CHAPTER 1: INTRODUCTION

1.1 Waste

Generation of waste continues to increase in response to rapid population growth, accelerated urbanization and industrialization. Waste generation rate in Malaysia was found to depend very much on the sources of municipal solid waste (MSW). The per capita generation of MSW has reached 1.3kg per day giving a total generation of more than 31000 tonnes daily (Agamuthu, 2009) compared to 15,000 tonnes/day in 1997 (Agamuthu,2001). This clearly indicates more than 100% rise in waste due to rapid development and urbanization in Malaysia for the past 12 years. This condition makes the management of municipal solid waste one of Malaysia's most critical environmental issues (Chong, 2005). An estimated 10 million tonnes of total waste was produced in 2008 in Malaysia which was sent to 260 landfills (Agamuthu, 2009). Most of the landfills are not sanitary and lacked facilities to collect and/or treat leachate and the infrastructure to exploit landfill gas (LFG) (Agamuthu, 2001).

The passive emission of LFG into the atmosphere is generally caused from the uncovered waste and gas being released via top covers or by LFG can lead to malodorous circumstances, adverse health effects, explosive conditions and global warming (Reinhart, 1998). MSW composition varies from one country to other, due to different lifestyles of contributing population and socio-economic groups. The physical and chemical characteristic also vary within the same geographic location in different seasons. Knowledge on the composition and characteristic of waste is essential in order to decide the type of disposal method and estimation on the quality and quantity of LFG generated.

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1.2 Landfill Gases

LFG is the product of biological decomposition of organic waste materials deposited in a landfill. LFG will be continuously produced until all of the organic matter in the waste is decomposed. According to Burdekin (2003) LFG production results from chemical reactions and microbes acting upon the waste as the putrescible materials begin to break down in the landfill. Due to the constant production of LFG, pressure increases within the landfill and provoke its release into the atmosphere. Such emissions lead to important environmental, hygiene and security problems in the landfill (Brosseau, 1994, Christensen et al., 1999).

LFG consists mainly of methane (CH₄) and carbon dioxide (CO₂) at about 55% and 35% by volume respectively and smaller amounts of other gases including oxygen (O₂), H₂S (hydrogen sulfide) and nitrogen (NH₄) (Themelis, 2007). Both CH₄ and CO₂ are widely known as greenhouse gases and recognized as the primary global warming contributors with CH₄ being 24 times more infrared absorptive capacity than CO₂. Methane gas was recorded to increase by approximately one percent/year over the past 15 years and the estimated global emission from landfills is between 20 and 70 Tg of CH₄ (Kightley, 1995).

LFG is a significant greenhouse gas (GHG) which, due to its high energy content, also has potential for energy production. The collection and subsequent use of LFG for heat and electricity production is on the increase in many countries (Bove and Lunghi, 2006; Henigin and Eymann, 1996; Reinicke, 1996), both to reduce GHG emissions from landfills and to replace fossil fuels in energy production. Upgrading LFG for biofuel enhanced the energy density of the fuel and minimized the transportation cost of the LFG, thereby enabling better utilization of the recovered gas in cases where landfills are located at a long distance from the heat-consuming infrastructure. So far, studies and applications on upgrading LFG usage are relatively few, while the use of biogases from sewage and biowaste digesters is rapidly increasing in some countries (Tynell, 2005).

LFG monitoring is the process by which gases that are released from landfill are electronically monitored. For measuring the emission from small area, some techniques are used, such as chamber method, method of subsurface vertical gradient of the concentration, while for large area measurements, micrometeorological methods, the isotope ratio technique, the trace method and infrared spectroscopy are utilized (Biszek et al., 2006)

Many factors interfere in the generation of methane in a landfill, but the most important factors include the waste composition and the presence of readily degradable organic components, the moisture content, the age of the residue, the pH and temperature. The pH and the temperature are relevant for the existence and action of bacteria (McBean et al., 1995) and they influence the type of bacteria that predominate and the rate of gas generation. According to Mehta et al. (2002) and Barlaz et al. (1990), the moisture content is a parameter that controls methane generation, since it stimulates microbial activity by providing better contact between soluble and insoluble substrates and microorganisms.

The emissions from landfills account for 21% of the total anthropogenic CH₄ sources in Canada, 30% in Europe, 34% in US and 10% globally (EC, 2006; EEA, 2001; NRCan, 2002; USEI, 2003, 2005). Worldwide, the CH₄ emission from the waste sector is about 18% of the global anthropogenic CH₄ emission (Bogner *et* at. 2007). In the United States, the second largest anthropogenic CH₄ emission originates from landfills. In Europe, landfills are reported as the second largest source of anthropogenic CH₄ (22%) (EEA 2008). Worldwide, landfills have been estimated previously to release between 35 and 69 Tg year⁻¹ of CH₄ to the atmosphere, out of an estimated annual global emission of approximately 600 Tg CH₄ (Denman *et* al. 2007, Bogner *et* al. 2007).

.1.3 Methane Oxidation

Landfill sites are widely reported as significant CH_4 emission sources (Borjesson et al., 2000; Barlaz et al., 2004; Powell et al., 2006; Lohila et al., 2007; Zhang et al., 2008a). Methane can be degraded by methanotrophic bacteria, which can grow using CH_4 as a sole carbon source in aerated soil and thus soil can serve as an important biological sink of atmospheric CH_4 (Adamsen and King, 1993).

Methane produced in landfills can be converted to carbon dioxide which is a less harmful GHG by oxidation. The process of methane oxidation consists of the conversion of methane into water, carbon dioxide and biomass by microbial activity.

 $CH_4 + O_2 \longrightarrow CO_2 + H_2O + biomass$

According to Christophersen et al. (2000) the methane oxidation rate depends on different physicochemical factors such as temperature, water content and organic matter. Meanwhile according to Park et al. (2002, 2004) the methane oxidation depends on temperature and water content. De Visscher et al. (2001) found out that temperature and nitrogen affects the methane oxidation. Therefore, microbially mediated CH_4 oxidation can play an important role in reducing the atmospheric CH_4 emission from landfills constructed with conventional cover soil (Kightley et al., 1995; Boeckx et al., 1996; De Visscher et al., 1999).

Biological CH₄ oxidation plays an important role in controlling the emission of CH₄ and it was reported that microbial CH₄ oxidation has significant rates in many natural environments (Whalen, 1990). Generally, a large number of methanotropic bacteria in landfill cover serve to minimize CH₄ emissions by optimizing the CH₄ oxidation (Stern, 2007). Microbial methane oxidation in the landfill cover is an important process in controlling and reducing methane emission from landfills at a lower cost association (Tanthachoon et al., 2007). According to Navarani (2009), CH₄ oxidation rate for garden waste compost was 3 times and 5.5 times higher compared to black soil and compost residue, respectively.

This source of methane emissions partly results from the lack of a gas collection system in thousands of old landfills and uncontrolled dumps around the world. Among design advances to reduce CH_4 emissions, gas collection systems have greatly reduced the environmental impact of new landfills and are now mandatory in most parts of the world. However, installation of a gas collection system in small or old landfills with low CH_4 production is not economically feasible (Mor et al., 2006; Streese and Stegmann, 2003), and in new landfills, gas collection systems are not 100% efficient (Spokas et al., 2006). This means that there will always be a certain amount of fugitive emissions. Therefore, any technology or approach that could help reduce atmospheric emissions of CH_4 from old or new landfills will make an important contribution to reducing the overall atmospheric CH_4 budget.

The control of CH_4 emissions in landfills can be achieved, in addition to the recovery and utilization of CH_4 for energy, via microbial oxidation of CH_4 to CO_2 , in landfill cover soils or in biofilters (Czepiel et al., 1996; De Visscher et al., 1999; Bo[°]rjesson et al., 2001, 2004; Streese and Stegmann, 2003; Hilger and Humer, 2003; Wilshusen et al., 2004; Gebert and Gröngröft, 2006). Microbial CH_4 oxidation, which is mediated by methanotrophic bacteria, takes place spontaneously in landfill soils and can be enhanced by management of the important controlling factors, which include environmental conditions such as temperature and moisture (e.g., Boeckx and Van Cleemput, 1996; Czepiel et al., 1996; Christophersen et al., 2000; Scheutz and Kjeldsen, 2004), the properties of the support medium (Hilger et al., 2000; Hilger and Humer, 2003; Kettunen et al., 2006), as well as gas flow and gas distribution to CH_4 -oxidisers.

1.4 Biocover

Landfill top covers, which optimize environmental conditions for methanotrophic bacteria and enhance biotic methane consumption, are often called "biocovers". In landfill cover soils, the microbial population of methane-oxidizing (methanotrophic) bacteria has been highly developed because of CH₄ fumigation, which was formed from anaerobic decomposition of the landfilled waste. Previous laboratory investigations have demonstrated a high oxidation capacity in diverse, mature and well-structured compost materials (Humer and Lechner, 1999; Wilshusen et al., 2004a). Moreover, preliminary field trials (Humer and Lechner, 2001a; Barlaz et al., 2004; Huber-Humer, 2004; Bogner et al., 2005) have provided indications as to the suitability of compost biocovers for practical application and their high efficiency in mitigating methane emissions. Manipulation of landfill covers to maximize oxidation capacity provides a promising complementary strategy for the control of methane emissions escaping gas collection, as well as for emission mitigation at smaller or older sites where the methane production is too low for energy recovery or flaring, and installation of a gas extraction system is inefficient.

Numerous studies has been carried out mainly under laboratory conditions and to the lesser extent in the landfill environment, to attenuate methane through design of landfill cover using selection of materials with optimum methane attenuation capacity. It has been reported that by creating optimal ambient conditions for methanotropic bacteria in cover layers, it is possible to foster the natural potential of methane oxidation and attain very high oxidation rates (Humer and Lechner, 2001). Similar studies indicated that compost as the basic landfill capping material offered the higher oxidation capacity due to higher organic matter, water holding capacity and porosity than typical soil.

1.5 Problem Statement

The storage of MSW in landfills contributes to the GHG effect. Methane gas is one of the most important GHGs because its global warming potential more than 20 times carbon dioxide (Ishigaki et al., 2005). Atmospheric CH4 gas has more than doubled in concentration over the last 150 years (Stern et al., 2007). Since methane is a potential GHG, it is essential to mitigate its emission from landfills. Studies have been conducted widely by many scientists all over the world on means to reduce the CH_4 from the landfill since 18^{th} century.

1.6 Objectives of study

The objectives of this research are as follows:

- 1. To analyze the physical and chemical characteristic of the biocover samples (compost and landfill soil).
- 2. To assess the methane oxidation capacity of garden waste compost and landfill soil for tropical conditions.
- 3. To evaluate the effects of temperature, pH and moisture on the methane oxidation rate.
- To evaluate rate of methane oxidation using Biocover Performance Index (BPI) and Kinectics.
- 5. To propose suitable landfill covers for methane oxidation under tropical conditions.

The contribution of this research is to establish basic methane oxidation parameters under laboratory conditions. The hypothesis / theory are the Biocover will decrease the methane rate.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Human activities have always generated waste. This was not a major issue when the human population was relatively small, but became a serious problem with urbanization and the growth of large conurbations. Poor management of waste led to contamination of water, soil and atmosphere and caused a major impact on public health. The mass of waste produced in the world has been growing considerably for many decades especially in affluent countries as shown by the link between national gross domestic product (GDP) and waste generation per capita (World Bank, 1992; OECD, 2003). Statistics show that the world population reached six billion in 2001 with 46% of this population is residing in urban areas (HMGN and MoPE, 2003).

2.2 Waste

Solid waste is invariably a by-product of human activity. Solid wastes are defined as wastes arising from human and animal activities that are normally solid and unwanted (Agamuthu, 2001). There are 4 main categories of solid waste which includes MSW, hazardous waste, agricultural waste and industrial waste. Municipal refuse is composed of largely unnecessary packaging materials and items that have been discarded because they weren't built to last in the first place (Agamuthu, 2001).

Waste can be classified as follows:

- 1) Organic/ inorganic (solid, semi-solid, liquid and gases)
- 2) Combustible/ non-combustible wastes
- 3) Compostable/ non-compostable wastes

2.3 Solid Waste Generation and Characteristics

2.3.1 Malaysia

The waste generation rate in Kuala Lumpur Malaysia is continuously rising up every year due to the uncontrollable consumption owing to the increasing population, the attitude towards shopping and the high living standard. It is expected that the amount of solid waste generated in Kuala Lumpur would double in the next twenty years; from 3.2 million metric tons a year today, to 7.7 million metric tons a year (Hassan, 2002; Hassan et al., 2000). Today SWM is the biggest environmental problem in Malaysia. The amount of waste generated continues to increase due to rapid increase in population, accelerated urbanization and industrialization process (Hassan et al., 1999). The amount of solid waste in Malaysia has put pressure on local authorities making them continually seeking new management strategies to deal with these wastes generation, i.e. demand management, as well as, find new sites for landfill, i.e. supply management (Nesadurai, 1999). In 2006, about 7.34 million metric tons of solid wastes were generated in Malaysia, enough to fill up 42 buildings (Siraj, 2006). In 2008, approximately 31,000 tonnes of waste were disposed off daily into 260 landfills in Malaysia (Agamuthu, 2009)

MSW composition varies from one country to other mainly due to different lifestyles of contributing population and socio-economic groups. Knowledge on the composition and characteristics of waste is essential in order to decide the type of disposal method and also gives estimation on the quality and quantity of LFG generated.

The official reported that Kuala Lumpur's population in 2007 was 1.604 million according to statistic department 2007. In Kuala Lumpur alone, the estimated solid waste generation was 4000 metric tons per day in the year 2000 (Murad and Siwar, 2006).

The Malaysian population has been increasing at a rate of 2.4% per annum or about 600,000 per annum since 1994. With this population growth, the MSW generation also

increased, which makes MSW management crucial. In 2003, the average amount of MSW generated in Malaysia was 0.5–0.8 kg/ person/day; it has increased to 1.7 kg/person/day in major cities (Kathirvale et al., 2003). By the year 2020, the quantity of MSW generated is estimated to have increased to 31,000 metric tons.

Malaysian solid waste contains a very high concentration of organic waste (Figure 2.1) and consequently has high moisture content and a bulk density of about 200 kg/m³. A waste characterization study found that the main components of Malaysian waste were food, paper, and plastic which comprise 80% of overall weight (Kathirvale et al., 2003). These characteristics reflect the nature and lifestyle of the Malaysian population.

Despite the aggressive economic development in Malaysia, the solid waste management is relatively poor and haphazard (Hassan et al., 1999). Waste minimization strategy and control is the objective for Kuala Lumpur to achieve the UN Agenda 21 which emphases on human and environment.

With the increase in municipal waste generation from 5.6 million tons in 1997 up to 8.0 million tons in 2000, there is an urgent need for a better managed disposal option (Fauziah and Agamuthu, 2003). Figure 2.1 shows the waste composition for Malaysia. Waste generation within Malaysia was found to depend very much on the sources of MSW. Malaysians generate about 72% compostable waste comprising organic waste, paper, textile/leather and wood. Plastic waste in Malaysia is 15% which is considered high. According to Agamuthu (2003), high generation of plastic waste is typical in fast developing nation.

The Agenda 21 of the UNCED 1992, defined environmentally sound technologies protect the environment; moreover, recycling most of the wastes and handle residual wastes in more acceptable manner. Though recycling activity in Malaysia is rising up, the recycling industry still needs to be enhanced. The Malaysian's attitude towards recycling is higher, but only few practice it (Mamat and Chong, 2007). Since 1993 a major effort of recycling was lunched by the Ministry of Housing and Local Government but unfortunately limited recycling activities taken place (Agamuthu, 2001).

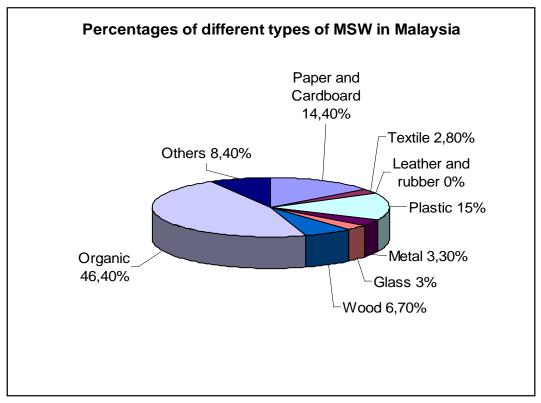


Figure 2.1: Waste composition for Malaysia (Agamuthu et al., 2003)

2.3.2 Global

In 2006, the USA produced more than 228 million tons (EPA, 2008; OECD, 2008a, b) of MSW, or 750 kg per capita per year. The quantity of MSW generated in the OECD countries in 2006 was more than 619 million tons, or 580 kg per inhabitant per year (OECD, 2008b). Figure 2.2 shows the MSW arising in selected OECD countries and in China, as total weight and as kg/yr/capita, respectively. In 2006, the 15 countries of the European Union generated 219 million tons of MSW, or 560 kg/yr/capita (OECD, 2008a,b). As less developed countries such as China and India industrialize and their populations urbanize, huge amounts of MSW are disposed of, though the production per

capita (less than 0.5 kg/day/capita in India and less than 0.9 kg/day/capita in China) is still relatively small compared to the production in the USA (up to 2.1 kg/day/capita). However, this masks the fact that a large proportion of the MSW is produced in urban centres.

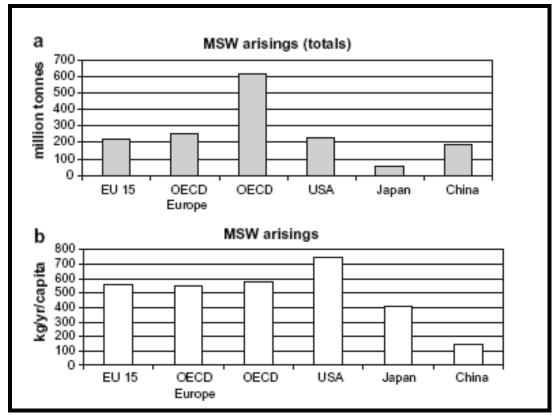


Figure 2.2: MSW arising in selected OECD countries and in China, in million tones per year, and MSW arising in selected OECD countries and in China, as kg/yr/ capita. Sources of data: OECD, 2008a, 2008b; EASUR, 2005.

In 2002, more than one billion tonnes of industrial waste (about five times the amount of MSW) was produced in China, mostly mine tailings, coal ash, and slag. The published projections of municipal waste generation for China were based on three different waste growth scenarios (i.e. waste generation increasing gradually from 0.9 kg/day/capita to 1.2 kg/day/capita, 1.5 kg/day/capita, and 1.8 kg/day/capita).

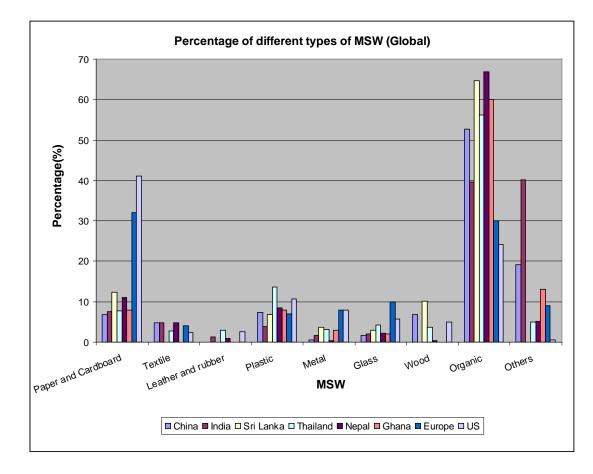
Table 2.1 shows the percentage of different types of MSW for some countries. For most countries, organic waste is the most waste produced which accounts almost 30-70%.

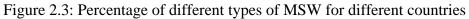
Generally Europe and US has the highest percentage of different type of waste. Figure 2.3 summarizes the percentage of different types of MSW from Table 2.1.

	Paper And Cardboard	Textile	Leather and rubber	Plastic	Metal	Glass	Wood	Organic	Others
China	6,9	4,7	0,0	7,3	0,5	1,6	6,9	52,6	19,2
India	7,6	4,7	1,3	3,8	1,7	2,1	0,0	39,6	40,1
Sri									
Lanka	12,3	0,0	0,0	6,8	3,7	3,0	10,2	64,7	0,0
Thailand	7,7	2,7	3,0	13,7	3,1	4,3	3,6	56,2	5,0
Nepal	11,0	4,8	1,0	8,4	0,3	2,2	0,3	66,8	5,2
Ghana	8,0	0,0	0,0	8,0	3,0	2,0	0,0	60,0	13,0
Europe	32,0	4,0	0,0	7,0	8,0	10,0	0,0	30,0	9,0
US	41,0	2,4	2,6	10,7	7,9	5,8	5,0	24,1	0,5

Table 2.1: Percentage of different types of MSW for different countries

Source: (Hogland et al., 2005, Agamuthu et al., 2003)





2.4 Solid Waste Management Practices

Solid Waste Management (SWM) may be defined as that discipline associated with the control of generation, storage, collection, transfer & transport, processing and finally disposing of solid wastes in a manner that is in accord with the best principles of public health, economics, engineering, conservation, aesthetics and environmental considerations (Agamuthu, 2001). Generally, landfill is an important component in the hierarchy of integrated waste management practice. Therefore, designing landfill for MSW require an integrated input from multidiscipline (Mantell, 1975). The Waste Management Hierarchy (Agamuthu, 2001) can be listed as:

- 1. Prevent the creation of waste, or reduce the amount generated.
- 2. Reduce the toxicity or negative impacts of the waste that is generated.
- 3. Reuse in their current forms the materials for use as direct or indirect inputs to new products.
- 4. Recycle, compost or recover materials for use as direct or indirect input to new products.
- 5. Recover energy by incineration, anaerobic digestion or similar processes
- 6. Reduce the volume of waste prior to disposal
- 7. Dispose of waste in an environmentally acceptable manner, generally in landfills.

2.4.1 Malaysia

Essentially, MSW management in Malaysia is under the responsibility of the local authority, as stipulated in Section 72 of the Local Government Act 1976. Under this act, the local authority is expected to provide, directly or through contract, public cleansing services of equitable and acceptable quality to all urban and semiurban communities within its jurisdiction, and must dispose of all the waste collected in a sanitary manner. On average,

20-70% of the local authority's operating budget is spent on MSW and of this more than 50% is spent on the collection of waste.

Therefore, the government has set up a new solid waste management structure. Under the Ministry of Housing and Local Government, Malaysia has set up the National Solid Waste Management Department as the regulatory body and the Solid Waste and Public Cleansing Management Corporation to conduct the operations. The corporation would take over the role of managing solid waste from local authorities and watch over the concessionaires. However, local authorities would continue to monitor cleanliness in areas under their jurisdiction.

At present, landfilling is the only method used for the disposal of MSW in Malaysia, and most of the landfill sites are open dumping areas, which pose serious environmental and social threats (Yunus and Kadir, 2003). Disposal of wastes through landfilling is becoming more difficult because existing landfill sites are filling up at a very fast rate. At the same time, constructing new landfill is becoming more difficult because of land scarcity and the increased of land price.

In 2001, there were 155 disposal sites under the responsibility of local authorities in Malaysia (Wan and Kadir, 2001) ranging in size from 8 to 60 ha, depending on the location and amount of waste disposed (Hassan et al., 2001). Till date, there are 261 landfills in Malaysia (Agamuthu et al., 2008). Table 2.2 shows landfills in central Malaysia in accordance to states. Most of these sites are open dumpsites, and the capacity has been overloaded. The operation of these sites has been extended due to the absence of appropriate and cost-effective alternatives to treat the waste.

Table 2.2: Number of closed disposal facilities and facilities proposed for closure in
Malaysia 2008.

State	Closed Facilities over the	Facilities proposed		
State	last 17 years	for closure		
Perlis	1	1		
Kedah	3	1		
Penang	2	0		
Perak	9	1		
Pahang	12	1		
Selangor	11	4		
Wilayah Persekutuan	7	0		
Negeri Sembilan	10	4		
Malacca	5	0		
Johor	21	4		
Kelantan	5	0		
Terangganu	12	0		
Labuan	0	0		
Sabah	1	0		
Sarawak	12	0		
Total	111	16		

Source: Agamuthu et al., 2008

2.4.1.1 National Strategic Plan for Solid Waste Minimization 2005

Under The Ninth Malaysia Plan 2006-2010, the National Strategic Plan for Solid Waste Minimization 2005 will be implemented (Economic Planning Unit, 2006) with emphasis on the upgrading of unsanitary landfills as well as the construction of new sanitary landfills and transfer stations with integrated material recovery. Priority will continue to be accorded to the reduction, reuse, recovery and recycling of waste as well as greater use of environment friendly material such as bioplastics.

The aim of National Strategic Plan for Solid Waste Minimization are to provide a strategic framework related to the overall SWM in Malaysia and recommended an affective management plan, which identifies the roles of each stakeholders and actions that are required to be taken to meet the objectives of the National Development Plan. According to Nadzri (2007a), for maintaining the quality and services of solid waste facilities, three categories of action under The National Strategic Plan were outlined as listed below:

- 1. First category establishing a regulatory framework includes development of legislation and institution
- Second category service operation includes privatization and development of solid waste management facilities.
- 3. Third category supporting infrastructure includes waste reduction, reuse and recovery as well public awareness program and waste database.

2.4.1.2 National Policy on Solid Waste Management 2006

A year later in September 2006, National Policy on Solid Waste Management was endorsed by the Cabinet which fully supports the National Strategic Plan as reported in Utusan Malaysia (September 17, 2006). The purpose of the policy is to establish a holistic, integrated and cost effective, sustainable and socially acceptable SWM.

2.4.1.3 Solid Waste and Public Cleansing Management Act 2007 and Solid Waste and Public Cleansing Corporation Act 2007

The Solid Waste and Public Cleansing Act 2007 was gazetted on 30 August 2007 with the focus to pave away for federal government to take-over of solid waste management and privatization of solid waste handling. Consequential amendments were also made to three other policies. They were Local Government Act 1976, Site, Drainage and Building 1974, and the Town and Country Planning 1976. The Act covers eight categories of controlled solid waste from commercial centers, public sites, construction sites, households, industrial zones, institutions, imported, and others which can be prescribed from time to time. SWM services provided include separation, storage, collection, transportation, transfer, processing, recycling, treatment, and disposal of controlled solid waste.

2.4.2 Global

In Europe, landfilling is the main disposal method. In 1999, 57% of MSW was landfilled (67% in 1995) in west Europe, and 83.7% in central and east Europe (DHV CR, 2001). In 2000, about 18% of MSW was incinerated and 25% recycled in western Europe, whereas incineration and recycling accounted for 6% and 9%, respectively, in central and eastern Europe (Eurostat, 2002). Overall, recycling is increasing in West Europe. Lack of data makes it difficult to identify trends for east Europe. In 2006 the USA landfilled 54% of MSW, incinerated 14%, and recovered, recycled or composted the remaining 32% (EPA, 2008). Figure 2.4 shows the weight of MSW generated and some contrasting examples of waste management practice in different countries. The data for Japan refers to 2003, for Germany to 2004, and for UK, France, Italy and the USA to 2005. The percentage of MSW disposed at landfills accounted for 3% in Japan, 18% in Germany, 36% in France, 54% in Italy and the USA, and 64% in the UK. As legislation becomes more stringent, and

landfilling becomes a less cheap option, alternative solutions are considered. For example, there has been a significant reduction in the amount of waste landfilled in the UK and Italy. In 1995, Italy landfilled 93% of MSW, and the UK 83%.

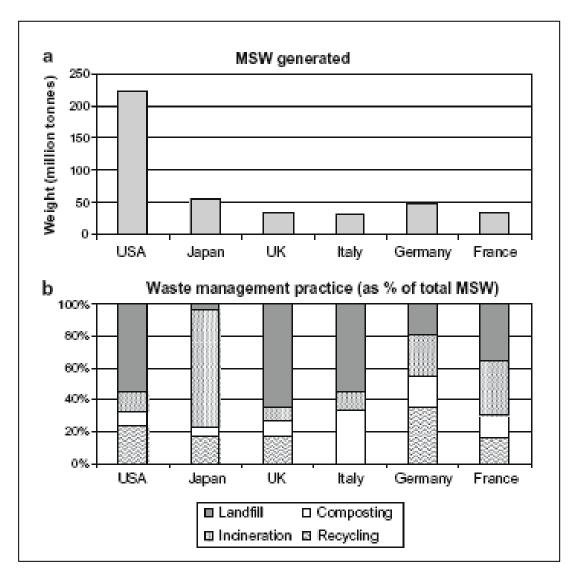


Figure 2.4: (a) MSW generated in selected countries, and (b) contrasting waste management practice in selected countries. Source of data: OECD, 2008b.

2.5 Landfill as disposal method

Landfilling is defined as a method of refuse disposal significantly limiting volume where waste is systematically covered by layers of earth (Agamuthu, 2001). It is one of the most common disposal methods in developing countries. Landfilling is preferred the most as it is the only waste disposal method that can deal with all materials in the solid waste stream. It is also considered simplest and cheapest compared to other waste disposal methods. The placement of solid waste on land is called a dump in the USA and a tip in Great Britain (as in tipping) (Christensen et al., 2007). Large quantities of MSW are currently disposed of in landfill sites, resulting in rapid exhaustion of the landfill capacity (Moldes et al.,2007).

The disposal of solid wastes is a misnomer. The only two realistic options for storing waste on a long-term basis are in the oceans (or other large bodies of water) or on land. The former is becoming illegal in most developed nations. Waste dumping means an important source of anthropogenic CH₄ emissions (EPA, 2002). Behind agriculture, waste landfills contribute to the worldwide anthropogenic CH₄ emissions with 17% (Wuebbles and Hayhoe, 2002). Das et al.(2002) carried out a field scale aerobic bioreduction process in a landfill, but the process required 14 months of bioreduction to obtain a biologically stable product, with a C/N ratio as high as 27.1 which could be used as a soil amendment. Although landfill seemed to be the best disposal option, it posed many perilous hazards to the environment and public health.

According to Agamuthu (2008), there are 261 landfills in Malaysia. As almost 90% of the landfills in Malaysia are non-sanitary landfills, they lack proper gas and leachate collection system.

2.6 Landfill outputs

The ever growing MSW load has many effects on the environment and public health, such as the bad odour from MSW landfill sites, explosions resulting from the generation of combustible gases (CO_2 and CH_4) – which also contribute to the greenhouse effect – and contamination of groundwater and soil by hazardous organic and heavy metals. The three main outputs from a sanitary landfill are:

- 1. gas
- 2. leachate
- 3. inert solid waste

LFG is characterized by the gas quantity and quality. Both factors are highly dependent of the age of the landfill. The LFG composition is shown in Table 2.3 below.

%(dry volume basis) ^a			
45 - 60			
40 - 60			
2-5			
0.1 - 1.0			
0.1 - 1.0			
0 - 0.2			
0-1.0			
0-0.2			
0.01-0.6			

Table 2.3: Typical landfill gas composition

^aExact percentage distribution will vary with the age of the landfill. Source: Tchobanoglous, et al (1993) The chemical process that converts wastes into LFG is known as waste decomposition or degradation. This process is influenced by several factors such as temperature, moisture content, waste composition and diversity of substrates for microbial degradation. The gas quantity will vary significantly through the time phase of the landfill. To estimate the amount of methane produced in a landfill in a given year, information is needed on the type and quantity of waste in the landfill, as well as the landfill characteristics (e.g., size, aridity, waste density). For the stable methanogenic phase the highest gas production rates are expected in the beginning of the phase, while the production rate is expected to be very small in the later phases. Cossu et al.(1995) presents an overview of observed production rates together with several models of LFG production (only covering the stable methanogenic phase).

2.7 LFG emissions

The LFG emissions typically consist of up to 64% CH₄, 35% CO₂, and <1% volatile odorous compounds (Allen et al., 1997). Meanwhile (Khalil, 1999) reported that typically, LFG consists of 50-60 vol. % of CH₄ and 30-40 vol. % of CO₂ and trace amounts of numerous chemical compounds such as aromatics, chlorinated organic compounds and sulphur compounds. Meanwhile recent findings reported by Bove and Lunghi, 2006 stated that the main components of LFG are CH₄ (from 40% to 60%), CO₂ (from 35% to 50%), N (from 0% to 20%), O₂ (from 0% to 1%) and H₂S (from 50 to 200 ppm). LFG is typically 40–60% CH₄ (Senior, 1990), with CH₄ having 25 times the global warming potential of CO₂ over a hundred year period (IPCC, 2007) Landfills are estimated to be the largest source of anthropogenic methane. LFG can also contain trace compounds such as aliphatic and aromatic hydrocarbons, halogenated compounds and silicon-containing compounds up to a total concentration of 2000 mg/m³ (Schweigkofler and Niessner, 2001). Some of these

compounds may cause corrosion or other damage to engines if they are not removed from the gas before utilization.

The emissions from landfills account for 21% of the total anthropogenic CH₄ sources in Canada, 30% in Europe, 34% in US, and 10% globally (EC, 2006: EEA, 2001: NRCan, 2002: USEI, 2003, 2005). The CH₄ emissions from MSW landfills depend on the quantity and composition of the solid waste dumped at the site (Hoeks, 1983; US EPA, 1994) and a significant amount of LFG eventually makes its way to the atmosphere (Mor et al., 2006).

Landfilling is considered to be an important global source of GHG. Worldwide, landfills have been estimated previously to release between 35 and 69 Tg yr⁻¹ (Denman et al., 2007, Bogner et al., 2007). These emissions are mainly caused by inadequate gas collection systems, from uncontrolled emissions from old dumps and from unauthorized open dumping. Furthermore, because of the increase in population in developing countries, CH₄ emissions are estimated to increase by up to 60% within the next two decades (Meadows et al., 1997).

 CH_4 and CO_2 are produced in landfills when anaerobic bacteria decompose the organic constituents of solid waste. Although the gases are produced in about equal quantities, CH_4 traps and retains radiation more efficiently and is a potent GHG (Augenstein 1990). Since CH_4 is produced only during the anaerobic decay of organic matter, and not during aerobic decay, the diversion of organic waste from landfills to composting reduces CH_4 production (Thompson and Tanapat, 2005). Municipal waste landfills are large heterogeneous areas in which organic wastes undergo degradation in anaerobic, acidic environments resulting in a high generation rate of LFG (Davoli et al., 2003; Schmidt et al., 1998). Figure 2.5 illustrates global anthropogenic CH₄ budget by source in year 2000. USEPA estimated that the total anthropogenic emissions of methane

were 282.6 million tonnes in 2000 (USEPA, 2002), of which 13% or 36.7 million tonnes were due to landfill emissions.

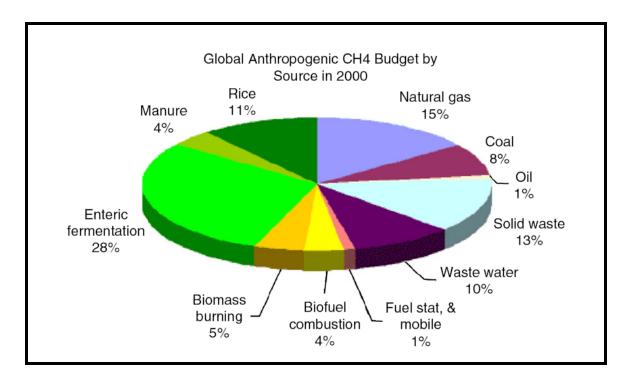


Figure 2.5: Global anthropogenic methane in year 2000 (Source: USEPA. International analyses of methane emissions, 2002)

When organic wastes are degraded, CO_2 and CH_4 are produced. Although these originate deep in the landfill, they can readily migrate to the surface and enter the atmosphere. The biochemical reactions that produce them typically continue long after a landfill is capped, so that even after closure, emissions can continue (Tchobanoglous *et al.*, 1993). Since both of these gases contribute to global climate change, gas collection systems are recommended and sometimes required at landfills. While some of the gas escapes capture, gas collection systems can significantly reduce LFG emissions. Although CO_2 and CH_4 are produced in about equal amounts during waste degradation, the CH_4 is of greater concern. As sanitation imperatives are changing waste disposal practices from open waste pits to landfills, anaerobic decay will result in greater CH_4 production (Hilger and Humer, 2003), unless waste diversion and/or CH_4 recovery programs and regulations are implemented. To evaluate appropriate CH_4 reduction strategies, LFG production rates must be accurately quantified. The design and operation of LFG extraction and utilization projects require reliable emission forecasts for project feasibility and to ensure environmental compliance (Huitric and Soni, 1997; Oonk and Boom, 1995).

2.7.1 LFG production

Biodegradation of wastes within landfills produces various gases that consist of primarily CH₄ and CO₂. This biogenerated gas, i.e., LFG will increase the pressure within landfills and thereby escape from landfills to the atmosphere. Where CH₄ is not controlled, fire and explosions could occur. Concentrations above the lower explosive limit of CH₄ have been reported at a distance up to 300 m off-site (Izadi and Stephenson, 1992). The Loscoe, UK and Masserano, Italy incidents, which resulted in extensive property damage and loss of lives, show the importance of controlling migration of gas from landfills (Didier et al., 2000; Vangpaisal and Bouazza, 2004). There have been reports of fires due to CH₄ around landfills (Christensen et al. 1989, Jones et al 1990, Kjeldsen et al. 1995, Boltze et al. 1997). Moreover it could cause suffocation of personnel in unventilated places (Robinson 1986).

According to Agamuthu (2001), the rate of LFG production depends on:

- 1. size and composition of solid waste
- 2. age of solid waste and age of landfill
- 3. moisture content
- 4. temperature conditions in landfill
- 5. quantity and quality of nutrients

- 6. organic content of refuse
- 7. pH and alkalinity of liquids in the landfill and
- 8. presence of toxic or hazardous materials

Atmospheric CH₄ concentration has more than doubled during the past several 100 years and continues to rise (IPCC, 2001). Of the global anthropogenic CH₄ emissions, more than 10% originate from MSW landfills (IPCC, 2001). Landfill CH₄ is produced from anaerobic biodegradation of organic matter in the land-filled waste (Bogner et al., 1995; Kumar et al., 2004). CH₄ emissions vary significantly among the landfill sites and are affected by, e.g. gas recovery, microbial CH₄ oxidation, landfill age, the thickness of landfill cover, and meteorological conditions. Atmospheric CH₄ concentrations have increased by 30% in the last 25 years (IPCC, 2007) and multiplied by a factor of 2–3 since the 1700s due to human activities. This CH₄ addition has increased radioactive forcing by 0.47Wm⁻² (IPCC, 2007, 2006). Approximately 70% of CH₄ emissions are anthropogenic (e.g., agriculture, natural gas activities, landfills, etc) and 19% (70 Tg/ year) of these are attributed to LFG generation (Lay et al., 1996; Czepiel et al., 2003).

Shortly after MSW is landfilled, the organic components start to undergo biochemical reactions. In the presence of atmospheric air that is near the surface of the landfill, the natural organic compounds are oxidized aerobically, a reaction that is similar to combustion because the products are CO_2 and water vapour. However, the principal bioreaction in landfills is anaerobic digestion that takes place in three stages. In the first, fermentative bacteria hydrolyze the complex organic matter into soluble molecules. In the second, these molecules are converted by acid forming bacteria to simple organic acids, CO_2 and H_2 ; the principal acids produced are acetic acid, propionic acid, butyric acid and ethanol. Finally, in the third stage, CH_4 is formed by methanogenic bacteria, either by breaking down the acids to CH_4 and CO_2 , or by reducing CO_2 with H_2 . Two of the representative reactions are shown below:

Acetogenesis

 $C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$

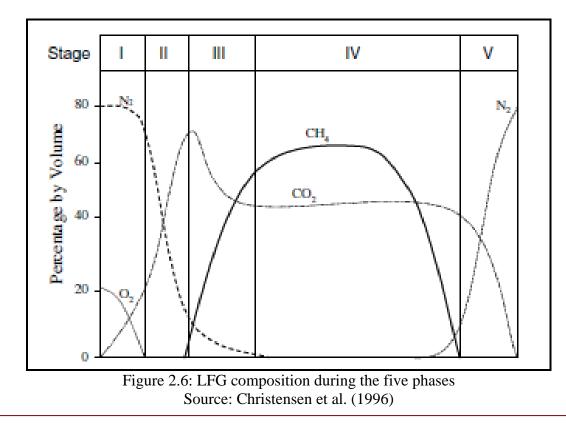
Methanogenesis

 $CH_3COOH \longrightarrow CH4 + CO$

 $CO_2 + 4H_2 \longrightarrow CH4 + 2H_20$

2.7.2 LFG Composition

The chemical process that converts wastes into LFG is known as waste decomposition or degradation. This process is influenced by several factors, such as temperature, moisture content, waste composition and diversity of substrates for microbial degradation. The phenomena and chemical reactions involved in this process are quite complex. Typical gas quality composition of the main LFG components is given in Figure 2.6 below.



The process is composed of five different phases:

1. Aerobic decomposition. In this phase, wastes are digested by bacteria, in the presence of air. Heat is produced, while O_2 is consumed for CO_2 production. The time frame, depending on specific conditions, ranges from months to one year.

2. Acidogenic. In this phase, anaerobic conditions are established. As results, H_2 , CO_2 , H_2O and organic acids are produced. Because of the anaerobic conditions, the energy release rate is low. Because of acid formation, the leachate pH can drop below 5.

3. Acetogenesis. In this phase, the oxidation of acids and alcohols to acetic acids plus CO_2 and H_2 takes place. The chemical oxygen demand (COD) noticeably increases due to the dissolution of acids and the leachate.

4. Methanogenesis. Products of acetogensis are converted to methane and CO_2 , and H_2 is consumed. The methane content depends on the available substrates.

5. Maturation. Because of substrate depletion, gas production drops-off.

In Figure 2.6, the gases concentrations variation during the five phases of the waste decomposition are depicted

2.7.3 LFG generation process

The gas generation from landfills is resulted from the process of waste decomposition and related to the waste landfilled and landfill technologies used. The waste receiving in landfills included amount of organic waste, the microbial conversion of biodegradable organic carbon to CH₄, CO₂, and tracer gases such as: H₂S, volatile organic compounds (VOC). The degradation processes of biodegradable waste were divided into five stages, Fig. 2.7 shows the decomposition pathways of the major organic and inorganic components of biodegradable wastes (Williams, 2005).

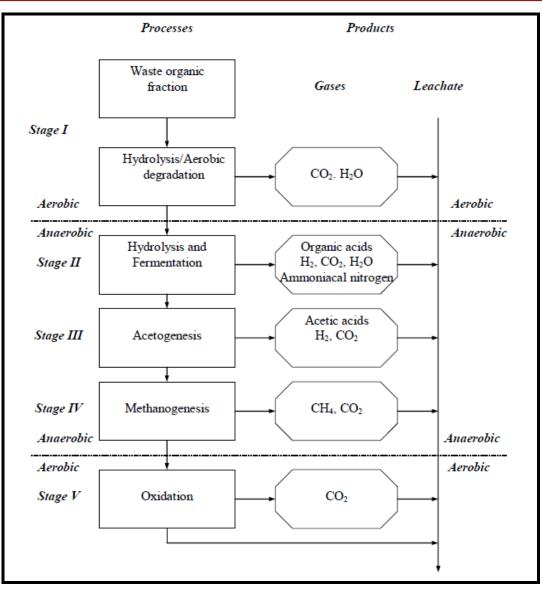


Figure 2.7: Major stages of waste degradation in landfills (Williams, 2005)

Stage I: Aerobic bacteria are responsible for degradation of organic matter and produces CO₂, H₂O and heat. CO₂ may be releases as a gas or adsorbs in the H₂O to form carbonic acid (H₂CO₃), which gives acidity for the leachate generation.

Stage II: A facultative bacterium grows during the second stage, which can survive in aerobic and anaerobic conditions. Carbohydrates, proteins and lipids hydrolyzed to sugars, which decomposed to CO₂, H₂, ammonia (NH₃) and organic acids.

Stage III: Organic acids from the second stage convert to acetic acid (CH₃COOH), H₂ and CO₂ by acetogen microorganisms available in the third stage under anaerobic conditions

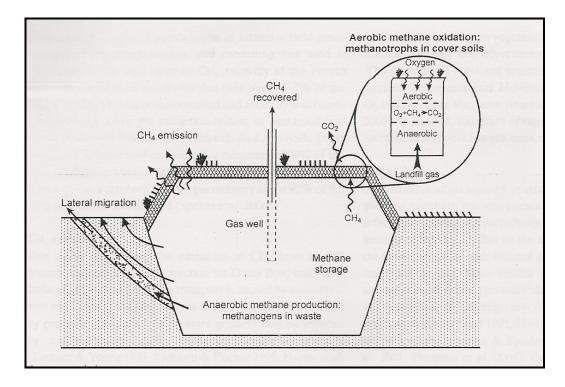
(Williams, 2005), as well H₂S may produced by the reduction of sulphate (SO₄₋₂) compounds in the waste by SO₄₋₂ reduction bacteria.

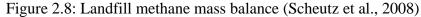
Stage IV: Considers the main stage for LFG production and the longest time stage. Methanogenic microorganisms under anaerobic conditions degrade the organic acids produced from the third stage to produce CH₄ and CO₂, while another microorganism directly converted H₂ and CO₂ to CH₄ and H₂O.

Stage V: In the final stage, an aerobic condition occurred with aerobic microorganisms convert the CH₄ generated in the previous stage to CO₂ and H₂O; as well H₂S gas may forms in waste with high concentration of SO₄₋₂

2.8 Landfill CH₄ mass balance and controlling processes and factors

Many processes other than microbial CH_4 oxidation affect the landfill CH_4 mass balance and the quantities of CH_4 emitted from landfills. To effectively engineer microbial CH_4 oxidation process at a landfill, it is necessary to understand other processes affecting the CH_4 mass balance. These processes are summarized in Figure 2.8.





The CH₄ mass balance (Bogner & Spokas, 1993) is described by the relationship: CH₄ production = CH₄ recovered + CH₄ emitted + Lateral CH₄ migration + CH₄ oxidized + Δ CH₄ storage

(all units= mass t⁻¹; from Bogner & Spokas, 1993)

2.9 LFG usage

2.9.1 LFG for vehicle fuel

The potential for the use of LFG exists if the gas is upgraded to natural gas quality. In New Zealand, many vehicles already run on upgraded LFG and the number is increasing (Nyns,1992). However, in most countries the use of LFG as a vehicle fuel is limited to landfill or other range of operations. According to Stahl (1992), the use of LFG in vehicles offers greater economic benefits than power generation using treated or even untreated LFG. So expensive is the conversion of LFG to natural gas that only large landfills can attain the economics of scale necessary to support operation. Other examples where LFG is successfully being used as fuel are in food production factories, in cement and brick kilns (Sperl, 1988), in bitumen production, ore processing, knackery, sludge drying facility, leachate treatment plant (reverse osmosis, condensate drying)(Gendebien et al.,1992), heating of private houses in Austria (Tscherner, 1985) and district heating in Sweden.

2.9.2 Electrical Power Generation

This is the most common landfill-gas-to-electricity application. According to Vesilind (2002), there were 85 landfill-gas-to-electricity projects in United States of America in 2000 that was capable of generating 344MW of electricity. These represented three fourths of landfill-gas-to-electricity projects in the United States. Electricity generated can either used by the producer or sold to the public utility company. Of course, it is the

most economic way if the producer utilizes the electricity. In Malaysia, only one landfill in Air Itam, Puchong is capable of generating 2MW of electricity, (Agamuthu, 2008)

2.9.3 Boilers and other direct combustion applications

This method of LFG utilization is by far the cheapest and easiest option. The LFG is directly used to replace or supplement coal, oil, propane, and natural gas for boiler firing, space heating, cement and brick kilns, sludge drying, and leachate drying and incineration in United States of America. However, the efficiency in the utilization of LFG in this method is highly dependent on gas quality, use, and continuity of supply. According to Thorneloe (1992), the ideal situation is one where a user, located within a two mile radius of the landfill, could accept all of the gas generated on a continuous basis. The gas is then treated to upgrade the gas through a range of processes depending on the required end-use for the gas. This may involve a condensate removal system, particulate filter, absorption and adsorption systems to scrub the gases and other gas clean-up systems such as membranes and molecular sieves to remove carbon dioxide and trace contaminants (Brown et al., 1994).

2.10 Environmental impacts of landfill

2.10.1 Greenhouse effects/ Global Warming

In recent years, landfills have been implicated in greenhouse warming scenarios as significant sources of atmospheric CH₄ (illustrated in Figure 2.9). CH₄ emission control is of utmost importance for global warming reduction. The worldwide anthropogenic emission of the GHG CH₄ is actually about 360 TgCH₄/a (Wuebbles and Hayhoe, 2002. CH₄ is one of the most important GHG, with a global warming potential 25 times higher than that of CO₂ (averaged over 100 years) (IPCC, 2007) estimated at 0.7 ppm, whereas that in 1998 was 1.745 ppm (IPCC, 2001).USEPA estimated that the total anthropogenic

emissions of CH_4 were 282.6 million tonnes in 2000 (USEPA, 2002), of which 13% or 36.7 million tonnes were due to landfill emissions.

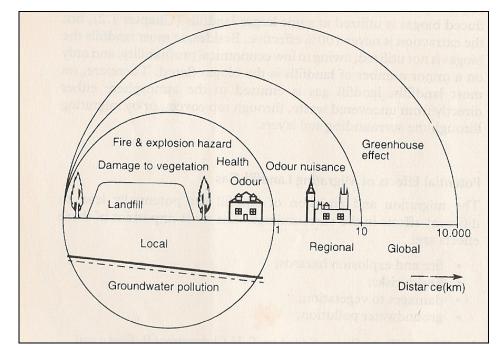


Figure 2.9: The different scales of landfill affects (after Luning and Tent, 1993)

In average, Malaysian landfills produced about 1.3-7.5 L/kg/year of CH₄ gas (Agamuthu, 2009). Almost 90% of Malaysian landfills are not equipped with any engineering waste containment system, (e.g. compacted clay liner, geomembrane or geosynthetic clay liners). Malaysia's total GHG emissions were equivalent to 1.5×10^{11} CDE in 2004 (CDE). Highest CH₄ emissions were reported from LFG (53%). According to Star Daily, Malaysians collectively spewed 177 million tonnes of GHG in 2004 (The Star, 2009), Malaysia was marked No.26 among the world's top 30 emitters. Based on Human Development Report 2007/2008, each Malaysian averages carbon footprints of 7.5 tonnes in 2004, although this figure is smaller compared to American's which 20.6 tonnes is, it is still 6 times larger than India's and 2 times of China's. Reduction of the CH₄ by chemical or biochemical oxidation is of great importance for minimization of the greenhouse effect.

2.10.2 Ozone depletion

The LFG content of volatile chlorinated and fluorinated hydrocarbons poses a special problem. The fluorinated hydrocarbons reach the stratosphere, where the chlorine atom is separated and the radical causes ozone to break down (Deipser et al., 1995).Fluorinated hydrocarbons (the "freons") which are disposed of at landfill are quite volatile and are expected to escape from the landfill within the first years of disposal (Christensen et al.,1995b). However the freons are often contained in metal containers (spray cans etc) while disposed of, and may not be readily available for volatilization.

2.10.3 Toxic VOCs in air

Main components of LFG such as CO_2 and H_2S are potentially toxic to humans, but most concern is generally assumed to be related to organic trace components in the LFG. The most critical compounds are believed to be related to organic trace components in the LFG. The most critical compound are believed to be vinyl chloride and benzene, due to their carcinogenic effects, but also dioxins and furans are potential toxic compounds if the LFG is flared (Eikman, 1995).

2.10.4 Odour

The LFG compounds that give rise to odour problems are H_2S and organic sulphur compound (mercaptanes). The main problems exist during operation and from releases from waste in the acetogenic phase. The threshold levels where odour is significant are often below levels where in the acetogenic health effects arise. Odour problems have been recognized at several landfills (Frechen, 1995).

2.10.5 Explosion and Fire Hazards

LFG is explosive mainly due to the CH_4 content. The explosive limit range for CH_4 lies between 5 and 15% in air at atmospheric pressure and ambient temperature. The limits are only slightly affected by the presence of other constituents (Gendebien et al., 1992). If

LFG is vented directly to the atmosphere, no explosion hazard exists, but surface fires have been observed. One of the main environmental hazard related to LFG is believed to be the explosion hazard by LFG entering houses through cracks in foundations, penetrating services etc. After mixing of the gas with air, an energizer (spark in electrical components, striking a match etc.) can initiate the explosion. Many cases of elevated CH₄ concentrations in houses due to LFG are reported in the literature. Gendebien et al.(1992) describes 60 cases from UK, USA, Germany and Canada of elevated CH₄ concentrations, and 55 cases from USA,UK and Canada involving explosion, fire and human injuries.

2.10.6 Vegetation Damage

Many cases of damages to vegetation in the vicinity of landfills are reported in the literature. Gendebien et al. (1992) describes 31 different cases from UK, USA, Germany, Canada and Japan. The main reason for damages to vegetation from LFG is asphyxia by removal of oxygen in root zone. This removal can either be due to displacement of the oxygen by LFG or by oxidation of CH_4 . High concentration of CO_2 (20%) is also toxic to plants (Neumann & Christensen, 1995) and some trace compounds (H₂S, haloorganics compounds, etc) are toxic to plants as well.

2.11 Methanotrophs Activity

Landfill CH_4 is produced from a complex process of waste decomposition and subsequent fermentation under anaerobic conditions (Thorneloe et al., 2000). Due to these conditions, landfills produce an estimated 6–12% of the CH_4 entering the atmosphere (Kightley et al., (1995); Houghton et al., (2001); Howeling et al., (1999); Lelieveld et al., (1998); Olivier et al., 1999). However, oxic zones of landfill cover soils were shown to consume significant amounts of the CH_4 produced. They contain methanotroph populations with the highest CH_4 oxidation capacity reported (Jones and Nedwell, 1993; Whalen et al., 1990).

Methanotrophic bacteria have a ubiquitous distribution in the environment and play an important role in global climate warming by lowering CH_4 emission into the atmosphere. Globally, landfill sites produce about 10% of the CH_4 entering the atmosphere, and soils above landfill sites have been shown to contain methanotrophic populations with the highest CH_4 oxidation capacity measured. CH_4 oxidizing bacteria or methanotrophs has the unique ability of utilizing CH_4 as their sole carbon and energy source (Hanson and Hanson, 1996; Murrell, 1994). Methanotrophs significantly reduce biological and anthropogenic CH_4 emissions via their activity, thus contributing to the mitigation of global warming (Hanson and Hanson, 1996).

CH₄ reduction can also be regulated by methanotrophic bacteria that develop in the aerobic zone of the landfill cover. It is well established that methanotrophs are capable of efficiently converting CH₄ to CO₂ and biomass (Hanson and Hanson, 1996; Hakemian and Rosenzweig, 2007).) CH₄ emissions from landfills can be mitigated through microbial oxidation in the aerobic surface of cover soils, and this process has been estimated to reduce 35% (22 of 62 Tg) of the CH₄ produced in landfills before it enters the atmosphere (Reeburgh 1996). CH₄ oxidation can be disturbed by the presence of inhibitory substances. In this respect, methanotrophic bacteria share many of the features characteristics for ammonium-oxidizing bacteria and these two groups are inhibited by the same substances. The inhibitory concentrations of these substances often fall within one order of magnitude for ammonium and methane-oxidizing bacteria (Bedard and Knowles 1989).

2.12 Methanotrophs bacteria

Methanotrophic bacteria that can oxidize CH₄ in oxic conditions were isolated for the first time from soil close to a leakage of natural gas by Songen in 1906 (Mancinelli et al., 1981; Topp and Pattey,1997). Methanotrophs are a unique group of methylotrophic bacteria, which utilize CH₄ as their sole carbon and energy source (Hanson and Hanson 1996, Murrell 1994). These organisms have been isolated from a wide variety of environments including soils (Whittenbury et al, 1970), sediments (Smith, et al., 1997), landfills (Wise et al., 2000), groundwater (Fliermans et al., 1988), seawater (Holmes et al., 1995, and Murrell and Holmes 1995, Seiburth et al., 1997), peat bogs (Dedysh, et al., 1998, McDonald, et al., 1996 and Ritchie, et al, 1997), hotsprings (Bodrossy, et al. 1995 and 1997), plant rhizosphere (Gilbert et al., 1998), salt reservoirs (Khmelenina et al, 1996) and the Antarctic (Bowman et al., 1997). Methanotrophs are classified into two groups, type I and type II, differing in many characteristic, including the carbon assimilation pathway and the arrangement of intracellular membranes (Anthony, 1982; Whittenbury and Dalton, 1981).

Type I – Type I methanotrophs (including two genera named type X) utilise the ribulose monophosphate pathway as the primary pathway for carbon assimilation. Type I methanotrophs (the family *Methylococcaceae* (Bowman, 2000)) are methylotrophs belonging to the g-subdivision of *Proteobacteria* and assimilate formaldehyde via the ribulose monophosphate pathway. The family *Methylococcaceae* includes the genera *Methylomonas, Methylobacter, Methylomicrobium, Methylosarcina, Methylosphaera, Methylococcus, Methylocaldum and "Methylothermus*" (Bodrossy et al., 1997; Wise et al., 2001).

Type II – Type II methanotrophs use the serine pathway. Type II methanotrophs (the family *Methylocystaceae* (Bowman, 2000) cluster in the a-subclass of *Proteobacteria* and

utilise the serine pathway as primary pathway for formaldehyde assimilation. Type II methanotrophs are comprised of the genera *Methylosinus*, *Methylocystis*, *Methylocapsa* and *Methylocella* (Dedysh et al., 2000, 2002).

Figure 2.10 shows the complete pathway for the microbial oxidation of CH_4 to CO_2 by methanotrophs, including intermediate steps for oxidation of CH_4 to methanol, followed by oxidation of methanol to formaldehyde (CHOH) and the subsequent oxidation of formaldehyde to formate (CHOOH).

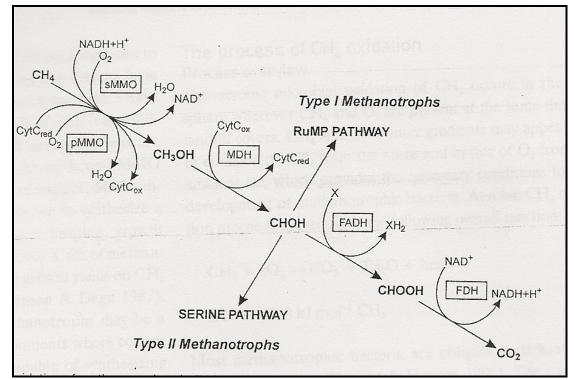


Figure 2.10: The pathway for the oxidation of methane and assimilation of formaldehyde by Methanotrophs. Reproduced from Hanson R.S..Hanson (1996)

It has been observed that shifts in the methanotroph populations in soils can occur in response to environmental stimuli such as changes in concentrations of CH_4 and O2, temperature, pH and nitrogen sources (Hanson and Hanson, 1996). Furthermore, several studies have indicated that type I and type II methanotrophs seem to occupy different niches. For instance, type I strains are likely to dominate in nutrient-rich environments (Graham et al., 1993; Amaral et al., 1996; Borjesson et al., 1998; Wise et al., 1999) which agrees with the finding that nitrogen fixation is more common in type II methanotrophs (Auman et al., 2000)

With respect to the oxygen demand, methanotrophic bacteria are classified into two functional groups: obligatory aerobic bacteria that cannot live in anaerobic conditions and bacteria that can survive in anaerobic period and reactivate in aerobic conditions. Most of methanotrophs belong to obligatory microaerophiles. They prefer oxygen concentrations below atmospheric (Mancinelli, 1995). Microorganisms responsible for this process, so-called methanotrophs, are common bacteria that can utilize CH₄ as the sole carbon and energy source.

2.13 Factors affecting methanotrophs bacteria

Some of the factors that influence microbial CH₄ oxidation in landfills include climate variables such as moisture and temperature (Jones and Nedwell, 1993 ; Bogner et al., 1995; Czepiel et al., 1995; Boeckx and Van Cleemput, 1996; Borjesson and Svensson, 1997), as well as CH₄ concentration (Czepiel et al., 1996; Bogner et al., 1997), soil type (Kightley et al., 1995) and pH (Hilger et al., 2000).

2.13.1 Temperature

Temperature is of the utmost importance for the ability of the methanotroph community to oxidise CH_4 , and a better understanding of the optimal conditions for oxidation would improve predictions of oxidation rates and would also help in the construction of better landfill covers. The best temperature conditions are within the range of 30 to 35°C. Investigations carried out by Whalen et al. (1990) on a sandy clay soil of the landfill cover surface layer, within the temperature range of 5-46°C indicate that there is a temperature optimum of 31°C. Temperatures decrease below that value bring about a

smooth decline of methanotrophic activity, where an increase of the temperature up to the values exceeding the optimum causes a rapid drop in the activity to almost zero at 46°C. This is related to denaturation processes of proteins contained in methanotrophic cells. A similar value of the temperature optimum contained within the range of 25°C-30°C has been obtained for a soil of a prevalent sand fraction also taken from a landfill cover (Boeckx and Van Cleemput, 1994: Boeckx and Van Cleemput, 1996).

Temperature has a profound effect on all biological processes, including CH₄ oxidation activity. Most methanotrophs available in pure cultures are mesophiles (Hanson & Hanson 1996). Optimum temperatures are around 25—35 °C for CH₄ oxidation in soil environments, although CH₄ oxidation can occur down to 1—2 °C (Prime & Christensen 1997, Christophersen *et* al. 2000, Scheutz & Kjeldsen 2004, Einola *et* al. 2007). Omel'chenko *et* al. (1993) isolated methanotrophs from acid soils in a bog in the Arctic that had optimum growth at temperatures of 10 °C or lower indicating that some populations of methanotrophs can adapt to lower temperatures in nature. All of the bacteria found in low temperature environments belong to type I methanotrophs (Borjesson *et al.* 2004), indicating that temperature could exhibit a selecting effect that determines which of the two main types of methanotrophs will predominate in a given environmental system. It appears that in landfill conditions type I methanotrophs tend to have a lower temperature optimum than type II methanotrophs (Gebert *et* at. 2003). Consequently, type I methanotrophs are more dominant at 10 °C than at 20 °C (Börjesson *et al.* 2004).

A little lower optimum value of 23°C has been obtained for Alaskan waterlogged soils (Whalen and Reeburgh, 1996). Results of Boeckx et al (1996), investigations performed on a sandy-clay soil of a landfill cover indicate that the temperature optimum value varies depending on the moisture content of the soil material. Within the moistness range of 10-30% of weight, the temperature optimum decrease along with the increasing

moisture content from 27.1°C at the lowest moistness level to 20.1°C at the upper limit of the range. Increasing the moisture content results in a reducing effect on the gas transport to the bacteria cell. This can eventually lead to a situation in which the substrate supply is smaller than the oxidizing capacity of microorganisms at a given temperature. Thus, at higher moisture content, the CH₄ transport becomes a limiting factor for the oxidation process. When the moisture content is low, the limiting factor is the activity of microorganisms.

In cold areas or during winter season with temperatures below 5-10°C the CH₄ oxidation might be significantly reduced or even come to standstill. Börjesson & Svensson (1997b) investigated the seasonal as well as the diurnal variation in CH₄ emissions from a small Swedish landfill and found temperature to be the controlling factor. CH₄ emissions were negatively correlated with soil temperature, indicating that microbial oxidation was an important regulating factor. Christophersen *et* al. (2001) also found higher CH₄ emissions during winter, while no CH₄ was emitted during summer at Skellingsted landfill in Denmark, which was attributed to temperature.

The active temperature for methanogenic microorganisms is in the range 30-50°C. The temperature for mesophilic bacteria in the range 30-35°C, while 45-65°C for the thermophilic bacteria (Williams, 2005). The optimum temperature range of gas generation between 30-45°C during the main LFG generation phase (Williams, 2005).

2.13.2 Moisture content

The moisture content of the substrate influences CH_4 oxidation in many ways. Moisture content is the most important parameters affecting CH_4 oxidation in landfill cover soil. The moisture strongly affects the capacity for CH_4 consumption by determining the extent of CH_4 diffusion between the soil gas phase and the atmosphere (Schnell and King, 1995). There is a strong correlation between the actual water content and oxygen respectively CH₄ permeability, which also has a big impact on CH₄ oxidation. Moisture is an essential factor for micro-organisms to sustain their activity as it is the transport medium for nutrient supply and also for removal of residual metabolic compounds. However, too much moisture may slow down gaseous transport processes in the soil because molecular diffusion in water is about 10^4 times slower than in the air (Cabral *et* al. 2004). When the soil's degree of saturation (volume of water/volume of voids) reaches a value in the vicinity of 85%, the air- filled voids are no longer interconnected and the gases have to diffuse in the liquid phase (Cabral *et al.* 2004), drastically reducing the availability of CH₄ and O₂, thereby limiting CH₄ oxidation. In contrast, a decrease in moisture content can also reduce the oxidation rates significantly due to microbial water stress resulting from desiccation.

Moisture contents reported to be optimum for CH_4 uptake in landfill cover soils range from 10–20% (Whalen *et al.*, 1990; Boeckx and VanCleemput, 1996; Czepiel *et al.*, 1996). However, in some cases higher soil moisture optima have been observed (Börjesson *et al.* 1998a, Christophersen *et al.* 2000, Scheutz & Kjeldsen 2004). The oxidation activity is significantly reduced when soil moisture content decreases below 5% (Whalen *et al.* 1990, Czepiel *et al.* 1996b, Stein & Hettiaratchi 2001, Scheutz & Kjeldsen 2004).

Boeckx *et al.* (1996) found that the CH_4 emission was controlled by soil moisture content in a field experiment conducted at a small landfill in Belgium. Likewise, Jones & Nedwell (1990) measured the highest CH_4 emissions from a landfill in England during the warmest and driest periods. In arid areas or during periods with very low precipitation, moisture content can be a critical factor in limiting the oxidation capacity in landfill soil covers. Jones and Nedwell (1993) speculated that the capacity of cover soil to sustain substantial moisture content throughout its depth is likely to promote more uniform methanotroph distribution and greater opportunity for CH_4 removal throughout the cover depth. In a combined field and laboratory study, Scheutz *et al.* (2003) found that reduced methanotrophic activity in the upper part of the soil cover was due to moisture limitation rather than substrate limitation.

Gas permeability decreases with increasing water content (Humer and Lechner, 2000). At moisture content below 13% of the maximum water capacity, methanotrophic microorganisms tend to become inactive. (Bender, 1992). Tests carried out by Figueroa (1993) on different landfill cover materials show that optimum conditions for CH_4 oxidation are found in areas with a relatively high moisture content. The highest CH_4 turnover rate could be achieved under the same ambient conditions in biowaste composts with moisture content of approx 40-80% of the maximum water-holding capacity. Boeckx et al.(1996) indicated that water content widely regulates the activity of methanotrophic bacteria. They found that the optimum moisture content is situated at about 50% of the water capacity. In laboratory test carried out by Humer and Lechner (2001), the activity of the methanotrophic bacteria was strongly inhibited at a moisture content of 20% w/w in compost (corresponding to <15% of maximum water capacity). The high water holding capacity of organic-rich composts is beneficial in arid climates to preserve moisture for the microbes, although under wet conditions, a high moisture content can reduce gas transport and hinder methane uptake, an in extreme cases, even can produce CH₄ (Barlaz et al.,2004).

2.13.3 pH and alkalinity

According to McBean et al (1995), suitable top cover to encourage vegetation growth should have pH in the range of 5 to 8. If the pH is over 8, necessary elements for plant growth may not be soluble. A pH of less than 5 may cause some elements to become toxic. In general, soil pH should be above 6. The CH₄ oxidation process occurs within a comparatively wide pH range from pH <4 in sandy (Hoeks, 1972) and bog soils (Powlson et al., 1997) up to >9 in bog soils (King, 1990). At lower pH values it is possible that the dropping CH₄ concentration could result from the activity of yeast that easily adapts to an acidified medium. The optimal pH for the growth of methanotrophic bacteria isolated from dune sands located in vicinity of natural gas leakage was 7.0, although their growth was also observed in the pH range 5.5-8.0 (Adamse et al., 1972). Arif et al. (1996) have noted a slightly narrower pH range (5.9-7.7) in agriculturally used sandy soils. The optimum pH in an acid forest luvisol was 6.3 (Bender and Conrad, 1995), while in bog soils the most intensive oxidation occurred at pH 6-8 (King, 1990).

The methanogenic bacteria operate efficiently only within a narrow pH-range of 6-8 (Zehnder et al.,1982). The pH range for the fermentative and acetogenic bacteria is much wider than for the methanogenic bacteria. If the methanogens are stressed by other factors, their conversion of hydrogen and acetis acids decreases, leading to an accumulation of volatile organic acids and a decrease in pH (Pawloska,2008). This will furthermore inhibit the CH₄ formation and lead to further decrease in pH. Eventually, the CH₄ generation may stop. Rozej and Stepniewski (2008) who used sand as the material for CH₄ oxidation in column experiment observed a strong increase in methanotrophic activity when the pH of the material declined below 8.0. Pawloska (1999) did not observe any significant changes in the CH₄ oxidation rate in the pH range 7.61-8.89, although Hilger et al.(2008b) found that increasing soil pH will increase the intensity of CH₄ oxidation.

Methanotrophic bacteria are treated as neutrophiles lacking in any clear adaptations to extreme conditions. The highest CH_4 oxidation rate is usually observed at pH values of 6-7 (Hutsch, 1994; Dunfield et al., 1993). The optimal pH for the methanogenic bacteria is in the range of 6.7 to 7.5. However, there is still some activity with pH in the range of 5.0 to 9.0. pH (Hilger et al., 2000). Recently, some authors have observed methanotrophic activity in highly alkaline environments (at pH 10-11) (Khmelenina et al., 1997; Sorokin et al., 2000; Kaluzhnaya et al., 2001), but acidophilic methanotrophs have also been found

(Dedysh et al., 2004; Trotsenko & Khmelenina, 2005) comfirming the significant adaptive capacity of some methanotrophs.

2.13.4 O₂ supply

 O_2 concentration plays an important role in the regulation of CH₄ oxidation and the microbial ecology of methanotrophs. Methanotrophic bacteria are obligate aerobes, which can optimum CH₄ oxidation rates even under mesophilic conditions, i.e. at very low O_2 concentrations (Pawloski and Pawloska, 2008). CH₄ oxidation is an aerobic microbial process and oxygen availability in landfill cover soil is a major limitation to the growth and activity of methanotrophs (Stralis-Pavese et al., 2006). Humer and Lechner (1999) and Börjesson et al. (2004) found that soils with high porosity and particle size distribution can retain CH₄ and O_2 longer in the pores, resulting in higher oxidation rates. Czepiel et *al.* (1996b) who found that CH₄ oxidation dropped significantly at O_2 -mixing ratios below 3%. Wilshusen *et* al. (2004a) showed that in pure methanotrophic cultures, O_2 concentrations ranging from 0.45 to 20 % could support maximum CH₄ oxidation rates in both type I and II bacteria.

2.14 Landfill Cover

Historically, landfills are among the largest anthropogenic CH₄ sources worldwide, ranking third after agriculture (livestock farming and rice cultivation) and losses from fossil fuel distribution, processing and mining (Forster et al., 2007). An important cost-effective means of reducing greenhouse active methane emissions from existing MSW landfills is to exploit the natural process of microbial CH₄ oxidation through improved landfill cover design. This oxidation process is usually mediated by a group of bacteria known as the methanotrophs, and has already been well documented in landfill cover soils and biofilters (e.g., Kightley et al., 1995; Boeckx et al., 1996; Bogner et al., 1997; Gebert and Gröngröft, 2006). Landfill top covers, which optimise environmental conditions for methanotrophic bacteria and enhance biotic CH_4 consumptions, are often called "biocovers", functioning as vast bio-filters.

A biocover usually consists of a suitable cover material and a subjacent gas distribution layer to homogenize LFG fluxes. Since biocovers are typically spread over an entire landfill area or sector, availability and cost become critical factors in material selection, consequently, often waste materials, such as diverse composts, mechanicallybiologically treated waste, dewatered sewage sludge or yard waste, are used.

Considerations to be reflected in selection of landfill cover components (McBean, 1995)

- 1. Cost
- 2. Erosion and slope stability concerns
- 3. Selection of cover materials, slope and thickness
- 4. Estimation of runoff quantities on to adjacent lands
- 5. Long term durability
- 6. Estimation of percolation quantities

One of the major design components of landfill is the final cover besides liners, the leachate collection and management system, gas management facilities, storm water management and the final landfill cover (Vesilind et al., 2002). MSW landfills have the following components as shown in Figure 2.11.

- (i) Bottom and lateral system (act as barrier system that encapsulate the waste)
- (ii) Leachate collection and removal system,
- (iii) Gas collection and control system,
- (iv) Final cover system,
- (v) Storm water management system,
- (vi) Groundwater monitoring system and

(vii) Gas monitoring system

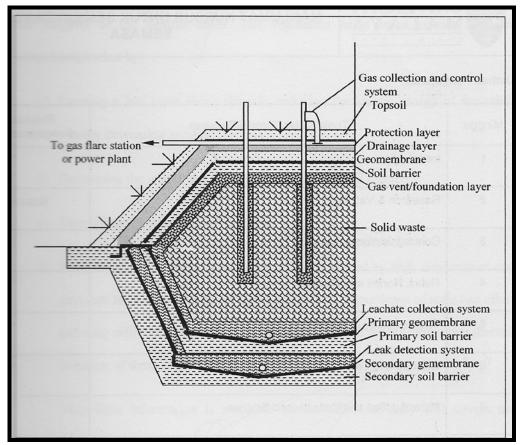


Figure 2.11: Schematic diagram of MSW landfill containment system (Sharma, 1995)

Cover material is classified as daily, intermediate, or final cover according to the frequency with which the material is applied. Daily cover is placed at the end of the working day (or more frequently, as the situation warrants). According to McBean (1995), the primary functions of daily cover are:

- 1. Moisture control, helps reduce odors and prevent fires
- 2. Capping of refuse as a litter control measure
- 3. Limits rodent and bird contact with the refuse
- 4. As an operational requirement for vehicle access to the active face
- 5. Decreases the unsightliness of the facility.

Intermediate cover provides the same general functions as daily cover, with its primary objective being the reduction of moisture entering the refuse. Meanwhile to be

effective, final cover must be compacted (except the top soil in which vegetative growth is desired) ,uniformly applied, and sloped to enhance surface runoff as opposed to allowing infiltration. According to McBean (1995), purposes of final-soil cover are:

- 1. To encourage surface runoff while discouraging erosion of the cover itself; provide an effective low-permeability cap/cover to the landfill site that serves to control the infiltration of surface water into the waste and hence limit the generation of leachate.
- 2. To retain moisture for growth of vegetative root.
- 3. To reduce or enhance landfill gas migration (depending on the design objectives)
- 4. To provide a base for the establishment of a suitable ground cover.
- 5. To provide the final shaping and contouring of the site in accordance with the end use objectives.

Both soil materials and non-soil materials are utilized, although soils are most commonly used. Table 2.4 below gives the advantage and disadvantages of using various non-soil materials for final cover.

Material	Advantages	Disadvantages
Asphalt	 Traditional used as hydraulic barrier Ductile and often chemically durable. Wide variety of water based emulsions Available in panels or rolls 	 Low tensile strength; needs geotextile reinforcement Need careful design and installation
Soil-Cement	Relatively low permeabilityCan be formulated on site	 Inflexible and brittle Difficult to utilize as major cover component

Table 2.4: The advantages and disadvantages of using various non-soil materials for final cover.

Material	Advantages	Disadvantages
Geotextiles	• Ideal for filtration, drainage, separation, reinforcement and armouring	• Limited to essentially secondary roles, in conjuction with use of soil
Geomembranes	 Thin sheets take the place of thicker soil layers Preformed as relatively large panels Small leaks less serious than when used as liners Very low permeability Large body of geotechnical knowledge in application 	 May be vapour-gas degradable Uncertain life span under various in-place conditions Cannot be exposed to elements Low tensile strength Requires careful installation
Industrial Wastes	 Abundant and cheap where available Predictable chemistry; often inert to vapours/gases Ideal for drainage and load-bearing application 	• Many available only as less desirable fine grained materials

 Table 2.4 (Continued): The advantages and disadvantages of using various non-soil materials for final cover.

Source: Hatheway and McAneny (1987)

2.15 Compost as landfill cover

Previous laboratory investigations have demonstrated a high oxidation capacity in diverse, mature and well-structured compost materials (Humer and Lechner, 1999; Wilshusen et al., 2004a). Laboratory studies to assess the factors that influence microbial CH₄ oxidation have been conducted on MSW and sewage sludge composts_(Humer & Lechner 1999a, b, Huber-Humer 2004, Wilshusen *et al.* 2004a, b), compost mixtures with soil or sand_(Huber-Humer 2004, Scheutz *et al.* 2009), compost mixed with perlite_(Melse & Van der Werf 2005), biowaste composts of different ages (Felske 2003), leaf compost, commercially available compost, and unscreened wood-chips compost (Wilshusen *et al.* 2004b). Moreover, preliminary field trials (Humer and Lechner, 2001a; Barlaz et al., 2004;

Huber-Humer, 2004; Bogner et al., 2005) have provided indications as to the suitability of compost biocovers for practical application and their high efficiency in mitigating CH_4 emissions.

Compost instead of soil was used as the basic material because it is known to offer a higher CH_4 oxidation capacity due to its higher organic matter, water holding capacity, and porosity (Agnew and Leonard, 2003; Barlaz et al., 2004; Hilger and Humer, 2003; Humer and Lechner, 2001; Nikiema et al., 2005; Wilshusen et al., 2004a). Furthermore, it does not require additional nutrients for the growth of methanotrophic micro-organisms. Moreover, it was decided to use mature compost in this study to avoid further composting, which would produce CO_2 and cause an increase in temperature. Both field observations at landfills and results from laboratory studies have demonstrated that organic cover soils have a high capacity to mitigate CH_4 emissions (Borjesson et al., 1998b; Humer and Lechner, 2001). Research so far indicates that compost should be capable of oxidizing CH_4 at rates two to three times higher than that of mineral soils (Wilshusen et al., 2004). Streese and Stegmann (2003) studied compost as biofilter material for microbial CH_4 degradation and reported high degradation rates of up to $63g CH_4m^{-3}h^{-1}$.

Humer and Lechner (1999, 2001) studied MSW compost and sewage sludge compost as cover soil to increase oxidation of CH_4 and found that complete CH_4 oxidation is possible. Barlaz et al. (2004) reported that compost covers oxidized more CH_4 than conventional clay covers in field trials, but warned that compost covers can also produce CH_4 if the moisture content is too high. In the present study, experiments were performed at laboratory scale to examine how CH_4 oxidation depends on temperature and moisture for different types of compost and to assess the suitability of compost as landfill cover. Previous studies have shown that microbial CH_4 oxidation in landfill cover soil can be enhanced when using substrates that are rich in organic matter, such as compost, rather than pure clay covers (Abichou et al., 2006; Stern et al., 2007). . The ability of compost to remove chlorinated hydrocarbons and sulphur compounds has been reported by Muntoni and Cossu (1997).

It seems logical that a landfill cover could be designed to promote optimum growth of methane-oxidizing bacteria and thus enhance biological oxidation of CH₄. Various landfill covers or biofilter designs, using different configurations and substrates to support growth of methanotrophs, have been evaluated elsewhere (Hilger and Humer, 2003; Gebert and Gröngröft, 2006). However, results from efficiency tests under field conditions are mostly available for covers or biofilters working under temperate climatic conditions.

Stern et al. (2007) reported the performance of three biocover cells relative to three control cells from March 2004 to April 2005. Stern et al. (2007) observed that placing a layer of compost over the landfill cover soil led to more resistance to gas flow associated with the longer flow path. They added that flow resistance was also increased because the compost layer kept the underlying cover soils at higher water content. Compost has a high capacity to retain moisture, which kept the entire soil profile at higher water content, resulting in lower gas permeability and lower diffusion coefficients. This effect of biocover was referred to as blockage (Stern et al., 2007). Stern et al. (2007) added that, because CH₄ loading was lower, the biocover was able to oxidize a greater portion of the CH₄ flux entering it from below, even though the absolute CH₄ oxidation rate was less than in the control soils.

Siminiss and Manios (1990), proposed mixing peat with MSW compost. Ribeiro et al. (2000) carried out a study to evaluate the use of MSW compost as a fertilizer for potted geraniums, mixing MSW compost with a peat-based medium and observing that concentrations of MSWC of around 10–20% promoted the highest plant growth; Castillo et

al. (2004) proposed the use of MSW compost rather than peat, as a tomato transplant medium.

Compost has proved capable of providing suitable chemical and physical properties for methane oxidising micro-organisms (Humer and Lechner, 1999, 2001b). The most beneficial feature of compost is the high content of organic matter, providing numerous favourable conditions for micro-organisms, such as a high specific surface area, a high water retention capacity combined with adequate porosity and suitable texture for gas exchange (meaning a high air-filled pore volume even at higher moisture contents), low thermal conductivity and, consequently, good temperature insulation effect. However, when applied for methane oxidation purposes, organic matter in the compost must be stable and mature. CH₄ turnover rates in mature composts are clearly higher than in humic-poor soils and the cohesive, mineral clay soils usually used for landfill covers, while fresh and finely sieved composts may exert an opposite effect due to oxygen limitation and competition by respiration of the compost material followed by formation of exopolymeric substances (Humer and Lechner, 1999; Huber-Humer, 2004; Wilshusen et al., 2004b). Moreover, compost materials which are not fully mature and well textured may produce methane rather than oxidise it under unfavourable water-saturated, anaerobic conditions, as observed in field investigations with biocovers made of one meter yard waste compost by means of isotopic evidence (Barlaz et al., 2004).

Important influencing factors on CH_4 oxidation such as temperature and moisture content can be controlled by the unique physical properties of the compost. Usually, compost materials have a high water retention capacity due to their high organic content and high specific surface area. While this is a beneficial property in arid climates to preserve moisture for the microbes, under wet conditions, the high water content can block gas transport, reduce CH_4 uptake, and in extreme cases, contribute to CH_4 production (Scheutz *et al.* 2009). Some studies have suggested that the high water retention capacity of biocover compost materials, particularly when combined with the evapotranspirative capacity of vegetation will be sufficient to prevent high levels of infiltration and leachate production (Gomiscek *et al.* 2001, Huber-Humer & Lechner 2003, Huber-Humer 2004).

2.16 Methane Oxidation

Landfill sites are widely reported as significant CH₄ emission sources (Borjesson et al., 2000; Barlaz et al., 2004; Powell et al., 2006; Lohila et al., 2007; Zhang et al., 2008a). Methane can be degraded by methanotrophic bacteria, which can grow using CH₄ as a sole carbon source in aerated soil and thus soil can serve as an important biological sink of atmospheric CH₄ (Adamsen and King, 1993). CH₄ oxidation in conventional landfill cover soil has been reported to be effective in reducing the amount of CH₄ emitted (Kightley et al., 1995; Bogner et al., 1997; De Visscher et al., 1999; Hilger et al., 2000; De Visscher et al., 2001). Studies on CH₄ oxidation in landfill have been extensively conducted. Fauziah and Agamuthu (2002) have reported Wheaton bottle trials using landfill cover soil at temperature from 4°C to 35°C. Based on their results, trials conducted at 35°C recorded the highest CH₄ oxidation rate within 28 hours. The high oxidation rate could have been contributed by the suitable temperature (35°C) for optimum microbial growth.

 CH_4 produced in landfills can be converted to CO_2 which is a less harmful greenhouse gas by oxidation. The process of CH_4 oxidation consists of the conversion of CH_4 into H_2O , CO_2 and biomass by microbial activity.

 $CH_4 + O_2 \longrightarrow CO_2 + H_2O + biomass$

According to Christophersen et al. (2000) the CH_4 oxidation rate depends on different physicochemical factors such as temperature, water content and organic matter. Meanwhile according to Park et al. (2002, 2004) the CH_4 oxidation depends on temperature

and water content. De Visscher et al. (2001) found out that temperature and nitrogen effects the CH₄ oxidation water. Meanwhile according to Wilshusen et al. (2004a) the rate at which CH₄ is biologically oxidized depends on several factors such as moisture content, temperature, soil characteristics and composition, pH, nutrients and O_2 concentrations. Oxidation rates of CH₄ differ within and between landfill sites due to seasonal climate changes, physical heterogeneities in the soil cover and CH₄ concentrations (Whalen and Reeburgh, 1996; Bogner et al. 1997; Borjesson et al. 1994). Therefore, microbially mediated CH₄ oxidation can play an important role in reducing the atmospheric CH₄ emission from landfills constructed with conventional cover soil (Kightley et al., 1995; Boeckx et al., 1996; De Visscher et al., 1999).

The kind of soil is also an important determinant of CH_4 oxidation. Gebert et al. (2003 a,b) reported even 100 times more methanotrophic bacteria in the biofilter filled with mineral soil. Rozej&Stepniewski (2008) observed highest CH_4 oxidation rate of $387 \text{dm}^3 \text{m}^2$ $^2\text{d}^{-1}$ in column with sewage sludge, while Kightley et al.(1995) obtained a range of 225 and 227 $\text{dm}^3\text{m}^{-2}\text{d}^{-1}$ using sand, Pawlowska (1999) observed 227 $\text{dm}^3\text{m}^{-2}\text{d}^{-1}$ using sand. CH_4 oxidation rate values obtained by de Visscher et al (1999) and Stein & Hettiarachi (2001) using landfill cover were in the range of 256-447 $\text{dm}^3\text{m}^{-2}\text{d}^{-1}$ obtained for landfill cover.

Another important factor that determines CH_4 oxidation is CH_4 concentration. Stein and Hettiaratchi (2001) studied that the presence of CH_4 caused the methanotrophic bacteria to proliferate. In their landfill cover soil, there were apparently large populations of methanotrophs, which adapted to the new laboratory conditions within a short period of time in an experiment conducted by Stein and Hettiaratchi (2001).

Diffusion also determines the depth of the oxidation zone in soil. According to Born et al.(1990) and Dorr et al.(1993) the methanotrophic capacity of soils of prevalent clay and silt fractions is diffusion-limited. Diffusion also determinates the depth of the oxidation

zone in soil. Bender and Conrad(1995) found that, when a grain diameter decreases from above 2mm to below 0.05mm, the maximal methanotrophic activity is reduced and the time for soil to reach it lengthened although the number of methanotrophs remains basically unchanged. This was probably due to easier gas diffusion in the more porous material.

CH₄ oxidation rates in conventional soils have been studied extensively, but there are fewer studies on environmental factors influencing the rate of CH₄ oxidation in compost. Streese and Stegmann (2003) studied compost as biofilter material for microbial CH₄ degradation and reported high degradation rates of up to 63 g CH₄ m⁻³ h⁻¹. Wilshusen et al. (2004a,b) studied CH₄ oxidation and formation of exopolymeric substances in woodchips compost for the performance of CH₄ biofilters and the effect of oxygen concentration. Humer and Lechner (1999, 2001) studied MSW compost and sewage sludge compost as cover soil to increase oxidation of CH₄ and found that complete CH₄ oxidation is possible. Barlaz et al. (2004) reported that compost covers oxidized more CH₄ than conventional clay covers in field trials, but warned that compost covers can also produce CH₄ if the moisture content is too high.

Boeckx et al. (1996) determined CH₄ oxidation in a cover soil by removing the cover from part of the landfill and measuring the CH₄ flux using a closed chamber method directly on the waste and the surrounding cover soil; however, the cover layer is extensively disturbed by this CH₄ and a bypass for LFG may be created. Yet another approach performed by Kjeldsen et al. (2007) involves the use of "deep flux chambers", which are placed beneath biocover layers prior to their installation, in order to determine the CH₄ load going into a biocover. Sub-surface chambers may reflect CH₄ load sufficiently when diffusive fluxes are assumed, but may fail when advection occurs. This method together with other monitoring strategies is currently undergoing evaluation in a Danish research project "BIOCOVER".

De Visscher et al. (2001) have reported a V_{max} value of 0.820µmol kgdw⁻¹ s⁻¹ in soil on day 34 after the start of an incubation experiment, while Whalen et al. (1990) have reported a V_{max} value of 0.039 µmol kgdw⁻¹ s⁻¹ in soil samples that were taken from a landfill. Streese and Stegmann (2003) observed a V_{max} value of 2.43 µmol kgdw⁻¹ s⁻¹ in compost, which was a mixture of an equal volume of yard waste, peat and squeezed spruce wood fibre. Wilshusen et al. (2004a) observed a V_{max} value of 3.77 µmol kgdw⁻¹ s⁻¹ after one month and 2.77 µmol kgdw⁻¹ s⁻¹ after two months in compost, which was prepared from municipal green waste such as leaves mixed with manure.

Powelson et al.(2006) conducted a field test using biofilter filled with compost made of garden waste (mainly leaves and tree branches) with expanded polystyrene pellets added. A CH₄ charged supplied to biofilter of $375-750 \text{dm}^3 \text{m}^{-2} \text{d}^{-1}$ showed that the CH₄ oxidation rate of $362.3 \text{dm}^3 \text{m}^{-2} \text{d}^{-1}$ compared to bi-layer biofilter filled with coarse sand covered with a fine sand layer ($303.9 \text{dm}^3 \text{m}^{-2} \text{d}^{-1}$). Thomas et al.(2002) used loamy sand which exhibited highest CH₄ oxidation activity which began on Day 2. .Pawlowska, et al (2006),Stein and Hettiaratchi (2001) reported that highest CH₄ oxidation rate was noted around 66cm using landfill soils.Thomas (2002) who used loamy sand indicated active zone were at a depth 0-20cm from the surface. Scheutz and Kjeldsen (2004) used soil samples from Skellingsted Landfill, Denmark and they obtained an average oxidation rate of 70 µg g⁻¹h⁻¹ at 60cm column height.

2.17 Kinetics of Landfill Gases

Pawloska and Stepniewski (2006) used kinetics described by the Michaelis-Menten equation to study the kinetics of CH_4 oxidation using column experiment with continuous flow of CH_4 . A curve that illustrates its course is often called a substrate saturation curve and can be described as follows:

$$V = V_{\text{max}} \qquad 1 \\ 1 + \frac{K_{M}}{C}$$

where:

V = actual methane oxidation rate $(m^3m^{-3}s^{-1})$,

 V_{max} = maximum methane oxidation rate (m³m³s⁻¹)

 K_m = Michaelis constant (m^3m^{-3})

C = CH₄ concentration (
$$m^3m^{-3}$$
)

Based on the kinetics, Pawloska and Stepniewski (2006) found that the rate or reaction increases initially as the concentration of CH_4 increases, until such time as the substratum is saturated. The K_m value obtained by Pawloska and Stepniewski(2006) was in the range of 0.6% (at a depth of 80cm) to 2.9% (10cm down).

A similar relationship for high concentrations of CH₄ was observed by other authors (Whalen et al.,1990; Reeburgh, 1996; Bestead and King,1997;Dammann et al.,1999;Gebert et al.,2003). Also known is work (like Bender and Conrad, 1995, Roslev et al.,1997;Streese and Stegmann,2003) pointing to CH₄ oxidation reactions whose course is in line with first-order kinetics, the result being that the upper limit value for the studied range of CH₄ concentrations is below the saturation value. In the case of the work by Streese and Stegmann(2003), the upper value for the concentration did not exceed 3.2% CH₄. In contrast the saturation value in the experiment conducted by Pawloska and Stepniewski (2006) always exceeded 4 % (v/v) CH₄. Table 2.5 shows the summary of maximal methane oxidation rates for landfill cover soils obtained from batch studies by several authors.

 Table 2.5: Summary of maximal methane oxidation rates for landfill cover soils obtained from batch studies.

Reference	Landfill soil material	Maximum CH ₄ oxidation rate	Initial CH ₄ concentration	Investigated temperature range	Optimum temperature
		$(\mu g C H_4 g^{-1} h^{-1})$	(%v/v)	(°C)	(°C)
Park et al. (2009)	5 year old compost cover	16	10	5-35	25-35
Einola et al. (2007)	5 year old compost cover	2.5	8-9	1-19	19
Scheutz <i>et al.</i> (2007)	Loam	28	15	22	30
Park et al. (2005)	Sandy soil	25	5-53	4-40	30
Börjesson at al. (2004)	Sandy loam ^a	18.8	5	3-20	≥20
Börjesson at al. (2004)	Sandy loam ^a	25.2	5	3-20	≥20
Scheutz & Kjeldsen (2004)	Loamy sand	118	15	2—50	30
Scheutz et al. (2003)	Silt, sandy	1.5	15	22	30
Stein & Hettiaratchi (2001)	Loam	16	2.5	4-40	30
De Visscher et al. (2001)	Sandy loam	47.2	2	22	30
Börjesson (2001)	Sand	16	0.2-0.67	20	20-25
Hilger et al. (2000a)	Sandy loam	2.4	8	22	30
Christophers en <i>et al</i> . (2000)	Sandy loam	19	18	2-15	15
De Visscher et al. (1999)	Sandy loam	26	3	22	30
Börjesson (1997)	Silty loam ^a	173	5	2-37	31
Börjesson (1997)	Sandy loam	48	5	25	38
Börjesson & Svensson (1997b)	Sand ^a	16	0.2-0.67	25	20-25

Reference	Landfill soil material	Maximum CH ₄ oxidation rate	Initial CH4 concentration	Investigated temperature range	Optimum temperature
		$(\mu g C H_4 g^{-1} h^{-1})$	(%v/v)	(°C)	(°C)
Bogner et al. (1997a)	Sand	11.8	8.4	25	20-25
Boeckx & Van Cleemput (1996)	Sandy loam	0.0024	0.001	5-30	20-30
Czepiel et al. (1996b)	Sand clay loam	41.5	1.7-2	5-45	36
Boeckx et al. (1996)	Sandy loam	0.01	0.001	5-30	20-30
Kightley et al. (1995)	Coarse sand	16	5	20	30
Figueroa (1993)	Humic soil Till Biowaste compost	86.4 40 128	10 10 10	20 10-40 20	30
Jones & Nedwell (1993)	Sandy loam	0.2	12.5	22	30

Table 2.5 (continued): Summary of maximal methane oxidation rates for landfill cover soils obtained from batch studies.

^aAccording to ISSS (International Society of Soil Science: clay = < 0.002 mm, silt = 0.002—0.02 mm, sand = 0.02-2.0 mm) Source: Scheutz et al., (2008)

The V_{max} obtained in the experiment conducted by Pawloska and Stepniewski (2006) was in the range of 0.11 x 10⁻³ to 0.86x10⁻³ units. These were approximately one order of magnitude lower than the potential methanotrophic activity measured by Kightley et al.(1995) in coarse-grained sand taken from 'landfill cover' by Stein and Hettiaratchi(2001) in 'loam soil from the landill cover', by Gebert et al.(2003)in crushed expanded clay material tested as a biofilter for LFG, being equal to 6.49-7.29 x 10⁻³, 6.2x10⁻³ and 11.08x10⁻³ units, respectively.

The results obtained by Pawloska and Stepniewski (2006) were similar to those obtained by Whalen et al.(1990)in a soil from the top of the landfill cover; these varying

across the range 0.88×10^{-3} to 1.09×10^{-3} cm³ kg⁻¹s⁻¹. For comparison, the V_{max} values measured in forest soils were several orders of magnitude lower, and varied between 4.9 x 10^{-6} and 56.8 x 10^{-6} cm³kg⁻¹s⁻¹(Bender and Conrad, 1993;Whalen and Reeburgh,1996;Benstead and King,1997).

De Visscher et al. (2001) have reported a V_{max} value of 0.820µmol kgdw⁻¹ s⁻¹ in soil on day 34 after the start of an incubation experiment, while Whalen et al. (1990) have reported a V_{max} value of 0.039 µmol kgdw⁻¹ s⁻¹ in soil samples that were taken from a landfill. Streese and Stegmann (2003) observed a V_{max} value of 2.43 µmol kgdw⁻¹ s⁻¹ in compost, which was a mixture of an equal volume of yard waste, peat and squeezed spruce wood fibre. Wilshusen et al. (2004a) observed a V_{max} value of 3.77µmol kgdw⁻¹ s⁻¹ after one month and 2.77µmol kgdw⁻¹ s⁻¹ after two months in compost, which was prepared from municipal green waste such as leaves mixed with manure.

2.18 Biocover Performance Index

Biocover Performance Index (BPI) is used to evaluate the efficiency of a biocover material. BPI is inversely proportional to the period of CH_4 oxidation. Period complete of CH_4 oxidation is taken into account to determine BPI. Other parameters which influence BPI are the CH_4 concentration oxidized and the weight of the Biocover material used.

The performance of the Biocover was expressed in terms of Biocover PerformanceIndex(BPI). Derivation of the performance parameters are detailed below:

 $BPI = (CH_4)_0 \quad (CH_4)_n \quad (Equation 1)$

where

 $(CH_4)_0 =$ Initial concentration of CH_4 (mL)

 $(CH_4)_n = \text{concentration of } CH_4 \text{ at time } n (mL)$

W = amount of Biocover (g)

N= time taken for complete methane oxidation (hours)

2.19 Literature Review Conclusion

Numerous studies has been carried out mainly under laboratory conditions and to the lesser extent in the landfill environment, to attenuate CH_4 through design of landfill cover using selection of materials with optimum CH_4 attenuation capacity. It has been reported that by creating optimal ambient conditions for methanotropic bacteria in cover layers, it is possible to foster the natural potential of CH_4 oxidation and attain very high oxidation rates (Humer and Lechner, 2001). Therefore this research investigates the suitability of compost from garden waste and black soil as landfill biocover to achieve maximum oxidation of CH_4 under tropical condition, as most study carried out was not under tropical conditions. Some other present work (Table 2.5) shows the summary of maximal CH_4 oxidation rates for landfill cover soils obtained from batch studies.

This study conducted is quite similar to Navarani, V. (2009) study which was on Bioremediation of Landfill Gas Under Laboratory Conditions, but the difference is in Navarani's study, she conducted column experiment, meanwhile in this study Wheaton bottles experiment were carried out .In this study, materials used was garden waste compost and black soil, also similar to Navarani's study, but her additional material used was residue compost.

CHAPTER 3: MATERIALS AND METHODS

3.1 EXPERIMENTAL MATERIALS

3.1.1 Garden Waste Compost

Compost was prepared by mixing grass clippings and cow dung in the ratio 3: 1 based on previous trials (Navarani, 2009). For optimum composting, the grass clippings and the cow dung were mixed thoroughly to ensure the microbes are distributed evenly. Heap method was used and composting was carried out under a rain shelter. The heap was 0.5m high and 1m wide at base.

Water was added to the compost mixture to maintain the moisture level in the range of 50-60%. Aerobic condition was maintained by manual daily turning of composting mixture for the first 8 days and one turn in 2 days thereafter. Temperatures of the composting mixture were measured daily using electronic thermometer model Oregon Scientific SA880SSX.



Plate 3.1: Garden Waste Compost heap

3.1.2 Black Soil



Black soil was obtained from a local nursery in Bukit Rahman Putra, Sungai Buloh.

Plate 3.2: Black Soil

The Biocover materials were sieved using 5mm mesh size grid to provide large surface area.

3.2 EXPERIMENTAL METHODS

3.2.1 Experimental Design

In order to meet the objectives of this study, replicate trials using Wheaton bottles was conducted using garden waste compost and black soil. The experimental design focused on evaluating the interactions between the variables (Table 3.1) affecting CH_4 oxidation in the Biocover, namely: temperature, pH and moisture content.

The experiments were conducted for 15 days in a continuous batch operation in triplicates and samples were incubated at various parameters including temperature, moisture content and pH to determine the most optimum parameters for methane oxidation.

The analysis was determined using a Gas Chromatography (GC) equipped with a thermal conductivity detector (TCD).

	Parameter			
Samples	Temperature (°C)	Moisture Content (%)	pН	
	20	30	4	
Compost &	30	40	5	
Black Soil	35	50	6	
	40	60	7	
		70	8	

Table 3.1: The parar	neter used in the s	study of CH ₄ of	oxidation in tl	ne Biocover
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Moisture content was determined gravimetrically by oven-drying the Biocover materials at 104 °C for 24 hours and expressed as the mass ratio of water to dry Biocover material, following the ASTM (2004) procedure. Organic content was determined by loss on ignition. Impo Electronic pH meter model pH100 Type 13.50 was utilized to measure pH of the Biocover materials. Further chemical analyses were conducted on the Biocover materials according to standard procedures.

3.2.2 Experimental Set Up

Wheaton bottles, with 125mL total volume each were used to conduct the batch experiment. After placing 20g of Biocover, the bottles were sealed with rubber septum and aluminium seal to ensure it was gas tight. Afterwards, 15mL of air from the headspace was withdrawn using a syringe and replaced with 10mL of O_2 gas (99.8% purity) and 5mL of CH₄ (99.9% purity). These amounts provided a mixing ratio of approximately 4% of CH₄ (v/v) and 8% of O_2 (v/v) of the total headspace. The aim of adding O_2 gas into the Wheaton bottles was to ensure that the aerobic conditions prevailed during the experiment. The

experimental runs were conducted in triplets for every variables and parameters studied. A

schematic diagram in Figure 3.1 shows the work flow for this experimental set up.

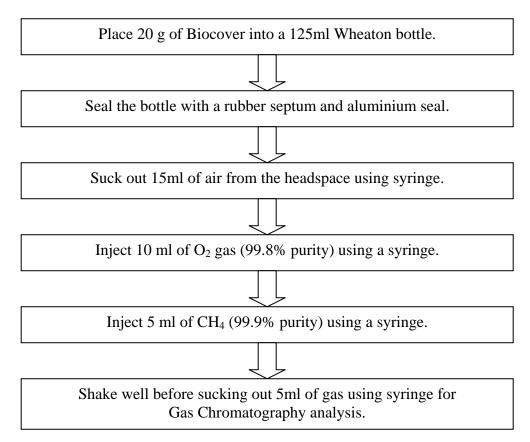


Figure 3.1: Schematic work flow diagram for experimental set up

3.2.3 Gas Chromatography Analysis

The concentrations of CH_4 , CO_2 and O_2 in the headspace were measured daily using Gas Chromatography model Shimadzu 8A attached to a C-R8A Chromatopac Integrator. The GC-8A supports a single detector, manual pressure or flow control, on column injection port(s), and analog output. Isothermal or single temperature ramp program models are available. The specifications and settings used for the GC machine used are indicated in Table 3.2 below. Table 3.2: Specifications and settings for GC-8A

Specifications	Description
Dimensions	440mm(W) x 570mm(H) x 410mm(D)
Weight	34.5kg
Injection ports and detectors temperature used	110°C
Initial temperature used	130°C
Final temperature used	130°C
Carrier gas flowrate	Helium at 7 PSI at 100°C



Plate 3.3: The Gas Chromatography model Shimadzu 8A used for the analysis.

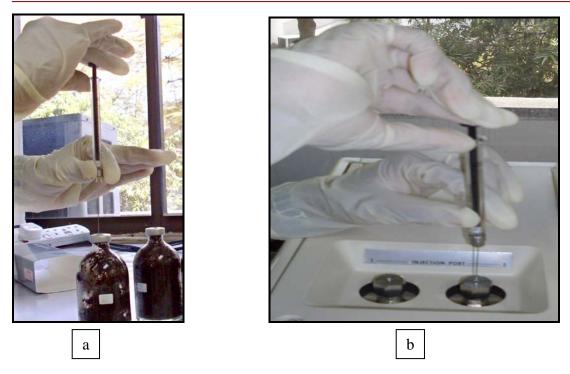


Plate 3.4: (a) Injecting out gas sample from Wheaton bottle

(b) Injection of gas into GC

3.2.4 Effects of Temperature, pH and Moisture Content Experimental Set Up

For Wheaton Bottles experiment, Figure 3.2 shows the schematic diagram workflow for the temperature experimental set up. For pH parameter, the workflow is shown in Figure 3.3 and for moisture content the workflow is shown in Figure 3.4

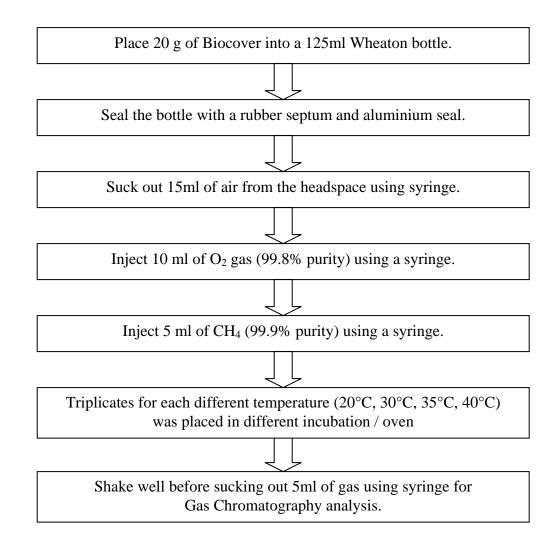


Figure 3.2: Schematic workflow diagram for temperature experimental set up

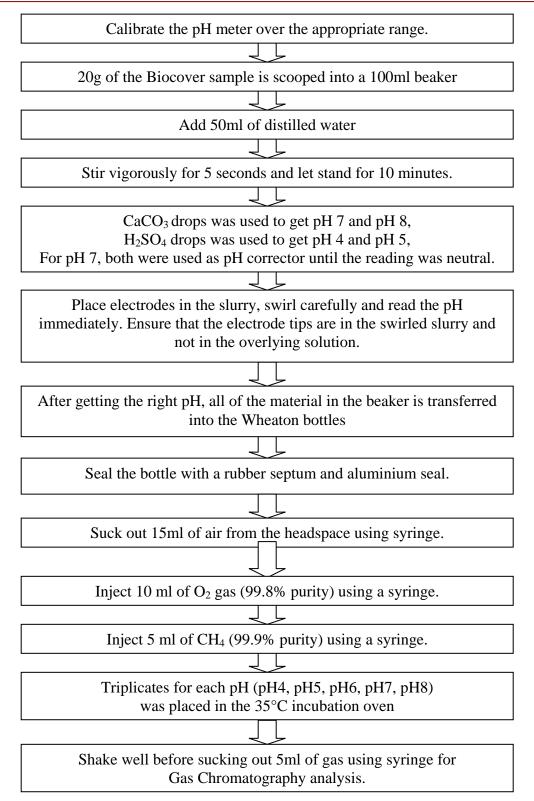


Figure 3.3: Schematic workflow diagram for pH experimental set up

3.3 BIOCOVER PERFORMANCE

3.3.1 Biocover Performance Index (BPI)

The performance of the Biocover was expressed in terms of Biocover Performance Index (BPI). Derivation of the performance parameters are detailed below:

$$BPI = (CH_4)_0 \quad (CH_4)_n \quad (Equation 1)$$

where

 $(CH_4)_0 =$ Initial concentration of CH_4 (mL)

 $(CH_4)_n = concentration of CH_4 at time n (mL)$

W = amount of Biocover (g)

N= time taken for complete methane oxidation (hours)

3.3.2 Kinetics of the Methane Oxidation Process

Further analysis on methane oxidation capacity was conducted with the kinetics model described by the Michaelis-Menten equation (Pawloska, 2006):

 R_{p} = R_{max} _____ (Equation 2) 1 - ($K_{M}/\,C$)

where

 R_p = potential methane oxidation rate (mL / d)

 R_{max} = maximum methane oxidation rate (mL/ d)

K_m= Half- saturation reaction rate (mL/d)

 $C = initial CH_4$ concentration (%)

Since C is a constant (4% v/v) for all batch incubation, C was eliminated from Equation 2 to modify the kinetics, where R_p is now described as follows:

 $R_{p} = R_{max} \qquad \underline{1} \qquad (Equation 3)$ $1 - (K_{M})$

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Properties of study Material

Compost has a higher moisture content value compared to black soil (Table 4.1). Moisture is an important physical factor that indirectly influences gas diffusion by changing the porosity of the medium and directly affects the development. Wilshusen et al. (2004), Barlaz et al. (2004), Hilger and Humer, (2003) have indicated that compost is known to offer a higher CH₄ oxidation capacity due to its higher organic matter, water holding capacity, and porosity. According to Pawloska (2008), CH₄ oxidation becomes limited if there is lack of water as it causes a physiological stress to methanotrophs.

Table 4.1 also shows that compost has a higher percentage of organic matter. Both field observations at landfills and results from laboratory studies have demonstrated that organic cover soils have a high capacity to mitigate CH_4 emissions (Borjesson et al., 1998b; Humer and Lechner, 2001). Previous studies have shown that microbial CH_4 oxidation in landfill cover soil can be enhanced when using substrates that are rich in organic matter, such as compost, rather than pure clay covers (Abichou et al., 2006; Stern et al., 2007). According to Chanton and Liplay (2000), methane oxidation is higher in organic-rich soils.

Compost has a higher C/N ratio with 16.9 due to high cellulose in the garden waste. The final carbon to nitrogen ratio (C:N) of the compost also indicates that it was a mature substrate (Navarani, 2009). According to previous laboratory tests by Boeckx et.al (1996), a high maturity of compost materials is crucial for efficient CH_4 consumption. The C/N ratio obtained by Suman et al. (2001) for the garden waste compost was in the range of 11.2 to 26.9. Compost is least acidic meanwhile black soil is more acidic. Suitable pH will favor a balanced microbial population particularly to optimize methane oxidation activities and the pH of any compost should be neutral to slightly acidic (Moldes *et al.*, 2007). The physical properties of the Biocover materials used are indicated in Table 4.1

TEST PARAMETER	RESULTS		
	Compost	Black Soil	
Moisture Content(%)	61.7	43	
рН	6.35	5.78	
Organic matter (%)	52	40	
Total Carbon(%)	20.30	16.20	
Total Nitrogen(%)	1.20	1.10	
C:N ratio	16.9	14.7	
Total Potassium(ppm)	13.75	20.73	
Total Boron(ppm)	< 0.01	< 0.01	
Calcium(ppm)	32.71	38.55	
Iron(ppm)	22.89	30.47	
Manganese(ppm)	4.20	3.29	
Magnesium(ppm)	4.65	8.83	
Sodium(ppm)	5.85	6.68	
Copper(ppm)	0.51	2.71	
Total Phosphorus(ppm)	600	700	
Zinc(ppm)	1.42	0.65	
Lead(ppm)	<0.06	< 0.06	
Cadmium(ppm)	< 0.01	< 0.01	
Mercury(ppm)	< 0.01	< 0.01	
Chromium(ppm)	< 0.02	< 0.02	
Nickel(ppm)	< 0.01	<0.01	
Aluminium(ppm)	1.53	1.85	
Total Sulphur(ppm)	<0.01	<0.01	

 Table 4.1: Properties of Biocover Materials

Biocover materials tested in this study have less than 0.01ppm concentration of sulphur. Based on studies conducted by Christensen et al. (1996) and Stegmann and Spendlin, (1985), presence of sulphur in substantial concentrations can reduce CH_4 oxidation dramatically. The ability of compost to remove chlorinated hydrocarbons and sulphur compounds has also been reported by Muntoni and Cossu (1997).

Nitrogen is an essential parameter in determining the fertility of a soil. According to Mor et.al (2006), garden waste used in their batch incubation experiment contains N concentration in the range of 1.08 to 1.54 ppm. In this study, total nitrogen for compost is 1.20ppm while black soil contains 1.10ppm, similar to Navarani (2009)

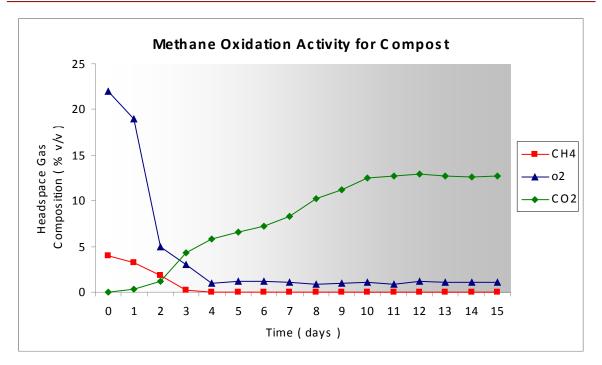
Compost has the lowest Cu concentration compared to other Biocover materials tested. According to Kjeldsen (2004) and Tsien et al.,(1989), methane degradation rates are higher when Cu concentration is very low as methanotrophs only express soluble methane monooxygenase (sMMO) enzyme which facilitates methane oxidation at low copper concentration.

4.2 Batch Experiments

Results of the triplicate Wheaton bottle batch experiments were averaged and graphs were tabulated to study methane oxidation activity of Biocovers. Figure 4.1 depicts the headspace gas analysis for CH_4 , O_2 and CO_2 for the Biocovers tested. Compost took the shortest period (4 days) for complete methane oxidation compared to black soil (7 days).

Compost took the shortest acclimatization period (1 day) compared to black soil (4 days). By day 1, compost oxidized almost 18% of the initial CH_4 injected. Black soil took 2 days to attain the same 18% CH_4 oxidation rate. High organic matter could have attributed to the shortest acclimatization period in compost as organic matter serves as the main carrier and improves soil substrate (Christensen et al.,1996).

From figure 4.1, the sharp fall in CH_4 between days 1 and 3 (compost) and day 4 and 6 (black soil) was an indicative of active methanotrophic activity in compost after acclimatization period. Muna and Leta (2008) observed sharp fall of CH_4 between 2-12 hours of incubation using yard waste, meanwhile Perdikea et al. (2007) observed between day 3 and 5 in batch incubation conducted using garden compost.



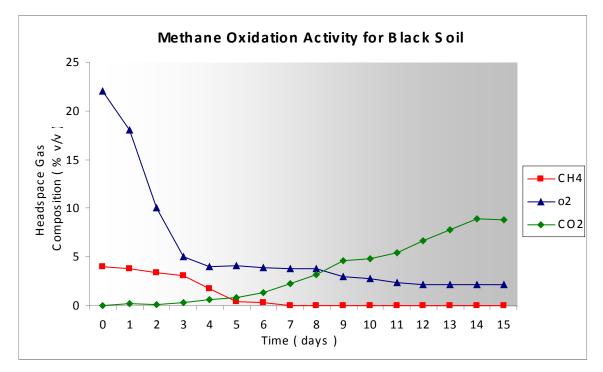


Figure 4.1: Headspace Gas Composition for the Biocover material studied using Wheaton bottles.

From this study, peak CH_4 oxidation occurred between day 2 and day 3 compared to black soil which only occurred between day 4 and day 5. This shows that compost has high capacity for faster CH_4 oxidation. Thomas et al. (2002) also observed similar results using loamy sand in which peak CH₄ oxidation began on day 2. Previous laboratory investigations have demonstrated a high oxidation capacity in diverse, mature and wellstructured compost materials (Humer and Lechner, 1999; Wilshusen et al., 2004a). Laboratory studies to assess the factor that influence microbial CH₄ oxidation have been conducted on MSW and sewage sludge compost (Humer and Lechner, 1999a,b; Huber-Humer, 2004; Wilshusen et al., 2004a,b), compost mixture with soil or sand (Huber-Humer, 2004; Scheutz et al., 2009), compost mixed with perlite (Melse & Van der Werf, 2005), biowaste composts of different ages (Felske, 2003), leaf compost, commercially available compost and unscreened wood-chipscompost (Wilshusen et al., 2004b)

Moreover, preliminary field trials (Humer and Lechner, 2001a; Barlaz et al., 2004; Huber-Humer, 2004; Bogner et al., 2005) have provided indications as to the suitability of compost biocovers for practical application and their high efficiency in mitigating methane emissions. Compost instead of soil was used as the basic material because it is known to offer a higher CH₄ oxidation capacity due to its higher organic matter, water holding capacity, and porosity (Agnew and Leonard, 2003; Barlaz et al., 2004; Hilger and Humer, 2003; Humer and Lechner, 2001; Nikiema et al., 2005; Wilshusen et al., 2004a). Furthermore, it does not require additional nutrients for the growth of methanotrophic micro-organisms. Both field observations at landfills and results from laboratory studies have demonstrated that organic cover soils have a high capacity to mitigate CH₄ emissions (Borjesson et al., 1998b; Humer and Lechner, 2001). Research so far indicates that compost should be capable of oxidizing CH₄ at rates two to three times higher than that of mineral soils (Wilshusen et al., 2004). . Streese and Stegmann (2003) studied compost which was a mixture of an equal volume of yard waste, peat and squeezed spruce wood fibre as biofilter material for microbial CH₄ degradation and reported high degradation rates of up to 63 g $CH_4 m^{-3} h^{-1}$.

Black soil took longer time for complete CH_4 reduction (7 days) compared to the garden waste compost. This could be due to the moisture content in black soil was low (43%) compared to compost (61.7%). According to Boeckx et al.(1996), water content widely regulates the activity of methanotrophic bacteria. They found that optimum moisture content was about 50% w/w where else black soil used in this study has lesser moisture content than suggested by Boeckx et al. (1996). Another possible reason for lower CH_4 oxidation capacity in black soil is due to its acidic soil condition which inhibits the methanotrophic activity in black soil. Pawloska (2008) reported that at lower pH values, it is possible that the drop in CH_4 concentration could result from the activity of yeast that easily adapts to an acidified medium.

Similar batch incubation experiments were conducted by Muna and Leta (2008) using yard waste compost at a temperature of 35°C with much higher CH₄ concentration (10%). Based on their results, complete CH₄ oxidation occurred in less than 12 hours. Higher temperature and CH₄ concentration used in their studies could have greatly contributed to optimum environmental conditions for tremendously enhanced CH4 oxidation. In addition, similar experiment was conducted by Perdikea et al. (2007) using garden waste compost, but with higher amount of CH₄ (5%) at laboratory temperature of 22°C. Based on their results, CH₄ was completely oxidized only on day 6 compared to day 4 in this study. The possible explanation for longer CH₄ oxidation period found by Perdikea et al. (2007) could simply be due to the higher CH₄ concentration and incubation temperature used in their study. Although Perdikea et al. (2007) used higher CH4 concentration which theoretically should indicate faster CH₄ oxidation; lower incubation temperature could have inhibited CH₄ oxidation activity. This reason could be further supported by findings of King and Adamsen (1992) who concluded that the bacterial enzymatic processes at low temperature limit their performance more than any other environmental conditions. Fauziah and Agamuthu (2002) recorded that at temperature 35°C, methanotrophic activity was the highest compared to other incubation temperature studied (20-40°C).

Figure 4.2 indicates that compost had the fastest speed of CH₄ oxidation with a slope gradient of 27.55 compared to black soil's slope gradient of 16.52. Slope gradient for compost was 1.67 times higher than black soil. Perdikea et al. (2008) obtained a lower slope gradient (15.63) for CH₄ oxidation using garden waste compost indicating a lower CH₄ capacity compared to garden waste compost and black soil used in this study. Peak methane oxidation occured between day 2 and day 3 compared to black soil which only occured between day 4 and day 5. Similar results were obtained by Thomas et al.(2002) using loamy sand in which peak methane oxidation began on Day 2.

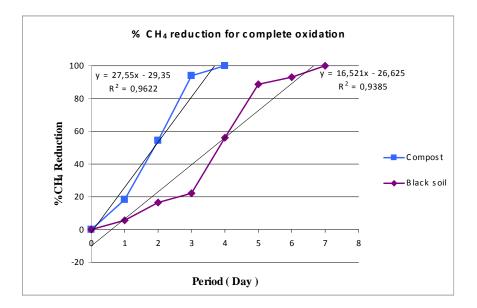


Figure 4.2: Percentage of complete CH₄ oxidation for Biocover materials

 CH_4 was completely oxidized by day 4 and day 7 for compost and black soil respectively (Figure 4.1) and no CH_4 was detected in all the Wheaton bottles thereafter. The slow rate in CH_4 oxidation was obviously due to lack of O_2 (substrate in CH_4 oxidation activity). The increase in percentage of CO_2 correlates to the theoretical aspect of CH_4 oxidation. The same condition (absence of CH_4) prevailed till day 15. CO_2 however increased even after the completion of CH_4 with simultaneous decrease of O_2 . Perdikea et al. (2008) and Charlotte & Kjeldsen (2000) also obtained similar results. In both their experiments, increase of CO_2 and decrease of O_2 was observed after complete CH_4 oxidation in the Wheaton bottles. The possible reason for this phenomenon could be due to the decomposition of organic matter by other groups of microbes present in the Biocover materials. Biocover materials used in this study were rich in organic matter which was able to facilitate the growth of other microbes such as fungi and bacteria (Wilshusen et al., 2004) besides methanotrophs. Methanotrophs are obligate aerobes; they are able to conduct CH_4 oxidation even at low O_2 concentration (Pawloski & Pawloska, 2008). This explains why although the condition in Wheaton bottles containing compost and black soil was anaerobic by the end of day 2 and 6, but CH_4 reduction still occurred but at a slower rate. This could be due to the unique adaptation of methanotrophs to anaerobic conditions.

Lag phases were never observed in this study indicating that the microbes were well adapted to oxidizing CH₄. Charlotte and Kjeldsen (2004) who conducted batch incubation trials using landfill soil from Denmark also did not observe any lag phase in their experiment. In contrast, Perdikea et al. (2007) observed a lag phase of approximately 2.5 days in batch incubation conducted using garden waste. This could probably due to low incubation temperature (22°C) which provided less suitable condition for methanotrops growth, thus increasing the acclimatization period and significantly contributing to longer lag phase. Oxygen gas was utilized to oxidize methane to carbon dioxide and the presence of water droplets on the inner surface of the Wheaton bottle indicated that water was a byproduct of methane oxidation.

4.3 Wheaton bottle experiments using compost and black soil

The experiments were conducted for 15 days in a continuous batch operation in triplicates and samples were incubated at various parameters including temperature, moisture content and pH to determine the most optimum parameters for methane oxidation.

4.3.1 Parameter: Temperature

The results for experiments using different temperature is indicated in Figure 4.3 and 4.4. Temperature is an essential parameter in determining the efficiency of methanotrophic activity.

The results obtained in this experiment showed that the Biocovers favoured optimal temperature of 35°C. At 35°C, the Biocover materials exhibited the fastest methane oxidation where garden waste compost took 5 days meanwhile black soil required 6 days for complete methane oxidation. For compost, at 20°C it took 11 days for complete methane exidation meanwhile for black soil it took 13 days. At 30°C, there was not great difference seen as compost took 8 days and blacksoil took only 9 days. Both took 9 days for complete methane oxidation at 40°C. A further increase in temperature to 40°C resulted in a steep decline in oxidation rates.

The active temperature for methanogenic microorganisms is in the range 30-50°C. The temperature for mesophilic bacteria in the range 30-35°C, while 45-65°C for thermophilic bacteria (Williams, 2005). The optimum temperature range of gas generation during the main landfill gas generation phase was between 30-45°C (Williams, 2005). The change of temperature will have an impact on the growth of biomass and the activity of the micro-organisms (Naranjo et al., 2004).

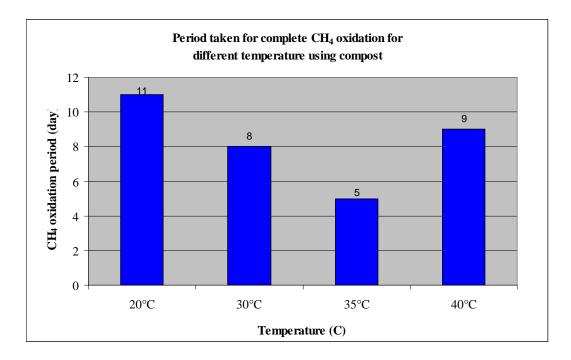
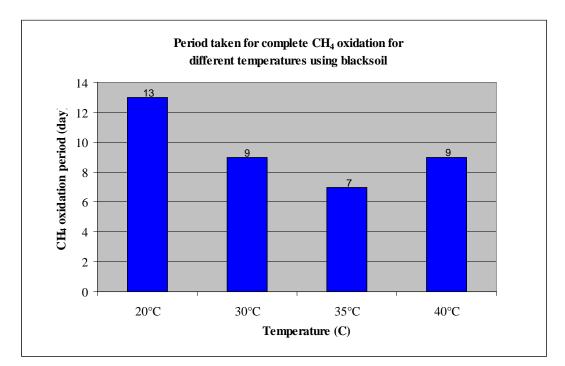


Figure 4.3 : Period taken for complete CH₄ oxidation for different temperatures



using compost

Figure 4.4: Period taken for complete CH₄ oxidation for different temperatures

using black soil

Investigations carried out by Whalen et al. (1990) on a sandy clay soil from landfill cover surface layer, within the temperature range of 5-46°C, indicate that the optimum temperature was 31°C. Temperatures lower than that value bring about a smooth decline of methanotrophic activity, where an increase of the temperature up to the values exceeding the optimum causes a rapid drop in the activity to almost zero at 46°C. This is related to denaturation processes of proteins contained in methanotrophic cells. A similar value of the temperature optimum was observed within the range of 25°C-30°C taken from a landfill cover soil and prevalent with sand fraction also taken from a landfill cover (Boeckx and Van Cleemput, 1994: Boeckx and Van Cleemput, 1996). A little lower optimum value of 23°C has been obtained for Alaskan waterlogged soils (Whalen and Reeburgh, 1996).

Results of Boeckx et al (1996), investigations performed on a sandy-clay soil of a landfill cover indicate that the temperature optimum value varies depending on the moisture content of the soil material. Within the moistness range of 10-30% of weight, the temperature optimum decrease along with the increasing moisture content from 27.1°C at the lowest moistness level to 20.1°C at the upper limit of the range. Increase in the moisture content results in a reducing effect on the gas transport to the bacteria cell (Boeckx, 1996). This can eventually lead to a situation in which the substrate supply is smaller than the oxidizing capacity of microorganisms at a given temperature. Thus, at higher moisture content, the CH₄ transport becomes a limiting factor for the oxidation process. When the moisture content is low, the limiting factor is the activity of microorganisms (Boeckx, 1996).

In this study, although the moisture content of the Biocover materials varied, the optimum temperature for methane oxidation was the same (35°C). One of the possible reasons is the high degree of adaptation of methanotrophs in Biocover materials in tropical conditions. A better understanding of the optimal temperature conditions for oxidation

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would improve predictions of oxidation rates and would also help in the identification of better landfill covers

4.3.2 Parameter: Moisture Content

The results for experiments using different moisture content % is indicated in Figure 4.5 and 4.6.

The optimal moisture content from the experiment was 60%, where garden waste compost was the fastest and it took only 4 days, compared to blacksoil where it almost doubled bringing it to 7 days for complete methane oxidationThe results shows that at 30% MC, both biocovers used took 11 days for complete methane oxidation. Meanwhile at 40% MC , there was not much difference as compost took 8 days and blacksoil took 9 days. Same goes to 50% MC as compost took 7 days and blacksoil took 8 days. For compost at 70% MC, it took 6 days for complete methane oxidation meanwhile blacksoil took 10 days.

The moisture content (MC) of the substrate influenced methane oxidation in many ways. Moisture is an essential factor for microorganisms to sustain their activity as it is the transport medium for nutrient supply and also for removal of residual metabolic compounds (Cabral et al., 2004). A high moisture content (MC) in the sample would lead to decreasead air porosity, which would impact the CH₄ capacity (Perdikea et al., 2007). In this study, the Biocover material had the highest CH₄ oxidation efficiency at moisture level of 60%. At higher moisture level (70%), the CH₄ oxidation efficiency reduced. The observation obtained in this exepriment agree well with the findings of Das and Keener (1997) that the free air spaces in compost becomes limiting at MC> 60% w/w. A strong dependence of methanotrophic capacity on the water content in soil has been experimentally confirmed (Pawloska, 2008). Moisture content is the most important parameters affecting CH₄ oxidation in landfill cover soil.

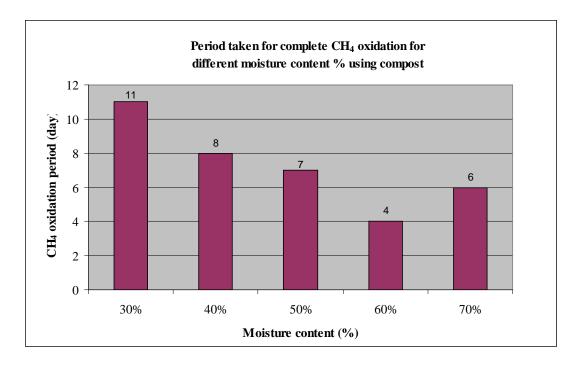
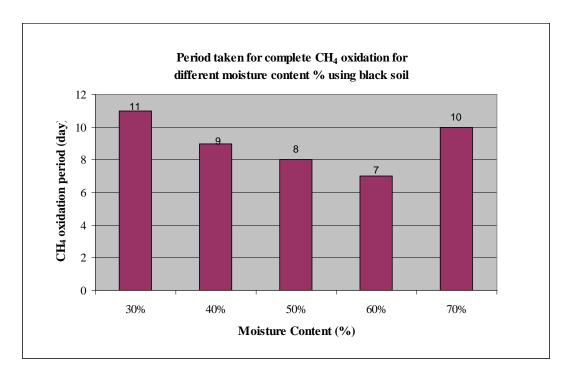
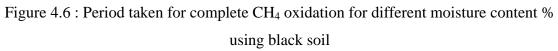


Figure 4.5 : Period taken for complete CH_4 oxidation for different moisture content % using compost





Moss, (1997) reported that the range for moisture content in a typical landfill cover soil is 15 to 40% with a typical average 30% (Williams, 2005). Some studies have indicated that refuse samples containing greater than 55% (wt/wt) moisture content produced increased amounts of CH_4 while those that contained less than 33% moisture content did not produce any CH_4 (Gurijala et al., 1997). The rate of gas generation increased with the increment of moisture in landfill site (Naranjo et al., 2004; Williams, 2005; Sormunen et al., 2008). The water content in landfill sites assists to exchange substrate, nutrients, buffer, and dilution of inhibitors and spreading of microorganisms (Cernuschi and Giugliano, 1996; and Tecle et al., 2008).

The moisture strongly affects the capacity for CH_4 consumption by determining the extent of CH_4 diffusion between the soil gas phase and the atmosphere (Schnell and King, 1995). Moisture contents reported to be optimum for CH_4 uptake in landfill cover soils range from 10–20% (Whalen *et al.*, 1990; Boeckx and VanCleemput, 1996; Czepiel *et al.*, 1996). Jones and Nedwell (1993) speculated that the capacity of cover soil to sustain substantial moisture content throughout its depth is likely to promote more uniform methanotroph distribution and greater opportunity for CH_4 removal throughout the cover depth.

Gas permeability decreased with increasing water content (Humer and Lechner, 2000). At moisture content below 13% of the maximum water capacity, methanotrophic microorganisms tend to become inactive (Bender, 1992). Tests carried out by Figueroa (1993) on different landfill cover materials showed that optimum conditions for methane oxidation are found in areas with a relatively high moisture content. The highest methane turnover rate could be achieved under the same ambient conditions in biowaste composts with moisture content of approx 40-80% of the maximum water-holding capacity.

Boeckx et al.(1996) indicated that water content widely regulates the activity of methanotrophic bacteria. They found that the optimum moisture content is situated at about 50% of the water capacity. In laboratory tests carried out by Humer and Lechner (2001), the activity of the methanotrophic bacteria was strongly inhibited at a moisture content of 20% w/w in compost (corresponding to <15% of maximum water capacity). The high water holding capacity of organic-rich composts is beneficial in arid climates to preserve moisture for the microbes, although under wet conditions, a high moisture content can reduce gas transport and hinder methane uptake while in extreme cases it can even produce CH_4 (Barlaz et al.,2004).

In contrast, Scheutz and Kjeldsen (2004), found that an increase in soil moisture from 30% w/w resulted in reduced methane oxidation rate by using soil samples collected from landfill in Denmark. Based on their findings, the range of soil moisture for optimum methane oxidation was between 18 and 34% w/w. The differences in the results could be due to the climate dissimilarity in Malaysia (tropical) and Denmark (four-seasons).

The optimal soil moisture content for CH_4 oxidation in a loamy sand has been shown to be 13% by weight (Park et al.,2002) while for meadow cambisol ranged from 15 to 22% (Bender & Conrad, 1995). Lessard et al., (1994) who conducted tests on forest soil of temperate climate zone found a negative correlation between CH_4 uptake rate and the moisture content in soil within the range of 30-50% v/v. The above results are similar with the observation of Whalen & Reeburgh (1996), who have also indicated a decrease in methanotrophic activity within the mentioned range of moisture contents in soils that are not exposed to permanent flooding.

4.3.3 Parameter: pH

The results for experiments using different pH value is indicated in Figures 4.7 and 4.8

The results obtained shows that the optimal pH is 6 for both biocovers, where garden waste compost took 5 days meanwhile black soil took 8 days for complete methane oxidation. As the biocover become more acidic (pH 4), the process for methane oxidation is longer as shown by compost which took 11 days and for black soil it was 13 days. At pH 5, compost took 9 days, meanwhile black soil took 10 days. At pH 7, compost took 8 days meanwhile at pH 8 it took 10 days for complete methane oxidation. As for black soil, at pH 7 it took 11 days, and at pH 8 it took 13 days for complete methane oxidation.

According to McBean et al (1995), suitable top cover to encourage vegetation growth should have a pH in the range of 5 to 8. If the pH is over 8, necessary elements for plant growth may not be soluble. A pH of less than 5 may cause some elements to become toxic. In general, soil pH should be above 6. The methanogenic bacteria operate efficiently only within a narrow pH-range of 6-8 (Zehnder et al.,1982). The optimum pH values for methanotrophic growth and CH₄ oxidation in soils generally lie between 5.5 and 8.5 (Dunfield et al., 1993; Hütsch et al., 1994; Bender & Conrad 1995; Scheutz & Kjeldsen 2004) and are generally consistent with those of pure cultures of methanotrophs which are between pH 6.6 and 6.8 (Whittenbury et al., 1970; Hanson & Hanson, 1996).

The optimal pH for the growth of methanotrophic bacteria isolated from dune sands located in vicinity of natural gas leakage was 7.0, although their growth was also observed in the pH range 5.5-8.0 (Adamse et al., 1972). Arif et al. (1996) have noted a slightly narrower pH range (5.9-7.7) in agriculturally used sandy soils. The optimum pH in an acid forest luvisol was 6.3 (Bender and Conrad, 1995), while in bog soils the most intensive oxidation occurred at pH 6-8 (King, 1990).

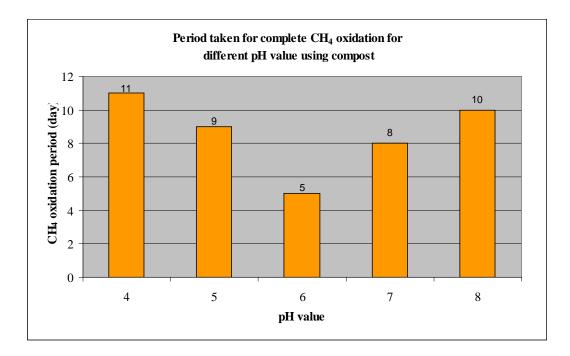


Figure 4.7 : Period taken for complete CH₄ oxidation for different pH value using compost

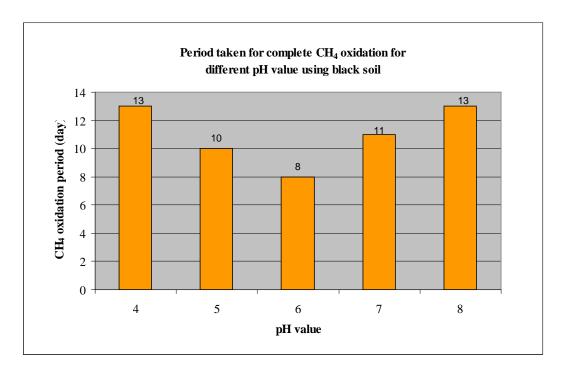


Figure 4.8 : Period taken for complete CH_4 oxidation for different pH value using black soil

The pH range for the fermentative and acetogenic bacteria is much wider than for the methanogenic bacteria. If methanogens are stressed by other factors, their conversion of hydrogen and acetic acids decreases, leading to an accumulation of volatile organic acids and a decrease in pH (Pawloska, 2008). This will furthermore inhibit the methane formation and lead to further decrease in pH. Eventually, the methane generation may stop. Rozej and Stepniewski (2008) used sand as the material for CH₄ oxidation in column experiment and observed a strong increase in methanotrophic activity when the pH of the material declined below 8.0. Pawloska (1999) did not observe any significant change in the methane oxidation rate in the pH range 7.61-8.89, although Hilger et al.(2008b) found that increasing soil pH will increase the intensity of CH₄ oxidation. The CH₄ oxidation process occurs within a comparatively wide pH range from pH <4 in sandy (Hoeks, 1972) and bog soils (Powlson et al., 1997) up to >9 in bog soils (King, 1990).

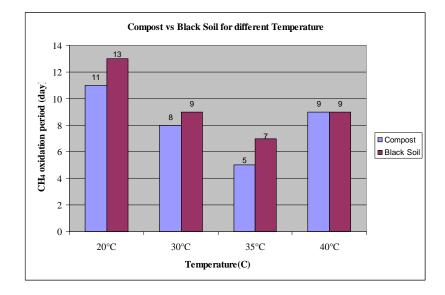
Methanotrophic bacteria are treated as neutrophiles lacking in any clear adaptations to extreme conditions. The highest CH₄ oxidation rate is usually observed at pH values of 6-7 (Hutsch, 1994; Dunfield et al., 1993). The optimal pH for the methanogenic bacteria is in the range of 6.7 to 7.5. However, there is still some activity with pH in the range of 5.0 to 9.0. pH (Hilger et al., 2000). Recently, some authors have observed methanotrophic activity in highly alkaline environments (at pH 10-11) (Khmelenina et al., 1997; Sorokin et al., 2000; Kaluzhnaya et al., 2001), but acidophilic methanotrophs have also been found (Dedysh et al., 2004; Trotsenko & Khmelenina, 2005) confirming the significant adaptive capacity of some methanotrophs.

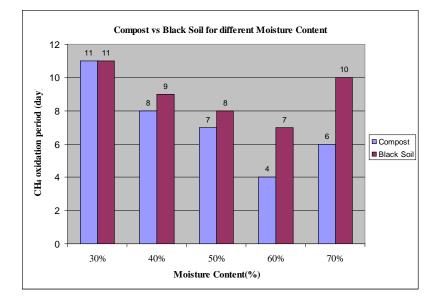
4.4 Compost Vs Black soil

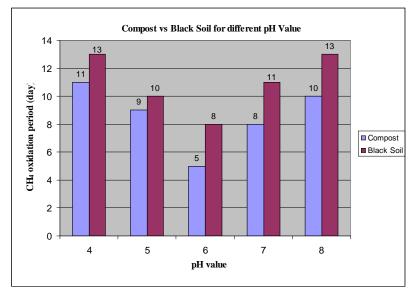
Figure 4.9 shows the comparison of CH_4 oxidation for compost and black soil using different parameters used in this study. It clearly shows that for all parameters, garden waste compost has shown very fast reaction in oxidizing methane.

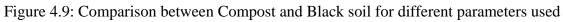
Compost from sewage sludge has proved capable of providing suitable chemical and physical properties for methane oxidising micro-organisms (Humer and Lechner, 1999, 2001b). The most beneficial feature of compost is the high content of organic matter, providing numerous favourable conditions for micro-organisms, such as a high specific surface area, a high water retention capacity combined with adequate porosity and suitable texture for gas exchange (meaning a high air-filled pore volume even at higher moisture contents), low thermal conductivity and, consequently, good temperature insulation effect (Humer and Lechner, 1999, 2001b). However, when applied for methane oxidation purposes, organic matter in the compost must be stable and mature.

Methane turnover rates in mature composts are clearly higher than in humic-poor soils and the cohesive, mineral clay soils usually used for landfill covers, while fresh and finely sieved composts may exert an opposite effect due to oxygen limitation and competition by respiration of the compost material followed by formation of exopolymeric substances (Humer and Lechner, 1999; Huber-Humer, 2004; Wilshusen et al., 2004b). Moreover, compost materials which are not fully mature and well textured may produce methane rather than oxidise it under unfavourable water-saturated, anaerobic conditions, as observed in field investigations with biocovers made of one meter yard waste compost by means of isotopic evidence (Barlaz et al., 2004).









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Methane oxidation is dependent upon a number of determining factors, such as the water content, temperature, soil conditions and nutrient compounds. Oxidation rates of CH_4 differ within and between landfill sites due to seasonal climate changes, physical heterogeneities in the soil cover and CH_4 concentrations (Whalen and Reeburgh, 1996; Bogner et al. 1997; Borjesson et al. 1994). The rate at which CH_4 is biologically oxidized depends on several factors such as moisture content, temperature, soil characteristics and composition, pH, nutrients and oxygen concentrations (Wilshusen et al. 2004a).

Methane oxidation rates in conventional soils have been studied extensively, but there are fewer studies on environmental factors influencing the rate of CH₄ oxidation in compost. Streese and Stegmann (2003) studied compost from a mixture of an equal volume of yard waste, peat and squeezed spruce wood fibre as biofilter material for microbial CH₄ degradation and reported high degradation rates of up to 63 g CH₄ m⁻³ h⁻¹. Wilshusen et al. (2004a,b) studied CH₄ oxidation and formation of exopolymeric substances in compost from a) MSW compost and b) compost (leaves, garden, wood chips) for the performance of CH₄ biofilters and the effect of oxygen concentration. Humer and Lechner (1999, 2001) studied municipal solid waste compost and sewage sludge compost as cover soil to increase oxidation of CH₄ and found that complete CH₄ oxidation is possible. Barlaz et al. (2004) reported that compost covers oxidized more CH₄ than conventional clay covers in field trials, but warned that compost covers can also produce CH₄ if the moisture content is too high.

In addition to that, Figure 4.10 summarizes the comparison of CH_4 oxidation for optimum parameter used for garden waste compost and black soil. It clearly shows that compost took shorter period for complete CH_4 oxidation compared to black soil.

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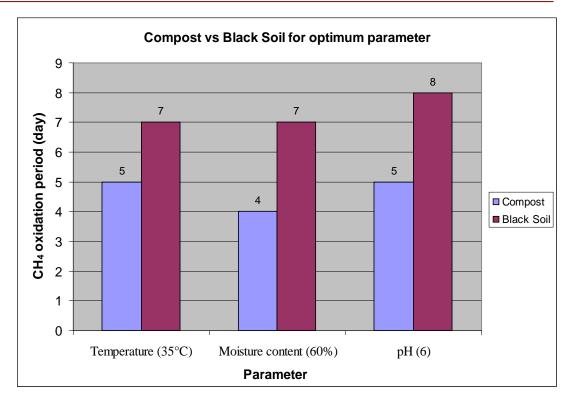


Figure 4.10: Optimum Parameter for Compost and Black soil

At 35°C, compost took 5 days for complete CH_4 oxidation meanwhile black soil took 7 days. Investigations carried out by Whalen et al. (1990) on a sandy clay soil of the landfill cover surface layer, within the temperature range of 5-46°C, indicate that there is a temperature optimum of 31°C. The active temperature for methanogenic microorganisms is in the range 30-50°C. The temperature for mesophilic bacteria in the range 30-35 °C, while 45-65 °C for the thermophilic bacteria (Williams, 2005).

At 60% moisture content, black soil also took 7 days upon completion but compost took almost half of what black soil obtained (4 days).

At pH 6, compost took 5 days meanwhile black soil took a longer time (8 days) for complete CH₄ oxidation.

4.5 Biocover Performance Index (BPI)

Table 4.2 summarized the Biocover Performance Index (BPI) value for Wheaton bottle experiment. It clearly shows that garden waste compost scored the highest BPI value, which proved its efficiency in CH_4 oxidation. Meanwhile black soil only scored almost half of the BPI that was obtained by compost.

Table 4.2: Biocover Performance Index (BPI) for Biocover from batch incubation

Biocover Material	Biocover Performance Index (µgg ⁻¹ h ⁻¹)
Garden Waste Compost	2.08×10^{-3}
Black Soil	1.19 × 10 ⁻³

The performance of the Biocover was expressed in terms of Biocover Performance Index (BPI). Derivation of the performance parameters are detailed below:

 $BPI = (CH_4)_0 - (CH_4)_n$ $W \ge N$

where

 $(CH_4)_0 =$ Initial concentration of CH_4 (mL)

 $(CH_4)_n$ = concentration of CH_4 at time n (mL)

W = amount of Biocover(g)

N= time taken for complete methane oxidation (hours)

BPI for Compost

$$BPI = (CH_4)_0 - (CH_4)_n$$

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BPI for Black Soil

$$BPI = (CH_4)_0 - (CH_4)_n$$

$$W \ge N$$

$$= \frac{(4) - (0)}{(20g) \times (168 \text{ hours})}$$

= $\frac{4}{3360}$
= **1.19 × 10⁻³**

4.6 Kinetic Modelling

Michaelis-Menten equation (modified) was used to evaluate the kinetic for garden waste compost and black soil.

$$R_{p} = R_{max} \underline{1} \qquad (Equation 1)$$

$$1 - (K_{M}/C)$$

where

 R_p = potential methane oxidation rate (mL / d)

 R_{max} = maximum methane oxidation rate (mL/ d)

K_m= Half- saturation reaction rate (mL/d)

 $C = initial CH_4$ concentration (%)

Since C is a constant (4% v/v) for all batch incubation and column experiments, C was eliminated from Equation 2 to modify the kinetics, where R_p is now described as follows :

$$R_p = R_{max}$$
 _1 (Equation 2)

$$1 - (K_M)$$

Volume of CH₄, S (% v/v) was plotted against time (day). R_{max} and K_m was obtained from the graph plotted. Figure 4.11 and 4.12 shows the graph for compost and black soil. From the Wheaton bottle experiments (batch incubation), compost scored highest potential rate ($R_p = 17.036$) which was almost two times higher than for black soil ($R_p = 10.806$). The value for R_{max} , K_m and R_p for compost and black soil is summarized in Table 4.3.

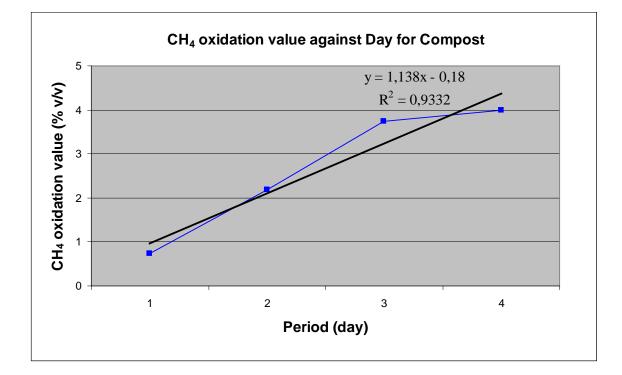


Figure 4.11: CH₄ oxidation value for compost

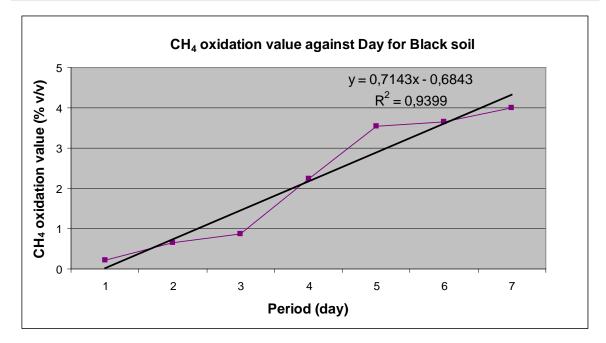


Figure 4.12: CH₄ oxidation value for black soil

Table 4.3: The kinetic constant of the kinetic model used for Wheaton bottle experiments

Material	R _{max}	K _m	R _p
Compost	1.138	0.9332	17.036
Black soil	0.7143	0.9339	10.806

 R_p = potential methane oxidation rate (mL / d)

 R_{max} = maximum methane oxidation rate (mL/ d)

K_m= Half- saturation reaction rate (mL/d)

From the results obtained, it clearly shows that compost definitely was a better Biocover in relation to CH_4 oxidizing capacity. Even though K_m value for both media was not much different, but the R_{max} value showed that compost had twice the value than black soil, which explains why the R_p value for compost was also almost double that for black soil. The V_{max} obtained in the experiment conducted by Pawloska and Stepniewski (2006) using coarse sand with continuous flow of CH₄ ranging from 1.0-16.0 % (v/v) was in the range of 0.11 x 10⁻³ to 0.86x10⁻³ units. R_{max} value obtained in this study was 0.7143 – 1.138 which is much higher than values obtained by the authors. The vast difference in the R_{max} value could be due to variation in experimental methods. The authors mentioned above used continuous flow of CH₄ in their experiments compared to on-off injection (static flow) of CH₄ in this study. Continuous flow of CH₄ can cause high saturation of the gas in the columns thus impeding CH₄ oxidation tremendously. Another possible reason for high kinetics value obtained in this study could be the suitability of tropical climate in facilitating microbial growth for optimum CH₄ oxidation.

Figueroa (1993), who studied biowaste compost under laboratory conditions comparable to those of the present study, and obtained a maximum potential oxidation rate of $128\mu g \ CH_4h^{-1}gdw^{-1}$. De Visscher et al. (1999) obtained a potential activity of $26\mu g \ CH_4h^{-1} \ gdw^{-1}$ for a sandy loam cover soil; Scheutz and Kjeldsen (2004) obtained 118µg $CH_4h^{-1} \ gdw^{-1}$ for a loam soil; and Börjesson and Svensson (1997) obtained 173µg CH_4h^{-1} g dw⁻¹ for a silty loam soil.

Dubey (2003) reported values of V_{max} in the range of 105-615 µmoles CH₄d⁻¹kg⁻¹ dry soil weight, and Horz et al. (2002) reported V_{max} values in the range from 21 to 88 µmoles CH₄d⁻¹kg⁻¹ dry soil weight. In the study conducted by Dubey (2003) to determine the biological kinetics constants, chemical fertilizers in the form of NH₄Cl, NH₄NO₃, and urea were applied to the tested soil that contained 43% moisture content. Horz et al. (2002) performed their field study using non-grazed, managed (fertilized with 50-80 kg N Ha⁻¹ year⁻¹) meadow.

De Visscher et al. (2001) have reported a V_{max} value of 0.820µmol kg_{dw}⁻¹ s⁻¹ in soil on day 34 after the start of an incubation experiment, while Whalen et al. (1990) have reported a

 V_{max} value of 0.039 µmol kg_{dw}⁻¹ s⁻¹ in soil samples that were taken from a landfill. Streese and Stegmann (2003) observed a V_{max} value of 2.43µmol kg_{dw}⁻¹ s⁻¹ in compost, which was a mixture of an equal volume of yard waste, peat and squeezed spruce wood fibre. Wilshusen et al. (2004a) observed a V_{max} value of 3.77µmol kg_{dw}⁻¹s⁻¹ after one month and 2.77µmol kg_{dw}⁻¹s⁻¹ after two months in compost, which was prepared from municipal green waste such as leaves mixed with manure. Values of V_{max} are not easy to interpret mechanistically because they are the result of both the number of micro-organisms in the medium and their activity (Bender and Conrad, 1992; Dunfield and Conrad, 2000)

4.7 General Discussion

From the study conducted the results over all shows that compost from garden waste was more effective than black soil in oxidizing methane. Compost has a higher moisture content (61.7%) compared to black soil (43%). Moisture is an important physical factor that indirectly influences gas diffusion by changing the porosity of the medium and directly affects the development. Wilshusen et al. (2004), Barlaz et al. (2004), Hilger and Humer, (2003) have indicated that compost is known to offer a higher CH₄ oxidation capacity due to its higher organic matter, water holding capacity, and porosity. According to Pawloska (2008), CH₄ oxidation becomes limited if there is lack of water as it causes a physiological stress to methanotrophs. Best CH₄ oxidation performance of compost could also be explained by its high percentage of organic matter (52%) compared to black soil (42%).

Both field observations at landfills and results from laboratory studies have demonstrated that organic cover soils have a high capacity to mitigate CH_4 emissions (Borjesson et al., 1998b; Humer and Lechner, 2001). Previous studies have shown that microbial CH_4 oxidation in landfill cover soil can be enhanced when using substrates that are rich in organic matter, such as compost, rather than pure clay covers (Abichou et al.,

2006; Stern et al., 2007). According to Chanton and Liplay (2000), methane oxidation is higher in organic-rich soils. Slightly acidic property of compost (6.35) allows methanogenic bacteria to operate efficiently (Moldes et al., 2007). Compost has a higher C/N ratio with 16.9 due to high cellulose in the garden waste. The final C:N ratio of the compost also indicates that it was a mature substrate. According to previous laboratory tests by Boeckx et.al (1996), a high maturity of compost materials is crucial for efficient CH_4 consumption. The C/N ratio obtained by Suman et al. (2001) for the garden waste compost was in the range of 11.2 to 26.9.

Compost has proved capable of providing suitable chemical and physical properties for methane oxidising micro-organisms (Humer and Lechner, 1999, 2001b). The most beneficial feature of compost is the high content of organic matter, providing favourable conditions for micro-organisms, such as a high specific surface area, a high water retention capacity combined with adequate porosity and suitable texture for gas exchange (meaning a high air-filled pore volume even at higher moisture contents), low thermal conductivity and, consequently, good temperature insulation effect (Humer and Lechner, 1999, 2001b). However, when applied for methane oxidation purposes, organic matter in the compost must be stable and mature. Methane turnover rates in mature composts are clearly higher than in humic-poor soils and the cohesive, mineral clay soils usually used for landfill covers, while fresh and finely sieved composts may exert an opposite effect due to oxygen limitation and competition by respiration of the compost material followed by formation of exopolymeric substances (Humer and Lechner, 1999; Huber-Humer, 2004; Wilshusen et al., 2004b). Moreover, compost materials which are not fully mature and well textured may produce methane rather than oxidise it under unfavourable water-saturated, anaerobic conditions, as observed in field investigations with biocovers made of one meter yard waste compost by means of isotopic evidence (Barlaz et al., 2004).

Biocover Performance Index (BPI) value for Wheaton bottle experiment revealed that compost scored the highest BPI value ($2.08 \times 10^{-3} \mu gg^{-1}h^{-1}$), which proved it efficiency in CH₄ oxidation. Meanwhile black soil only scored almost half ($1.19 \times 10^{-3} \mu gg^{-1}h^{-1}$) of the BPI that was obtained by compost.

Similar to BPI, kinetics also revealed compost as the best Biocover material for CH₄ oxidation. The V_{max} obtained in the experiment conducted by Pawloska and Stepniewski (2006) using coarse sand with continuous flow of CH₄ ranging from 1.0-16.0 % (v/v) was in the range of 0.11 x 10⁻³ to 0.86x10⁻³ units. R_{max} value obtained in this study was 0.7143 – 1.138 was much higher than values obtained by the authors. The vast difference in the R_{max} value could be due to variation in experimental methods. The authors mentioned above used continuous flow of CH₄ in their experiments compared to on-off injection (static flow) of CH₄ in this study. Continuous flow of CH₄ can cause high saturation of the gas in the columns thus impeding CH₄ oxidation tremendously. Another possible reason for high kinetics value obtained in this study could be the suitability of tropical climate in facilitating microbial growth for optimum CH₄ oxidation.

CHAPTER 5: CONCLUSION

From the study conducted, garden waste compost was identified as the best Biocover compared to black soil. Compost only took four days for complete methane oxidation, meanwhile black soil took seven days. Compost had a higher moisture content (61.7%) and organic matter (52%) compared to black soil (43%) and (40%), which explains why compost is more effective in methane oxidation. Compost took the shortest acclimatization period (one day) compared to black soil (four days). Compost had the fastest speed of CH_4 oxidation with a slope gradient of 27.55 compared to black soil's slope gradient of 16.52. Slope gradient for compost was 1.67 times higher than black soil.

The optimum parameter identified for compost and black soil was at 35° C, with 60% moisture content and pH value of 6. A strong dependence of methanotrophic capacity on the water content in soil has been experimentally confirmed. Moisture content is the most important parameter affecting CH₄ oxidation in landfill cover soil. A pH of less than 5 may cause some elements to become toxic. In general, soil pH should be above 6. The methanogenic bacteria operate efficiently only within a narrow pH range of 6-8.

BPI obtained for garden waste compost $(2.08 \times 10^{-3} \mu gg^{-1}h^{-1})$ was higher than for black soil $(1.19 \times 10^{-3} \mu gg^{-1}h^{-1})$.

Meanwhile the R_p (potential oxidation rate) value for compost (17.036 mL/d) also almost doubled the value of black soil (10.806 mL/d). This clearly indicates that compost was the most effective and suitable Biocover for methane oxidation under tropical conditions.

The summary for the result obtained from this study is indicated in Table 5.1

	Biocover Material		
Properties studied	Compost	Black soil	
Complete methane oxidation (for batch experiments) Temperature: 35°C Moisture content: 60%	Day 4	Day 7	
Temperature : Optimum at 35°C	Day 5	Day 7	
Moisture content: Optimum at 60%	Day 4	Day 7	
pH: Optimum at pH 6	Day 5	Day 8	
BPI value	$2.08 \times 10^{-3} \mu gg^{-1}h^{-1}$	$1.19 \times 10^{-3} \mu gg^{-1}h^{-1}$	
Rmax	1.138mL/d	0.7143mL/d	
Rp	17.036mL/d	10.806mL/d	

Table 5.1: Summary of results obtained in this study

This clearly indicates that compost from garden waste was the most effective and suitable Biocover compared to black soil for methane oxidation under tropical conditions. This study therefore supports the hypothesis / theory that the biocover will decrease the methane production rate.