisture content (MC). The temperature levels were 5, 22, and 35°C to reflect different climatic conditions. The compost samples were acclimatized by running three laboratory scale columns; the columns had CH_4 inlet ports at the bottom and air inlet ports at the top to simulate the landfill cover system. The designated saturation levels of the compost in the columns were 30, 50 and 75%. The compost samples were taken from these simulated columns to conduct the batch experiments and had 57, 100 and 142% w/w MC, respectively. The selected NMOCs in

this study were TCA, TCE, and DCM because these compounds were recognized in LFG in most sites (USEP 1999). Also, they have harmful effects on human health as their emission factor rating is either "A or B" based on a USEPA (1999) report, which means that these selected compounds are classified as "proven or probable human carcinogens" (Watts 1997). Table 5.1 shows the experimental variables and their levels.

Table 5.1 Variables and their levels

Variables→ / Levels↓	NMOC Concentration (ppmv)	Temperature (°C)	Moisture Content (% w/w)*
1	No NMOC = 0	5	57
2	TCA = 1	22	100
3	TCE = 3	35	142
4	DCM = 14.3		
5	Mix = 18.3		

* Compost samples were taken from columns that had 30, 50 and 75% S.L.s. Moisture content was based on dry weight bases.

This experimental design resulted in 45 experimental run in triplicates, in addition to control reactors. The CH_4 oxidation kinetics parameters were determined by incubating compost samples under a range of CH_4 concentrations varying from 0 to 14% v/v.

5.2.2 EXPERIMENTAL MATERIALS

Compost samples were collected from Trail Road composting facility in Ottawa. The compost used was mature and stabilized yard waste compost. The stability of the compost at the beginning of the experiments was checked and the respiration rates were measured by incubating compost samples in batch reactors with air. The O_2 consumption rate was

0.45 μmol O_2 h^{-1} $g^{-1}_{wet\ wt}$ and CO_2 evolution rate was 0.33 μmol CO_2 h^{-1} $g^{-1}_{wet\ wt}$ at 22°C. The compost's initial moisture content was 107% w/w and was determined gravimetrically by oven-drying soil or compost samples at 105°C for 24 hours and expressed as the mass ratio of water to dry soil or compost following the ASTM D2974-87 procedure. Initial organic matter was 31% and was determined by loss on ignition following ASTM D7348-08. The compost's initial bulk density was 890 kg/m^3. The percentage of nitrogen and carbon were 1.24 and 14.81%, respectively and were obtained using Thermo-Finnigan Flash 1112 elemental analyzer.

The compost obtained from the composting facility had not been exposed to CH_4; to ensure adequate population of methanotrophs, the compost was acclimatized by running three laboratory scale columns that contained compost samples with the designated saturation levels. Before filling the columns, the moisture content of the compost was adjusted according to the designed saturation level in each column and then the samples were packed in the columns and compacted. Moisture content was increased by adding sterilized water, and decreased by air drying the water content to the desired level. Bulk density and specific gravity were measured, and void ratio and saturation level were calculated accordingly. Void ratio was calculated based on bulk density, specific gravity and moisture content. Saturation level was calculated based on the voids ratio, specific gravity and moisture content (Holtz and Kovacs, 1981).

The columns were kept covered to reduce light exposure and minimize the growth of other microorganisms that can compete with the methanotrophs and consequently increase the respiration rate in the compost. The compost samples used in the

experiments were taken from the columns simulating LFC, which were purged with CH_4 for 30 days. The compost samples used in the experiments were taken from the top 50-150 mm of the simulation columns. The chemicals used in the experiments were obtained from Sigma-Aldrich Canada, in liquid form and high purity (98.0-99.5%).

5.2.3 EXPERIMENTAL METHODS

Each experimental run was conducted in glass bottle of 160 mL total volume. Thirty grams of wet compost were added to each reactor. For the first experimental set where CH_4 alone was tested without any NMOCs, each bottle was tightly sealed after adding the compost sample using a gas tight aluminum seal of a tan Teflon/silicone (PTFE) septum which enabled gas sampling from the reactor's headspace by a gas tight needle and syringe. For the other four sets of experiments where CH_4 combined with NMOCs was tested, the compounds in liquid form were transferred into small size tubes which were placed inside the glass bottle reactors containing the compost samples using a gas tight syringe (Hamilton syringe type 10ULPT2). The initial concentrations used were based on the default concentrations reported by USEPA (1999) as follows: DCM = 14.3 ppmv, TCE = 3 ppmv, and TCA = 1 ppmv. The reactors were immediately closed tightly using Mininert valves with auxiliary septum seal (VICI Precision Sampling, Inc.). Immediately after the closure of each reactor and for all the experimental sets, 40 mL of air from the headspace was withdrawn using a syringe and replaced with 16 mL of CH_4 gas (99% purity) and 24 mL of O_2 gas (100% purity). These amounts provided a mixing ratio of approximately 10% CH_4 (v/v) and 30% O_2 (v/v) of the total headspace. The O_2 was added to ensure that the aerobic conditions prevailed during the experiment. The bottles

that contain the NMOCs were incubated at 35°C for one hour to ensure the complete volatilization of NMOCs. Afterwards, all reactors were kept on top of orbital shakers at the designated temperatures to ensure good mixing conditions. The pressure inside each reactor for all the experiments was atmospheric pressure. Headspace gas samples were withdrawn regularly and analyzed by gas chromatograph.

To determine CH_4 oxidation kinetics parameters, compost samples were incubated under at least five CH_4 concentrations varying from 0 to 14% v/v for all sets of experiments.

There were control reactors for each experimental run. The compost samples in the control reactors were autoclaved and then a sufficient amount of sodium azide (25mg per kg of wet compost (Scheutz et al. 2004a; Kjeldsen et al. 1997) was added to inactivate the microorganisms.

5.2.4 GAS CHROMATOGRAPHS

The concentrations of headspace gases CH_4, O_2, N_2 and CO_2 were monitored by withdrawing 200 µL samples from the headspace using a gas tight syringe and injected manually into the inlet of series 400 Gow-Mac gas chromatograph equipped with a thermal conductivity detector (TCD) and two columns. The type of the column is capillary column. The carrier gas was helium, and the detector, injection port and column temperatures were 130, 130 and 120°C, respectively.

The gas samples were also analyzed for NMOCs concentrations by withdrawing 5 µL samples from the headspace using gas tight syringes and injecting the samples manually into a Hewlett Packard 5890 gas chromatograph equipped with electron-capture detector

(ECD). The detector and injection port temperatures were 300, 200°C respectively. The selected NMOCs were analyzed with an isothermal column temperature of 40°C for 3 minutes and then increased at a rate of 30°C/min to a temperature of 70°C for 2 minutes and finally increased at a rate of 40°C/min to 110°C for 3 minutes. All peaks were quantified using LabView integration software on the laboratory computer.

To measure the concentrations of the proposed compounds using ECD gas chromatograph, calibration curves were established for each compound by a minimum of ten concentration levels. Calibration standards were established by injecting a specific amount of an NMOC into a five liters gas sampling bag after filling the bag with air.

5.3 RESULTS AND DISCUSSION

5.3.1 CH_4 OXIDATION KINETIC PARAMETERS WITHOUT NMOCs

To evaluate the effects of organic compounds on the CH_4 oxidation uptake of the bio-cover, the first experimental run was conducted in compost incubated with CH_4 under different environmental conditions. In all active reactors, CH_4 and O_2 concentrations decreased with time, while CO_2 concentration increased except in the control reactors as shown in Figure 5.1.

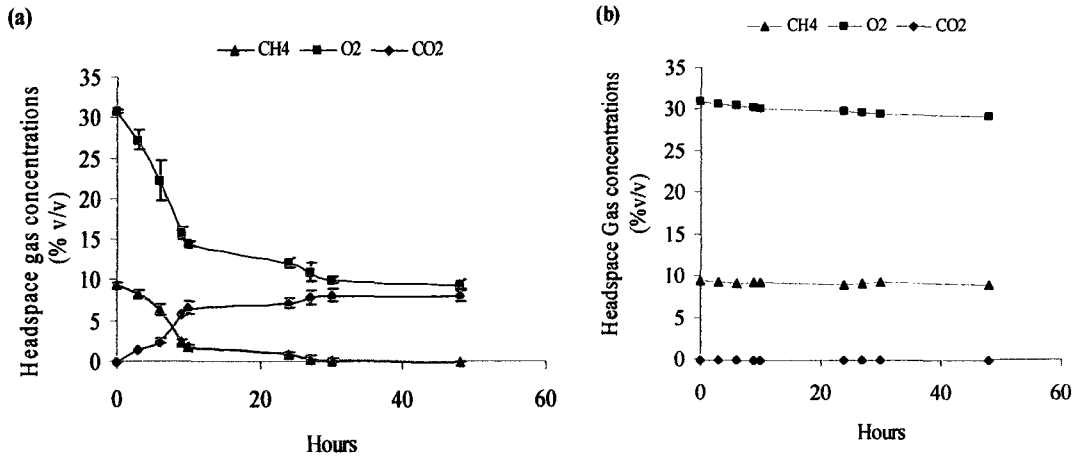


Figure 5.1 Headspace gas concentrations versus time in batch reactors using compost with 100%MC at 22°C (a) active reactors (b) control.

Figure 5.1 shows CH_4, O_2 and CO_2 concentrations versus time in batch reactors using compost with 100% MC (compost samples were taken from columns with 50% S.L.) at 22°C, as an example. The error bars are standard deviation from experiments on triplicates samples. The results illustrated in Figure 5.1.a indicated that biological CH_4 oxidation was taking place in the active batch reactors. Methane and O_2 concentrations decreased over time while CO_2 concentration increased, signifying that CH_4 oxidation was taking place. Also, there was no decrease in CH_4 or increase in CO_2 concentrations in the headspace of the control reactors (as shown in Figure 5.1.b). In all active reactors, O_2 concentration was never below 10% v/v which indicates that O_2 was not limiting factor. Also, CH_4 oxidation followed zero-order kinetics which indicated that the oxidation process was not limited by CH_4 as a substrate. There was no lag phase in any of the active experiments, which implied that there were well established methanotrophic bacteria in the compost samples. Bottle headspaces were sampled 5-10 times during the experiments by removing 200 μL of gas in each sample, and CH_4 concentrations were quantified using the Gow-Mac gas chromatograph.

The CH_4 oxidation kinetic parameters for the compost were obtained by supplying varying quantities of CH_4 into the batch reactors containing active compost according to the experimental protocol in section 5.2.3. The resulting oxidation rates were used to calculate the maximum rate of CH_4 oxidation (V_{max}) and the apparent half-saturation constant (K_m). Michaelis-Menten kinetics parameters were fitted to the experimental data using non-linear regression software (SYSTAT 11) in keeping with the following equation:

$$V_{CH\,4} = \frac{V_{max} \times [CH_4]}{K_m + [CH_4]} \qquad [5.5]$$

where, V_{CH4} is the CH_4 oxidation rate ($\mu gCH_4\ h^{-1}g^{-1}_{wet\ wt.}$), V_{max} is the maximum CH_4 oxidation rate ($\mu gCH_4\ h^{-1}g^{-1}_{wet\ wt.}$), $[CH_4]$ is the CH_4 concentration of compost gas phase (ppm), and K_m is the apparent half-saturation constant (ppm).

Methane oxidation rate data were expressed in substrate saturation curves as a function of initial CH_4 concentrations as shown in Figure 5.2.

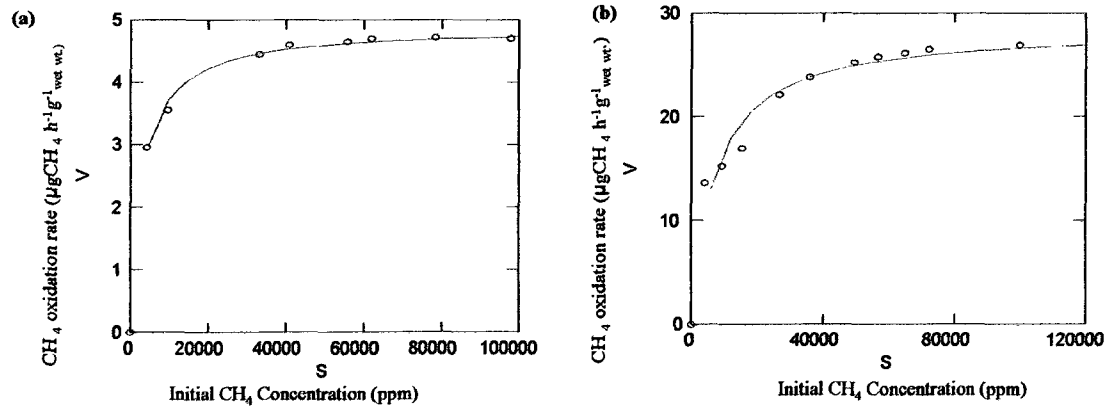


Figure 5.2 **CH_4 oxidation rates as a function of initial headspace CH_4 concentrations using compost samples with 142% MC; (a) at 5°C, (b) at 35°C.**

Figure 5.2 illustrates (as an example) CH_4 oxidation rates ($\mu gCH_4\ h^{-1}g^{-1}_{wet\ wt}$) versus initial substrate concentration (ppm) for the experiments conducted at 5 and 35°C using compost with 142% MC. Methane oxidation results demonstrated typical Michaelis-Menten characteristics. Table 5.2 provides the values of V_{max} and K_m that best fitted the experimental data at different temperature and moisture levels without any NMOCs.

Table 5.2 Kinetic parameters of CH_4 oxidation in compost at different temperature and moisture levels without NMOCs.

Temperature (°C)	Compost MC (% w/w)	V_{max} ($\mu gCH_4\ h^{-1}g^{-1}_{wet\ wt.}$)	K_m (ppm)
5	57	7.4	3,717.4
5	100	5.5	3,135.3
5	142	4.8	2,727.3
22	57	30.2	9,524.1
22	100	20.4	8,695.7
22	142	13.2	6,694.9
35	57	38.2	10,057.7
35	100	35.0	9,017.3
35	142	28.6	7,051.8

The compost showed a high capacity for CH_4 oxidation; V_{max} values ranged between 4.8 – 38.2 $\mu gCH_4\ h^{-1}g^{-1}_{wet\ wt.}$ (11.1 - 71.7 $\mu gCH_4\ h^{-1}g^{-1}_{dry\ wt.}$), and K_m values between 2,727 – 10,057 ppm. The kinetic parameters were within the range reported by other researchers. Gebert et al. (2003) reported values of V_{max} value of 28.5 $\mu gCH_4\ h^{-1}g^{-1}_{wet\ wt.}$ and K_m value of 10,067 ppm in bio-filters. De Visscher et al. (2001) reported V_{max} values using LFC soil in the range of 1.3 $\mu gCH_4\ h^{-1}g^{-1}_{dry\ wt.}$ at 5°C and 29 $\mu gCH_4\ h^{-1}g^{-1}_{dry\ wt.}$ at 35°C, and K_m values in the range of 787 to 4,675 ppm.

The kinetic parameters reflected the effect of different temperature and moisture levels. The temperature had a significant effect on the bacterial oxidation activities as shown in Table 5.2. The values of V_{max} and K_m increased with temperature and the highest activities were noted at 35°C, the highest temperature tested. The values of maximum oxidation rates at 5°C were 3 to 4 times lower than the rates at 22°C; this is in accordance with findings by (Kjeldsen et al. 1997; Whalen et al. 1990). As discussed by Albanna and Fernandes (2009), the low temperature levels affect the methanotrophic bacteria type existing in the landfill cover system, as well as the diffusion of gases (CH_4 and O_2) within the cover, which was reflected on reduced oxidation capacities at low temperatures.

5.3.2 CH_4 OXIDATION KINETIC PARAMETERS IN THE PRESENCE OF NMOCs

The effects of single and mixed NMOCs on CH_4 oxidation activities were studied by monitoring the headspace gases reductions with time in another 36 experimental runs. The investigations have been performed on compost incubated with CH_4 and NMOCs under different environmental conditions and various organic compounds concentrations as illustrated in Table 5.1. Figure 5.3 displays the results of CH_4 concentration (% v/v) in the headspace batch reactors versus time for the experimental run conducted using compost with 57% MC at 22°C.

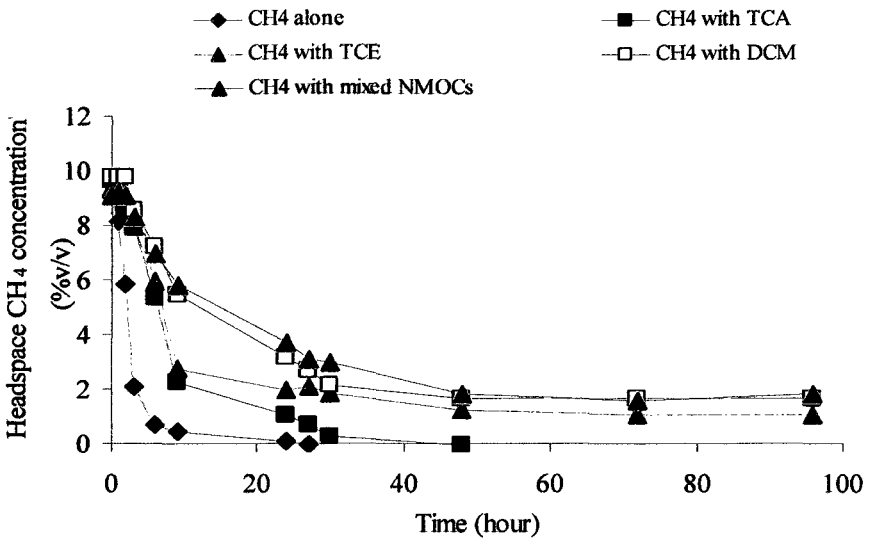


Figure 5.3 Methane concentration (%v/v) versus time in batch reactors using compost with 57% MC at 22°C with different NMOCs concentrations.

In all the experiments where NMOCs were introduced, CH_4 and O_2 concentrations declined with time while CO_2 increased, indicating that CH_4 oxidation was taking place. However, the presence of NMOCs affected the CH_4 oxidation process quite significantly as shown in Figure 5.3. Complete CH_4 oxidation occurred within 24 hours when CH_4 was present alone in the reactors headspace, while CH_4 oxidation was not complete in more than 50 hours when DCM or the mixed NMOCs were introduced with CH_4 in the headspace. The concentration of NMOCs affected the oxidation process; almost complete CH_4 oxidation within 30 hours was monitored in the batch reactors were TCA was added, while CH_4 oxidation was not completed during this time in the batch reactors when TCE was added. The trends shown in Figure 5.3 were observed in all the experimental runs.

In order to evaluate the effects of NMOCs on the biological CH_4 oxidation in the compost, CH_4 oxidation kinetic parameters in the presence of different NMOCs types and concentrations were obtained. Methane oxidation rates when NMOCs were present

versus initial CH_4 substrate concentrations for each experiment were plotted and the CH_4 oxidation kinetic parameters (V_{max} and K_m) were estimated by applying the growth model (equation 5.5) using non-linear regression software. Figure 5.4 demonstrates the values of the maximum oxidation rate (V_{max}) for all the experimental runs.

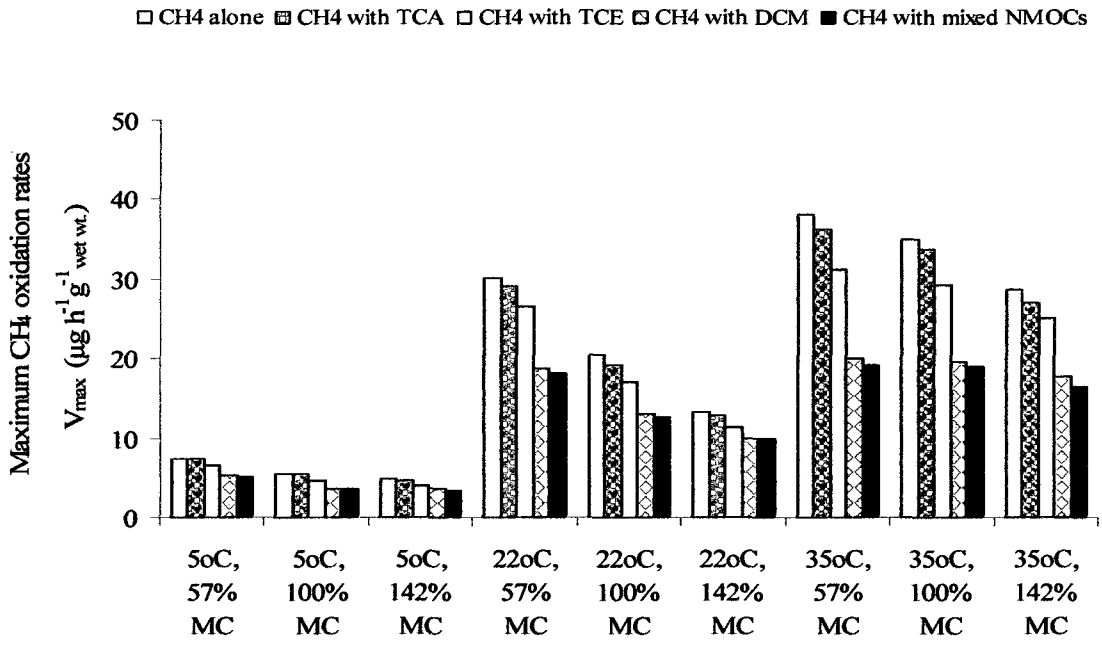


Figure 5.4 Maximum CH_4 oxidation rates (V_{max}) under different operating condition in the presence of NMOCs.

Figure 5.4 illustrates the effect of NMOCs on the CH_4 kinetic parameter (V_{max}) and shows that the NMOCs present in different concentrations result in decreased CH_4 maximum oxidation rates. For example, in the experiment using compost with 57% MC at 22°C without any NMOCs, the V_{max} value was 30.2 $\mu gCH_4\ h^{-1}g^{-1}_{wet\ wt}$. This value was reduced to 18.1 $\mu gCH_4\ h^{-1}g^{-1}_{wet\ wt}$ when mixed NMOCs were present in the batch reactors under same environmental conditions. The same trend was monitored in all other experimental runs. The reduction in CH_4 oxidation capacity was assumed to be a result of the presence of NMOCs with different concentrations. Increasing NMOCs concentrations

appeared to cause decreased CH_4 oxidation rates. Very few researches discussed the effects of NMOCs on the biological CH_4 oxidation in the LFC based on batch experiments. These researches were presented by Scheutz et al. (2004a, b), Chiemchaisri et al. (2001) and Kjeldsen et al. (1996); the results of this study were in accordance with their findings. The presence of mixed NMOCs reduced the V_{max} about 25-50%; this can be attributed to a combination of inhibition due to toxicity of the chemical compounds or their transformation products, and the increased competition of CH_4 and organic compounds for the enzyme MMO which stimulates the oxidation. This competition can result in overall decreased transformation rates of CH_4 substrate and enzyme inhibition afterwards. The binding of the NMOCs to the enzyme can stop the CH_4 from entering the enzyme's active site and hinder the enzyme from catalyzing its reaction, which eventually was reflected on the kinetic parameters, as shown in Figure 5.4.

The values of K_m also decreased with the increase of NMOCs concentrations under the same environmental conditions as shown in Figure 5.5. In the experiments conducted using compost with 57% MC at 22°C without any NMOCs, the K_m value was 9524 ppm. This value was reduced to 4968 ppm when mixed NMOCs were present in the batch reactors under same environmental conditions. LaGrega et al. (2001) stated that K_m is an indication of the efficiency with which degradation will occur. Monitoring the change of kinetic parameters (V_{max} and K_m) obtained from batch experiments would assist in identifying the inhibition type that has occurred between the growth substrate and NMOCs.

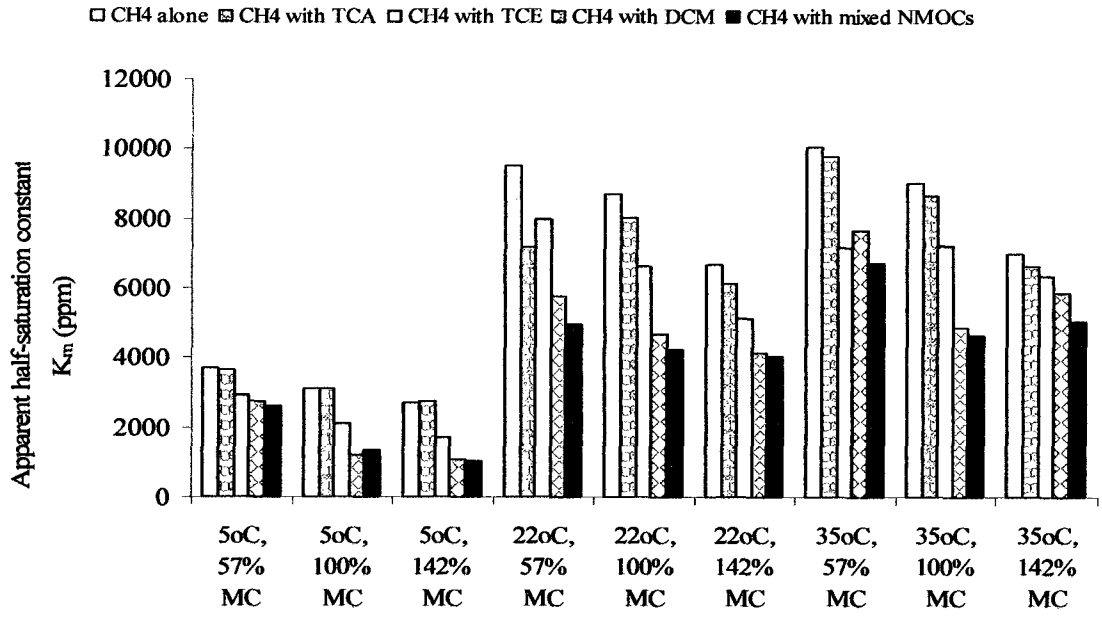


Figure 5.5 Apparent half-saturation constant (K_m) values under different operating condition in the presence of NMOCs.

Detailed results that demonstrate the effect of NMOCs present in different concentrations -along with CH_4- on the bacterial kinetic parameters are presented in Appendix V-3.

5.3.3 KINETICS OF ENZYME INHIBITION

It was confirmed from the results of this study that NMOCs influenced negatively the biological CH_4 capacity in the LFC system due to inhibition effects, and this finding was in agreement with previous studies. The second objective of this study was to identify the enzyme inhibition type caused by concurrent degradation of growth substrate (CH_4) and co-metabolic substances (NMOCs) in LFC experiments. The method for identification of inhibition mechanism was based on the best fit of the experimental data to various models of inhibition described in the introduction section of this study (i.e., competitive, uncompetitive and noncompetitive types of inhibition, in addition to Haldane Inhibition). The kinetic constants were fitted by using nonlinear regression

analysis of the CH_4 oxidation rates in the absence and presence of NMOCs versus the initial headspace CH_4 concentrations. The kinetic experiments conducted and presented in section 5.3.2 were essential and provided information regarding the inhibition mechanism that might have occurred. The data used were the CH_4 oxidation rates versus substrate (CH_4) consumed in the presence CH_4 alone (I=0) and in the presence of CH_4 and each NMOC compound (I= 5.5, 16.35, and 52.8 μg/L respectively) in addition to the mixed compounds (I= 74.7 μg/L) into each model. The output showed that experimental results of CH_4 oxidation rates at various concentration fit well to the uncompetitive model with the biological kinetic parameters shown in Table 5.3.

Table 5.3 Kinetic parameters of CH_4 oxidation in presence of NMOCs with different concentrations at various environmental conditions applying uncompetitive inhibition model.

Temperature (°C)	Compost MC (%w/w)	V_{max} ($\mu gCH_4\ h^{-1}g^{-1}_{wet\ wt.}$)	K_m^* ($\mu gCH_4/L$)	K_i^{**} (μg/L)
5	57	7.5	2,473.3	133.2
5	100	5.4	1,757.9	148.0
5	142	4.4	1,383.2	462.4
22	57	30.0	5,667.5	102.5
22	100	19.8	5,273.5	128.7
22	142	13.3	4,620.4	155.1
35	57	38.6	6,815.1	61.0
35	100	35.4	5,851.7	75.8
35	142	28.9	4,663.2	88.3

* K_m is the CH_4 apparent half saturation constant.
** K_i is the dissociation constant for the enzyme-inhibitor complex.

Table 5.3 demonstrates the kinetic parameters of CH_4 oxidation in presence of mixed NMOCs at different environmental conditions applying uncompetitive inhibition model.

Appendix V-4 shows a sample of the uncompetitive model simulation, compared to the other models presented and discussed in section 5.1. The results illustrate the lack of fit of the other models to the experimental results.

Good agreement was achieved between independently measured values of V_{max} and K_m and presented in Table 5.2, and these obtained from the nonlinear inhibition equation and presented in Table 5.3. The values of the dissociation constant for the enzyme-inhibitor complex (K_i) ranged from 61 to 462 μg/L. The environmental conditions affected the value of K_i. Higher values of K_i were obtained for the experiments conducted at lower temperature level. The dissociation constant values for the enzyme-inhibitor indicate the strength of binding between the enzyme and the chemical compound; the smaller K_i the stronger the binding would be. Therefore, at higher temperature levels the K_i values were smaller, which indicates that at higher temperature levels the binding is stronger between the enzyme MMO and NMOCs. This observation was supported by the inhibition levels observed in the experiments. At the lower temperature (5°C), the V_{max} values obtained from the experiments with mixed NMOCs were around 30% lower than the V_{max} values obtained from the experiments conducted without any NMOCs at the same temperature, while the experiments conducted at 35°C showed higher inhibition levels. The V_{max} values for the experiments conducted with NMOCs at 35°C were around 45% lower than the V_{max} values obtained for the experiments without NMOCs. Additionally, in the case

of uncompetitive inhibition as mentioned in the introduction of this study, the value of K_i is much greater than the total organic compound concentration.

Figure 5.6 shows samples of the surface responses of the uncompetitive model for the same experiment with CH_4 and NMOCs conducted at 5 and 35°C using compost with 142% MC (75% S.L).

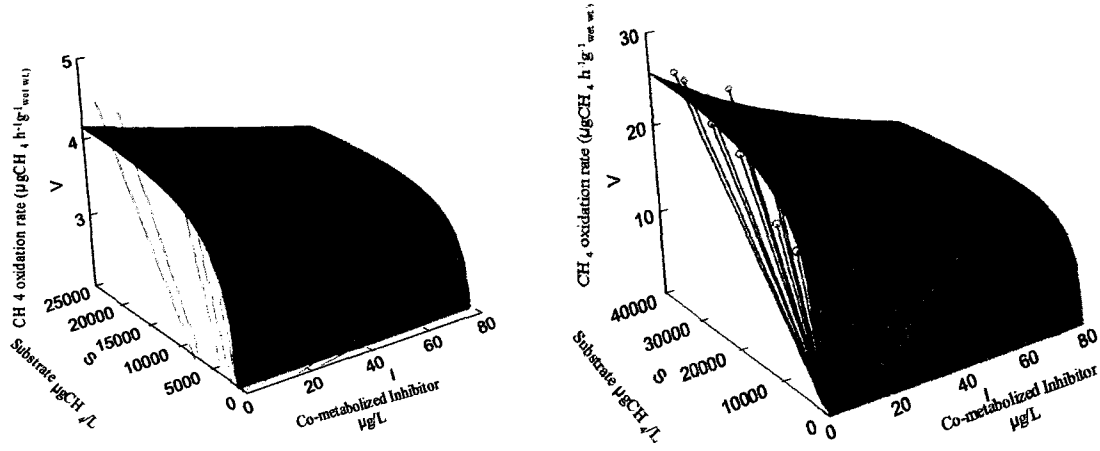


Figure 5.6 Example of Surface responses of the uncompetitive model of CH_4 and NMOCs for the experiment conducted at 5 and 35°C using compost with 142% MC (75%S.L.)

There was good fit between the model predictions and experimental observations for each set and this finding was supportive of the model assumption (R^2 values were in the range of 97 to 99.5% for the experimental runs). Figure 5.7 illustrates comparison between the measured versus simulated CH_4 oxidation rates in presence of (a) mixed NMOCs, I =74.7 μg/L, and (b) TCA – I = 5.5 μg/L.

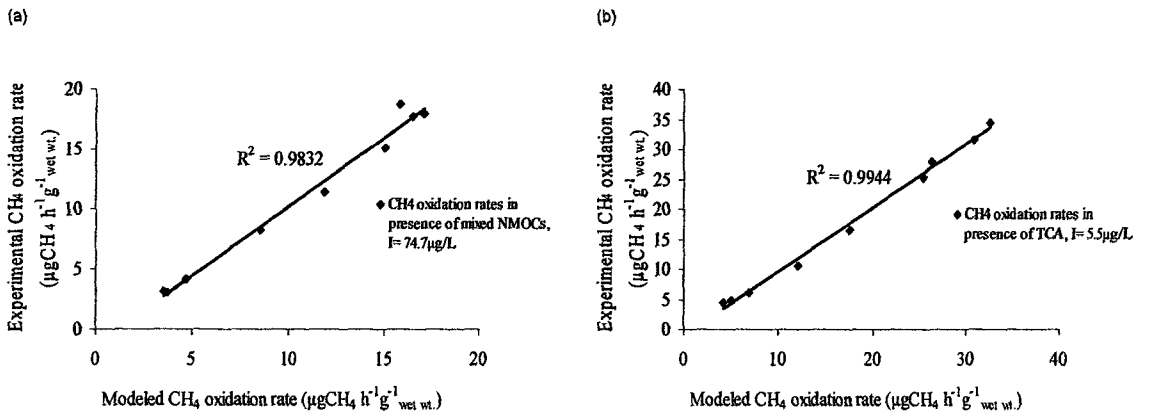


Figure 5.7 Measured and simulated CH_4 oxidation rates in presence of mixed NMOCs.

The results shown in Figure 5.7 suggest that the reduction of CH_4 oxidation rates in bio-cover was the result of uncompetitive inhibition mechanisms. Previous researchers who conducted experiments using methanotrophic pure cultures with small CH_4 concentrations with TCE only have proposed that the competition between the organic compound and CH_4 for the enzyme MMO would cause inhibition. The results of this experiment confirmed that the inhibition mechanism in LFC system would be the uncompetitive inhibition, where the CH_4 concentration is much higher than the concentration of the organic compounds. The uncompetitive inhibition decreases the V_{max} as well as the K_m, which is in agreement with the experimental results of this study.

5.3.4 NMOCs BIODEGRADATION RATES

The third objective of this study was to examine the co-metabolic abilities of methanotrophic bacteria in the LFC system by estimating the degradation rates of the different NMOCs under different temperatures and moisture content levels.

The NMOCs concentrations were described as existing in solid, liquid, and gas phases of the compost; therefore, the total amount of all NMOCs were expressed as a function of the gas concentration using Henry's law, fraction of organic carbon and the organic carbon partition coefficient for each NMOC. The decrease in concentration of each NMOC in the headspace of each batch experiment was observed over time under different environmental conditions. The degradation curves of NMOCs were presented as relative degradation curves, where all concentrations were normalized to the initial concentration. Figure 5.8 illustrates the degradation curves of DCM at different temperature, in addition to the control experiment.

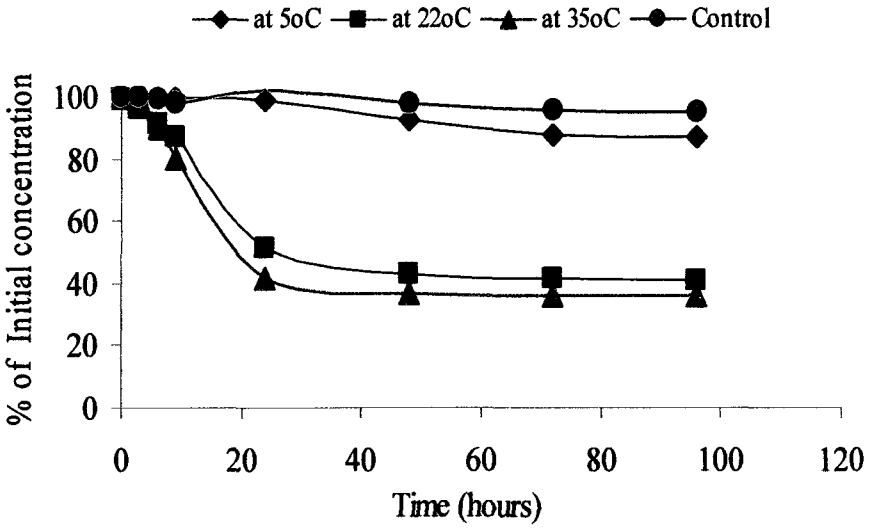


Figure 5.8 Relative DCM concentration in the headspace with time in batch experiments using compost samples with 57% MC at different temperatures, in addition to the control.

Figure 5.8 shows that degradation of DCM was observed at higher temperature levels in the batch experiments. The same trends were observed in the experiments of TCA and TCE. All NMOCs were degraded in the presence of CH_4 and O_2. These observations indicate that NMOCs can be co-oxidized by methanotrophic bacteria; however, the co-

oxidation process is affected by temperature. The effect of low temperature on the co-oxidation process is related to the type of methanotrophic bacteria present at these temperatures. There are two main groups of methanotrophic bacteria, which are designated as Type I and Type II (Borjesson et al. 2004). All methanotrophs are capable of forming a particulate or membrane-bound form of the enzyme (pMMO) when grown in the presence of copper, while Type II synthesize a soluble form (sMMO) under copper limiting growth (Hanson and Hanson 1996). It was reported that sMMO can rapidly co-metabolize a variety of aliphatic compounds, including halogenated hydrocarbons (Scheutz et al. 2004a; Hanson and Hanson 1996). Many researchers reported that only Type I methanotrophic bacteria grow at low temperatures between 3 and 10°C while both types (Type I and Type II) grow at 20°C (Borjesson et al. 2004; Gebert et al. 2003). Alvarez-Cohen and McCarty (1991b) reported that higher TCE oxidation rates can only be obtained when Type II methanotrophs were present under conditions that permitted expression of sMMO; on the other hand, Type I methanotrophs containing pMMO have been reported to oxidize TCE at much slower rate. These specifics explain the experimental observations of this study at 5°C.

The degradation rates of different NMOCs used in this study were calculated over time based on triplicates, and normalized to the wet compost mass. Table 5.4 shows degradation rates for DCM, TCE and TCA at different temperatures using compost samples that contained 57% MC. The data obtained were the results from triplicate batch reactors. Almost the same rates (within 87 to 93% of the values in Table 5.4) were obtained for the experiments conducted using compost samples with 100 and 142% MC.

Table 5.4 Biological co-oxidation rates for NMOCs at different temperatures using compost samples that contained 57% MC.

Temperature	DCM co-oxidation rate ($\mu gDCM\ h^{-1}\ g^{-1}_{wetwt.}$)	TCE co-oxidation rate ($\mu gTCE\ h^{-1}\ g^{-1}_{wetwt.}$)	TCA co-oxidation rate ($\mu g\ h^{-1} g^{-1}_{wetwt.}$)
5°C	6.3×10^{-3}	9.8×10^{-4}	5.1×10^{-4}
22°C	0.035	0.013	0.004
35°C	0.046	0.017	0.005

The co-oxidation rates obtained from this study were in agreement with the rates reported by previous researchers as shown in Table 5.5.

Table 5.5 Biological NMOCs co-oxidation rates reported previously compared to the results obtained in this study.

Researcher	NMOC	Co-oxidation rates reported previously	Co-oxidation rates obtained in this study
Kjeldsen et al. (1997)	TCE	12.5×10^{-4} µg TCE h^{-1} g^{-1}_{drywt} at 10°C using soil samples in batch reactors.	15×10^{-4} µgTCE h^{-1} g^{-1}_{drywt} (9.8×10^{-4} µgTCE h^{-1} g^{-1}_{wetwt}) at 5°C using compost
Scheutz et al. (2007)	TCE	0.017 µgTCE h^{-1} g^{-1}_{drywt} at 22°C using soil samples	0.021 µgTCE h^{-1} $g^{-1}_{drywt.}$ (0.013 µgTCE h^{-1} g^{-1}_{wetwt}) at 22°C using compost
Scheutz et al. (2003)	DCM	0.037 µgDCM h^{-1} g^{-1}_{drywt} at 22°C using soil samples	0.055 µgDCM h^{-1} g^{-1}_{drywt} (0.035 µgDCM h^{-1} g^{-1}_{wetwt}) at 22°C using compost

The results from this study confirmed that the NMOCs can be co-oxidized in LFC system, but with lower rates than the oxidation of the main substrate (CH_4).

The transformation yield was calculated to describe the co-metabolic rates of DCM and TCE; transformation yield is defined as the amount of compound transferred per amount of substrate utilized. The transformation yield at 22 and 35°C for DCM was around 2.6 µgDCM mg^{-1} CH_4, while it was less than 1 µg TCE mg^{-1} CH_4. Alvarez-Cohen and Speitel

(2001) reported that the type of inhibition caused by TCE is competitive inhibition in pure culture; also stated that TCE transformation yield was ranging from 15 to 50 μgTCE mg^{-1} CH_4. The lower transformation yields obtained in this study indicate that not all the methanotrophs present in LFC are capable of co-metabolizing NMOCs and confirm that the type of inhibition in LFC system is not the competitive inhibition.

5.4 SUMMARY

In this study, the kinetics parameters of biological CH_4 oxidation in the presence of NMOCs were obtained and the effects of these chemicals on the oxidation capacity of LFC were estimated. The increase in NMOCs concentrations (single or mixed) resulted in decreased CH_4 oxidation rates. Methanotrophic activities in LFC can be affected by inhibition that may result from the co-metabolic uncompetitive inhibition to CH_4 oxidation. Although many recent studies have expanded knowledge about microbial CH_4 oxidation in the LFC system, and the environmental conditions that can enhance this process. Still, a knowledge gap exists and should be addressed regarding the NMOCs present in LFG and the effect of these compounds on the bacterial enzyme that induce the CH_4 oxidation.

This research confirmed that bio-cover can reduce the CH_4 emissions through the biological oxidation. However, the methanotrophic activities could be affected by the NMOCs presence in LFG. Therefore, the NMOCs concentrations are a significant

parameter to be taken into consideration in designing LFC system to mitigate the harmful emissions from landfill sites.

5.5 REFERENCES

Albanna, M., and Fernandes, L. (2009). "Capacity for Biological Methane Oxidation in Different Types of Soils and Compost." Submitted to Journal of Solid Waste Technology and Management.

Alvarez-Cohen, L., and McCarty, P.L. (1991a), "Effects of Toxicity, Aeration, and Reductant Supply of Trichloroethylene Transformation by Mixed Methanotrophic Cultures," *Applied Environmental Microbiology,* 57, pp. 228-235.

Alvarez-Cohen, L., and McCarty, P.L. (1991b), "Product Toxicity and Cometabolic Competitive Inhibition Modeling of Chloroform and Trichloroethylene Transformation by Methanotrophic Resting Cells," *Applied Environmental Microbiology*, 57, 1031-1037.

Alvarez-Cohen, L. and Speitel Jr. G.E. (2001), "Kinetics of Aerobic Cometabolism of Chlorinated Solvents," Biodegradation, 12: pp. 105–126.

ASTM D2974-87, American Society for Testing and Materials (2000), "Standard Test Method for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils". ASTM International, PA, USA.

ASTM D7348-08, American Society for Testing and Materials (2000), "Standard Test Methods for Loss on Ignition of Solid Combustion Residues". ASTM International, PA, USA.

Barlaz, M.A., Green, R.B., Chanton, J.P., Goldsmith, C.D., and Hater, G.R. (2004), "Evaluation of a Biologically Active Cover for Mitigation of Landfill Gas Emissions," *Environmental Science and Technology*, 38, pp. 4891-4899.

Borjesson, G., Sundh, I., and Svensson, B.H. (2004), "Microbial Oxidation of CH_4 at Different Temperatures in Landfill Cover Soils," *FEMS Microbiology Ecology*, 48, pp. 305-312.

Chiemchaisri, W, Chettiyappan, V. and Shing Wu, J. (2001), "Effects of Trace Volatile Organic Compounds on Methane Oxidation," *Brazilian Archives of Biology and Technology*, 44, 2, pp.135-140.

De Visscher, A. and Schippers, M. (2001), "Short-Term Kinetic Response of Enhanced Methane Oxidation in Landfill Cover Soils to Environmental Factors," *Biological Fertile Soils*, 33, pp. 231-237.

Gebert, J., Groengroeft, A., and Miehlich, G. (2003), "Kinetics of Microbial Landfill Methane Oxidation in Biofilters," *Waste Management*, 23, pp. 609-619.

Hanson, R. and Hanson, T.E. (1996), "Methanotrophic Bacteria," *Microbiological Reviews*, 60, pp. 439- 471.

Intergovernmental Panel on Climate Change, (2001). IPCC Working Group I, The Scientific Basis, http://www.grida.no/climate/ipcc_tar/wg1/248.htm.

Jeremy, B. M., Tymoczko, J.L. and Stryer, L. (2007), Biochemistry. 6th edition. W. H. Freeman and Company, New York, USA.

Krogsgaard-Larsen, P., and Liljefors, T., (2002), "Textbook of Drug Design and Discovery," CRC Press, Boca Raton, Florida.

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.

LaGrega, M., Buckingham, P., and Evans, J., (2001), "Hazardous Waste Management," McGraw-Hill Higher Education, Boston, USA.

Leskovac, V. (2003), "Comprehensive Enzyme Kinetics," Kulwer Academic/Plenum Publisher, New York.

Lontoh, S., and Semrau, J. (1998), "Methane and Trichloroethylene Degradation by Methylosinus trichosporium OB3b Expressing Particulate Methane Monooxygenase," *Applied and Environmental Microbiology*, 64(3), pp. 1106-1114.

McFarland, M.J. , Vogel C.M., and Spain J.C (1992), " Methanotrophic Cometabolism of Trichloroethylene (TCE) in a Two Stage Bioreactor System," *Water Resource,* 26, pp. 259-265.

Mor, S., De Visscher, A., Ravindra, K., Dahiya, R.P., Chandra, A., and Van Cleemput, O. (2006),"Induction of Enhanced Methane Oxidation in Compost: Temperature and Moisture Response," *Waste Management,* 26(2006), pp. 381-388.

Oldenhuis, R., Oedzes, J.Y., Van Der Waarde, J.J., and Janssen, D.B. (1991), "Kinetics of Chlorinated Hydrocarbon Degradation by Methylosinus Trichosporium OB3b and Toxicity of Trichloroethylene", *Applied and Environmental Microbiology,* 57(1), pp. 7-14.

Scheutz, C., Bogner, J., Chanton, J., Blake, D., Morcet, M., and Kjeldsen, P. (2003),"Comparative Oxidation and Net Emissions of Methane and Selected Non-Methane Organic Compounds in Landfill Cover soils," *Environmental Science and Technology.,* 37, pp. 5150-5158.

Scheutz, C., Mosbaek, H., and Kjeldsen, P. (2004a),"Attenuation of Methane and Volatile Organic Compounds in Landfill Soil Covers," *Environmental Quality,* 33, pp. 61-71.

Scheutz, C., and Kjeldsen, P. (2004b),"Environmental Factors Influencing Attenuation of Methane and Hydrochloroflorocarbons in Landfill Cover Soils," *Environmental Quality*, 33, pp. 72-79.

Scheutz, C., Bogner, J., Chanton, J., Blake, D., Morcet, M., Aran, C., and Kjeldsen, P. (2007),"Atmospheric Emissions and Attenuation of Non-Methane Organic Compounds in Cover Soils at a French Landfill," *Waste Management,* 28, pp. 1892-1908.

Silverman, R. (2000), "The Organic Chemistry of Enzyme Catalyzed Reactions," Academic Press, London, UK.

SYSTAT 11, (2004). Systat Software Inc., Chicago, USA.

Tsien, H.C, Brusseau, G., Hanson, R., and Wackett, L.P. (1989),"Biodegradation of Trichloroethylene by Methylosinus trichosprium OB3b," *Applied and Environmental Microbiology,* 55(12), pp. 3155-3161.

USEPA (1999), Municipal Solid Waste Landfills, Volume I: Summary of the Requirements for the New Performance Standards and Emissions Guidelines for Municipal Solid Waste Landfills. 453/R-96-004. Research Triangle Park, NC. USA.

USEPA (2006), State of Knowledge, October, 2006, http://www.epa.gov/climatechange/science/stateofknowledge.html.

Watts, R.J. (1997), "Hazardous Wastes: Sources, Pathways and Receptors", John Wily and Sons Inc., New York, USA.

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.

CHAPTER 6

LONG-TERM BEHAVIOR OF BACTERIAL METHANE AND NMOCs OXIDATION IN LANDFILL BIO-COVERS: COLUMN STUDY

Muna Albanna, Mostafa Warith and Leta Fernandes

ABSTRACT

The potential of CH_4 oxidation and NMOCs co-oxidation by methanotrophic bacteria was studied in compost columns that simulate landfill bio-cover environments. Methane uptake was monitored with time in two phases: phase 1 where CH_4 was fed into the compost matrix and phase 2 where a blend of CH_4 and NMOCs was introduced into the cell matrix. The biological CH_4 oxidation rates in phase 1 ranged between 124 and 175 $gCH_4\ m^{-2}\ d^{-1}$. While in phase 2, the oxidation rate dropped to a range of 90 to 120 $gCH_4\ m^{-2}\ d^{-1}$ due to the presence of NMOCs. The methanotrophic bacteria were able to bio-degrade the chemical compounds in parallel with CH_4, and they were very active in oxidizing methane and the selected NMOCs in the zone between 50 to 150 mm from the surface of the compost column.

6.1 INTRODUCTION

The solid waste sector is responsible for 13% of global anthropogenic methane (CH_4) gas emissions (USEPA 2006). Methane is an important greenhouse gas (GHG), whose atmospheric life time is 9-15 years; this means that its global warming potential is higher for shorter time horizons (IPCC 2001). Landfill gas (LFG) generated from organic waste anaerobic decomposition inside landfills is composed of primarily 50-65% CH_4, 35-50% carbon dioxide (CO_2), and trace constituents of non-methane organic compounds (NMOCs) (USEPA 2006). The vast majority of existing landfill sites around the world does not have biogas capturing setups. Methane emissions from these sites are entirely released to the environment, in addition to millions of tonnes of volatile organic compounds. The net GHGs emissions from Canadian landfills in 2002 were estimated to be 22 million metric tonnes (Mt) of carbon dioxide equivalent (eCO_2) but only 6.6 Mt eCO_2 were captured (Environment Canada 2005).

Landfill cover soils are critical for attenuating fluxes of CH_4 from landfill sites to the atmosphere. Oxidation of CH_4 by methanotrophic bacteria can be an efficient and practical technology to control the emissions from the surfaces of the landfills across daily, intermediate and final covers. Methanotrophs are capable of efficiently converting CH_4 to CO_2 and biomass by means of CH_4 oxidation. This simple and efficient technology could take the form of soil medium supporting methanotrophic bacteria or bio-covers.

Landfill cover can be designed to promote optimum growth of methanotrophic bacteria and thus enhance the biological oxidation. Based on the results of Albanna and Fernandes

(2009a), and supported by other researchers (Jugnia et al. 2008; Wilshusen et al. 2004b; Barlaz et al. 2004; Hilger and Humer 2003) it appears that compost can maintain higher CH_4 oxidation rates than conventional soil and therefore offers an effective medium for landfill cover (LFC). Compost provides mixture of porosity, water holding capacity, pH and nutrients supply, and therefore it can support good microbial growth which will be reflected on the CH_4 oxidation capacity of the cover.

To explore the effects of environmental conditions on the biological process, some researches have based their findings on laboratory batch reactor experiments. However, short-term incubation studies may not be representative of long-term performance, since the cover profile is significant when studying the CH_4 oxidation in LFC system. Therefore, some researchers presented long-term CH_4 oxidation experiments using laboratory LFC soil columns (De Visscher et al. 1999; Kightley et al. 1995, Hilger et al. 2000); others conducted laboratory bio-filters column experiments (Kettunen et al 2006; Wilshusen et al. 2004b), while Einola et al. (2008) presented laboratory column experiments using mechanically-biologically treated municipal solid waste as a support LFC medium. However, all of these studies were based on feeding only CH_4 into the columns. Though NMOCs are part of the landfill gas, none of the researches included these compounds in their studies. It was confirmed, from the experiments conducted using batch reactors, that the NMOCs present with CH_4 affect negatively the biological oxidation capacity in LFC system (Albanna et al. 2009b; Scheutz et al. 2004; Chiemchaisri et al. 2001). A recent scanning of literature revealed that there are no attempts made so far to study the CH_4 and NMOCs oxidation in laboratory controlled column experiments. To realistically simulate the biological oxidation in the LFC,

NMOCs present in the LFG cannot be ignored. Moreover, the NMOCs can be co-metabolized by methanotrophic bacteria in the presence of CH_4; this will add to the value of the LFC system which provides a sink for the GHGs harmful fugitive emissions. To this end, long-term laboratory experiments were carried out in this research to investigate the methanotrophic oxidation performance in CH_4 and NMOCs-fed columns using compost as LFC medium with different saturation levels. This research presents results from a comparative study of CH_4 oxidation performance of two phases: phase I where CH_4 was migrated through the compost columns until the oxidation process reached the steady state then, phase II, where the CH_4 was replaced by the blend of CH_4 and NMOCs. This experimental strategy was adopted to make sure that the methanotrophic bacteria were well established in the simulated LFC, also to minimize the risk that NMOCs might cause any inhibition or toxicity for the CH_4 oxidizers at the beginning of the experiments.

6.2 MATERIALS AND METHODS

6.2.1 EXPERIMENTAL DESIGN

Long-term column experiments were conducted by feeding fluxes of CH_4 and selected NMOCs through the bottom of the columns. A 1-D column experiments, using compost with three levels of saturation limits (S.L.) of 30, 50 and 75% at 22°C, were conducted in duplicate and in the two phases. The first phase was accomplished in 50 days by feeding CH_4 only into the compost matrix until CH_4 oxidation steady state is reached, and then

CH_4 was replaced by a blend of CH_4 and selected NMOCs in the second phase and kept running for another 50 days. Figure 6.1 illustrates the experimental setups and phases.

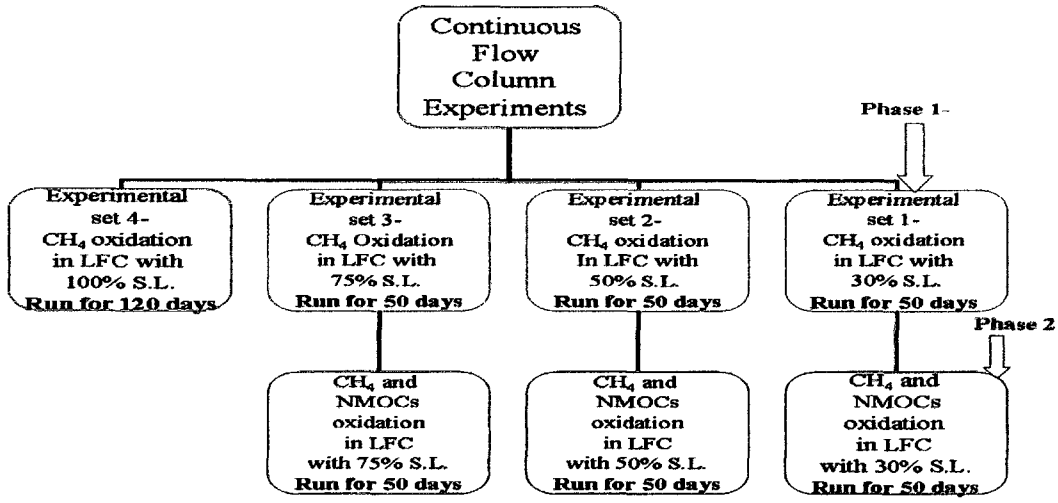


Figure 6.1 Experimental setups and phases.

As shown in Figure 6.1, experimental setups 1, 2, and 3 had two phases: phase 1 was based on feeding only CH_4 into the compost matrix. This phase was terminated after 50 days when the compost's CH_4 oxidation rates reached the steady state level, then the reactors were opened and samples were collected from several depths and tested for moisture content, organic matter content and pH. The second phase was initiated immediately by replacing CH_4 with the blend of CH_4 and NMOCs. The same laboratory experiments were conducted for another 50 days, where CH_4 oxidation's steady state level, were reached in phase 2.

The selected NMOCs in this study were a mix of: trichloroethane (TCA); trichloroethylene (TCE); and dichloromethane (DCM), because these compounds were recognized in LFG in most sites. Also, they have harmful effects on human health as their emission factor rating is either "A or B" based on a USEPA (1999) report, which means

that these selected compounds are classified as "proven or probable human carcinogen" (Watts 1997). The initial concentrations used were based on the default concentrations reported by USEPA (1999) as follows: DCM = 14.3 ppmv, TCE = 3 ppmv, and TCA = 1 ppmv.

Experimental set No. 4 was based on feeding only CH_4 into the compost matrix. This experimental set kept running for 120 days, and was designed to report on longer-term CH_4 oxidation performance in landfill bio-covers, and on the duration that the high oxidation rates can be maintained in the system.

Inflow and outflow concentrations were measured to obtain changes in the masses of CH_4 and NMOCs entering and leaving the columns in each phase. Gas tight sampling ports along the vertical axis of the columns were used to collect samples to measure the CH_4 and NMOCs concentrations along the profile. The study consisted of four experimental sets in duplicates and was conducted at 22°C in addition to control and blank.

6.2.2 EXPERIMENTAL MATERIALS

Compost samples were collected from Trail Road composting facility in Ottawa. The compost to be used as LFC medium had to be biochemically stable so that the respiration by other microorganism does not divert oxygen (O_2) from the methanotrophs; therefore, the compost's stability was a significant issue to check before using the compost samples. The respiration rate was tested in both batch and column reactors. Compost samples were incubated with air in batch reactors for 54 hours and the O_2 consumption rate was on average 0.45 μmol O_2 h^{-1} $g^{-1}_{wet\ wt}$, while CO_2 evolution rate of 0.33 μmol CO_2 h^{-1} $g^{-1}_{wet\ wt}$

on average. The stability of the compost was also checked by running a separate laboratory scale column that contained compacted compost samples. The column had an inlet port where air was fed continuously through the bottom, and an outlet port for sampling. The O_2 and CO_2 concentrations in the column headspace were measured continuously to calculate the O_2 consumption and CO_2 production rates due to respiration. The column was kept running for 30 days. The respiration rate was taken into consideration when calculating the mass balances in the reactors afterwards.

The compost's initial moisture content was 107% (%w/w) and was determined gravimetrically by oven-drying samples at 105°C for 24 hours and expressed as the mass ratio of water to dry compost following the ASTM D2974-87 procedure. Initial organic matter content was 31% and was determined by loss on ignition following the D7348-08 procedure. The compost's initial bulk density was 890 kg/m^3 and was determined by weighing compost-filled cylinders, subtracting the cylinder weight, and dividing by the cylinder volume. Compost's pH was 7.1; the compost pH was determined in 1:2.5 compost-water mixture using a digital pH meter (530 pH meter by Corning Pinnacle). The percentages of nitrogen and carbon were estimated using a Thermo-Finnigan Flash 1112 elemental analyzer. The percentage of initial nitrogen (%N) and carbon (%C) were 1.24 and 14.81, respectively.

In the first phase of the experiments, CH_4 gas cylinders (99% purity) were obtained from the BOC Gases Company. In the second phase, the blend of CH_4 and chosen NMOCs were prepared and delivered by Praxair Distribution Inc. according to order number 06985054-00, where the certificate of analysis showed that the blend certified

concentration was 1,1,2-trichloroethane = 0.997 ppm, dichloromethane = 14.6 ppm, trichloroethylene = 3.0 ppm, and methane is the balance. The air source used was the continuous in-house air setup.

6.2.3 EXPERIMENTAL METHODS

Figure 6.2 is a schematic diagram of the bio-cover column set-up used for this research.

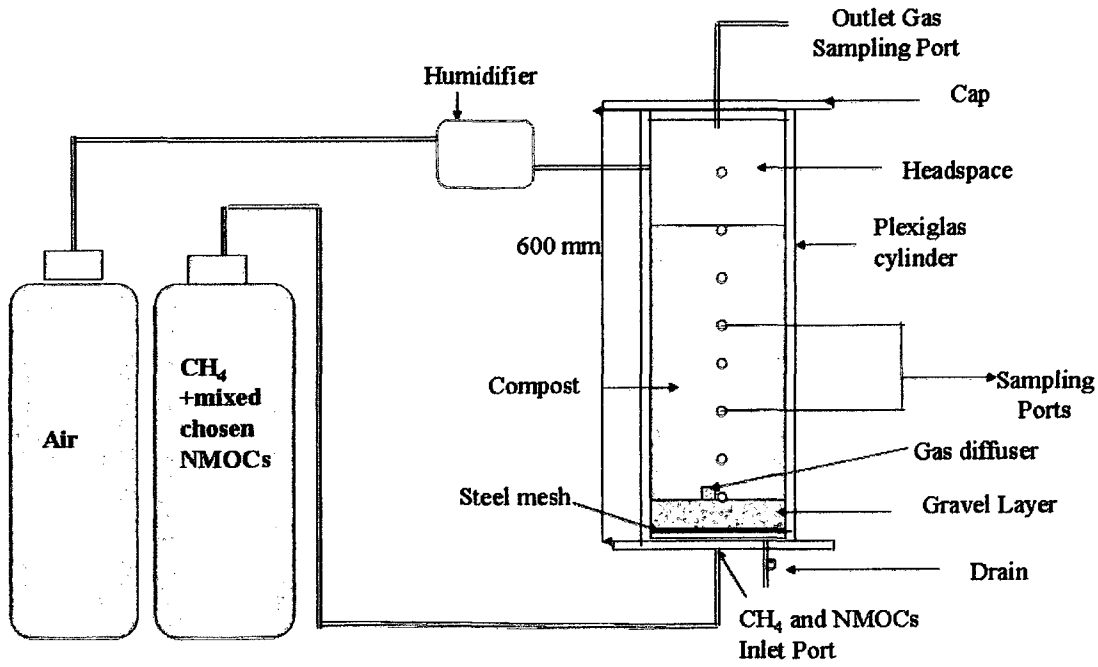


Figure 6.2 Schematic of compost column set-up.

Each column consisted of a gas tight cylinder reactor made of Plexiglas tubing 150 mm in diameter, 600 mm long and 6 mm thickness. The compost medium was compacted and supported by a 50 mm layer of sterile autoclaved gravel to distribute the gas from the inlet into the compost matrix. The gas inlet was connected to gas diffuser type Hagen A-983. The compost layers were 300 mm maximum. The columns were built up with an inlet port for CH_4 and NMOCs at the bottom, an inlet port for the air at the top, and an

outlet port at the top to vent the gas mix to obtain soil gas profiles over the column. Inlet CH_4 gas concentrations were controlled with flow controllers. Pure CH_4 gas (>=99% purity) was fed through the bottom of the columns in the first phase, and a blend of CH_4 and selected NMOCs in the second phase. The flow rate of CH_4 fluxes was 5.0 mL/min, which corresponds to a CH_4 flux of 310 g CH_4 m^{-2} d^{-1} and is similar to the fluxes observed in municipal solid waste landfills (Kightley et al. 1995). Air was passing through a humidifier and then passed across the top of the column at a nominal rate of 85 mL/min. This permitted measurement of CH_4 flux from the compost surface and maintained almost natural O_2 concentration at the top of the compost. The changes in the mass rate of CH_4 and NMOCs entering and leaving the reactor were quantified by measuring the inlet and exit gas concentrations.

The columns were threaded and fitted with 15.0 mm Parker thread fittings, and 17.5 mm type P4MC4 connectors for gas sampling. The sampling ports were located at 50 mm intervals. Sampling ports were fitted with 17.0 mm Tegrabond Disc Teflon-Silicon Septa. A drain with a valve was located at the bottom of each column to collect any possible leachate for testing.

Both ends of the column were closed with Plexiglas end caps that are fitted with rubber O-rings. The bottom and top end caps will be 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.

Methane inflow concentrations were measured using Lab-Crest Century-Mark II flow meters. The CH_4 flow rate was controlled using Swagelok metering valves type L-31

series with vernier handles. Air inflow and gas outflow concentrations were measured daily using Alltech air flow meter 12-192762-01. The inlet CH_4 and O_2 flow rates and the outlet gas flow rates were measured daily to calculate the consumption (CH_4 and O_2) or production (CO_2) of gases by subtracting the influent and effluent flow rates of each gas. The CH_4 flux from the surface of each compost column was calculated by measuring the CH_4 concentration and flow rates of the effluent air stream exiting each column. The difference between the CH_4 fed to the base of the column and the CH_4 flux from the surface of the column was then calculated. The difference was attributed to CH_4 oxidation within the compost. The mass balance for the system was calculated accordingly in each column. The gas composition (CH_4, O_2 and CO_2) with depth was measured weekly by taking samples from the different elevation ports. Between sampling, the columns were kept covered to reduce light exposure and minimize the growth of other microorganisms that can compete with the methanotrophs and consequently increase the respiration rate in the compost.

For each experimental set, there were control and blank reactors. The abiotic controls were autoclaved and then a sufficient amount of sodium azide (25mg per kg of wet compost according to Scheutz et al. (2004) and Kjeldsen et al. (1997)) was added to inactivate the microorganisms. The controls ran at different treatments levels to determine if biological activity is the main process responsible for CH_4 and NMOCs reduction. The blanks did not contain any soil or compost, only gases were injected according to the experimental design, to account for losses due to leaks.

Before filling the columns, the moisture content of the compost was adjusted according to the designed saturation level in each column and then the samples were placed in the columns and compacted. Moisture content was increased by adding sterilized water, and decreased by air drying the water content to the desired level. Bulk density and specific gravity were measured, and void ratio and saturation level were calculated accordingly. Void ratio was calculated based on bulk density, specific gravity and moisture content. Saturation level was calculated based on the voids ratio, specific gravity and moisture content (Holtz and Kovacs 1981).

6.2.4 ANALYTICAL PROCEDURE AND INSTRUMENTS

Samples were analyzed for CO_2, O_2, CH_4 and N_2 concentrations, as well as the NMOCs concentrations. Column gas profiles were established by analyzing the samples at different depths for determining changes in CH_4 and NMOCs concentrations in order to be able to measure the gases concentrations decrease with depth. The gas composition (CH_4, O_2 and CO_2) with depth was measured weekly by taking samples from the different elevation ports.

The gas samples from columns sampling ports were analyzed for CH_4, CO_2 and N_2 by withdrawing 200 μL samples from the ports using a gas tight syringe and injected manually into the inlet of a 400 Gow-Mac Thermal Conductivity Gas Chromatograph. The carrier gas was helium, and the detector, injection port and column temperatures were 130, 130 and 120°C, respectively.

The gas samples were also analyzed for NMOCs concentrations by withdrawing 5 μL samples from the ports using gas tight syringes and injecting the samples manually into a Hewlett Packard 5890 gas chromatograph equipped with electron-capture detector (ECD). The carrier gases were helium and nitrogen, and the detector and injection port temperatures were 300 and 200, respectively. The column type is capillary column. The selected NMOCs were analyzed with an isothermal column temperature of 40°C for 3 minutes and then increased at a rate of 30°C/min to a temperature of 70°C for 2 minutes and finally increased at a rate of 40°C/min to 110°C for 3 minutes. All concentration peaks were quantified using LabView integration software on the laboratory computer. To measure the concentrations of the proposed compounds using ECD gas chromatograph, calibration curves were established based on peaks height for each compound by a minimum of ten concentration levels. Calibration standards were established by injecting a specific amount of an NMOC into a 5 L gas sampling bag after filling the bag with air.

Samples were also analyzed for changes in CH_4 and NMOCs concentrations at different depth, as dictated by the location of the sampling ports. These concentrations were used to establish column gas concentration profiles.

6.3 RESULTS AND DISCUSSION

6.3.1 CH_4 OXIDATION RATES: PHASE 1 RESULTS

The ability of the compost to promote CH_4 oxidation in the LFC was assessed by determining CH_4 oxidation rate and the changes in depth distribution. The oxidation rates were calculated by measuring CH_4 concentration and flow rates of the effluent air stream exiting each column. Then the difference between the mass of CH_4 fed to the column base and the mass of CH_4 flux from the surface of the column was calculated. The difference in CH_4 mass with time was normalized to the surface area of the soil in the column, and was attributed to CH_4 oxidation within the compost layer. The CH_4 oxidation rates of three compost columns with different saturation levels over 50 days are illustrated in Figure 6.3.

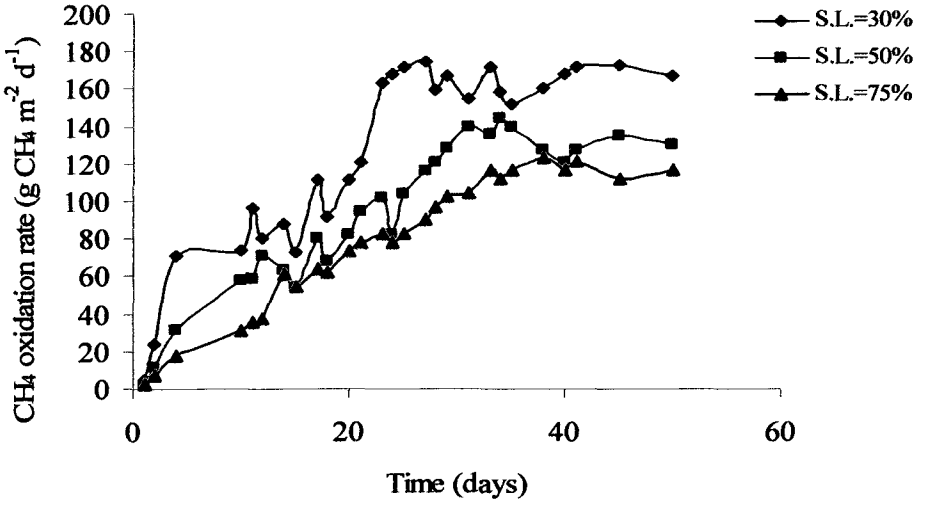


Figure 6.3 CH_4 oxidation rates versus time in compost columns at 22°C.

All columns demonstrated similar trends as shown in Figure 6.3. In the three experimental sets, CH_4 flux from the surface of the compost decreased with time,

indicating the growth of methanotrophic bacteria capable of oxidizing CH_4. Each data point is an average of the duplicates readings. It was observed that CH_4 concentration started to decrease and CO_2 concentration began to increase during rapid acclimation period within 10 to 20 days. After the acclimation phase, CH_4 oxidation rates started to increase gradually until the oxidation reached the steady state phase. According to the experimental strategy, this high-rate of CH_4 oxidation or steady state phase was targeted; reaching the high-rate steady state phase meant that there were well established methanotrophic communities in the compost matrix in each experimental set. A similar pattern has been observed in compost microcosm simulation performed by Kettunen et al. (2006) and Wilshusen et al. (2004b). Experimental set 1 which contained compost with 30% S.L. showed the highest CH_4 oxidation efficiencies and rates. The highest CH_4 oxidation rates observed in experimental set 1 was 175.5 $gCH_4\ m^{-2}\ d^{-1}$ in day 27. The highest oxidation rate monitored in experimental set 2 that contained compost with 50% S.L. was 145.3 $gCH_4\ m^{-2}\ d^{-1}$ in day 34, while the highest oxidation rate observed in experimental set 3 with compost that had 75% S.L. was 123.6 $gCH_4\ m^{-2}\ d^{-1}$ in day 38. The differences in the maximum oxidation rates can be attributed to the increased saturation levels which affect the CH_4 and O_2 movements through the pores. Under higher moisture conditions, CH_4 must reach the methanotrophs by aqueous diffusion, which is much slower than gas diffusion; the diffusion coefficient of CH_4 in water ($1.49 \times 10^{-9}\ m^2\ s^{-1}$ at 22°C) is four orders of magnitude lower than in air ($2.12 \times 10^{-5}\ m^2\ s^{-1}$ at 22°C). It is also the same for O_2 diffusion; the diffusion coefficient of O_2 in water ($1.97 \times 10^{-9}\ m^2\ s^{-1}$ at 22°C) is four orders of magnitude lower than in air ($2.19 \times 10^{-5}\ m^2\ s^{-1}$ at 22°C) (Welty et al. 1984). Still, the proper moisture levels are essential for the bacteria;

very low moisture levels can drastically affect the oxidation activities, Czepiel et al. (1996) observed a major decrease in LFC soil oxidizing capacity at lower moisture content (5% by weight in soil), and concluded that the methanotrophic activities are limited at this low moisture level.

The O_2 consumption and the CO_2 production in the three experimental sets followed same trends as CH_4 consumption. Figure 6.4(a) demonstrates O_2 consumption rates, and Figure 6.4 (b) illustrates CO_2 production rates versus time in the three experimental sets.

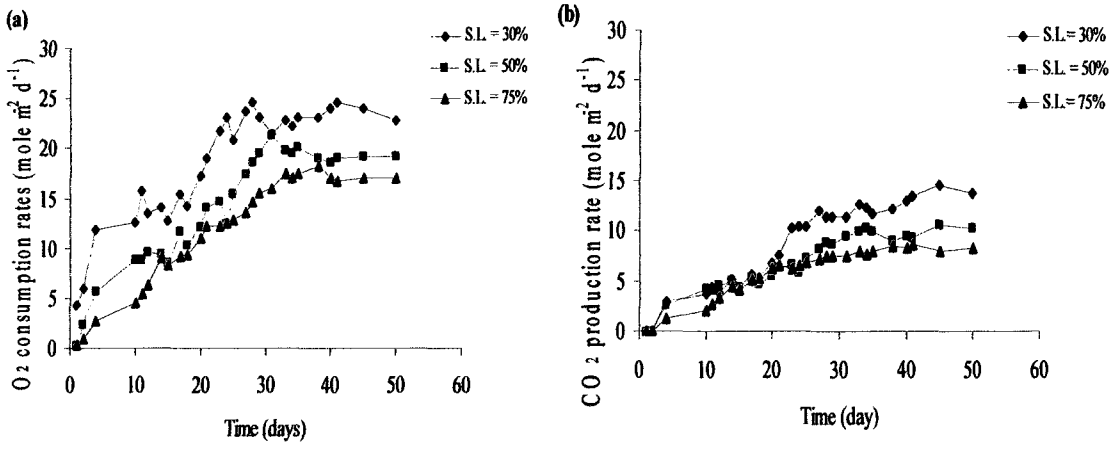


Figure 6.4 (a) O_2 consumption rates, (b) CO_2 production rates versus time in the three experimental sets.

As shown in Figure 6.4, the highest O_2 consumption rate observed was 24.7 mole O_2 m^{-2} d^{-1} and the highest CO_2 production rate monitored was 14.6 mole CO_2 m^{-2} d^{-1}. In all the experimental sets, the highest molar ratio of O_2 consumed to CH_4 consumed was 2.2±0.29 in proportion to CH_4 consumption. The highest molar ratio of CO_2 produced to CH_4 consumed was 1.3±0.14. The results are in agreement with the equation presented by Borjesson et al. (1998) that describe the biological oxidation process, and as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \qquad \Delta G^o = -780 \text{ kJ/mol}CH_4 \qquad [6.1]$$

Kettunen et al. (2006) reported that in optimal conditions, the theoretical molar ratio for methanotrophic process in the LFC system are O_2:CH_4 = 2.0, CO_2:CH_4 = 1.0 and CO_2:O_2 = 0.5. The results obtained from the experimental studies in this research are in agreement when taking into consideration the respiration rate of the compost.

In the control and blank reactors, no reactions occurred in both columns experiments. These experiments allowed a check of CH_4 balance; the mass balance was 95-97%, so the losses were negligible. Moreover, there was no leachate coming out from any columns during the experiments; compost's water holding capacity is one of the advantages of this medium as LFC that can maintain suitable condition for the bacterial growth and activities.

Methane, O_2 and CO_2 in compost's pore gas were measured at different depths in all the experimental runs to assess the movement and exchange of gases in columns vertical profiles. Figure 6.5 depicts gas concentration profiles for the experimental sets 1 and 2 on day 45.

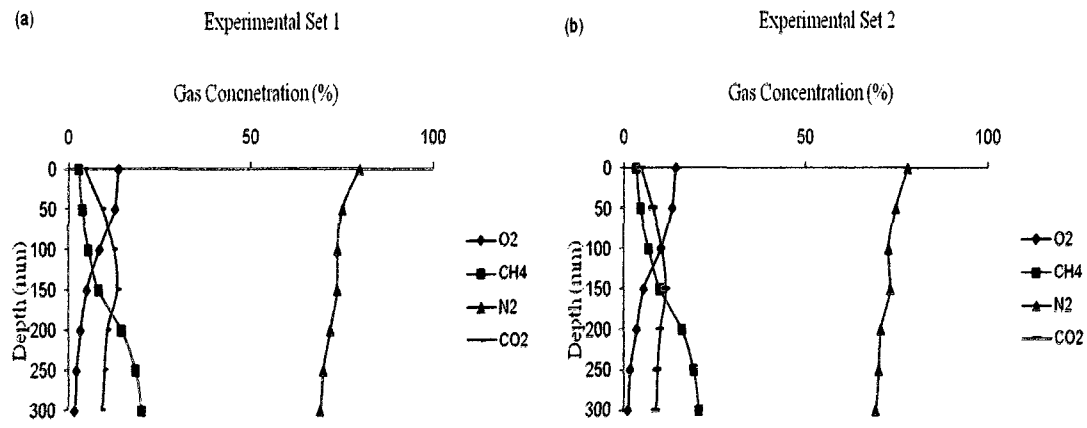


Figure 6.5 Gas concentration profiles as a function in compost columns (a) with 30% S.L. (b) with 50% S.L.

Figure 6.5 shows the profile of the gas concentrations in the compost with different saturation levels on day 45. Each data point is an average of the duplicates readings; results from duplicate columns were almost identical in all the experimental runs. In the three active experimental runs, CH_4 and CO_2 concentrations decreased and O_2 concentration increased from bottom to top. The O_2 concentrations in all the columns were much higher in the top 100 mm when compared to the rest of the column, and were always around or below 3% at depths of 200-300 mm. Methane and O_2 concentrations decreased in the top 50 -150 mm of the simulated LFC as CO_2 concentration increased. These results indicate that the active oxidation zones were observed around the 50-150 mm depth in all the experimental runs, and were in agreement with the observations reported by Kettunen et al. (2006), and Wilshsen et al. (2003a), and De Visscher et al. (1999). In comparing the concentrations profiles between the columns with different saturation levels, the compost with 30% S.L. showed lower concentrations of O_2 and CH_4 in the active zones as well as higher CO_2 evolution than the experimental run with 50% S.L. as shown in Figure 6.5. This observation indicates that the oxidation rate was higher in the compost with lower saturation levels. The O_2 concentrations were less than 3% at 200 mm in depth onward; this concentration is critical for the oxidation process where proper O_2 concentrations are essential for CH_4 to be microbially oxidized.

The oxidation steady state was reached within 27 to 40 days for all the experimental runs and maintained. Afterwards, phase 1 of the experiment was terminated in day 50 and the columns were opened. Samples of the compost were taken at 50 mm intervals to determine the kinetic parameters, changes in moisture content, organic matter content and pH. The tested moisture levels at the end of phase I were around 1% lower than the initial

levels in the beginning of the experiments at the top 50 mm; this is because water evaporated at the surface due to incomplete saturation of the air passing over the compost, despite having the humidifier as part of the experimental setup. However, the moisture levels was 3-5% higher than the initial moisture in the beginning of the experiments from depth 50 mm onward; this is attributed to the CH_4 oxidation below the surface which led to water production as part of the oxidation process. At the top 200 mm, the compost pH was not markedly different from initial compost pH. The organic matter content values were not substantially different from the initial value; this suggests that the growth of the biomass was balanced by degradation of organic matter. The compost in the columns settled from 3-5 cm in all the columns compared to the original compost layer measured at the beginning of the experiments.

To quantify the kinetic parameters for CH_4 oxidation, compost samples were collected from different depths (50, 100, 150 and 200 mm) and subjected to batch incubation experiments. Batch incubation experiments were performed in duplicates using 30 g of compost in 160 mL air tight glass bottles at 22°C. A headspace CH_4 concentration of approximately 10% was achieved by injecting 15 mL of CH_4 into the bottles. Batch headspace was sampled not less than 5 times during the experiment by removing 200 µL of gas, and CH_4 concentrations were quantified using the Gow-Mac gas chromatograph. The resulting data were used to plot substrate saturation curves, and nonlinear regression software was used to derive the kinetic parameter V_{max}. The kinetic parameters followed typical Michaelis-Menton characteristics. The highest values of maximum oxidation rate (V_{max}) were obtained in compost samples collected from 50-150 mm in depth, and for all experimental runs as shown in Figure 6.6.

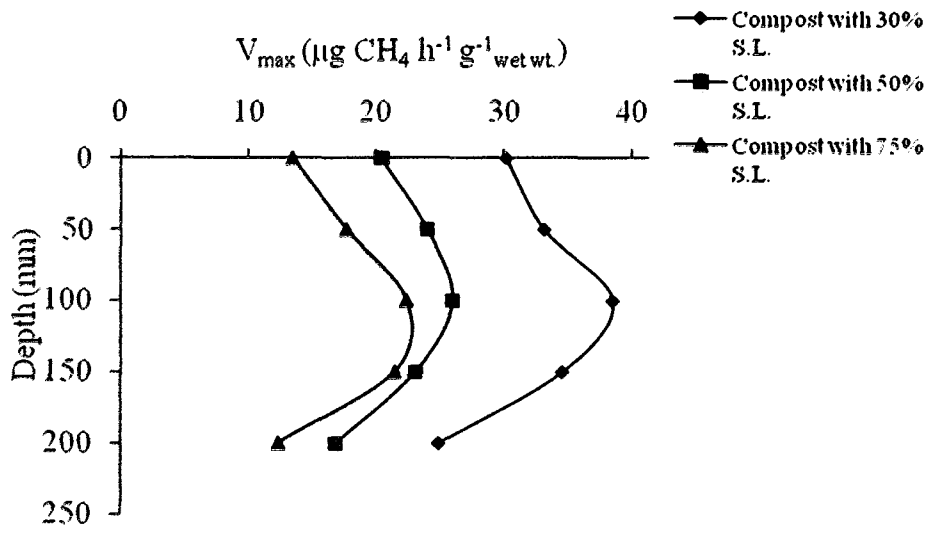


Figure 6.6 Values of V_{max} at the end of phase 1 for experimental runs 1, 2 and 3.

As shown in Figure 6.6, the highest values of (V_{max}) were obtained in samples collected at 100 mm depth, where CH_4 and O_2 concentrations overlapped together. The values of V_{max} at 200 mm in depth were lower than V_{max} values in the active zone between 50- 150 mm; which can be related to the lower O_2 concentration at 200 mm depth. Also, V_{max} values were higher using the compost with 30% S.L. due to the fact that the diffusion coefficients of CH_4 and O_2 in air are higher than the diffusion coefficients in water. This was also reflected on the V_{max} values between compost with 50 and 75% S.L. In general, V_{max} values ranged between 13 – 39 µgCH_4 $h^{-1}g^{-1}_{wet\ wt.}$ (31 – 62 µgCH_4 $h^{-1}g^{-1}_{dry\ wt.}$). The values of V_{max} in this study were within the range reported by Mor et al. (2006) who conducted batch experiments using compost and stated that the V_{max} values were in the range of 46 to 102 µg CH_4 h^{-1} $g^{-1}_{dry\ wt.}$ Gebert et al. (2003) tested the CH_4 oxidizing biolfilter system and reported that the CH_4 V_{max} was 28.5 µgCH_4 $h^{-1}g^{-1}_{wet\ wt.}$. De Visscher et al. (1999) conducted column experiments using LFC soil and reported values in the range of 2.9 to 25.9 µg CH_4 $h^{-1}g^{-1}_{drywt.}$

The column experiments provided the opportunity to evaluate whether the use of batch experiments for estimating CH_4 oxidation rates in the field is valid procedure. It was assumed that the oxidation rates of the compost on site would be equal to the rates determined from a batch incubation experiments on a disturbed compost sample. However, because batch experiments were conducted at different O_2 concentrations, and atmospheric pressure, there were differences between the highest CH_4 oxidation rates observed throughout the columns and the rates obtained from batch experiments in the range of (14 to 19%). Therefore, the oxidation rates from the batch experiments should be adjusted accordingly. It is suggested that the effect of sub-saturating O_2 concentrations on CH_4 oxidation can be explicitly accounted for with a modified Michaelis-Menton, which is:

$$V_{CH4} = V_{\max}\left(\frac{C_{CH4}}{K_{CH4}+C_{CH4}}\right)\left(\frac{C_{O2}}{K_{O2}+C_{O2}}\right) \qquad [6.2]$$

In general, the estimate of the total CH_4 uptake based on batch experiments are reasonably close to those determined using a mass balance equation.

6.3.2 CH_4 OXIDATION RATES IN THE PRESENCE OF NMOCs: PHASE 2 RESULTS

On day 50, all the experimental runs were stopped; reactors were opened and tested as mentioned in section 6.3.1. Compost inside each column was removed, mixed and returned to the column after adding extra compost to compensate for the amounts taken for testing at the end of phase 1. Immediately after closing the columns, the cylinder that

contained the blend of CH_4 and NMOCs was connected to the experimental setup in addition to the air source. The same experimental strategy followed in phase 1 was resumed in phase 2.

It was perceived that the oxidation efficiencies dropped to low levels in the first 10 days of resuming the experiments with the blend of CH_4 and NMOCs. Figure 6.7 shows the CH_4 oxidation efficiencies with time monitored in the two phases.

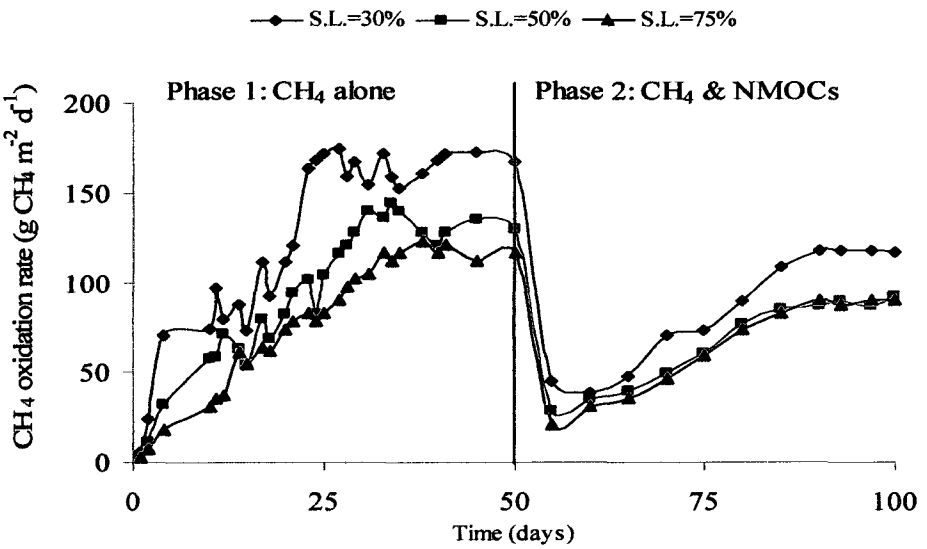


Figure 6.7 Methane oxidation rates versus time in the three experimental runs over 100 days.

As shown in Figure 6.7, CH_4 oxidation rates in the three experimental sets dropped to a range of 31- 39 $gCH_4\ m^{-2}\ d^{-1}$ in the first 10 days of phase 2. Then, with time, the oxidation rates rebounded to levels approaching 119 $gCH_4\ m^{-2}\ d^{-1}$ in experimental set 1, 93 $gCH_4\ m^{-2}\ d^{-1}$ in experimental run 2, and 90 $gCH_4\ m^{-2}\ d^{-1}$ in experimental run 3. These findings show that there was healthy population of methanotrophs maintained in the compost, so the bacteria were able to perform their oxidation activities, still the NMOCs as part of the blend affected their performance. For experimental set 1 that contained

compost with 30% S.L., the maximum CH_4 oxidation rate in phase 1 was 175.5 $gCH_4\ m^{-2}\ d^{-1}$ when CH_4 alone was flowing into the compost matrix, while the maximum monitored CH_4 oxidation efficiency when the blend of CH_4 and NMOCs was flowing into the compost was 119 $gCH_4\ m^{-2}\ d^{-1}$ over 50 days for each phase. The reduction in CH_4 oxidation rates (32%) was attributed to NMOCs present with CH_4. The same trend was observed in experimental runs 2 and 3 using compost with 50 and 75% S.L., respectively. The observed reductions in the maximum CH_4 oxidation rates between the two phases in experimental run 2 and 3 were 36 and 27%, respectively. The presence of mixed NMOCs reduced CH_4 maximum oxidation rates and this can be attributed to a combination of inhibition due to the chemical compounds presence or their transformation products, and the increased competition between CH_4 and NMOCs for the enzyme methane monooxygenases (MMO) which is considered the defining characteristic of methanotrophic bacteria. The phase 2 high level oxidation performances were sustained for almost 15 days before terminating phase 2. Evidently, the CH_4 performance among the two phases of the experiments followed a similar trend. This study revealed important observations concerning the CH_4 oxidation capacity of the LFC in the presence of NMOCs, Though, longer term experiments are recommended to confirm the extent of CH_4 oxidation steady state in the presence of NMOCs as part of the LFG.

Analyzing the concentrations of CH_4, O_2 and CO_2 with depth in this phase indicated that the active zone was between 50 and 150 mm from the top of the columns, where O_2 had the highest concentrations. The concentrations profiles had the same trends as the profiles in the first phase except that concentrations of CH_4 and O_2 were higher due to lower oxidation efficiencies in this phase where NMOCs were present with CH_4. After 50 days

of commencing phase 2, the column incubation experiments were terminated, and the column reactors were opened. According to the experimental protocol, the duration of each phase was 50 days; where the high steady state performance was expected. Compost samples were taken from different depths and tested for moisture content, organic matter content and pH. The moisture level was 2-4% higher than the initial levels in the beginning of the experiments from depth 50 mm onward, and the organic matter content values were not substantially different from the initial value in the experimental sets in phase 2. The change in pH did not exceed 2% of the original pH for the compost in all the experiments. The increase in biomass was in the range of 52 to 58%, and was calculated as

6.3.3 NMOCs BIOLOGICAL CO-OXIDATION IN LANDFILL BIO-COVERS

There are number of factors that affect the transport and fate of NMOCs in LFCs including sorption and biodegradation (Barlaz et al. 2004). When a NMOC is released into the LFG as vapor it will partition onto the LFC system; compost with its higher organic carbon fraction grants higher partitioning in gas-solid phases than conventional soil. In addition, methanotrophic bacteria are capable of performing oxidative conversions of a number of organic compounds in LFC system. Therefore, it was hypothesized that a bio-cover which can enhance CH_4 oxidation may also result in decreased emissions of trace organic compounds to the atmosphere. However, the objective of this research was to investigate the NMOCs biological degradation in the LFC system. In order to do so, the concentration of each NMOC selected in this study at

the top layer was measured daily using ECD gas chromatograph and analyzed. From the measured gas concentrations, the total mass of the each NMOC was determined by phase distribution calculations. The model used was presented by Scheutz et al. (2004) and verified in details in Appendix 6. The total mass of the chemical compound in the three phases can be expressed as follows (assuming steady state):

$$\text{Total mass of NMOC} = C_{gas} \times \left(\frac{V_{water}}{K_H} + V_g + mass_{compost} \frac{f_{OC} \times K_{OC}}{K_H} \right) \quad [6.3]$$

Where K_H is the dimensionless Henry's law constant, f_{oc} is the dimensionless fraction of organic carbon, and K_{oc} is the organic carbon partition coefficient (mL/g).

Figure 6.8 shows the relative concentrations of DCM and TCE, where (C in μg/L) was the concentration of the compound measured at the top of the compost in each column, and (C_o in μg/L) is the initial concentration of the chemical compound measured at the top of the compost.

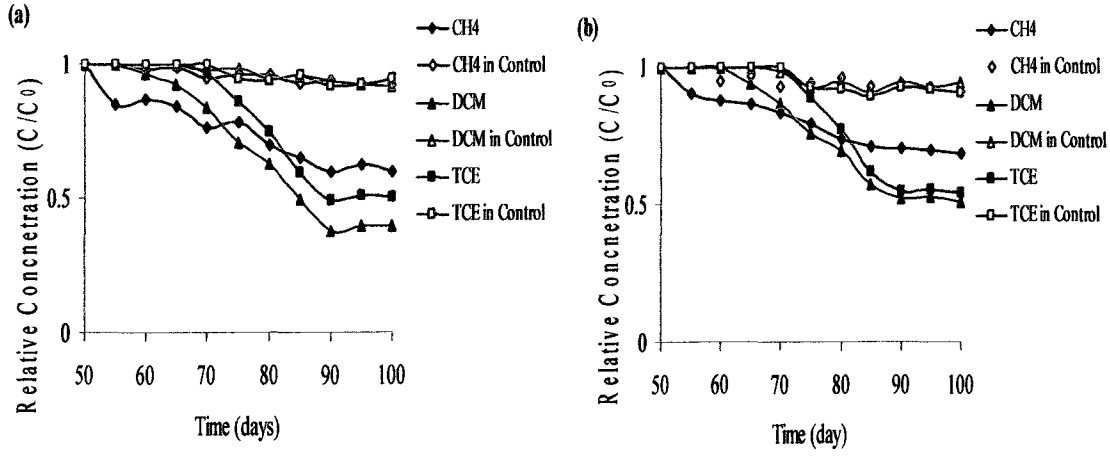


Figure 6.8 Relative headspace concentrations versus time of CH_4, DCM and TCE in (a) compost with 30% S.L., (b) compost with 50% S.L.

As illustrated in Figure 6.8, the concentrations of both DCM and TCE were decreased with time; each point is the average reading of duplicates. However, TCA was not detected at the top layer of the compost in the active column reactors, but it was observed in the blank and control. It was assumed that since TCA had a very low concentration in the blend (1 ppm), the final mass at the top layer remained after water and compost phases' distribution and co-oxidation was below detection limit of the gas chromatograph. The degradation of DCM was much faster than TCE in all the experimental runs; this is attributed to the concentration of the organic compound. The same observation was reported by Scheutz et al. (2004) in batch experiments using LFC soil. The biological co-oxidation rates of DCM and TCE were calculated based on the linear section of the degradation curves shown in Figure 6.8, the co-oxidation rates are presented in Table 6.1.

Table 6.1 Biological co-oxidation rates for DCM and TCE in experimental sets 1, 2 and 3.

Compost Saturation Level	DCM co-oxidation rate ($mgDCM\ m^{-2}\ d^{-1}$)	TCE co-oxidation rate ($mgTCE\ m^{-2}\ d^{-1}$)
30%	427.815	94.230
50%	311.670	88.110
75%	294.300	83.880

The results presented in Figure 6.8 and Table 6.1 showed that the DCM and TCE were degraded in the simulated LFC columns and this was related to the methanotrophic co-oxidation of NMOCs. The degradation of the chemical compounds in compost with different saturation levels followed the same trend of CH_4, where the biological degradation monitored was higher in compost with 30% S.L. followed by compost with

50 and 75% S.L., respectively. This can be referred to the methanotrophic bacteria established in each compost medium due to gases diffusion through air and water as explained in section 6.3.1. There are evidences in the literature that methanotrophic bacteria possess the enzyme monooxygenase (MMO) which facilitates the oxidation of CH_4 in addition to the co-oxidation of many chlorinated solvents (Alvarez-Cohen and Speitel 2001; Hanson and Hanson 1996). The degradation of DCM and TCE in these experiments was related to the co-oxidation capabilities of the well established methanotrophic bacteria in the compost matrix in all experimental runs. Alvarez-Cohen and Speitel (2001) stated that the co-metabolic transformations of chemical compounds were reported to occur relatively slowly in comparison to metabolism of the growth substrate (CH_4); it was observed in all experimental runs that CH_4 oxidation was faster in the first 25 days than the co-oxidation of DCM and TCE, which confirms the statement reported. However, the degradation declined after 30-35 days of the experiment and this was attributed to the inhibition effects due to the accumulation of degradation products or the chemical-CH_4-enzyme products. In a previous study by Albanna et al. (2009b), there were indications that the presence of NMOCs in the LFG affected the biological oxidation processes due to uncompetitive inhibition effects; the chemical compound binds to the enzyme-CH_4 complex and with time the accumulation of the degradation products will cause inhibition of the biological oxidation process. However, further microbiological studies should address the methanotrophic co-oxidation in the LFC system, and the type of enzyme inhibition caused by the NMOCs present in LFG.

6.3.4 METHANE OXIDATION PERFORMANCE: RESULTS OF EXPERIMENTAL SET 4

The objective of experimental set 4 was to report on the duration for which high CH_4 oxidation rate can be maintained in landfill bio-covers. Methane was fed alone in this experimental set, and the column experiments where monitored over 120 days. Figure 6.9 shows the CH_4 oxidation rates in compost with 50% S.L. The experiment was conducted at 22°C.

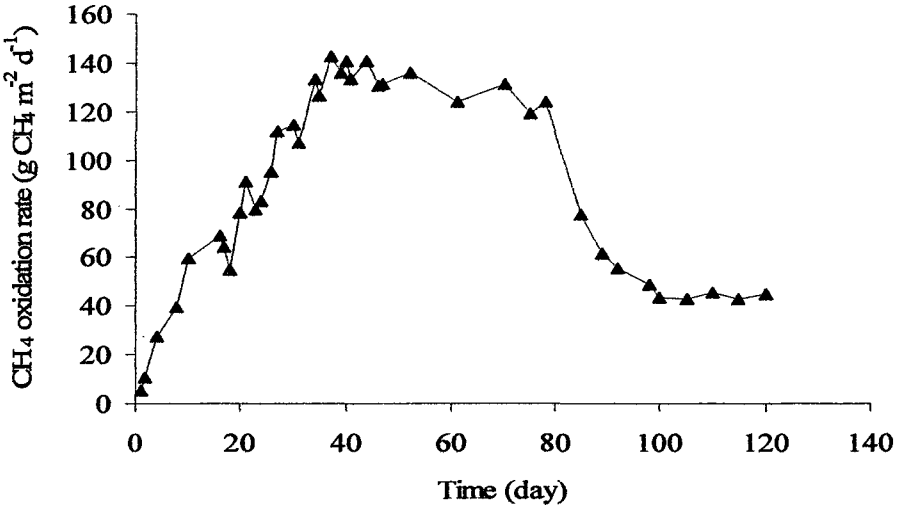


Figure 6.9 Methane oxidation rates versus time in the compost contained with 100% S.L. at 22° C.

As illustrated in Figure 6.9, the CH_4 oxidation performance changed with time: first there was a short acclimation phase, followed by a rapid increase in oxidation efficiency, then a plateau of high oxidation rate and finally a decline in the oxidation efficiency to a steady low rate. The column performance over the first 50 days resembled the columns performance in experimental set 2 since both were operating under same conditions. The highest CH_4 oxidation rate observed was 140.6 $gCH_4\ m^{-2}\ d^{-1}$ in day 40. The CH_4

oxidation rate in the range of 130 to 140 gCH_4 m^{-2} d^{-1} was sustained until day 75, and then a decline in oxidation performance was observed. The decline was most evident between day 80 and 100, on day 100 the CH_4 oxidation rate was 42 gCH_4 m^{-2} d^{-1}. The low oxidation steady state continued for the last 20 days of the experiment. After day 80, it was observed that top of compost layer had discoloration zones. On day 120, the gases concentrations were measured at different depths; afterwards the experimental set was terminated. Figure 6.10 shows the gas concentration profiles for the experimental 4 on day 120.

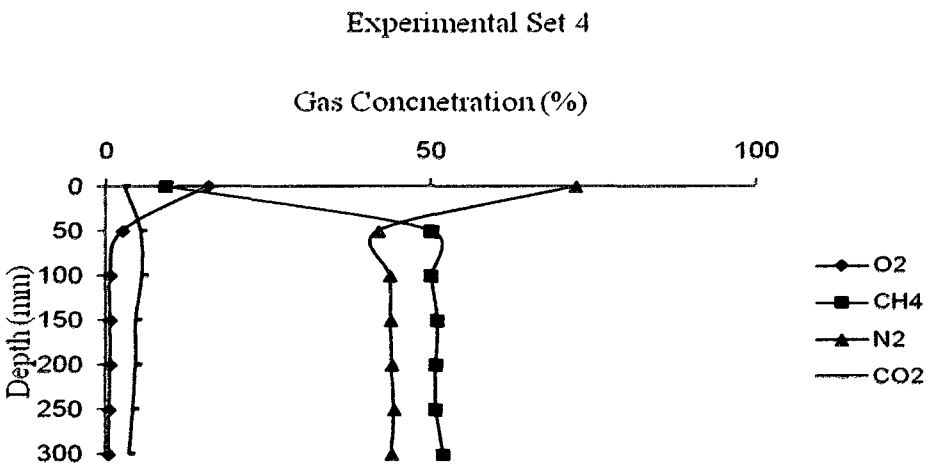


Figure 6.10 Gas concentration profile as function of depth in experimental set 4 after 120 days.

The gas profile illustrated in Figure 6.10 looked different compared to the active profile shown in Figure 6.5(b). Between 0 and 100 mm depths in the compost, the concentration of CH_4 was reduced by 80%, and the concentration of O_2 reduced by 95%. The reduction in CH_4 oxidation rates after day 100 can be attributed to the formation of exopolymeric substances (EPS) that blocked the compost pores at the top 100 mm and prevented O_2 from migrating to the lower regions of the LFC. Exopolymeric substances are growth

products that impact the diffusion of substrates and reducing the CH_4 oxidation in LFC system. Wilshusen et al. (2004a) and Hilger et al. (2000) reported similar observations in long-term experiments with CH_4 alone, and suggested that the CH_4 oxidation decreasing trend is correlated with the production of the exopolymeric substances in the upper layer of the LFC column which could limit gas diffusion into the cover pores, and therefore reduce methanotrophic activities. No information until now available on the techniques to prevent the formation of the EPS in order to avoid the decrease in oxidation rates, However, Wilshusen et al. (2004b) suggested the mixing of the medium as means of returning the high level performance, since mixing could prevent the concentration of EPS and methanotrophic bacteria in a certain zone, thereby prevent negative consequences of EPS formation. Future studies should address the substances occurrence, the quantification methods, and the on site maintenance, in order to optimize the oxidation rates expected in the cover system.

6.4 SUMMARY

This is a comparative study of the bio-cover's CH_4 oxidation efficiency between the two phases based on type of gas fed (CH_4 alone versus CH_4 with NMOCs) using controlled column experiments. This study showed that compost promotes optimum growth of methanotrophic bacteria and thus enhance the biological oxidation of CH_4 and co-oxidation of selected organic compounds. However, the NMOCs present with CH_4 to simulate LFG affected negatively the compost's CH_4 oxidation rates. The column experiments conducted for 50 days with CH_4 and another 50 days with a blend of CH_4

and NMOCs showed that the presence of mixed NMOCs reduced CH_4 maximum oxidation rates in a range from 27 to 36% of the maximum CH_4 oxidation rates. This can be attributed to a combination of inhibition due to the chemical compounds presence or their transformation products, and the increased competition between CH_4 and NMOCs for the enzyme methane monooxygenases.

6.5 REFERENCES

Albanna, M., and Fernandes, L. (2009a). "Capacity for Biological Methane Oxidation in Different Types of Soils and Compost." Submitted to Journal of Solid Waste Technology and Management.

Albanna, M., Warith, M., and Fernandes, L. (2009b). "Kinetics of Biological Methane Oxidation in the Presence of Non-Methane Organic Compounds in Landfill Bio-Covers." Submitted to Waste Management Journal.

Alvarez-Cohen, L. and Speitel Jr. G.E. (2001), "Kinetics of Aerobic Cometabolism of Chlorinated Solvents," *Biodegradation*, 12: pp. 105–126.

ASTM D2974-87, American Society for Testing and Materials (2000), "Standard Test Method for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils". ASTM International, PA, USA.

ASTM D7348-08, American Society for Testing and Materials (2000), "Standard Test Methods for Loss on Ignition of Solid Combustion Residues". ASTM International, PA, USA.

Barlaz, M.A., Green, R.B., Chanton, J.P., Goldsmith, C.D., and Hater, G.R. (2004), "Evaluation of a Biologically Active Cover for Mitigation of Landfill Gas Emissions," *Environmental Science and Technology*, 38, pp. 4891-4899.

Borjesson, G., Sundh, I., Tunlid, A., Frostegard, A., and Svensson, B.H. (1998), "Microbial Oxidation of CH_4 at High Partial Pressures in an Organic Landfill Cover Soil under Different Moisture Regimes," *Microbiology Ecology*, 26, pp. 207-217.

Chiemchaisri, W, Chettiyappan, V. and Shing Wu, J. (2001), "Effects of Trace Volatile Organic Compounds on Methane Oxidation," *Brazilian Archives of Biology and Technology*, 44, pp.135-140.

Czepiel, P.M., Mosher, B. and Harris, R.C. (1996), "Landfill Methane Emissions Measured by Enclosure and Atmospheric Tracer Method," *Journal of Geophysical Research*, 101, pp. 16711-16719.

De Visscher, A. Thomas, D., Boeckx, P., and Van Cleemput, O. (1999), "Methane Oxidation in Simulated Landfill Cover Soil Environments," *Environmental Science and Technology*, 33, pp. 1854-1859.

Einola J-K.M., Kettunen, R.H., and Rintala, J.A. (2008), "Mechanically-Biologically Treated Municipal Solid Waste as a Support Medium for Microbial Methane Oxidation to Mitigate Landfill Greenhouse Emissions," *Waste Management,* 28, pp. 97-111.

Environment Canada (October, 2005), Landfill Gas Management in Canada Report, http://www.ec.gc.ca/pdb/ghg/inventory_report/2005_report/tdm-toc_eng.cfm.

Gebert, J., Groengroeft, A., and Miehlich, G. (2003), "Kinetics of Microbial Landfill Methane Oxidation in Biofilters," *Waste Management*, 23, pp. 609-619.

Hanson, R. and Hanson, T.E. (1996), "Methanotrophic Bacteria," *Microbiological Reviews*, 60, pp. 439- 471.

Hilger, H., Cranford, D., and Barlaz, M. (2000), "Methane Oxidation and Microbial Exopolymer Production in Landfill Cover Soil," *Soil Biology and Biochemistry*, 32, pp. 457-467.

Hilger, H. and Humer, M. (2003), "Biotic Landfill Cover Treatments for Mitigating Methane Emissions," *Environmental Monitoring and Assessment,* 84, pp. 71-84.

Holtz, R., and Kovacs, W. (1981), "An Introduction to Geotechnical Engineering," Prentice-Hall, Englewood Cliffs, N.J., USA.

Intergovernmental Panel on Climate Change, (2001). IPCC Working Group I, The Scientific Basis, http://www.grida.no/climate/ipcc_tar/wg1/248.htm.

Jugnia, L.B., Cabral, A.R., and Greer, C. W. (2008), "Biotic Methane Oxidation with an Instrumented Experimental Landfill Cover," *Ecological Engineering,* 33, pp. 102-109.

Kettunen, R., Einola, J-K.M. and Rintala, J.A. (2006), "Landfill Methane Oxidation in Engineered Columns at Low Temperature," *Water, Air and Soil,* 177, pp. 313-334.

Kightley, D., Nedwell, DB. and Cooper, M. (1995), "Capacity for Methane Oxidation in Landfill Cover Soils Measured in Laboratory-Scale Soil Microcosms," *Applied and Environmental Microbiology,* 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.

Mor, S., De Visscher, A., Ravindra, K., Dahiya, R.P., Chandra, A., and Van Cleemput, O. (2006),"Induction of Enhanced Methane Oxidation in Compost: Temperature and Moisture Response," *Waste Management,* 26, pp. 381-388.

Scheutz, C., Mosbaek, H., and Kjeldsen, P. (2004),"Attenuation of Methane and Volatile Organic Compounds in Landfill Soil Covers," *Environmental Quality,* 33, pp. 61-71.

SYSTAT 11, (2004). Systat Software Inc., Chicago, USA.

USEPA (2006), "Global Anthropogenic Non-CO_2 Greenhouse Gas Emissions: 1990-2020, U.S. Environmental Protection Agency, Office of Atmospheric Programs, Climate Change Division, U.S. Environmental Protection Agency, 1200 Pennsylvania Avenue, NW, Washington, DC 20460.

USEPA (1999), Municipal Solid Waste Landfills, Volume I: Summary of the Requirements for the New Performance Standards and Emissions Guidelines for Municipal Solid Waste Landfills. 453/R-96-004. Research Triangle Park, NC. USA.

Watts, R.J. (1997), "Hazardous Wastes: Sources, Pathways and Receptors", John Wiley and Sons Inc., New York, USA.

Welty, J.R., C.E. Wicks, and R.E. Wilson. (1984), "Fundamentals of Momentum, Heat, and Mass Transfer", 3rd Ed. John Wiley & Sons, New York, USA.

Wilshusen, J.H., Hettiaratchi, J.P.A., De Visscher, A., and Saint-Fort, R. (2004a), "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., and Stein, V.B. (2004b), "Long-Term Behavior of Passively Aerated Compost Methanotrophic Biofilters Columns," *Waste Management*, 24, pp. 643-653.

CHAPTER 7

APPLICATION OF NEURAL NETWORK FOR SIMULATION OF BIOLOGICAL CH_4 OXIDATION IN LANDFILL BIO-COVERS

Muna Albanna, Mostafa Warith and Leta Fernandes

ABSTRACT

Biological methane (CH_4) oxidation in landfill cover system plays an important role in reducing CH_4 emissions from landfill sites into the atmosphere. The oxidation rate depends on different environmental factors, mostly temperature and moisture content. The non-methane organic compounds (NMOCs) present in landfill gas can affect the extent of biological CH_4 oxidation rates expected in the cover system. Artificial neural networks (ANN) are non-linear statistical modeling tools that can be used to model complex relationships between input and output data sets to find and learn their performance patterns. The purpose of this study is to develop a model based on ANN to estimate the CH_4 oxidation rates in landfill bio-covers under various levels of temperature, moisture content and NMOCs concentration. The best model for prediction of CH_4 oxidation rates was selected based on minimum errors and highest coefficient of determination values. The selected model successfully simulated the effect of each input data on the oxidation capacity of the bio-cover.

7.1 INTRODUCTION

Recent attention has been drawn to the increase in average global temperatures which was attributed to the growing greenhouse gases emissions mainly: carbon dioxide (CO_2) and methane (CH_4). One important source which adds to the anthropogenic CH_4 emissions is solid waste disposal. The biogas generated from biodegradation of solid waste in landfills, known as landfill gas (LFG), consists of CH_4, CO_2, plus trace amounts of non-methane organic compounds (NMOCs). Oxidation of CH_4 by methanotrophic bacteria within the landfill cover (LFC) provides a sink for these harmful fugitive emissions and is considered a significant biological process for attenuating fluxes of CH_4 to the atmosphere. The trace constituents of NMOCs present in LFG affect the CH_4 oxidation rates expected in LFC system. The experimental results presented by Albanna et al. (2009) showed a decrease in CH_4 oxidation capacity of the landfill bio-cover with an increase in NMOCs concentrations. Therefore, NMOCs presence is critical and it should be to taken into consideration when simulating and/or predicting the biological CH_4 capacity of the LFC system.

Modeling the biological oxidation processes that occur within the LFC can be used to estimate the CH_4 oxidation potential of the methanotrophic bacteria under different environmental conditions; such estimation can successfully lead to the optimization of design parameters of an effective LFC system that will reduce the CH_4 emissions from landfill sites and open dumps to the atmosphere. The previous mathematical models (De Visscher and Cleemput 2003; Stein 2001; Hilger et al. 1999; Bogner et al. 1997; El-Fadel et al. 1995) were developed based on transport-reactive simulation models and imparted

quantitative perceptions of biological and physical processes, with reference to CH_4 transport, oxidation and reaction rates. However, these models were based on the flow of CH_4 alone into the cover matrix; NMOCs presence and their inhibition effects were not taken into consideration. There is definitely a need to develop a comprehensive landfill gas transport model that simulates the LFC system, evaluates the physical and biochemical processes, and includes NMOCs transport and oxidation, as well as their effect on CH_4 oxidation rates.

The complexity and the multi-factorial interactions between the various factors affecting biological oxidation of CH_4 and NMOCs in LFC system impose a challenge for simulating this system and the coupled processes using conventional mathematical methods. Recently, advanced methods, such as the artificial neural networks analyses, established their reputation as alternative modeling techniques. Artificial neural networks (ANN) are non-linear statistical data modeling tools; they can be used to model complex relationships between inputs and outputs and/or to find patterns in data and they can be utilized to solve many complex and real-world problems (Basheer and Hajmeer 2000; Hassoun 1995; Haykin 1994). The power of ANN lies in implementing the learning algorithms of neural networks to describe the behavior of the system without the need to know the exact interrelationships (Lu and Rosenbaum 2003). The significant information processing capabilities of ANN approach, and the ability to learn from examples, make this method very efficient problem-solving tool (Lu and Rosenbaum 2003; Basheer and Hajmeer 2000; Yeh 1998; Baum and Haussler 1989), and thus can offer advantages in simulating the complex biological oxidation processes in the LFC system. Recently, the application of ANN in modeling different complex engineering problems has received

positive and widespread attention, where dynamic characteristics and uncertainty may be important (Yeh 2007; Lu and Rosenbaum 2003; Lee 2003). Basheer and Hajmeer (2000) stated the ANN models are attractive because: nonlinearity allows better fit to the data; noise-insensitivity provides accurate predictions; learning and adaptivity allow the system to modify its internal structure in response of changing environmental conditions; and, generalization enables application of the model to the unlearned data.

ANN-based models are empirical in nature, but they can provide practically accurate solutions for processes and phenomena that are understood through the experimental data. From this perspective, it was decided to use ANN modeling techniques to estimate the bio-cover's CH_4 oxidation capacity under different environmental conditions. The objective of this study was to develop a neural network's structure that has the capability to predict CH_4 oxidation rates in landfill bio-cover, when NMOCs are present in different concentrations, under various temperature and moisture levels, based on previous experimental results.

7.2 ARCHITECTURE OF ARTIFICIAL NEURAL NETWORKS

Artificial neural networks are computational models that involve a network of simple, highly interconnected processing elements (neurons), which manage information by its dynamic state response to external inputs (Solomatine 2003; Yeh 1998; Graupe 1997). Artificial neural networks consist of a set of input units (senses), connected to vast arrays of processing units (hidden neurons), which connect the senses to the decision making

neurons. Artificial neural networks can learn complex input-output mapping; the learning process is used to determine proper interconnection weights, and the network is trained to properly associate the inputs with their corresponding outputs (Yeh 2007).

The perceptron, which is historically the earliest artificial that was proposed by Rosenblatt in 1958, is the basic building block of nearly all ANN (Chow and Cho 2007, Graupe 1997). The perceptron can be trained on a set of examples using special learning rule, and the perceptron weights are changed in proportion to the difference (error) between the target output (experimental observation) and the solution for each example (Basheer and Hajmeer 2000). In order to handle the nonlinearity discrete problems, additional layer/layers of neurons placed between the input layer- that contains the input nodes- and the output neuron are needed, which lead to the multilayer perceptron architecture. The intermediate layer/layers is called hidden layer/layers with hidden neurons because they do not interact with the external environment; the addition of intermediate layer/layers invigorates the perceptron by extending its ability to solve nonlinear problems. The multilayer perceptron (MLP) is generally considered the most powerful and universally applicable type of ANN (Basheer and Hajmeer 2000; Dowla and Rogers 1995). The widely accepted way of training MLP is the back-propagation algorithm (Yeh 2007; Lee 2003; Basheer and Hajmeer 2000). The back-propagation algorithm usually uses a gradient descent method to systematically modify the weights in the network so as to minimize the network output error. The algorithm gives instructions for changing the connection strength between nodes, in layered network, to teach the network a certain task by using a set of training inputs-outputs pairs with a gradient decent through two passes (Hassoun 1995). The term back-propagation refers to the way

the error computed at the output side is propagated backward from the output layer, to the hidden layer and finally to the input layer. The algorithm has an iterative gradient designed to minimize the mean square error between the desired and actual outputs (Lu and Rosenbaum 2002). The algorithm is simple, can efficiently solve multi-dimensional as well as multi-variable problems, and can be implemented practically although it may take a large number of iterations especially for systems with many layers (Lee 2003).

In general, the network is trained so that the application of the set of inputs produces the desired set of outputs. Each input or output set is referred to as a vector. Training is achieved by successively applying input vectors. During training, the network weights gradually converge to values such that each input vector produces the output vector. To test the accuracy of a trained network, the coefficient of determination (R^2) is adopted. The higher the R^2 value is, the better the prediction relationship will likely be (Yeh 1998). Overtraining is a problem that should be avoided during the training of a network; it occurs when the network is forced to make the output error very small by continued exercise of error minimization. Overtraining is minimized by using large and well distributed set of examples and by comparing the performance of the training and testing events (Dowla and Rogers 1995).

7.3 MODELING OF CH_4 OXIDATION IN LANDFILL BIO-COVERS: METHODS

7.3.1 SYSTEM MODEL

The basic approach for developing a neural based model for biological CH_4 oxidation behavior in landfill bio-covers was to train a neural network on the results of a series of experiments that were conducted to estimate that CH_4 oxidation capacity of the bio-cover. The experimental results presented by Albanna et al. (2009) were used as the training and validation data sets. The experimental results were the values of the CH_4 oxidation rates obtained using laboratory batch experiments. The experiments were conducted using compost as the landfill cover medium, under three levels of temperature (5, 22 and 35°C) and moisture content (57, 100 and 142% w/w), and five concentrations of various NMOCs (without NMOCs, with trichloroethane (TCA) = 1 ppm, trichloroethylene (TCE) = 3 ppm, dichloromethane (DCM) = 14.3 ppm and the mix of these compounds = 18.3 ppm). The domain of temperature and moisture content levels was selected to simulate various climatic conditions that might affect microbial activities. The batch experiments were conducted in triplicates. It was hypothesized in this study that since these data sets contained the relevant information about the biological CH_4 oxidation behavior in landfill bio-cover under different environmental conditions and NMOCs concentrations, the trained neural network would contain sufficient information about the process's behavior, to qualify as the biological process model. Additionally, it was assumed that such a trained neural network would be able to reproduce the experimental results, and through its generalization capability, it should be able to

approximate the expected results of other applications of the bio-cover under different environmental conditions. Figure 7.1 illustrates the flow chart of the proposed training cycle of the ANN adapted in the biological CH_4 oxidation model design.

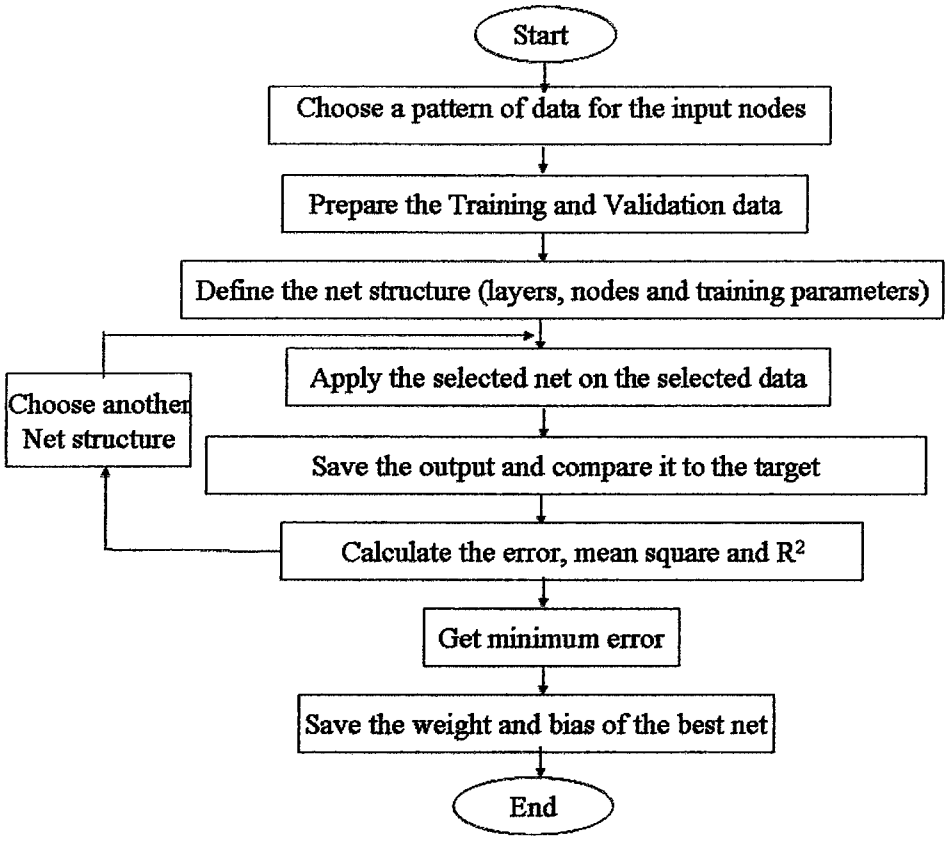


Figure 7.1 Flow chart of the training cycle of ANN.

The consolidated data set of 135 experiments (5 levels of NMOCs concentration, 3 levels of temperature, and 3 levels of moisture content, in triplicates) was used to build the model. The experimental results were the biological CH_4 oxidation rates ($\mu g\ CH_4\ h^{-1}\ g^{-1}_{wet\ wt.}$) and they were used as the target output.

7.3.2 DATA BASE USED IN THE MODEL DEVELOPMENT

Preprocessing

The software NeuralMachine Version 2 was used to build the model. NeuralMachine is a general purpose data-driven modeling tool with an executable code generator. NeuralMachine allows creation of ANN with one hidden layer and supports multilayer preceptron (MLP). Multilayer preceptron trained through error back propagation algorithm is the most used type of ANN and its applications to function approximation have been proven in several studies (Jalili and Noori 2008; Yeh 2007; Lee 2003; Basheer and Hajmeer 2000). For MLP of continuous nonlinear hidden-layer activation functions, one hidden layer is very precise and adequate (Hornik et al 1989). In the case of MLP network, all neurons are of sigmoid-type and the direct input-output link can be made as well. The software defines the hidden and output nodes as linear or sigmoid nodes; the model was based on sigmoid nodes for better accuracy. Therefore, it was hypothesized that the use of this software was practical and adequate.

The ranges for the input variables (temperature, moisture content and concentration of NMOC) and the output (CH_4 oxidation in landfill bio-cover) in the database are shown in Table 7.1. Once properly trained and tested, the ANN was used to predict the value of the CH4 oxidation rate expected in compost under this range of temperature, moisture content and NMOCs concentrations.

Table 7.1 Ranges of input variables used for the model

Input variable	Level 1	Level 2	Level 3	Level 4	Level 5
Medium - Compost	1				
Temperature (°C)	5	22	35		
Moisture Content (%w/w)	57	100	142		
NMOCs concentration (ppm)	0	1	3	14.3	18.3

The database used in the model development exhibited a close behavior to a normal distribution; a verification check by way of a normal distribution shape of the output variable, was important to obtain, in order to guarantee the appropriate fitting of the model in the domain of study.

Since the input variables had different scale of numerical range, a typical standardization was used in order to avoid the saturation of the model towards the variable with the bigger numerical numbers (Basheer and Hajmeer 2000). The standardization method used was according to the following equation:

$$z_i = \frac{x_i - mean(x)}{stdev(x)} \qquad [7.1]$$

Where, z_i is the standardized value of the variable, x is the variable analyzed, *mean* and *stdev.* are mean and standard deviation values of variable x.

Data Set Size and Partitioning

It was important to assess the data set size and partitioning between training, testing and validation subsets before proceeding with the model development. In order to estimate the proper data size for the model, the following architecture of the ANN was considered based on the details presented in the preprocessing section:

- Type of the ANN: The Multilayer perceptron which was trained through error back-propagation algorithm;
- Input neurons: From the experimental input variables show in Table 7.1, the input neurons in the first layer were "three";
- Hidden layer: "One";
- Neurons in the hidden layer: The methodology in this study was to test the optimum number of neurons in the hidden layer and to assess several configurations: two, three, four, five, six seven and eight nodes in the hidden layer; and,
- Number of outputs: "One", which estimated the CH_4 oxidation rate in the bio-cover.

The model's learning parameters (which include convergence criteria, the values of the back propagation learning rate and momentum constant) were as follows:

- The convergence criteria that was "training error,
- Absolute increase of step, if previous step reduced error (Kappa) = 0.02,
- Relative decrease of step, if previous step increased error (Phi) = 0.5,

- Relative influence of the previous values of error (Theta) = 0.5,
- Momentum: relative speed of the weights' change (Mu) = 0.7. The value of the momentum (Mu) can be increased to help pass local minima.

The network are frequently described as (P-n-O), where P was the number of input variables, n represented the number of neurons or nodes in the hidden layer, and O was the number of output variables. The determination of the appropriate number of hidden nodes was the most critical task in the ANN development. Unlike the input and output layers, the design of the ANN starts with no prior knowledge as to the size of hidden layer. It was important to define the "examples or training set to weights ratio (EWR)" for the proposed ANN, therefore, the number of data sets were divided by the number of weighing factors. Dowla and Rogers (1995) stated that the simplest network is the one with the fewest number of weights that satisfy all the input-output relations given by the training set, and therefore this network is expected to have the best generalization properties. Overfitting in regression analysis and memorization of the examples by the network will occur if the number of weights is higher than needed. These authors confirmed that a network with smaller numbers of weights may generalize better on data than a network with a larger number of weights that has memorized the examples. From this perspective, Dowla and Rogers (1995) recommended that the EWR should be > 10, while Masters (1994) suggested EWR should be > 4. Sarle (1995) proposed that the training set should be at least 30 times the number of nodes in the hidden layer. Based on such analysis and taking into consideration the experimental data base available, the ANN optimum configuration may have from 3-6 neurons in the hidden layer. Therefore, it was decided to train and test different configurations that had two, three, four, five, six,

seven and eight nodes in order to assess the optimum number of nodes in the hidden layer. Figure 7.2 illustrates an example of the proposed architecture of the mode based on six nodes in the hidden layer and 24 numbers of weights.

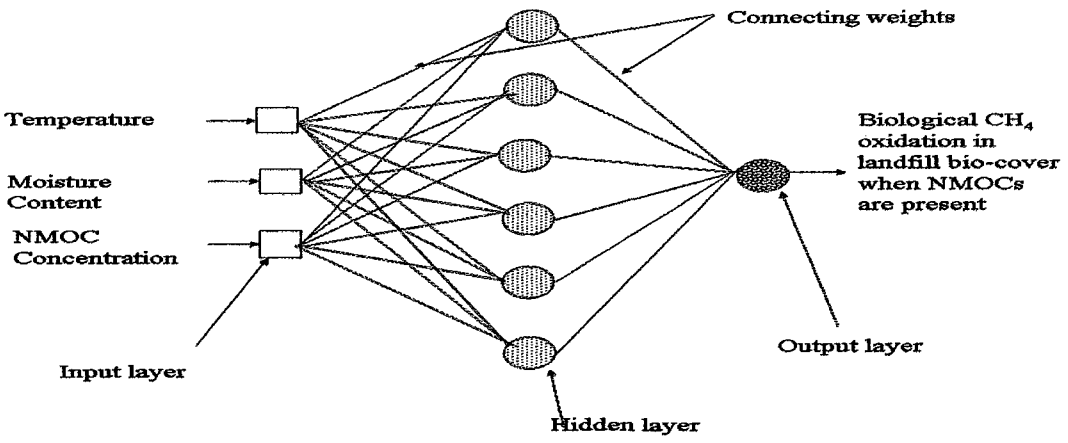


Figure 7.2 Schematic of the architecture of the ANN with six nodes in the hidden layer.

Subsequently, it was decided to continue with the model development, and split the 135 lines of data into training, testing (also called verification) and validation data by arrangement of 80, 10 and 10%, respectively. For the training data there were 107 lines of data, for the testing there were 14 lines of data, and for the validation there were also another 14 lines of data. Each line of data consisted of one level of each input variable and the corresponding experimental output result (the CH_4 oxidation rate obtained experimentally). The training, testing and validation data sets were selected strategically to ensure that all data sets included data from each NMOCs concentration.

7.3.3 MODEL EVALUATION CRITERIA

The commercial software NeuralMachine 2 was used for the development of the model. It was decided to check several ANN models that had different hidden neurons (2, 3, 4, 5, 6, 7 and 8 nodes in the hidden layer) to confirm the optimum number of nodes in the hidden layer. In order to avoid overtraining of the network, the training was stopped when the testing error increased. In the training process, the network used pairs of input and target values to create the weights accordingly. The network used the training sets to predict the target for the validation set using the input values of this set and compares it to the measured values. Consequently, statistical indictors were used in order to evaluate the performance of each ANN model. These values were derived in statistical calculations of observed results to the predicted ones as follows (Jalili et al. 2008):

- the mean absolute error (MAE);

$$MAE = \left(\frac{1}{n}\right)\sum_{i=1}^{n} | x_o - x_p | \qquad [7.2]$$

- the mean absolute relative error (MARE);

$$MARE = \left(\frac{1}{n}\right)\sum_{i=1}^{n} \frac{| x_o - x_p |}{x_o} \qquad [7.3]$$

- the root mean square error (RMSE);

$$RMSE = \sqrt{\left(\frac{1}{n}\right)\sum_{i=1}^{n} (x_o - x_p)^2} \qquad [7.4]$$

- the mean square error (MSE);

$$MSE = \left(\frac{1}{n}\right)\sum_{i=1}^{n}(x_o - x_p)^2 \qquad [7.5]$$

- and the coefficient of determination (R^2);

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(x_o - x_p)^2}{\sum_{i=1}^{n}(x_o - x'_o)^2} \qquad [7.6]$$

where, x_o, is the actual value of CH_4 oxidation rate in landfill bio-cover, n is the total observation number, x'_o, is the average of observed methane oxidized and x_p is the predicted CH_4 oxidation rate through modeling.

Gauch et al. (2003) suggested another approach to confirm the judgment on the ANN models results and to better understand the sources of error from each model. This approach was based on partitioning the MSE into three components: the square bias (SB), which is the translational discrepancy; the non-unity slope (NU), which is the rotational discrepancy; and, the lack of correlation (LC), which describes the scatter around the regression line. The mathematical definitions for these partitioned values of the MSE are as follows (Gauch et al. 2003)

$$SB = (x'_p - x'_0)^2 \qquad [7.7]$$

$$NU = (1-b)^2 * (\sum X_p^2 / N) \qquad [7.8]$$

$$LC = (1-R^2) * (\sum X_0^2 / N) \qquad [7.9]$$

where, x'_p is the average of predicted CH_4 oxidation rate, b, is the slope of the least squares regression of the observed and predicted methane oxidized, X_p and X_0 are also defined as:

$$X_0 = x_0 - x'_0 \quad \text{and } X_p = x_p - x'_p \qquad [7.10]$$

The three components (SB, NU and LC) added together give the MSE, which have distinct geometrical interpretations, including transparent relationships with regression parameter R^2 (Gauch et al. 2003).

7.4 RESULTS AND DISCUSSION

The structure of trained network in this study was (3-n-1); this structure means that the input variables were three as indicated in Table 7.1 and the output variable was one (CH_4 oxidation rate in landfill bio-covers), while the numbers of neurons in the hidden layer (n) were from 2 to 8. Figure 7.3 shows a comparison between measured and estimated values of CH_4 oxidation rates for the 14 data set used in the validation of (3-4-1) ANN structure as an example.

Validation set	Input Variables
1	5°C, 142% MC, NMOCs= 0 ppm
2	5°C, 142% MC, NMOCs= 1 ppm
3	5°C, 57% MC, NMOC = 3 ppm
4	5°C, 100% MC, NMOCs= 14.3 ppm
5	5°C, 57% MC, NMOCs= 18.3 ppm
6	22°C, 100%MC, NMOCs= 0 ppm
7	22°C, 100%MC, NMOCs= 1 ppm
8	22°C, 142%MC, NMOCs= 3 ppm
9	22°C, 100%MC, NMOCs= 14.3 ppm
10	22°C, 57% MC, NMOCs= 18.3 ppm
11	35°C, 57% MC, NMOCs= 0 ppm
12	35°C, 57% MC, NMOCs= 1 ppm
13	35°C, 100%MC, NMOCs= 3 ppm
14	35°C, 142%MC, NMOCs= 18.3 ppm

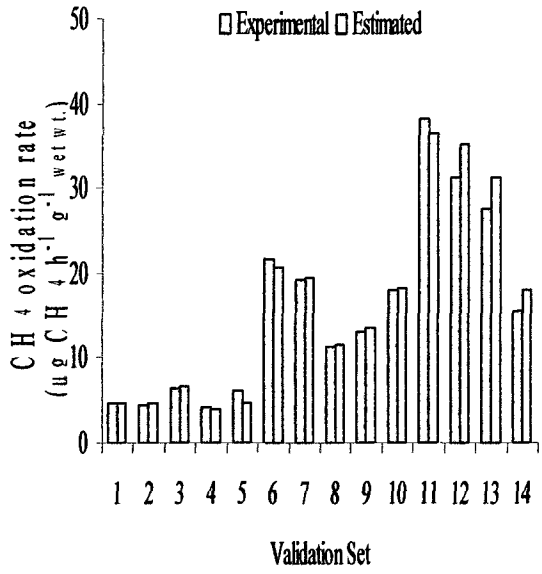


Figure 7.3 The experimental versus estimated CH_4 oxidation rates for the validation data set using the (3-4-1) ANN structure.

Figure 7.3 provides an example to illustrate the estimation by the (3-4-1) ANN for the values of CH_4 oxidation rates in landfill bio-cover under different levels of temperature and moisture as well as different NMOCs concentrations. The results estimated by the ANN were close to the oxidation rates obtained from the experimental program.

To analyze the results of different ANN structures, Table 7.2 and 7.3 demonstrate the training and verification values of the root mean square error (RMSE), the mean square error (MSE), the mean absolute error (MAE), the mean absolute relative error (MARE) and the coefficient of determination (R^2) for the different hidden neurons tested.

Table 7.2 Training errors of different number of ANN configurations

ANN Configuration	RMSE	MSE	MAE	MARE	R^2
3-2-1	1.738	3.022	1.288	0.097	0.9728
3-3-1	1.633	2.773	1.268	0.098	0.9750
3-4-1	1.545	**2.388**	1.151	0.089	**0.9787**
3-5-1	1.537	**2.350**	1.147	0.088	**0.9788**
3-6-1	1.532	**2.331**	1.142	0.088	**0.9790**
3-7-1	1.528	**2.339**	1.150	0.089	**0.9789**
3-8-1	1.525	**2.335**	1.147	0.088	**0.9790**

Table 7.3 Verification errors of the different ANNs configurations

ANN Configuration	RMSE	MSE	MAE	MARE	R^2
3-2-1	1.959	3.836	1.281	0.077	0.9722
3-3-1	1.972	3.887	1.344	0.083	0.9716
3-4-1	1.756	**3.083**	1.308	0.086	**0.9792**
3-5-1	2.029	4.117	1.279	0.076	0.9758
3-6-1	2.034	4.136	1.349	0.079	0.9738
3-7-1	2.017	4.068	1.281	0.073	0.9741
3-8-1	2.022	4.087	1.209	0.071	0.9745

The statistical values reported in Tables 7.2 and 7.3 shows that the mean square error (MSE) values in the training and verification sets were less than 5%. Also the coefficients of determination values (R^2) were high; this was possible because the training input data set were obtained from controlled and consistent laboratory batch experiments. From the results presented in Table 7.2, it was determined that with a higher number of nodes in the hidden layer, the mean square training errors (shown in bold) for the networks were lower, and almost similar for the networks with 4 to 8 number of nodes. The values of coefficient of determination (R^2) were higher for these networks as well; therefore, the results of the training errors of different ANN configurations indicated that the optimum network could have from 4 to 8 nodes in the hidden layer.

To further assess the different configuration performance, the relation between the number of nodes and the values of MSE and R^2 for the verification process was examined. The results of the error values associated with the verification process and presented in Table 7.3 specified that the ANN with (3-4-1) configuration had the lowest MSE value as well as the highest R^2; which might lead that this configuration could be the optimal. A four node structure was consistent with Sarle (1995) and Masters (1994) recommendation of EWR value, where the EWR for (3-4-1) ANN structure was 6.7 and greater than 4.

Figure 7.4 shows the experimental CH_4 oxidation rates obtained from batch experiments compared to the estimated values of CH_4 oxidized using the designated ANN with four neurons in the hidden layer.

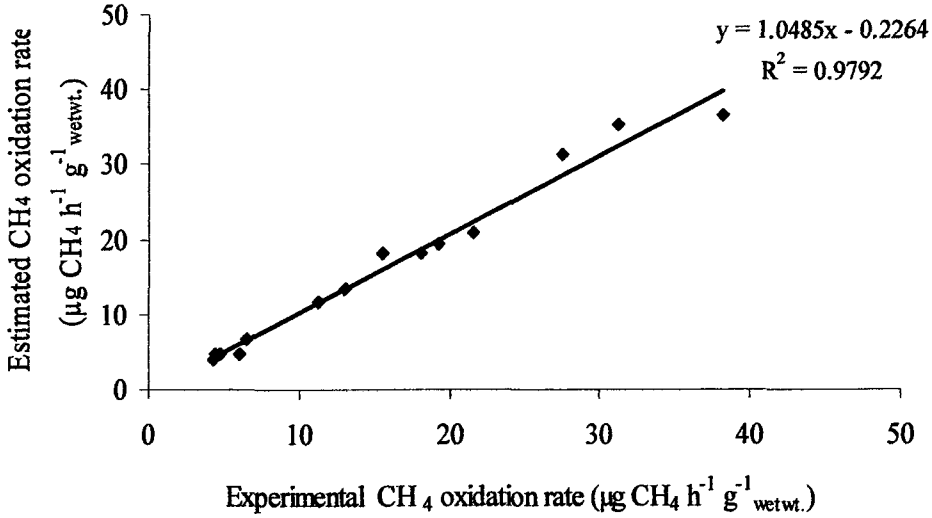


Figure 7.4 The experimental versus predicted CH_4 oxidation rates from the verification process of the ANN (3-4-1).

As shown in Figure 7.4, there was a very good fit between the verification experimental data and the estimated results provided by the designed ANN. The R^2 value was 97.9%.

The coefficient of determination was a key output of regression analysis. It was interpreted as the proportion of the variance in the dependent variable (CH_4 oxidation rate) that was predictable from the independent variables. With such a value, it means that CH_4 oxidation rates could be predicted with little error from the independent variables (temperature, moisture content and NMOCs concentrations).

To confirm the optimum network structure, a comparison of the percentage of contribution of the SB, NU and LC to the MSE for all nodes for the verification data set is shown in Table 7.4. This approach was suggested by Gauch et al. (2003) to confirm the judgment on the ANN different network structure as discussed in section 7.3.3.

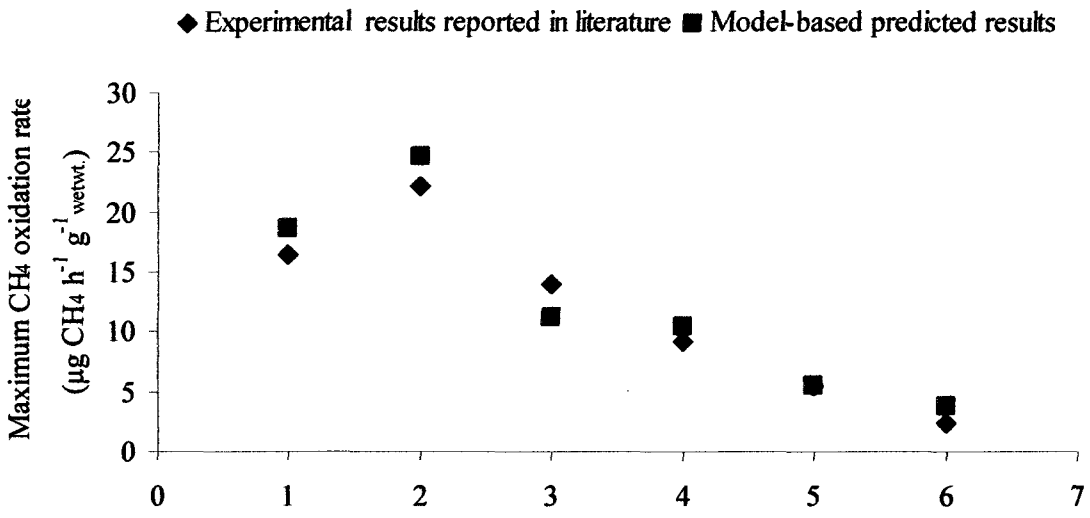
Table 7.4 The percentage of contribution of the standard bias (SB), Non-unity (NU), and lack of correlation (LC) to the mean square error (MSE) of the verification data

ANN Configuration	SB (%)	NU (%)	LC (%)
3-2-1	14.07	16.56	69.37
3-3-1	13.00	15.79	71.21
3-4-1	11.88	23.96	**64.16**
3-5-1	13.54	20.59	65.87
3-6-1	14.71	16.34	68.94
3-7-1	13.07	17.80	69.13
3-8-1	12.57	17.07	70.35

Gauch et al. (2003) stated that the parameters in linear regression of the observed and predicted methane oxidized account for the bias and the non-unity, and only residual errors from the lack of correlation reduce a regression's fit. This means that the regression was responsive to lower values of the lack of correlation only but not the standard bias or non-unity. Table 7.4 shows that the contribution of LC for the (3-4-1) network structure was the lowest. From all of above statistical indices, it was confirmed

that ANN structure of (3-4-1) had the lower value of LC, minimum standard error, and highest value of R^2 for the verification set. Therefore, the network with (3-4-1) structure was used to estimate the CH_4 oxidation rates in landfill bio-covers for any values of input variables. The optimal number of iterations was 1200. Almost in most of the runs, lowest mean square error values were obtained.

The selected ANN model with (3-4-1) structure was verified using experimental CH_4 oxidation rates in compost reported previously in literature but without any NMOCs (concentration of NMOCs = 0). Figure 7.5 demonstrates a comparison between the experimental CH_4 oxidation rates in compost as landfill cover medium reported previously by Einola et al. (2007); Mor et al. (2006); Kettunen et al. (2006) and the ANN model- based rates. The figure also shows the operating conditions reported by the mentioned researches.



	Medium	Temperature (oC)	M/C (%w/w)	NMOCs (ppm)
Mor et al., 2006	Compost	30	50	0
		22	50	0
		22	110	0
		7	59	0
Einola et al, 2007	Compost	12	21	0
Kuttenun et al., 2006	Compost	4-6	64	0

Figure 7.5 Comparison between reported CH_4 oxidation rates and the ANN modeled results under different temperatures and moisture content without NMOCs, and the reported operating conditions.

Figure 7.5 demonstrates that the selected ANN with the (3-4-1) configuration confirmed the experimental results reported by other researchers and estimated the CH_4 oxidation capacity of the bio-cover reasonably well, by applying the knowledge learned about the factors that influenced the biological process.

To study the effect of each input data on the CH_4 oxidation performance in the bio-cover, sensitivity analyses were performed. The model successfully simulated the effects of NMOCs concentration, temperature and moisture content on the biological oxidation process; examples of the model simulations are depicted in Figures 7.6, 7.7 and 7.8.

Figure 7.6 illustrates the model simulation of the CH_4 oxidation rates expected in compost with 57% MC at 22°C under different concentrations of NMOCs as an example. The figure shows the experimental results as well.

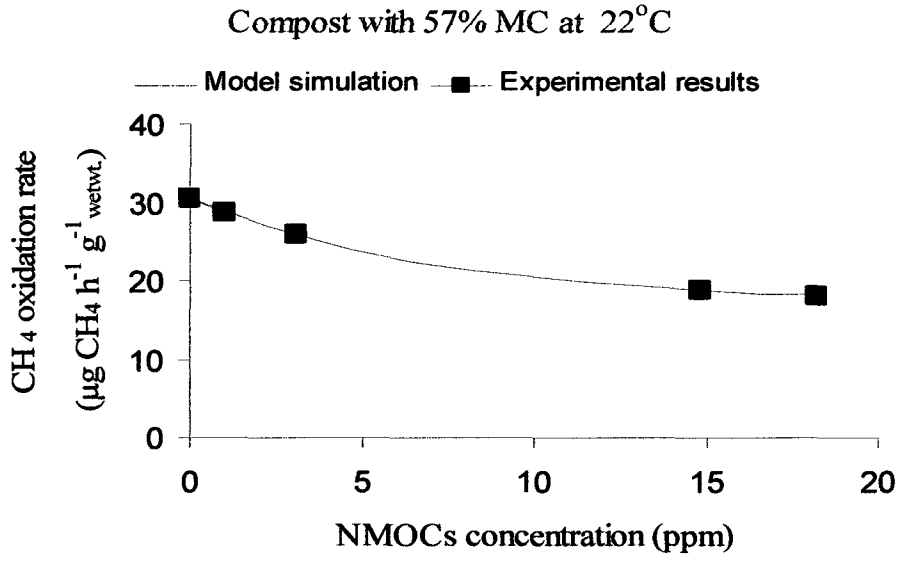


Figure 7.6 Model simulation of the biological CH_4 oxidation rates in compost with 57% MC at 22°C and different NMOCs concentration.

The model's simulation presented in Figure 7.6 showed that the increase in NMOCs concentrations affect negatively the CH_4 oxidation rates expected in the bio-covers. The presence of NMOCs can reduce the oxidation rates up to 40% of the initial oxidation rates at the same levels of temperature and moisture content; this can be attributed to a combination of inhibition due to toxicity of the chemical compounds or their transformation products, and the increased competition of CH_4 and organic compounds for the enzyme CH_4 monooxygenase which stimulate the oxidation. This competition can result in overall decreased transformation rates of CH_4 substrate and enzyme inhibition afterwards as discussed thoroughly by Albanna et al. (2009). The model simulated

successfully the effect of the organic compounds on the biological oxidation process. Additionally, the model results had a very good agreement with the experimental results.

To study the effect of temperature on the biological oxidation process in landfill bio-cover, Figure 7.7 shows the model simulation of the CH_4 oxidation rates in compost with 100% MC as an example under different temperature levels with NMOCs concentrations of zero and 18.3 ppm.

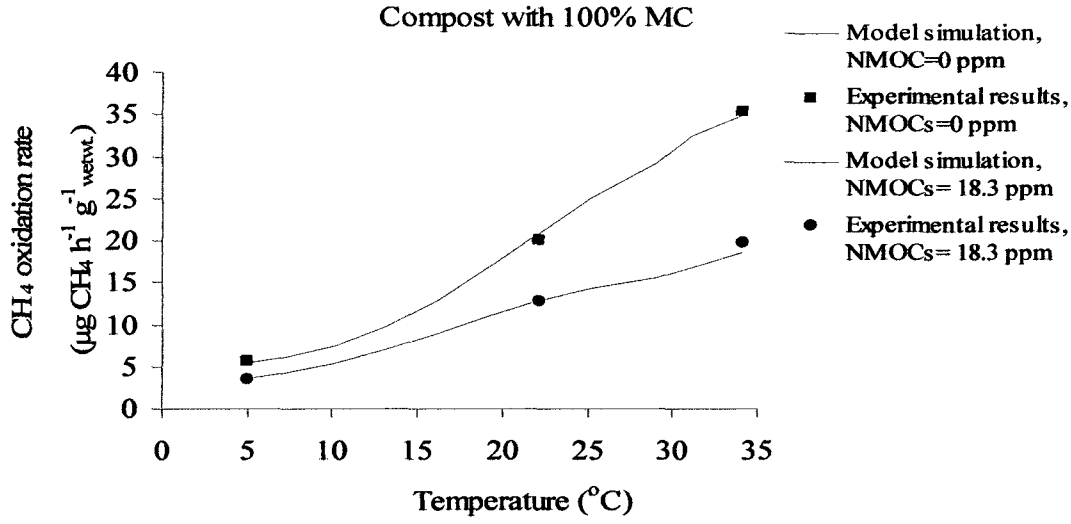


Figure 7.7 Model simulations of the CH_4 oxidation rates in compost with 100% MC at different temperatures with NMOCs concentrations of 0 and 18.3 ppm.

The model simulation results presented in Figure 7.7 shows that the CH_4 oxidation rates increases with the increase in temperature. The simulated oxidation rates increased from 5.9 to 35.4 $\mu gCH_4\ h^{-1}\ g^{-1}_{\ wetwt.}$ when the temperature increased from 5 to 35°C in compost with 100% MC and no NMOCs. Also, the simulated oxidation rates increased from 3.8 to 19.5 $\mu gCH_4\ h^{-1}\ g^{-1}_{\ wetwt.}$ when the temperature increased from 5 to 35°C in compost with 100% MC and NMOCs concentration of 18.3 ppm. The temperature has a critical effect on the CH_4 oxidation rates expected in landfill bio-covers; this is attributed to the

type of methanotrophic bacteria that can be active at different levels of temperature. At low temperatures between 3 and 10°C only Type I methanotrophic bacteria grow, while two types of methanotrophic bacteria (Type I and Type II) grow at 20°C. Moreover, lower temperatures affect negatively the O_2 diffusion within the cover, where the diffusion coefficient in soil decreases with declining temperature. In all cases, the model had a very good fit with the experimental results obtained previously, as shown in Figure 7.7.

To assess the effect of moisture content, Figure 7.8 shows the model simulation of the CH_4 oxidation rates in compost with 100% MC, as an example, under different temperature levels with NMOCs concentrations of zero and 18.3 ppm.

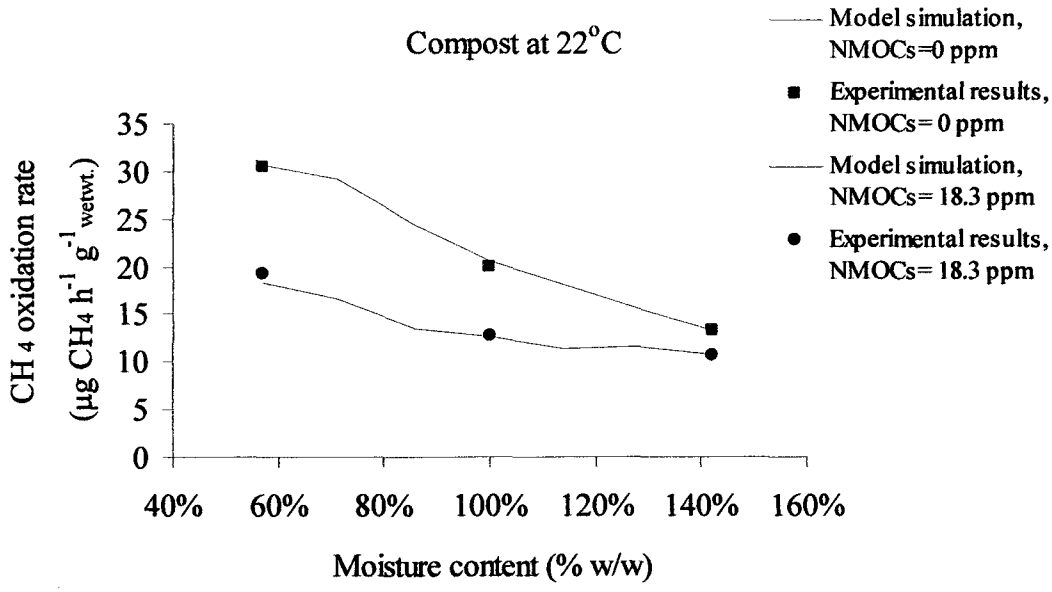


Figure 7.8 Model simulations of the CH_4 oxidation rates in compost with different moisture contents at 22°C with NMOCs concentrations of 0 and 18.3 ppm.

The model simulation results presented in Figure 7.8 indicate that the CH_4 oxidation rates decrease with the increase in bio-cover moisture content levels. The simulated oxidation

rates decreased from 30.1 to 13.3 $\mu gCH_4\ h^{-1}\ g^{-1}_{wetwt}$ when moisture content was increased from 57 to 142% at 22°C without the presence of NMOCs. The same observation was viewed when the moisture content levels were increased from 57 to 142% in the presence of 18.3 ppm of NOMCs; the CH_4 oxidation rates dropped from 18.5 to 10.4 $\mu g\ CH_4\ h^{-1}\ g^{-1}_{wetwt}$. The differences in the oxidation rates can be attributed to increased moisture levels which affect the CH_4 and oxygen (O_2) movements through the pores.

Based on the findings of this study, it can be concluded that the use of ANN technique to predict the CH_4 oxidation in landfill covers can be considered as a successful simulation tool without describing the complicated physical and biochemical processes in the LFC system. However, ANN modeling technique is based on learning patterns from a large number of experimental observations, which may be site or case specific. The ANN models are not comprehensive, as they cannot simulate the process outside the input variables domain. These limitations are critical and the ANN modeling technique provides a viable tool only for situations where significant quantities of data are available.

7.5 SUMMARY

Artificial neural networks are nonlinear statistical data modeling tools that can be used to describe complex relationships between input and output data sets to find and learn patterns in the data. With the broad variations of environmental conditions, physical characteristics of the LFC medium, and the NMOCs concentrations in landfill gas, it is difficult to provide an accurate mathematical model that can describe and predict the

biological CH_4 oxidation rates in the cover system. This study was aimed at demonstrating the possibility of adapting ANN to estimate the oxidation rates in the bio-cover. The developed ANN was assessed through a series of steps to evaluate and to minimize its errors. In the preliminary testing, an ANN with one hidden layer was evaluated by changing the number of neurons in the layer. Using the regression analysis on statistical parameters to evaluate the fit of the selected ANN, it was found that the structure with four nodes in the hidden layer had the least errors and the highest coefficient of determination value. Prediction results by the selected architecture showed good results with the test and validation data sets, which has not been used in the training process. The model was also validated using some of the experimental result for CH_4 oxidation reported in literature when the NMOCs concentration was zero. It can be concluded that the extent to which an ANN can be successful for predicting the biological oxidation capacity in LFC system depends upon the input data available. It would appear that ANN already provides a viable tool for situations where significant quantities of data are available. Comparison between the model results and the experimental data showed that ANN is an effective tool to predict CH_4 oxidation rates in landfill bio-covers under various environmental conditions.

7.6 REFERENCES

Albanna, M., Warith, M., and Fernandes, L. (2009). "Kinetics of Biological Methane Oxidation in the Presence of Non-Methane Organic Compounds in Landfill Bio-Covers." Submitted to Waste Management Journal.

Basheer, I.A. and Hajmeer, M. (2000), "Artificial Neural Networks: Fundamentals, Computing, Design and Application," *Journal of Microbiological Methods*, 43, pp. 3-31.

Baum, E.B., and Haussler, D. (1989), "What Size Net Gives Valid Generalization?", *Neural Computation*, 1, pp. 151-160.

Bogner, J., Meadows, M., and Czepiel, P. (1997), "Fluxes of Methane between Landfills and the Atmosphere: Natural and Engineered Controls," *Soil Use and Management*, 13, pp. 268-277.

Chow, T.W.S., and Cho, S.Y. (2007), Neural Networks and Computing, Learning Algorithms and Applications, Imperial College Press, Singapore; Hackensack, NJ.

Czepiel, P.M., Mosher, B. and Harris, R.C. (1996), "Landfill Methane Emissions Measured by Enclosure and Atmospheric Tracer Method," *Journal of Geophysical Research*, 101, pp. 16711-16719.

El-Fadel, M., Findikakis, A.N., and Leckie, J.O. (1995), "Numerical Modelling of Generation and Transport of Gas and Heat in Landfills: I. Model Formulation," *Waste Management and Research*, 14, pp. 483-504.

Einola J-K.M., Kettunen, R.H., and Rintala, J.A. (2007), "Responses of Methane Oxidation to Temperature and Water Content in Cover Soil of a Boreal Landfill," *Soil Biology and Biochemistry*, 39, pp. 1,156-1,164.

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.

Dowla, F.U., and Rogers, L.L. (1995), Solving problems in Environmental Engineering and Geosciences with Artificial Neural Networks, The MIT Press Cambridge, Massachautts.

Hassoun, M.H. (1995), Fundamentals of Artificial Neural Networks, The MIT Press, Cambridge, Massachusetts,.

Haykin, S. (1994), Neural Network: A Comprehensive Foundation, Edition: 3rd, IEEE Computer Society, Wiley, New York.

Hilger, H., Cranford, D., Barlaz, M. (1999), "Methane Oxidation and Microbial Exopolymer Production in Landfill Cover Soil," *Soil Biology and Biochemistry*, 32, pp. 457-467.

Hornik, K., Stinchcombe M., and White, H. (1989), "Multilayer Feed-Forward Networks are Universal Approximators", *Neural Networks,* 2, pp. 359–366.

Gauch, H.G., Hwang, G., Fick, G., (2003), "Model Evaluation by Comparison of Model-Based Predictions and Measured Values", *Agronomy Journal*, 95, pp. 1442-1446.

Graupe, D., (1997), "Principles of Artificial Neural Networks", World Scientific Publishing Co., Singapore.

Jalili G., and Noori M., (2008), "Prediction of Municipal Solid Waste Generation by Use of Artificial Neural Network", International Journal of Environmental Research, 2, pp. 13-22.

Kettunen, R., Einola, J-K.M. and Rintala, J.A. (2006). "Landfill Methane Oxidation in Engineered Columns at Low Temperature," *Water, Air and Soil*, 177, pp. 313-334.

Lee, S.C. (2003), "Prediction of Concrete Strength Using Artificial Neural Networks," *Engineering Structures*, 25, pp. 849-857.

Lu, P. and Rosenbaum M.S., (2003), "Artificial Neural Networks and Grey Systems for the Prediction of Slope Stability," *Natural Hazards*, 30, pp. 383-398.

Masters, T. (1994), Signal and Image Processing with Neural Networks, John Wiley & Sons, Inc. New York.

Mor, S., De Visscher, A., Ravindra, K., Dahiya, R.P., Chandra, A., and Van Cleemput, O. (2006),"Induction of Enhanced Methane Oxidation in Compost: Temperature and Moisture Response," *Waste Management,* 26, pp. 381-388.

Neural Machine Version 2 (2004), Solomatine, D.P., UNESCO-IHE Institute for Water Education, the Netherlands.

Sarle, W.S., (1995), "Stopped Training and Other Remedies for Over-Fitting", Proceedings of the 27th Symposium on the Interface of Computing Science and Statistics, http://mars.elcom.nitech.ac.jp/~anto/NEURO/inter95.ps.gz.

Solomatine, D.P., (2003), Neural Machine: neural network Tool, UNESCO-IHE Institute for Water Education, The Netherlands.

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.

Yeh, L.C. (1998), "Modeling of Strength of High-Performance Concrete Using Artificial Neural Networks," *Cement and Concrete Research*, 28, pp. 1797-1808.

Yeh, C. (2007), "Modeling Slump Flow of Concrete Using Second-Order Regressions and Artificial Neural Networks," *Cement & Concrete Composites*, 29, pp. 474-480.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

Methane oxidation and NMOCs co-oxidation in landfill bio-cover can offer effective and practical technology to reduce the harmful emissions from landfill sites to the atmosphere. Promoting biological CH_4 oxidation within the landfill bio-cover can provide a significant management practice for smaller and older landfills with lower CH_4 generation where gas extraction is not economically feasible. From the results of this research projects, it can be concluded that:

- ✓ Methane emissions from existing landfill sites and open dumps can be mitigated by methanotrophic bacteria that develop in the aerobic zone of the landfill cover.
- ✓ The type of cover medium influences the amount of methane (CH_4) that can be biologically degraded through it. Bio-covers promote conditions suitable for aerobic biological activity that would result in lower emissions of CH_4 and non-methane organic compounds (NMOCs) relative to conventional soil covers.
- ✓ The steady-state rate of CH_4 oxidation rate observed in this research was between 124 and 175 $gCH_4\ m^{-2}\ d^{-1}$, with an active oxidation zone between 50 and 200 mm in depth of the simulated bio-cover.

- ✓ Methane oxidizing bacteria can co-metabolize the NMOCs present in the landfill gas; this will add to the value of the landfill bio-cover which provides a sink for the greenhouse gases' harmful fugitive emissions.
- ✓ The results of this research revealed that NMOCs could decrease the kinetics of bacterial growth and consequently bacterial CH_4 oxidation activities. The rate at which CH_4 biologically degraded in the presence of NMOCs depended on the concentration of these organic compounds. The steady state CH_4 oxidation efficiency of the landfill bio-cover when mixed NMOCs were present along with CH_4 was reduced up to 36% of the initial steady-state CH_4 oxidation efficiency when CH_4 was flowing separately into the simulated landfill cover (LFC). The vast majority of the previous works on biological landfill cover performance were based on CH_4 alone; most of the previous researchers did not consider NMOCs presence which would have affected the reported results.
- ✓ One of the research significant outcomes was that the competition between CH_4 as the main substrate and NMOCs as the co-metabolized substrate, presumably on the enzyme methane monooxygenases (MMO) active site which caused inhibition. This competition resulted in an overall decreased transformation rates of CH_4 substrate and enzyme inhibition afterwards. The experimental data of this research best fit the uncompetitive inhibition model, which was justified by the decrease in kinetic parameters values with the increase of the chemical compound concentrations and the transformation yield factor.
- ✓ This research was the first attempt to report on controlled column experiments using a blend of CH_4 and NMOCs; the experimental setup offered a chance to

adequately simulate the landfill bio-cover system and gases mass transfer limitations.

- ✓ Methane oxidation performance is challenged by the exopolymeric substances (EPS); EPS are bacterial growth products that will be produced in the active zone of the LFC system and will limit gas diffusion into the cover pores, and therefore reduce methanotrophic activities.
- ✓ The biological oxidation of CH_4 and co-oxidation of NMOCs processes in the LFC are also challenged by temperature. The temperature was found to be the main environmental condition that would affect the oxidation rates. In the experiments conducted using the compost samples and within the tested range of temperatures, CH_4 oxidation rates were 3-5 times higher when the temperature changed from 5 to 22° C and 6-7 times higher when the temperature changed from 5 to 35° C. The significant effect of temperature is related to the type of bacteria present at different temperature levels. Only Type I methanotrophic bacteria grow at low temperatures between 3 and 10° C while both types grow at 20° C.
- ✓ The research results showed that moisture content (MC) or saturation level (S.L.) appeared to be a critical environmental condition that would affect the CH_4 oxidation potential of the LFC. Within the tested range in this research, compost with 30% S.L. showed higher oxidation rates compared to compost with 50 and 75% S.L. The same observation was noted using existing LFC soil samples; higher CH_4 oxidation rates were monitored using the soil with 20% MC compared to the samples with 25 and 30% MC. It appears that increased saturation levels affect the CH_4 and O_2 movements through the pores. Under higher moisture

conditions, CH_4 must reach the methanotrophs by aqueous diffusion, which is much slower than gas diffusion; the diffusion coefficient of CH_4 in water (1.49×10^{-9} m^2 s^{-1} at 22° C) is four orders of magnitude lower than in air (2.12×10^{-5} m^2 s^{-1} at 22° C). It is also the same for O_2 diffusion; the diffusion coefficient of O_2 in water (1.97×10^{-9} m^2 s^{-1} at 22° C) is four orders of magnitude lower than in air (2.19×10^{-5} m^2 s^{-1} at 22° C).

8.2 RECOMMENDATIONS

1- In view of the negative effects of NMOCs on the biological CH_4 oxidation process, future design, engineering and modeling of the landfill cover system should not only focus on CH_4 but also on the organic compounds found in the LFG.

2- Further microbiological studies are needed to confirm the type of inhibition in the LFC caused by NMOCs, to investigate the degradation products from the co-oxidation of NMOCs by methanotrophs and to report on kinetics parameters including the dissociation constants. Biological degradation kinetics of the primary substrate (CH_4) and co-metabolized organic compounds are of major importance for the design and implementation of the cover system. Also, kinetic parameters are significant components of fate and transport models, which are used to design, and monitor the cover on site.

3- Additional investigations should address the microbial community and their response to shifts in environmental conditions over longer timeframe, and report on the stability of the oxidation and co-oxidation processes.

4- The results of this study confirmed that compost can be incorporated into the design of LFC system to enhance the biological attenuation of CH_4 and NMOCs in LFC. However, subsequent investigations of bio-covers need to address the durability, maintenance and active life of the cover material under different environmental conditions.

5- There is a need to simulate the coupled processes of the LFC system using numerical modeling, and include NMOCs transport and oxidation, as well as their effect on CH_4 oxidation rates.

APPENDIX I

GAS CHROMATOGRAPHS USED IN THE RESEARCH

Throughout the research, analyses of different gases (CH_4, O_2 and CO_2) were carried out using Gow-Mac 400 gas chromatograph equipped with thermal conductivity detector. (Figure A-1.1).

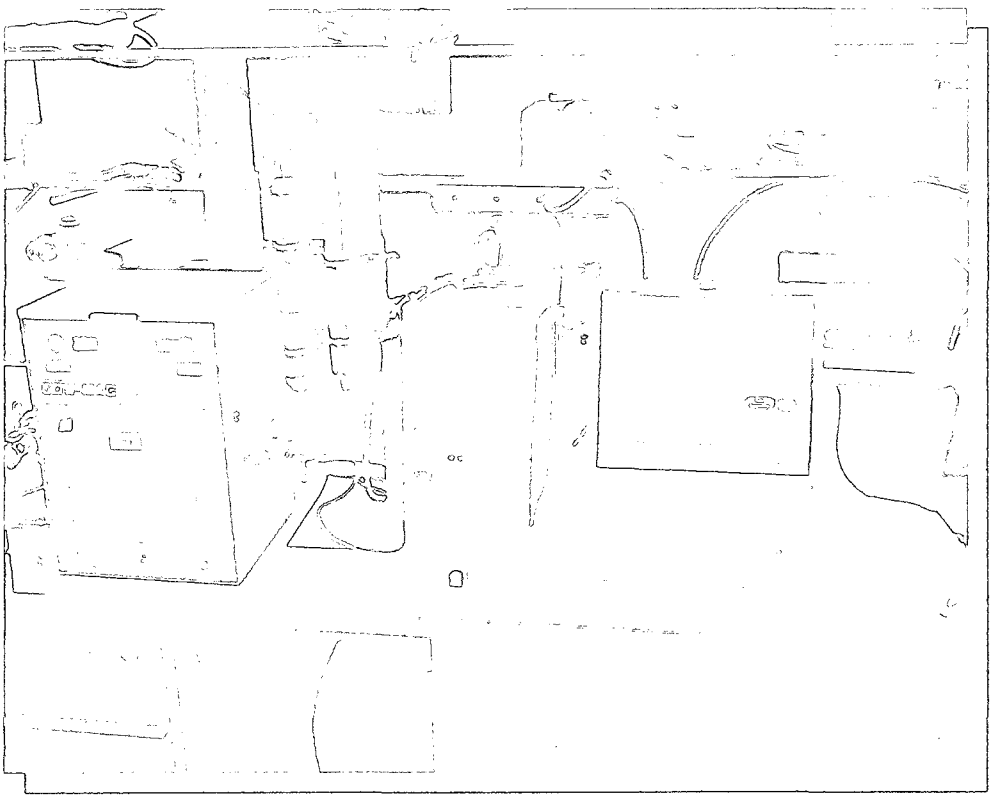


Figure A.1 Gow-Mac 400 gas chromatograph equipped with thermal conductivity detector.

The non-methane organic compounds' concentrations were analyzed using Hewlett Packard 5890 gas chromatograph equipped with electron-capture detector (ECD) shown in Figure A-1.2.

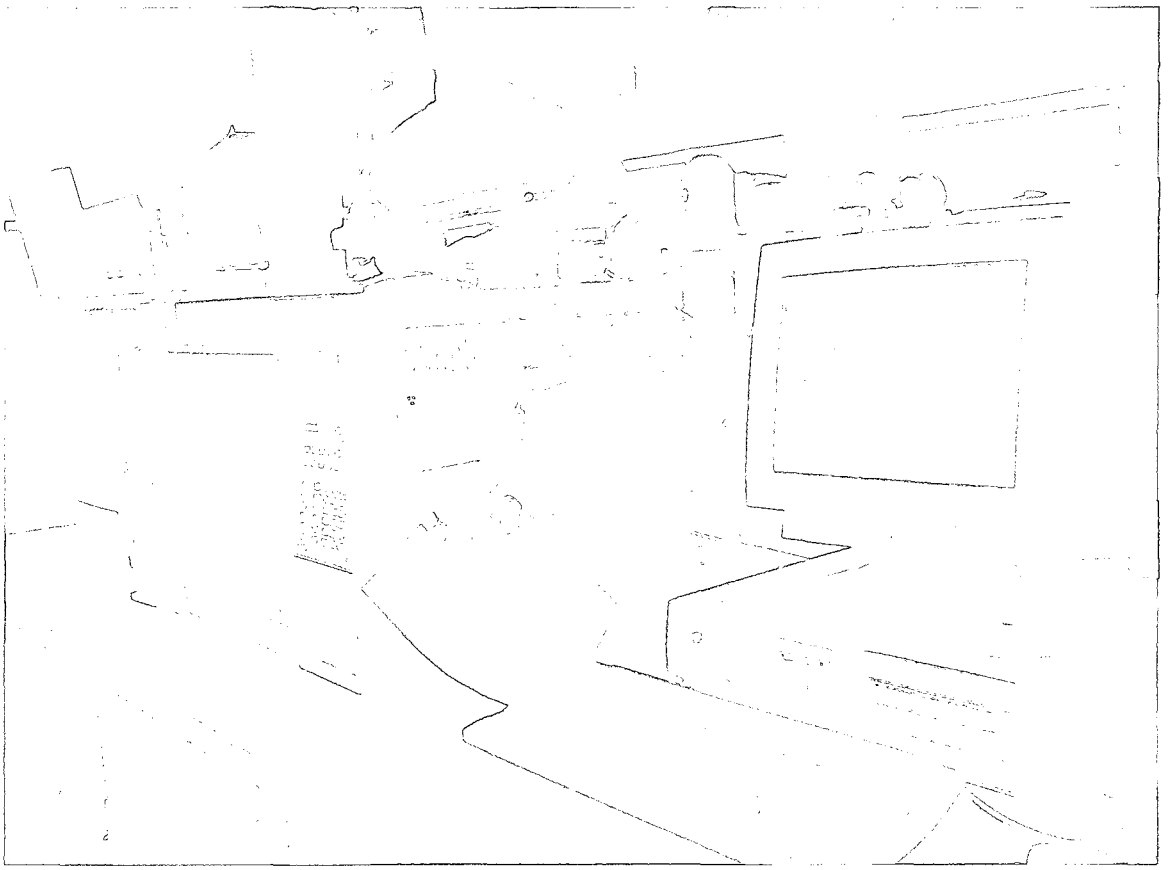


Figure A.2 Hewlett Packard 5890 gas chromatograph equipped with electron-capture detector (ECD).

APPENDIX II

EXPERIMENTAL SETUPS

The experiments to estimate the methane (CH_4) oxidation capacities of the soils and compost were conducted in standard glass bottles, each of 160 ml total volume. In each experiment, 30 g of sieved soil or compost were added to the batch reactor. After placing the soil or compost in each reactor, the glass bottle was sealed with gas tight aluminum seal and tan Teflon/silicone (PTFE) septum, which enabled gas sampling from the reactor's headspace with a gas tight needle and syringe (Figure A.3).

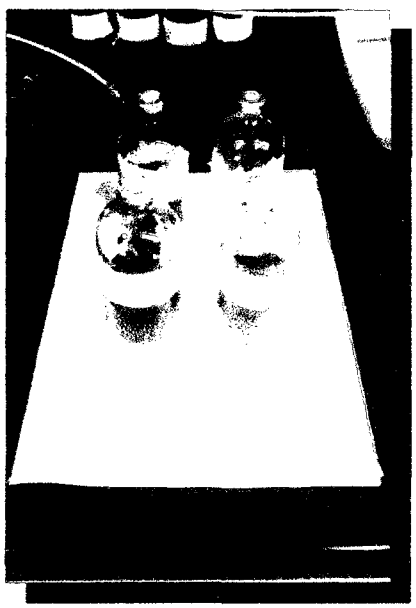


Figure A.3 Batch Reactors Experiments- Methane oxidation capacity in landfill cover soils and compost.

In the experiments where CH_4 oxidation was tested in the presence of the NMOCs, the batch reactors were closed tightly using Mininert valves with auxiliary septum seal (VICI Precision Sampling, Inc.) as shown in Figure A.4.

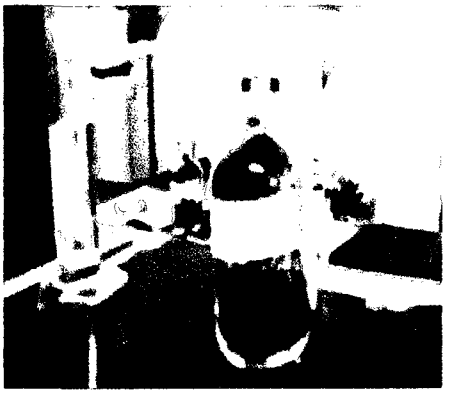


Figure A.4 Batch Reactors Experiments- Methane and non-methane organic compounds oxidation capacity in landfill bio-covers.

The compost obtained from the composting facility had not been exposed to CH_4; to ensure adequate population of methanotrophs, it was decided to acclimatize the compost by running a laboratory scale columns that contained the compost samples with three designated saturation levels (30, 50 and 75% S.L.). The columns had CH_4 inlet ports at the bottom and air inlet ports at the top to simulate the landfill cover system. Before filling the columns, the moisture content of the compost was adjusted according to the designed saturation level in each column and then the samples were packed in the columns and compacted (Figure A.5).

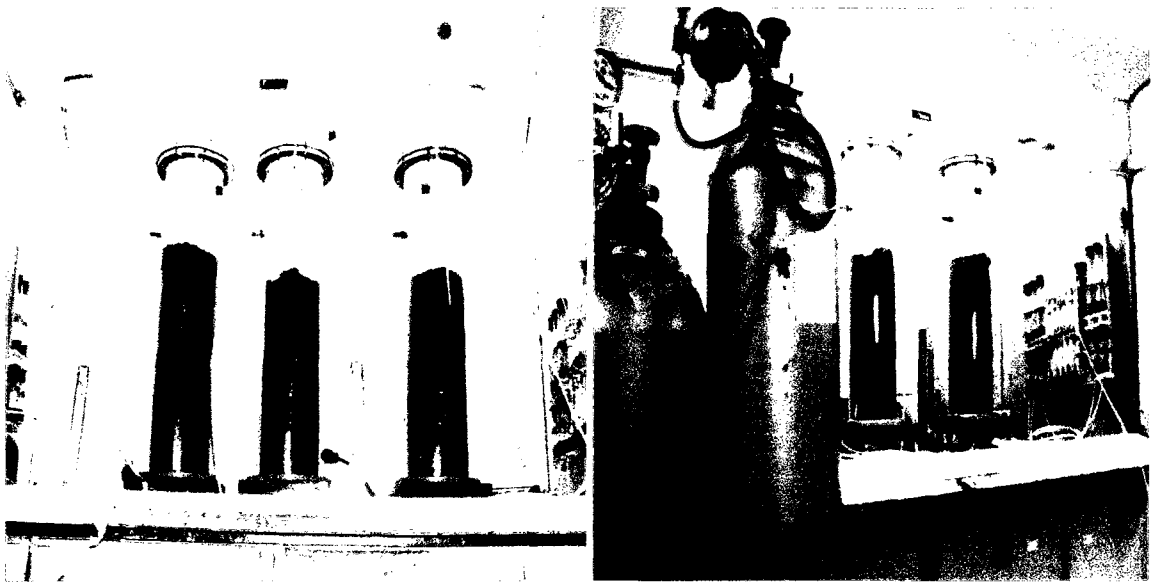


Figure A.5 Laboratory Scale Column Experiments- Columns experiments to acclimatize compost samples.

Long-term column experiments were conducted by passing fluxes of CH_4 and selected NMOCs through the bottom of the columns. Air was passing through a humidifier and then passed across the top of the column. For each experimental set, there were control and blank reactors (Figure A.6).

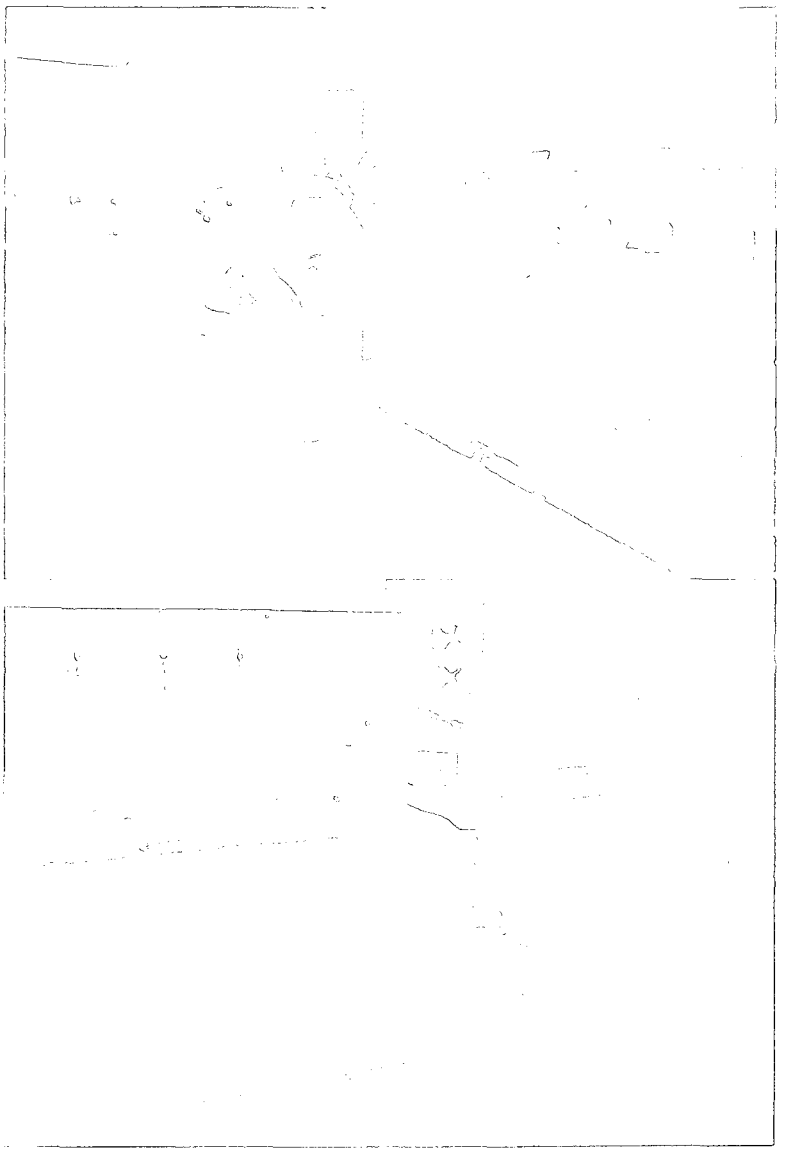


Figure A.6 Laboratory Scale Column Experiments- Methane and non-methane organic compounds oxidation in landfill bio-covers.

Aerobic methane oxidation proceeds according to the overall reaction:

$$\mathbf{CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + Heat} \qquad \mathbf{\Delta G^o (\ -780\ kJ/mol\ CH_4).}$$

Figure A.7 shows an active column.

Figure A.7 Active column

The columns were kept covered away from light in order to reduce the possibility of having other microorganisms that can compete with the methanotrophs and consequently increase the respiration rate in the compost (Figure A.8)

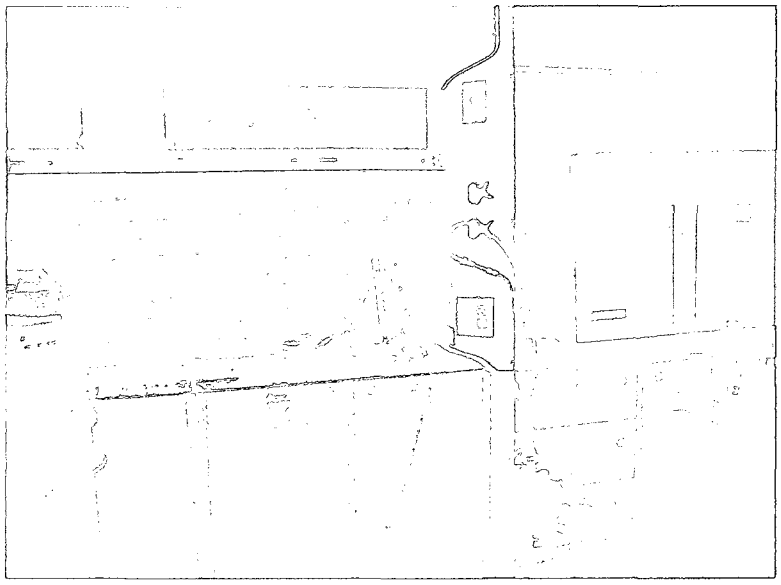


Figure A.8 Laboratory scale columns were kept covered from light.

APPENDIX III

ANALYSIS AND SAMPLE CALCULATIONS –

EFFECTS OF TEMPERATURE, MOISTURE CONTENT AND FERTILIZER ADDITION ON BIOLOGICAL METHANE OXIDATION IN LANDFILL COVER SOILS

Appendix III includes samples of raw data, detailed analysis, and statistical results for the experiments conducted and discussed in Chapter 3.

Appendix III-1 Methane reduction versus time in triplicates

Table A.1 shows as an example, CH_4 concentrations versus time in triplicate batch reactors, as well as control experiments. The example shown is for clayey silt soil samples that contained 30% MC with no added nutrients. The experiments were conducted at 22°C.

Table A.1 Methane concentrations with time in triplicates and controls using clayey silt soil with 30% MC at 22°C.

Time (hour)	CH_4 concentration in the headspace (%) → Sample 1	Sample 2	Sample 3	Control 1	Control 2
0	9.9	9.6	9.7	9.7	9.5
3	9.3	8.8	9.2	9.6	9.5
6	8.9	8.6	9.1	9.7	9.4
9	8.6	8.3	8.7	9.6	9.3
24	7.1	7.6	7.6	9.5	9.4
27	6.3	7.4	7.4	9.6	9.4
30	6.1	6.8	7	9.5	9.1
48	3.9	4.7	4.1	9.4	9.2
51	3.7	4.2	3.8	9.3	9.1
54	3.3	3.8	3.6	9.4	9.2
72	2.1	3.1	2.4	9.2	8.9
75	1.8	3	2.3	9.2	8.9
96	0.9	1.7	1.5	9.1	9
120	0.2	0.6	0.4	9.2	8.9

Appendix III-2 Methane Oxidation Rates in the Two Types of Soils

Table A.2 shows the determined CH_4 oxidation rates in the two types of soil tested with standard deviation between triplicates.

Table A.2 Methane oxidation rates in the two types of landfill cover soils.

Experimental Set Up	Clay Soil CH_4 Oxidation Rate ($\mu gCH_4\ h^{-1}g^{1}_{drysoil}$)	Clayey Silt Soil CH_4 Oxidation Rate ($\mu gCH_4\ h^{-1}g^{1}_{drysoil}$)
5C, 20% m/c, no nutrients	3.9 ± 0.2	4.7 ± 0.6
5C, 25% m/c, no nutrients	3.6 ± 2.0	3.7 ± 0.4
5C, 30% m/c, no nutrients	3.5 ± 3.4	3.3 ± 1.0
5C, 20% m/c, with nutrients	3.8 ± 2.7	4.4 ± 1.3
5C, 25% m/c, with nutrients	4.6 ± 4.0	4.7 ± 0.3
5C, 30% m/c, with nutrients	5.0 ± 3.0	8.1 ± 1.7
22° C, 20% m/c, no nutrients	6.6 ± 3.6	8.9 ± 1.4
22° C, 25% m/c, no nutrients	4.9 ± 0.2	6.0 ± 1.0
22° C, 30% m/c, no nutrients	4.1 ± 0.8	5.6 ± 0.2
22° C, 20% m/c, with nutrients	5.0 ± 1.4	6.8 ± 1.1
22° C, 25% m/c, with nutrients	6.6 ± 1.1	6.8 ± 0.6
22° C, 30% m/c, with nutrients	8.5 ± 5.6	10.3 ± 1.7
35° C, 20% m/c, no nutrients	9.3 ± 0.2	12.0 ± 1.3
35° C, 25% m/c, no nutrients	8.1 ± 1.6	9.5 ± 1.7
35° C, 30% m/c, no nutrients	7.7 ± 0.5	8.7 ± 1.8
35° C, 20% m/c, with nutrients	6.3 ± 0.4	10.1 ± 1.7
35° C, 25% m/c, with nutrients	9.6 ± 2.2	10.3 ± 1.8
35° C, 30% m/c, with nutrients	10.5 ± 3.2	12.3 ± 0.7

Appendix III-3 Multi-Factor Analysis of Variance (ANOVA)

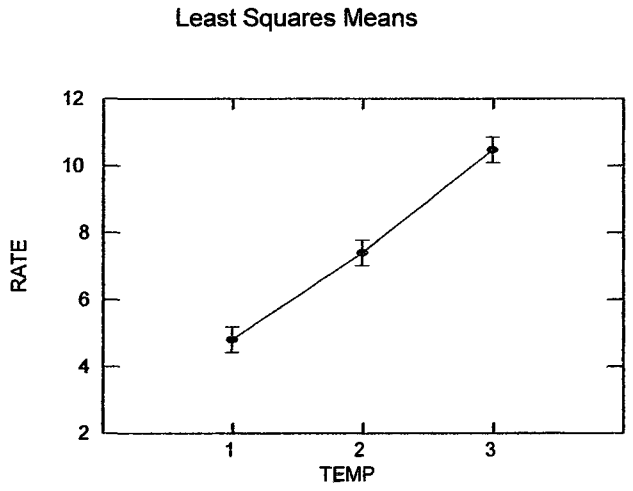
The ANOVA analysis for the results presented in Chapter 3 was carried out using SYSTAT 11. The detailed results were:

```
Categorical values encountered during processing are:
TEMP (3 levels)
          1,        2,        3
MC (3 levels)
          1,        2,        3
NUTRIENTS (2 levels)
          1,        2

Dep Var: RATE   N: 54   Multiple R: 0.901   Squared multiple R: 0.812

Analysis of Variance
```

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
TEMP	290.133	2	145.067	54.625	0.000
MC	14.935	2	7.468	2.812	0.073
NUTRIENTS	22.532	1	22.532	8.485	0.006
TEMP*MC	5.442	4	1.360	0.512	0.727
TEMP*NUTRIENTS	2.521	2	1.260	0.475	0.626
MC*NUTRIENTS	75.378	2	37.689	14.192	0.000
TEMP*MC*NUTRIENTS	1.778	4	0.444	0.167	0.954
Error	95.604	36	2.656		

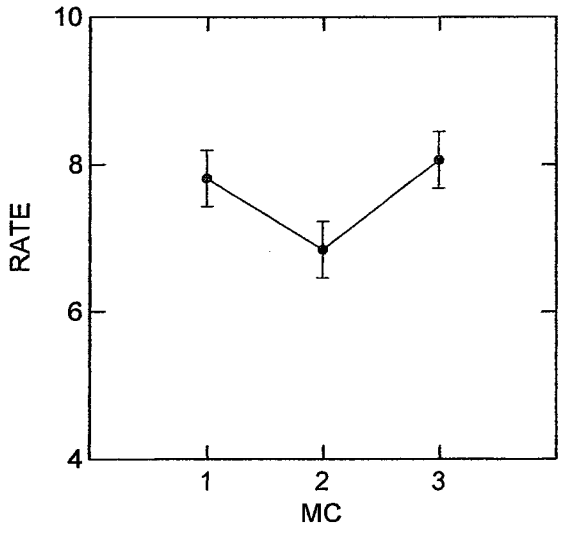
Least squares means

		LS Mean	SE	N
TEMP	1	4.827	0.384	18
TEMP	2	7.419	0.384	18
TEMP	3	10.498	0.384	18



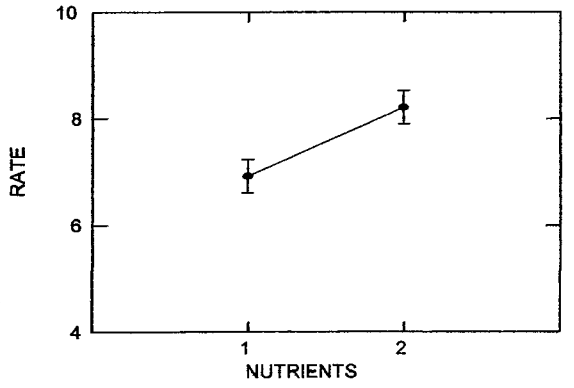
MC	1	7.820	0.384	18
MC	2	6.852	0.384	18
MC	3	8.072	0.384	18

Least Squares Means



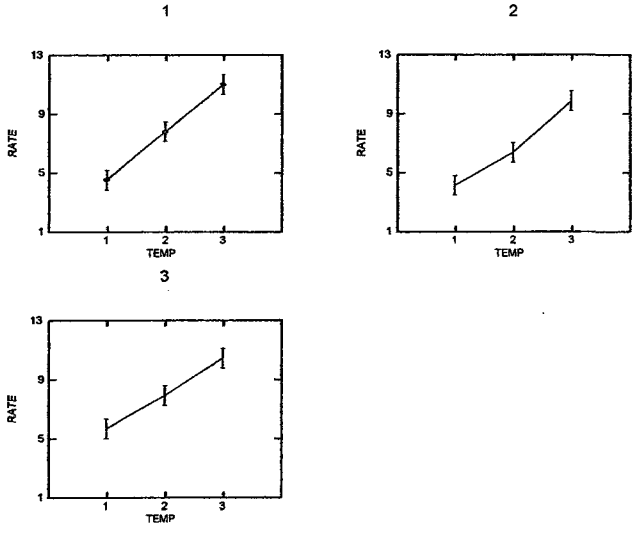
NUTRIENTS	1	6.935	0.314	27
NUTRIENTS	2	8.227	0.314	27

Least Squares Means



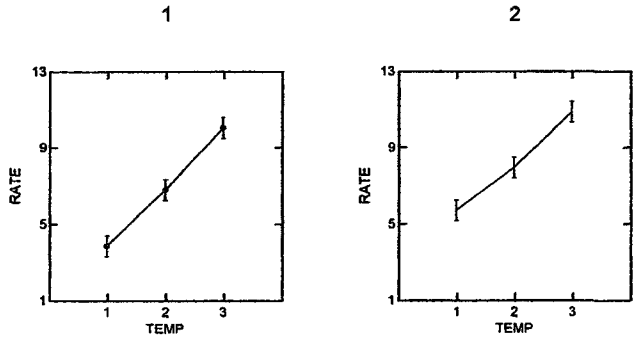
TEMP	1			
MC	1	4.556	0.665	6
TEMP	1			
MC	2	4.199	0.665	6
TEMP	1			
MC	3	5.725	0.665	6
TEMP	2			
MC	1	7.850	0.665	6
TEMP	2			
MC	2	6.424	0.665	6
TEMP	2			
MC	3	7.982	0.665	6
TEMP	3			
MC	1	11.053	0.665	6
TEMP	3			
MC	2	9.932	0.665	6
TEMP	3			
MC	3	10.508	0.665	6

Least Squares Means



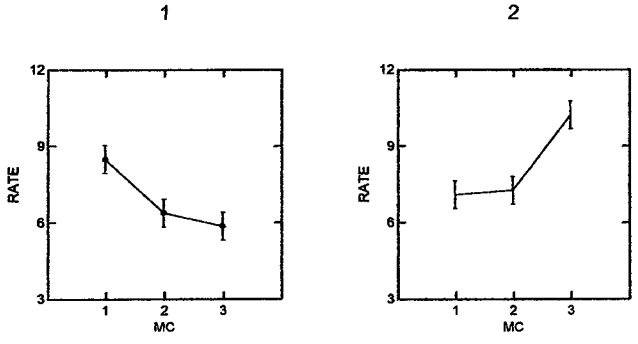
TEMP	1			
NUTRIENTS	1	3.890	0.543	9
TEMP	1			
NUTRIENTS	2	5.764	0.543	9
TEMP	2			
NUTRIENTS	1	6.837	0.543	9
TEMP	2			
NUTRIENTS	2	8.001	0.543	9
TEMP	3			
NUTRIENTS	1	10.078	0.543	9
TEMP	3			
NUTRIENTS	2	10.917	0.543	9

Least Squares Means



MC	1			
NUTRIENTS	1	8.510	0.543	9
MC	1			
NUTRIENTS	2	7.129	0.543	9
MC	2			
NUTRIENTS	1	6.406	0.543	9
MC	2			
NUTRIENTS	2	7.298	0.543	9
MC	3			
NUTRIENTS	1	5.889	0.543	9
MC	3			
NUTRIENTS	2	10.255	0.543	9

Least Squares Means



TEMP	1			
MC	1			
NUTRIENTS	1	4.673	0.941	3
TEMP	1			
MC	1			
NUTRIENTS	2	4.439	0.941	3
TEMP	1			
MC	2			
NUTRIENTS	1	3.664	0.941	3
TEMP	1			
MC	2			
NUTRIENTS	2	4.735	0.941	3
TEMP	1			
MC	3			
NUTRIENTS	1	3.333	0.941	3
TEMP	1			
MC	3			
NUTRIENTS	2	8.117	0.941	3
TEMP	2			
MC	1			
NUTRIENTS	1	8.867	0.941	3
TEMP	2			
MC	1			
NUTRIENTS	2	6.833	0.941	3
TEMP	2			
MC	2			
NUTRIENTS	1	6.006	0.941	3
TEMP	2			
MC	2			
NUTRIENTS	2	6.842	0.941	3
TEMP	2			
MC	3			
NUTRIENTS	1	5.638	0.941	3
TEMP	2			
MC	3			
NUTRIENTS	2	10.327	0.941	3
TEMP	3			
MC	1			
NUTRIENTS	1	11.991	0.941	3
TEMP	3			
MC	1			
NUTRIENTS	2	10.115	0.941	3
TEMP	3			
MC	2			
NUTRIENTS	1	9.548	0.941	3

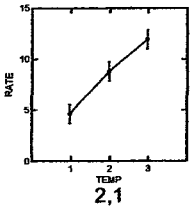
TEMP	3			
MC	2			
NUTRIENTS	2	10.317	0.941	3

TEMP	3			
MC	3			
NUTRIENTS	1	8.697	0.941	3

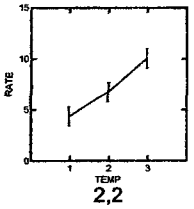
TEMP	3			
MC	3			
NUTRIENTS	2	12.320	0.941	3

Least Squares Means

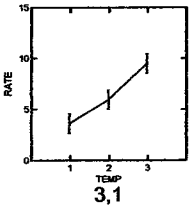
1,1



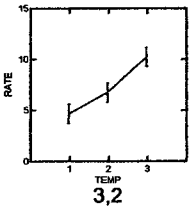
1,2



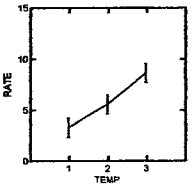
2,1



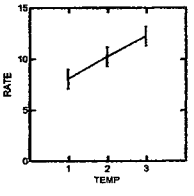
2,2



3,1



3,2



Appendix III-4 Mathematical Description

The details of the mathematical description presented in Chapter 3 using SYSTAT 11 were as follows:

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\Journal Paper2 - revision.syd, created Sat Sep 27, 2008 at 17:45:12, contains variables:
RATE TEMP MC NUTRIENTS

Dependent variable is CH4 OXIDATION RATE

Source	Sum-of-Squares	df	Mean-Square
Regression	3497.286	8	437.161
Residual	114.596	46	2.491
Total	3611.882	54	
Mean corrected	508.324	53	

Raw R-square (1-Residual/Total) = 0.968
Mean corrected R-square (1-Residual/Corrected) = 0.775
R(observed vs predicted) square = 0.775

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper
B0	4.353	4.755	0.916	-5.217 13.923
B1	4.829	2.201	2.194	0.399 9.259
B2	-2.966	2.201	-1.348	-7.397 1.464
B3	-2.939	3.007	-0.977	-8.992 3.114
B12	-0.609	1.019	-0.597	-2.659 1.442
B13	-0.758	1.392	-0.544	-3.560 2.044
B23	2.633	1.392	1.892	-0.169 5.435
B123	0.120	0.644	0.186	-1.177 1.417

Case	CH4 OXIDATION RATE Observed	CH4 OXIDATION RATE Predicted	Residual
1	4.976	4.663	0.313
2	3.379	3.841	-0.462
3	2.300	3.019	-0.719
4	3.180	3.719	-0.539
5	4.471	5.650	-1.179
6	10.796	7.582	3.214
7	8.252	8.246	0.006
8	6.754	6.935	-0.181
9	5.735	5.625	0.110
10	6.612	6.664	-0.052
11	6.225	8.227	-2.002
12	10.860	9.790	1.070
13	11.220	11.828	-0.608
14	10.644	10.029	0.615
15	11.200	8.230	2.970
16	8.696	9.609	-0.913
17	9.370	10.804	-1.434
18	13.040	11.998	1.042
19	4.000	4.663	-0.663
20	3.425	3.841	-0.416
21	3.500	3.019	0.481
22	4.440	3.719	0.721
23	4.742	5.650	-0.908
24	9.656	7.582	2.074

25	10.892	8.246	2.646
26	6.437	6.935	-0.498
27	5.400	5.625	-0.225
28	5.836	6.664	-0.828
29	6.870	8.227	-1.357
30	12.220	9.790	2.430
31	13.440	11.828	1.612
32	7.580	10.029	-2.449
33	7.590	8.230	-0.640
34	9.672	9.609	0.063
35	8.150	10.804	-2.654
36	12.239	11.998	0.241
37	5.044	4.663	0.381
38	4.187	3.841	0.346
39	4.200	3.019	1.181
40	5.696	3.719	1.977
41	4.992	5.650	-0.658
42	3.900	7.582	-3.682
43	7.456	8.246	-0.790
44	4.825	6.935	-2.110
45	5.780	5.625	0.155
46	8.052	6.664	1.388
47	7.430	8.227	-0.797
48	7.900	9.790	-1.890
49	11.312	11.828	-0.516
50	10.420	10.029	0.391
51	7.300	8.230	-0.930
52	11.976	9.609	2.367
53	13.430	10.804	2.626
54	11.680	11.998	-0.318

Asymptotic Correlation Matrix of Parameters

	B0	B1	B2	B3	B12
B0	1.000				
B1	-0.926	1.000			
B2	-0.926	0.857	1.000		
B3	-0.949	0.878	0.878	1.000	
B12	0.857	-0.926	-0.926	-0.813	1.000
B13	0.878	-0.949	-0.813	-0.926	0.878
B23	0.878	-0.813	-0.949	-0.926	0.878
B123	-0.813	0.878	0.878	0.857	-0.949

	B13	B23	B123
B13	1.000		
B23	0.857	1.000	
B123	-0.926	-0.926	1.000

Appendix III-5 Clay Soil Characteristics

Dry Bulk Density

The dried bulk density of the clay soil was conducted by drying a certain amount of the clay in bulk as obtained from the site for 24 hours. Then the sample was weighed to get the dry weight, which was (23.65) g.

The volume was obtained by immersing the bulk dried weight with was, and then the waxed bulk was put in water, and the volume of the displaced water was calculated. The water displacement was 20 cm. The calculations were as follows:

Weight of the waxed bulk clay = 30.079 g

Weight of wax= 30.079 – 23.65 = 6.42 g.

Volume of wax = weight of wax/density of wax = 6.42/0.85 = 7.55 cm^3.

Volume of soil = Total volume displaced – Volume of wax = 12.45 cm^3.

Dry bulk density = Weight of dry sample / Volume of dry sample= 23.02/12.45=

1.9 g/cm^3 or 1900 kg/m^3.

Porosity

- $\delta_{dry} = \frac{G}{1+e}$

- where: G is the specific gravity, e is the voids ration.

- 1.9 = 2.63/ (1+e)

- e = 0.384

- Porosity = e/ (1+e)

- **Porosity = 0.277**

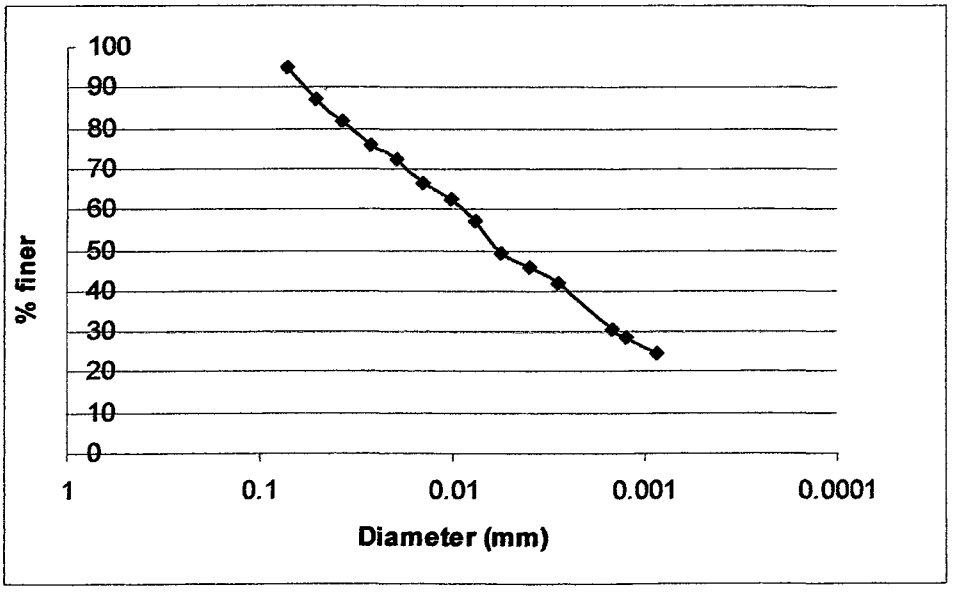
Hydrometer Test (Grain Size Analysis)

To obtain the grain size, the hydrometer test was conducted according to ASTM D 422.

The following results were obtained and analyzed.

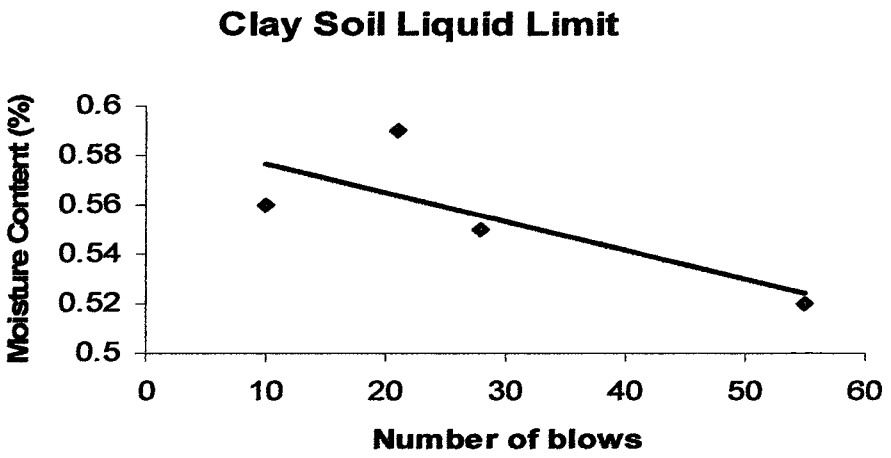
Time (min)	Hydrometer Reading	Corrected Hydrometer Reading	%finer	Correction for meniscus	Effective Length	Length/time	K	Diameter
0	60	53	**100.7**	59	7.6			
0.25	57	50	**95**	56	7.9	31.6	0.013	**0.073078**
0.5	53	46	**87.4**	52	8.1	16.2	0.013	**0.052324**
1	50	43	**81.7**	49	8.4	8.4	0.013	**0.037678**
2	47	40	**76**	46	8.8	4.4	0.013	**0.027269**
4	45	38	**72.2**	44	9.2	2.3	0.013	**0.019715**
8	42	35	**66.5**	41	9.6	1.2	0.013	**0.014241**
16	40	33	**62.7**	39	10.1	0.631	0.013	**0.010329**
30	37	30	**57**	36	10.6	0.353	0.013	**0.007727**
60	33	26	**49.4**	32	10.9	0.182	0.013	**0.005541**
120	31	24	**45.6**	30	11.2	0.093	0.013	**0.003972**
240	29	22	**41.8**	28	11.5	0.048	0.013	**0.002846**
960	23	16	**30.4**	22	12.5	0.013	0.013	**0.001483**
1380	22	15	**28.5**	21	12.7	0.009	0.013	**0.001247**
2880	20	13	**24.7**	19	13	0.004	0.013	**0.000873**

The % finer were plotted against the diameter for each reading and the following curve was obtained:



Clay Soil Liquid Limit Calculations:

The liquid limit test was conducted according to ASTM D 4318. For each sample the number of blows was calculated and then the moisture content for each sample was estimated. The numbers of blows versus the moisture content were plotted and the reading on the number 25 blow was estimated as the liquid limit, according to the following graph.



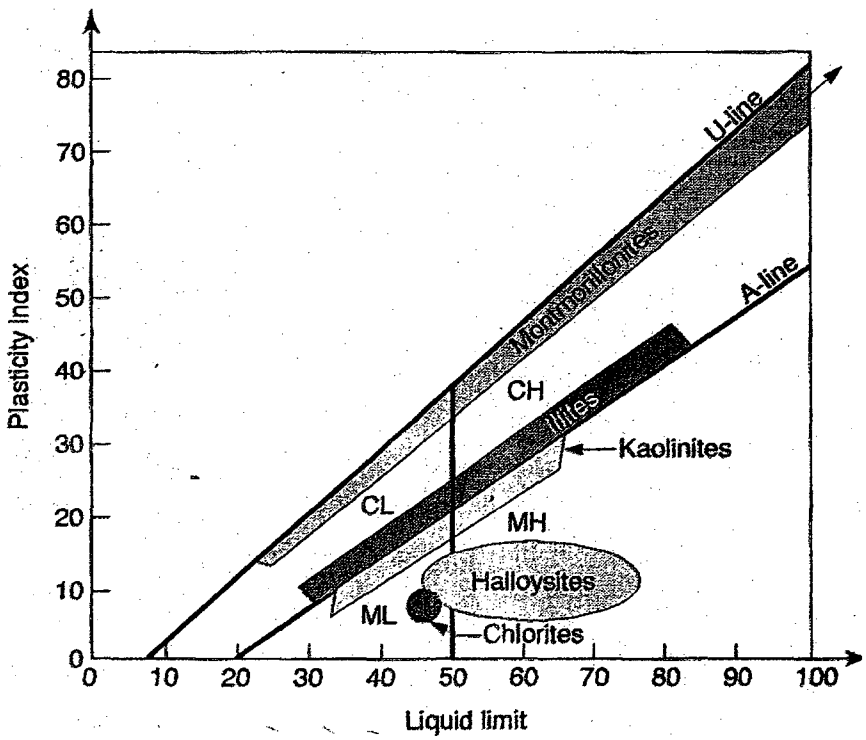
Plastic Limit

Plastic limit experiment was conducted according to ASTM D 4318, and was estimated as follows:

PL= 0.55g/2.23g = 0.25 = 25%.

Type of Clay

Based on the laboratory experiments' results, and according to the following plasticity characteristics (adapted from Day 2001), the clay soil was characterized as "inactive Illites clay".



Plasticity Characteristics of Common Clay Minerals (Adapted from Day 2001)

APPENDIX IV

ANALYSIS AND SAMPLE CALCULATIONS –

CAPACITY FOR BIOLOGICAL METHANE OXIDATION IN DIFFERENT TYPES OF SOILS AND COMPOST

Appendix IV includes examples of raw data, detailed analysis for the experiments conducted and discussed in Chapter 4.

Appendix IV-1 Raw Data - Methane concentrations versus time in the triplicates under different conditions.

	Clay Soil			Clayey Silt Soil			Compost		
	Time (hour)	CH_4 concentration in the headspace (%)							
5°C, MC level 1		S1	S2	S3	S1	S2	S3	S1	S2	S3
	0	9.4	9.2	9.3	9.7	9.5	9.3	9.2	9.3	9.5
	3	9.1	8.8	8.8	8.2	9.7	9.1	9.1	9.3	9.4
	6	9.2	8.7	8.5	7.9	9.1	8.6	9	9.3	9.4
	9	8.8	8.3	7.6	7.7	8.8	8.4	9	9.1	9.2
	24	6.5	6.6	3.2	4.5	7.2	4.8	5.2	5.4	5.6
	27	6.3	6.5	3	3.8	6.8	4.3	4.9	4.8	5.2
	30	5.9	5.9	2.6	3.6	6.6	4.1	4.7	4.5	4.7
	48	4	3.4	1.1	2.3	4.3	2.3	3.1	3.3	3.1
	51	3.7	3.2	0.9	1.8	4.1	1.9	2.8	2.9	3
	54	3.5	3	0.5	1.5	3.7	1.8	2.2	2.1	2.7
	72	2.7	1.9	0	0.9	2.5	0.5	1.9	1.7	2.4
	75	2.6	1.8	0	0.8	1.8	0.3	0.8	0.7	1.6
	96	1.7	1.1	0	0	0.7	0	0	0	0.9
	120	0.5	0.6	0	0	0	0	0	0	0

5°C, MC level 2	Time (hour)	Clay Soil			Clayey Silt Soil			Compost		
		CH_4 concentration in the headspace (%)								
		S1	S2	S3	S1	S2	S3	S1	S2	S3
	0	9.3	9.7	9.5	9.3	9.6	9.3	9.8	8.9	9.9
	3	7.8	9.4	8.6	9.1	9.4	7.8	9.7	8.9	9.7
	6	7.2	9.5	8.4	8.8	8.8	7.3	9.6	8.7	9.7
	9	6.8	9.4	8.1	8.6	8.7	6.8	9.5	8.5	9.4
	24	5.4	9.2	7.3	7.4	6.5	5.4	5.4	4.8	5.2
	27	4.8	9	6.9	6.7	6.1	4.8	5.1	4.7	5
	30	4.3	8.8	6.6	6.1	6	4.1	5	4.5	4.7
	48	3	8	5.5	4.1	4.6	3	3.4	2.9	3.1
	51	2.6	7.9	5.3	3.9	4.3	2.6	3.3	2.7	3
	54	2.2	7.9	5.1	3.8	3.8	2.3	3.1	2.4	2.7
	72	1.4	7.4	4.4	2.7	2.8	1.4	2.6	1.9	2.4
	75	1.3	7.3	4.3	2.4	2.5	1.4	2.5	1.9	2.2
	96	1	7	4	1.4	1.1	1	1.1	0.6	1.3
	120	0.4	6.3	3.4	0.4	0.2	0.4	0	0	0

	Clay Soil			Clayey Silt Soil			Compost		
	Time (hour)	CH_4 concentration in the headspace (%)							
5°C, MC level 3		S1	S2	S3	S1	S2	S3	S1	S2	S3
	0	9.4	9	9.2	10.3	9.9	9.4	9.6	9.8	9
	3	7.2	8.7	8	9.5	9.4	9.1	9.6	9.7	9.0
	6	6.8	8.3	7.6	9.1	8.9	8.4	9.2	9.2	8.8
	9	6.5	8.2	7.4	8.6	8.7	8.2	9.0	9.1	8.5
	24	2.5	8	5.3	7.2	7.7	5.3	8.1	8.4	7.1
	27	2.2	8	5.1	6.8	7.4	4.7	7.7	8.1	6.8
	30	1.7	7.9	4.8	6.6	7.2	4.2	7.4	7.9	6.6
	48	1.1	7.8	4.5	3.8	6.1	3.1	5.7	6.1	5.3
	51	0.8	7.6	4.2	3.2	5.4	2.8	5.5	5.9	5.1
	54	0.7	7.7	4.2	3.1	5.1	2.6	4.3	4.5	4.8
	72	0.2	6.6	3.4	1.9	3.5	1.6	3.7	4.2	2.8
	75	0	6.5	3.3	1.7	3.3	1.3	3.4	3.9	2.6
	96	0	6.3	3	0.8	2.2	0.7	1.7	1.4	1.1
	120	0	6.7	2.7	0.3	1.3	0.1	0.8	0.6	0.4

	Clay Soil			Clayey Silt Soil			Compost		
	Time (hour)	CH_4 concentration in the headspace (%)							
22°C, MC level 1		S1	S2	S3	S1	S2	S3	S1	S2	S3
	0	9.4	9.6	9.4	9.3	9.4	9.5	9.5	9.1	9.7
	3	9.6	8.8	9	9.2	9.1	9.2	8	8.2	8.9
	6	9.4	7.2	8.7	8.6	9	8.4	6.2	5.9	7.2
	9	9.3	6.3	8.5	8.1	8.6	7.9	2.5	2.1	2.7
	24	9.1	2.7	6.6	5	4.7	5.6	0.9	0.7	1.1
	27	8.8	1.8	6.3	4.3	2.2	4.8	0.2	0.5	0.7
	30	8.7	1.5	5.5	3.1	1.5	3.5	0	0.1	0.3
	48	6.5	0	2.1	0.1	0	0	0	0	0
	51	6.2	0	1.9	0	0	0	0	0	0
	54	6.1	0	1.9	0	0	0	0	0	0
	72	5.8	0	1.5	0	0	0	0	0	0
	75	5.5	0	1.1	0	0	0	0	0	0
	96	4.6	0	0	0	0	0	0	0	0
	120	3.7	0	0	0	0	0	0	0	0

		Clay Soil			Clayey Silt Soil			Compost		
	Time (hour)	CH_4 concentration in the headspace (%)								
22°C, MC level 2		S1	S2	S3	S1	S2	S3	S1	S2	S3
	0	9.6	9.6	9.3	9.5	9.4	9.3	9.2	9.3	10.2
	3	8.5	9.3	9.5	9.5	9.3	9.1	8.3	8.6	9.3
	6	8.1	9.1	9.1	8.5	8.8	8.7	6.6	6.3	8.6
	9	7.5	8.7	8.6	7.8	8.5	8.1	4.9	4.5	7.1
	24	4.9	6.7	6.7	5.7	7.7	6.1	1.4	1.2	1.8
	27	4.6	6.6	6.7	5.7	6.4	5.8	0.7	0.6	1.3
	30	3.9	6.5	6.2	4.2	5.9	5.5	0.4	0.5	0.9
	48	2.5	4.7	4.6	1.8	2.1	3.2	0	0	0
	51	2	4.2	4.3	1.4	1.7	3.1	0	0	0
	54	1.7	3.9	4.1	0.8	1.4	2.7	0	0	0
	72	0.5	3.1	3.3	0	0	1.5	0	0	0
	75	0.2	3	3	0	0	0.5	0	0	0
	96	0	2.1	2.3	0	0	0	0	0	0
	120	0	1.3	1.7	0	0	0	0	0	0

		Clay Soil			Clayey Silt Soil			Compost		
	Time (hour)	CH_4 concentration in the headspace (%)								
22°C, MC level 3		S1	S2	S3	S1	S2	S3	S1	S2	S3
	0	9.5	9.1	9.2	9.9	9.6	9.7	10.2	10.6	9.5
	3	8.9	8.7	8.5	8.8	8.8	9.2	9.6	10	9
	6	8.6	8.1	8	8.9	8.6	9.1	8.6	8.8	8
	9	8.5	7.7	8.1	8.6	8.3	8.7	7.1	7.7	6.4
	24	7.6	4	7.7	7.1	7.8	8.4	2.5	2.9	1.8
	27	7.3	3.8	7.5	6.3	7.4	8.1	2.1	2.5	1.5
	30	7.2	3.3	7.4	6.1	6.8	7	1.6	1.9	1.2
	48	6.7	2.2	7.1	5.4	4.7	4.1	0	0	0
	51	6.7	1.9	6.9	3.7	3.9	3.8	0	0	0
	54	6.4	1.7	6.8	3.3	3.8	3.6	0	0	0
	72	6	0.8	6	2.1	3.1	2.4	0	0	0
	75	5.7	0.5	6	1.8	3	2.3	0	0	0
	96	4.9	0	5.6	0.9	1.7	1.5	0	0	0
	120	4.8	0	4.5	0.2	0.6	0.4	0	0	0

		Clay Soil			Clayey Silt Soil			Compost		
	Time (hour)	CH_4 concentration in the headspace (%)								
35°C, MC level 1		S1	S2	S3	S1	S2	S3	S1	S2	S3
	0	9.4	9.6	9.8	9.5	9.4	9.2	9.3	9.5	9.5
	3	9	9.3	9.5	8.7	9.1	8.2	7.5	6.3	6.2
	6	8.8	8.9	9	5.4	8.7	6.1	4.8	3.4	3.8
	9	8.5	8.7	8.8	2.3	2.9	3.4	3.2	1.9	2.1
	24	7.8	7.8	7.7	0.6	1.1	1.6	1.9	0.5	0.9
	27	7.3	7.4	7.4	0.2	0.4	0.9	0	0	0
	30	7	7.2	7.3	0	0.1	0.2	0	0	0
	48	5.6	5.8	6	0	0	0	0	0	0
	51	5.1	5.5	5.8	0	0	0	0	0	0
	54	5	5.3	5.5	0	0	0	0	0	0
	72	4.1	4.5	4.8	0	0	0	0	0	0
	75	3.8	4.2	4.6	0	0	0	0	0	0
	96	3.4	3.8	4.1	0	0	0	0	0	0
	120	2.1	2.6	3.1	0	0	0	0	0	0

		Clay Soil			Clayey Silt Soil			Compost		
	Time (hour)	CH_4 concentration in the headspace (%)								
35°C, MC level 2		S1	S2	S3	S1	S2	S3	S1	S2	S3
	0	9.4	9	9.7	9.5	9.2	9.1	10.9	9.5	9.8
	3	8.5	7.9	9	9.3	9	8.6	7.5	6.3	6.5
	6	7.9	7.3	8.4	9.3	8.9	7.3	4.8	3.4	3.8
	9	7.3	6.6	8	8.9	8.3	6.6	3.3	1.1	0.9
	24	5	3.7	6.2	3.4	4.2	2.6	0	0	0
	27	4.3	2.8	5.8	3.5	3.9	1.9	0	0	0
	30	3.5	2.1	4.9	2.1	3.2	1.6	0	0	0
	48	2	1	2.9	0	0.6	0	0	0	0
	51	1.6	0.7	2.5	0	0.3	0	0	0	0
	54	1.2	0.3	2.1	0	0	0	0	0	0
	72	0.8	0	1.5	0	0	0	0	0	0
	75	0.6	0	1.1	0	0	0	0	0	0
	96	0.4	0	0.8	0	0	0	0	0	0
	120	0	0	0	0	0	0	0	0	0

	Clay Soil			Clayey Silt Soil			Compost		
	Time (hour)	CH_4 concentration in the headspace (%)							
35°C, MC level 3		S1	S2	S3	S1	S2	S3	S1	S2	S3
	0	9.2	9.5	9.7	9.5	9.8	9.9	9.2	9.7	9.2
	3	8.3	8.1	8.6	7.9	9.1	8.2	7	6.9	6.5
	6	7.6	6.9	8.2	7	8.3	6.9	4.6	4.4	4
	9	6.5	4.8	7.7	6.8	8.1	6.4	2.4	2.7	2.2
	24	3.9	2.4	5.2	4.7	5.2	4.5	0	0	0
	27	3.5	1.9	4.9	1.2	4.5	3.9	0	0	0
	30	3.2	1.1	4.2	0.8	3.9	3.2	0	0	0
	48	2.2	0	3.3	0	1.1	0.8	0	0	0
	51	2	0	3.1	0	0.7	0.4	0	0	0
	54	1.7	0	2.8	0	0.4	0	0	0	0
	72	1.3	0	2.6	0	0	0	0	0	0
	75	0.5	0	2	0	0	0	0	0	0
	96	0	0	1.5	0	0	0	0	0	0
	120	0	0	0.4	0	0	0	0	0	0

Appendix IV-2 Methane Oxidation Rates in Triplicates under different conditions.

Cover medium levels: (1) Clay, (2), clayey silt and (3) Compost

Temperature Levels: (1) 5°C, (2) 22°C and (3) 35°C.

Moisture Content Levels: (1) 20% w/w for soils, 57% for compost,

(2) 25% w/w for soils, 100% for compost,

(3) 30% w/w for soils, 142% for compost.

Table A.1 Methane oxidation rates under different levels of tested environmental conditions in triplicates

CH_4 Oxidation Rates ($\mu g\ CH_4\ h^{-1}\ g^{-1}_{wet\ wt.}$)	Cover Medium Levels	Temperatures Levels	MC Levels
2.97	1	1	1
3.27	1	1	2
6.43	1	1	3
3.47	1	2	1
4.03	1	2	2
2.84	1	2	3
7.94	1	3	1
6.70	1	3	2
6.29	1	3	3
3.16	1	1	1
0.97	1	1	2
0.77	1	1	3
9.00	1	2	1
3.68	1	2	2
3.85	1	2	3
7.61	1	3	1
6.60	1	3	2
5.82	1	3	3
3.52	1	1	1
4.29	1	1	2
0.77	1	1	3
4.06	1	2	1
4.10	1	2	2
2.64	1	2	3

7.73	1	3	1
6.00	1	3	2
5.60	1	3	3
4.15	2	1	1
2.70	2	1	2
1.76	2	1	3
6.88	2	2	1
5.40	2	2	2
4.40	2	2	3
9.35	2	3	1
8.51	2	3	2
8.59	2	3	3
3.33	2	1	1
2.74	2	1	2
2.68	2	1	3
9.08	2	2	1
5.15	2	2	2
4.14	2	2	3
11.20	2	3	1
7.06	2	3	2
5.82	2	3	3
4.20	2	1	1
3.35	2	1	2
3.22	2	1	3
6.21	2	2	1
3.86	2	2	2
4.43	2	2	3
8.34	2	3	1
7.32	2	3	2
5.60	2	3	3
5.57	3	1	1
4.80	3	1	2
4.66	3	1	3
27.93	3	2	1
17.35	3	2	2
11.47	3	2	3
31.97	3	3	1
29.44	3	3	2
28.03	3	3	3
5.67	3	1	1
4.99	3	1	2
4.65	3	1	3
27.89	3	2	1
16.64	3	2	2

11.09	3	2	3
37.63	3	3	1
32.38	3	3	2
26.66	3	3	3
5.70	3	1	1
4.97	3	1	2
4.27	3	1	3
27.22	3	2	1
17.51	3	2	2
11.04	3	2	3
36.97	3	3	1
35.35	3	3	2
27.17	3	3	3

Appendix IV-3 Oxygen Consumption and Carbon Dioxide Production in Original Compost (Compost's Respiration Rate)

The stability of the compost was checked and the respiration rates of the compost were measured by incubating compost samples in batch reactors with air (base on triplicates). The O_2 and CO_2 concentrations in the batch reactors were measured continuously to calculate the O_2 consumption and CO_2 production rates due to respiration. Table (A.4) shows the O_2 consumption with time at 22°C, for the original compost obtained from Trail Road composting facility. Each reading is the average of triplicates.

Table A.2 Oxygen consumption in batch reactors at 22°C, using original compost to calculate respiration rates

Time (hour)	O_2 concentration in the headspace (%)	Moles of O_2 reduction in the headspace (μmole O_2)*1	Rate of O_2 reduction (μmole O_2/ h^{-1} g^{-1} $_{wet\ wt}$) **2
0	20.9	0	0
2	20.8	6.2	0.103
3	20.6	18.6	0.207
5	19.8	68.2	0.455
9	19.2	99.2	0.367
24	18.3	161.2	0.224
48	17.3	223.2	0.155
72	16.4	279.0	0.129

Sample Calculations (between time1 = 0 hours and time2= 5 hours):

*1 - the moles of O_2 reduction in the headspace was calculated as follows:

- Percentage of O_2 reduced in the batch's headspace in 5 hours = 20.9%-19.8%= 1.1%.

- Volume of O_2 reduced = 1.1% * 0.15 L (volume of headspace gases)= 1.65×10^{-3} L.

- Convert the volume reduced to moles using Ideal gas law (PV=nRT, where R= 0.082 L.atm K^{-1} $mole^{-1}$, T= 295 K, P= 1 atm)

  O_2 moles reduced in 5 hours= 6.82×10^{-5} moles = 62.0 μmole O_2.

**2- Rate of O_2 reduction (μmole O_2/ h^{-1} $g^{-1}_{\text{wet wt}}$) = Moles reduced/ time × mass of compost sample. = 62.0 μmole O_2/ 5 hours × 30 g of wet compost sample = 0.455 μmole O_2/ h^{-1} $g^{-1}_{\text{wet wt.}}$

Table (A.5) shows the CO_2 production with time at 22°C, for the original compost obtained from Trail Road composting facility. Each reading is the average of triplicates.

Table A.3 Carbon dioxide production in batch reactors at 22°C, using original compost to calculate respiration rates.

Time (hours)	CO_2 concentration in the headspace (%)	Moles of CO_2 in the headspace (μmole O_2)	Rate of CO_2 production (μmole CO_2/ h^{-1} $g^{-1}_{\text{wet wt}}$)
0	0	0	0
2	0	0	0
3	0	0	0
5	0.8	49.6	0.330
9	1.1	68.2	0.253
24	2.0	124.0	0.172
48	2.6	161.2	0.112
72	3.3	204.63	0.095

Appendix IV-4 Empirical Models Tested to Determine Single and Multi-Parameter Interactions of CH4 Oxidation in Landfill Cover System

Model 1

81 cases and 4 variables processed and saved.

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\June2.syd,
created Tue Jun 02, 2009 at 08:32:48, contains variables:

VAR00001 VAR00002 VAR00003 VAR00004

Iteration No.	Loss	B0	B1	B2	B3
0	0.674513D+04	0.101000D+01	0.102000D+01	0.103000D+01	0.104000D+01
1	0.259184D+04	-.119029D+02	0.694254D+01	0.589057D+01	-.211235D+01
2	0.259184D+04	-.119029D+02	0.694254D+01	0.589057D+01	-.211235D+01
3	0.259184D+04	-.119029D+02	0.694254D+01	0.589057D+01	-.211235D+01

Dependent variable is OXIDATION

Source	Sum-of-Squares	df	Mean-Square
Regression	12087.176	4	3021.794
Residual	2591.840	77	33.660
Total	14679.016	81	
Mean corrected	7309.265	80	

Raw R-square (1-Residual/Total)	0.823
Mean corrected R-square (1-Residual/Corrected)	0.645
R(observed vs predicted) square	0.645

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
B0	-11.903	2.810	-4.236	-17.498	-6.308
B1	6.943	0.790	8.793	5.370	8.515
B2	5.891	0.790	7.461	4.318	7.463
B3	-2.112	0.790	-2.675	-3.684	-0.540

Case	OXIDATION Observed	OXIDATION Predicted	Residual
1	2.967	-1.182	4.149
2	3.272	-3.295	6.567
3	6.432	-5.407	11.839
4	3.473	4.708	-1.235
5	4.030	2.596	1.434
6	2.837	0.484	2.353
7	7.940	10.599	-2.659
8	6.699	8.487	-1.788
9	6.287	6.374	-0.088

10	3.160	-1.182	4.342
11	0.970	-3.295	4.265
12	0.774	-5.407	6.180
13	9.000	4.708	4.292
14	3.687	2.596	1.091
15	3.856	0.484	3.373
16	7.607	10.599	-2.992
17	6.600	8.487	-1.887
18	5.819	6.374	-0.555
19	3.521	-1.182	4.703
20	4.292	-3.295	7.587
21	0.767	-5.407	6.174
22	4.063	4.708	-0.645
23	4.100	2.596	1.504
24	2.645	0.484	2.161
25	7.733	10.599	-2.866
26	6.000	8.487	-2.487
27	5.597	6.374	-0.778
28	4.147	5.760	-1.614
29	2.703	3.648	-0.945
30	1.763	1.536	0.228
31	6.877	11.651	-4.774
32	5.403	9.539	-4.135
33	4.397	7.426	-3.029
34	9.350	17.542	-8.192
35	8.515	15.429	-6.914
36	8.587	13.317	-4.730
37	3.333	5.760	-2.427
38	2.740	3.648	-0.908
39	2.683	1.536	1.148
40	9.077	11.651	-2.574
41	5.150	9.539	-4.389
42	4.140	7.426	-3.286
43	11.200	17.542	-6.342
44	7.064	15.429	-8.365
45	5.819	13.317	-7.498
46	4.203	5.760	-1.557
47	3.350	3.648	-0.298
48	3.220	1.536	1.684
49	6.213	11.651	-5.438
50	3.860	9.539	-5.679
51	4.431	7.426	-2.995
52	8.336	17.542	-9.206
53	7.317	15.429	-8.112
54	5.597	13.317	-7.720
55	5.570	12.703	-7.133
56	4.800	10.591	-5.791
57	4.660	8.478	-3.818
58	27.933	18.593	9.340
59	17.353	16.481	0.872
60	11.467	14.369	-2.902
61	31.967	24.484	7.483
62	29.443	22.372	7.072
63	28.027	20.259	7.767
64	5.670	12.703	-7.033
65	4.993	10.591	-5.597
66	4.650	8.478	-3.828
67	27.890	18.593	9.297
68	16.640	16.481	0.159
69	11.090	14.369	-3.279
70	37.633	24.484	13.149
71	32.380	22.372	10.008
72	26.663	20.259	6.404

73	5.700	12.703	-7.003
74	4.967	10.591	-5.624
75	4.267	8.478	-4.212
76	27.223	18.593	8.630
77	17.507	16.481	1.026
78	11.043	14.369	-3.325
79	36.967	24.484	12.483
80	35.350	22.372	12.978
81	27.170	20.259	6.911

Asymptotic Correlation Matrix of Parameters

	B0	B1	B2	B3
B0	1.000			
B1	-0.562	1.000		
B2	-0.562	0.000	1.000	
B3	-0.562	0.000	0.000	1.000

Model 2

Iteration
No. Loss B0 B1 B2 B3 B4
B5 B6 B7

0 0.488587D+04 0.101000D+01 -.102000D+00 0.103000D+01 -.104000D+00
0.105000D+01
-.106000D+00 0.107000D+01 -.108000D+00
1 0.126293D+04 0.766188D+01 -.451282D+01 -.731020D+01 -.439399D+00
0.105000D+01
0.638686D+01 0.872709D+00 -.854592D+00
2 0.126293D+04 0.766188D+01 -.451282D+01 -.731021D+01 -.439399D+00
0.105000D+01
0.638686D+01 0.872709D+00 -.854592D+00
3 0.126293D+04 0.766188D+01 -.451282D+01 -.731021D+01 -.439399D+00
0.105000D+01
0.638686D+01 0.872709D+00 -.854592D+00

Dependent variable is OXIDATION

Source	Sum-of-Squares	df	Mean-Square
Regression	13416.088	8	1677.011
Residual	1262.929	74	17.067
Total	14679.016	81	
Mean corrected	7309.265	80	

Raw R-square (1-Residual/Total) = 0.914
Mean corrected R-square (1-Residual/Corrected) = 0.827
R(observed vs predicted) square = 0.827

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
B0	7.662	4.379	1.750	-1.063	16.387
B1	-4.513	1.487	-3.034	-7.477	-1.549
B2	-7.310	2.395	-3.053	-12.082	-2.539
B3	-0.439	1.487	-0.295	-3.403	2.524
B4	1.050	.	.	.	.
B5	6.387	0.938	6.807	4.517	8.256
B6	0.873	0.938	0.930	-0.997	2.742
B7	-0.855	0.319	-2.681	-1.490	-0.220

Case	OXIDATION Observed	OXIDATION Predicted	Residual
1	2.967	2.854	0.112
2	3.272	2.433	0.839
3	6.432	2.012	4.420
4	3.473	2.999	0.474
5	4.030	2.596	1.434
6	2.837	2.193	0.644
7	7.940	3.144	4.796
8	6.699	2.759	3.940
9	6.287	2.374	3.913
10	3.160	2.854	0.306
11	0.970	2.433	-1.463
12	0.774	2.012	-1.238
13	9.000	2.999	6.001
14	3.687	2.596	1.091
15	3.856	2.193	1.663
16	7.607	3.144	4.463
17	6.600	2.759	3.841
18	5.819	2.374	3.445
19	3.521	2.854	0.666
20	4.292	2.433	1.859
21	0.767	2.012	-1.245
22	4.063	2.999	1.064
23	4.100	2.596	1.504
24	2.645	2.193	0.452
25	7.733	3.144	4.589
26	6.000	2.759	3.241
27	5.597	2.374	3.223
28	4.147	4.924	-0.777
29	2.703	3.648	-0.945
30	1.763	2.372	-0.609
31	6.877	11.651	-4.774
32	5.403	9.539	-4.135
33	4.397	7.426	-3.029
34	9.350	18.378	-9.028
35	8.515	15.429	-6.914
36	8.587	12.480	-3.894
37	3.333	4.924	-1.591
38	2.740	3.648	-0.908
39	2.683	2.372	0.311
40	9.077	11.651	-2.574
41	5.150	9.539	-4.389
42	4.140	7.426	-3.286
43	11.200	18.378	-7.178
44	7.064	15.429	-8.365
45	5.819	12.480	-6.661
46	4.203	4.924	-0.721
47	3.350	3.648	-0.298
48	3.220	2.372	0.848
49	6.213	11.651	-5.438
50	3.860	9.539	-5.679
51	4.431	7.426	-2.995
52	8.336	18.378	-10.042
53	7.317	15.429	-8.112
54	5.597	12.480	-6.884
55	5.570	6.993	-1.423
56	4.800	4.863	-0.063
57	4.660	2.732	1.928
58	27.933	20.303	7.631
59	17.353	16.481	0.872
60	11.467	12.660	-1.193
61	31.967	33.612	-1.645

62	29.443	28.099	1.344
63	28.027	22.587	5.440
64	5.670	6.993	-1.323
65	4.993	4.863	0.130
66	4.650	2.732	1.918
67	27.890	20.303	7.587
68	16.640	16.481	0.159
69	11.090	12.660	-1.570
70	37.633	33.612	4.021
71	32.380	28.099	4.281
72	26.663	22.587	4.077
73	5.700	6.993	-1.293
74	4.967	4.863	0.104
75	4.267	2.732	1.534
76	27.223	20.303	6.921
77	17.507	16.481	1.026
78	11.043	12.660	-1.616
79	36.967	33.612	3.355
80	35.350	28.099	7.251
81	27.170	22.587	4.583

Asymptotic Correlation Matrix of Parameters

	B0	B1	B2	B3	B4
B0	1.00				
B1	-0.679	1.000			
B2	-0.784	0.532	1.000		
B3	-0.679	0.000	0.532	1.000	
B4	.	.	.	.	.
B5	0.462	-0.679	-0.784	0.000	.
B6	0.462	0.000	-0.784	-0.679	.
B7	0.000	0.000	0.532	0.000	.

	B5	B6	B7
B5	1.000		
B6	0.462	1.000	
B7	-0.679	-0.679	1.000

Model 3

Iteration
No. Loss B0 B1 B2 B3 B4
B5 B6

0 0.509503D+04 0.101000D+00 0.102000D+01 0.103000D+00 0.104000D+01
0.105000D+00
0.106000D+01 0.107000D+00

1 0.193891D+04 0.100560D+02 -.170721D+02 0.541155D+01 -.396939D+01
0.600367D+01
0.119757D+00 0.464261D+00

2 0.193891D+04 0.100560D+02 -.170721D+02 0.541155D+01 -.396939D+01
0.600367D+01
0.119757D+00 0.464261D+00

3 0.193891D+04 0.100560D+02 -.170721D+02 0.541155D+01 -.396939D+01
0.600367D+01
0.119757D+00 0.464261D+00

Dependent variable is OXIDATION

Source	Sum-of-Squares	df	Mean-Square
Regression	12740.107	7	1820.015
Residual	1938.909	74	26.201
Total	14679.016	81	
Mean corrected	7309.265	80	

Raw R-square (1-Residual/Total)	=	0.868
Mean corrected R-square (1-Residual/Corrected)	=	0.735
R(observed vs predicted) square	=	0.735

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
B0	10.056	7.394	1.360	-4.676	24.788
B1	-17.072	4.876	-3.501	-26.788	-7.356
B2	5.412	4.876	1.110	-4.304	15.127
B3	-3.969	4.876	-0.814	-13.685	5.746
B4	6.004	1.206	4.976	3.600	8.408
B5	0.120	1.206	0.099	-2.284	2.524
B6	0.464	1.206	0.385	-1.940	2.868

Case	OXIDATION Observed	OXIDATION Predicted	Residual
1	2.967	1.014	1.953
2	3.272	-1.563	4.835
3	6.432	-3.211	9.643
4	3.473	6.785	-3.311
5	4.030	4.208	-0.178
6	2.837	2.560	0.277
7	7.940	12.795	-4.855
8	6.699	10.218	-3.520
9	6.287	8.570	-2.284
10	3.160	1.014	2.146
11	0.970	-1.563	2.533
12	0.774	-3.211	3.985
13	9.000	6.785	2.215
14	3.687	4.208	-0.521
15	3.856	2.560	1.296
16	7.607	12.795	-5.188
17	6.600	10.218	-3.618
18	5.819	8.570	-2.751
19	3.521	1.014	2.507
20	4.292	-1.563	5.855
21	0.767	-3.211	3.978
22	4.063	6.785	-2.721
23	4.100	4.208	-0.108
24	2.645	2.560	0.085
25	7.733	12.795	-5.062
26	6.000	10.218	-4.218
27	5.597	8.570	-2.974
28	4.147	1.953	2.194
29	2.703	-0.624	3.327
30	1.763	-2.272	4.035
31	6.877	7.723	-0.847
32	5.403	5.147	0.257
33	4.397	3.499	0.898
34	9.350	13.734	-4.384
35	8.515	11.157	-2.642
36	8.587	9.509	-0.922
37	3.333	1.953	1.381

38	2.740	-0.624	3.364
39	2.683	-2.272	4.955
40	9.077	7.723	1.353
41	5.150	5.147	0.003
42	4.140	3.499	0.641
43	11.200	13.734	-2.534
44	7.064	11.157	-4.093
45	5.819	9.509	-3.690
46	4.203	1.953	2.251
47	3.350	-0.624	3.974
48	3.220	-2.272	5.492
49	6.213	7.723	-1.510
50	3.860	5.147	-1.287
51	4.431	3.499	0.933
52	8.336	13.734	-5.398
53	7.317	11.157	-3.840
54	5.597	9.509	-3.912
55	5.570	14.899	-9.329
56	4.800	12.322	-7.522
57	4.660	10.674	-6.014
58	27.933	20.670	7.264
59	17.353	18.093	-0.740
60	11.467	16.445	-4.978
61	31.967	26.680	5.287
62	29.443	24.103	5.340
63	28.027	22.455	5.571
64	5.670	14.899	-9.229
65	4.993	12.322	-7.329
66	4.650	10.674	-6.024
67	27.890	20.670	7.220
68	16.640	18.093	-1.453
69	11.090	16.445	-5.355
70	37.633	26.680	10.953
71	32.380	24.103	8.277
72	26.663	22.455	4.208
73	5.700	14.899	-9.199
74	4.967	12.322	-7.356
75	4.267	10.674	-6.407
76	27.223	20.670	6.554
77	17.507	18.093	-0.586
78	11.043	16.445	-5.402
79	36.967	26.680	10.287
80	35.350	24.103	11.247
81	27.170	22.455	4.715

Asymptotic Correlation Matrix of Parameters

	B0	B1	B2	B3	B4
B0	1.000				
B1	-0.565	1.000			
B2	-0.565	0.000	1.000		
B3	-0.565	0.000	0.000	1.000	
B4	0.544	-0.990	0.000	0.000	1.000
B5	0.544	0.000	-0.990	0.000	0.000
B6	0.544	0.000	0.000	-0.990	0.000

	B5	B6
B5	1.000	
B6	0.000	1.000

Model 4

```
Iteration
 No.      Loss        B0            B1            B2            B3            B4
                   B5           B6           B7           B8           B9
                   B10
   0  0.741061D+04  -.101000D+00  0.102000D+01  -.103000D+00  0.104000D+01  -
.105000D+00
                    0.106000D+01    -.107000D+00    0.108000D+01    -.109000D+00
0.110000D+01
                    -.111000D+00
   1   0.344741D+04   0.999900D+01   -.922959D+01   -.264308D+01   0.700890D-01
0.205769D+01
                    0.727119D+00    0.952474D-01    0.324000D+01    -.176066D+00
0.928968D+00
                    -.328977D+00
   2   0.609540D+03   0.284271D+02   -.279306D+02   -.727763D+01   -.169958D+01
0.600367D+01
                    0.119757D+00    0.464261D+00    0.718106D+01    -.298433D+00
0.616909D+00
                    -.726692D+00
   3   0.609540D+03   0.284271D+02   -.279306D+02   -.727763D+01   -.169958D+01
0.600367D+01
                    0.119757D+00    0.464261D+00    0.718106D+01    -.298433D+00
0.616909D+00
                    -.726692D+00
   4   0.609540D+03   0.284271D+02   -.279306D+02   -.727763D+01   -.169958D+01
0.600367D+01
                    0.119757D+00    0.464261D+00    0.718106D+01    -.298433D+00
0.616909D+00
                    -.726692D+00

Dependent variable is OXIDATION

    Source   Sum-of-Squares    df  Mean-Square
 Regression       14069.476    11    1279.043
   Residual         609.540    70       8.708

      Total       14679.016    81
Mean corrected     7309.265    80

       Raw  R-square (1-Residual/Total)        =        0.958
Mean corrected R-square (1-Residual/Corrected) =        0.917
         R(observed vs predicted) square       =        0.917
```

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
B0	28.427	7.280	3.905	13.908	42.947
B1	-27.931	3.955	-7.062	-35.819	-20.043
B2	-7.278	3.955	-1.840	-15.166	0.610
B3	-1.700	3.955	-0.430	-9.587	6.188
B4	6.004	0.696	8.632	4.616	7.391
B5	0.120	0.696	0.172	-1.267	1.507
B6	0.464	0.696	0.667	-0.923	1.851
B7	7.181	1.301	5.519	4.586	9.776
B8	-0.298	1.301	-0.229	-2.894	2.297

B9	0.617	1.301	0.474	-1.978	3.212
B10	-0.727	0.602	-1.206	-1.928	0.475

Case	OXIDATION Observed	OXIDATION Predicted	Residual
1	2.967	4.880	-1.913
2	3.272	4.165	-0.893
3	6.432	4.378	2.054
4	3.473	5.033	-1.559
5	4.030	4.208	-0.178
6	2.837	4.312	-1.475
7	7.940	5.425	2.515
8	6.699	4.491	2.208
9	6.287	4.485	1.802
10	3.160	4.880	-1.720
11	0.970	4.165	-3.195
12	0.774	4.378	-3.605
13	9.000	5.033	3.967
14	3.687	4.208	-0.521
15	3.856	4.312	-0.455
16	7.607	5.425	2.182
17	6.600	4.491	2.109
18	5.819	4.485	1.334
19	3.521	4.880	-1.359
20	4.292	4.165	0.127
21	0.767	4.378	-3.612
22	4.063	5.033	-0.969
23	4.100	4.208	-0.108
24	2.645	4.312	-1.667
25	7.733	5.425	2.308
26	6.000	4.491	1.509
27	5.597	4.485	1.112
28	4.147	1.116	3.031
29	2.703	-0.624	3.327
30	1.763	-1.436	3.199
31	6.877	7.723	-0.847
32	5.403	5.147	0.257
33	4.397	3.499	0.898
34	9.350	14.570	-5.220
35	8.515	11.157	-2.642
36	8.587	8.673	-0.086
37	3.333	1.116	2.217
38	2.740	-0.624	3.364
39	2.683	-1.436	4.119
40	9.077	7.723	1.353
41	5.150	5.147	0.003
42	4.140	3.499	0.641
43	11.200	14.570	-3.370
44	7.064	11.157	-4.093
45	5.819	8.673	-2.854
46	4.203	1.116	3.087
47	3.350	-0.624	3.974
48	3.220	-1.436	4.656
49	6.213	7.723	-1.510
50	3.860	5.147	-1.287
51	4.431	3.499	0.933
52	8.336	14.570	-6.234
53	7.317	11.157	-3.840
54	5.597	8.673	-3.076
55	5.570	9.360	-3.790

56	4.800	6.595	-1.795
57	4.660	4.758	-0.098
58	27.933	22.421	5.512
59	17.353	18.093	-0.740
60	11.467	14.693	-3.226
61	31.967	35.723	-3.756
62	29.443	29.831	-0.388
63	28.027	24.868	3.159
64	5.670	9.360	-3.690
65	4.993	6.595	-1.601
66	4.650	4.758	-0.108
67	27.890	22.421	5.469
68	16.640	18.093	-1.453
69	11.090	14.693	-3.603
70	37.633	35.723	1.911
71	32.380	29.831	2.549
72	26.663	24.868	1.795
73	5.700	9.360	-3.660
74	4.967	6.595	-1.628
75	4.267	4.758	-0.491
76	27.223	22.421	4.802
77	17.507	18.093	-0.586
78	11.043	14.693	-3.650
79	36.967	35.723	1.244
80	35.350	29.831	5.519
81	27.170	24.868	2.302

Asymptotic Correlation Matrix of Parameters

	B0	B1	B2	B3	B4
B0	1.000				
B1	-0.773	1.000			
B2	-0.773	0.433	1.000		
B3	-0.773	0.433	0.433	1.000	
B4	0.318	-0.703	0.000	0.000	1.000
B5	0.318	0.000	-0.703	0.000	0.000
B6	0.318	0.000	0.000	-0.703	0.000
B7	0.715	-0.658	-0.658	-0.564	0.000
B8	0.715	-0.658	-0.564	-0.658	0.000
B9	0.715	-0.564	-0.658	-0.658	0.000
B10	-0.662	0.609	0.609	0.609	0.000

	B5	B6	B7	B8	B9
B5	1.000				
B6	0.000	1.000			
B7	0.000	0.000	1.000		
B8	0.000	0.000	0.857	1.000	
B9	0.000	0.000	0.857	0.857	1.000
B10	0.000	0.000	-0.926	-0.926	-0.926

	B10
B10	1.000

Model 5

```
Iteration
 No.       Loss        B0            B1            B2            B3            B4
                     B5            B6            B7            B8            B9
                     B10           B11           B12           B13
   0   0.478104D+04   0.101000D+00   0.102000D+00   0.103000D+00   0.104000D+00
0.105000D+00
                     0.106000D+00     0.107000D+00     0.108000D+00     0.109000D+00
0.110000D+00
                     0.111000D+00 0.112000D+00 0.113000D+00 0.114000D+00
   1   0.420309D+03   -.315058D+01   0.103020D+02   0.529224D+01   -.734095D+00   -
.970468D+01
                     -.552585D+00     0.527675D+00     -.360662D+01     0.872704D+00
0.239801D+00
                     -.580095D+00 0.430887D+01 -.357639D+00 0.101182D+00
   2   0.282541D+03   -.384031D+01   0.124656D+02   0.639300D+01   -.911873D+00   -
.117855D+02
                     -.692285D+00     0.616909D+00     -.439458D+01     0.103470D+01
0.267335D+00
                     -.726692D+00 0.519912D+01 -.457473D+00 0.984630D-01
   3   0.282541D+03   -.384031D+01   0.124656D+02   0.639300D+01   -.911873D+00   -
.117855D+02
                     -.692285D+00     0.616909D+00     -.439458D+01     0.103470D+01
0.267335D+00
                     -.726692D+00 0.519912D+01 -.457473D+00 0.984630D-01
   4   0.282541D+03   -.384031D+01   0.124656D+02   0.639300D+01   -.911873D+00   -
.117855D+02
                     -.692285D+00     0.616909D+00     -.439458D+01     0.103470D+01
0.267335D+00
                     -.726692D+00 0.519912D+01 -.457473D+00 0.984630D-01

Dependent variable is OXIDATION

    Source   Sum-of-Squares    df  Mean-Square
 Regression       14396.475    14    1028.320
   Residual         282.541    67       4.217

      Total       14679.016    81
Mean corrected     7309.265    80

       Raw  R-square (1-Residual/Total)        =        0.981
Mean corrected R-square (1-Residual/Corrected) =        0.961
```

R(observed vs predicted) square = 0.961

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
B0	-3.840	8.516	-0.451	-20.838	-3.158
B1	12.466	6.154	2.026	0.182	24.750
B2	6.393	5.828	1.097	5.241	18.027
B3	-0.912	5.483	-0.166	-11.856	10.033
B4	-11.786	3.474	-3.393	-18.719	-4.852
B5	-0.692	2.538	-0.273	-9.759	-1.374
B6	0.617	0.906	0.681	-1.191	2.424
B7	-4.395	1.281	-3.432	-6.951	-1.838
B8	1.035	1.281	0.808	-1.521	3.591
B9	0.267	1.281	0.209	-2.289	2.823
B10	-0.727	0.419	-1.734	-1.563	0.110
B11	5.199	0.593	8.770	4.016	6.382
B12	-0.457	0.593	-0.772	-1.641	0.726
B13	0.098	0.593	0.166	-1.085	1.282

Case	OXIDATION Observed	OXIDATION Predicted	Residual
1	2.967	3.266	-0.300
2	3.272	2.650	0.622
3	6.432	2.765	3.667
4	3.473	4.695	-1.222
5	4.030	3.969	0.061
6	2.837	3.974	-1.137
7	7.940	7.278	0.662
8	6.699	6.442	0.257
9	6.287	6.337	-0.051
10	3.160	3.266	-0.106
11	0.970	2.650	-1.680
12	0.774	2.765	-1.991
13	9.000	4.695	4.305
14	3.687	3.969	-0.282
15	3.856	3.974	-0.118
16	7.607	7.278	0.329
17	6.600	6.442	0.158
18	5.819	6.337	-0.518
19	3.521	3.266	0.254
20	4.292	2.650	1.642
21	0.767	2.765	-1.998
22	4.063	4.695	-0.632
23	4.100	3.969	0.131
24	2.645	3.974	-1.329
25	7.733	7.278	0.455
26	6.000	6.442	-0.442
27	5.597	6.337	-0.741
28	4.147	4.582	-0.436
29	2.703	2.842	-0.139
30	1.763	2.030	-0.267
31	6.877	7.723	-0.847
32	5.403	5.147	0.257
33	4.397	3.499	0.898
34	9.350	11.104	-1.754
35	8.515	7.691	0.824
36	8.587	5.206	3.380
37	3.333	4.582	-1.249
38	2.740	2.842	-0.102
39	2.683	2.030	0.653
40	9.077	7.723	1.353
41	5.150	5.147	0.003
42	4.140	3.499	0.641

43	11.200	11.104	0.096
44	7.064	7.691	-0.627
45	5.819	5.206	0.613
46	4.203	4.582	-0.379
47	3.350	2.842	0.508
48	3.220	2.030	1.190
49	6.213	7.723	-1.510
50	3.860	5.147	-1.287
51	4.431	3.499	0.933
52	8.336	11.104	-2.768
53	7.317	7.691	-0.374
54	5.597	5.206	0.390
55	5.570	7.507	-1.937
56	4.800	4.643	0.157
57	4.660	2.905	1.755
58	27.933	22.759	5.174
59	17.353	18.332	-0.979
60	11.467	15.031	-3.564
61	31.967	37.336	-5.369
62	29.443	31.346	-1.903
63	28.027	26.481	1.545
64	5.670	7.507	-1.837
65	4.993	4.643	0.350
66	4.650	2.905	1.745
67	27.890	22.759	5.131
68	16.640	18.332	-1.692
69	11.090	15.031	-3.941
70	37.633	37.336	0.297
71	32.380	31.346	1.034
72	26.663	26.481	0.182
73	5.700	7.507	-1.807
74	4.967	4.643	0.323
75	4.267	2.905	1.362
76	27.223	22.759	4.464
77	17.507	18.332	-0.826
78	11.043	15.031	-3.988
79	36.967	37.336	-0.369
80	35.350	31.346	4.004
81	27.170	26.481	0.689

Asymptotic Correlation Matrix of Parameters

	B0	B1	B2	B3	B4
B0	1.000				
B1	-0.861	1.000			
B2	-0.752	0.614	1.000		
B3	-0.632	0.375	0.103	1.000	
B4	0.744	-0.822	-0.868	-0.074	1.000
B5	0.585	-0.405	-0.095	-0.926	0.080
B6	0.425	-0.252	-0.311	-0.330	0.223
B7	0.501	-0.832	-0.314	0.000	0.632
B8	0.501	-0.297	-0.879	0.000	0.632
B9	0.501	-0.297	0.000	-0.934	0.000
B10	-0.394	0.272	0.288	0.306	-0.241
B11	-0.464	0.771	0.339	0.000	-0.683
B12	-0.464	0.321	0.814	0.000	-0.683
B13	-0.464	0.321	0.000	0.865	0.000

Appendix IV-5 Comparison between the Experimental and the Modeled CH_4 Oxidation Rates in Soils and Compost.

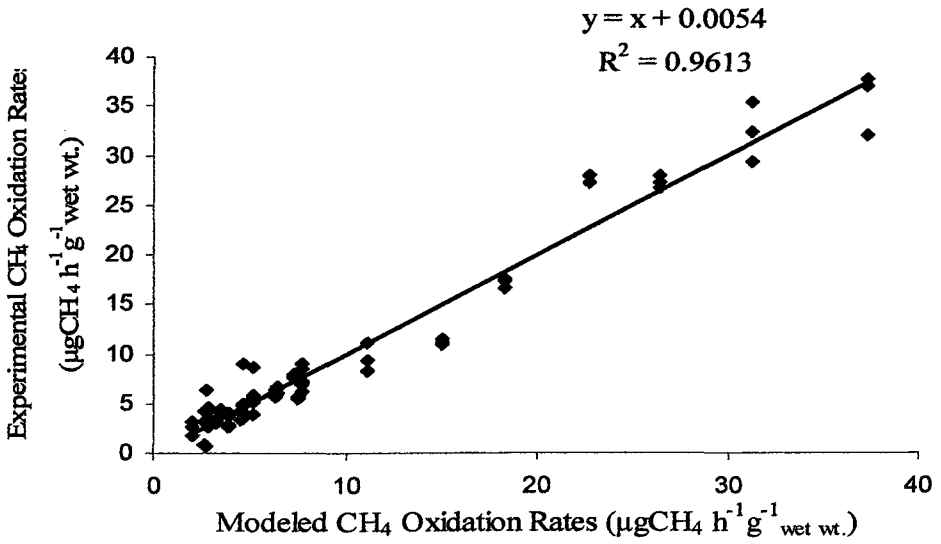


Figure A.9 The predicted CH_4 oxidation rates (using the empirical model) versus experimental data.

APPENDIX V

ANALYSIS AND SAMPLE CALCULATIONS –

KINETICS OF BIOLOGICAL METHANE OXIDATION IN THE PRESENCE OF NON-METHANE ORGANIC COMPOUNDS IN LANDFILL BIO-COVERS

Appendix V includes examples of raw data, detailed analysis for the experiments conducted and discussed in Chapter 5.

Appendix V-1 Methane Oxidation Kinetic Parameters using SYSTAT 11

The following are two typical examples for the determination of the kinetics constants using SYSTAT 11. The experimental data of CH_4 reaction rate and initial CH_4 substrate concentration were fitted using nonlinear regression growth model. 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. The software performed a comparison between some values of experimental CH_4 reaction rate and the predicted reaction rate and calculated the residuals. The calculated residuals are the least possible. Each data point is the average of duplicate experiments.

Compost with 142% w/w MC at 5°C

9 cases and 2 variables processed and saved.

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\try.syd,

V S

Iteration

No.	Loss	VMAX	KM
0	0.892194D+02	0.101000D+01	-.102000D+01
1	0.870812D+02	0.105547D+01	0.100980D+03
2	0.401415D+01	0.477137D+01	0.809033D+04
3	0.609433D+00	0.474445D+01	0.407757D+04
4	0.440900D-01	0.488675D+01	0.298274D+04
5	0.406635D-01	0.489142D+01	0.310507D+04
6	0.406597D-01	0.489200D+01	0.311002D+04
7	0.406597D-01	0.489202D+01	0.311014D+04
8	0.406597D-01	0.489202D+01	0.311015D+04

Dependent variable is V

Source	Sum-of-Squares	df	Mean-Square
Regression	150.367	2	75.183
Residual	0.041	7	0.006
Total	150.407	9	
Mean corrected	19.458	8	

Raw R-square (1-Residual/Total) = 1.000

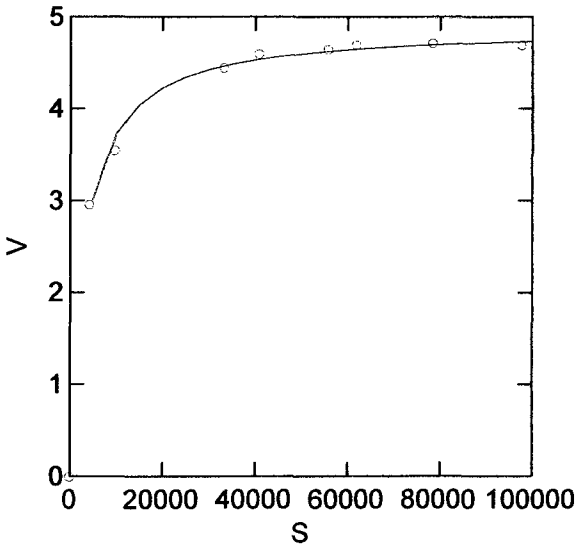
Mean corrected R-square (1-Residual/Corrected) = 0.998
R(observed vs predicted) square = 0.998

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
VMAX	4.892	0.042	117.415	4.794	4.991
KM	2727.347	200.126	15.541	2636.924	3583.370

Case	V Observed	V Predicted	Residual
1	0.000	0.000	0.000
2	2.960	2.860	0.100
3	3.550	3.702	-0.152
4	4.450	4.475	-0.025
5	4.600	4.546	0.054
6	4.650	4.634	0.016
7	4.700	4.658	0.042
8	4.720	4.706	0.014
9	4.700	4.741	-0.041

Asymptotic Correlation Matrix of Parameters

	VMAX	KM
VMAX	1.000	
KM	0.684	1.000



Compost with 142% w/w MC at 35°C

11 cases and 2 variables processed and saved.

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\try.syd,
created Thu Feb 12, 2009 at 17:22:44, contains variables:

V S

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\try.SYD,
created Thu Feb 12, 2009 at 17:22:44, contains variables:

V S

Iteration No.	Loss	VMAX	KM
0	0.170776D+04	0.101000D+02	-.102000D+02
1	0.120530D+04	0.127385D+02	0.100980D+04
2	0.349085D+02	0.264791D+02	0.624282D+04
3	0.181614D+02	0.284728D+02	0.693671D+04
4	0.181428D+02	0.285580D+02	0.703432D+04
5	0.181425D+02	0.285677D+02	0.704926D+04
6	0.181425D+02	0.285691D+02	0.705147D+04
7	0.181425D+02	0.285693D+02	0.705180D+04

Dependent variable is V

Source	Sum-of-Squares	df	Mean-Square
Regression	5166.991	2	2583.496
Residual	18.142	9	2.016
Total	5185.134	11	
Mean corrected	680.234	10	

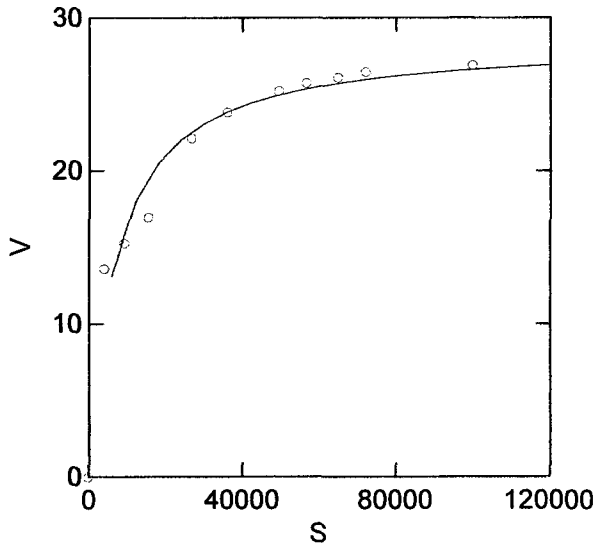
Raw R-square (1-Residual/Total)	=	0.997
Mean corrected R-square (1-Residual/Corrected)	=	0.973
R(observed vs predicted) square	=	0.974

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
VMAX	28.569	0.963	29.657	26.390	30.749
KM	7051.800	1205.400	5.850	4324.995	9778.605

Case	V Observed	V Predicted	Residual
1	0.000	0.000	0.000
2	13.630	10.541	3.089
3	15.300	16.232	-0.932
4	17.000	19.622	-2.622
5	22.160	22.619	-0.459
6	23.866	23.899	-0.033
7	25.264	25.006	0.258
8	25.788	25.409	0.379
9	26.149	25.771	0.378
10	26.500	26.026	0.474
11	26.950	26.687	0.263

Asymptotic Correlation Matrix of Parameters

	VMAX	KM
VMAX	1.000	
KM	0.810	1.000



Appendix V-2 Methane Oxidation Rates Kinetic Parameters using Uncompetitive Inhibition Model

The uncompetitive inhibition model is:

$$V = V_{max} \frac{[S]}{K_m + [S]\left(1 + \frac{I}{K_i}\right)}$$

where, V is the reaction rate, V_{max} is the maximum reaction rate, [S] is the substrate concentration, I is the concentration of the inhibitor, K_m is the half saturation constant and K_i is the dissociation constant for the E-I complex.

The kinetic constants were fitted by using nonlinear regression analysis of the CH_4 oxidation rates in the absence and presence of NMOCs versus the initial headspace CH_4 concentrations. The following are examples of the nonlinear regression modeling to obtain the kinetic parameters including the dissociation constant.

Compost with 57% w/w MC at 5°C

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\enzyme-dec27.SYD,
created Sun Dec 28, 2008 at 08:33:55, contains variables:

V S I

```
 Iteration
 No.      Loss          VMAX          KII           KM
   0 0.123616D+03 0.101000D+02 0.102000D+02 0.103000D+02
   1 0.319484D+02 0.658016D+01 0.210639D+02 0.836750D+03
   2 0.845803D+01 0.702482D+01 0.512484D+02 0.212628D+04
   3 0.128392D+01 0.742380D+01 0.947748D+02 0.248748D+04
   4 0.488386D+00 0.748195D+01 0.124989D+03 0.246692D+04
   5 0.468037D+00 0.749009D+01 0.132696D+03 0.247157D+04
   6 0.467985D+00 0.749112D+01 0.133147D+03 0.247311D+04
```

```
   7 0.467985D+00 0.749122D+01 0.133154D+03 0.247327D+04
   8 0.467985D+00 0.749123D+01 0.133154D+03 0.247328D+04

Dependent variable is V
```

Source	Sum-of-Squares	df	Mean-Square
Regression	286.193	3	95.398
Residual	0.468	12	0.039
Total	286.661	15	
Mean corrected	20.995	14	

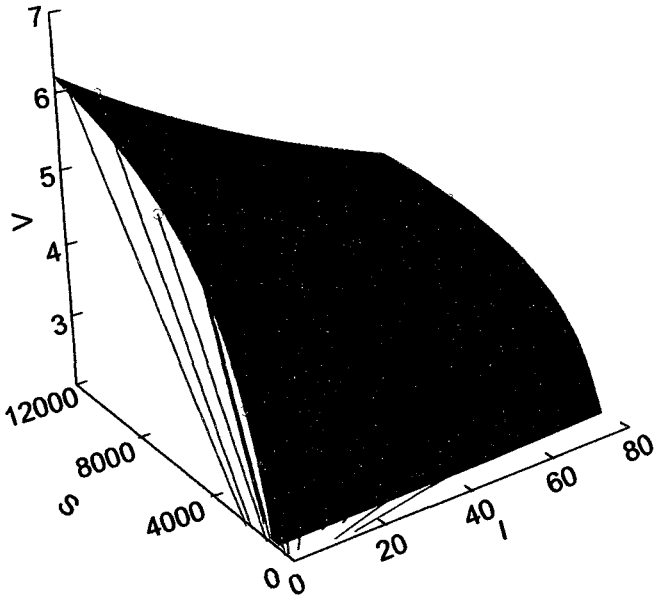
Raw R-square (1-Residual/Total) =	0.998
Mean corrected R-square (1-Residual/Corrected) =	0.978
R(observed vs predicted) square =	0.978

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
VMAX	7.491	0.240	31.164	6.967	8.015
KII	133.154	16.726	7.961	96.711	169.598
KM	2473.278	240.087	10.302	1950.172	2996.383

Case	V Observed	V Predicted	Residual
1	3.481	3.437	0.044
2	5.222	5.377	-0.155
3	6.189	6.134	0.054
4	3.409	3.335	0.074
5	5.114	5.191	-0.077
6	6.061	5.911	0.151
7	3.634	3.325	0.309
8	4.240	4.661	-0.421
9	5.653	5.488	0.165
10	2.371	2.394	-0.023
11	3.556	3.794	-0.238
12	4.346	4.376	-0.030
13	2.273	2.224	0.049
14	3.409	3.463	-0.053
15	4.167	3.964	0.203

Asymptotic Correlation Matrix of Parameters

	VMAX	KII	KM
VMAX	1.000		
KI	-0.448	1.000	
KM	0.874	-0.149	1.000



Compost with 57% w/w MC at 22°C

27 cases and 3 variables processed and saved.

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\enzyme-c4.syd, created Mon Dec 29, 2008 at 11:28:46, contains variables:

V S I

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\enzyme-c4.SYD, created Mon Dec 29, 2008 at 11:28:46, contains variables:

V S I

Iteration No.	Loss	VMAX	KII	KM
0	0.508290D+04	0.101000D+02	0.102000D+02	0.103000D+02
1	0.372501D+04	0.129363D+02	0.181385D+02	0.104030D+04
2	0.282406D+03	0.268139D+02	0.758234D+02	0.575982D+04
3	0.858613D+02	0.300520D+02	0.100677D+03	0.565924D+04
4	0.857742D+02	0.300697D+02	0.102451D+03	0.566471D+04
5	0.857741D+02	0.300723D+02	0.102460D+03	0.566687D+04
6	0.857741D+02	0.300729D+02	0.102458D+03	0.566735D+04

7 0.857741D+02 0.300730D+02 0.102458D+03 0.566745D+04

Dependent variable is V

Source	Sum-of-Squares	df	Mean-Square
Regression	9962.860	3	3320.953
Residual	85.774	24	3.574
Total	10048.634	27	
Mean corrected	851.333	26	

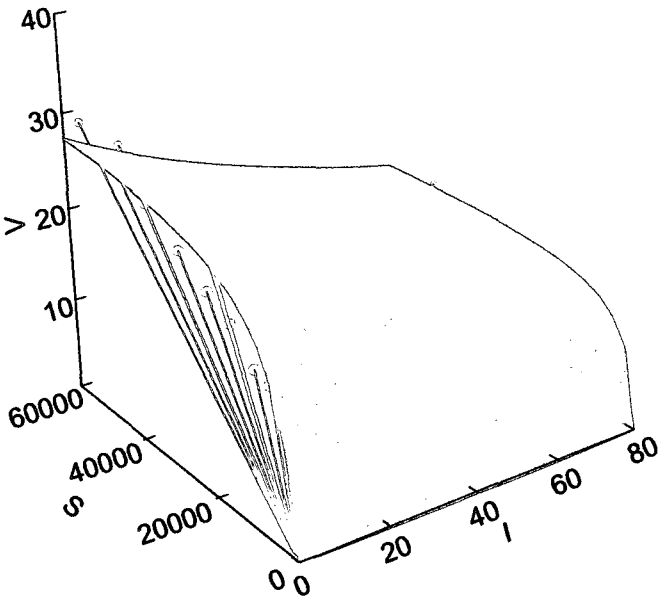
Raw R-square (1-Residual/Total) = 0.991
Mean corrected R-square (1-Residual/Corrected) = 0.899
R(observed vs predicted) square = 0.904

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
VMAX	30.073	1.215	24.761	27.566	32.580
KII	102.458	16.192	6.328	69.039	135.877
KM	5667.448	846.972	6.691	3919.383	7415.513

Case	V Observed	V Predicted	Residual
1	13.925	9.933	3.991
2	15.665	15.819	-0.153
3	16.246	19.042	-2.797
4	19.147	21.973	-2.826
5	20.887	23.673	-2.786
6	23.208	25.004	-1.796
7	25.860	26.016	-0.155
8	27.850	26.691	1.159
9	30.171	27.241	2.930
10	10.228	7.885	2.344
11	17.047	15.979	1.068
12	19.320	19.514	-0.194
13	24.434	24.125	0.309
14	28.033	25.794	2.239
15	7.036	5.815	1.222
16	14.073	13.905	0.168
17	16.418	17.355	-0.936
18	19.937	21.547	-1.610
19	25.800	23.471	2.329
20	13.499	13.590	-0.091
21	14.061	16.253	-2.192
22	16.123	17.584	-1.460
23	18.279	18.288	-0.008
24	13.326	12.347	0.978
25	14.537	14.648	-0.111
26	15.345	15.551	-0.206
27	17.868	16.159	1.709

Asymptotic Correlation Matrix of Parameters

	VMAX	KII	KM
VMAX	1.000		
KI	-0.520	1.000	
KM	0.818	-0.241	1.000



Compost with 57% w/w MC at 35°C

29 cases and 3 variables processed and saved.

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\enzyme-dec27.syd, created Sat Jan 03, 2009 at 20:46:11, contains variables:

V S I

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\enzyme-dec27.SYD, created Sat Jan 03, 2009 at 20:46:11, contains variables:

V S I

Iteration No.	Loss	VMAX	KII	KM
0	0.909490D+04	0.101000D+02	0.102000D+02	0.103000D+02
1	0.719209D+04	0.129265D+02	0.159774D+02	0.104030D+04
2	0.457738D+03	0.338997D+02	0.654751D+02	0.798658D+04
3	0.120266D+03	0.389221D+02	0.593887D+02	0.685089D+04
4	0.119903D+03	0.386402D+02	0.609861D+02	0.681851D+04
5	0.119903D+03	0.386386D+02	0.610069D+02	0.681577D+04
6	0.119903D+03	0.386379D+02	0.610075D+02	0.681524D+04
7	0.119903D+03	0.386377D+02	0.610077D+02	0.681512D+04

Dependent variable is V

Source	Sum-of-Squares	df	Mean-Square
Regression	15451.878	3	5150.626
Residual	119.903	26	4.612
Total	15571.781	29	
Mean corrected	1393.400	28	

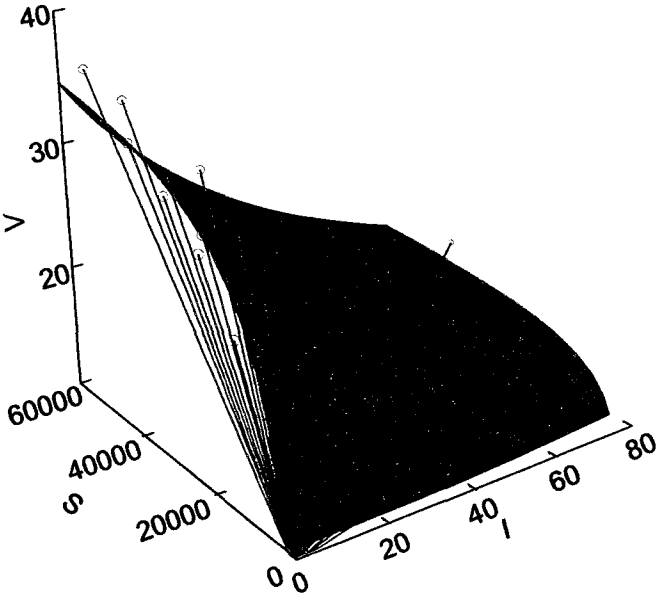
Raw R-square (1-Residual/Total)	=	0.992
Mean corrected R-square (1-Residual/Corrected)	=	0.914
R(observed vs predicted) square	=	0.917

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
VMAX	38.638	1.610	23.992	35.327	41.948
KII	61.008	7.855	7.766	44.861	77.155
KM	6815.121	999.429	6.819	4760.764	8869.477

Case	V Observed	V Predicted	Residual
1	17.406	13.096	4.310
2	19.147	20.481	-1.334
3	23.208	25.973	-2.765
4	27.850	29.613	-1.763
5	30.635	31.628	-0.993
6	33.072	32.993	0.078
7	36.801	34.139	2.663
8	14.000	11.111	2.889
9	17.780	18.891	-1.110
10	21.336	23.836	-2.499
11	24.004	26.753	-2.750
12	27.737	28.933	-1.195
13	30.819	30.322	0.497
14	34.545	31.386	3.158
15	14.000	10.572	3.428
16	17.780	17.382	0.398
17	21.336	21.483	-0.146
18	24.004	23.825	0.179
19	25.604	25.198	0.405
20	26.671	26.101	0.569
21	29.465	26.967	2.497
22	13.181	14.181	-1.000
23	14.379	17.099	-2.720
24	15.178	18.271	-3.094
25	19.771	18.960	0.811
26	13.039	12.493	0.546
27	14.224	14.732	-0.507
28	15.410	15.644	-0.235
29	18.847	16.065	2.782

Asymptotic Correlation Matrix of Parameters

	VMAX	KII	KM
VMAX	1.000		
KI	-0.561	1.000	
KM	0.846	-0.283	1.000



Appendix V-3 **The Effect of NMOCs different Concentrations on the Bacterial Kinetic Parameters Applying the Uncompetitive Inhibition Model.**

The Uncompetitive Inhibition Models is :

$$V = V_{max} \frac{[S]}{K_m + [S]\left(1 + \frac{[I]}{K_i}\right)}$$

The NMOCs present with CH4 in different concentrations affected the bacterial kinetic parameter as follows:

- The maximum CH_4 Reaction Rate (V_{max}) in $\mu g\ h^{-1} g^{-1}_{wet\ wt}$..

Environmental Conditions	CH_4 alone	TCA (1ppm)	TCE (3 ppm)	DCM (15.4 ppm)	Mix (18.4 ppm)
5°C, 57% MC	7.45	7.30	6.45	5.26	5.04
5°C, 100% MC	5.54	5.48	4.69	3.66	3.50
5°C, 142% MC	4.78	4.57	3.94	3.56	3.44
22°C, 57% MC	30.21	29.18	26.65	18.78	18.10
22°C, 100% MC	20.37	19.23	17.14	13.00	12.59
22°C, 142% MC	13.21	12.91	11.29	9.90	9.87
35°C, 57% MC	38.22	36.25	31.21	20.07	19.28
35°C, 100% MC	35.03	33.69	29.42	19.72	19.08
35°C, 142% MC	28.68	26.97	25.09	17.79	16.38

- The Apparent Half-Saturation Constant (Km) in ppm:

Environmental Conditions	CH_4 alone	TCA (1ppm)	TCE (3 ppm)	DCM (15.4 ppm)	Mix (18.4 ppm)
5°C, 57% MC	3717.4	3640.7	2936.4	2746.4	2633.1
5°C, 100% MC	3135.3	3103.6	2133.7	1216.6	1332.0
5°C, 142% MC	2727.3	2745.3	1720.0	1075.3	1041.7
22°C, 57% MC	9524.1	7168.8	7985.1	5780.5	4967.9
22°C, 100% MC	8695.7	8049.6	6625.6	4682.6	4248.5
22°C, 142% MC	6694.9	6141.5	5150.1	4150.2	4039.7
35°C, 57% MC	10057.7	9789.4	7168.4	7683.0	6704.9
35°C, 100% MC	9017.3	8675.0	7214.0	4883.2	4637.0
35°C, 142% MC	7009.4	6614.5	6344.7	5874.0	5056.7

- The Dissociation Constant (Ki) in(μg/L):

Temperature (°C)	Compost MC (%w/w)	K_i** CH_4, No NMOCs	K_i CH_4 with 1ppm of TCA	K_i CH_4 with 3ppm of TCE	K_i CH_4 with 15.4 ppm of DCM	K_i CH_4 with 18.4 ppm of mixed NMOCs
5	57	1	71.2	83.5	112.7	133.2
5	100	1	73.5.1	89.4	129.6	148.0
5	142	1	231.0	259.3	391.1	462.4
22	57	1	53.7	59.2	85.7	102.5
22	100	1	63.2	77.3	109.0	128.7
22	142	1	77.8	90.7	132.0	155.1
35	57	1	30.5	36.7	52.1	61.0
35	100	1	37.9	41.7	64.4	75.8
35	142	1	45.1	52.9	75.0	88.3

**K_i is the dissociation constant for the enzyme-inhibitor complex in (μg/L).

Appendix V-4 An Example of the Lack of Correlation of Competitive, Model Compared to Uncompetitive Models Results

The following is an example of the lack of correlations applying the competitive to the experimental results. The competitive, noncompetitive and Haldane model could not estimate a reasonable value of the dissociation constant (K_i). This case is an example of compost with 100% MC at 22°C. The same trend was observed in all the other experiments.

The Uncompetitive Inhibition Model is:

$$V = V_{max} \frac{[S]}{K_m + [S]\left(1 + \frac{[I]}{K_i}\right)}$$

Model v=vmax*s / (s*(1+I/kII)+km)

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\enzyme-c5.SYD, created Tue Dec 23, 2008 at 09:06:30, contains variables:

V S I

Iteration No.	Loss	VMAX	KII	KM
0	0.718091D+03	0.101000D+02	0.102000D+02	0.103000D+02
1	0.535516D+03	0.115265D+02	0.142389D+02	0.104030D+04
2	0.538713D+02	0.196577D+02	0.419327D+02	0.685323D+04
3	0.658563D+01	0.209131D+02	0.640130D+02	0.610412D+04
4	0.628469D+01	0.211465D+02	0.675365D+02	0.632658D+04
5	0.628417D+01	0.211601D+02	0.676835D+02	0.634172D+04
6	0.628417D+01	0.211606D+02	0.676860D+02	0.634239D+04
7	0.628417D+01	0.211606D+02	0.676861D+02	0.634240D+04

Dependent variable is V

Source	Sum-of-Squares	df	Mean-Square
Regression	2056.909	3	685.636
Residual	6.284	12	0.524
Total	2063.193	15	
Mean corrected	247.049	14	

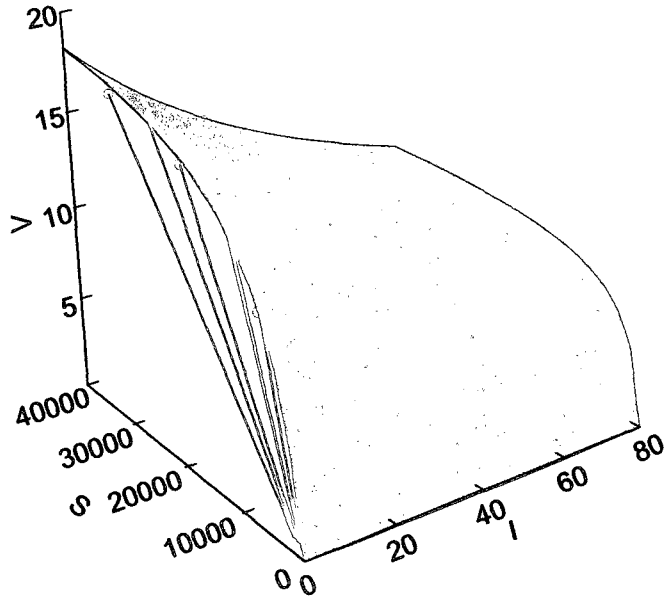
Raw R-square (1-Residual/Total)	=	0.997
Mean corrected R-square (1-Residual/Corrected)	=	0.975
R(observed vs predicted) square	=	0.975

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
VMAX	19.811	0.911	23.219	17.175	23.146
KII	**128.686**	8.611	7.860	88.923	156.449
KM	5273.494	891.302	7.116	4400.422	8284.385

Case	V Observed	V Predicted	Residual
1	10.784	10.706	0.078
2	15.577	15.815	-0.237
3	17.175	17.569	-0.395
4	10.668	10.228	0.440
5	14.224	14.575	-0.350
6	16.595	16.363	0.233
7	10.808	9.548	1.259
8	11.888	12.561	-0.673
9	15.491	14.411	1.080
10	3.481	4.403	-0.922
11	7.543	8.537	-0.994
12	9.283	9.802	-0.519
13	4.741	4.892	-0.151
14	7.705	7.591	0.114
15	9.088	8.497	0.591

Asymptotic Correlation Matrix of Parameters

	VMAX	KII	KM
VMAX	1.000		
KII	-0.442	1.000	
KM	0.874	-0.150	1.000



The Competitive Inhibition Model is:

$$V = V_{max} \frac{[S]}{K_m\left(1+\frac{[I]}{K_i}\right)+[S]}$$

15 cases and 3 variables processed and saved.

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\enzyme-c5.syd, created Tue Dec 23, 2008 at 09:06:30, contains variables:

V S I

SYSTAT Rectangular file C:\Program Files\SYSTAT 11\Data\enzyme-c5.SYD, created Tue Dec 23, 2008 at 09:06:30, contains variables:

V S I

Iteration No.	Loss	VMAX	KM	KIS
0	0.252084D+03	0.101000D+02	0.102000D+02	0.103000D+02
1	0.167555D+03	0.136324D+02	0.103020D+04	0.775290D+03
2	0.159398D+03	0.149605D+02	0.170379D+04	-.199086D+05
3	0.157443D+03	0.150651D+02	0.176981D+04	-.201077D+07
4	0.157425D+03	0.150661D+02	0.177042D+04	-.203088D+09
5	0.157403D+03	0.150663D+02	0.177082D+04	0.201057D+11
6	0.825002D+02	0.167649D+02	0.463990D+04	0.201057D+11
7	0.695183D+02	0.188591D+02	0.746631D+04	0.201057D+11
8	0.680826D+02	0.199216D+02	0.890822D+04	0.201057D+11
9	0.680003D+02	0.202327D+02	0.932082D+04	0.201057D+11
10	0.679972D+02	0.202977D+02	0.940450D+04	0.201057D+11
11	0.679971D+02	0.203096D+02	0.941972D+04	0.201057D+11
12	0.679971D+02	0.203117D+02	0.942243D+04	0.201057D+11
13	0.679971D+02	0.203121D+02	0.942291D+04	0.201057D+11

Dependent variable is V

Source	Sum-of-Squares	df	Mean-Square
Regression	1995.196	2	997.598
Residual	67.997	13	5.231
Total	2063.193	15	
Mean corrected	247.049	14	

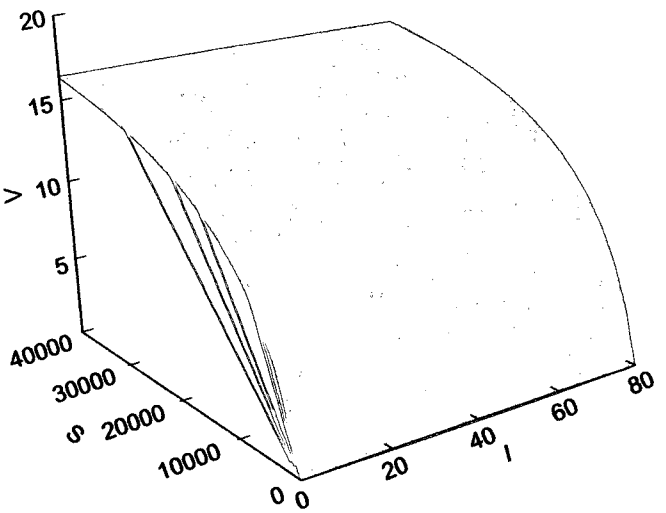
Raw R-square (1-Residual/Total)	=	0.967
Mean corrected R-square (1-Residual/Corrected)	=	0.725
R(observed vs predicted) square	=	0.726

Parameter	Estimate	A.S.E.	Param/ASE	Wald Confidence Interval Lower < 95%> Upper	
VMAX	20.312	3.150	6.449	13.508	27.116
KM	9422.912	3785.786	2.489	1244.218	17601.606
KIS	**2.01057E+10**	.	.	.	.

Case	V Observed	V Predicted	Residual
1	10.784	8.288	2.496
2	15.577	13.521	2.056
3	17.175	15.581	1.594
4	10.668	8.235	2.434
5	14.224	13.105	1.120
6	16.595	15.455	1.140
7	10.808	8.298	2.509
8	11.888	12.251	-0.362
9	15.491	15.196	0.295
10	3.481	3.697	-0.216
11	7.543	9.971	-2.428
12	9.283	13.005	-3.722
13	4.741	4.724	0.018
14	7.705	10.079	-2.374
15	9.088	12.906	-3.818

Asymptotic Correlation Matrix of Parameters

	VMAX	KM	KIS
VMAX	1.000		
KM	0.944	1.000	
KIS	.	.	.



The Noncompetitive Inhibition Model is:

$$V = \frac{V_{max}[S] \Big/ \left(1 + \frac{[I]}{K_i}\right)}{K_m + [S]}$$

Iteration

No.	Loss	VMAX	KI	K
0	0.798815D+10	-.101000D+01	-.102000D+01	-.103000D+01
1	0.484243D+10	-.101000D+01	-.364867D+01	-.206611D+01
2	0.416822D+10	-.553690D+00	-.422387D+01	-.206611D+01
3	0.381819D+10	-.202820D+00	-.487158D+01	-.206611D+01
4	0.373084D+10	-.202820D+00	-.504919D+01	-.269737D+01
5	0.366332D+10	-.202820D+00	-.520274D+01	-.367658D+01
6	0.365471D+10	-.202820D+00	-.522819D+01	-.400814D+01
7	0.356685D+10	0.971447D+00	-.672781D+01	-.400814D+01
8	0.345396D+10	0.516360D+00	-.634825D+01	-.400814D+01
9	0.344599D+10	0.516360D+00	-.646160D+01	-.350584D+01
10	0.344316D+10	0.600653D+00	-.662574D+01	-.350584D+01
11	0.344244D+10	0.569290D+00	-.653711D+01	-.350584D+01
12	0.344227D+10	0.569290D+00	-.658426D+01	-.336152D+01
13	0.344224D+10	0.559919D+00	-.656044D+01	-.336152D+01
14	0.344224D+10	0.559919D+00	-.657247D+01	-.332888D+01
15	0.344224D+10	0.557509D+00	-.656645D+01	-.332888D+01
16	0.344224D+10	0.557509D+00	-.656947D+01	-.332094D+01
17	0.344224D+10	0.557509D+00	-.656796D+01	-.332455D+01
18	0.344224D+10	0.557840D+00	-.656871D+01	-.332455D+01
19	0.344224D+10	0.557840D+00	-.656834D+01	-.332545D+01
20	0.344224D+10	0.557840D+00	-.656852D+01	-.332496D+01
21	0.344224D+10	0.557840D+00	-.656843D+01	-.332518D+01
22	0.344224D+10	0.557861D+00	-.656848D+01	-.332518D+01
23	0.344224D+10	0.557851D+00	-.656845D+01	-.332518D+01
24	0.344224D+10	0.557851D+00	-.656846D+01	-.332515D+01

Dependent variable is V

Source	Sum-of-Squares	df	Mean-Square
Regression	.	2	.
Residual	3.44224E+09	13	.64787E+08
Total	2672.247	15	
Mean corrected	59.850	14	

Raw R-square (1-Residual/Total)	=	0.000
Mean corrected R-square (1-Residual/Corrected)	=	0.000
R(observed vs predicted) square	=	0.010

The Haldane Toxic Inhibition Model
The model is:

$$V = V_{max} \frac{[S]}{K_m + [S] + \frac{[S^2]}{K_i}}$$

Iteration

No.	Loss	VMAX	KM	KI
0	0.236613D+04	-.101000D+03	0.102000D+03	-.103000D+03
1	0.236613D+04	-.101062D+03	0.104024D+03	-.102937D+03
2	0.236613D+04	-.101125D+03	0.106088D+03	-.102874D+03
3	0.236613D+04	-.101189D+03	0.108193D+03	-.102809D+03
4	0.236613D+04	-.101255D+03	0.110339D+03	-.102743D+03
5	0.236613D+04	-.101322D+03	0.112529D+03	-.102675D+03
6	0.236613D+04	-.101390D+03	0.114761D+03	-.102607D+03
7	0.236613D+04	-.101460D+03	0.117038D+03	-.102537D+03
8	0.236613D+04	-.101531D+03	0.119361D+03	-.102466D+03
9	0.236613D+04	-.101604D+03	0.121729D+03	-.102393D+03
10	0.236613D+04	-.101678D+03	0.124144D+03	-.102319D+03
11	0.236613D+04	-.101753D+03	0.126607D+03	-.102244D+03
12	0.236612D+04	-.101830D+03	0.129119D+03	-.102168D+03
13	0.236612D+04	-.101908D+03	0.131681D+03	-.102090D+03
14	0.236612D+04	-.101988D+03	0.134294D+03	-.102010D+03
15	0.236612D+04	-.102070D+03	0.136958D+03	-.101930D+03
16	0.236612D+04	-.102153D+03	0.139676D+03	-.101847D+03
17	0.236612D+04	-.102238D+03	0.142447D+03	-.101764D+03
18	0.236612D+04	-.102324D+03	0.145274D+03	-.101678D+03
19	0.236612D+04	-.102412D+03	0.148156D+03	-.101591D+03
20	0.236612D+04	-.102502D+03	0.151096D+03	-.101503D+03
21	0.236612D+04	-.102594D+03	0.154094D+03	-.101413D+03
22	0.236612D+04	-.102687D+03	0.157151D+03	-.101321D+03
23	0.236612D+04	-.102783D+03	0.160269D+03	-.101228D+03
24	0.236612D+04	-.102880D+03	0.163449D+03	-.101133D+03
25	0.236612D+04	-.102979D+03	0.166692D+03	-.101036D+03

Maximum number of iterations exceeded. Current estimates suspect.

Dependent variable is V

Source	Sum-of-Squares	df	Mean-Square
Regression	.	3	.
Residual	14815.680	12	1234.640
Total	2672.247	15	
Mean corrected	59.850	14	

Raw R-square (1-Residual/Total)	=	0.000
Mean corrected R-square (1-Residual/Corrected)	=	0.000
R(observed vs predicted) square	=	0.313

Appendix V-5 Raw Data of Relative Degradation of NMOCs

The decrease in concentration of each NMOC in the headspace of each batch experiment was observed over time. Relative headspace concentrations with time in batch experiments using compost sample under different temperature and moisture levels. All the concentrations were normalized to the initial concentration. Each data point is the average of triplicates.

Compost with 57% MC at 5°C

Time (hours)	DCM(% of initial Concentration) in the batch headspace	TCE (% of initial Concentration) in the batch headspace	TCA (% of initial Concentration) in the batch headspace
0	100	100	100
3	100	100	99.5
6	100	100	98.6
9	100	100	97.4
24	100	100	93.5
27	98.7	100	93.1
30	97.4	100	93.2
48	92.7	97.3	93.1
51	91.2	96.1	93.3
54	88.2	95.4	92.7
72	87.9	92.3	90.5
75	88.1	92.5	90.3
96	87.7	92.1	91.3

Compost with 100% MC at 5°C

Time (hours)	DCM(% of initial Concentration) in the batch headspace	TCE (% of initial Concentration) in the batch headspace	TCA (% of initial Concentration) in the batch headspace
0	100	100	100
3	100	100	98.2
6	100	100	100
9	99.8	100	100
24	99.6	99.2	95.7
27	98.3	95.4	95.2
30	97.5	94.6	95.5
48	93.7	93.5	93.6
51	93.2	93.1	93.2
54	88.7	93.3	92.9
72	88.5	92.9	92.4
75	88.1	93.0	92.0
96	88.3	92.8	91.9

Compost with 142% MC at 5°C

Time (hours)	DCM(% of initial Concentration) in the batch headspace	TCE (% of initial Concentration) in the batch headspace	TCA (% of initial Concentration) in the batch headspace
0	100	100	100
3	100	100	98.5
6	99.2	100	98.9
9	99.5	100	98.7
24	98.6	98.5	95.7
27	98.5	96.4	95.5
30	96.9	95.2	95.2
48	94.2	94.8	93.9
51	93.5	94.3	92.5
54	89.0	94.0	92.7
72	88.9	93.9	92.7
75	88.5	93.5	91.8
96	88.7	93.1	91.7

Compost with 57% MC at 22°C

Time (hours)	DCM(% of initial Concentration) in the batch headspace	TCE (% of initial Concentration) in the batch headspace
0	100	100
3	96.6	99.4
6	91.9	97.7
9	87.7	90.1
12	85.9	82.3
15	80.6	75.5
24	51.9	53.9
27	51.2	54.2
30	51.5	53.7
48	43.2	51.4
72	41.8	51.1
96	41.6	50.4

Compost with 100% MC at 22°C

Time (hours)	DCM(% of initial Concentration) in the batch headspace	TCE (% of initial Concentration) in the batch headspace
0	100	100
3	96.6	99.7
6	91.9	99.1
9	87.7	94.2
12	85.9	85.7
15	80.6	82.1
24	55.3	59.8
27	54.8	57.3
30	55.0	54.7
48	46.2	52.9
72	46.8	53.3
96	46.2	53.0

Compost with 142% MC at 22°C

Time (hours)	DCM(% of initial Concentration) in the batch headspace	TCE (% of initial Concentration) in the batch headspace
0	100	100
3	99.7	98.3
6	99.1	97.6
9	79.9	82.7
24	65.5	59.1
27	63.5	58.7
30	54.7	57.5
48	48.9	55.2
72	48.1	54.3
96	48.4	54.3

Compost with 57% MC at 35°C

Time (hours)	DCM(% of initial Concentration) in the batch headspace	TCE (% of initial Concentration) in the batch headspace
0	100	100
3	99.5	95.1
6	89.9	89.5
9	80.2	65.3
24	42.3	42.7
27	40.7	42.2
30	40.9	42.8
48	37.9	40.5
72	37.0	40.7
96	36.3	40.5

Compost with 100% MC at 35°C

Time (hours)	DCM(% of initial Concentration) in the batch headspace	TCE (% of initial Concentration) in the batch headspace
0	100	100
3	93.6	94.3
6	90.7	84.8
9	85.9	72.2
24	47.3	45.9
27	45.2	44.7
30	46.2	44.9
48	42.5	44.1
72	42.3	43.8
96	42.3	43.7

Compost with 142% MC at 35°C

Time (hours)	DCM(% of initial Concentration) in the batch headspace	TCE (% of initial Concentration) in the batch headspace
0	100	100
3	91.1	95.2
6	85.9	90.5
9	77.6	80.0
24	52.2	52.4
27	48.1	51.7
30	47.2	51.9
48	46.9	50.4
72	46.0	49.8
96	45.8	49.5

APPENDIX VI

ANALYSIS AND SAMPLE CALCULATIONS –

LONG-TERM BEHAVIOR OF BACTERIAL METHANE AND NMOCs OXIDATION IN LANDFILL BIO-COVERS: COLUMN STUDY

Appendix VI includes examples of raw data, detailed analysis for the experiments conducted and discussed in Chapter 6.

Appendix VI-1 Gases Mass Balances in the Column Experiments

Methane oxidation is a bacterial process that occurs wherever CH_4 is present with O_2 at the same time. It occurs in landfill top cover system, where CH_4 and O_2 counter gradients intersect in the active zone of the final cover. The biological oxidation proceeds according to the following equation reported by Borjesson et al., 1997:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \quad \Delta G^o = -780 \text{ kJ/mol}CH_4$$

The mass balance of the gases (CH_4, O_2 and CO_2) was monitored during the column experiments. The following are some of the raw data and mass balance calculations for one of the column experiments with compost that contained 30% S.L. at 22°C. The first 50 days of the experiment, CH_4 fluxes were fed into the compost. At day 50 and after taking the gases readings, the columns were opened and samples were tested, according to the protocol mentioned in Chapter 6. Extra amounts of compost were added to the columns to compensate for the compost samples used for testing. The experiments proceeded by replacing the CH_4 gas cylinder with the blend of CH_4 and NMOCs cylinder. Sample calculations are presented also in the following section.

The readings and analysis presented in Table A.6 are all for the **(EXIT PORT).**

ıble A.6 **Raw data from the exit port and mass balance calculations Table**

Time	Reading	Using	GC Port A	Reading Using GC Port B			CH4 Oxidation Efficiency	Moles of CH4 Oxidized			Moles of O2 consumed			Moles of CO2 Produced
(Day)	% O2	% N2	%CH4	%CO2		(mL)	(%)	(mmoles/min)		(mL)	(mmoles/min)		(mL)	(mmoles/m
1	19.8	74	6.2		Flow out	79	2.04	0.004	O2 in	16.8	0.05			
					CH4 in	5			O2 out	15.642				
					CH4 out	4.90								
2	19.2	75	5.8		Flow out	79	8.36	0.02	O2 in	16.80	0.07			
					CH4 in	5			O2 out	15.17				
					CH4 out	4.58								
4	17.9	77.1	5	1.1	Flow out	76	24.00	0.05	O2 in	16.80	0.13	CO2 out	0.84	0.03
					CH4 in	5			O2 out	13.60				
					CH4 out	3.80								
10	17.2	78	4.8	1.3	Flow out	78	25.12	0.05	O2 in	16.80	0.14	CO2 out	1.01	0.04
					CH4 in	5			O2 out	13.42				
					CH4 out	3.74								
11	15.7	80.1	4.2	1.5	Flow out	80	32.80	0.07	O2 in	16.80	0.18	CO2 out	1.20	0.05
					CH4 in	5			O2 out	12.56				
					CH4 out	3.36								
12	16.5	79	4.5	1.3	Flow out	81	27.10	0.06	O2 in	17.01	0.15	CO2 out	1.05	0.04
					CH4 in	5			O2 out	13.37				
					CH4 out	3.65								

14	16.1	79.4	4.5	1.8	Flow out	78	29.80	0.06	O2 in	16.38	0.16	CO2 out	1.40	0.06
					CH4 in	5			O2 out	12.56				
					CH4 out	3.51								
15	16.7	65.4	4.7	1.5	Flow out	80	24.80	0.05	O2 in	16.80	0.14	CO2 out	1.20	0.05
					CH4 in	5			O2 out	13.36				
					CH4 out	3.76								
17	15.9	80.3	3.8	1.9	Flow out	82	37.68	0.08	O2 in	17.22	0.17	CO2 out	1.56	0.06
					CH4 in	5			O2 out	13.04				
					CH4 out	3.12								
18	16.2	79.5	4.3	1.8	Flow out	80	31.20	0.06	O2 in	16.80	0.16	CO2 out	1.44	0.06
					CH4 in	5			O2 out	12.96				
					CH4 out	3.44								
20	15.2	80.9	3.9	2.3	Flow out	80	37.60	0.08	O2 in	16.80	0.19	CO2 out	1.84	0.08
					CH4 in	5			O2 out	12.16				
					CH4 out	3.12								
21	14.7	81.7	3.6	2.5	Flow out	82	40.96	0.08	O2 in	17.22	0.21	CO2 out	2.05	0.08
					CH4 in	5			O2 out	12.05				
					CH4 out	2.95								
23	14.2	83.0	2.8	3.5	Flow out	80	55.20	0.11	O2 in	17.22	0.24	CO2 out	2.80	0.12
					CH4 in	5			O2 out	11.36				
					CH4 out	2.24								
24	13.7	83.5	2.8	3.7	Flow out	77	56.88	0.12	O2 in	16.80	0.26	CO2 out	2.85	0.12
					CH4 in	5			O2 out	10.55				
					CH4 out	2.16								

25	13.5	83.7	2.8	3.8	Flow out	75	58.00	0.12	O2 in	15.75	0.23	CO2 out	2.85	0.12
					CH4 in	5			O2 out	10.13				
					CH4 out	2.10								
27	13.7	83.6	2.7	4.3	Flow out	76	58.96	0.12	O2 in	15.96	0.23	CO2 out	3.27	0.14
					CH4 in	5			O2 out	10.41				
					CH4 out	2.05								
28	13.2	83.8	3.0	4.0	Flow out	77	53.80	0.11	O2 in	16.80	0.27	CO2 out	3.08	0.13
					CH4 in	5			O2 out	10.16				
					CH4 out	2.31								
29	14.1	83.0	2.9	4.1	Flow out	75	56.50	0.12	O2 in	16.80	0.26	CO2 out	3.08	0.13
					CH4 in	5			O2 out	10.58				
					CH4 out	2.18								
31	14.3	82.6	3.1	4.0	Flow out	77	52.26	0.11	O2 in	16.80	0.24	CO2 out	3.08	0.13
					CH4 in	5			O2 out	11.01				
					CH4 out	2.39								
33	13.9	83.4	2.7	4.4	Flow out	78	57.88	0.12	O2 in	17.01	0.25	CO2 out	3.43	0.14
					CH4 in	5			O2 out	10.84				
					CH4 out	2.11								
34	13.5	83.6	2.9	4.2	Flow out	80	53.60	0.11	O2 in	16.80	0.25	CO2 out	3.36	0.14
					CH4 in	5			O2 out	10.80				
					CH4 out	2.32								
35	13.3	83.7	3.0	3.9	Flow out	81	51.40	0.11	O2 in	17.01	0.26	CO2 out	3.16	0.13
					CH4 in	5			O2 out	10.77				
					CH4 out	2.43								

38	13.1	84.0	2.9	4.2	Flow out	79	54.18	0.11	O2 in	16.59	0.257999	CO2 out	3.32	0.14
					CH4 in	5			O2 out	10.35				
					CH4 out	2.29								
40	12.9	84.4	2.7	4.4	Flow out	80	56.80	0.12	O2 in	16.80	0.27	CO2 out	3.52	0.15
					CH4 in	5			O2 out	10.32				
					CH4 out	2.16								
41	12.5	84.8	2.7	4.7	Flow out	78	57.88	0.12	O2 in	16.38	0.27	CO2 out	3.67	0.15
					CH4 in	5			O2 out	9.75				
					CH4 out	2.11								
45	13.4	83.9	2.7	5.1	Flow out	77	58.42	0.12	O2 in	16.80	0.27	CO2 out	3.93	0.16
					CH4 in	5			O2 out	10.32				
					CH4 out	2.08								
50	13.1	84.1	2.8	4.8	Flow out	78	56.32	0.12	O2 in	16.38	0.25	CO2 out	3.74	0.15
					CH4 in	5			O2 out	10.22				
					CH4 out	2.18								
55	18.3	76.4	5.3	1.3	Flow out	80	15.20	0.03	O2 in	16.80	0.09	CO2 out	1.04	0.04
					CH4 in	5			O2 out	14.64				
					CH4 out	4.24								
60	19.2	75.5	5.3	1.1	Flow out	82	13.08	0.03	O2 in	17.22	0.06	CO2 out	0.90	0.04
					CH4 in	5			O2 out	15.74				
					CH4 out	4.35								
65	18.4	76.5	5.1	1.4	Flow out	82	16.36	0.03	O2 in	17.22	0.09	CO2 out	1.15	0.05
					CH4 in	5			O2 out	15.09				
					CH4 out	4.18								

70	17.7	77.6	4.7	1.8	Flow out	81	23.86	0.05	O2 in	17.01	0.11	CO2 out	1.46	0.06
					CH4 in	5			O2 out	14.34				
					CH4 out	3.81								
75	17.6	77.5	4.9	1.7	Flow out	80	21.60	0.04	O2 in	16.80	0.11	CO2 out	1.36	0.06
					CH4 in	5			O2 out	14.08				
					CH4 out	3.92								
80	16.5	79.3	4.2	1.8	Flow out	83	30.28	0.06	O2 in	17.43	0.15	CO2 out	1.49	0.06
					CH4 in	5			O2 out	13.70				
					CH4 out	3.49								
85	15.7	80.2	4.1	2.1	Flow out	79	35.22	0.07	O2 in	16.59	0.17	CO2 out	1.66	0.07
					CH4 in	5			O2 out	12.40				
					CH4 out	3.24								
90	14.9	81.2	3.9	2.2	Flow out	77	39.94	0.08	O2 in	16.17	0.19	CO2 out	1.69	0.07
					CH4 in	5			O2 out	11.47				
					CH4 out	3.00								
93	14.7	81.4	3.9	2.5	Flow out	80	37.60	0.08	O2 in	16.80	0.21	CO2 out	2.00	0.08
					CH4 in	5			O2 out	11.76				
					CH4 out	3.12								
97	14.6	81.5	3.8	2.4	Flow out	79	39.96	0.08	O2 in	16.59	0.21	CO2 out	1.90	0.08
					CH4 in	5			O2 out	11.53				
					CH4 out	3.00								
100	14.9	81.4	3.7	2.7	Flow out	81	40.06	0.08	O2 in	17.01	0.20	CO2 out	2.19	0.09
					CH4 in	5			O2 out	12.07				
					CH4 out	3.00								

Sample Calculations – Day 45:

45	13.4	83.9	2.7	5.1	Flow out	77	58.42	0.12	O2 in	16.80	0.27	CO2 out	3.93	0.16
					CH4 in	5			O2 out	10.32				
					CH4 out	2.08								

n day 45: The GC reading using port A, which analyzes CH_4, O_2 and the balance is N_2 was (14.1% O_2, 2.7% CH_4 and the rest is N_2)

Methane Analysis:

Methane inflow measured using the flow meter was (5 mL/min).

Methane out flow was calculated as follows: flow out×% of CH_4 = 77 mL/min× 2.7%= 2.08 mL/min.

Methane oxidation efficiency = [(5-2.08)/5] ×100%= 58.4%.

CH_4 volume oxidized = (5-2.08) = 2.92 mL/min

No. of CH_4 moles oxidized = P × V/ R × T= (1.0 × 2.92 mL)/ (0.082 × 295) = 0.121 mmole CH_4/min.

Oxygen Analysis:

O_2 Inflow = Air flow in × GC reading for O_2 percentage in the air inflow = 80 mL/min × 21% = 16.80 mL/min

O_2 outflow = 77 mL/min × 13.4% = 10.32 mL/min

O_2 volume consumed = 16.8 – 10.32 = 6.48 mL/min.

No. of O_2 moles consumed = P × V/ R × T = (1.0 × 6.48mL)/ (0.082 × 295) = 0.27 mmole O_2 /min consumed.

Carbon Dioxide Analysis:

CO_2 inflow = zero

CO_2 produced = Flow out × % CO_2 in the sample from the exit port= 77 mL/min × 5.1 = 3.93 mL of CO_2 produced/min.

No. of CO_2 moles produced = P × V/ R × T = (1.0 × 3.93mL)/ (0.082 × 295) = 0.16 mmole CO_2 Produced/min.

Check mass balances Calculated:

CH_4 moles Oxidized = 0.121 mmole CH_4/min, O_2 moles Consumed =0.27 mmole O_2/min, CO_2 moles Produced= 0.16 mmole CO_2 /min

Take into consideration the respiration rate from batch experiments to test original compost respiration rate: O_2 respiration rate = 0.03 mmole/min,

CO_2 respiration rate = 0.02 mmole/min

Therefore, the mass balance check is as follows:

$CH_4 : O_2 : CO_2 \rightarrow$ 0.121 mmole CH_4/min : 0.24 mmole O_2/min: 0.14 mmole CO_2/min.

Appendix VI-2 Sample Calculation of moles of CH_4, O_2 and CO_2 in m^2 of compost in day

The following sample calculations are for the columns that contained compost with 30% S.L. at 22°C. The first 50 days of the experiment, CH_4 fluxes were fed into the compost. At day 50 and after taking the gases readings, the columns were opened and samples were tested, according to the protocol mentioned in Chapter 6. Extra amounts of compost were added to the columns to compensate for the compost samples used for testing. The experiments proceeded by replacing the CH_4 gas cylinder with the blend of CH_4 and NMOCs cylinder. Each data point is the average of the duplicates.

Table A.7 CH_4 oxidation efficiencies and rates, O_2 consumption rates and CO_2 production rates in experimental set 1 that contained compost with 30% S.L. at 22°C.

Time (day)	CH_4 Oxidation Efficency (%)	CH_4 moles Oxidized (mmole min^{-1})	CH_4 moles Oxidized (mole m^{-2} d^{-1}	Mass of CH_4 oxidized ($mgCH_4$ min^{-1})	Mass of CH_4 oxidized ($mgCH_4$ m^{-2} d^{-1})	O_2 moles consumed (mmoles min^{-1})	moles of O_2 Consumed (mole m^{-2} d^{-1})	CO_2 moles produced (mmoles min^{-1})	moles of CO_2 produced(mole m^{-2} d^{-1})
1	**2.04**	0.00	0.38	0.07	**6.07**	0.05	4.31		
2	**8.36**	0.02	1.56	0.28	**24.88**	0.07	6.07		
4	**24.00**	0.05	4.46	0.79	**71.43**	0.13	11.89	0.03	3.11
10	**25.12**	0.05	4.67	0.83	**74.77**	0.14	12.59	0.04	3.77
11	**32.80**	0.07	6.10	1.08	**97.63**	0.18	15.78	0.05	4.46
12	**27.10**	0.06	5.04	0.90	**80.66**	0.15	13.56	0.04	3.92
14	**29.80**	0.06	5.54	0.99	**88.70**	0.16	14.22	0.06	5.22
15	**24.80**	0.05	4.61	0.82	**73.82**	0.14	12.80	0.05	4.46
17	**37.68**	0.08	7.01	1.25	**112.15**	0.17	15.56	0.06	5.80
18	**31.20**	0.06	5.80	1.03	**92.86**	0.16	14.29	0.06	5.36
20	**37.60**	0.08	6.99	1.24	**111.91**	0.19	17.26	0.08	6.85
21	**40.96**	0.08	7.62	1.35	**121.91**	0.21	19.22	0.08	7.63
23	**55.20**	0.11	10.27	1.83	**164.30**	0.24	21.80	0.12	10.42
24	**56.88**	0.12	10.58	1.88	**169.30**	0.26	23.26	0.12	10.60
25	**58.00**	0.12	10.79	1.92	**172.63**	0.23	20.93	0.12	10.60
27	**58.96**	0.12	10.97	1.95	**175.49**	0.26	23.77	0.14	12.16
28	**53.80**	0.11	10.01	1.78	**160.13**	0.27	24.69	0.13	11.46
29	**56.50**	0.12	10.51	1.87	**168.17**	0.26	23.16	0.13	11.44
31	**52.26**	0.11	9.72	1.73	**155.55**	0.24	21.54	0.13	11.46

33	**57.88**	0.12	10.77	1.91	**172.28**	0.25	22.95	0.14	12.77
34	**53.60**	0.11	9.97	1.77	**159.54**	0.25	22.32	0.14	12.50
35	**51.40**	0.11	9.56	1.70	**152.99**	0.26	23.21	0.13	11.75
38	**54.18**	0.11	10.08	1.79	**161.26**	0.26	23.22	0.14	12.34
40	**56.80**	0.12	10.57	1.88	**169.06**	0.27	24.11	0.15	13.10
41	**57.88**	0.12	10.77	1.91	**172.28**	0.27	24.67	0.15	13.64
45	**58.42**	0.12	10.87	1.93	**173.88**	0.27	24.12	0.16	14.61
50	**56.32**	0.12	10.48	1.86	**167.63**	0.25	22.93	0.15	13.93
55	**15.20**	0.03	2.83	0.50	**45.24**	0.09	8.04	0.04	3.87
60	13.08	0.03	2.43	0.43	**38.93**	0.06	5.49	0.04	3.36
65	**16.36**	0.03	3.04	0.54	**48.69**	0.09	7.93	0.05	4.27
70	**23.86**	0.05	4.44	0.79	**71.02**	0.11	9.95	0.06	5.42
75	**21.60**	0.04	4.02	0.71	**64.29**	0.11	10.12	0.06	5.06
80	**30.28**	0.06	5.63	1.00	**90.13**	0.15	13.90	0.06	5.56
85	**35.22**	0.07	6.55	1.16	**104.83**	0.17	15.58	0.07	6.17
90	**39.94**	0.08	7.43	1.32	**118.88**	0.19	17.48	0.07	6.30
93	**37.60**	0.08	6.99	1.24	**111.91**	0.21	18.75	0.08	7.44
97	**39.96**	0.08	7.43	1.32	**118.94**	0.21	18.81	0.08	7.05
100	**40.06**	0.08	7.45	1.32	**119.24**	0.20	18.38	0.09	8.14

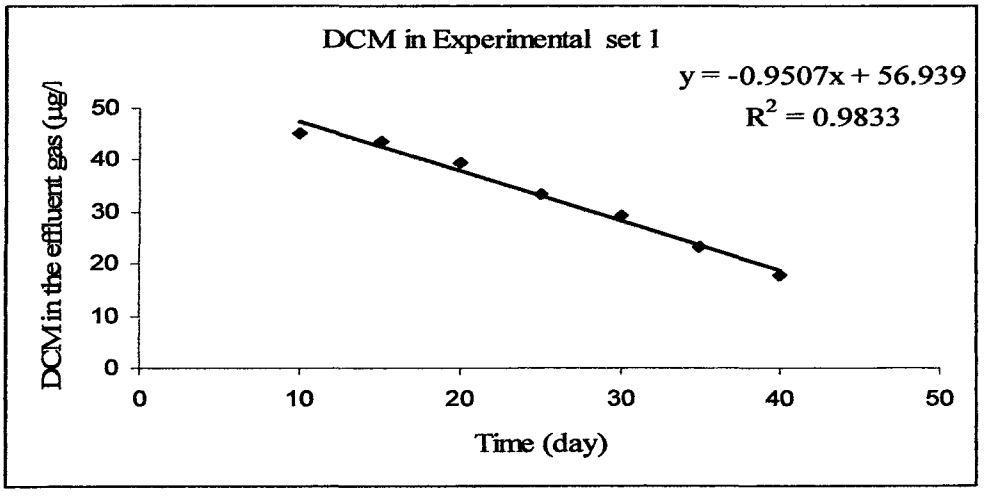
Appendix VI-3 NMOCs Biological Co-oxidation Rates

Table A.8 shows sample calculations for the biological degradation of DCM and TCE in experimental set 1. Each data point is the average of duplicates.

Table A.8 Sample calculations for the biological co-oxidation of DCM and TCE in experimental set 1

Experimental Set 1						
	DCM			TCE		
day	µg/L in the effluent gas	µg/L biologically co-oxidized	C/C_0	µg/L in the effluent gas	µg/L biologically co-oxidized	C/C_0
0	46.7	0	1	8.7	0	1
10	45.2	1.5	0.97	8.7	0	1
15	43.7	3	0.93	8.7	0	1
20	39.4	7.3	0.84	8.4	0.3	0.965517
25	33.4	13.3	0.71	7.52	1.18	0.864368
30	29.4	17.3	0.63	6.52	2.18	0.749425
35	23.4	23.3	0.5	5.21	3.49	0.598851
40	17.7	29	0.38	4.32	4.38	0.496552
45	18.5	28.2	0.4	4.46	4.24	0.512644
50	18.2	28.5	0.39	4.4	4.3	0.505747

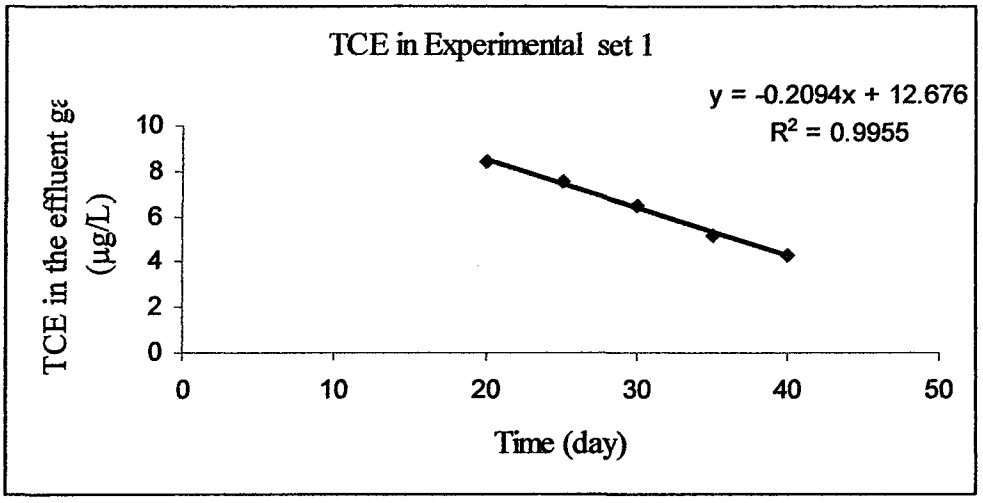
The co-oxidation rate was obtained from the zero-order degradation curves, as follows:



The DCM degradation rate is 0.9507 μgDCM/L day, but in 1 day there is 5mL/min of gas, therefore the amount of DCM degraded in a day = 0.9507 × 5 mL × 60 (min/hour) × 24 hour/day= 6845 μg of DCM/day. Divide by the compost area in the column,

The biological degradation rate of DCM= 427.815 mg DCM day^{-1} m^{-2}

The same method was used to calculate the TCE biological degradation.



The degradation rate is 0.2094 μgTCE/L day, the amount of TCE degraded in a day = 0.2094 × 5 mL × 60 (min/hour) × 24= 1507.68 μg of TCE/day. Divide by the compost area in the column,

The biological degradation rate of TCE= 94.230 mg DCM day^{-1} m^{-2} .

Appendix VI-4 NMOCs Mass Distribution between Solid-Water-Gas Phases of the Compost Column Experiments

When an organic compound is released into the LFG as vapor, it will partition onto the cover system (soil or compost).

Mass of compound (I) = mass in gas + mass in water + mass in compost [AVI-1]

Mass in gas = Concentration of compound in gas (μg/L) × Volume of gas (L)[AVI-2]

Mass in water =

From the definition of partial pressure, Henry's constant also represent the ratio of the concentration to the concentration in liquid:

$H = C_g/C_L$

C_g = Concentration of the compound in gas phase,

C_L = Concentration of compound in liquid phase, therefore,

$C_L = Cg/K_H$ [AVI-3]

Mass in water = Concentration of compound in water (μg/L) × Volume of water

Mass in water = $C_L \times V_L$ substitute from AVI-3

Mass of compound in water = Cg/H × Volume of water [AVI-4]

Furthermore, the compost-water partition coefficient K_{sw} is a dimensionless constant that describes the tendency of a chemical to be absorbed by a soil/compost in aqueous suspension, K_{sw} is defined as:

Ksw = X/C, where, [AVI-5]

X= Concentration of the chemical in soil/compost (μg/ Kg of compost), and

C= Concentrations of chemical in water (ppb or μg/Kg)

A general expression for organic compound sorption in the LFC system is the soil/compost distribution coefficient. Almost all of the sorption of organic chemical by a soil/compost is due to the organic carbon of the soil,

$K_{oc} = C_{soil}/C_{water}$ [AVI-6]

C_{soil} = concentration of chemical in organic carbon component of soil (μg adsorbed/ kg organic carbon).

C_{water} = Concentration of chemical in water (μg /kg of water)

The concentration of compound in the soil/compost can be calculated using the soil water partition coefficient (K_{sw}) and the organic carbon partition coefficient (K_{oc}). The coefficient K_{sw} is equal to K_{oc} multiplied by the fraction of organic carbon in the soil (f_{oc}). The organic matter content (by loss on ignition) contains approximately 58% carbon; therefore, a correction factor is applied to estimate the organic carbon content of soil/compost from the measurement of organic matter content

$K_{sw} = K_{oc} \times f_{oc}$ [AVI-7]

From [AVI-3] and [AVI-5],

Concentration of compound in compost = $\frac{K_{sw} \times C_g}{K_H}$, and from [AVI-7]

Concentration of compound in compost = $\frac{K_{oc} \times f_{oc} \times C_g}{K_H}$ [AVI-8]

Mass of compound will be the sum of (AVI-2], [AVI-4] and [AVI-8], which is:

Mass of compound = $= C_{gas} \times \frac{V_{water}}{K_H} + C_{gas} \times mass_{compost} \times \frac{f_{OC} \times K_{OC}}{K_H} + C_{gas} \times V_{gas}$

The fraction of organic carbon f_{oc} :

The mass lost on ignition is an estimate of soil organic matter which contains approximately 58% carbon. A correction factor (0.58) is applied to estimate the organic carbon content of the compost/soil from the measurement of mass lost on ignition according to ASTM 2974-87.

Reference:

LaGrega, M., Buckingham, P., Evans, J., (2001), "Hazardous Waste Management," McGraw-Hill Higher Education, ISBN-13: 978-0-07-039365-3, ISBN-10: 0-07-039365-6.

Appendix VI-5 Chemical Properties of Selected NMOCs

Table A.9 shows chemical names and properties for the NMOCs selected in this study.

Table A.9 Chemical properties of the selected NMOCs

Chemical Full Name	Compound		Molecular weight (g/mole)	K_{oc} (mL/g)	K_H
Dichloromethane	DCM	CH_2Cl_2	84.93	8.8	0.11
Trichloroethylene	TCE	C_2HCl_3	131.38	126	0.403
1,1,2-trichloroethane	TCA	$C_2H_3CL_3$	133.40	56	0.037

APPENDIX VII

ANALYSIS AND SAMPLE CALCULATIONS –

APPLICATION OF NEURAL NETWORK FOR SIMULATION OF BIOLOGICAL CH_4 OXIDATION IN LANDFILL BIO-COVERS

Appendix VII includes examples of raw data, detailed analysis for the experiments conducted and discussed in Chapter 7.

Appendix VII-1 Training and Verification Report for the ANN (3-4-1)

*** NeuralMachine: neural network tool ***
*** Training and Verification Report ***

Date: 3/10/2009 2:22:48 PM

Project file : C:\Documents and Settings\User\Desktop\MUNA\MunaANN.anf
Working folder : C:\Documents and Settings\User\Desktop\MUNA
Project title : Oxidation of CH_4 in presence of NMOCs
Problem type : Numerical prediction

Training data file : MunaTraining.csv
Examples in training set : 107
Number of input attributes : 3
Number of output attributes : 1
--- Cross-validation and verification ---
Cross-validation data file : MunaValidation.csv
Examples in cross-validation : 14

Verification data file : MunaVerification.csv
Examples in verification : 14

--- Model description ---
Model type : Multi-layer perceptron (MLP)
File with ANN weights used to perform verification:
MunaTraining.wei

Hidden nodes type : Sigmoid
Output nodes type : Sigmoid
Number of hidden nodes : 4
Number of iterations made : 1207

===== TRAINING: Calculated values and errors =====

[1] 1. Var 1

Examples	Measured	Calculated	Difference
1	7.454E+00	7.963E+00	-5.090E-01
2	8.600E+00	7.963E+00	6.370E-01
3	7.900E+00	7.414E+00	4.863E-01
4	7.189E+00	7.414E+00	-2.247E-01
5	6.300E+00	7.414E+00	-1.114E+00
6	8.100E+00	6.638E+00	1.462E+00
7	5.500E+00	6.638E+00	-1.138E+00
8	4.300E+00	5.021E+00	-7.211E-01

9	5.900E+00	5.021E+00	8.789E-01
10	5.300E+00	5.021E+00	2.789E-01
11	4.100E+00	4.768E+00	-6.679E-01
12	4.800E+00	4.768E+00	3.210E-02
13	4.700E+00	5.544E+00	-8.437E-01
14	5.700E+00	5.544E+00	1.563E-01
15	7.000E+00	5.544E+00	1.456E+00
16	4.700E+00	5.264E+00	-5.644E-01
17	6.500E+00	5.264E+00	1.236E+00
18	5.900E+00	4.884E+00	1.016E+00
19	4.000E+00	4.884E+00	-8.840E-01
20	5.200E+00	4.884E+00	3.160E-01
21	3.100E+00	4.017E+00	-9.168E-01
22	5.200E+00	4.017E+00	1.183E+00
23	3.000E+00	3.743E+00	-7.425E-01
24	4.200E+00	3.743E+00	4.575E-01
25	4.000E+00	4.788E+00	-7.878E-01
26	5.900E+00	4.788E+00	1.112E+00
27	5.300E+00	4.616E+00	6.842E-01
28	3.900E+00	4.616E+00	-7.158E-01
29	3.445E+00	4.387E+00	-9.424E-01
30	4.017E+00	4.387E+00	-3.704E-01
31	3.556E+00	3.926E+00	-3.695E-01
32	3.958E+00	3.926E+00	3.246E-02
33	2.900E+00	3.757E+00	-8.571E-01
34	4.200E+00	3.757E+00	4.429E-01
35	3.700E+00	3.757E+00	-5.706E-02
36	3.125E+01	3.070E+01	5.462E-01
37	3.009E+01	3.070E+01	-6.138E-01
38	2.918E+01	2.911E+01	7.473E-02
39	2.842E+01	2.911E+01	-6.893E-01
40	2.923E+01	2.911E+01	1.227E-01
41	2.730E+01	2.619E+01	1.106E+00
42	2.595E+01	2.619E+01	-2.437E-01
43	2.470E+01	2.619E+01	-1.494E+00
44	2.090E+01	1.909E+01	1.811E+00
45	1.760E+01	1.909E+01	-1.489E+00
46	1.850E+01	1.909E+01	-5.892E-01
47	1.866E+01	1.813E+01	5.348E-01
48	1.975E+01	1.813E+01	1.623E+00
49	2.037E+01	2.079E+01	-4.203E-01
50	1.997E+01	2.079E+01	-8.183E-01
51	2.067E+01	1.943E+01	1.238E+00
52	2.116E+01	1.943E+01	1.724E+00
53	1.636E+01	1.735E+01	-9.989E-01
54	1.662E+01	1.735E+01	-7.319E-01

55	1.252E+01	1.352E+01	-1.003E+00
56	1.480E+01	1.352E+01	1.275E+00
57	1.259E+01	1.283E+01	-2.495E-01
58	1.314E+01	1.283E+01	3.075E-01
59	1.277E+01	1.283E+01	-6.346E-02
60	1.320E+01	1.344E+01	-2.373E-01
61	1.401E+01	1.344E+01	5.697E-01
62	1.313E+01	1.344E+01	-3.093E-01
63	1.360E+01	1.263E+01	9.622E-01
64	1.190E+01	1.263E+01	-7.378E-01
65	1.270E+01	1.263E+01	6.223E-02
66	1.310E+01	1.157E+01	1.526E+00
67	1.030E+01	1.157E+01	-1.274E+00
68	9.902E+00	1.081E+01	-9.127E-01
69	1.146E+01	1.081E+01	6.473E-01
70	9.867E+00	1.083E+01	-9.698E-01
71	1.148E+01	1.083E+01	6.462E-01
72	3.820E+01	3.650E+01	1.696E+00
73	3.640E+01	3.650E+01	-1.042E-01
74	3.420E+01	3.525E+01	-1.053E+00
75	3.720E+01	3.525E+01	1.947E+00
76	2.921E+01	3.221E+01	-3.001E+00
77	3.093E+01	3.221E+01	-1.282E+00
78	3.505E+01	3.221E+01	2.837E+00
79	2.420E+01	2.042E+01	3.782E+00
80	1.920E+01	2.042E+01	-1.218E+00
81	1.850E+01	2.042E+01	-1.918E+00
82	1.928E+01	1.920E+01	7.856E-02
83	1.966E+01	1.920E+01	4.656E-01
84	1.696E+01	1.920E+01	-2.238E+00
85	3.203E+01	3.567E+01	-3.644E+00
86	3.950E+01	3.567E+01	3.826E+00
87	3.630E+01	3.433E+01	1.970E+00
88	3.120E+01	3.433E+01	-3.130E+00
89	3.308E+01	3.433E+01	-1.247E+00
90	3.520E+01	3.135E+01	3.848E+00
91	3.070E+01	3.135E+01	-6.523E-01
92	1.730E+01	2.094E+01	-3.641E+00
93	2.220E+01	2.094E+01	1.259E+00
94	1.680E+01	1.913E+01	-2.330E+00
95	2.270E+01	1.913E+01	3.570E+00
96	2.668E+01	2.967E+01	-2.983E+00
97	2.984E+01	2.967E+01	1.750E-01
98	3.107E+01	2.967E+01	1.399E+00
99	3.193E+01	2.810E+01	3.825E+00
100	2.528E+01	2.810E+01	-2.825E+00

101	2.730E+01	2.523E+01	2.069E+00
102	2.250E+01	2.523E+01	-2.731E+00
103	1.879E+01	1.896E+01	-1.770E-01
104	1.805E+01	1.896E+01	-9.150E-01
105	2.150E+01	1.896E+01	2.535E+00
106	1.630E+01	1.804E+01	-1.739E+00
107	1.922E+01	1.804E+01	1.181E+00

*** Overall training mean squared errors (MSE) ***
Training MSE of outputs averaged for all examples : 2.388E+00
Total training MSE : 2.388E+00
Total training root mean squared error (RMSE) : 1.545E+00

===== CROSS-VALIDATION: Calculated errors =====

Total cross-val. MSE : 1.186E+00
Total cross-val. root mean squared error (RMSE) : 1.089E+00

===== VERIFICATION: Calculated values and errors =====

[1] 1. Var 1

Examples	Measured	Calculated	Difference
1	4.782E+00	4.788E+00	-5.780E-03
2	4.472E+00	4.616E+00	-1.438E-01
3	6.500E+00	6.638E+00	-1.381E-01
4	4.300E+00	4.017E+00	2.832E-01
5	6.100E+00	4.768E+00	1.332E+00
6	2.157E+01	2.079E+01	7.787E-01
7	1.923E+01	1.943E+01	-2.053E-01
8	1.129E+01	1.157E+01	-2.790E-01
9	1.300E+01	1.352E+01	-5.249E-01
10	1.810E+01	1.813E+01	-2.322E-02
11	3.823E+01	3.650E+01	1.724E+00
12	3.125E+01	3.525E+01	-4.000E+00
13	2.750E+01	3.135E+01	-3.852E+00
14	1.550E+01	1.804E+01	-2.539E+00

*** Overall verification mean squared errors (MSE) ***
Verification MSE of outputs averaged for all examples : 3.083E+00
Total verification MSE : 3.083E+00
Total verification root mean squared error (RMSE) : 1.756E+00

*** End of report.

Appendix VII-2 Training and Verification Results Analyses for the ANN (3-4-1)

Training	Examples	Measured	Calculated	Difference	ABS DIFF (MAE)	ABS DIFF
	1	7.45E+00	7.96E+00	-5.09E-01	0.509	0.068285
	2	8.60E+00	7.96E+00	6.37E-01	0.637	0.07407
	3	7.90E+00	7.41E+00	4.86E-01	0.4863	0.061557
	4	7.19E+00	7.41E+00	-2.25E-01	0.2247	0.031256
	5	6.30E+00	7.41E+00	-1.11E+00	1.114	0.176825
	6	8.10E+00	6.64E+00	1.46E+00	1.462	0.180494
	7	5.50E+00	6.64E+00	-1.14E+00	1.138	0.206909
	8	4.30E+00	5.02E+00	-7.21E-01	0.7211	0.167698
	9	5.90E+00	5.02E+00	8.79E-01	0.8789	0.148966
	10	5.30E+00	5.02E+00	2.79E-01	0.2789	0.052623
	11	4.10E+00	4.77E+00	-6.68E-01	0.6679	0.162902
	12	4.80E+00	4.77E+00	3.21E-02	0.0321	0.006688
	13	4.70E+00	5.54E+00	-8.44E-01	0.8437	0.179511
	14	5.70E+00	5.54E+00	1.56E-01	0.1563	0.027421
	15	7.00E+00	5.54E+00	1.46E+00	1.456	0.208
	16	4.70E+00	5.26E+00	-5.64E-01	0.5644	0.120085
	17	6.50E+00	5.26E+00	1.24E+00	1.236	0.190154
	18	5.90E+00	4.88E+00	1.02E+00	1.016	0.172203
	19	4.00E+00	4.88E+00	-8.84E-01	0.884	0.221
	20	5.20E+00	4.88E+00	3.16E-01	0.316	0.060769
	21	3.10E+00	4.02E+00	-9.17E-01	0.9168	0.295742
	22	5.20E+00	4.02E+00	1.18E+00	1.183	0.2275
	23	3.00E+00	3.74E+00	-7.43E-01	0.7425	0.2475
	24	4.20E+00	3.74E+00	4.58E-01	0.4575	0.108929
	25	4.00E+00	4.79E+00	-7.88E-01	0.7878	0.19695
	26	5.90E+00	4.79E+00	1.11E+00	1.112	0.188475
	27	5.30E+00	4.62E+00	6.84E-01	0.6842	0.129094
	28	3.90E+00	4.62E+00	-7.16E-01	0.7158	0.183538
	29	3.45E+00	4.39E+00	-9.42E-01	0.9424	0.273556
	30	4.02E+00	4.39E+00	-3.70E-01	0.3704	0.092208
	31	3.56E+00	3.93E+00	-3.70E-01	0.3695	0.103909
	32	3.96E+00	3.93E+00	3.25E-02	0.03246	0.008201
	33	2.90E+00	3.76E+00	-8.57E-01	0.8571	0.295552
	34	4.20E+00	3.76E+00	4.43E-01	0.4429	0.105452
	35	3.70E+00	3.76E+00	-5.71E-02	0.05706	0.015422
	36	3.13E+01	3.07E+01	5.46E-01	0.5462	0.017478
	37	3.01E+01	3.07E+01	-6.14E-01	0.6138	0.020399
	38	2.92E+01	2.91E+01	7.47E-02	0.07473	0.002561
	39	2.84E+01	2.91E+01	-6.89E-01	0.6893	0.024254
	40	2.92E+01	2.91E+01	1.23E-01	0.1227	0.004198

	41	2.73E+01	2.62E+01	1.11E+00	1.106	0.040513
	42	2.60E+01	2.62E+01	-2.44E-01	0.2437	0.009391
	43	2.47E+01	2.62E+01	-1.49E+00	1.494	0.060486
	44	2.09E+01	1.91E+01	1.81E+00	1.811	0.086651
	45	1.76E+01	1.91E+01	-1.49E+00	1.489	0.084602
	46	1.85E+01	1.91E+01	-5.89E-01	0.5892	0.031849
	47	1.87E+01	1.81E+01	5.35E-01	0.5348	0.02866
	48	1.98E+01	1.81E+01	1.62E+00	1.623	0.082177
	49	2.04E+01	2.08E+01	-4.20E-01	0.4203	0.020633
	50	2.00E+01	2.08E+01	-8.18E-01	0.8183	0.040976
	51	2.07E+01	1.94E+01	1.24E+00	1.238	0.059894
	52	2.12E+01	1.94E+01	1.72E+00	1.724	0.081474
	53	1.64E+01	1.74E+01	-9.99E-01	0.9989	0.061057
	54	1.66E+01	1.74E+01	-7.32E-01	0.7319	0.044037
	55	1.25E+01	1.35E+01	-1.00E+00	1.003	0.080112
	56	1.48E+01	1.35E+01	1.28E+00	1.275	0.086149
	57	1.26E+01	1.28E+01	-2.50E-01	0.2495	0.019817
	58	1.31E+01	1.28E+01	3.08E-01	0.3075	0.023402
	59	1.28E+01	1.28E+01	-6.35E-02	0.06346	0.004969
	60	1.32E+01	1.34E+01	-2.37E-01	0.2373	0.017977
	61	1.40E+01	1.34E+01	5.70E-01	0.5697	0.040664
	62	1.31E+01	1.34E+01	-3.09E-01	0.3093	0.023557
	63	1.36E+01	1.26E+01	9.62E-01	0.9622	0.07075
	64	1.19E+01	1.26E+01	-7.38E-01	0.7378	0.062
	65	1.27E+01	1.26E+01	6.22E-02	0.06223	0.0049
	66	1.31E+01	1.16E+01	1.53E+00	1.526	0.116489
	67	1.03E+01	1.16E+01	-1.27E+00	1.274	0.123689
	68	9.90E+00	1.08E+01	-9.13E-01	0.9127	0.092173
	69	1.15E+01	1.08E+01	6.47E-01	0.6473	0.056483
	70	9.87E+00	1.08E+01	-9.70E-01	0.9698	0.098287
	71	1.15E+01	1.08E+01	6.46E-01	0.6462	0.056289
	72	3.82E+01	3.65E+01	1.70E+00	1.696	0.044398
	73	3.64E+01	3.65E+01	-1.04E-01	0.1042	0.002863
	74	3.42E+01	3.53E+01	-1.05E+00	1.053	0.030789
	75	3.72E+01	3.53E+01	1.95E+00	1.947	0.052339
	76	2.92E+01	3.22E+01	-3.00E+00	3.001	0.102739
	77	3.09E+01	3.22E+01	-1.28E+00	1.282	0.041448
	78	3.51E+01	3.22E+01	2.84E+00	2.837	0.080942
	79	2.42E+01	2.04E+01	3.78E+00	3.782	0.156281
	80	1.92E+01	2.04E+01	-1.22E+00	1.218	0.063438
	81	1.85E+01	2.04E+01	-1.92E+00	1.918	0.103676
	82	1.93E+01	1.92E+01	7.86E-02	0.07856	0.004075
	83	1.97E+01	1.92E+01	4.66E-01	0.4656	0.023683
	84	1.70E+01	1.92E+01	-2.24E+00	2.238	0.131958
	85	3.20E+01	3.57E+01	-3.64E+00	3.644	0.113768
	86	3.95E+01	3.57E+01	3.83E+00	3.826	0.096861
	87	3.63E+01	3.43E+01	1.97E+00	1.97	0.05427
	88	3.12E+01	3.43E+01	-3.13E+00	3.13	0.100321

	89	3.31E+01	3.43E+01	-1.25E+00	1.247	0.037696
	90	3.52E+01	3.14E+01	3.85E+00	3.848	0.109318
	91	3.07E+01	3.14E+01	-6.52E-01	0.6523	0.021248
	92	1.73E+01	2.09E+01	-3.64E+00	3.641	0.210462
	93	2.22E+01	2.09E+01	1.26E+00	1.259	0.056712
	94	1.68E+01	1.91E+01	-2.33E+00	2.33	0.13869
	95	2.27E+01	1.91E+01	3.57E+00	3.57	0.157269
	96	2.67E+01	2.97E+01	-2.98E+00	2.983	0.111807
	97	2.98E+01	2.97E+01	1.75E-01	0.175	0.005865
	98	3.11E+01	2.97E+01	1.40E+00	1.399	0.045027
	99	3.19E+01	2.81E+01	3.83E+00	3.825	0.119793
	100	2.53E+01	2.81E+01	-2.83E+00	2.825	0.111748
	101	2.73E+01	2.52E+01	2.07E+00	2.069	0.075788
	102	2.25E+01	2.52E+01	-2.73E+00	2.731	0.121378
	103	1.88E+01	1.90E+01	-1.77E-01	0.177	0.00942
	104	1.81E+01	1.90E+01	-9.15E-01	0.915	0.050693
	105	2.15E+01	1.90E+01	2.54E+00	2.535	0.117907
	106	1.63E+01	1.80E+01	-1.74E+00	1.739	0.106687
	107	1.92E+01	1.80E+01	1.18E+00	1.181	0.061446
					126.2072	9.641243
Training MSE of outputs averaged for all examples : 2.388E+00					1.179507	0.090105
Total training MSE : 2.388E+00					0.978635	
Total training root mean squared error (RMSE) : 1.545E+00						
Verification	**Examples**	**Measured**	**Calculated**	**Difference**		
	1	4.78E+00	4.79E+00	-5.78E-03	0.00578	0.001209
	2	4.47E+00	4.62E+00	-1.44E-01	0.1438	0.032156
	3	6.50E+00	6.64E+00	-1.38E-01	0.1381	0.021246
	4	4.30E+00	4.02E+00	2.83E-01	0.2832	0.06586
	5	6.10E+00	4.77E+00	1.33E+00	1.332	0.218361
	6	2.16E+01	2.08E+01	7.79E-01	0.7787	0.036101
	7	1.92E+01	1.94E+01	-2.05E-01	0.2053	0.010676
	8	1.13E+01	1.16E+01	-2.79E-01	0.279	0.024712
	9	1.30E+01	1.35E+01	-5.25E-01	0.5249	0.040377
	10	1.81E+01	1.81E+01	-2.32E-02	0.02322	0.001283
	11	3.82E+01	3.65E+01	1.72E+00	1.724	0.045095
	12	3.13E+01	3.53E+01	-4.00E+00	4	0.128
	13	2.75E+01	3.14E+01	-3.85E+00	3.852	0.140073
	14	1.55E+01	1.80E+01	-2.54E+00	2.539	0.163806
					15.829	0.928955
Verification MSE of outputs averaged for all examples : 3.083E+00					1.130643	0.066354
Total verification MSE : 3.083E+00					0.979205	
Total verification root mean squared error (RMSE) : 1.756E+00						
==== CROSS-VALIDATION: Calculated errors =====						
Total cross-val. MSE : 1.186E+00						

Total cross-val. root mean squared error (RMSE) : 1.089E+00					
Hidden nodes type : Sigmoid					
Output nodes type : Sigmoid					
Number of hidden nodes : 4					
Number of iterations made : 1207					

Appendix VII-3 Training Regression Results for the ANN (3-4-1)

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.98926
R Square	0.978635
Adjusted R Square	0.978432
Standard Error	1.553004
Observations	107

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	11600.02	11600.02	4809.652	1.6E-89
Residual	105	253.2412	2.411821		
Total	106	11853.26			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-0.01934	0.284491	-0.06797	0.945938	-0.58343	0.544756
X Variable 1	1.001227	0.014437	69.35165	1.6E-89	0.972601	1.029853

RESIDUAL OUTPUT

Observation	*Predicted Y*	*Residuals*	*Standard Residuals*
1	7.953431	-0.49943	-0.32312
2	7.953431	0.646569	0.418312
3	7.403758	0.496242	0.321055
4	7.403758	-0.21476	-0.13894
5	7.403758	-1.10376	-0.7141
6	6.626806	1.473194	0.953116
7	6.626806	-1.12681	-0.72901

PROBABILITY OUTPUT

Percentile	*Y*
0.46729	2.9
1.401869	3
2.336449	3.1
3.271028	3.445
4.205607	3.556
5.140187	3.7
6.074766	3.9

8	5.007822	-0.70782	-0.45794	7.009346	3.958
9	5.007822	0.892178	0.577214	7.943925	4
10	5.007822	0.292178	0.189031	8.878505	4
11	4.754512	-0.65451	-0.42345	9.813084	4.017
12	4.754512	0.045488	0.02943	10.74766	4.1
13	5.531464	-0.83146	-0.53793	11.68224	4.2
14	5.531464	0.168536	0.109038	12.61682	4.2
15	5.531464	1.468536	0.950102	13.5514	4.3
16	5.25112	-0.55112	-0.35656	14.48598	4.7
17	5.25112	1.24888	0.807991	15.42056	4.7
18	4.870654	1.029346	0.665958	16.35514	4.8
19	4.870654	-0.87065	-0.56329	17.28972	5.2
20	4.870654	0.329346	0.213078	18.2243	5.2
21	4.002591	-0.90259	-0.58395	19.15888	5.3
22	4.002591	1.197409	0.774691	20.09346	5.3
23	3.728254	-0.72825	-0.47116	21.02804	5.5
24	3.728254	0.471746	0.305206	21.96262	5.7
25	4.774536	-0.77454	-0.5011	22.8972	5.9
26	4.774536	1.125464	0.728144	23.83178	5.9
27	4.602325	0.697675	0.451376	24.76636	5.9
28	4.602325	-0.70233	-0.45439	25.70093	6.3
29	4.373044	-0.92804	-0.60042	26.63551	6.5
30	4.373044	-0.35604	-0.23035	27.57009	7
31	3.911479	-0.35548	-0.22999	28.50467	7.189
32	3.911479	0.046521	0.030098	29.43925	7.454
33	3.742272	-0.84227	-0.54493	30.37383	7.9
34	3.742272	0.457728	0.296138	31.30841	8.1
35	3.742272	-0.04227	-0.02735	32.24299	8.6
36	30.71832	0.531676	0.34398	33.17757	9.867
37	30.71832	-0.62832	-0.40651	34.11215	9.902
38	29.12637	0.053627	0.034695	35.04673	10.3
39	29.12637	-0.70637	-0.457	35.98131	11.46
40	29.12637	0.103627	0.067044	36.91589	11.48
41	26.20279	1.097209	0.709864	37.85047	11.9
42	26.20279	-0.25279	-0.16355	38.78505	12.52
43	26.20279	-1.50279	-0.97226	39.71963	12.59
44	19.09408	1.805919	1.16838	40.65421	12.7
45	19.09408	-1.49408	-0.96663	41.58879	12.77
46	19.09408	-0.59408	-0.38435	42.52336	13.1
47	18.1329	0.527097	0.341017	43.45794	13.13
48	18.1329	1.617097	1.046217	44.39252	13.14
49	20.79617	-0.42617	-0.27572	45.3271	13.2
50	20.79617	-0.82617	-0.53451	46.26168	13.6
51	19.4345	1.235502	0.799336	47.19626	14.01
52	19.4345	1.725502	1.116352	48.13084	14.8
53	17.35195	-0.99195	-0.64176	49.06542	16.3
54	17.35195	-0.73195	-0.47355	50	16.36
55	13.51725	-0.99725	-0.64519	50.93458	16.62
56	13.51725	1.282752	0.829905	51.86916	16.8
57	12.8264	-0.2364	-0.15295	52.80374	16.96

58	12.8264	0.313598	0.202889	53.73832	17.3
59	12.8264	-0.0564	-0.03649	54.6729	17.6
60	13.43715	-0.23715	-0.15343	55.60748	18.05
61	13.43715	0.57285	0.370618	56.54206	18.5
62	13.43715	-0.30715	-0.19872	57.47664	18.5
63	12.62616	0.973844	0.63005	58.41121	18.66
64	12.62616	-0.72616	-0.4698	59.34579	18.79
65	12.62616	0.073844	0.047775	60.28037	19.2
66	11.56486	1.535144	0.993196	61.21495	19.22
67	11.56486	-1.26486	-0.81833	62.14953	19.28
68	10.80392	-0.90192	-0.58352	63.08411	19.66
69	10.80392	0.656076	0.424463	64.01869	19.75
70	10.82395	-0.95695	-0.61912	64.95327	19.97
71	10.82395	0.656052	0.424447	65.88785	20.37
72	36.52544	1.674561	1.083395	66.82243	20.67
73	36.52544	-0.12544	-0.08116	67.75701	20.9
74	35.27391	-1.07391	-0.69479	68.69159	21.16
75	35.27391	1.926095	1.24613	69.62617	21.5
76	32.23018	-3.02018	-1.95397	70.56075	22.2
77	32.23018	-1.30018	-0.84118	71.49533	22.5
78	32.23018	2.819824	1.824348	72.42991	22.7
79	20.42571	3.774287	2.44186	73.36449	24.2
80	20.42571	-1.22571	-0.793	74.29907	24.7
81	20.42571	-1.92571	-1.24588	75.23364	25.28
82	19.20422	0.075784	0.04903	76.16822	25.95
83	19.20422	0.455784	0.29488	77.1028	26.68
84	19.20422	-2.24422	-1.45195	78.03738	27.3
85	35.69442	-3.66442	-2.37078	78.97196	27.3
86	35.69442	3.805579	2.462105	79.90654	28.42
87	34.35278	1.947223	1.2598	80.84112	29.18
88	34.35278	-3.15278	-2.03976	81.7757	29.21
89	34.35278	-1.27278	-0.82345	82.71028	29.23
90	31.36912	3.830879	2.478473	83.64486	29.84
91	31.36912	-0.66912	-0.4329	84.57944	30.09
92	20.94635	-3.64635	-2.35909	85.51402	30.7
93	20.94635	1.253649	0.811077	86.4486	30.93
94	19.13413	-2.33413	-1.51012	87.38318	31.07
95	19.13413	3.56587	2.307019	88.31776	31.2
96	29.68706	-3.00706	-1.94548	89.25234	31.25
97	29.68706	0.15294	0.098948	90.18692	31.93
98	29.68706	1.38294	0.894724	91.1215	32.03
99	28.11513	3.814866	2.468113	92.05607	33.08
100	28.11513	-2.83513	-1.83425	92.99065	34.2
101	25.24161	2.058387	1.331719	93.92523	35.05
102	25.24161	-2.74161	-1.77375	94.85981	35.2
103	18.96392	-0.17392	-0.11252	95.79439	36.3
104	18.96392	-0.91392	-0.59128	96.72897	36.4
105	18.96392	2.536078	1.640773	97.66355	37.2
106	18.04279	-1.74279	-1.12754	98.59813	38.2
107	18.04279	1.177207	0.76162	99.53271	39.5

Appendix VII-4 Verification Regression Results for the ANN (3-4-1)

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.989548
R Square	0.979205
Adjusted R Square	0.977472
Standard Error	1.62288
Observations	14

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1488.233	1488.233	565.0644	1.84E-11
Residual	12	31.60487	2.633739		
Total	13	1519.837			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.540919	0.776269	0.696819	0.499193	-1.15043	2.232263
X Variable 1	0.933935	0.039289	23.77108	1.84E-11	0.848332	1.019537

RESIDUAL OUTPUT

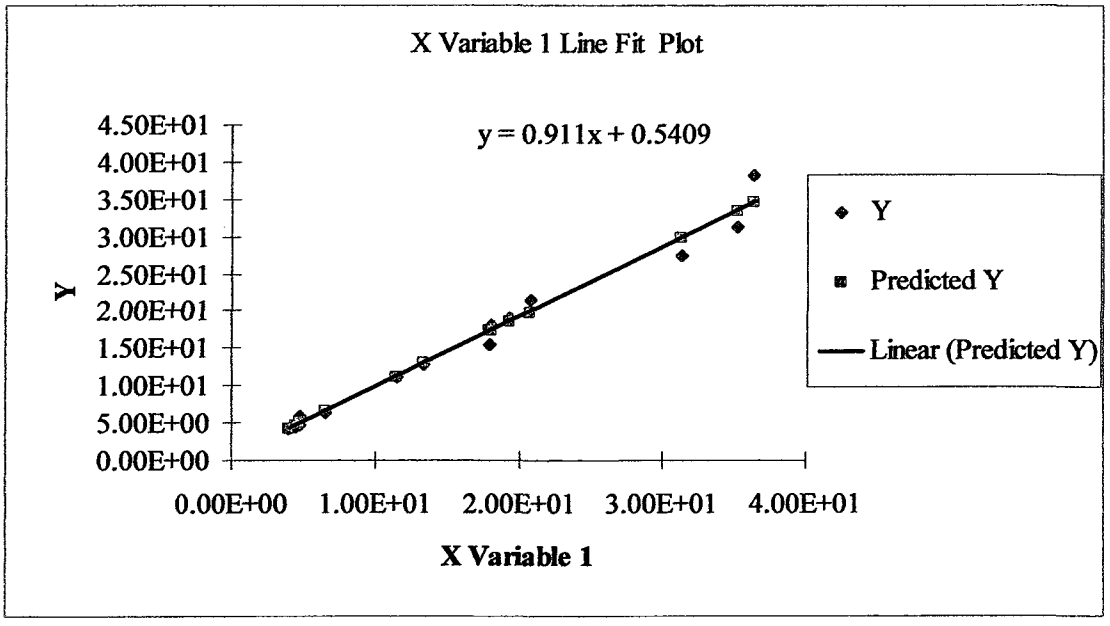
Observation	*Predicted Y*	*Residuals*	*Standard Residuals*
1	5.012598	-0.2306	-0.14789
2	4.851961	-0.37996	-0.24369
3	6.740377	-0.24038	-0.15417
4	4.292534	0.007466	0.004788
5	4.993919	1.106081	0.709384
6	19.95742	1.612581	1.034228
7	18.68727	0.542732	0.348081
8	11.34654	-0.05654	-0.03626
9	13.16771	-0.16771	-0.10756
10	17.47315	0.626847	0.402028
11	34.62953	3.600468	2.309158
12	33.46211	-2.21211	-1.41874
13	29.81977	-2.31977	-1.48778
14	17.3891	-1.8891	-1.21157

PROBABILITY OUTPUT

Percentile	*Y*
3.571429	4.3
10.71429	4.472
17.85714	4.782
25	6.1
32.14286	6.5
39.28571	11.29
46.42857	13
53.57143	15.5
60.71429	18.1
67.85714	19.23
75	21.57
82.14286	27.5
89.28571	31.25
96.42857	38.23

Appendix VII-5 Verification Using Gauch Method for the ANN (3-4-1)

			Sigma xn^2	sigma yn^2	
X hat	1.64E+01		134.5186	122.3805	
Y hat	1.58E+01		138.5379	129.3354	
b =	0.911		95.02768	87.32102	
			152.9975	133.2771	
			134.9829	94.95667	
			19.39333	32.78053	
			9.264631	11.46113	
			23.19592	20.74412	
			8.215184	8.091587	
			3.040789	5.086958	
			404.5644	501.1074	
			355.8424	237.3272	
			223.9149	135.849	
			2.735007	0.118729	
		SUM	1706.231	1519.837	%
		SB=		0.293377	**8.343512**
		NU=		0.965361	**27.45444**
		LC=		2.257491	**64.20204**
		MSE=		3.516229	

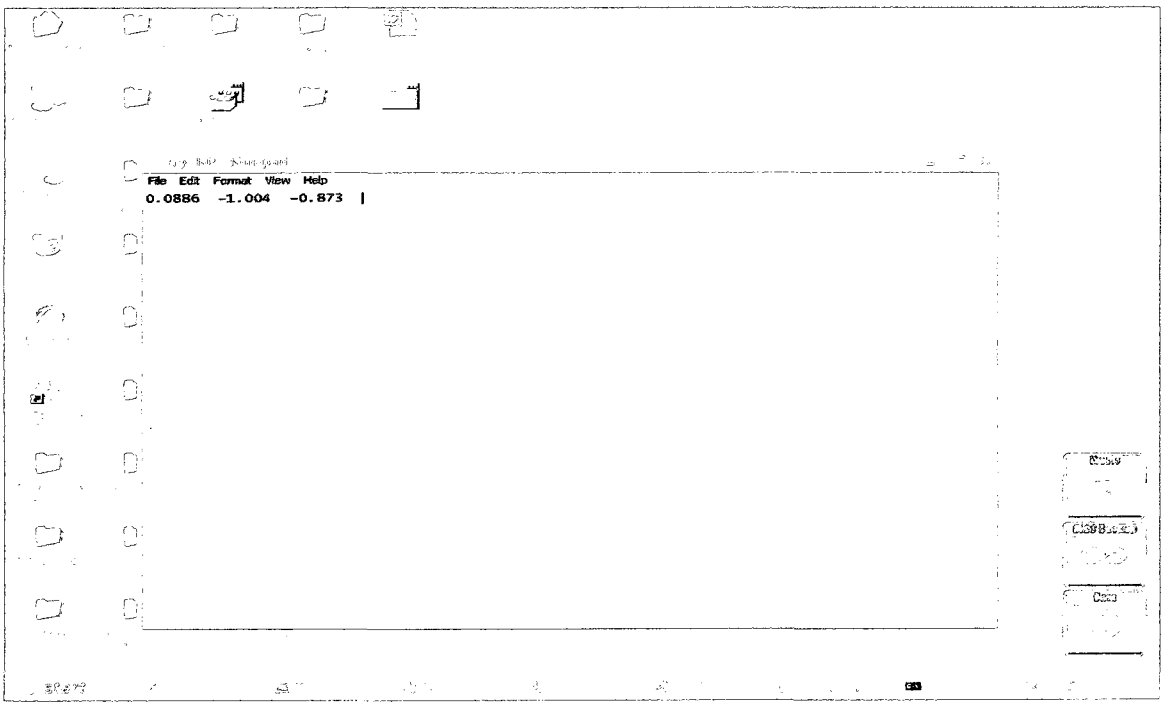


Appendix VII-6 Standardization of the input data set

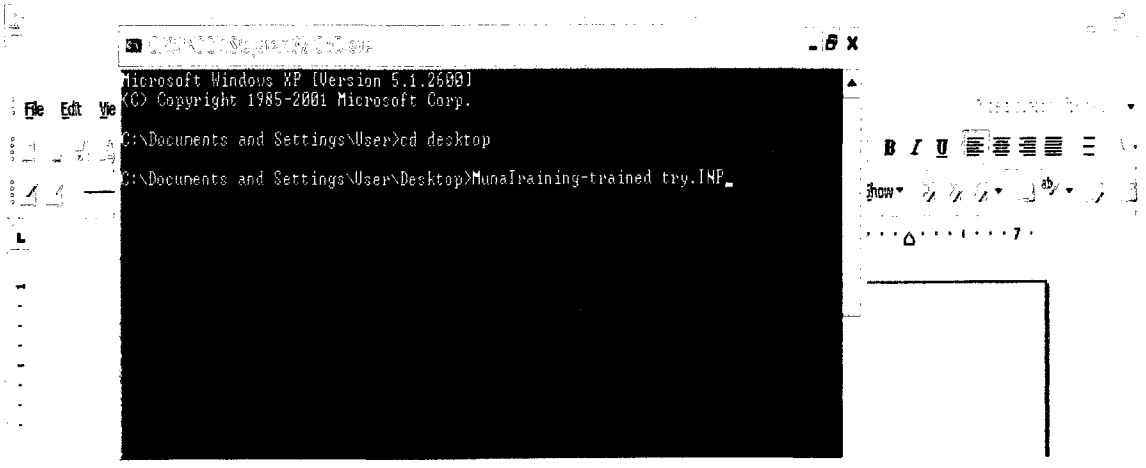
	Input Temperature °C	Standardized Temperature	Moisture content (%w/w)	Standardized Moisture content	NMOCs Concentration (ppm)	Standardized Concentration
	5	-1.041	57	-1.004	0	-0.873
	22	0.089	100	0.0078	1	-0.753
	35	0.953	142	0.996	3	-0.515
					14.3	0.8321
					18.3	1.3089
Average	20.67		99.67		7.32	
Standard Deviation	15.04		42.50		8.3885	

Appendix VII-7 Applying the Execution File for ANN with (3-4-1)

- Create an INP file with the input variables specified



- Run the EXE file and select the appropriate INP file that you would like the network to run against.



Appendix VII-8 Model Simulation

1. EFFECT OF NMOCs CONCENTRATION:

In put Parameters (standardized): Temp. M/C NMOC
0.089 -1.004 -0.873 (0ppm)

Model's result:

```
3.071E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE        (weight        file        C:\Documents        and
Settings\User\Desktop\MUNA\MunaTraining.wei)
```

Temp. M/C NMOC
0.089 -1.004 -0.753 (1ppm)

```
2.910E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 -1.004 -0.7 (1.448 ppm)

```
2.841E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 -1.004 -0.6 (2.287 ppm)

```
2.717E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 -1.004 -0.5 (3.126 ppm)

```
2.603E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 -1.004 -0.3 (4.803 ppm)

```
2.411E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 -1.004 -0.1 (6.481 ppm)

```
2.264E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 -1.004 0.1 (8.159 ppm)

2.152E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 -1.004 0.3 (9.836 ppm)

2.066E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 -1.004 0.5 (11.514 ppm)

1.998E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 -1.004 0.7 (13.191 ppm)

1.942E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 -1.004 0.9 (14.869 ppm)

1.893E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE
Temp. M/C NMOC
0.089 -1.004 1.1 (16.547 ppm)

1.851E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 -1.004 1.3 (18.225 ppm)

1.814E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. (Standardized)	MC (Standardized)	NMOCs Concentration (Standardized)	NMOCs concentration (ppm)	Predicted CH_4 oxidation rates ($\mu g\ CH_4\ h^{-1}\ g^{-1}_{wet\ wt}$)
0.088627	-1.0039	-0.873	0	30.71
		-0.753	1.00	29.1
		-0.7	1.44	28.41
		-0.6	2.29	27.17
		-0.5	3.12	26.03
		-0.3	4.80	24.11
		-0.1	6.48	22.64
		0.1	8.16	21.52
		0.3	9.84	20.66

		0.5	11.51	19.98
		0.7	13.19	19.42
		0.9	14.87	18.93
		1.1	16.55	18.52
		1.3	18.23	18.41

2. EFFECT OF TEMPERATURE:

Temp. M/C NMOC
-1.04136 0.0078 (100% MC) -0.873 (0 ppm)

```
5.545E+0000     ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
-1.04136 0.0078 (100% MC) 1.3 (18.3 ppm)

```
3.748E+0000     ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
-0.9 0.0078 (100% MC) -0.873 (0 ppm)

```
6.235E+0000     ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
-0.9 0.0078 (100% MC) 1.3 (18.3 ppm)

```
4.327E+0000     ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
-0.7 0.0078 (100% MC) -0.873 (0 ppm)

```
7.677E+0000     ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
-0.7 0.0078 (100% MC) 1.3 (18.3 ppm)

```
5.506E+0000     ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC

-0.5 0.0078 (100% MC) -0.873 (0 ppm)

```
9.866E+0000      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
-0.5 0.0078 (100% MC) 1.3 (18.3 ppm)

```
7.142E+0000      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
-0.3 0.0078 (100% MC) -0.873 (0 ppm)

```
1.295E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
-0.3 0.0078 (100% MC) 1.3 (18.3 ppm)

```
9.120E+0000      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
-0.1 0.0078 (100% MC) -0.873 (0 ppm)

```
1.682E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
-0.1 0.0078 (100% MC) 1.3 (18.3 ppm)

```
1.115E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.1 0.0078 (100% MC) -0.873 (0 ppm)

```
2.104E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.1 0.0078 (100% MC) 1.3 (18.3 ppm)

```
1.294E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC

0.3 0.0078 (100% MC) -0.873 (0 ppm)

2.517E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.3 0.0078 (100% MC) 1.3 (18.3 ppm)

1.438E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.5 0.0078 (100% MC) -0.873 (0 ppm)

2.905E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.5 0.0078 (100% MC) 1.3 (18.3 ppm)

1.562E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.7 0.0078 (100% MC) -0.873 (0 ppm)

3.252E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.7 0.0078 (100% MC) 1.3 (18.3 ppm)

1.700E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.9 0.0078 (100% MC) -0.873 (0 ppm)

3.515E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.9 0.0078 (100% MC) 1.3 (18.3 ppm)

1.871E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

MC (100%MC) (Standardized)	Temperature (Standardized)	Temperature (°C)	NMOCs = (0ppm)	Predicted CH_4 oxidation rates ($\mu g\ CH_4\ h^{-1}\ g^{-1}_{wet\ wt}$)	NMOCs = (18.3ppm)	Predicted CH_4 oxidation rates ($\mu g\ CH_4\ h^{-1}\ g^{-1}_{wet\ wt}$)
0.0078	-1.04	5.02	-0.873	5.545	1.3	3.748
	-0.9	7.13		6.235		4.327
	-0.7	10.14		7.677		5.506
	-0.5	13.14		9.866		7.142
	-0.3	16.15		12.95		9.12
	-0.1	19.16		16.82		11.15
	0.1	22.17		21.04		12.94
	0.3	25.17		25.22		14.38
	0.5	29.05		29.22		15.62
	0.7	31.20		32.52		17.00
	0.9	34.21		35.15		18.71

3. EFFECT OF MOISTURE CONTENT:

Temp. M/C NMOC
0.089 -1.004 (57% MC) -0.873 (0 ppm)

```
3.071E+0001     ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 -1.004 (57% MC) 1.3 (18.3 ppm)

```
1.814E+0001     ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 -0.674 (71% MC) -0.873 (0 ppm)

```
2.927E+0001     ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 -0.674 (71% MC) 1.3 (18.3 ppm)

```
1.681E+0001     ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 -0.32 (86% MC) -0.873 (0 ppm)

2.452E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 -0.32 (86% MC) 1.3 (18.3 ppm)

1.363E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 0.0078 (100% MC) -0.873 (0 ppm)

2.080E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 0.0078 (100% MC) 1.3 (18.3 ppm)

1.285E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 0.337 (114% MC) -0.873 (0 ppm)

1.829E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 0.337 (114% MC) 1.3 (18.3 ppm)

1.246E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 0.667 (128% MC) -0.873 (0 ppm)

1.582E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 0.667 (128% MC) 1.3 (18.3 ppm)

1.180E+0001 ;1 outputs by NeuralMachine executable MunaTraining-trained.EXE

Temp. M/C NMOC
0.089 0.996(142% MC) -0.873 (0 ppm)

```
1.345E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temp. M/C NMOC
0.089 0.996 (142% MC) 1.3 (18.3 ppm)

```
1.084E+0001      ;1 outputs by NeuralMachine executable MunaTraining-
trained.EXE
```

Temperature (22°C) (Standardized)	Moisture Content (Standardized)	Moisture Content (%w/w)	NMOCs = (0ppm) Stand.	Predicted CH_4 oxidation rates ($\mu g\ CH_4\ h^{-1}\ g^{-1}_{wet\ wt}$)	NMOCs = (18.3ppm) Stand.	Predicted CH_4 oxidation rates ($\mu g\ CH_4\ h^{-1}\ g^{-1}_{wet\ wt}$)
						18.3 ppm
0.089	-1.004	57%	-0.873	30.71	1.3	18.41
	-0.67449	71%		29.27		16.81
	-0.32156	86%		24.52		13.63
	0.007843	100%		20.8		12.85
	0.337247	114%		18.29		11.6
	0.666651	128%		15.82		11.8
	0.996055	142%		13.45		10.84