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Bio-Reactive Landfill Covers: An Inexpensive Approach to Mitigate Methane Emissions

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THE FLORIDA STATE UNIVERSITY

COLLEGE OF ENGINEERING

BIO-REACTIONAL LANDFILL COVERS:
AN INEXPENSIVE APPROACH TO MITIGATE METHANE EMISSIONS

By

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A thesis submitted to the
Department of Civil and Environmental Engineering
in partial fulfillment of the
requirements for the degree of
Master of Science

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ABSTRACT

Methane is one of two primary gases produced from the decomposition of landfill waste. Studies have been directed to collection and mitigation of methane gas. In small landfills, collection is not an economically feasible solution. Bio-cover placement is an inexpensive approach to mitigating methane emissions. The enhancing of oxidation processes by placement of bio-covers will reduce emissions even while gas extraction is employed and improve aesthetic quality of solid waste facilities.

The overall objective of the research is to mitigate methane emissions from landfills. To reach this objective, a test site was selected to evaluate the effects of compost placement over a closed landfill. The static chamber technique was used to estimate methane emissions and the stable isotope tracing method was used to determine oxidation rates. Hot spots were identified in the grid area and emissions at these spots were analyzed more in detail. Results obtained during the first year of the study are presented in this thesis.

In these investigative efforts, it was noted that moisture content plays a significant role in controlling emissions and oxidation. At high water contents, low flux emissions were measured observed and at low water contents, emissions were higher. Oxidation rates varied in much the same way. High water contents corresponded with low oxidation rates and vise versa. Further study on the effects of moisture content and other variables on flux emission and oxidation is warranted.
SECTION ONE
INTRODUCTION

Methane gas produced from landfills accounts for 15 to 20% of the anthropogenic greenhouse effect. Since methane is one of the two primary gases produced from the decomposition of landfill waste, studies have been directed to foster the collection and mitigation of methane gas. In small landfills, collection is not an economically feasible solution; therefore mitigation by means of oxidation enhancement may be the optimum solution.

Different factors affect methane flux rate and oxidation both directly and indirectly. Examples of these variables include: pH, temperature, moisture content, porosity, and barometric pressure. Altering cover soil can in-turn alter some of these variables, specifically moisture content, soil temperature and porosity, thereby reducing overall methane emissions.

The overall objective of the research project is to mitigate methane emissions from landfills. To reach this objective, a test site was selected to evaluate the effects of compost placement over a closed landfill. This thesis is a summary of the activities performed during the first year of the research project. Section Two of this thesis presents a literature review of past research on methane gas emissions and oxidation at solid waste landfill facilities. Section Three describes the experimental procedures during the study. A preliminary survey was conducted to decide on the location for compost placement. The static chamber technique was used to estimate methane emissions and the stable isotope tracing method was used to determine oxidation rates. Hot spots were identified in the grid area and emissions at these spots were evaluated in more detail. After these spots were identified, a glass dispersement layer along with compost placement commenced over one area of the site. A region similar to this area was used for comparison but was left devoid of compost. Results obtained during the first year of the study are presented in Section Four. A brief summary and conclusions are presented in Section Five.
SECTION TWO
BACKGROUND AND MOTIVATION

2.1 METHANE GENERATION

Methane generation in solid waste landfills is very complex. Measured methane emissions from landfills are very limited, and are typically performed at the surface of the landfill. The measured emissions do not account for the methane that had been already oxidized by the bacteria in the cover soil. Therefore the actual quantities of landfill gas generated by the waste itself have not been well studied. Bingemer and Crutzen (1987) developed a mass balance approach in which the annual landfill deposit of degradable organic carbon is used to estimate the generation of biogas. A model developed by Augenstein and Pacey (1991) uses a semi-empirical approach that accounts for less than ideal decomposition by assuming specific biogas yield and generation rates for three waste categories: readily degradable, moderately degradable, and slowly degradable. The assumed gas yields and generation rates are based on actual results from field-scale test cells and field gas recovery data. Landfills are considered to be a major global source of the greenhouse gas methane. Landfill gases are produced as organic materials decompose under anaerobic conditions. These gases are primarily composed of equal parts of methane and carbon dioxide, but have trace concentrations of other gases. The result of one ton of deposited municipal solid waste is roughly 160 to 250 m$^3$ of landfill gas. This gas is comprised of approximately 55% methane, 44% carbon dioxide and less than 1% of other potentially hazardous substances to the environment. Table 2.1 shows typical landfill gas composition.

Immediately after waste is deposited, a short phase of aerobic decomposition takes place. Degradable material is consumed first causing only carbon dioxide to be generated. After cover is placed, the first intermediate decomposition phase occurs. As the oxygen is consumed, aerobic bacteria decrease. The second intermediate phase is where methanogenic bacteria first appear. The generation of high-volume methane is delayed by the production of sulfate reducing bacteria occurring simultaneously. Sulfate-
Table 2.1 Landfill Gas Composition (El-Fadel et al. 1997).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Concentration Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>40-70</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>30-60</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>0-3</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3-5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0-3</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0-5</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>0-2</td>
</tr>
<tr>
<td>Trace Compounds</td>
<td>0-1</td>
</tr>
</tbody>
</table>
reducers are eventually limited and a steady production of methane gas is produced. This tends to be the longest phase of generation and typically starts between two and six months after waste is deposited. According to the United States Environmental Protection Agency (US EPA), this phase may take place for several decades (US EPA 1999a).

2.2 METHANE AS A GREENHOUSE GAS

Methane is an important and powerful greenhouse gas. Currently, methane concentrations are at a level unprecedented in the last 400,000 years. As reported by Humer et al. (1999), concentrations of CH$_4$ are currently responsible for 15 - 20% of the anthropogenic greenhouse effect. In the last century methane atmospheric concentration has doubled.

Le Mer and Roger (2001) indicate that methane, despite the short residence time of 10 years in the atmosphere, is 20 to 30 times (on a molar basis) more efficient as a greenhouse gas than carbon dioxide due to its stronger ability to absorb infrared radiation. Lashof et al. (1990) also has reported that CH$_4$ can be up to 70 times more efficient, gram per gram, even though its atmospheric concentration is significantly lower. The concentration of methane in the atmosphere is estimated to be about 200 times lower than that of carbon dioxide (Lashof et al. 1990). According to the Commission to the Council and to the European Parliament (CCEP), the extensive increase in methane concentration is primarily caused by human activity taking place. It was also indicated by the Commission that converting methane into carbon dioxide will eliminate 95% of its global warming potential (CCEP 2001).

2.3 METHANE OXIDATION

Methane migrates through zones of low pressure in cover soils, and eventually reaches the surface. The cover soil will oxidize about ten percent of the generated methane unless it is captured by a recovery system and used as an energy source (Liptay et al. 1998). Methane oxidation occurs in many natural systems and soils and serves as an important natural sink for natural and anthropogenic methane emissions. The process of methane oxidation consists of the conversion of methane into carbon dioxide, water,
and biomass by means of microbial activity. Microbial methane oxidation reduces methane released in certain methanogenic areas. The following are determining factors for methane oxidation:

- Existence of methanotrophic microorganisms
- Supply of oxygen
- Suitable carrier that offers adequate nutrient supply and facilitates colony formation
- Adequate moisture content and ambient conditions in the medium.

Environmental factors have a decisive impact on the activity of methanotrophic bacteria. Among these factors are pH, temperature, water content, oxygen supply, inhibitors, soil condition and nutrient supply, barometric pressure, and retention time.

### 2.3.1 pH

According to Humer et al. (1999) the optimum pH for growth and activity of methanotrophs ranges between 5.5 and 8.5. If soil pH drops below 6.0 or rises above 8.0, methanotrophic activity is generally halted as stated by Neue and Rogers (1993). Vegetation can directly influence the pH by means of nitrogen uptake, which then will inhibit methane oxidation. De Visscher et al (1999) noted that vegetative growth may be the cause of the pH change by inhibiting methane oxidation through nitrogen uptake. But the vegetation can also provide a channel for oxygen penetration. Vegetative root systems can also induce a more suitable microbiological environment for methane oxidation. In general, vegetation can be used to enhance methane oxidation (Maurice et al., 1999). According to Williams et al., (1993) higher pH at a reclaimed landfill golf course indicated greater methane consumption.

### 2.3.2 Temperatures

Most methanotrophic bacteria thrive in temperatures that range from 20 to 37 degrees Celsius. Many researchers have found that optimum temperatures for methane oxidation are around 25 to 35 °C (Christophersen et al, 2000; Bender and Conrad 1995). As reported by Christophersen et al, the lowest temperature studied in soil exposed to high concentrations of CH₄ was 5 (degree) °C. A study conducted by Whalen et al.
(1990) shows that an oxidation rate of 0.05 mmol g-1 h-1 at 5 (degree) °C was found and an oxidation rate of 0.1 mmol g-1 h-1 at 5 (degree) °C was found by Czepiel et al. (1996). Whalen et al. (1990) has also noted that during lab experimentation, an increase in temperatures from 15 to 25 (degree) °C doubled the oxidation rates. The EPA recognizes that in warm temperatures, the growth of methane producing bacteria increases. The actual temperature of the waste will depend upon the depth of the landfill and the number of layers of cover soil, along with the atmospheric temperatures.

Coleman et al. (1981) indicated that there is a strong temperature dependence for methane oxidation. Studies conducted by Chanton and Liptay (2000) indicate that there is a significant difference in oxidation rates between winter and summer months. Summer months seemed to produce lower flux rates and higher oxidation values. One month in their study showed a discontinuity and it was suggested that methane oxidation was retarded due to the large amount of rainfall occurring in that month. This would have hindered the oxygen flow to methanotrophs through the soil (Chanton et al. 2000).

2.3.3 Moisture Content

Landfills receive water from various sources including: incoming waste, surface water infiltration, groundwater infiltration, precipitation, and the decomposition reaction. Methanotrophic microorganisms tend to become inactive under ambient conditions where the moisture content falls 13% below maximum water capacity (Bender 1995). Higher oxidation rate is associated with high moisture content. Water effect plays three important roles. First, the optimum environment for methane oxidizing bacteria (methanotrophic) is obtained at certain water content. Second, water content affects the penetration of oxygen into the soils, which is main reactor for methane oxidation. As the water content increases, the oxygen diffusion into the soil is hindered. Thirdly, water content affects the air filled porosity of the soil and influences gas transport through the soil. As water fills up the pores in the soil, it blocks the flow of gas upward. At the same time, the blocking of flow might lead to increased methane emission due to the excess pressure built-up in the landfill (Boeckx et al., 1996).

At optimum water content, there is both rapid gas phase molecular diffusion and a sufficient microbial activity to oxidize the delivered methane. The reduced methane-
oxidizing capacity at higher moisture contents is caused by a shift of gas-phase molecular
diffusion to aqueous-phase molecular diffusion, which is about $10^4$ fold less rapid
(Boeckx et al., 1996). Low methane oxidation occurring at low ranges of soil water
content may be caused by decreased methanotrophic activity. Oxidation peaks when a
balance is achieved between moisture content and methanotrophic activity (Czepiel et al.,
1996). The optimum oxidation soil water content will vary for different soil types and
depends on temperature and other environmental factors.

The general range of optimum water content, as reported by Visvanathan et al.
(1999) is 15-20%. Boeckx et al. (1996) has stated a range of 10 to 20%. The optimal
oxidation water content ranged between 15.6 and 18.8% w/w for soils tested by Boeckx
et al. (1996) and Christophersen et al. (2000). Czepiel et al. (1996) measured an optimal
oxidation water content of 15.7%. Whalen et al. (1990) reported a value of 11%.
Visvanathan et al. (1999) also reported values ranging from 15 to 20%. At increasing
organic matter content both the optimal soil moisture content and the maximum oxidation
rate increased (Christophersen, 2000).

### 2.3.4 Porosity and Oxygen Penetration

Atmospheric oxygen can only penetrate a certain depth of cover soils; therefore
oxygen is often the limiting factor for methane oxidation. The porosity of soil directly
influences the penetration of oxygen into the soil. Oxygen is the main reactor of the
oxidation process. Porosity can provide the channel for oxygen penetration and the
contact surface area with methanotrophic bacteria. Borjesson et al. (2004) reported a
significant relationship between methane oxidation and particle size distribution. Soils
with high porosity retain methane and oxygen longer in the pores leading to higher
oxidation rate (Humer and Lechner, 1999).

Even at very low oxygen concentrations, methanotrophic bacterial can still obtain
optimum methane conversion rates. Methane oxidation takes place mainly in the top 30
cm of the soil surface (Bogner et al. 1997). Organic matter mainly serves as a carrier for
the microorganisms and improves soil properties and substrate. Methane oxidation rates
vary significantly depending on the flow rate and the physical properties of the substrate
sample.
Landfill cover soils are important for attenuating fluxes of methane to the atmosphere and transformation of methane to carbon dioxide via methane oxidation. Borjesson and Svensson (1997) demonstrated that the rate of oxidation varies depending on temperature and moisture, but their studies were restricted to the topsoil down to 0.12 m. Landfill cover soils contain a large quantity of methanotrophic bacteria allowing for higher rates of methane oxidation. Oxygen penetration is directly affected by the porosity of the soil. Soils that are compacted too tightly will prevent methane oxidation from occurring at detectible levels due to the minimization of oxygen penetration.

Soil depth also acts as a significant factor that is essential in the optimization of methane oxidation. Soil depth changes regionally for optimum methane oxidation, because soil temperature and soil moisture vary significantly from location to location. For example research on a Swedish landfill showed that the activity of methane oxidizing microorganisms was greatest around 0.5–0.6m depth in the soil profile (Borjesson and Svensson, 1997). In another study, it was indicated that methane oxidation takes place mainly in the top 30cm of the covering soil (De Visscher et al. 1999).

In order for methane to oxidize, adequate oxygen is necessary. Oxygen penetration to the oxidation zone is dependent on the soil moisture. Oxygen and water balance influences one another. When the soil surface is flooded with rain and its retention time is long, the methane oxidation is typically influenced negatively.

2.3.5 Barometric Pressure

Another factor influencing \( \text{CH}_4 \) emissions and oxidation is the barometric pressure. In models used to estimate oxidation rates, the change in pressure instead of pressure itself was the actual parameter used. Borjesson et al. (1996) has indicated that when air pressure decreases, landfill gas will be sucked out and vice versa. A very strong negative correlation was found by Czepiel et al (2003) between the methane emissions and air pressure. Borjesson and Svensson (1997) have maintained that there is not a significant seasonal correlation between concentration and air pressure.
2.4 ESTIMATED EMISSIONS FROM LANDFILLS

Annual methane emissions are estimated by summing total annual generation and subtracting any methane that is recovered or oxidized (Table 2.2). Table 2.3 shows the Municipal Solid Waste (MSW) contribution to methane emissions as well as the estimated methane emitted from landfills from 1994 to 1997. The atmospheric methane δ^{13}C (carbon isotopic composition) has been measured to be about -47 parts per thousand in air samples that were obtained between 1980 and 1985. The global average CH$_4$ source has a value of -57 parts per thousand. This value was obtained by making several assumptions including that the spatial pattern of sources and sinks is equal (Cicerone et al. 1988). Negative δ values indicate that the sample is being $^{13}$C depleted relative to the carbonate standard. More negative values indicate greater depletion of $^{13}$C.

2.5 POTENTIAL HAZARDS

The combustibility of methane is both an asset and liability to landfill owners. It is considered to be an asset when it is used as a source of energy, but a liability when migration of the landfill gas subsurface results in conditions considered to be hazardous. Methane accumulations of 5% or more will further damage vegetation and will increase the risk for explosion or fire.

Because methane is an odorless, colorless, flammable gas, several health and safety concerns have been expressed. Methane can seep up or migrate fairly easily through soils. Health and safety issues exist for workers and residents neighboring a landfill. Establishing cover soil standards and taking necessary precautions in the design of the facility and operations should aid in the mitigation of negative health impacts. It can also displace air and cause a suffocation hazard in low, enclosed spaces.

2.6 ALTERNATIVES AND AESTHETICS

Contrary to other sources, methane emission from landfills can be controlled easily. There are two main ways to reduce methane emission from landfills. One of the options is gas recovery and the other is the encouragement of methane oxidation. The use of landfill gas as an alternative energy source has become more attractive over the past few years. In many countries, landfill gases are extracted and used as fuel sources. Using
Table 2.2 Total Landfill Methane Emissions

<table>
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<tr>
<th>Total Landfill Methane Emissions</th>
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<tbody>
<tr>
<td>Equals</td>
</tr>
<tr>
<td>Methane Generated from Municipal Solid Waste (MSW Landfills)</td>
</tr>
<tr>
<td>Less</td>
</tr>
<tr>
<td>Methane Recovered and Flared or Used for Energy</td>
</tr>
<tr>
<td>Less</td>
</tr>
<tr>
<td>Methane Oxidized from MSW Landfills</td>
</tr>
<tr>
<td>Plus</td>
</tr>
<tr>
<td>Methane Emissions from Industrial Waste Sites</td>
</tr>
</tbody>
</table>

Table 2.3 Methane Emissions

<table>
<thead>
<tr>
<th>Municipal Solid Waste (MSW) Contributing to Methane Emissions (Tg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>---------------------------------------------------------------------</td>
</tr>
<tr>
<td>Total MSW Generated</td>
</tr>
<tr>
<td>Percent of MSW Landfilled</td>
</tr>
<tr>
<td>Total MSW Landfilled</td>
</tr>
<tr>
<td>Cumulative MSW Contributing to Emissions</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Methane Emissions from Landfills (million metric tons of carbon equivalent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSW Landfilling</td>
</tr>
<tr>
<td>Recovery</td>
</tr>
<tr>
<td>Oxidation from MSW</td>
</tr>
<tr>
<td>Industrial Waste Landfilling</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

Source: BioCycle (1998). The data, originally reported in short tons, are converted to metric tons. The EPA emissions model (EPA 1993) defines all waste younger than 30 years as contributing to methane emissions.
LFG as an energy source is advantageous for many reasons, including the direct reduction of greenhouse gas emissions. An LFG electricity project can capture approximately 85% of the emitted methane from MSW landfills. The methane that is collected is broken down to water and the less potent greenhouse gas of carbon dioxide. The CO$_2$ emitted is said not to contribute to the global climate change, because it would have been emitted as a result of natural decomposition.

This process also has indirect benefits such as the reduction of air pollution by the offset of using non-renewable resources. Using coal, oil, or natural gases to produce the same amount of electricity is not required. This in-turn reduces the production of pollutants such as sulfur dioxide, particulate matter, nitrogen oxides and trace hazardous air pollutants. Landfill odors are also reduced when LFG is collected as well as hazards from accumulation such as explosivity (U.S.EPA 2003). This is only an economical solution for larger landfills. There are several reasons why gas recovery is becoming more appealing, including increases in fossil fuel costs, government support of LFG-to-energy projects, and costs of complying with environmental regulations. For example, landfill owners can offset a portion of the pollution control cost that is required by Federal and State regulation, by selling the LFG that is recovered.

Methane emission can also be mitigated by using the microbiology of landfill soils (Whalen et al., 1990; Kightley et al., 1995; Czepiel et al., 1995; Borjesson and Svensson, 1997; Borjesson et al., 1998; Chanton and Liptay, 2000; Borjesson et al., 2001). Methane oxidation in landfill cover soils have been reported to vary from 7% to 50% (Reeburgh, 1996; Kightley et al., 1995; Gardner and Manley, 1993). Czepiel et al. (1996) reported methane oxidation of 10% even in landfill in the northeast of America, suggesting in warm climates, under similar conditions, methane oxidation would be much higher. Kjeldsen et al. (1997) reported that landfill soil can oxidize up 100% of methane emission. Under certain circumstance, the landfill cover can even consume atmospheric rather than emit methane to the atmosphere (Bogner et al., 1995; Borjesson and Svensson, 1997; Borjesson et al., 1998; Bogner et al., 1997)

Laboratory studies were also used to measure methane oxidation in columns. Kightley et al. (1995) reported a peak oxidation rate of 166 g CH$_4$ m$^{-2}$ d$^{-1}$. Visvanathan et al. (1999) had a maximum oxidation rate of 100g CH$_4$ m$^{-2}$ d$^{-1}$. Both were higher than the
oxidation rate of 45g CH$_4$ m$^{-2}$ d$^{-1}$ measured by Whalen et al. (1990). These results were measured on different soils and different laboratory methane feed conditions and therefore can’t easily be compared.

Research has shown that the landfill cover systems are very effective in methane oxidation. Landfill cover systems convert the methane to carbon dioxide at an efficiency of approximately 60 to 94% (Humer and Lechner 1999; Borjesson et al. 2001). If all old landfill areas were coated with suitable cover material, landfills would contribute a maximum of 5% and a minimum of 1%, of total methane emissions, annually to the atmosphere. Consideration must be given to oxidation rates during the winter when microbial degradation tends to be reduced. Researchers have demonstrated that different species of bacteria are active at different levels of methane concentration. Also suggested is the idea that methane consumption might occur at low temperatures as long as the soil water remains liquid. It was observed by Priemé and Christenson (1997) that methane oxidation remains active even at low temperatures down to 1 degree Celsius in the field and 2 degrees Celsius in soil core experiments.

2.7 THE LEON COUNTY LANDFILL

Leon County, which is approximately 671 square miles, with a population of 245,000 people has been disposing almost all of its municipal solid waste (MSW) at the Leon County Landfill since the inception of the landfill. The class III site strictly prohibits the disposal of any type of hazardous waste such as fluorescent tubes, tires, batteries, and paint. Odors emitted and visibility of the waste has caused a rise in much concern from nearby residents. Its capacity reached over 1,708,500 Mg. Because of many environmental issues brought forth the landfill closed officially for city-wide dumping in 2004. Currently no household waste is being deposited at this site. The refuse in place from the open to closing years has increased in over one order of magnitude from 130,100 Mg to an estimated value of 1,708,000 Mg. The methane emission rates have followed a similar pattern, increasing from 794.6 Mg/yr to an estimated 7,501 Mg/yr. After closure of the site, it has been predicted that the emission rates will steadily decrease in a linear fashion but at a very slow rate.
Studies performed on MSW landfill gas emissions have indicated that at certain concentrations, adverse effects may be found on both public health and welfare. Methane emissions present a hazardous threat because of danger of fire and explosion (in a 5 to 15 percent mixture with air) under extreme pressures. The main concern from methane emissions is the potential to increase global warming because methane (CH$_4$) is a greenhouse gas. When the methane is oxidized it produces carbon dioxide (CO$_2$) and water. Carbon dioxide is also a greenhouse gas, but its effects are nowhere as severe as that of methane. Also when landfill cover systems are not adequately constructed, Non-Methane Organic Compounds (NMOCs) contribute to ozone formation. Some of these compounds are known or suspected carcinogens or they may cause other health effects. These gases are a primary source for odor nuisances.
SECTION THREE
MATERIALS AND METHODS

3.1 SITE DESCRIPTION

A preliminary survey of emissions in the Leon County Landfill was conducted from June 2003 to February 2004. Based on the results of the preliminary work, S-1 Grid site was chosen for the Bio-cell study described in Section 3.7. Fig. 3.1 shows the location of each of the 4 sites investigated during the preliminary survey. The Bio-cell location resides on the side slopes of the landfill. Chanton and Liptay (2000) had previously studied the seasonal variation of methane flux and oxidation at this landfill. The Bio-cell location was chosen because it simulates the cover of an old landfill. The final cover at this site was placed over 7 years ago.

3.2 METHANE SURFACE EMISSION FLUX

The static chamber technique was used to determine the methane emission rates from the landfill surface. Each chamber covered an area of 0.4 m$^2$. The chambers used during this study were squares of 0.63 m and 0.2 m in height. Fig. 3.2 shows the chambers used in this study and a typical regression plot for methane emissions using the static chamber technique. A small fan was attached to the interior of the chamber to circulate the air trapped within the chamber. Collars were installed into the ground at fixed locations. The chambers were attached to the collars using 8 clamps (2 on each side). Prior to placement of chambers over collars, weather stripping was placed on the adjoining portion of the chamber.

Samples were taken using 60-mL disposable syringes immediately after sealing and at the 2, 5, 10, and 15 minute marks. These samples were then collected and taken to the laboratory to measure the concentrations. The gas concentrations were determined using a Shimadzu 8A gas chromatograph with a flair ionization detector. Methane flux was
Fig. 3.1. Elevation Contour and Location Map of Test Sites.
Fig. 3.2. Photograph of Static Chamber (a) and Typical Regression Plot of Methane Emissions (b).
determined using the concentration data in ppmv and plotting the concentration against elapsed time. Most of the data fit a linear regression; therefore, the slope of the fitted line dC/dt was then used to estimate the methane flux rate. Methane flux rate was calculated using the following equation:

$$F = \frac{PVMU(dC/dt)}{(ATR)}$$  \hspace{1cm} (3.1)

where, $F$ is flux rate (g/m²/d), $P$ is pressure (1 atm), $V$ is chamber volume (80 liters), $M$ is the molar mass of methane (16 g/mol), $U$ is the units conversion factor (0.00144 L min / (µL d)), $A$ is the area covered by the chamber (0.4 m²), $T$ is chamber temperature (Kelvin), and $R$ is the gas constant (0.08205 liter atm/(K mol)).

Volumes for each collar were determined by collecting all dimensions (L x W x H). The height was taken at each of the four sides of the collars. The 0.4 m² area of the chamber itself was then multiplied by the estimated height.

### 3.3 PERCENT OXIDATION

Percent oxidation was determined using the stable isotope tracing technique. Isotope samples were collected during flux measurements. The stable isotope tracing method is commonly used to determine the amount of oxidation that takes place in landfill cover soil (Liptay et al. 1998; Chanton and Liptay 2000; Borjesson et al. 2001; and Christophersen et al. 2001.) There are two stable isotopes of carbon, $^{13}$C and $^{12}$C. $^{13}$C makes up about 1% of the carbon atoms, while $^{12}$C makes up about 99% of the carbon atoms. Microbial methane (CH$_4$) is typically produced in landfills at values below -55‰. After oxidation takes place CH$_4$ may exhibit enriched values of $^{13}$C at -30 to -50‰. Negative δ values indicate that depletion of the $^{13}$C isotope is taking place relative to the carbonate standard. The lower the value of $^{13}$C, the more oxidation occurring.

The carbon isotopic composition is expressed by δ notation ($δ^{13}$C), which is calculated using the following equation:

$$δ^{13}C = [(R_{sample}/R_{standard}) - 1] * 1000$$  \hspace{1cm} (3.2)

where $R_{sample}$ is the $^{13}$C/$^{12}$C ratio of the sample and $R_{standard}$ is the $^{13}$C/$^{12}$C ratio of the marine carbonate standard (PDB, $R_{standard} = 0.01124$).
Local atmospheric methane must be accounted for when calculating isotope ratios for methane emissions ($\delta_E$) from the soil. The atmospheric methane is incorporated into the equation used for CH$_4$ emission computations.

$$\delta_E = \frac{(\delta_F - c_F) - (\delta_I - c_I)}{c_F - c_I} \tag{3.3}$$

where $\delta_I$ and $c_I$ are the methane $\delta$ and concentration for the initial gas sample and $\delta_F$ and $c_F$ refer to the final sample $\delta$ and concentration.

Studies have indicated that mehtanotrophic bacteria consume CH$_4$ containing the lighter isotope $^{12}$C more readily than the $^{13}$C (Coleman et al., 1981). The extent of oxidation can be calculated by using an estimate of the bacterial preference and is assigned by the variable $\alpha_{ox}$. This factor, $\alpha_{ox}$, is taken from the difference of the unaffected methane and the residual methane. The percent of CH$_4$ oxidized, which describes the fractionation in an open system is derived from the following equation:

$$f_o \% = 0.1 \frac{(\delta_E - \delta_A)}{(\alpha_{ox} - \alpha_{trans})} \tag{3.4}$$

where $\delta_A$ is the $\delta^{13}$C value of anoxic zone CH$_4$ (-55.4‰ determined from data), $\alpha_{ox}$ is the isotopic fractionation factor for bacterial oxidation and $\alpha_{trans}$ is the isotopic fractionation associated with gas transport.

To the extent that gas transport is dominated by advection of gases across the landfill cap $\alpha_{trans}$ will approach 1. However, if diffusion plays a significant role in gas transport, $\alpha_{trans}$ will be greater than 1 causing this approach to yield conservative values of methane oxidation (De Visscher et al., 2004). We assumed that gas transport across the landfill surface was dominated by advection so that $\alpha_{trans}$ approached 1. This is a reasonable assumption because there was no gas collection system at this landfill so gas pressure should be greater within the landfill due to CH$_4$ and CO$_2$ production. Consistent with this assumption, Czepiel et al. (2003) reported a strong negative relationship between landfill methane emission and atmospheric pressure. Berganaschi et al., (1998) also observed that landfill gas transport is dominated by advection. The fractionation factor ($\alpha_{ox}$) was determined from soil temperature ($T$, °C) using the regression equation for $\alpha_{ox}$ with temperature, for both the clay soil as well as the bio-cover material, at this same landfill reported in Chanton and Liptay (2000):

$$\alpha_{ox} = -0.000433 T + 1.0421 \tag{3.5}$$
Stable isotopic ratios were determined using a Hewlett Packard Gas Chromatograph coupled via a combustion interface to a Finnegan Mat Delta S Isotope Ratio Mass Spectrometer (GCC-IRMS) following methods adapted from Merrit et al. (1995). For chamber samples, a cryogenic focusing device was used on the front end of the gas chromatograph. The standard deviation of replicate analyses is generally about 0.15%. Stable isotopic ratios for the anoxic gases and soil gas profile were determined using direct injection on the GCC-IRMS.

3.4 MONITORING OF AMBIENT CONDITIONS

Atmospheric temperatures were measured using a thermometer. The air temperature was measured at the initial sample and at final sample during fluxing events. The average of these temperatures was used in the equation to determine the methane flux. Soil temperatures at a depth of 6 to 8 cm were also measured per cell using a thermometer. Soil samples were collected and sealed in aluminum cans and taken to the lab for moisture content testing. Initial weight of cans was predetermined. Soil samples were again weighed and placed in the oven for a period of at least 24 hours. Samples were again weighed and their water content calculated. Barometric pressures for the Tallahassee airport (19 km away from the site) were acquired via internet from intellicast.com. An average of the barometric pressures recorded per hour was used in comparison studies. For instance, if testing was done over a period of 4 hours, the barometric pressure was recorded for each of those hours and the mean was used in the analysis. The barometric pressures were then plotted against time and a best fit line was used to evaluate any correlation. The variation was noted to be minor. When the barometric pressure was compared to average fluxes, no correlation was found.

3.5 GAS CONCENTRATION PROFILE PROBES

The methane concentration profile in the soil cover was determined by installing gas probes, made of stainless steel, at different depths. These probes were used to sample gas at different depths ranging from 15 to 91 cm. A hammer was used to set probes into various depths. The gas concentrations were again determined using the Shimadzu 8A
gas chromatograph with a thermal conductivity detector. Figure 3.3 shows a nest of gas probes being sampled.

3.6 SPATIAL ANALYSIS (SURFER)

Golden Software, Inc. has developed a contouring and 3-dimensional surface mapping system, Surfer 8, for scientists and engineers. Surfer is a grid based graphics and mapping program that interpolates unevenly spaced data of all dimensions. Data can be imported into this program from numerous sources including the United States Geological Survey (USGS). Various maps were used in this study including contour, vector, wireframe, image, shaded relief or surface. Maps were also combined to produce a more complete representation of the data.

Contour plots were used extensively to evaluate any correlation between variables. Given the dimensions of the test site, contours were drawn to represent total existing cover depth, the flux and oxidation rates pre-compost, and the elevation over the entire grid area. Inverse distance weighing was used to estimate surrounding areas to the fixed locations. The two factors that influence this method of interpolation are the type of data and the interpolation setting. A setting of 2 was used for each of the contour plots developed. The interpolation procedure used, performed adequately in estimating methane concentrations over the entire grid area pre-compost as well as individualized cell contours over time. In studying the concentration at individualized cell locations over time, contours were plotted for each of the four seasons. These plots demonstrate the effect of climate/temperature on the methane emissions.
Fig. 3.3. Gas Probe Nest Being Sampled.
3.7 BIO-CELL STUDY

3.7.1 Grid Emission Survey

The selected area designated S-1 Grid, had 7-year old waste covered with about 45 cm of sandy clay and sandy loam. The area was thickly vegetated and entirely covered with a mixture of local grasses and occasional shrubs. The S1-Grid is representative of a typical older closed landfill with a vegetated soil cover. The S1-Grid was 60.8 by 60.8 m (200 by 200 feet) which was divided into eight rows and eight columns. The rows and columns were labeled A through H and one through eight respectively. Methane emissions were measured in the middle of each square with more sample locations added in selected squares to better define the flux distribution over a short distances. The average flux was used for locations where the flux was repeatedly measured. Six squares had additional sampling locations in each quadrant as well as one in the middle. In these squares the minimum separation distance between sampling locations was 2.69 m (8.84 ft). Flux and oxidation contours were obtained for the entire S1-Grid.

Hot spots were identified and further studied. Probes were inserted into these areas to the trash level. In this way, samples were collected to verify that no gas migration was occurring at these locations. Using probes would also indicate what layer of soil produced the most oxidation. Collars were placed directly above these spots to measure the difference in concentration from prior testing. Trace amounts of methane were observed at these spots. Based on all of the samples collected, six areas with high methane emissions were identified. Row B and Row D were chosen for the bio-cell study.

3.7.2 Layout of Bio-cell

Two rows, rows B and D, were chosen for the bio-cell study. Three squares were selected for compost treatment in Row D (Cells 2D, 4D, and 6D) and three were left as is in Row B (Cells 2B, 4B, and 8B) to monitor the change in emissions with time. Four collars were installed on each of the six cells. Fig. 3.4 shows a contour map of the thickness of cover soil in the S1-Grid a long with the locations selected for the bio-cell study. The selected areas were all squares with 7.6 meters sides. Once the areas were
chosen the methane flux was measured in several locations inside each hot spot area several times before the application of compost. A layer of crushed recycled glass was placed over each square to disperse the landfill gas as it emerges from the cover, thereby making the gas flux into the compost more uniform. The glass layer was placed with a low pressure skid steer to avoid disturbing the ground surface. The glass was then raked manually to achieve a uniform thickness of about 10 cm (Fig. 3.5a). The glass was placed only in the hot spot areas were compost will be used. Aged compost (chipped yard waste stockpiled for 5 years) was hauled, dumped, and spread with a bulldozer to a depth of 38 cm over the crushed glass, with spreading completed on March 17, 2004 (Fig. 3.5b)
Fig. 3.4. Location of Bio-Cell Study Prior to Bio-cover Placement.
Fig. 3.5. Placing of Glass Layer (a), Placing of Compost Layer (b).
SECTION FOUR
RESULTS AND DISCUSSION

S1-Grid is an area where the waste was covered 9 years prior to the measurement period. S1-Grid was located on the side slopes of the landfill. Contour plots were created using Surfer 8 developed by Golden Software. Surveys were conducted to evaluate topography, existing depth of cover, and average flux rates throughout the S1-Grid. Through this preliminary work on the site, two rows were chosen for the bio-cell study, one of which was selected for compost placement. After compost was placed, six cells were more thoroughly studied for seasonal variation. The six cells were selected based on continuous testing that indicated a very high to medium flux rate emission.

4.1 S1-GRID SURVEY: PRE-COMPOST

Fig. 4.1 shows a contour map of cover thickness in the S1-Grid. The soil cover in S1-Grid varied from 21 to 119 cm and averaged 45 cm in thickness. The Northwest corner of the S1-Grid seems to have the thickest soil cover. The Southeast corner on the other hand had the thinnest soil cover. The S1-Grid can then be assumed to simulate a typical cover for an older landfill with similar cover thickness. The vegetation in the S1-Grid was also well established. Fig. 4.2 shows a contour map of the topography of the S1-Grid. As can be noted from Fig. 4.2, the S1-Grid slopes from North to South with contour lines running East-West indicating little to no-sloping in the East-West direction. Elevations ranged from 30.6 to 29 m. Fig. 4.3 and Fig. 4.4 show methane emission flux and oxidation rate measured at the surface of the S1-Grid during one month period prior to the initiation of the bio-cell study.

The preceding contour maps show that methane emissions can occur even when the soil cover is as thick as 95 cm. Methane oxidation seems to be occurring throughout the S1-Grid (Fig. 4.4). The mean methane oxidation rate was 25.2% for S1-Grid. The peak oxidation rate was 63.9% for the S1-Grid. Some evidence of how methane
Fig. 4.1. Total Thickness (in Meters) of Existing Soil Cover in S1-Grid.
Fig. 4.2. Topography (in Meters) of S1-Grid.
Fig. 4.3 Average Flux (g/m²/d) Measured on the Surface of S1-Grid Prior to Compost Placement During the Period of September 2003 to February 2004.
Fig. 4.4 Average Fraction Oxidized Measured on the Surface of S1-Grid Prior to Compost Placement during the period of September 2003 to February 2004.
oxidation is affecting the measured emissions can be observed. For instance in the areas where the flux rate is 50 g/m²/d, the oxidation rate is around 20%. On the other hand, areas with flux rates of 20 g/m²/d show higher oxidation rates of about 40%. This suggests that the higher oxidation rate might be responsible for the lower surface emissions. However, as previously stated oxidation was evident over the entire area.

High emissions zones in the S1-Grid were isolated spots. The flux contours also show that emissions from most of the thicker vegetated cover are low. This flux contour pattern suggests that most of the emissions at the S1-Grid are occurring from a few spots with small surface areas. This emission pattern might be representative of emissions from older landfills having similar covers to S1-Grid (relatively thick and well vegetated). To mitigate emissions from such covers, biocells (layers of compost) can be placed only on high emission areas.

4.2 PRE/POST-COMPOST SURFACE EMISSIONS COMPARISON

Six squares of the S1-Grid have been selected as experimental units for the biocell study. A layer of compost was placed on 7.6 m by 7.6 m squares around high emissions spots (2D, 4D, and 6D). Three other high emission spots were left untreated and were monitored along with the compost experimental squares (2B, 4B, and 8B). Prior to compost placement, an intensive flux survey was performed on all six cells to establish pre-compost conditions. The flux in each cell was measured 12 to 14 times during the month prior to compost placement. The survey of methane flux emissions continued in all six cells after glass and compost was placed on Cell 2D, 4D, and 6D. Flux measurements were continued since the compost was placed and will continue to monitor the long term performance of the biocells. Tables 4.1 and 4.2 show the summary of fluxes measured at each cell prior to and after compost placement. Fluxes measured on each cell at a given date were averaged. Cells with flux emissions higher than 100 g/m²/day were classified as very high emission zones. Cells with average flux emissions between 50 and 100 g/m²/day were classified as medium emission cells, and cells with fluxes lower than 10 g/m²/day were classified as low emission cells.
Table 4.1 Classification of No-Compost Flux Emissions (g/m²/d).

<table>
<thead>
<tr>
<th>Cell</th>
<th>Average Flux Pre Compost</th>
<th>Peak Flux Pre Compost</th>
<th>Minimum Flux Pre-Compost</th>
<th>Emission Classification on Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>2B</td>
<td>70</td>
<td>247</td>
<td>5</td>
<td>High</td>
</tr>
<tr>
<td>4B</td>
<td>38</td>
<td>58</td>
<td>0</td>
<td>Medium</td>
</tr>
<tr>
<td>8B</td>
<td>3</td>
<td>8</td>
<td>0</td>
<td>Low</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cell</th>
<th>Average Flux Post Compost</th>
<th>Peak Flux Post Compost</th>
<th>Minimum Flux Post-Compost</th>
<th>Emission Classification on Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>2B</td>
<td>32</td>
<td>323</td>
<td>-0</td>
<td>Medium</td>
</tr>
<tr>
<td>4B</td>
<td>7</td>
<td>108</td>
<td>-0</td>
<td>Low</td>
</tr>
<tr>
<td>8B</td>
<td>4</td>
<td>49</td>
<td>-0</td>
<td>Low</td>
</tr>
</tbody>
</table>

Table 4.2. Classification of Compost Flux Emissions (g/m²/d).

<table>
<thead>
<tr>
<th>Cell</th>
<th>Average Flux Pre Compost</th>
<th>Peak Flux Pre Compost</th>
<th>Minimum Flux Pre-Compost</th>
<th>Emission Classification on Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>445</td>
<td>1743</td>
<td>0</td>
<td>Very High</td>
</tr>
<tr>
<td>4D</td>
<td>7</td>
<td>27</td>
<td>0</td>
<td>Low</td>
</tr>
<tr>
<td>6D</td>
<td>55</td>
<td>288</td>
<td>0</td>
<td>High</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cell</th>
<th>Average Flux Post Compost</th>
<th>Peak Flux Post Compost</th>
<th>Minimum Flux Post-Compost</th>
<th>Emission Classification on Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>60</td>
<td>1159</td>
<td>-0</td>
<td>High</td>
</tr>
<tr>
<td>4D</td>
<td>2</td>
<td>22</td>
<td>-0</td>
<td>Low</td>
</tr>
<tr>
<td>6D</td>
<td>1</td>
<td>11</td>
<td>-0</td>
<td>Low</td>
</tr>
</tbody>
</table>
In Cells 2B (no compost), the peak flux increased from 247 (pre-compost) on February 4, 2004 to 323 g/m²/day on August 17, 2004. In Cell 4B and 8B (no compost), the peak measured flux increased from 58 g/m²/day prior to compost placement to 108 g/m²/day and from 8 to 49 g/m²/day, respectively. The peak methane emissions were generally not frequent enough the affect the average emissions. For example, the average methane flux decreased from 37 to 7 g/m²/day in Cell 2B and from 28 to 7 g/m²/day in Cell 4B, but increased from 3 to 4 g/m²/day in Cell 8B. On the other hand, the average measured flux from the cells that received glass and compost all decreased dramatically. The average flux decreased from 445 to 60 g/m²/day in Cell 2D, from 7 to 2 g/m²/day in Cell 4D, and from 55 to less than 1 g/m²/day in Cell 6D. The measured peak emissions flux in all of these three cells also decreased, from 1743 to 1159 g/m²/day in Cell 2D, from 27 to 22 g/m²/day in Cell 4D, and from 288 to 11 g/m²/day in cell 6D.

The average methane flux in the cells that were not treated with compost varied from 3 g/m²/day in Cell 8B to 70 g/m²/day in Cell 2B. The peak emission flux in these cells was 8 g/m²/day for Cell 8B, 58 g/m²/day for Cell 4B, and 247 g/m²/day for Cell 2B. On the other hand, the pre-treatment average flux in the cells that were treated with compost varied from 7 g/m²/day in Cell 4D, to 445 g/m²/day in Cell 2D. In addition, the peak emission flux measured in these cells was 27 g/m²/day for Cell 4D, 288 g/m²/day for Cell 6D, and 1743 g/m²/day for Cell 2D.

Before compost placement, Cells 2B, and 6 D were classified as high emissions cells. Cell 2D was classified as a very high emission cell. Cells 8B, and 4D were classified as low emission cells. Cell 4 B was classified as medium emission cell. It was not anticipated that emissions from half of the cells were this low. After compost placement, Cells 4 B, 8B, and 4 D were classified as low emission cells. Cell 2B was classified medium emission cell during the post compost period. Bio-cell 2D was classified as a high emission cell even after compost placement, but had decreased from an emission of 1743 to 1159 g/m²/d.
4.3 TIME SERIES OF AVERAGE DAILY FLUX EMISSIONS

Fluxes were averaged both per day and per cell. The No-Compost cells were compared to Compost cells or biocells. Figs. 4.5a and b show the variation of average flux rates over time before and after placement of compost for cells without compost. Figs. 4.6a and b show the variation of the average flux over the same period of time for the cells with compost (Biocells). Emissions from cells without compost seemed to stay the same during the entire monitoring period except for the period between March 24 and May 18, where the flux was lowest for all three no-compost cells. This period was characterized by being one of the driest periods on records. Emissions from the cells with compost decreased just after compost placement then increased during the summer and then started to decrease again early late summer to early fall.

The average emissions from Cell 2B were higher than 10 g/m²/d before the compost was placed. Emissions from this cell were always higher than 10 g/m²/d except for the period between April 19 through May 18 when they were less than 10 g/m²/d. The average emissions from Cell 2D were higher than 100 g/m²/d on the days prior to compost placement. Emissions from Cell 2D were higher than 100 g/m²/d after the placement of compost only on two fluxing events. Emissions from Cell 2D seems to have peaked on June 1st and then started to decrease to below 10 g/m²/d on October 8. Pre-compost emissions from Cells 4D and 6D were initially high then decreased dramatically before the compost was placed (February 02). The post-compost emissions from Cells 4D and 6D remained relatively low (less than 1 g/m²/d) except for the period between June 3, and July 22.

In order to better contrast the emissions from the cells with compost and the cells without compost, the daily average flux was determined for all the cells in Row B (No-compost) and in Row D (Compost). Fig 4.7a indicates that pre-compost flux rates averaged higher in Row D which again is why it was chosen to be the compost treatment site. In some cases, Row D more than doubled the flux rates of Row B, the zone chosen as the no-compost zone. Emissions from Row D showed the same trend as the ones
Fig. 4.5 Average Flux Within No-Compost Cells a) Pre-Compost, b) Post-Compost.
Fig. 4.6 Average Flux Within Bio-Cells a) Pre-Compost b) Post-Compost.
Fig. 4.7  Average Flux From Row B (No-Compost) and Row D (Compost)

a) Pre-Compost  b) Post-Compost.
observed for Cell 2D, demonstrating that Cell 2D governs the average flux rates measured in Row D. The pre-compost fluxes in Row D were one order of magnitude higher (on average) than in Row B. After the compost was placed both Rows had an average flux around 10 g/m$^2$/d until June 3$^{rd}$. The average flux in Row D increased in the summer months to reach 100 g/m$^2$/d. After August 17$^{th}$, the average flux in row D decreased to well below 10 g/m$^2$/d (Fig. 4.7b).

4.4 SPATIAL DISTRIBUTION OF FLUX FROM BIO-CELLS

Fluxes measured on four sampling events on the surface of Cells 2D, 4D, and 6D were contoured to monitor the spatial pattern of emissions from these cells. Four specific dates were chosen. The first event was pre-compost and the remaining three were post-compost sampling events. Only Cell 2D contours are shown in Fig. 4.8. Contours for Cells 4D and 6D are included in the appendix. Prior to compost placement, high fluxes were measured in the northwest corner of Cell 2D and were as high as 1600 g/m$^2$/d. The flux elsewhere in Cell 2D was around 100 g/m$^2$/d, prior to compost placement. On April 28$^{th}$, the highest flux was also at the northwest corner of Cell 2D and was around of 55 g/m$^2$/d. Elsewhere the flux was as low as 5 g/m$^2$/d. The same pattern of emission is observed in all four contours in Fig. 4.8. That is, the highest emission in Cell 2D were always measured at northwest corner.

Cells 4D and 6D also show that spatial distribution of the flux is the same before and after compost placement. Locations with the highest fluxes before compost placement also had the highest flux after compost placement. This suggests that the crushed glass layer placed to function as a dispersing layer did not function well. The purpose of the crushed glass layer was to even-out the flux of methane into the compost. It is not clear why the glass layer did not disperse the flow at the bottom of the compost. This might be due to the graduation of the glass layer, i.e., the glass contained too much fines that were responsible for clogging the flow of gas through the glass layer. The
Fig. 4.8 Contour Maps of Flux Measured (g/m²/d) on Surface of Cell 2D (meters): Pre-compost (a), Post-Compost April 28, 2004 (b), July 27, 2004 (c) and October 8, 2004 (d).
thickness of the layer might not be enough to allow the flow of methane to move horizontally before starting to go through the compost. Further analysis of the dispersing layer is warranted.

4.5 AVERAGE METHANE OXIDATION: PRE-POST ANALYSIS

As described in Section 3, stable isotope techniques were used to measure the percent oxidation that the methane has undergone prior to appearing on the surface. Fig. 4.9a shows the percent oxidation measured in Cells without compost (2B, 4B, and 8B) throughout the monitoring period. Fig. 4.9b shows the percent oxidation measured in Cells with compost (2D, 4D, and 6D). In the no-compost region (fig 4.9a), consistently high oxidation rates were found amongst all three cells in April 28th. On July 27th, almost no oxidation took place over the entire region. On this date, flux emission rates for all three cells were fairly high in all three cells. An extremely high oxidation rate occurred within cell 2B on September 3rd. The testing period just prior to this measured rate showed the highest flux emission throughout the study. In cells where no emissions were reported, it may be assumed that oxidation was taking place at very near 100%.

No consistency in oxidation rates was found within the compost region as indicated by Fig. 4.9b. Very low oxidation rates were measured on July 27th and September 3rd. In Cell 6D, moderately constant oxidation rates were observed from March 24th through June 10th. Following this period, oxidation rates significantly decreased.

Fig. 4.10 compares the average oxidation rates of the no-compost zone to that of the compost zone and shows the number of samples collected for each date. Oxidation occurred within the same ranges from March 24th until June 10th. At this point, higher rates were observed in the compost zone but alternated to the no-compost zone in the following test (June 29th). Following this study, again the high rate shifted to the compost zone by almost 10%. September 3rd demonstrated a shift in performance, indicating the no-compost zone had higher oxidation rates. At the last test time (October 8th), almost no oxidation took place over the entire region. A more accurate estimate of oxidation could have been developed if more samples were correct.
Fig. 4.9 Daily Oxidation Rates  a) No-Compost Zone b) Compost Zone.
Fig. 4.10  Average Oxidation Comparison of Compost Zone and No-Compost Zone.  
(Numbers above columns indicate number of samples collected)
4.6 MASS OF METHANE OXIDIZED

The flux measured at each location along with the percent oxidation was used to calculate the mass of methane being oxidized by the cover material. Mass of methane oxidized was used to improve the estimate of the quantification of landfill gas being mitigated. Therefore, the mass of methane oxidized is a better index or measure of how effective a reactive layer is in consuming methane. Fig. 4.11a shows the mass of methane being oxidized during each sampling event in Cells without compost (2B, 4B, and 8B).

Fig. 4.11B shows the mass of methane being oxidized during each sampling event in Cells with compost (2D, 4D, and 6D). According to Fig. 4.11a, a high mass of methane oxidized was measured on the date of July 27th of 17 g/m²/d. All grid cells in the no-compost zone showed increased mass of methane being oxidized at the final sampling event (October 8th). In the cells with compost, a high mass of methane oxidized was observed on June 10th. Fig. 4.11c demonstrates the variation of the mass of methane oxidized between the compost zone and the no-compost zone.

4.7 WATER CONTENT, TEMPERATURE AND BAROMETRIC PRESSURE

The relationships between methane flux and water content, soil temperature, and barometric pressure can be very helpful when characterizing flux emission data from different locations and from different times. However, the effect of water content on flux is complicated by its effect on microbial oxidation and gas migration. Methanotrophs need water to be active, but too much water in soil reduces oxygen availability. Gas flux is also influenced by physical advection due to pressure gradients between the waste and the atmosphere.

Fig. 4.12 shows the average flux measured from Row B (no compost) and Row D (with compost) plotted with the measured water content at every sampling event. For both rows, there is no clear trend or correlation between the measured emissions and water content of the soil. Fig. 4.13 shows the variation of flux with soil temperatures measured on each sampling event. Once again, there is no clear correlation between the measured flux and the soil temperature. High water content may concentrate gas.
Fig. 4.11 Mass of Methane Oxidized a) No compost zone b) Compost Zone c) Average No-compost/Compost Comparison.
Fig. 4.12 Flux and Water Content Variation: Row B (a), and Row D (b).
Fig. 4.13 Flux and Soil Temperature Variation: Row B (a), and Row D (b).
advection by blocking small pores and reducing the strength of the clay cover soil, thereby allowing “piping” of gas through macropores. Landfill gas can often be seen bubbling from temporary puddles and wet mud after a rain. In wet conditions flux could be high or low depending on oxygen availability and whether a gas-conducting macropore was sampled. In dry conditions it was expected that flux would be high because oxidation would be low and gas conductivity would be high.

Fig. 4.14 shows the percent oxidation along with water content measured in Rows B and D. Lower percent oxidation is associated with high water contents. Periods with lower water content had higher percent oxidation. It appears that the water content controls oxygen penetration into the soil and therefore limited oxidation occurs when the water content is high. Fig. 4.15 shows percent oxidation plotted with soil temperature. There seems to be no correlation between percent oxidation and soil temperature within the no-compost zone, but it is demonstrated that within the compost, there is a correlation. High temperatures show low oxidation rates and low temperatures show higher oxidation rates.

**4.8 GAS CONCENTRATION PROFILES**

Fig. 4.16 shows the gas concentration profile during one sampling event (June 3, 2004) in Cell 2D, 4D, and Cell 6D (cells received compost) and in Cell 2B, 4B, and Cell 8B (cells without compost). In Cell 2D, methane concentration declined from around 55% at 20 cm to near zero at the surface. $N_2$, and $O_2$ concentrations declined with depth (from atmospheric levels on the surface to nearly zero at the same depth of 20 cm). The gas concentration profile shows that in Cell 2D oxygen only reached the top 20 cm of the compost. Therefore, only the top 20 cm of the compost was actively involved in the oxidation of methane as it moved upwards from the glass layer. The gas concentration profile in Cell 2D also shows that the glass layer along with the bottom half of the compost layer had methane concentrations equal to values measured in the waste mass.

In Cell 4D, oxygen reached to about 30 cm. The methane concentration was zero from the surface to a depth of 18 cm. The methane concentration then increased to 50% at the top of the glass layer and then increased gradually thereafter until it reached 60% at
Fig. 4.14 Percent Oxidation and Water Content: Row B (a), and Row D (b).
Fig. 4.15 Percent Oxidation and Soil Temperature: Row B (a), and Row D (b).
Fig. 4.16. Gas Concentration Profile at One Sampling Event (June 3, 2004) in Cell 2D and Cell 6D.
the waste level. In the case of Cell 6D, the methane concentration decreased from around 50% at the waste level to about 25% in the glass layer. The methane concentration decreased to zero at a depth of 18 cm. The oxygen concentration profile in Cell 6D shows that oxygen has diffused into the glass layer and maybe deeper.

The profiles in Cell 2B, 4B, and 8B (no compost) show that $O_2$ has diffused in to a depth of around 60 cm (on average), i.e., the oxygen has diffused through the entire thickness of the cover soil.
SECTION FIVE
SUMMARY AND CONCLUSIONS

The decomposition of landfill wastes produces harmful greenhouse gases which must be mitigated. Fifty five percent of landfill gas is methane, which accounts for fifteen to twenty percent of the global anthropogenic greenhouse effect. Methane collection and/or oxidation of methane are the two most common solutions. This study was directed towards the enhancement of oxidation capabilities of landfill covers using compost.

A square grid, 60.8 meters on a side, was chosen as the study area. Areas within the S1-Grid were selected for the bio-cell study after the detailed grid survey was completed. S1-Grid was chosen because it simulates a typical soil final cover. Methane emissions were measured using a static chamber technique. Fluxes were very non-uniform ranging from negative emissions to a rate of up to 1743 g/m²/d. Percent oxidation taking place within the cover was determined using the stable isotope tracing technique.

From an initial survey of the entire region, two rows were designated to conduct further research. Each row was then divided into separate cells measuring 7.6 meters on a side. Three cells were left as is to monitor emissions with time (Cell 2B, 4B, and 8B). The other three cells were covered by a 10 cm glass layer and a 38 cm layer of compost (Cell 2D, 4D, and 6D).

The average methane flux decreased from 70 to 32 g/m²/day in Cell 2B, and from 38 to 7 g/m²/day in Cell 4B, and increased from 3 to 4 g/m²/day in Cell 8B. On the other hand, the average measured flux from the cells that received glass and compost all decreased significantly. The average flux decreased from 445 to 60 g/m²/day in Cell 2D, from 7 to 2 g/m²/day in Cell 4D, and from 55 to less than 1 g/m²/day in Cell 6D. Before compost placement, Cells 2B, and 6 D were classified as high emissions cells. Cell 2D was classified as a very high emission cell. Cells 8B, and 4D were classified as low
emission cells. Cell 4 B was classified as medium emission cell. It was not anticipated that emissions from half of the cells would be this low. After compost placement, Cells 4 B, 8B, and 4 D were classified as low emission cells. Cell 2B was classified medium emission cell during the post compost period. Biocell 2D was classified as a high emission cell even after compost placement.

The flux contours obtained from the flux emission data seem to indicate that the glass layer was not able to disperse the high flux measured before the glass was placed, because these contours show that the high flux areas of each cell remained in the same location before and after the placement of compost.

Soil temperature as well as atmospheric temperature was analyzed to verify the optimum temperatures for methanotrophic bacteria. Minimal difference was found between flux emission and temperature. This could be attributed to the fact that soil temperatures varied little throughout testing time and never fell below 8.4°C. Atmospheric temperatures ranged from 6.9 to 37.1°C. There was, however, a correlation between soil temperature and oxidation rates only within the compost zone. Peak oxidation rates occurred at soil temperatures between 20 and 35 ºC. At soil temperatures above 40°C, oxidation rates were lowest at just above 10%. At higher atmospheric temperatures, some desiccation of the cover soil occurred. For this reason, moisture content and soil porosity were also reviewed.

Since water content was not collected daily, rainfall data was also used to substantiate effects on methane emissions. Rainfall data, in conjunction with air filled porosity demonstrated that for drier regions with greater porosity, high fluxes could be observed. This was indicated in comparing daily flux rates to the air filled porosity only in the compost zone. In some cases oxidation did not follow the same pattern. In Row B (no compost), low fluxes occurred in conjunction with high water contents of approximately 50%. When a significant reduction of water content occurred, flux emissions peaked before leveling out. In Row D (compost), an inverse relationship was noted between the water content and the average flux emissions. At high water contents, low flux emissions could be observed and at low water contents, flux emissions were high. Oxidation rates varied in much the same way. High water contents corresponded with low oxidation rates and vise versa.
Early on in the study, oxidation rates over 10% were found consistently in cells 2B and 8B. Any negative oxidation rates were omitted to take the conservative approach. Negative oxidation rates in essence indicate that methane is being taken in from the atmosphere. The purpose of this study is to reduce emissions into the atmosphere; therefore any amount that is being absorbed is more than satisfying of the goals presented herein. As indicated previously, saturation of cover soils reduces the oxidation ability of bacterial decomposition. Further study on the effects of moisture content and other variables to flux emission and oxidation is warranted.
APPENDIX
CONTOUR MAPS

Contour Maps of Flux Measured (g/m²/d) on Surface of Cell 4D (in Meters):
Pre compost (a) Post Compost – April 28th, (b) July 27th (c) and October 8th (d).
Contour Maps of Flux Measured (g/m²/d) on Surface of Cell 6D (in Meters):
Pre compost (a) Post Compost – April 28th, (b) July 27th (c) and October 8th (d).
REFERENCES


BIOGRAPHICAL SKETCH

OBJECTIVE
To begin a career in the Civil/Environmental Engineering Profession, which allows for utilization of my skills, knowledge of engineering, and conceptual ideas of design and management, while gaining experience and working towards my professional license.

EXPERIENCE

Summer 2003 to present  Dr. Abichou,  FAMU-FSU College of Engineering,  Tallahassee, FL
Research Assistant
✧ Field and lab testing for methane emissions
✧ Calculated fluxes for acquired data and data analysis for variability

Spring 2003  Dr. Awoniyi,  FAMU-FSU College of Engineering,  Tallahassee, FL
Teaching Assistant
✧ Graded papers/exams for First Year Engineering Lab
✧ Excel work regarding class averages for ABET reports

2001 to present  Jimmy Postich  The Moon Incorporated  Tallahassee, FL
Bartender
✧ Customer service
✧ Inventory

2001 to 2003  Dr. Nur Yazdani,  FAMU-FSU College of Engineering,  Tallahassee, FL
Student Assistant
✧ Edited papers for publication in recognized civil engineering journals
✧ Accounting for grant maintenance to ensure proper fund allocation and budget compliance
✧ Personnel appointment paperwork

2001 to 20003  Civil & Environmental Engineering Dept.,  FAMU-FSU COE,  Tallahassee, FL
Student Assistant
✧ International Graduate Admissions Assistant
✧ Graduate Web Page Reformatting

2000 to 2001  Alan Newman,  Doctor Mechanic,  Marianna, FL
Bookkeeper
✧ Responsible for all accounting information
✧ Inventory of supplies needed and used
1997 to 2000           Thad Richards             Hungry Howies                Marianna, FL

Assistant Manager
+ Management of store
+ Scheduling of employees
+ Weekly Inventory

EDUCATION
1998-2000           Chipola Junior College        Marianna, FL
+ A.A. in General Engineering
2000-2003           Florida State University        Tallahassee, FL
+ B.S. in Civil/Environmental Engineering GPA – 3.31
2003-2005           Florida State University        Tallahassee, FL
+ M.S. in Civil/Environmental Engineering GPA – 3.76

SKILLS
+ Proficient in Microsoft Office, MathCAD, Technical writing styles and techniques, knowledgeable in Pond Pak, Storm Cad, and AutoCAD
+ Organized, Responsible, Punctual, Hardworking, and Dependable

PROFESSIONAL AFFILATIONS AND OTHER ORGANIZATIONS
+ American Society of Civil Engineers (ASCE)
  - Treasurer of the FAMU-FSU COE Student Chapter Spring 03
  - 2002 to 2003, FAMU-FSU COE Concrete Canoe Committee
+ Society of Women Engineers (SWE)
+ Hispanic/Latino Student Union (HLSU)
+ Puerto Rican Student Association (PRSA)
+ Cuban American Student Association (CASA)
+ Sabrosura (Miami Style Salsa)
+ Lambda Tau Omega Sorority Incorporated-Founding Sister & President Spring 2003
+ Florida-Georgia Louis Stokes Alliance for Minority Participation (FGLSAMP) Fall 2003

HONORS AND AWARDS
+ Outstanding Member of Puerto Rican Student Association
+ Valedictorian of High School (CHS)
+ Florida-Georgia Louis Stokes Alliance for Minority Participation (FGLSAMP) Bridge to the Doctorate Scholarship Recipient (Fall 2003)