BIOREMEDIATION OF LANDFILL GAS UNDER LABORATORY CONDITIONS

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ABSTRACT
Per capita generation of municipal solid waste (MSW) in Malaysia has reached 1.3kg per day giving a total generation of more than 31000 tonnes daily. All the MSW collected are disposed into 260 landfills or dumps with 90% of the landfills being non-sanitary. Due to lack of proper gas collection facilities, almost all the methane produced are released passively to the atmosphere. Malaysian landfills produce 1.3-7.5 L/kg/year of methane gas. Since methane is 23 times more harmful as greenhouse gas than CO$_2$, it is essential to mitigate its emission from landfills. One option to reduce methane emissions is to oxidize the methane to CO$_2$ and water using “Biocover”. The objective of this study is to investigate various Biocover materials such as compost, for methane oxidation capabilities under tropical conditions and to establish suitable Biocover height for landfill application. Batch incubation experiments using Wheaton bottles revealed that compost was the best (Biocover) material compared to black soil and compost residue. It took the shortest duration (4 days) for complete methane oxidation. Subsequently 1-m high reactor columns were used to evaluate methane oxidation using compost and black soil. Fresh Biocover material and mixture of used + fresh Biocover material ranging from 10-100cm in height was tested for methane reduction. Column height of 60cm compost and 80 cm black soil took the shortest time for CH$_4$ oxidation indicating optimum Biocover height. Column trials with mixture of 90cm used+10cm fresh Biocover materials exhibited highest CH$_4$ oxidation capacity for both compost and black soil. The Biocover Performance Index (BPI) ranged from 1.04-2.60 x 10³, where the latter value was for compost. Kinetics of methane oxidation and statistical analysis were performed to determine the efficiency of biocover material. CH$_4$ oxidation rate for compost was 3 times and 9 times higher compared to black soil and compost residue, respectively. It is evident that the use of compost as biocover could reduce methane emission
from landfills; however, field conditions would also influence the rate of oxidation.
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Chapter 1: INTRODUCTION

1.1 MSW Generation

Waste is discards that has no value. Generation of waste is inevitable in our daily lives. The amount of waste generated by the human population is constantly growing, especially in developing countries. According to the Organization for Economic Cooperation and Development (OECD, 2004), the greatest amount of municipal waste is generated in the most developed countries. This could be due to high socio-economic affluence and costly lifestyle by the people in these countries. In Malaysia, due to rapid increase in population size and urbanization, waste generation increases at 3% annually (Agamuthu, 2001). In 2008, Malaysians generated approximately 10 million tonnes of solid waste which were disposed off to 260 landfills throughout the country (Agamuthu, 2009). The per capita generation of municipal solid waste (MSW) in Malaysia has reached 1.3kg per day giving a total generation of more than 31000 tonnes daily. This figure indicates an alarming rise of more than 100% compared to only 15 000 tonnes daily in 1997 (Agamuthu, 2001). These wastes have to be managed properly to minimize its negative impacts to the environment and to public’s health. The management of municipal waste is one of the major problems of modern civilization due to the complexity of waste. Despite recent advances in technology of waste management, there is still a great need for environmentally-friendly management systems.

1.2 Landfilling

The oldest and most popular method of disposal of municipal waste is landfilling. The oldest landfill was opened in Athens about 500 B.C., and since that time the number of landfills has been growing steadily. However, a recent decrease in the number of new landfills, especially in developed countries, has been observed. The number of landfills in the
United States decreased from 8000 in 1998 to 1654 in 2005 (CSO, 2002-2006). In Poland, landfill surface area increased about 5.6% between 2001 and 2004 (from 3207 to 3385 ha) but fell to 3359.5 ha by 2005 (CSO, 2002-2006). Such trends reflect changes in waste management systems. In many countries, including Mexico, Poland, New Zealand, Greece, Italy, and Hungary, about 90% of waste is deposited in landfills. But in other countries, this type of waste management is not popular, mainly due to the long-term negative impacts of landfills on the environment. In Japan, Switzerland and Denmark, for example, only 11%, 13% and 17% of municipal solid waste, respectively, is disposed of in landfills (OECD, 2004). In contrast, the number of landfills in Malaysia is increasing to accommodate the current high waste generation. All the MSW collected are disposed into 260 landfills or dumps as other waste management methods such as incineration or composting are not widely practised in Malaysia. The landfills or dumps, most being non-sanitary pose perilous hazard to the environment. Landfill gas (LFG) and leachate generation are some of the major issues in Malaysian landfills.

1.3 Landfill Gas

Landfill gas (LFG) is produced in the waste layer due to anaerobic decomposition of waste. The quantity and quality of LFG is governed by many factors such as the type of waste landfilled and its composition. The LFG primarily contains CH\textsubscript{4} (usually between 50% and 60% by volume) and CO\textsubscript{2} (35%), volatile organic compounds (VOCs) which is less than 1%, small amounts of N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2} trace amounts of inorganic compounds (Kettunen et al., 2003). LFG is produced for about 10-15 years (methanogenic phase) after which methane emissions gradually decrease for years; however the actual trend in LFG emissions depends on the duration of the lifespan of landfill.

1.4 Global Warming
Landfills pose major threats to the environment if improperly managed. Decomposition of the biodegradable fraction of wastes deposited in a landfill make a significant source of methane emission to the atmosphere. Landfill gas (LFG) and leachate production are the major issues in Malaysian landfills. Of all the gases produced in landfill, CH₄ pose very serious threat to the environment as it contributes largely to global warming. The role of CH₄ on the green-house effect has been known since the 1940’s, when Migeotte had found strong absorption band in the infra-red region of the solar spectrum attributed to the presence of CH₄ (Pawloska, 2008). Methane absorbs infrared radiation 23 times more efficiently than CO₂, over a 100-year time period, and is 62 times more active than CO₂ on a 20-year time scale (IPCC, 2007). It absorbs long wave radiation emitted from the Earth’s surface in the 4-100µm atmospheric window (Whalen et al.,1996).

Almost 90 % of Malaysian landfills are not equipped with any engineering waste containment system, (e.g. compacted clay liner, geomembrane or geosynthetic clay liners). In average, Malaysian landfills produced about 1.3-7.5 L/kg/year of methane gas (Agamuthu, 2009). Malaysia’s total GHG emissions were equivalent to 1.5×10¹¹ CDE in 2004 (Agamuthu, 2009). Waste treatment or waste disposal operations have been estimated to contribute at least 50% of methane (CH₄), <1% of carbon dioxide (CO₂) and negligible amounts of nitrous oxide (N₂O) emissions. Malaysia’s CH₄ emission in 1994, 4.6×10⁹ CDE, was 32% of total GHG emissions. Highest CH₄ emissions were reported from landfill gas (53%). According to Star Daily, Malaysians collectively spewed 177 million tonnes of greenhouse gases 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 methane by chemical or biochemical oxidation is of great importance for minimization of the greenhouse effect.

1.5 LFG Use

LFG is a useful but underutilized gas. In USA, LFG is directly used for boilers and other combustion applications to replace or supplement coal or oil. LFG is also used as fuel for vehicle in countries such as New Zealand (Nyns, 1992) or heating private houses in Austria (Tscherner, 1995). The most common LFG use is in electrical power generation. However, if LFG production is insufficient to support at least one MW of power generation, it is generally deemed economically unsustainable. However, this collection system is not 100% efficient in mitigating the CH\textsubscript{4} produced as some amount of gas may just escape to the atmosphere. Since most of the landfills or dumps in Malaysia are non-sanitary, LFG produced are just allowed to escape (passive release) to the atmosphere without any prior treatment.

1.6 Landfill Cover

The design of final-cover systems of landfill is an important issue because it determines the performance of landfill. Landfill cover is mainly designed and aimed to reduce water infiltration into landfills. Mohamed Kamil (1999) reported that, almost 95 % of Malaysian landfills were not equipped with any engineering waste containment system, (e.g. compacted clay liner, geomembrane or geosynthetic clay liners). In Malaysia, clay is extensively used as landfill cover in order to minimize leachate volume. This might, however, have a very significant effect on LFG, owing to pressure build up within the landfill due to the non-permeability to LFG. Both Kjeldsen and Fischer (1995) and Zeiss (2006) reported that landfills were covered with a clay soil cover a few months before serious explosion accidents occurred. Witmann (1985) observed that the trees surrounding a landfill died off one month
after clay cover was constructed. Also, off-site odour problems have been observed as a result of covering a landfill with clay soil (Powelson et al., 2006). Cracks formed by differential settlement in the underlying waste, ‘rodent digging’ etc. could lead to higher emission rates locally. Therefore, an optimum landfill cover should also focus on mitigation of gaseous emissions from landfill.

1.7 LFG mitigation

Since CH$_4$ is a potential greenhouse gas, 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$^{th}$ centuries. Reduction or elimination of methane emission from landfill is possible even at the absence of a degassing installation; by making use of the methanotrophic properties of microorganism (Pawloska et al, 2006a). Microorganisms responsible for this process are called methanotrophs. They are the common bacteria which can utilize methane as the sole carbon and energy source (Pawloska, 2008). Methanotrophs convert CH$_4$ to CO$_2$ and water, in the presence of oxygen. Instead of CH$_4$, CO$_2$ which is 23 times less harmful is released to the atmosphere, hence reducing the greenhouse effect. Methanotrophs are found in most landfill covers. However, landfill covers such as clay is not a suitable medium for methanotrophs to thrive in due to lack of oxygen supply for methanotrophic activity.

Since methanotrophic bacteria are essential in reducing the methane emission to the atmosphere, suitable medium is needed for the growth of methanotrophs. An optimum medium should provide favourable conditions for the methanotrophs to thrive-in as the microbes are sensitive to changes in environmental conditions. According to Humer and Lechner (2001), most of the referenced investigations show that a high methane oxidation capacity could be found in porous, coarse and organic-rich substrates such as compost.
1.8 Objectives

Therefore, the objectives of this research are follows:

1) To identify and analyse landfill cover materials such as compost, compost residue and black soil.

2) To assess the efficiency of these materials in reducing landfill gas emissions using Wheaton bottle experiments.

3) To assess the methane oxidation by landfill cover materials in column trials at room temperature.

4) To evaluate and propose suitable height of landfill cover for optimum methane oxidation.

5) To assess methane oxidation capacity of landfill cover materials using kinetics modelling and Biocover Performance Index
Chapter 2: Literature Review

2.1 Waste

Waste is a by product of human activity. Any material or product that has no value in the perception of the generator is considered waste. The quantity of waste generated is increasing simultaneously with the human development. Even the complexity of the waste has increased with the rapid changes in society. These changes in waste composition complicate waste management and disposal methods.

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

Solid waste is defined as wastes arising from human and animal activities that are normally solid and that are discarded as useless or unwanted (Agamuthu, 2001). There are four main categories of solid waste which includes municipal solid waste (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). Municipal solid waste (MSW) is made up of different organic and inorganic fractions like food, vegetables, paper, wood, plastic, glass, metal and other inert materials (Wilshusen et al., 2004). In short, it is mainly household waste including commercial and institutional waste.
2.2 MSW Generation

Waste management studies in developing countries, including some in Africa; have shown that the MSW generation is always higher than 0.2 tonnes per capita (Themelis et al., 2007). Most of the waste are food and yard wastes and are landfilled (Themelis et al., 2007). This results in an estimate of 1080 million tonnes for the 5.4 billion people in the developing world. Adding up these estimates indicates that the global MSW landfilled is somewhere close to 1.5 billion tonnes of MSW per year.

Waste generation within Malaysia was found to depend very much on the sources of MSW. The per capita generation of municipal solid waste (MSW) has reached 1.3kg per day giving a total generation of more than 31,000 tonnes daily compared to 15,000 tonnes/day in 1997 (Agamuthu, 2001). This clearly indicates more than 100% rise in waste generation due to rapid development and uncontrolled urbanization in Malaysia for the past 12 years.

2.3 MSW Composition

MSW composition varies from one country to other mainly due to different lifestyles of contributing population and socio-economic groups. The characteristics, both physical and chemical, 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 also gives estimation on the quality and quantity of LFG generated. Table 2.1 shows the waste composition for Malaysia and other countries.

Malaysians generate about 72% compostable waste comprising organic waste, paper, textile/leather and wood. Plastic waste in Malaysia and Thailand are 15% and 13.7% respectively which are considered high compared to US which generates about 10% of plastic
waste. According to Agamuthu (2003), high generation of plastic waste is typical in fast developing nations.

Table 2.1: Percentages of different types of MSW

<table>
<thead>
<tr>
<th>Country</th>
<th>Paper and Cardboard</th>
<th>Textile</th>
<th>Leather and rubber</th>
<th>Plastic</th>
<th>Metal</th>
<th>Glass</th>
<th>Wood</th>
<th>Others</th>
<th>Organic</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>6.9</td>
<td>4.7</td>
<td>-</td>
<td>7.3</td>
<td>0.5</td>
<td>1.6</td>
<td>6.9</td>
<td>19.2</td>
<td>52.6</td>
</tr>
<tr>
<td>India</td>
<td>7.6</td>
<td>4.7</td>
<td>1.3</td>
<td>3.8</td>
<td>1.7</td>
<td>2.1</td>
<td>-</td>
<td>40.1</td>
<td>39.6</td>
</tr>
<tr>
<td>Sri Lanka</td>
<td>12.3</td>
<td>-</td>
<td>-</td>
<td>6.8</td>
<td>3.7</td>
<td>3.0</td>
<td>10.2</td>
<td>-</td>
<td>64.7</td>
</tr>
<tr>
<td>Thailand</td>
<td>7.7</td>
<td>2.7</td>
<td>3.0</td>
<td>13.7</td>
<td>3.1</td>
<td>4.3</td>
<td>3.6</td>
<td>5.0</td>
<td>56.2</td>
</tr>
<tr>
<td>Nepal</td>
<td>11.0</td>
<td>4.8</td>
<td>1.0</td>
<td>8.4</td>
<td>0.3</td>
<td>2.2</td>
<td>0.3</td>
<td>5.2</td>
<td>66.8</td>
</tr>
<tr>
<td>Ghana</td>
<td>8.0</td>
<td>-</td>
<td>-</td>
<td>8.0</td>
<td>3.0</td>
<td>2.0</td>
<td>-</td>
<td>13.0</td>
<td>60.0</td>
</tr>
<tr>
<td>Europe</td>
<td>32.0</td>
<td>4.0</td>
<td>-</td>
<td>7.0</td>
<td>8.0</td>
<td>10.0</td>
<td>-</td>
<td>9.0</td>
<td>30.0</td>
</tr>
<tr>
<td>US</td>
<td>41.0</td>
<td>2.4</td>
<td>2.6</td>
<td>10.7</td>
<td>7.9</td>
<td>5.8</td>
<td>5.0</td>
<td>0.5</td>
<td>24.1</td>
</tr>
<tr>
<td>Malaysia</td>
<td>14.4</td>
<td>2.8</td>
<td>-</td>
<td>15.0</td>
<td>3.3</td>
<td>3.0</td>
<td>6.7</td>
<td>8.4</td>
<td>46.4</td>
</tr>
</tbody>
</table>

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

2.4 Solid Waste Management

Solid waste management may be defined as the 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).

The integrated waste management should be introduced in the current MSW management practice as to make every component in the hierarchy function effectively. According to Agamuthu (1997), an effective solid waste management hierarchy consists of four main functions to reduce waste generation by practicing waste minimization, reuse the materials recovered from waste stream, and recycle the waste as indirect input to the new
products (3R’s; Reduce, Reuse and Recycle concept). Furthermore, energy can be recovered by anaerobic digestion to reduce the volume of waste. Generally, landfill is an important component in the hierarchy of integrated waste management practice. It is obvious that the ultimate disposal of the solid waste and waste residual is landfilling. Therefore, designing landfill for MSW require an integrated input from multidiscipline (Frechen, 1989). 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.

2.5 Solid Waste Treatment

Solid waste can be treated by various means as listed below:
1) Biological treatment which is either aerobic (composting) or anaerobic (biogasification)

2) Thermal treatment which is either aerobic (incineration) or anaerobic (pyrolysis)

3) Reuse, Recycle, Reduce (3R)

4) Landfill.

Biological treatment of MSW is very rare in Malaysia while thermal treatment (incineration) is only used for clinical and hazardous waste. Reuse, Recycle, Reduce (3R) activities among the public are still at infancy level in Malaysia. Therefore, almost all the MSW generated in Malaysia is dumped into the landfills. Table 2.2 indicates the waste management methods practised since 2002 and the proposed technology for the future in Malaysia. However, these targets were not achieved due to absence of proper regulations and enforcement (Agamuthu et al., 2007).

Table 2.2: Methods of waste disposal in Malaysia

<table>
<thead>
<tr>
<th>Treatment</th>
<th>2002</th>
<th>2006</th>
<th>2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recycling</td>
<td>5.0</td>
<td>5.5</td>
<td>22.0</td>
</tr>
<tr>
<td>Composting</td>
<td>0</td>
<td>1.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Incineration</td>
<td>0</td>
<td>0.0</td>
<td>16.8</td>
</tr>
<tr>
<td>Inert landfill</td>
<td>0</td>
<td>3.2</td>
<td>9.1</td>
</tr>
<tr>
<td>Sanitary landfill</td>
<td>5.0</td>
<td>30.9</td>
<td>44.1</td>
</tr>
<tr>
<td>Other disposal sites</td>
<td>90.0</td>
<td>59.4</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Source: Agamuthu et al. (2007)

2.6 Landfill as Disposal Method
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 (Christensen et al., 2007). The former is becoming illegal in most developed nations. According to Moldes (2007), some authors proposed the incineration of MSW, but this type of process generally produced significant amounts of polluting flue gases and also gives rise to toxic solid residues. On the other hand, the European Landfill Directive (EU 1999/31) requires the phased reduction of landfill disposal of such biodegradable organic materials. 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 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. 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). 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 others waste disposal methods. Large quantities of MSW are currently disposed off in landfill sites, resulting in rapid exhaustion of the landfill capacity (Moldes et al., 2007). Sanitary landfill differs markedly from open dumps. Open dumps are simply places to dump wastes, while sanitary landfills are engineered operations, designed and operated according to acceptable standards (Christensen et al., 2007).

Till date, there are 261 landfills in Malaysia (Agamuthu et al., 2008). Table 2.3 shows landfills in central Malaysia in accordance to states. As almost all the landfills in

Table 2.3: Number of closed disposal facilities and facilities proposed for closure in
Malaysia in 2008.

<table>
<thead>
<tr>
<th>State</th>
<th>Closed Facilities over the last 17 years</th>
<th>Facilities proposed for closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perlis</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Kedah</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Penang</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Perak</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Pahang</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>Selangor</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>Wilayah Persekutuan</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>Negeri Sembilan</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>Malacca</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Johor</td>
<td>21</td>
<td>4</td>
</tr>
<tr>
<td>Kelantan</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Terengganu</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>Labuan</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sabah</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Sarawak</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>111</strong></td>
<td><strong>16</strong></td>
</tr>
</tbody>
</table>
Malaysia are non-sanitary landfills, they lack proper gas and leachate collection system. The landfill gas poses a potential threat to the environment thus contributing to global warming.

2.7 LFG generation

The initial aerobic phases immediately after landfilling of the waste will only last weeks. The acidic phase where high concentrations of fatty acids are formed and the initial methanogenic phase, where methane production begins, typically last for months (Palowska, 2008). The duration of the last phases is not known since no data exists, but will be from years to decades depending of the waste composition and landfill technology used (Christensen, 2007).

The rate of landfill gas production is influenced by

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 material

(Agamuthu, 2001)

Shortly after MSW is landfilled, the organic components start to undergo biochemical reactions. In the presence of atmospheric air, which is near the surface of the landfill, the
natural organic compounds are oxidized aerobically. This reaction is similar to combustion because the products are CO₂ and water vapour (Pawloska, 2008, Kallistova et al., 2005). However, the principal bio-reaction 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, CO₂ and H₂; the principal acids produced are acetic acid, proponoic acid, butyric acid and ethanol. Finally, in the third stage, methane is formed by methanogenic bacteria, either by breaking down the acids to methane and carbon dioxide, or by reducing CO₂ with H₂. Two of the representative reaction is shown below:

**Acetogenesis**

\[ C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \]

**Methanogenesis**

\[ CH_3COOH \rightarrow CH_4 + CO \]
\[ CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \]

Figure 2.1 illustrates the most important interactions in an anaerobic landfill between the bacterial groups involved, the substrates involved, and intermediate products. The anaerobic degradation can be viewed as consisting of three stages. In the first stage, solid and complex dissolved organic compounds are hydrolysed and fermented by fermenters to primarily volatile fatty acids, alcohols, hydrogen and carbon dioxide. In the second stage, an acetogenic group of bacteria converts the products from
Figure 2.1: Substrates and major bacterial groups in the methane-generating ecosystems
the first stage to acetic acid, hydrogen and carbon dioxide. In the final stage, methane is produced by methanogenic bacteria. This may be done by acetophilic bacteria converting hydrogen and carbon dioxide to methane.

The hydrolysis process is a very important process in the landfill environment, as the solid organic waste must be solubilised before the micro-organisms can convert it. After the smaller, easily soluble part of the organic matter has been converted, the hydrolysis may prove to be the overall rate-limiting process in the landfill environment (Leuschner, 1983; McInerney and Bryant, 1983; Barlaz et al., 1989; El-Fadel et al., 1989). The hydrolysis is caused by extracellular enzymes produced by the fermenting bacteria (Jones et al., 1983).

The fermenters are a large, heterogeneous group of anaerobic and facultative anaerobic bacteria. The acetogenic bacteria are also a large heterogenic group. Acetogenic bacteria produce acetic acid, hydrogen and also carbon dioxide (McInerney and Bryant, 1983), if the volatile fatty acid converted contains an odd number of carbon atoms. The acetogenic bacteria may also convert aromatic compounds containing oxygen (e.g. benzoic acid and phenols), while aromatic hydrocarbons (e.g. benzene and toluene) are apparently not degraded. The methanogenic bacteria are obligate anaerobic and require very low redox potentials.

One group, the hydrogenophilic, converts hydrogen and carbon dioxide to methane, while another group, the acetophilic, converts primarily acetic acid to methane and carbon dioxide. The methanogenic bacteria may also convert formic acid and methanol. The conversion of acetic acid to methane is believed to be the most important part of the methane-forming process.
Finally, the sulphate reducing bacteria, dominated by *Desulfovibrio* and *Desulfotomaculum* (Postgate, 1979) play an important role, as this group of bacteria in many ways resembles the methanogenic group as sulphate is a major compound of many waste types. The sulphate-reducing bacteria are obligate anaerobic and may convert hydrogen, acetic acid and higher volatile fatty acids during sulphate reduction. However, the organic carbon is always oxidized to carbon dioxide as opposed to the conversion by the methanogenic group of bacteria.

### 2.8 LFG composition

The amount and rate of methane generation depends upon the quantity and composition of the landfilled material, as well as the surrounding landfill environment. The gas emissions are characterized by the gas quantity and gas quality. Both factors are highly dependent of the age of the landfill. 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). First accounts on atmospheric methane were given by Hutchinson (1954). Systematic worldwide measurements of the tropospheric methane concentration were started in 1978 (Whalen, 1993). In the following years, multiple measurements of the mixing ratio of CH$_4$ in the atmosphere have been performed and atmospheric methane changes have been analyzed.

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) reported an overview of observed production rates together with several models of LFG production (only covering the stable methanogenic phase)
Typical gas quality composition of the main LFG components is given in Figure 2.2 for the whole lifetime of a landfill. The shown composition for the later phases is solely based on speculations (Christensen et al., 1996). After the initial relatively short phases (I-III) an often very long stable methanogenic phase begins, where typical contents of CH₄ and CO₂ are 55 vol % and 44 vol% respectively. In the end of this phase and especially in the beginning of the next phase (V) CH₄ tends to increase and CO₂ decreases.

![Figure 2.2: Illustration of developments in gas composition in a landfill cell](image)

Source: Christensen et al. (1996)

At this time the gas production is relatively low (which allows air to intrude into the waste layers) and a significant proportion of the CO₂ having a much higher solubility than CH₄ is transferred to leachate. Later in phase V the air intrusion increases which decreases both CH₄ and CO₂ by dilution and CH₄ further by an increasing methane oxidation. In phase VI methane oxidation prevails significantly decreasing the CH₄/CO₂ ratio. In phase VII the
methane production stops and O\textsubscript{2} begins to appear in the LFG. The LFG in the last phase resembles soil air.

LFG also contains several trace components especially different organic compounds originating from the microbial degradation of the organic waste and from volatile organic chemicals which have been disposed of together with the MSW. The most frequently found chemicals are the aromatic hydrocarbons (BTEX) and halogenated aliphatic hydrocarbons (Rettenberger & Stegmann, 1995).

### 2.9 Landfill Gas - Impact of LFG to Environment and Health

Landfill gas is a mixture of substances generated when bacteria decompose the organic materials contained in municipal solid waste (MSW). By volume, MSW landfill gas is about half methane and carbon dioxide (Gebert et al., 2003). According to Williams (2002), landfill gas consists of mainly H\textsubscript{2} and CO\textsubscript{2} in the early stages followed by mainly CH\textsubscript{4} and CO\textsubscript{2} in the later stages. Landfill gas also contains small amounts of nitrogen, oxygen, and hydrogen, less than one percent non-methane volatile organic compounds (NMVOCs), and trace amounts of inorganic compounds (Kallistova et al., 2005). Gases generated in the landfill will move throughout the mass of waste in addition to movement or migration out of the site. The mechanism of gas movement is via gaseous diffusion and advection or pressure gradient. This means, the gas moves from high to low gas concentration regions or from high to low gas pressure regions (Christensen et al., 2007). Movement of gas within the mass of waste is controlled by the permeability of the waste, overlying daily or intermittent cover and the degree of compaction of waste. Lateral movement of the gases is caused by overlying low permeability layers such as the daily cover and surface and sub-surface accumulations of water. Vertical movements of gas may occur through natural settlement of the waste, between bales of waste if a baling system is used to compact and bale
the waste or through layers of low permeability inert wastes such as construction waste rubble (Pawloska, 2008, Borjesson et al., 2004 and Einola et al., 2007).

Greenhouse effect is produced by certain gases in the atmosphere which allow transmission of short wave radiation from the sun but are opaque to long wave radiation reflected from the Earth’s surface, thereby causing warming of the Earth’s atmosphere.

2.9.1 Greenhouse Effects

Landfills significantly contribute to the global anthropogenic methane emissions (illustrated in Figure 2.3). Methane is a more powerful greenhouse gas than carbon dioxide due to its radioactive forcing ability. Of the anthropogenic emissions, CH$_4$ is estimated to contribute 18% of the global integrated radioactive forcing by gas (Thorneloe, 1995). The global emissions of methane from landfill have been estimated to be between 22 to 46 Tg/year equivalents to between 6 and 13% of the global methane emission (Einola et al., 2007). The estimation is based upon data from landfills where gas is collected. However, for landfills where no gas collection is taking place the gas will migrate through the top cover soil layers adjacent to the landfill and passively released to the atmosphere. Several climatic and environmental anomalies have been attributed to global warming (IPCC, 2007). One of it was the highest global temperatures were recorded between 1995 and 2006. Average temperature deviations between 1995 and 2006 were between 0.29 C and 0.54 C. This is higher than average temperature deviation between 1961 and 1990, which was between 0.1C and 0.4C.

2.9.2 Ozone depletion
The LFG content of volatile chlorinated and fluorinated hydrocarbons poses a special problem. Due to their chemical stability especially the fluorinated hydrocarbons reach the stratosphere, where the chlorine atom is separated and the radical cause ozone to break down (Deipser et al., 1995). Fluorinated hydrocarbons (Freon) 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., 1995). However the freons are often contained in metal containers (spray cans etc) while disposed of, and may not be readily available for volatilization. Therefore an increased emission of Freon in the later phases, where the metal containers are corroded, cannot be excluded.

Figure 2.3: The different scales of landfill gas effects (after Luning and Tent, 1993)

2.9.3 Toxic VOCs in air
Main components of LFG such as carbon dioxide and hydrogen sulphide are potentially toxic to humans, but most concern is generally assumed 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 (Dorr, 1995).

2.9.4 Odour

The LFG compounds that give rise to odour problems are hydrogen sulphide 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).

2.9.5 Explosion and Fire Hazards

One of the main environmental hazards related to landfill gas is believed to be the explosion hazard. Landfill gas is explosive mainly due to the CH₄ content. The explosive limit range for CH₄ lies between 5 and 15% in air at atmospheric pressure and ambient temperature (Christensen et al., 1995). The limits are only slightly affected by the presence of other constituents (Gendebien et al., 1992). If landfill gas is vented directly to the atmosphere, no explosion hazard exists, but surface fires have been observed. Landfill gas entering houses through cracks in foundations, or other penetrating means can initiate explosion after mixing of the gas with air with an energizer (spark in electrical components, striking a match etc). Many cases of elevated methane concentrations in houses due to landfill gas are reported in the literature. Gendebien et al. (1992) describes 60 cases from UK, USA, Germany and Canada of elevated methane concentrations, and 55 cases from USA, UK and Canada involving explosion, fire and human injuries.
2.9.6 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 landfill gas is asphyxia by removal of oxygen in root zone. This removal can either due to displacement of the oxygen by landfill gas or by oxidation of methane. High concentrations of carbon dioxide (20%) are also toxic to plants (Neumann & Christensen, 1995) and some trace compounds (hydrogen sulphide, haloorganics compounds, etc) are toxic to plants as well.

2.9.7 Health Impacts

Emission of landfill gas has much impact on people that can deteriorate one’s health condition. If the landfill gas in not managed properly, their impacts may include, as well as the basis of explosion and fire, odour nuisance, harm to flora and fauna, noise pollution, photochemical air pollution, acidic precipitation, stratospheric ozone depletion and global warming. These harmful impacts can cause many major illnesses which can lead to fatality in long run.

2.10 Global Landfill Gas Emissions

The gas emission from a landfill is a consequence of the biochemical stabilization processes taking place inside the waste (Kjeldsen and Christensen, 1995). According to Scheutz & Kjeldsen (2004) anaerobic decomposition of organic matter in refuse generates landfill gases consisting of CH₄ (55-60% v/v) and CO₂ (40-45% v/v). Agnew et al. (2003), reported a slightly different amount of landfill gas which is up to 64% CH₄, 35% CO₂, and <1% volatile odorous compounds. The emissions from landfill account for 21% of the total anthropogenic CH₄ sources in Canada, 30% in Europe, 34% in US and 10% globally.
(Neumann & Christensen, 1995). Chemicals emitted from landfills enhance the global climate change mainly due to methane emissions (Bogner et al. 1995). According to the official data from the IPCC framework, CH$_4$ emissions in 2000 from landfills in Greece were 548Gg per year; which contributed to 7.6% of total global anthropogenic CH$_4$ emissions (CSO, 2002-2006) (7.23 Tg per year), (IPCC 1996). Figure 2.4 illustrates global anthropogenic CH$_4$ budget by source in 2000. According to Pawloska (2006), solid waste contributes 13% of global anthropogenic CH$_4$ in 2000.

Methane is also emitted from older and smaller landfill sites, where the subsequent application of a gas collection system is too costly, as well as from open, unauthorized dumps. USEPA estimated that the total anthropogenic emissions of methane were 282.6 million tonnes in 2000 (CSO, 2002-2006), of which 13% or 36.7 million tonnes were due to landfill emissions. According to Themelis (2007), the global MSW landfilled was estimated at about 1.5 billion tonnes of MSW per year. In average, methane generation is at least 50Nm$^3$ of methane per tonne of MSW (i.e., at the low level of reported anaerobic digestion rates), the global generation of methane from landfilled MSW is in order of 75 billion standard cubic meters or 54 million tonnes of methane (Einola et al., 2007). Stern and Kaufman (1998) extrapolated the 1985 estimate of Subak et al. (1993) of 36 million tonnes of CH$_4$ to earlier years, by assuming that MSW generation and landfilling were proportional to economic growth.

Atmospheric methane (CH$_4$) in 2005 was approximately 1774ppb, exceeding levels for the past 650 000 years (320 – 790 ppm) (Kettunen et al., 2006). The increase is partially attributed to agriculture and the use of fossil fuels. CH$_4$ has 23 times higher global warming potential than CO$_2$ as it has a stronger molar absorption coefficient for infrared radiation and stays Earth’s atmosphere longer. It is said to be responsible for 15 to 20% of the anthropogenic greenhouse effect (Humer and Lechner, 1999).
Methane migration through landfill caps is the fourth largest source of anthropogenic CH₄ emissions worldwide (Stern and Kaufmann, 1996) and it is the largest source in the United States (US Department of Energy, 1997). These emissions alter the global CH₄ budget, and since CH₄ is a potent greenhouse gas, they contribute to global climate change. Landfills contribute about 20-70Tg to global methane emissions each year (Kettunen et al., 2006). Mancinelli (1995) estimated that total global methane emissions from landfills will increase significantly by 2025. The authors assumed that this will mainly be due to growing populations and urbanization in developing countries (such as regions in Asia or Africa) which most likely will lead to increased waste generation and disposal in landfills.

Figure 2.4: Global anthropogenic methane
Source: Pawloska (2006)

Presumably landfills in these countries will not have gas collection systems because of inadequate or missing technical and financial facilities. Although today’s sanitary landfills usually operate a gas extraction system, by which landfill gas is collected and burned in flares or used as an energy source, a high amount of gas still escapes into the atmosphere.
2.11 Application of Landfill Gas Use

Landfill gas is being managed or utilized by many means in some developed countries. According to Directive 31/1999/Ce “LFG shall be collected from all landfills receiving biodegradable waste and the LFG must be treated and used. If the gas collected cannot be used to produce energy, it must be flared”.

2.11.1 Flaring / Passive venting system

Figure 2.5 illustrates passive collecting and venting systems reported by McBean, 1995. A flare is sometimes referred to as a “Controlled combustion unit.” Flaring is a common treatment method when enough methane (e.g., greater than approximately 20 percent by volume) is present in the gas.

Flaring reduces odours and is more effective and more environmentally friendly than passive venting. Passive venting systems are used where landfill gas concentrations are low such as in older sites or for landfill sites which are used for non-bioreactive wastes such as inert materials. In many cases, landfill gas is flared without energy recovery to destroy the methane and organic micro-pollutants as a means of gas hazard and odour control. In addition, the flare may be required to burn off any excess gas or to act as a standby for any plant shutdowns. The flare may be an exposed open flame, usually on a pedestal or enclosed in a ceramic furnace. Most flares designed today are enclosed flares, which allow longer residence times, elevated combustion temperatures, and greater thermal destruction efficiency than open flares (Qian, 2002). The open type flare has to maintain a flame even under extremes of weather conditions. The stability of the
flame is related to the gas composition, weather conditions, burner design and other factors. However, the flame will be stable at CH$_4$ concentrations of between 30 and 60%. Minimum flame temperatures of between 850 and 1100°C are recommended to destroy any hazardous trace components (William et al, 1998). Landfill gas can be flared on site, but this is not a beneficial application of this resource. Beneficial energy recovery systems include direct use, electricity generation, and conversion to chemicals or fuels.

**2.11.2 Boilers and Other Direct Combustion Applications**

This method of landfill gas utilization is by far the cheapest and easiest use options. The landfill gas 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
Landfill gas 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 three kilometre 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).

### 2.11.3 Landfill Gas for Vehicle Fuel

The potential for the use of landfill gas for vehicle exists if the gas is upgraded to natural gas quality. In New Zealand, many vehicles are already running on upgraded landfill gas and the number is increasing (Nyns, 1992). However, in most countries the use of landfill gas as a vehicle fuel is limited to landfill or other range of operations. According to Stahl (1992), the use of landfill gas in vehicles offers greater economic benefits than power generation using treated or even untreated landfill gas. So expensive is the conversion of landfill gas to natural gas that only large landfills can attain the economics of scale necessary to support operation (Kallistova et al., 2005). 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.

### 2.11.4 Electrical Power Generation

This is the most common landfill-gas-to-electricity application. Stegmann (1996) reported that 120-150m$^3$ of landfill gas has a calorific value of 5.9kWh/m$^3$. According to Wheless et
al. (1993), there were 85 landfill-gas-to-electricity projects in United States of America by 2000 that was capable of generating 344MW of electricity. These represented three fourths of landfill-gas-to-electricity projects in the United States. If landfill gas production is insufficient to support at least one MW of power generation, it is generally deemed economically unsuitable. 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. There are other points that have to be considered before constructing the LFG-powered gas engines are listed as below:

a) Have a constant LFG quality

b) Respect and react on the problems associated with H$_2$S, halogenated hydrocarbons and other trace constituents

c) Observe the oil quantity in the engines and exchange at relevant intervals

d) Keep the engine at constant temperature also during breaks or maintenance and repair

e) Observe the emissions in the exhaust gas

f) Do general maintenance and inspection of the engine at shorter intervals (compared to natural gas powered engines)

However, the cost of setting up electrical power generators in landfill is very high. Therefore, electrical power generation using LFG is unfavourable in many underdeveloped and developing countries such as in Malaysia. Once all the LFG has depleted, the electrical power generators will be underutilized and wasted. Besides that, the inconsistent production of CH$_4$ in Malaysian landfill due to the highly heterogeneous waste is one of the reasons for the unpopularity of this LFG gas utilization method in Malaysia.
2.12 Technical Issues in LFG use

Many problems and technical issues arise in utilizing LFG. The physical, chemical and combustion characteristics of landfill gas can have significant impact on energy recovery equipment selection and operation. Trace organics, such gases as hydrogen sulphide and others, and particulates can cause corrosion and excessive wear on the gas collection wells. CO₂, N₂ and water vapour, with various inert materials, may reduce the efficiency of gas recovery system.

Although most trace gases, primarily hydrocarbons, are harmless to energy use, halogenated hydrocarbons may cause problems upon acids formed in untreated landfill gas. The acidic gas is also highly corrosive. Trace constituents have been reported to cause corrosions, combustion chamber melting, and deposits on blades of turbine engines, as well as internal combustion engines (Thorneloe, 1992).

Landfill gas is very corrosive and water saturated. Hydrogen sulphide and water vapour can also have corrosive effects. The use of landfill gas as a vehicle fuel requires the removal of hydrogen sulphide and water due to corrosion problems when they condense during gas compressions and cooling. Hydrogen sulphide in concentrations as low as 100ppm may lead to corrosion in piping, storage tanks, and engines (Wheless et al., 1993).

2.13 Methanotrophic Activity

The annual global CH₄ emission is many times larger than the annual amount of methane accumulating in the atmosphere, which indicates that there are mechanisms of CH₄ uptake in nature (Pawloska, 2008). The main mechanism of these processes is a set of chemical reactions of CH₄ with OH· radicals in the troposphere. However, the significance of microbial pathway of the atmospheric methane oxidation cannot be ignored (Christensen et
al., 2007). According to IPCC data (2007) the contribution of the microbial oxidation to the methane uptake from the atmosphere is about 5%, which makes 30Tg of methane annually,

The main global methane sinks are chemical reactions in the troposphere and microbial methane oxidation in soils. Microorganisms responsible for microbial methane oxidation, so-called methanotrophs, are common bacteria that can utilize methane as the sole carbon and energy source. Microorganisms which are capable of oxidizing methane have been known since the turn of the 19th century. These microorganisms are mainly so-called obligate methylotrophic (=methanotrophic) bacteria which specialize in the assimilation of C1 compounds (such as methane and methanol). Obligate methanotrophic bacteria use methane and its decomposed compounds, methanol and formaldehyde, as their sole source of energy and carbon. This process is catalyzed by an enzyme called methane mono-oxygenase) which can be found in all methanotrophic organisms and is essential to methane oxidation.

Methane mono-oxygenase (MMO) acts as a non-specific catalyst, which may lead to the co-oxidation of NH$_4^+$ and other hydrocarbons, such as halogenated ones, which are also found mainly in landfill gas. Methane non-oxygenase is available in either soluble or membrane-bound form, depending on the concentration of copper available in the substrate (Bender, 1992).

Microbial methane oxidation is very effective in many natural systems, such as the aerobic layers of topsoil in wetlands, and it is determining factor in the natural carbon cycle. For example, in the Florida swamps and in the marsh lands in Germany, it was demonstrated that CH$_4$ produced in anaerobic zones was reduced by 70-90% in the covering aerobic zones by methane oxidation before reaching the atmosphere (King et al., 1990).

According to Whittenbury (1970), the scientific community has long known about the presence of methane oxidizing microorganisms in different natural systems, e.g. aerobic soils,
water and marine habitats. Microbial methane oxidation, that means the conversion of CH$_4$ to CO$_2$ and water by microbial activity, is very important and accounts for about 80% of global CH$_4$ consumptions (Kightley et al., 1995). The effect of methane oxidation in natural landfill cover soils has already been described by a number of authors (Whalen et al., 1990). Microbial oxidation of methane plays a vital role in reducing emission of methane to the atmosphere. (Lelieveld et al., 1998, Oremland & Culbertson, 1992). Microbial CH$_4$ consumption in the aerobic portions of a landfill cap reduces CH$_4$ emissions to the atmosphere and the degree to which this occurs and the conditions that promote it are all under investigation (Whalen et al., 1990; Jones and Nedwell, 1993, Kjeldsen et al., 1997). Laboratory and field studies indicate that CH$_4$ oxidizers typically consume 10-20% of the CH$_4$ passing through a landfill cover, although under laboratory conditions, up to 60% CH$_4$ oxidation has been reported (Kightley et al., 1995). Bogner et al. (1995) have shown that under certain conditions, landfill covers are even a sink for atmospheric CH$_4$ due to presence of methanotrophs in the cover. Methanotrophic microorganisms are mainly bacteria, but a methane oxidizing ability has also been observed in the case of yeast (Adamse et al., 1972). Apart from CH$_4$, almost all known methanotrophs can also use methanol as a carbon and energy source (Whittenbury et al.,1970; Mancinelli et al.,1981), but not all bacteria that use methanol can also oxidize methane (Mancinelli et al.,1981). Methanotrophic bacteria that can oxidize CH$_4$ 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 & Pattey,1977).

According to Todd et al. (2007) methanotrophic bacteria have been classified into three types (I, II and X) based on the structures of their internal membranes and their carbon assimilation pathways. There are two types of the methane monooxygenase: sMMO, of low substrate specificity and limited dependence on copper availability and pMMO, of high substrate specificity and strong dependence on copper availability (Buchholz et al., 1995).
Methanotrophs of type I have a membrane-bound (particulate) methane monooxygenase enzyme (pMMO), cluster phylogenetically with the *Gammaproteobacteria*, and are considered to proliferate under high-oxygen and low methane conditions (Hanson and Hanson, 1996). Type II methanotrophs have pMMO enzymes, but can also produce a more reactive cytoplasmic (soluble) methane monooxygenase enzyme (sMMO) under copper-limiting conditions (Hanson and Hanson, 1996). Type X methanotrophs exhibit characteristics of both Type I and Type II methanotrophs, and cluster phylogenetically with the *Gammaproteobacteria* (Hanson and Hanson, 1996). The sMMO presence in a bacteria cell (methanotrophs of the types II and X) is coupled with low affinity to CH₄, which is the reason why those bacteria cannot oxidize CH₄ when its concentration is low. Most of methanotrophs are gram-negative bacteria (Whittenbury et al., 1970).

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 level (Mancinelli, 1995).

### 2.14 Factors affecting Methanotrophic Activity / Methane Oxidation

Environmental factors have a decisive impact on the activity of methanotrophic bacteria i.e. methane turnover rates. Methanotrophic organisms on the whole are fairly adaptive, but some certain ambient factors are required. 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).
2.14.1 pH and alkalinity

Nearly all methanotrophs grow at pH values >5 (Pawloska, 2008). 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 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. The highest CH$_4$ oxidation rate is usually observed at pH values of 6-7 (Hutsch, 1994; Dunfield et al., 1993). Some authors have observed methanotrophic activity in highly alkaline environment (at pH 10-11) (Khmelenina et al., 1997; Sorokin et al., 2000; Kaluzhnaya et al., 2001). Rozej&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 methane oxidation rate in the pH range 7.61-8.89, although Hilger et al. (2000b) found that increasing soil pH will increase the intensity of CH$_4$ oxidation.

2.14.2 Temperature

According to Pawloska (2008), methanotrophs prefer mesophilic conditions with optimum temperature above 15°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. According to Whalen (1990), when temperatures decrease below that value, a smooth decline of methanotrophic activity occurs. Meanwhile, an increase of the temperature up to the values exceeding the optimum temperature 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 & Van Cleemput, 1994: Boeckx & Van Cleemput, 1996). A little lower optimum value of 23°C has been obtained for Alaskan waterlogged soils (Whalen & Reeburgh, 1996). Results of investigations by Boeckx et al. (1996) performed on a sandy-clay soil of a landfill cover indicated that the temperature optimum value varies depending on the moisture content of the soil material. There are differing scientific statements concerning the dependency of methane oxidation on temperature. Most methanotrophic bacteria live and multiply best at temperatures ranging from 15 to 30°C. In laboratory landfill simulators, methane oxidation rate has been shown to increase significantly (up to 100 times), when the temperature is raised from 20 to 30 and 40°C (e.g. Buivid, 1980; Scharf, 1982, Ehrig, 1984). Although the anaerobic degradation of organic compounds yield much less heat than the aerobic process (about 7% according to Christensen and Kjeldsen, 1989), elevated temperatures (30-45°C) in landfills have been reported (e.g. Rees, 1980). Elevated temperatures primarily develop in landfills with a good CH₄ oxidation, a moderate water flux and substantial waste thickness providing good insulation. At elevated temperatures, the CH₄ oxidation is more vigorous and produced more heat, and as such is self-enhancing. Laboratory experiments conducted by Whalen et al. (1990) show that a temperature increase from 15°C to 25°C causes the CH₄ oxidation rate to nearly double, and the authors indicate that CH₄ turnover rates depend heavily on temperature. However, an investigation conducted by Boeckx et al. (1996) show only a slight temperature effect on methane oxidation. Test conducted by Humer and Lechner (2001) indicated that wider temperature with the range of 5°C to 35°C for rather higher and constant methane oxidation activity.

2.14.3 Moisture Content
Moisture Content of the soil plays an essential role in determining the size of methanotrophic population. Several laboratory investigations have shown that the methane production rate increases with increasing moisture content of the waste (e.g. Buid, 1980; Rees, 1980). Rees (1980) summarized findings from the literature suggesting an exponential increase in gas production between 25 to 60% water content. The main effect of the increased water content, besides limiting the oxygen transport from the atmosphere, is probably the facilitated exchange of substrate, nutrients buffer, and possibly dilution of inhibitors and spreading of micro-organisms between the micro-environments. The moisture content of the substrate influenced methane oxidation in many ways. There is a strong correlation between the actual water content and oxygen permeability and it has a big impact on methane oxidation. 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 CH₄ oxidation are found in areas with relatively high moisture content. The highest CH₄ turnover rate could be achieved under the same ambient conditions in bio-waste 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 was 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). Some authors have found that
0.06kg H₂O kg⁻¹ as the critical value of water content for methanotrophic activity in their soils (Stein & Hettiaratchi, 2001; Visvanathan et al., 1999).

The highest number of methanotrophic bacteria cells, within the range from 10⁵ to 10¹⁰ cells in 1g of moist material has been found in the upper part of wastes, in landfill cover soils or in biofilters for methane oxidation (Nozhevnikova et al., 1993; Lebedev et al., 1994, Gebert et al., 2003, Kallistova et al., 2005). However, authors have identified a strong dependence of moisture content and temperature of the soil. Within the moistness range of 10-30% of weight, the temperature optimum decreased 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. According to Pawloska (2008), increase in 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. However, the high water content and can restrict the presence of oxygen to the top 60cm (Lebedev et al., 1994) or even 30cm (Kightley et al., 1995) thus limiting methane oxidation capacity. A negative correlation between CH₄ uptake rate and the moisture content in soil within the range of 30-50%v/v has been proved by tests performed on forest soil of the temperate climate zone (Lessard et al., 1994). Whalen & Reeburgh (1990) has also indicated a decrease of methanotrophic activity within the mentioned range of moisture content in soils that are not exposed to permanent flooding. In waterlogged soils, a decrease of methanotrophic capacity occurs for higher moisture contents. The above mentioned authors have shown that there is an optimal value that can be expressed as a percentage of the total water holding capacity (WHC) of soils. The optimal moisture content for CH₄ oxidation in Alaskan forest soils have been shown to be 21-27% of the WHC, while in waterlogged
soils of that area it reached up to 50% of the capacity. The optimal soil moisture content for 
CH$_4$ oxidation in loamy sand has been shown to be 13% by weight (Park et al., 2002). The 
optimal weight moisture content in a meadow cambisol ranged from 15 to 22% (Bender & 
Conrad, 1995).

2.14.4 Methane Concentration

Methanotrophs contribute to the reduction of atmospheric methane concentration not 
only by capturing it from the atmosphere (acting as an absorbent) but also by preventing 
methane emissions from various environments. According to estimates by Reeburgh et al. 
(1993), soils exposed to high methane concentrations such as landfill cover soils prevent the 
emissions of about 700Tg of CH$_4$ annually in a global scale.

2.14.5 Oxygen supply

Methanotrophic bacteria are obligate aerobes, which can achieve optimum methane 
oxidation rates even under microaerophilic conditions, i.e. at very low oxygen concentrations 
(Pawloski & Pawloska, 2008). Bender (1992) carried out experiments on a paddy field soil 
and demonstrated that the microbial activity of methanotrophic bacteria is reduced 
significantly only below oxygen concentrations of 2% v/v in the gaseous phase. According to 
the total formula in stoichiometry, two molecules of oxygen per molecule of methane are 
required for microbial methane oxidation: \[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} = 210.8\text{kJ/mol} \] 

This equation results in an ideal O$_2$/CH$_4$ ratio of 2:1 in the substrate. This 
stoichiometric calculation works only if no carbon is converted into biomass. If biomass is 
accumulated, less oxygen is needed for methane oxidation (Mennerich, 1986). This indicates 
that 3.6 to 4.0 g O$_2$/g CH$_4$ is actually needed for methane oxidation. Kjeldsen et al. (1997)
indicated 5 g O₂/g CH₄ is required. Substrates, in which maximum CH₄ conversion rates should be achieved, must have a suitable pore volume to ensure a satisfactory supply of oxygen and methane as well as an adequate retention time for methane in the substrate.

2.14.6 Soil condition and nutrients supply

The anaerobic ecosystem must have access to all the required nutrients, in particular phosphorus and nitrogen for methane oxidation in landfills. All the necessary micronutrients, e.g. sulphur, calcium and magnesium, potassium, iron, zinc, copper, cobalt, molybdenite and selenium are considered to be fully available in most landfills. The anaerobic ecosystem assimilates only a very small part of the substrate into new cells and therefore requires much less nitrogen and phosphorus than the aerobic system. Optimal ratios between organic matter (expressed as chemical oxygen demand), nitrogen and phosphorus are listed by McInerney et al. (1983) as 100:0.44:0.08. On average, the mixed waste landfill will not be limited by nitrogen and phosphorus, but insufficient homogenization of the waste may result in nutrient-limited environments. Phosphorus is the nutrient most likely to limit the anaerobic degradation processes. The substrate must also be rich in organic matter and provide a satisfactory supply of nutrients. The nutrient supply and the content of organic matter in a substrate are vitally important in CH₄ oxidation for two reasons (Christensen et al., 1996). On the one hand, organic matter serves mainly as a carrier for microorganisms and improves the soil properties and substrates while on the other hand, a satisfactory nutrient supply is a prerequisite to the build-up of methanotrophic biomass. According to investigations by Kightly et al. (1995), the admixture of sewage sludge (2.5 g per kg of soil) to coarse-grained sand raises the specific methane oxidation rates by 26%, admixtures of peat leads to an
increase by 27% and admixture of compost derived from green waste leads to an increase by even 41%. No increase in the conversion rates was achieved by admixing mineral fertilizer.

2.15 Landfill Cover

2.15.1 Landfill Components

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 (Pawlowska, & Stepniewski, 2006a).

MSW landfills have the following components as shown in Figure 2.6.

(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

Cover material is classified as daily, intermediate, or final cover according to the frequency with which the material is applied. The final cover is usually compacted, uniformly applied and sloped to enhance surface runoff as opposed to allow infiltration. The final cover is to encourage surface runoff while discouraging erosion of the cover itself. It is intended to provide an effective low-permeability cap to the landfill site that serves to control
the infiltration of surface water into the waste, thus limiting the generation of leachate. The use of low-permeability soil as daily cover of the waste will impede uniform gas permeabilities in the landfill and create a wide diversity of gas pressures. Conversely, the use of very permeable materials, temporary road constructions and venting systems might create localized zones of high permeability where gas pressures are low (Baghi, 1989). According to McBean et al. (1995), final soil cover should also serve as the purpose to retain moisture for vegetative root growth, reduce or enhance landfill gas migration (depending on the design objectives), provide the final shaping and contouring of the site in accordance with the end use objectives and to provide a base for the establishment of a suitable ground cover (Table 2.4). Both soil materials and non-soil materials are utilized, although soils are most commonly used as landfill cover.

Figure 2.6 Schematic diagram of MSW landfill containment system (Sharma, 1995).
Completed landfill sites are sometimes developed to include such features as parks, golf course, nature areas and bicycle paths. The topsoil forming the protective top cover must be selected and constructed to support vegetation by allowing surface water to infiltrate into the topsoil and by retaining enough plant-available water to sustain plant growth through drought periods. Vegetation serves other relevant purposes to the water

Table 2.4 Purposes of final-soil cover

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

balance and maintenance of the integrity of the landfill cover. The vegetation helps resist erosion and promotes evapotranspiration by:

a) Creating a leaf layer above the soil, reducing the kinetic energy of the rainfall and thereby decreasing erosion

b) Decreasing the wind velocity, thereby decreasing soil erosion

c) Decreasing the water runoff velocities

d) Minimizing soil crusting.

Heavy loams, characterized by high clay content and dense structure have excessive swell/shrink behaviour. These types of soils can often crack, allowing infiltration through the cover. However, the cracks close soon thereafter due to nature of these soils. Negative effects of soil covers may be expected if the upper layer is supposed to undergo aerobic degradation. A soil cover will decrease the diffusion of oxygen into the waste layer and thus decrease the composting rate. Instead, anaerobic decomposition of waste would occur causing high production of CH$_4$ which can cause the emission of landfill gas or in worst cases, cause soil erosion or explosion. Landfill gas contains components which are flammable and toxic and uncontrolled leakage of landfill gas which can lead to problems associated with explosive and asphyxiation hazards.

Besides that, the heavier the soil, the more adverse the effect expected. Use of heavy clayish soil as daily covers may at later stage cause heterogeneous water distribution in the landfill, and eventually perched water-tables in the waste or very dry zones below soils of low permeability. Positive effects of daily soil covers may be expected if the soil provides important buffer capacity to the landfill, avoiding low pH values inhibitory to methane formation and mitigating the CH$_4$ emissions. Table 2.5
Table 2.5 Advantages and disadvantages of various non-soil materials for final cover

<table>
<thead>
<tr>
<th>Material</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt</td>
<td>- Traditional used as hydraulic barrier</td>
<td>- Low tensile strength; needs geo-textile reinforcement</td>
</tr>
<tr>
<td></td>
<td>- Ductile and often chemically durable. Wide variety of water-based emulsions</td>
<td>- Need careful design and installation</td>
</tr>
<tr>
<td></td>
<td>- Available in panels or rolls</td>
<td></td>
</tr>
<tr>
<td>Industrial Wastes</td>
<td>- Abundant and cheap where available</td>
<td>- Many available only as less-desirable fine-grained materials</td>
</tr>
<tr>
<td></td>
<td>- Predictable chemistry; often inert to vapours/gases</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Ideal for drainage and load-bearing application</td>
<td></td>
</tr>
<tr>
<td>Geo-membranes</td>
<td>- Thin sheets take the place of thicker soil layers</td>
<td>- May be vapour-gas degradable</td>
</tr>
<tr>
<td></td>
<td>- Pre-formed as relatively large panels</td>
<td>- Requires careful installation</td>
</tr>
<tr>
<td></td>
<td>- Small leaks less serious than when used as liners</td>
<td>- Cannot be exposed to elements</td>
</tr>
<tr>
<td></td>
<td>- Very low permeability</td>
<td>- Low tensile strength</td>
</tr>
<tr>
<td></td>
<td>- Large body of geo-technical knowledge in application</td>
<td>- Uncertain life span under various in-place conditions</td>
</tr>
<tr>
<td>Geo-textiles</td>
<td>- Ideal for filtration, drainage, separation, reinforcement and armouring</td>
<td>- Limited to essentially secondary roles, in conjunction with use of soil</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Lack information on long-term performance</td>
</tr>
<tr>
<td>Soil-Cement</td>
<td>- Relatively low permeability</td>
<td>- Inflexible and brittle</td>
</tr>
<tr>
<td></td>
<td>- Can be formulated on site</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Difficult to utilize as major cover component</td>
</tr>
</tbody>
</table>

Source: McInerney (1983)

gives the advantage and disadvantages of using various non-soil materials for final cover.
2.16 Compost as Landfill Cover

Various kinds of compost comprise the most often tested biofilter filling (Wilshusen et al., 2004b, Powelson et al., 2006; Zeiss, 2006, Haubrichs and Widmann, 2006). According to Rozej & Stepniewski (2008), mature composts show higher microbial methane consumption relative to conventional soil, which can most probably be related to nutritional factors provided by the compost or to changes in the microbial activity. Moreover, physical factors such as the increased porosity, water holding capacity, or thermal insulation properties of compost seem to be responsible for effectiveness of CH$_4$ oxidation by compost. Based on Agnew and Leonars, 2003, Barlaz et al., 2004, Hilger and Humer, 2003, Humer and Lechner, 2001, Nikiema et al., 2005 Wilshusen et al., 2004, Perdikea et al., 2007, compost instead of soil was used as the basic material in their experiments because it is known to offer a higher CH$_4$ oxidation capacity due to its high organic matter, water holding capacity, and porosity. According to Humer and Lechner (2001), most of the referenced investigations show that a high CH$_4$ oxidation capacity could be found in porous, coarse and organic-rich substrates such as compost. According to investigation conducted by Humer and Lechner in 2001, ripe compost was a suitable substrate for methane oxidation. Compost also acts as a suitable fertilizer for vegetation growth on landfill further enhancing the stability of the landfill cover. In general, soil pH should be above 6. According to McBean et al (1995), suitable top cover to encourage vegetation growth should have pH in the range of 5 to 8. Compost has a pH of 6.35 which falls comfortably in the range indicated by the author. If the pH is over 8, necessary elements for plant growth may not be soluble and at pH of less than 5 may cause some elements to become toxic.

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

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{biomass} \]

Studies on methane oxidation depth in landfill have been extensively conducted. Fauziah and Agamuthu (2002) conducted Wheaton bottle trials using landfill cover soil at temperature ranging from 4°C to 35°C. Based on their results, trials conducted at 35°C recorded the highest CH\textsubscript{4} oxidation rate within 28 hours. The high oxidation rate could have been contributed by the suitable temperature (35°C) for optimum microbial growth.

The oxidation depth (active zone) is highly dependent on the availability and penetration level of O\textsubscript{2}. Nozhevnikova & Lebedev (1995) cited by Pawlowska (1999), observed oxygen penetration by diffusion even to a depth of one meter in a landfill experiment conducted in Poland. Lebedev et al., (1994) observed a very low methane oxidation rate in the top 25 cm layer of a landfill cover soil. The latter authors as well as Stein & Hettiaratchi (2001) who used the results of Lebedev et al., (1994) for modelling, explained this observation by the low concentration of CH\textsubscript{4} at this depth. An experiment conducted by Rozej & Stepniewski (2008) using sand amended with sewage sludge showed that highest methanotrophic activity was observed at 10cm depth in the sand. In the control column (without sewage sludge), the maximum CH\textsubscript{4} oxidation activity was noted at a depth of 60cm. Other authors have observed highest CH\textsubscript{4} oxidation rates at similar depths: e.g. 60cm (Pawloska,1999), 40-60cm (Lebedev et al., 1994), 46 cm ( Stein & Hettiaratchi, 2001 ) and 15-40cm (Visvanathan et al.,1999) dependent on the kind of soil.

The kind of soil is also an important determinant of CH\textsubscript{4} oxidation. Gebert et al. (2003) reported even 1000 times more methanotrophic bacteria in the biofilter filled with
mineral soil. Rozej & Stepniewski (2008) observed highest methane oxidation rate of 387 dm$^3$ m$^{-2}$ d$^{-1}$ in column with sewage sludge while Kightley et al. (1995) obtained in a range of 225 to 227 dm$^3$ m$^{-2}$ d$^{-1}$ using sand. Pawlowska (1999) observed 227 dm$^3$ m$^{-2}$ d$^{-1}$ using sand. Methane oxidation rate values obtained by de De Visscher et al. (1999) and Stein & Hettiarachchi (2001) using landfill cover were in the range of 256-447 dm$^3$ m$^{-2}$ d$^{-1}$.

Methane concentration is also an important factor that determines methane oxidation. In the study of Stein & Hettiarachchi (2001), the presence of CH$_4$ caused the methanotrophic bacteria to proliferate. In their landfill cover soils, 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 Hettiarachchi (2001).

Column experiments are aimed to determine the appropriate depth of biocover to be applied on landfills. In all the column experiment conducted by Rozej & Stepniewski (2008), a decrease in the CH$_4$ oxidation rate was observed after the soil cores had reached the maximum. Such an effect was also reported by Hilger et al. (1999), Visvanathan et al. (1999) and Stein & Hettiarachchi (2001). Wilshusen et al. (2004) conducted column experiment using leaf-based compost which exhibited the highest methanotrophic activity (590 dm$^3$ m$^{-2}$ d$^{-1}$) compared to MSW compost, Home Depot garden store compost and un-screened wood chips for the first 100 days. With time, the value gradually decreased and finally became equal to the activity level of the MSW and wood chip compost. The lowest value was observed in Home Depot compost. In soil layers with optimum ambient conditions (oxygen-methane ratio) for microorganisms, an oxidation horizon of 0.1 to 0.3m is usually formed. This horizon is where most of the active methanotrophic bacteria accumulate and the major methane oxidation processes take place.
Powelson et al. (2006) conducted column experiments using biofilter filled with compost made of garden waste (mainly leaves and tree branches) with expanded polystyrene pellets added. Methane volume supplied to biofilter of $375-750 \text{dm}^3 \text{m}^{-2} \text{d}^{-1}$ showed that the \( \text{CH}_4 \) 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 methane oxidation activity which began on Day 2. Pawlowska et al. (2006), Stein and Hettiaratchi (2001) reported that highest methane oxidation rate was noted around 66cm using landfill soils. Thomas et al. (2002) who used loamy sand indicated active zone at a depth 0-20cm from the surface. Scheutz and Kjeldsen (2004) used soil samples from Skellingsted Landfill, Denmark obtained an average oxidation rate of $70 \mu \text{g g}^{-1} \text{h}^{-1}$ at 60cm column height.

King (1990) has emphasized the significance of the methane oxidation process applied to reduce its emissions from wetlands to the atmosphere, while Borjesson & Svensson (1997) as well as Czepiel et al. (1996) have analysed the reducing effect of \( \text{CH}_4 \) oxidation on the emission of that gas from landfills.

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. Bender and Conrad (1995) found that, when a grain diameter decreased 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.

2.18 Kinetics of Landfill Gas
Several methods have been described for modelling landfill gas oxidation (Augenstein and Pacey, 1991; Popov and Power, 1999). According to Mor et al (2006), landfill gas formation models are not based on microbiological or biochemical principles, but more on a practical description of formation, as observed in laboratory experiments or in full-scale recovery projects. There are numerous experimental results which indicate that the kinetics of the CH$_4$ oxidation process can be described by the Michaelis-Menten equation originally introduced to describe enzyme kinetics. The Michaelis curve shape and kinetic parameters of the reaction ($V_{\text{max}}$ and $K_m$) mainly depend on the CH$_4$, concentration in the natural environment from whence the soil was sampled. Soils exposed to high CH$_4$ concentration like those taken from a landfill cover, rice fields and waterlogged areas are characterized by high methanotrophic activity and low affinity to CH$_4$ (high $K_m$). The situation is different in the case of soils exposed to the atmospheric concentration of CH$_4$. Their methanotrophic activity is low but they can oxidize CH$_4$ even if its concentration is insignificant. Such kinetics can be observed in forest, meadow and arable soils. Pawloska and Stepniewski (2006) used kinetics described by the Michaelis-Menten equation \(V = V_{\text{max}} \frac{1}{1+([K_m/C])}\) to study the kinetics of methane oxidation using column experiment with continuous flow of CH$_4$, where $V$ was the actual methane oxidation rate (m$^3$ m$^{-3}$ s$^{-1}$), $V_{\text{max}}$ is the maximum methane oxidation rate (m$^3$ m$^{-3}$ s$^{-1}$), $K_m$ was the Michaelis constant for CH$_4$ [%], $C$ is the CH$_4$ concentration [%]. Based on the kinetics described, Pawloska and Stepniewski (2006) found that the rate or reaction increased initially as the concentration of methane increases, until such time as the substratum is saturated. $V_{\text{max}}$ values obtained in a sand material exposed to high methane concentration ranged from $0.11 \times 10^{-3}$ to $0.86 \times 10^{-3}$ cm$^3$ kgdw$^{-1}$ s$^{-1}$ and they are similar to those obtained by Whalen et al. (1990) in a soil from the top of the landfill cover. These values were approximately one order of magnitude lower than the potential methanotrophic activity measured by Kightley et al., (1995) in coarse-grained sand taken from a landfill cover; by
Stein and Hettiaratchi (2001) in loam soil from a landfill cover, and by Gebert et al. (2003b) in crushed expanded clay material tested as a biofilter for landfill gas and equal to 6.49-7.29 X10^{-3} and 11.08 X10^{-3} cm^3 kg d^{-1}s^{-1}, respectively. For comparison, the $V_{\text{max}}$ values measured in forest soils were lower by several orders of magnitude, and varied between 4.9X10^{-6} and 56.8 X 10^{-6}cm^3kgdw^{-1}s^{-1} (Bender and Conrad, 1993; Whalen & Reeburgh, 1996; Benstead & King, 1997). A similar relationship for high concentrations of methane was observed by other authors (Whalen et al., 1990; Reeburgh, 1996; Bestead and King, 1997; Dammann et al., 1999; Gebert et al., 2003a). Also known is work (like Bender and Conrad, 1995, Roslev et al., 1997; Streese and Stegmann, 2003) pointing to methane oxidation reactions whose course is in line with first-order kinetics, the result being that the upper limit value for the studied range of CH$_4$ 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% CH$_4$. In contrast the saturation value in the experiment conducted by Pawloska and Stepniewski (2006) always exceeded 4 % (v/v) CH$_4$. $K_m$ values for CH$_4$ measured in field conditions or in conditions of a simulated landfill cover or biofilter given in a literature range between 0.08 and 2.9 (Whalen et al., 1990; Kightley et al., 1995; Bogner et al., 1997; De Visscher, 2004; Gebert et al., 2003a; Scheutz & Kjeldsen, 2004; Pawloska & Stepniewski, 2006).

The measured affinity for methane in forest soils is several orders of magnitude greater. The Michaelis constant found by Benstead & King (1997) was 0.8 X10^{-3} and by Whalen & Reeburgh (1996) was 9.9X10^{-3} % of CH$_4$. Comparison of kinetic parameters measured in waterlogged and forest soils of the boreal zone show that affinity for CH$_4$ in the first type of soils, exposed too high CH$_4$ concentration is about 10 times lower, and the $V_{\text{max}}$ about 1000 times higher (Whalen & Reeburgh, 1996).
The $V_{\text{max}}$ obtained in the experiment conducted by Pawloska and Stepniewski (2006) were in the range of $0.11 \times 10^{-3}$ to $0.86 \times 10^{-3}$ 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 landfill cover’, and by Gebert et al. (2003) in crushed expanded clay material tested as a biofilter for landfill gas, being equal to $6.49-7.29 \times 10^{-3}$, $6.2 \times 10^{-3}$ and $11.08 \times 10^{-3}$ 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 $0.88 \times 10^{-3}$ to $1.09 \times 10^{-3}$ cm$^3$ kg$^{-1}$ s$^{-1}$. For comparison, the $V_{\text{max}}$ values measured in forest soils were several orders of magnitude lower, and varied between $4.9 \times 10^{-6}$ and $56.8 \times 10^{-6}$ cm$^3$ kg$^{-1}$ s$^{-1}$ (Bender and Conrad, 1993; Whalen and Reeburgh, 1996; Benstead and King, 1997). 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). Table 2.6 summarizes kinetic parameters for CH$_4$ oxidation obtained by various authors.

Table 2.6: Summary of kinetic parameters for CH$_4$ oxidation

<table>
<thead>
<tr>
<th>Authors</th>
<th>Biocover</th>
<th>Range of CH$_4$ concentration (%v/v in gaseous phase)</th>
<th>$V_{\text{max}}$ (units)</th>
<th>$K_m$ for CH$_4$(% v/v in gaseous phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whalen et al. (1990)</td>
<td>Composite of soil from landfill cover</td>
<td>$1.7 \times 10^{-4} - 1.0$</td>
<td>$0.88- 1.09 \times 10^{-3}$</td>
<td>0.18</td>
</tr>
<tr>
<td>Kightley et al. (1995)</td>
<td>Coarse sand soil from landfill cover</td>
<td>$0.05 - 5.0$</td>
<td>$6.49 \times 7.29 \times 10^{-3}$</td>
<td>2.35</td>
</tr>
<tr>
<td>Study</td>
<td>Description</td>
<td>Period</td>
<td>Concentration (CH₄)</td>
<td>Weight (g)</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------------------------------------</td>
<td>--------</td>
<td>---------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Bogner et al. (1997)</td>
<td>Clay topsoil from landfill</td>
<td>0.016-8.0</td>
<td>4.65 X 10⁻³</td>
<td>2.54</td>
</tr>
<tr>
<td>De Visscher et al. (1999)</td>
<td>Soil with agricultural origin</td>
<td>0.005-3.0</td>
<td>1.5 -16.8 X 10⁻³</td>
<td>0.15-0.5</td>
</tr>
<tr>
<td>De Visscher et al. (1999)</td>
<td>Sandy loamy cover soil from landfill</td>
<td>&lt;2.0</td>
<td>0.52-11.27 X 10⁻³</td>
<td>0.08-0.5</td>
</tr>
<tr>
<td>Stein and Hettiaratchi (2001)</td>
<td>Loam from landfill cover</td>
<td>&lt;10.0</td>
<td>6.2 X 10⁻³</td>
<td>0.75</td>
</tr>
<tr>
<td>Gebert et al. (2003)</td>
<td>Crushed expanded clay in biofilter</td>
<td>0.2-10.0</td>
<td>11.08 X 10⁻³</td>
<td>1.1</td>
</tr>
<tr>
<td>Pawloska and Stepniewski (2006)</td>
<td>Coarse sand purged by 99% CH₄</td>
<td>1.0-16.0</td>
<td>0.11-0.86 X 10⁻³</td>
<td>0.6-2.9</td>
</tr>
<tr>
<td>Bender and Conrad (1993)</td>
<td>Forest cambisol</td>
<td>0.02 X 10⁻⁴ - 0.03</td>
<td>2.23 X 10⁻⁶</td>
<td>2.2 X 10⁻⁴</td>
</tr>
<tr>
<td>Whalen and Reeburgh (1996)</td>
<td>The Alaskan soil - Bog - Forest</td>
<td>1.7 X 10⁻⁴ - 0.12</td>
<td>1.48 X 10⁻³ , 4.9 -56.8 X 10⁻⁶</td>
<td>8.4 X 10⁻² , 2.9-9.9 X 10⁻³</td>
</tr>
<tr>
<td>Benstead and King (1997)</td>
<td>Forest soil</td>
<td>1.7 X 10⁻⁴ -0.1</td>
<td>6.2 X 10⁻⁶</td>
<td>0.8 X 10⁻³</td>
</tr>
</tbody>
</table>

### 2.19 Biocover Performance Index

Biocover Performance Index (BPI) is aimed to evaluate the efficiency of a biocover material. Period of complete methane oxidation is taken into account to determine BPI. BPI is inversely proportional to the period of methane oxidation. Other parameters which influence BPI are the methane concentration oxidized and the weight of the Biocover material used.
BPI may also be used to assess methane oxidation capacity of different Biocover height in column experiments.

Chapter 3: Material and Methods

3.1 Experimental Design

In order to meet the objectives of this study, a multilevel factorial design was conducted using compost, black soil and compost residue. The experimental design focused on evaluating the interactions between the variables affecting CH$_4$ oxidation in the Biocover, namely: temperature, pH and moisture content.

The chosen variables were to stimulate various environmental conditions that might affect the CH$_4$ oxidation.

3.2 Experimental Materials

Compost was obtained by composting a mixture of 75% grass clippings and 25% cow dung. The grass clippings and the cow dung were uniformly mixed to ensure the even distribution of microbes for optimum composting. Heap method was used and composting were carried out under a shade. The heap was 0.5 m high and 1m wide at the base. Water was added to the compost mixture to increase the moisture level in a range of 50-60%. Aerobic
condition is maintained by manual turning of composting mixture with 1 turn daily for the first 8 days and 1 turn in 2 days thereafter. Temperatures of the composting mixture were measured daily using electronic thermometer model Oregon Scientific SA880SSX. Black soil was obtained from a local nursery while compost residue was obtained from a local composting plant that comports plant waste comprised of branches and tree barks.

Figure 3.1: Compost residue, black soil and compost

The Biocover materials were sieved using 5mm mesh size grid to provide large surface area for CH₄ oxidation. Moisture content was determined gravimetrically by oven-drying 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 in duplicates according to standard procedures.

3.3 Experimental Methods

The experiments were conducted in two phases which are:

Phase I: Wheaton bottle experiments
Phase II: Column Reactor experiments

3.3.1. Phase I: Wheaton bottle experiments

Phase I acts as the preliminary stage to investigate the Biocover performance for CH$_4$ oxidation. Wheaton bottles, with 125mL total volume each were used to conduct the batch experiments. After placing 20g of material, the bottles were sealed with rubber septum and aluminium seal to ensure gas tight. Afterwards, 15mL of air from the headspace were withdrawn using a syringe and replaced with 10mL of O$_2$ gas (99.8% purity) and 5mL of CH$_4$ (99.9% purity). These amounts provided a mixing ratio of approximately 4% of CH$_4$ (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 quadruplets for every variables and parameters studied. The concentrations of CH$_4$, CO$_2$ and O$_2$ in the headspace were measured daily using Gas Chromatography model Shimadzu 8A.

Figure 3.2: Injecting out gas sample from Wheaton Bottle (a) Injection of gas into GC
3.3.2 Phase II: Column Reactor Experiments

Phase II of the experiment represented the next step in determining suitable height of Biocover to be applied in landfills for optimum bioremediation of CH$_4$. All the column experiments were conducted at 24°C. One-metre high columns were fabricated using 10mm thick PVC with an internal diameter of 0.14m. Sampling ports were embedded in the columns at an interval of 0.1m to enable gas sampling at different heights. Biocover materials are placed into the columns and the top of the column was sealed with 5mm thick plexiglass to ensure air-tight. At the bottom of the column, 4% CH$_4$ gas (v/v) (99% purity) is introduced using a flow meter through an inlet. Introduction of CH$_4$ at the bottom represented the movement of methane gas from the bottom of the landfill. Gas sampled at each port was analysed using gas chromatography (GC) for CH$_4$, O$_2$ and CO$_2$. Column reactor experiments were run in duplicates for all column heights (10-100cm) studied. Column reactor experiments were conducted using fresh Biocover material and mixture of fresh and used Biocover material. Columns were filled with entirely fresh material for every height for
column experiment using fresh compost. Utilized Biocover materials were entirely removed before fresh Biocover materials were filled in the column for a different column height experiments. On the other hand, for column reactor experiments using a mixture of fresh and used Biocover materials, fresh Biocover material (10cm height) was added to the used material in the columns to increase the height without removing the utilized Biocover material in the columns.

3.4 Biocover Performance Index

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

\[
BPI = \frac{(\text{CH}_4)_0 - (\text{CH}_4)_n}{W \times N} \quad \text{(Equation 1)}
\]

where

\[
(\text{CH}_4)_0 = \text{Initial concentration of CH}_4 \ (\text{mL})
\]

\[
(\text{CH}_4)_n = \text{concentration of CH}_4 \text{ at time n (mL)}
\]

\[
W = \text{amount of Biocover (g)}
\]

\[
N = \text{time taken for complete methane oxidation (hours)}
\]

3.5 Statistical Analysis

The software package, SYSTAT 11 was used to statistically analyse the performance of the Biocover. Analysis on least square regression was conducted to get determination coefficients (R^2) and adjusted determination coefficient (R^2_a) values.
3.6 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):

\[ R_p = \frac{R_{\text{max}}}{1 - (K_M / C)} \]  
(Equation 2)

where

- \( R_p \) = potential methane oxidation rate (mL/d)
- \( R_{\text{max}} \) = 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:

\[ R_p = \frac{R_{\text{max}}}{1 - (K_M)} \]  
(Equation 3)

3.7 Control Experiments

To check if any disappearance of methane could be due to non-microbial processes, Biocover materials were autoclaved before tested in batch incubation and column experiments.
Chapter 4: Results and discussion

4.1 Properties of study materials

The physical properties of the Biocover materials used are indicated in Table 4.1

Compost has the highest moisture content among the three samples used. Ability of compost to retain water is important to sustain microbial population for CH₄ oxidation. According to Pawloska (2008), CH₄ oxidation becomes limited if there is lack of water, as it causes a physiological stress to methanotrophs. On the other hand, an excess of water obstructs diffusion of CH₄ and O₂ as the diffusion rate of these gases is 10⁴ times slower in water than in air (Boeckx et al., 1996). Humer & Lechner (1999) found that CH₄ emission was controlled by soil moisture content in an experiment conducted at a small landfill in Belgium. Wilshusen et al. (2004), Barlaz et al. (2004), Hilger and Humer (2003) have indicated that compost can offer a good water-holding capacity to optimize CH₄ oxidation.

The final carbon to nitrogen ratio (C: N) of the compost, which was 16.9, indicates that it was a mature substrate. A high maturity of compost materials is crucial for efficient CH₄ consumption, as was shown in previous laboratory tests (Boeckx et al., 1996). Compost residue has the highest C/N ratio with 17.25 due to high cellulose in the garden waste. The C/N ratio obtained by Mor et al. (2006) for the garden waste compost was in the range of 11.2 to 26.9. All the materials tested in this study has C: N ratio which falls in the range obtained by Mor et al. (2006).

Black soil is the most acidic and compost being least acidic. Suitable pH will favour a

<table>
<thead>
<tr>
<th>TEST PARAMETER</th>
<th>RESULTS</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Properties of Biocover Materials
<table>
<thead>
<tr>
<th></th>
<th>Compost</th>
<th>Black Soil</th>
<th>Compost residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture Content( % )</td>
<td>61.7</td>
<td>43</td>
<td>39</td>
</tr>
<tr>
<td>pH</td>
<td>6.35</td>
<td>6.02</td>
<td>6.12</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>52</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>Total Carbon( % )</td>
<td>20.30</td>
<td>16.20</td>
<td>20.70</td>
</tr>
<tr>
<td>Total Nitrogen (%)</td>
<td>1.20</td>
<td>1.10</td>
<td>1.20</td>
</tr>
<tr>
<td>Carbon : Nitrogen ratio</td>
<td>16.9</td>
<td>14.7</td>
<td>17.3</td>
</tr>
<tr>
<td>Total Potassium(ppm)</td>
<td>13.75</td>
<td>20.73</td>
<td>14.29</td>
</tr>
<tr>
<td>Total Boron(ppm)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Calcium(ppm)</td>
<td>32.71</td>
<td>38.55</td>
<td>36.4</td>
</tr>
<tr>
<td>Iron(ppm)</td>
<td>22.89</td>
<td>30.47</td>
<td>31.84</td>
</tr>
<tr>
<td>Manganese(ppm)</td>
<td>4.20</td>
<td>3.29</td>
<td>7.16</td>
</tr>
<tr>
<td>Magnesium(ppm)</td>
<td>4.65</td>
<td>8.83</td>
<td>5.55</td>
</tr>
<tr>
<td>Sodium(ppm)</td>
<td>5.85</td>
<td>6.68</td>
<td>5.78</td>
</tr>
<tr>
<td>Copper(ppm)</td>
<td>0.51</td>
<td>2.71</td>
<td>3.20</td>
</tr>
<tr>
<td>Total Phosphorus(ppm)</td>
<td>600</td>
<td>700</td>
<td>600</td>
</tr>
<tr>
<td>Zinc(ppm)</td>
<td>1.42</td>
<td>0.65</td>
<td>1.61</td>
</tr>
<tr>
<td>Lead(ppm)</td>
<td>&lt;0.06</td>
<td>&lt;0.06</td>
<td>&lt;0.06</td>
</tr>
<tr>
<td>Cadmium(ppm)</td>
<td>&lt;0.01 m</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Mercury(ppm)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Chromium(ppm)</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Nickel(ppm)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Aluminium(ppm)</td>
<td>1.53</td>
<td>1.85</td>
<td>1.76</td>
</tr>
<tr>
<td>Total Sulphur(ppm)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>
pH of any compost should be neutral to slightly acidic (Moldes et al., 2007). The methanogenic bacteria operate efficiently only within a narrow pH-range of 6-8 (Zehnder et al., 1982). All the materials tested in this study falls into the range proposed by Zehnder confirming its suitability for CH$_4$ oxidation.

Compost has the highest organic matter as compared to other materials used. According to Chanton and Liplay (2000), CH$_4$ oxidation is higher in organic-rich soils. Christensen et al. (1996) reported that organic matter serves mainly as a carrier for microorganisms and improves the soil properties and substrate. The presence of heavy metal in all the Biocover materials was negligible as their concentrations were very low. Presence of heavy metal in compost can affect the activity of the methanotrophs.

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, compost and compost residue have the same concentration of N which is 1.20ppm while black soil contained slightly lower amount of N. N is an essential parameter in determining the fertility of a soil. Compost has the lowest Cu concentration compared to other Biocover materials tested. According to Kjeldsen (1997) and Tsien et al., (1989), CH$_4$ degradation rates were higher when Cu concentration was very low, as methanotrophs only express sMMO (soluble CH$_4$ monooxygenase enzyme which facilitates CH$_4$ oxidation) at low copper concentration.

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. This was due to simple substrate competition as higher energy yielded by sulphate reduction favours the growth of sulphate reducers instead of methanotrophs (Zehnder et al., 1982).
4.2 Batch experiments

Results of the quadruplet Wheaton bottle batch experiments were averaged and graphs were tabulated to study CH$_4$ 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 CH$_4$ oxidation compared to black soil (7 days) and compost residue (10 days). Oxygen gas was utilised to oxidize CH$_4$ to carbon dioxide and the presence of water droplets on the inner surface of the Wheaton bottle indicated that water was a by-product of CH$_4$ oxidation.

Compost took the shortest acclimatization period (1 day) compared to black soil (4 days) and compost residue (6 days) as depicted in Figure 4.1. 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 to provide suitable conditions for methanotrophs growth (Christensen et al., 1996). By day 1, compost oxidized almost 18% of the initial CH$_4$ injected. Black soil and compost residue took 2 and 4 days respectively to attain the same 18% CH$_4$ oxidation rate. This clearly indicates the ability of compost to facilitate speedier CH$_4$ oxidation rate compared to other Biocover material tested in this study.

Black soil took longer time for complete CH$_4$ reduction (7 days) compared to compost (Figure 4.1). This could be due to its acidic soil condition which inhibits the methanotrophic activity in black soil. Pawloska (2008) has 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. Another possible reason for lower CH$_4$ oxidation capacity in black soil was lower moisture content (43%) compared to compost (61.7%) Boeckx et al. (1996).
indicated that water content widely regulates the activity of methanotrophic bacteria. They found that the 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). There was a
sharp increase in CH$_4$ consumption between days 4-6 for black soil which indicated high methanotrophic activity. This could be due to an increase in moisture level in the Wheaton bottles containing black soil as water was a by-product of CH$_4$ oxidation. Water produced from the oxidation process could have contributed to higher moisture content of black soil in the Wheaton bottles. An increase in moisture level could significantly increase CH$_4$ oxidation rate (Whalen et al., 2001). Another plausible reason for high CH$_4$ oxidation from day 4-6 could be the high degree of acclimatization by methanotrophs which sped CH$_4$ oxidation rate from day 4 onwards.

Compost residue took the longest period (11 days) for complete CH$_4$ oxidation. There was a steady decrease in CH$_4$ concentration from day 1 to day 6. This period (day 1-6) indicated rather longer acclimatization phase compared to compost or black soil. Longer acclimatization phase in compost residue could have been contributed to its low moisture content which inhibits microbial activity (Barlaz et al., 2004). Furthermore, compost residue has the lowest content of organic matter compared to other Biocover material tested in this study. The deficiency of organic matter could have contributed to overall low CH$_4$ oxidation capacity in compost residue. According to Christensen et al. (1996), organic matter significantly contribute to CH$_4$ oxidation as it served as a carrier for microorganisms and improves the soil properties, substrates and also a prerequisite to the build-up of methanotrophic biomass. Higher methanotrophic activity was only observed from day 6 to day 9 in compost residue which was much later than the time recorded by compost or black soil for optimum CH$_4$ oxidation.

Similar experiment was conducted by Perdikea et al. (2007) using garden waste compost, but with higher amount of CH$_4$ (5%) at laboratory temperature of 22°C. Based on their results, CH$_4$ was completely oxidised only on day 6 compared to day 4 in this study. The possible explanation for longer CH$_4$ oxidation period could simply be due to the higher
CH₄ concentration and incubation temperature used in the study conducted by Perdikea et al. Although, Perdikea et al 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 the 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. In addition, Whalen et al. (1990) has reported that CH₄ oxidation rate nearly doubled when incubation temperature was increased from 15 to 25°C while low temperature slows down methanotrophs activity. 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. Fauziah and Agamuthu (2002) who conducted similar batch incubation using landfill cover soil reported that CH₄ oxidation was the fastest (within 28 hours) at 35°C. Similarly, findings by Humer and Lechner (2001) recorded that at temperature 35°C, methanotrophic activity was the highest compared to other incubation temperature studied (15-35°C). These findings further support the results obtained by Muna and Leta (2008). Suitable temperature decreases the acclimatization period of the methanotrophs thus speeding CH₄ oxidation process (Pawloska, 2008).

The sharp fall in CH₄ between day 1 and 3 (in compost), day 4 and 6 (in black soil) and day 6 and 8 (in compost residue) was an indicative of active methanotrophic activity in compost after acclimatization period. Perdikea et al. (2007) observed sharp fall of CH₄ between day 3 and 5 in batch incubation conducted using garden compost while Muna and Leta (2008) between 2-12 hours of incubation using yard waste. As mentioned earlier, the
difference in CH₄ concentration and temperature used by other authors could be the possible reasons for the variation in results obtained in this study. Peak CH₄ oxidation occurred between day 2 and day 3 compared to black soil which only occurred between day 4 and day 5 and compost residue between day 5 and day 6 in this study. Optimum CH₄ oxidation in compost started off earlier than other Biocover materials due to its high initial microbial content. This shows that compost has high capacity for speedier CH₄ oxidation. Similar results were obtained by Thomas et al. (2002) using loamy sand in which peak CH₄ oxidation began on day 2. There were no changes in the Wheaton bottles containing sterilized Biocover material indicating that the methanotrophic activity was the main mechanism for CH₄ oxidation.

Although the condition in Wheaton bottles containing compost, black soil and compost residue was anaerobic by the end of day 2, 6 and 7 respectively, CH₄ reduction still occurred but in a slower rate. This could be explained by the unique adaptation of methanotrophs in anaerobic conditions. Methanotrophs are obligate aerobes; they are able to conduct CH₄ oxidation even at low O₂ concentration (Pawloska, 2008). The slow rate in CH₄ oxidation was obviously due to lack of O₂ (substrate in CH₄ oxidation activity). The increase in percentage of CO₂ correlates to the theoretical aspect of CH₄ oxidation. CH₄ was completely oxidized by day 4, 7 and 11 for compost, black soil and compost residue respectively and no CH₄ was detected in all the Wheaton bottles thereafter. The same condition (absence of CH₄) prevailed till day 15. CO₂ however, increased even after the completion of CH₄ oxidation with simultaneous decrease of O₂. Similar results were obtained by Perdikea et al. (2008) and Charlotte & Kjeldsen (2000). In both their experiments, increase of CO₂ and decrease of O₂ was observed after complete CH₄ oxidation in the Wheaton bottles. The possible reason for this phenomenon could be due to 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 as well such as fungi and bacteria (Wilshusen et al., 2004) besides methanotrophs. Scheutz & Kjeldsen (2004) has reported that various kinds of organic components are degraded particularly, components with halogenated combinations which could release CO\textsubscript{2} even after CH\textsubscript{4} oxidation in compost and most soils.

Lag phases were never observed in this study indicating that the microbes were well adapted to oxidizing CH\textsubscript{4}. Charlotte and Kjeldsen (2000) who conducted batch incubation trials using landfill soil from Denmark also did not observe any lag phases in their experiments. This could be due to presence of significant population size of methanotrophs and fast acclimatization of these microbes in highly exposed landfill soils. According to Reeburgh et al. (1993), soils exposed to high CH\textsubscript{4} concentrations such as landfill cover soils has higher capacity in CH\textsubscript{4} oxidation due to fast acclimatization process. 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 methanotrophs growth, thus increasing the acclimatization period and significantly contributing to longer lag phase.

From Figure 4.2, compost had the highest speed of CH\textsubscript{4} oxidation with slope gradient of 27.55 compared to black soil (slope gradient of 16.52) and compost residue (slope gradient 12.08). Slope gradient of compost was 1.67 times higher than black soil and 2.28 times higher than compost residue. Slope gradients obtained indicated that compost has the highest CH\textsubscript{4} oxidation rate compared to other Biocover materials tested. Perdikea at al. (2008) obtained lower slope gradient (15.63) for CH\textsubscript{4} oxidation using garden waste compost indicating a lower CH\textsubscript{4} oxidation capacity compared to compost and black soil used in this study. The difference could be attributed by the dissimilarity of incubation temperature and CH\textsubscript{4} volume used in this study compared to experiments conducted by Perdikea et al. (2008).
Highest bacterial colony counts were observed in compost followed by black soil and compost residue (Figure 4.3). High organic content (52%) in compost favoured the growth of bigger population of microbes in compost. Christensen et al. (1996) reported that compost is rich in organic matter and provide a satisfactory supply of nutrients for high microbial growth. Besides that, suitable moisture content (61.7% w/w) and very low copper (0.51 ppm) concentration found in compost provides an optimum condition for microbial growth in compost. Einola et al. (2007) reported that soil moisture content of 60% w/w was most suitable for optimum methanotrophic activity. Therefore, highest microbial growth in compost in this study can be explained by the its suitable moisture content which provided an optimum condition for microbial growth. Bacterial colony counts in black soil was almost double of compost residue. Higher moisture content and organic matter in black soil could be the reason for the difference. Compost residue provided the least favourable conditions for microbial growth as it recorded the lowest bacterial colony counts. Its low moisture content and higher copper concentration could have inhibited the growth of larger microbial population size.
4.3 Bioreactor column experiments

Column reactor experiments marked an advance stage in \( \text{CH}_4 \) mitigation studies aimed to determine suitable Biocover height for landfill application. In this study, column experiments were conducted for compost and black soil as these Biocover materials exhibited higher \( \text{CH}_4 \) oxidation rate compared to compost residue in Wheaton bottle experiments. Column experiments were conducted at laboratory temperature of 25°C with moisture content of 60 \%v/v. The results obtained for compost and black soil varied markedly although same experimental conditions (temperature: 25°C and moisture content: 60\%v/v) were used.

4.3.1 Column experiment using compost

Column experiment using compost exhibited higher rate of \( \text{CH}_4 \) oxidation for all heights tested compared to black soil. Time taken for complete \( \text{CH}_4 \) oxidation varied at different compost heights (Figure 4.4). From the column experiments conducted for compost
height ranging from (0-100cm), 60cm height proved to be the best height as it took only 4 days for complete CH$_4$ oxidation.

The column height of 10cm took the longest time (18 days) for complete CH$_4$ oxidation. Bacterial colony counts performed on the 10cm height compost indicated that it contained the lowest colony counts compared to other heights (Figure 4.5(a) and (b)). Lack of Biocover materials which means lack of nutrients could have attributed to the low colony counts at 10cm height. Therefore, it seemed logical that 10cm height took the longest period to complete CH$_4$ oxidation. Authors such as Muna and Leta (2008), Perdikea et al. (2007) and Pawloska (2008) who conducted column experiments using compost also obtained minimum CH$_4$ oxidation capacity at 10-15cm column heights which could be due to lack of compost. However, as the Biocover height was increased, period for CH$_4$ oxidation reduced indicating enhancement in methanotrophic activity. This could simply be due to increase of nutrients found in Biocover materials for methanotrophs to thrive in. Bacterial colony counts also showed a steady increment as column height was increased. Column heights of 80cm to 100 cm took similar period for CH$_4$ oxidation which was 7 days. This clearly showed that 60cm height column was
Figure 4.4: Time taken for complete CH$_4$ oxidation at different Biocover heights for compost sufficient for optimum CH$_4$ oxidation, and any addition in height thereafter did not increase CH$_4$ oxidation, but it will increase the cost of the cover material in real situation. Highest CH$_4$ oxidation capacity at 60cm column height could be due to the distribution pattern of microbes along the column (Figure 4.6).

Figure 4.5: Bacterial colony counts at different column heights for compost
Although, more bacterial colonies were detected at 0-30cm from the surface (active zone) of the 60cm height compost, a reasonable amount of colony counts were recorded from sampling ports below 30cm too.

This explains the overall speedy CH$_4$ oxidation of 60cm column. Pawlowska et al. (2006) and Stein & Hettiaratchi (2001) reported that highest CH$_4$ oxidation rate was noted around 66cm using landfill soils and garden waste compost respectively. Location and the horizon of active zone (range for highest CH$_4$ oxidation) (Figure 4.6) varied at different biocover heights. At all heights, the active zones were found to be situated closer to the surface of the compost. This indicated active methanotrophic activity closer to the surface of
Biocover materials as there were higher oxygen concentration at the surface. Pawloska & Stepniewski (2006), Perdikea et al. (2007) and Muna & Leta (2008) also found active zones located closer to the top surface of the cover material in the columns. They also indicated the abundance of $O_2$ at the top surface of the cover as the reason for active zone location. Similarly, Humer and Lechner (1999) reported high methanotrophic activity on the surface soil of landfill cover due to aerobic condition (presence of $O_2$).

![Active oxidation zone range (cm) for compost](image)

However, when column height was increased to 70cm, 80cm, 90cm and 100cm, the colony counts at deeper parts of the columns decreased. As more space in the column was being taken by the soil, the free space occupied by oxygen decreased which inhibited $CH_4$ oxidation in the column. Another possible reason would be longer time taken for oxygen to diffuse into the deeper zones of the column from the surface for higher column heights. Perdikea et al. (2007) also observed decreased $CH_4$ oxidation rate as column height was increased above 66cm. According to him, higher column height decreased $O_2$ availability in the columns. It was obvious that active zone shifted upwards as the height of Biocover materials in the columns were increased. Similar trend was observed by Pawloska and Stepniewski (2006) who reported the shifting of active zone towards the surface of the soil as
column height was increased. This could be explained by higher O₂ availability which favoured methanotrophs growth at the soil surface. Low colony counts in deeper zones at column height > 60cm is due to lack of oxygen permeability into deeper zones. At all column heights, the active zone were 0-30cm deep from the surface of the compost. On the other hand, Thomas (2002) conducted column experiments using loamy sand indicated active zone were at a depth 0-20cm from the surface. This shows that compost has a wider range of active zone compared to loamy sand used by Thomas (2002).

Changes in O₂ and CO₂ trend were similar for all sampling ports for every column heights tested. Figure 4.7 shows oxygen profile at all sampling ports of 60cm column height. Oxygen concentration at the top portion of the compost (40-60cm) was detected in much higher concentration compared to the bottom portion of the soil (0-30cm). This indicated O₂ diffusion was faster at the top layer of the compost compared to bottom part of the column. It was clear that more O₂ could be present in the empty space (60-100cm) of the column which was not filled with compost. The aerobic condition significantly sped up CH₄ oxidation rate at the top 30cm of the compost in the 60cm height column. Oxygen availability decreased at all sampling ports as incubation period increased indicating oxidation process. Availability of oxygen was one of the factors which allowed a more rapid CH₄ oxidation. Schnell & King (1995) have found that a reduction of O₂ concentration from the atmospheric value reflected a decline of the forest soil methanotrophic activity.
Figure 4.7: Concentration of O$_2$ for 60cm column height

Figure 4.8 illustrates concentration of CO$_2$ at sampling ports along column height of 60cm height. Production of CO$_2$ was the highest at 60cm sampling port with the highest slope gradient of 4.18 as compared to other sampling ports (slope range 2.26-2.98). Increase in CO$_2$ correlates well with the reduction of O$_2$.

Figure 4.8: Concentration of CO$_2$ for 60cm height column
The microbial count for compost varied for different column height. Bacterial colony counts at 60cm were the highest among all the Biocover height. At lower heights (10cm– 40 cm), colony counts were very low due to limited Biocover material (organic matter) for methonotrophs growth. Colony counts at column height of 70 and 80cm were lower than at 60cm although Biocover material was not the limiting factor. Hence, lack of oxygen could be the possible reason as more space has been filled with compost in the columns. Although the colony counts were relatively high in column heights of 70-100cm, CH\textsubscript{4} oxidation rate was much lower than of 60cm. This indicated that the lack of oxygen impedes methanotrophic activity.

4.3.2 Column rector experiments (used compost mixed with fresh compost)

Column experiments using mixture of used+fresh compost revealed much higher CH\textsubscript{4} oxidation capacity (Figure 4.9 (a) and (b)) compared to columns with entirely fresh compost. Graph of overall CH\textsubscript{4} oxidation capacity for mixture of used+fresh compost has higher slope gradient (4.374) compared to column experiments using fresh compost only (2.093). High oxidation capacity of used+fresh combination

![Graph](image)

Figure 4.9 (a): Results obtained from columns with mixture of used and fresh compost
compost could be due to existing population of methanotrophs in the used compost which was pre-incubated with CH$_4$ compared to fresh compost which were not exposed to CH$_4$ before. When fresh compost was added to the used compost, methanotrophs (in used compost) which has already acclimatize to CH$_4$ rich conditions reproduce even more rapidly resulting in higher CH$_4$ oxidation capacity. Bacterial colony counts conducted in the columns with the mixture of used+fresh compost also showed a clear increasing trend of microbial population along the column height (Figure 4.10). Bykova et al. (2007) noted an increase in CH$_4$ oxidizing capacity by $10^5$ times and a twofold increase in the total number of methanotrophs in an arable soil pre-incubated with CH$_4$. Methanotrophic capacity measured in soil taken out of landfill cover increased by more than fourfold with an increase of CH$_4$ concentration from 1.7 to 84000 ppm (Bogner et al., 1997) due to prior acclimatization of methanotrophs in the landfill cover. Fauziah et al. (2006) reported higher percentage of CH$_4$ oxidation in landfill cover soil. Landfill cover soil could possibly contain more microorganisms due to prior acclimatization of methanotrophs. Bacterial colony counts in used+fresh compost was relatively high compared to fresh compost. Slope gradient for
bacterial colony counts for used+fresh compost (5.374) was 6.7 times higher than slope gradient of fresh compost (0.794). Tremendously high performance of used+fresh compost was contributed by the high rate of microbial growth. Column height of 90cm used compost + 10cm fresh compost demonstrated the fastest CH$_4$ oxidation period which agree well with highest bacterial colony counts at this height. Figure 4.11 depicts the comparison of total bacterial colony counts for columns of used+fresh compost and columns with entirely fresh compost. It is evident that used+fresh compost has far more higher total bacterial colony counts compared to fresh compost.

![Figure 4.10: Total bacterial colony counts for used+fresh compost](image)

![Figure 4.11: Comparison of total bacterial counts for used+fresh compost and fresh compost](image)
4.3.3 Column experiments using Black soil

Column experiments conducted for black soil showed a slower pace in CH$_4$ oxidation rate compared to compost. Slope gradient for column experiment using black soil was 4 times lower than column experiment using compost. In general, black soil took longer period to oxidize CH$_4$ at all column height (Figure 4.12). This could be due to low moisture content in black soil compared to compost which can impede CH$_4$ and oxygen diffusion rate (Pawloska, 2008). Longest CH$_4$ oxidation period was recorded at 10cm column height which took 25 days. Black soil took exactly 1 week longer than compost to oxidize the same amount of CH$_4$ at the similar column height. Lower bacterial colony counts in black soil (Figure 4.13(a) and (b)) could have contributed to the delay in CH$_4$ oxidation. Black soil exhibited similar trend of CH$_4$ capacity as compost when column height was increased. CH$_4$ oxidation capacity in black soil increased as column height increased till an optimum height was reached. Column height 80 cm proved to be the best as it took the shortest period for CH$_4$ oxidation (8 days). The shortest period taken by black soil (8 days) was twice higher than compost which took only 4 days as for the shortest oxidation period at column height of 60cm. Furthermore, optimum column height of black soil was 20cm higher than the of compost (60cm). One possible reason for this difference could be the variation in methanotrophs population in both the Biocover materials tested. Colony counts recorded at 80cm black soil height was two fold lower compared to colony counts at 60cm height compost. Column height of 90 and 100 cm showed a slower pace in CH$_4$ oxidation rate. This clearly indicated that 80cm height of black soil was the optimum height and any increase of height thereafter failed to enhance CH$_4$ oxidation. In contrast, increase of height after 80cm reduced CH$_4$ oxidation rate. This could be due to reduction in availability of O$_2$ in higher column heights as more space of the column were now filled with black soil. Gebert et al. (2006) conducted column reactor experiment using black soil with continuous flow of CH$_4$ at a rate of 0.47g m$^{-2}$h$^{-1}$. Based on
their results, black soil exhibited lower CH$_4$ oxidation capacity than other materials tested (garden waste compost and landfill cover). Black soil used by Gebert et al. (2006) also had lower moisture content (40.2%) compared to other materials tested. Microorganisms were not so active at low moisture content due to lack of either sufficient water or lowered air porosity (Gebert et al., 2006).

![Figure 4.12: Time taken for complete CH$_4$ oxidation at different Biocover heights for black soil](image)

![Figure 4.13(a): Total bacterial colony counts at different column heights for black soil](image)
Bacterial colony counts conducted for black soil correlated well with the CH$_4$ oxidation rate for each column height. In average, bacterial colony counts for black soil were nearly half of the colony counts in compost. This could also explain the low CH$_4$ oxidation rate in black soil compared to compost as there were less methanotrophs to conduct CH$_4$ oxidation.

The highest bacterial colony counts at 80cm contributed to highest CH$_4$ oxidation capacity at this height. Colony counts at column height 90 and 100cm were quite similar, which explained the similarity in CH$_4$ oxidation period for both the heights. The same oxidation period (9days) were observed in column experiment using compost at 50cm height. Bacterial colony counts at column height of 90 and 100cm for black soil were similar to colony counts obtained at 50cm compost height. It was evident that microbial population plays an important role in determining CH$_4$ oxidation rate of Biocover materials. Highest bacterial colony counts were detected at 10cm depth from the surface for all column heights studies of black soil. The findings also correlated with faster CH$_4$ oxidation at the surface due to high availability of O$_2$. Figure 4.14 illustrates the actize zone recorded for black soil.
Therefore, it can be concluded that active zone for black soil was located at top 10cm of black soil height tested. In comparison, compost had a wider range of active zone in most of its column height. Column height of 60cm compost exhibited widest active zone of 30cm while compost height of 40, 70 and 80cm recorded active zone of 20cm each. Christensen et al. (2007) has reported that compost has wider range of active zone which supports high microbial growth due to its high porosity.

![Figure 4.14: Active oxidation zone range (cm) for black soil](image)

**4.3.4 Column rector experiments (used black soil + fresh black soil)**

Column trials using mixture of used + fresh black soil were conducted for column height of 10-100cm (Figure 4.15). As black soil height were increased in the columns, the time taken for CH$_4$ oxidation decreased just like the trend exhibited by mixture of used + fresh compost. This trend could be explained by high degree of acclimatization by methanotrophs in used soil compared to fresh soil. Prior exposure of CH$_4$ in used soil enhance oxidation capacity thus reducing CH$_4$ oxidation period (Pawloska, 2008). However, compared to used + fresh
compost and fresh compost, mixture of used + fresh black soil exhibited lower CH₄ oxidation capacity. Slope gradient obtained for used + fresh compost was 3 times higher (4.374) and fresh compost was 1.5 times higher (2.093) compared to used + fresh black soil (1.363). This indicated that compost was a better Biocover material than black soil as it has higher CH₄ oxidation capacity than either fresh soil or mixture of used + fresh soil.

Figure 4.15: Period for complete CH₄ oxidation for mixture of used+fresh black soil

Bacterial colony counts for used+fresh black soil (Figure 4.16) also clearly indicated an increasing trend as the black soil height was increased in the columns. Lowest colony counts were detected at column height of 10cm which could be explained by lesser nutrients for microbial growth due to lack of soil. However, as the soil height was increased, bacterial colony counts also increased owing to the increase in organic matter for microbial growth. Perdikea et al. (2007) has reported that inferior performance of lower soil height was attributed to lower residence time of CH₄ as well as a faster desiccation of active zone in comparison to that of higher soil height columns. Figure 4.17 depicts the comparison of total bacterial counts for used+fresh black soil and fresh black soil.
4.4 Biocover Performance Index

Table 4.2 summarized Biocover Performance Index (BPI) for Wheaton bottle experiment. Compost scored the highest BPI, which proved the efficiency in CH$_4$ oxidation.
Black soil and compost residue scored almost half of the BPI of compost which indicated poorer CH$_4$ oxidation competency. All the Biocover materials tested in the study showed very high oxidation rate compared to studies conducted by other authors. For example, Scheutz and Kjeldsen (2004) used soil samples from Skellingsted Landfill, Denmark and they obtained an average oxidation rate of 70 µg g$^{-1}$h$^{-1}$ compared to compost which scored 29.8 times higher oxidation rate in this study. The huge difference in the oxidation rate might be due to the extremely suitable/conducive climate for methanotrophic activity in tropical conditions.

An example of BPI calculation (for compost) is shown below:

$$\text{BPI} = \frac{(\text{CH}_4)_0 - (\text{CH}_4)_a}{W \times N} = \frac{(4 \times 10^6) \mu g - (0) \mu g}{20 \text{g} \times (4 \text{ days} \times 24 \text{ hour})} = 2.08 \times 10^3 \mu g \text{ g}^{-1} \text{h}^{-1}$$

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

<table>
<thead>
<tr>
<th>Biocover Material</th>
<th>Biocover Performance Index (µg g$^{-1}$h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compost</td>
<td>2.08 x 10$^3$</td>
</tr>
<tr>
<td>Black Soil</td>
<td>1.19 x 10$^3$</td>
</tr>
<tr>
<td>Compost Residue</td>
<td>0.83 x 10$^3$</td>
</tr>
</tbody>
</table>

For column experiments, BPI for compost was relatively higher than BPI for black soil (Figure 4.18), for all column heights. BPI of both the materials increased as the height of Biocover material was increased till maximum BPI was achieved. Maximum BPI for compost was 187.5 µg g$^{-1}$h$^{-1}$ while for black soil; it was 95.3 µg g$^{-1}$h$^{-1}$. The maximum BPI was recorded at 60 cm height for compost and 80 cm height for black soil (20 cm higher than compost). As BPI is highly dependent to CH$_4$ oxidation period, column height which recorded the shortest CH$_4$ oxidation period scored the highest BPI. Highest BPI for compost was almost double the highest BPI of black soil, indicating compost as the better Biocover
material for optimum CH$_4$ oxidation. Besides that, optimum height of compost (60cm) was 20% lesser than of black soil (80cm) which indicated compost as more cost-effective. BPI clearly indicated high CH$_4$ oxidation performance of compost and black soil at their optimum heights.

Figure 4.18: BPI for different column heights for compost and black soil

4.5 Statistical Analysis

Based on least square regression analysis conducted using SYSTAT 11 software, the results obtained were shown in Table 4.3. Compost scored the highest determination coefficient ($E^2$) of 0.981 and adjusted determination coefficient ($E^2_a$) of 0.962 compared to black soil and compost residue (Table 4.3). Muna & Leta (2008) obtained determination coefficient ($E^2$) of 0.991 and adjusted determination coefficient ($E^2_a$) of 0.978 for yard waste compost. Higher CH$_4$ volume (10%) and temperature (35°C) could have contributed to higher values obtained by Muna and Leta (2008). Although compost scored the highest values, this statistical analysis was not suitable to compare the CH$_4$ oxidation capacity as the differences were in very minimal range (0.02 to 0.038) for determination coefficients and adjusted determination coefficients respectively.

Table 4.3: Determination Coefficients and Adjusted Determination Coefficients for CH$_4$
### 4.6 Kinetic modelling

The kinetic evaluation of CH$_4$ oxidation of compost, black soil and compost residue was conducted using Michaelis-Menten equation (modified). Reciprocal of volume of CH$_4$, S$^{-1}$ (v/v) was plotted against time. The reaction rate, R was then determined by measuring the tangent of the resulting curve. The reaction rates (R), the concentration of CO$_2$ (V) and the reciprocals of CH$_4$ concentration (S$^{-1}$) are summarized in Table 4.4. Similar to BPI and statistical analysis, kinetics revealed that compost has the highest CH$_4$ oxidation capacity compared to black soil and compost residue. From the Wheaton bottle experiments, compost scored highest potential CH$_4$ oxidation rate ($R_p$=0.9102) which was almost 3 times higher than black soil ($R_p$=0.3065) and 5.5 times higher than compost residue ($R_p$=0.1648) as shown in Table 4.5. In the meantime, BPI of compost and black soil was 2.5 times and 1.74 times higher than compost residue respectively.

Kinetics was also used to evaluate performance of Biocover materials in column reactor experiments. Results obtained from kinetics varied at different column heights for both compost and black soil (Table 4.6 and 4.7). $R_p$ (potential CH$_4$ oxidation) increased as the column height increased for both the Biocover materials. This increasing trend showed enhanced CH$_4$ oxidation capacity as the column height was increased till optimum heights were reached. At compost height of 60cm, $R_p$ was the maximum indicating highest CH$_4$ oxidation.
oxidation rate. R_p for 60cm was 2.3 times higher than the lowest R_p (at 10cm). Any increase in column height above 60cm showed a decrease in R_p values.

An example of R_p calculation (compost) is shown below:

\[
R_p = \frac{R_{\text{max}}}{1 - (K_m)} = \frac{0.147 \times 1}{1 - 0.8385} = 0.9102
\]

(Value of R_{\text{max}} and K_m are obtained from Appendix 4)

Table 4.4: Data for S^{-1}, R and V for Biocover materials
### Compost

<table>
<thead>
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<th>Days</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
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<tr>
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<td>0.2446</td>
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<tr>
<td>R (mL/day)</td>
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<td>V (mL)</td>
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### Black Soil

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<td>R</td>
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<tr>
<td>V</td>
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### Compost Residue

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<td>0.2266</td>
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<tr>
<td>R</td>
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<td>0.15</td>
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</tr>
<tr>
<td>V</td>
<td>0.375</td>
<td>0.625</td>
<td>1.088</td>
<td>1.25</td>
</tr>
</tbody>
</table>

S=Volume of CH₄ (v/v) (mL)  R= Reaction rate (mL/day)  V=Volume of CO₂ (mL)

Table 4.5: The kinetic constants of the kinetic model used for Wheaton bottle experiments
Black soil exhibited lower $R_p$ value at all column heights indicating poorer CH$_4$ oxidation capacity compared to compost (Table 4.7). Similarly like compost, $R_p$ of black soil also increased as column height increased. $R_p$ obtained for black soil was highest at 80cm specifying the optimum column height for black soil. Any increase of column height above 80cm showed decreasing trend of $R_p$. Maximum $R_p$ obtained for black soil was 1.4 times lower than maximum $R_p$ obtained for compost. Therefore, it can be concluded that compost of column height 60cm was 1.4 times more efficient in CH$_4$ oxidation capacity than 80cm height black soil. As compost scored higher $R_p$ at all heights compared to black soil, it clearly indicated that compost was a more efficient Biocover material compared to black soil. At 60cm column height, the difference of $R_p$ between black soil and compost was very huge. This proved that compost works much more efficiently than black soil of the same height. Only at 80cm of column height, the difference of $R_p$ between compost and black soil was the smallest. In comparison,

<table>
<thead>
<tr>
<th>Material</th>
<th>$R_{max}$</th>
<th>$K_m$</th>
<th>$R_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compost</td>
<td>0.147</td>
<td>0.8385</td>
<td>0.9102</td>
</tr>
<tr>
<td>Black Soil</td>
<td>0.25</td>
<td>0.1845</td>
<td>0.3065</td>
</tr>
<tr>
<td>Compost Residue</td>
<td>0.15</td>
<td>0.09</td>
<td>0.1648</td>
</tr>
</tbody>
</table>

$R_{max} =$ maximum CH$_4$ oxidation rate (mL/ d)

$R_p =$ potential CH$_4$ oxidation rate (mL / d)

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

<table>
<thead>
<tr>
<th>Column Height(cm)</th>
<th>$R_{\text{max}}$</th>
<th>$K_m$ (half saturation)</th>
<th>$R_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.468</td>
<td>0.234</td>
<td>0.611</td>
</tr>
<tr>
<td>20</td>
<td>0.479</td>
<td>0.240</td>
<td>0.630</td>
</tr>
<tr>
<td>30</td>
<td>0.514</td>
<td>0.257</td>
<td>0.692</td>
</tr>
<tr>
<td>40</td>
<td>0.539</td>
<td>0.266</td>
<td>0.738</td>
</tr>
<tr>
<td>50</td>
<td>0.714</td>
<td>0.357</td>
<td>1.110</td>
</tr>
<tr>
<td>60</td>
<td>0.835</td>
<td>0.416</td>
<td>1.430</td>
</tr>
<tr>
<td>70</td>
<td>0.765</td>
<td>0.383</td>
<td>1.239</td>
</tr>
<tr>
<td>80</td>
<td>0.687</td>
<td>0.344</td>
<td>1.047</td>
</tr>
<tr>
<td>90</td>
<td>0.712</td>
<td>0.356</td>
<td>1.106</td>
</tr>
<tr>
<td>100</td>
<td>0.724</td>
<td>0.362</td>
<td>1.135</td>
</tr>
</tbody>
</table>

$R_{\text{max}}$ = maximum CH4 oxidation rate (mL/ d )

$R_p$ = potential CH4 oxidation rate (mL / d)

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

Table 4.7: The kinetic constant of the kinetic model proposed for Column experiments
using black soil

<table>
<thead>
<tr>
<th>Column Height(cm)</th>
<th>$R_{\text{max}}$</th>
<th>$K_m$ (half saturation)</th>
<th>$R_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.267</td>
<td>0.134</td>
<td>0.308</td>
</tr>
<tr>
<td>20</td>
<td>0.285</td>
<td>0.143</td>
<td>0.311</td>
</tr>
<tr>
<td>30</td>
<td>0.296</td>
<td>0.148</td>
<td>0.335</td>
</tr>
<tr>
<td>40</td>
<td>0.321</td>
<td>0.161</td>
<td>0.382</td>
</tr>
<tr>
<td>50</td>
<td>0.387</td>
<td>0.194</td>
<td>0.480</td>
</tr>
<tr>
<td>60</td>
<td>0.441</td>
<td>0.221</td>
<td>0.566</td>
</tr>
<tr>
<td>70</td>
<td>0.615</td>
<td>0.308</td>
<td>0.889</td>
</tr>
<tr>
<td>80</td>
<td>0.678</td>
<td>0.339</td>
<td>1.026</td>
</tr>
<tr>
<td>90</td>
<td>0.633</td>
<td>0.317</td>
<td>0.926</td>
</tr>
<tr>
<td>100</td>
<td>0.646</td>
<td>0.323</td>
<td>0.913</td>
</tr>
</tbody>
</table>

$R_{\text{max}}$ = maximum CH4 oxidation rate (mL/d)

$R_p$ = potential CH4 oxidation rate (mL/d)

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

Compost was definitely a better Biocover in relation to CH4 oxidizing capacity and also in terms of volume needed for landfill application. A summary of potential CH4 oxidation rate ($R_p$) at various column heights for compost and black soil is illustrated in Figure 4.19. Kightley et al. (1995) used similar kinetics to evaluate CH4 oxidation capacity in column
experiment using coarse sand soil from landfill cover and also with continuous CH$_4$ flow. They obtained $R_{\text{max}}$ value within the range of $6.49 \times 10^{-3}$ to $7.29 \times 10^{-3}$. Pawloska and Stepniewski (2006) who used coarse sand with continuous flow of CH$_4$ ranging from 1.0-16.0 % (v/v) obtained $R_{\text{max}}$ values in the range of $0.11 \times 10^{-3}$ to $0.86 \times 10^{-3}$ units. $R_{\text{max}}$ values obtained in this study ($4.07 \times 10^{-1}$ - $7.24 \times 10^{-1}$) were much higher than the values obtained by the authors. For example, $R_{\text{max}}$ of this study was about 80 times higher than the value obtained by Pawloska and Stepniewski (2006). The vast differences in the $R_{\text{max}}$ values could be due to variation in experimental methods. The authors mentioned above used continuous flow of CH$_4$ in their experiments compared to one-off injection (static flow) of CH$_4$ in this study. Continuous flow of CH$_4$ can cause high saturation of the gas in the columns thus impeding CH$_4$ oxidation tremendously. The difference in the type of soil used could also be the reason for the differences. Despite the differences, experiments conducted by Pawloska & Stepniewski (2006) proved that 60cm column height scored the highest $R_{\text{max}}$, similar to optimum column height of compost in this study. Another plausible reason for high kinetics value obtained in this study could be the suitability of tropical climate in facilitating microbial growth for optimum CH$_4$ oxidation.

Based on the results obtained by Whalen et al., 1990, Kightley et al., 1995, Bogner et al., 1997, De Visscher, 2004, Gebert et al., 2003, Scheutz & Kjeldsen, 2004 and Pawloska & Stepniewski, 2006, $K_m$ values for CH$_4$ measured in field conditions or in conditions of a simulated landfill cover or biofilter given were in range between 0.08 and 2.54. From this study, $K_m$ values obtained were in the range of 0.09-0.416 which falls in the range reported by the mentioned authors. However, the upper value of the range obtained in this experiment was much lower than in the literature review. This could be due to the static CH$_4$ flow used in this experiment, in which the CH$_4$ concentration is fixed in all the experiments conducted. $K_m$ value in Michaelis-Menten equation represented half-saturation reaction rate. Static flow of
CH₄ in this experiment provided less saturation level compared to continuous flow of CH₄ by other authors which explained low Kₘ value obtained in this study. Since Kₘ is inversely proportional to Rₚ (refer Section 3.6), it is plausible that Rₚ values obtained in this study was much higher than in the literature.

Figure 4.19: Summary of potential CH₄ oxidation rate at various column heights for compost and black soil.

4.7 General Discussion

Characterization of Biocover materials gave an in-depth analysis of chemical and physical properties of the materials. Moisture content, pH, organic matter and copper concentration were essential and significant parameters in determining CH₄ oxidation capacity of the Biocover materials (Humer & Lechner, 2001; Barlaz et al., 2004; Stein & Hettiaratchi, 2001; Figueroa, 1993; Pawloska, 2008; Sorokin et al., 2000; Rozej & Stepniewski, 2008; Kaluzhnaya et al., 2001). Results of chemical and physical properties of the essential parameters mentioned above were in optimum values for compost used in this study, contributing to its best performance among all Biocover materials tested. Highest moisture content of compost (61.7%) compared to other Biocover materials enhanced gas
diffusion, facilitated exchange of substrate, nutrients, buffer and spreading micro-organisms between the micro-environments (Boeckx et al., 1996). Slightly acidic property of compost (6.35) allows methanogenic bacteria to operate efficiently (Moldes et al., 2007). Best CH₄ oxidation performance of compost could also be explained by its high organic matter content which served as the main carrier for microorganisms (Christensen et al., 1996). Copper concentration have been known to inhibit CH₄ oxidation at high concentration (Kjeldsen, 2004 and Tsien et al., 1989). Compost contained negligible amount of copper which undoubtedly, gave no hindrance for CH₄ oxidation. In this study, moisture content and organic matter played most important role in CH₄ oxidation capacity compared to other parameters tested. Moisture level and organic matter content of compost was most significantly different compared to other Biocover materials, while other essential parameters scored very similar values.

Wheaton bottle experiments provided preliminary findings on CH₄ oxidation capacity of Biocover materials. Compost scored the highest CH₄ oxidation rate followed by black soil and compost residue. The high performance of compost in batch incubation also co-related with its highest microbial counts. Compost provided suitable conditions for microbes to thrive, thus promoting CH₄ oxidation (Wilshusen et al., 2004). Chanton & Liplay (2000), Perdikea et al.(2007), Wilshushen et al.(2004), Barlaz et al. (2004), Agnew & Leonars (2003), Hilger & Humer (2003), Humer and Lechner (2001) had reported highest CH₄ oxidation capacity in compost due to its porous and organic-rich substrate. Lowest CH₄ oxidation capacity in compost residue can be explained by its relatively low colony counts in compost residue. Compost residue failed to support high microbial growth due to its lowest moisture content and organic matter content. Period for CH₄ oxidation highly depend on acclimatization period of methanotrophs in the Biocover material (Barlaz et al., 2004). Faster acclimatization period means speedier CH₄ oxidation. High CH₄ oxidation rate which began
by day 2 marked an acclimatization period of less than 2 days in compost. Differences in acclimatization period observed in Biocover materials could be related to physical and chemical properties, mainly moisture content and availability of organic matter. Biocover material (compost) with higher moisture content and organic matter portrayed faster microbial acclimatization, thus contributing to higher CH₄ oxidation rate. Reduction of O₂, increase in CO₂ and presence of water droplets in the Wheaton bottle were observed simultaneously with CH₄ reduction confirming oxidation process. However, continuous increase of CO₂ even after CH₄ completion indicated organic matter degradation by other groups of microbes (Perdikea et al., 2007). Results from batch incubation conducted by other authors were different compared to the results obtained in this study. In comparison, this study exhibited higher CH₄ oxidation rate compared to other authors (Perdikea et al., 2007, Thomas, 2002, Stein & Hettiaratchi, 2001). The variation in results could be due to different experimental conditions used (lower temperature and moisture content) and type of materials used by the authors which affected the variation of microbial growth for CH₄ oxidation. Meanwhile, Muna & Leta (2008) and Fauziah & Agamuthu (2002) reported higher CH₄ oxidation rate than the results obtained in this study. These authors conducted batch incubation study using higher temperature (35°C) which could have provided more favourable conditions for CH₄ oxidation.

Column reactor trials marked an advanced stage in determining suitable height of Biocover material to be applied in landfill conditions. Compost and black soil were chosen to be experimented in column reactor based on their better performance in Wheaton bottle trials. In general, compost exhibited better CH₄ oxidation performance than black soil in column reactor trials. Time taken for CH₄ oxidation varied for each column heights for both the Biocovers tested. Period for CH₄ oxidation for compost and black soil ranged from 4-18 days and 8-25 days respectively. Time taken for CH₄ oxidation was longest at the minimum height
of 10cm for both Biocover materials tested. This could be due to lack Biocover materials (substrate) which inhibited the expansion of microbial population at minimum column height. Lack of Biocover material also meant lack of organic matter for microbial growth. Lowest colony counts observed at this height (10cm) justified the poor performance of CH$_4$ oxidation. As column height was increased, time taken for CH$_4$ oxidation decreased owing to the increase in substrate for higher microbial growth. Optimum CH$_4$ oxidation was recorded at 60cm height for compost on day 4 and at 80cm height for black soil on day 8.

Compost was a better Biocover material as it took shorter period for CH$_4$ oxidation and also recorded shorter optimum height indicating more cost-effectiveness. Bacterial colony counts also recorded highest counts at 60cm height compost and 80cm height black soil. Active zone for CH$_4$ oxidation was in a wider range (10-30cm depth) for compost compared to black soil (10cm depth) indicating favourability of microbes to compost. Compost also has wider active zone range compared to loamy sand (0-20cm depth) used by Thomas (2002). Wide active zone in compost could be due to speedier and deeper gaseous diffusion in this highly porous material. Shifting of active zones towards the surface of Biocover material were observed as column heights were increased indicating high sensitivity of active zone for O$_2$ availability. High availability of O$_2$ in deeper portions of 60cm compost height encouraged high microbial growth thus speeding CH$_4$ oxidation. Increase in column height above optimum height did not increase CH$_4$ oxidation. This could be due to decrease in O$_2$ availability as more air spaces have been replaced with Biocover materials. Column trials with mixture of used+fresh Biocover materials showed speedier performance in CH$_4$ oxidation. Mixture of 90cm of used+10cm of fresh Biocover proved to be the best height combinations for both the Biocover materials. Used biocover material was rich in microbial population reflected by its high colony counts. Addition of fresh Biocover materials to used Biocover materials induced the growth of bigger microbial population size thus increasing
CH$_4$ oxidation capacity. However, compost performed better in column trials using mixture of used+fresh Biocover materials in terms of CH$_4$ oxidation period. This could have been contributed by high organic content found in compost which encouraged higher microbial growth (1.4 times more) than black soil. Nevertheless, this study has been conducted using two variable (height and mixture of used+fresh Biocover materials) at the same time. Therefore, this study could be further improved by looking at one variable at a time for a better understanding of CH$_4$ oxidation capacity in column trials.

Biocover Performance Index (BPI) revealed that compost was the best Biocover material at 60cm column height. Compost scored 1.74 times and 2.5 times higher BPI than black soil and compost residue, respectively. BPI of compost height of 60cm was almost double than 80cm black soil height. Statistical analysis conducted for compost and black soil showed a very minimal difference of determination coefficients for both Biocover materials. Although compost had the highest score in statistical analysis, the differences between the values obtained by other Biocover materials were in very small range.

Similar to BPI and statistical analysis, kinetics revealed compost as the best Biocover material for CH$_4$ oxidation. However, kinetics showed much significant and obvious differences in CH$_4$ oxidation performance among the Biocover materials. $R_p$ (potential CH$_4$ oxidation rate) was 3 fold and 5.5 fold higher than black soil and compost residue, respectively. Compost height of 60cm and black soil of 80cm recorded highest $R_p$ for column experiments optimum for CH$_4$ oxidation. Authors [Pawloska & Stepniewski (2006), Kightley et al., (1995), Whalen et al., (1990),De Visscher et al., (1999), Stein & Hettiaratchi (2001), Gebert et al., (2003), Benstead & King (1997) and Whalen & Reeburgh (1996) ] obtained lower $R_p$ values compared to results in this study. The difference in $R_p$ value could be due to continuos flow of CH$_4$ used by other authors compared to static flow of CH$_4$ in this study. Continuos flow of CH$_4$ induces high level of gas saturation in the material thus impeding CH$_4$
oxidation capacity. Other factors that could have contributed to the differences in results were variation in type of Biocover material, volume of CH\textsubscript{4} used, and experimental conditions such as temperature. Results obtained from BPI, statistical analysis and kinetics revealed that compost was the best Biocover material and the optimum column height was 60cm. However, kinetics were more sensitive/reliable in expressing CH\textsubscript{4} oxidation capacity as it exhibited significant differences in Biocover performance.

This study facilitated in determining the suitable Biocover and the feasible height for optimum CH\textsubscript{4} oxidation for landfill application. Field experiments in actual landfill is ongoing and is the second segment of this project. Field conditions may affect the rate of CH\textsubscript{4} oxidation and it could be different compared to laboratory studies.

**Chapter 5: Conclusion**

Compost was identified as the best Biocover material as it completely oxidized CH\textsubscript{4} within the shortest period of time (4 days) compared to black soil (8 days) and compost residue (11 days) in Wheaton bottle experiments. Column reactor experiments also proved that compost was a better Biocover material for CH\textsubscript{4} oxidation as it took shorter period for complete CH\textsubscript{4} oxidation (4-18 days) compared to black soil (8-25 days). Optimum landfill cover height was 60cm for compost and 80cm for black soil for CH\textsubscript{4} oxidation. Kinetics modelling and Biocover Performance Index (BPI) revealed that compost at 60cm height was optimum for CH\textsubscript{4} mitigation. BPI obtained for compost (2.60 x 10\textsuperscript{3} µg g\textsuperscript{-1}h\textsuperscript{-1}) was the highest compared to black soil (1.49 x 10\textsuperscript{3} µg g\textsuperscript{-1}h\textsuperscript{-1}) and compost residue (1.04 x 10\textsuperscript{3} µg g\textsuperscript{-1}h\textsuperscript{-1}). Potential CH\textsubscript{4} oxidation rate (R\textsubscript{p}) obtained from the kinetics clearly indicated that compost was the most efficient Biocover with R\textsubscript{p} of 0.9122, and column height of 60cm was the most conducive
with the highest $R_p$ value of 0.5262. The significance of this work was methane oxidation capacity of different Biocover materials tested and analysed under tropical conditions.

Table 5.1: Summary of CH$_4$ Oxidation Capacity of Biocover Material tested

<table>
<thead>
<tr>
<th>Material</th>
<th>Compost</th>
<th>Black Soil</th>
<th>Compost Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period for CH$_4$ oxidation (day) in batch incubation experiments</td>
<td>4</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>Period for CH$_4$ oxidation (day) in column reactor experiments</td>
<td>4-18</td>
<td>8-25</td>
<td>-</td>
</tr>
<tr>
<td>Optimum landfill cover height</td>
<td>60 cm</td>
<td>80 cm</td>
<td>-</td>
</tr>
<tr>
<td>BPI (µg g$^{-1}$h$^{-1}$)</td>
<td>$2.60 \times 10^3$</td>
<td>$1.49 \times 10^3$</td>
<td>$1.04 \times 10^3$</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.9102</td>
<td>0.3065</td>
<td>0.1648</td>
</tr>
</tbody>
</table>

(BPI: Biocover Performance Index,  $R_p$: Potential CH$_4$ oxidation rate)
References


Hanson, R.S.& Hanson, T.E.(1996) Methanotrophic bacteria. Microbial Rev. 60:439-471


Pawloska, M. 2008. Reduction of methane emission from landfills by its microbial oxidation in filter bed.


The Star, Sizing Up, Section 2, pg 7, May 9 2009.


Appendix

Appendix 1: Volume of CH₄ against time for compost

Appendix 2: Volume of CH₄ against time for black soil

Appendix 3: Volume of CH₄ against time for compost residue
Appendix 4: Volume of CH$_4$ oxidized against time for compost