

Fall 1995

# Radiatively active trace gas emissions from waste management systems

Peter Matthew Czepiel  
*University of New Hampshire, Durham*

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RADIATIVELY ACTIVE TRACE GAS EMISSIONS FROM WASTE  
MANAGEMENT SYSTEMS

BY

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B.S., University of Rhode Island, 1982  
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DISSERTATION

Submitted to the University of New Hampshire  
in Partial Fulfillment of  
the Requirements for the Degree of

Doctor of Philosophy  
in  
Earth Sciences

September, 1995

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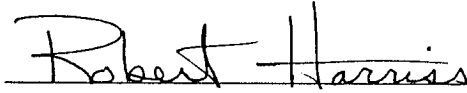
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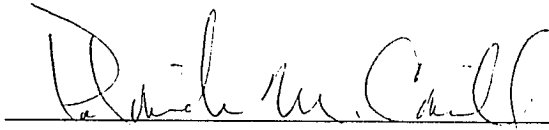
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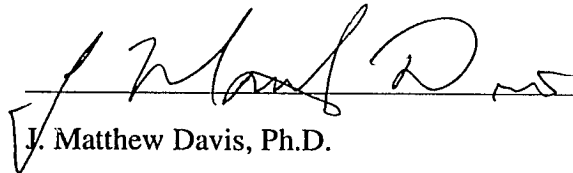
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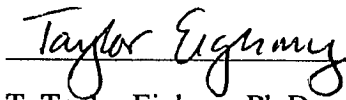
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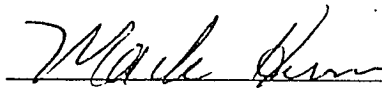
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I am deeply indebted to my trusty associates Ruth Kerwin, Paul Carroll, Mark Shipman, Barry Lefer, and Carolyn Jordan. Their company, and of course the pre-sampling Licker Store and post-sampling Press Room/Gaslight visits, made it all tolerable.

I must thank my parents for always believing in me and encouraging me to fulfill my potential. Finally, I must thank my wonderful wife, Robyn who encouraged and loved me through the peaks and valleys and never let me give up.

## PREFACE

The overarching theme of this dissertation is the quantitative assessment of emissions of methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ) from various waste management systems. The general goals of the 5 studies were to quantify emissions and to characterize the various factors that effect emissions.

Chapter 1 describes field measurements of  $\text{N}_2\text{O}$  from the liquid treatment processes at a wastewater treatment plant. Chapter 2 describes field measurements of  $\text{N}_2\text{O}$  from the composting of sludge, livestock manure, and yard wastes. Chapter 3 describes the influence of soil organic matter and moisture on the spatial distribution of  $\text{CH}_4$  oxidation in temperate zone soils. Chapter 4 describes a comparison study of  $\text{CH}_4$  emissions from a landfill using static chamber and atmospheric tracer methods. Chapter 5 describes a quantitative assessment of the capability of aerobic microorganisms to oxidize  $\text{CH}_4$  in a landfill soil cover.

Data collected from the experiments described in each chapter are presented in tabular form in Appendices A through E. Appendix F describes the methods utilized to collect the data.



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## ABSTRACT

### RADIATIVELY ACTIVE TRACE GAS EMISSIONS FROM WASTE MANAGEMENT SYSTEMS

by

Peter Czepiel

University of New Hampshire, September, 1995

Current waste management practices present significant potential for emissions of radiatively active trace gases to the atmosphere. This dissertation describes the quantitative assessment of nitrous oxide ( $\text{N}_2\text{O}$ ) emissions from liquid waste and residuals treatment, emissions of methane ( $\text{CH}_4$ ) from landfills, and the effects of microbial oxidation on landfill  $\text{CH}_4$  emissions.

$\text{N}_2\text{O}$  emissions were measured from liquid treatment process at a wastewater treatment plant where the highest emissions occurred during secondary aeration. Emission factors derived from the measurements included  $3.2 \text{ g N}_2\text{O person}^{-1} \text{ year}^{-1}$  and  $1.6 \times 10^{-6} \text{ g N}_2\text{O (liter wastewater}^{-1})$ . The potential for  $\text{N}_2\text{O}$  emissions from the composting of the residual wastewater sludge was also investigated. Treatment by composting resulted in significant emissions yielding an emission factor of  $0.7 \text{ g N}_2\text{O (dry kg of sludge)}^{-1}$ . In addition, potential  $\text{N}_2\text{O}$  emissions were predicted from the treatment of other organic wastes. Preliminary data from livestock waste and yard waste composting yielded emission factors of  $0.5 \text{ g N}_2\text{O (dry kg)}^{-1}$  and  $0.3 \text{ g N}_2\text{O (dry kg waste)}^{-1}$  from livestock and yard wastes, respectively. Livestock wastes were determined to present the greatest potential for global  $\text{N}_2\text{O}$  emissions, estimated to contribute  $1.2 \text{ Tg year}^{-1}$ .

$\text{CH}_4$  emissions from the landfilling of municipal solid wastes were determined using static enclosure and atmospheric tracer methods. Favorable agreement was observed between whole landfill emission estimates, yielding values of 16200 and 16740 liters  $\text{CH}_4 \text{ min}^{-1}$  using the chamber and tracer methods, respectively. The influence of microbial oxidation on landfill  $\text{CH}_4$  emissions was also investigated. Soil samples from locations of



CH<sub>4</sub> flux were returned to the laboratory and subjected to incubation experiments to quantify the response of oxidation in these soils to temperature, moisture, in-situ CH<sub>4</sub>, soil depth, and oxygen. The mathematical representations of the oxidation responses were combined with measured and predicted soil characteristics in a computer model to predict the rate of CH<sub>4</sub> oxidation in the soils. Air temperature and precipitation data were used in conjunction with an existing soil climate model to estimate an annual whole landfill oxidation rate in 1994 of 11 %.

**CHAPTER 1**  
**NITROUS OXIDE EMISSIONS FROM MUNICIPAL WASTEWATER**  
**TREATMENT**

CHAPTER 1  
NITROUS OXIDE EMISSIONS FROM MUNICIPAL WASTEWATER  
TREATMENT

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with co-authors P. M. Crill and R. C. Harriss

September, 1995

Summary

Nitrous oxide ( $N_2O$ ) emissions from primary and secondary wastewater treatment processes were measured during spring and summer 1993 in Durham, N. H. The most significant emissions occurred during secondary aeration. Dissolved  $N_2O$  generated as a result of denitrification during primary settling was stripped from the liquid during mechanical aeration. Emission factors derived from our field measurements included per capita emissions of  $3.2 \text{ g } N_2O \text{ person}^{-1} \text{ year}^{-1}$  and flow based emissions of  $1.6 \times 10^{-6} \text{ g } N_2O \text{ liter}^{-1} \text{ wastewater}$ . Data can be viewed in tabular form in Appendix A.

Introduction

Nitrous oxide ( $N_2O$ ) is an important trace gas that has been identified as a significant constituent in several aspects of atmospheric chemistry. It is important as a greenhouse gas due to its efficiency in absorbing infrared radiation (1).  $N_2O$  is also a major source of nitrogen oxides to the stratosphere where it plays a catalytic role in ozone destruction (2). The atmospheric mixing ratio of  $N_2O$  is about 310 ppbv and is increasing at a rate of 0.25 to 0.31 %  $\text{yr}^{-1}$  (3).

A key to formulating strategies to control and reduce the rate of increase of  $N_2O$  in the atmosphere is the identification and quantification of all sources, both natural and anthropogenic. Significant natural sources include undisturbed soils, oceanic waters and possibly atmospheric formation. These sources are estimated to account for about 60 % of the total global  $N_2O$  emissions which range from 12 to 20 Tg  $N_2O-N$  yr<sup>-1</sup> (3, 4). Many anthropogenic sources have also been identified but remain poorly quantified. These sources include cultivated soils, biomass burning, combustion, industrial processes, and waste treatment (4). The current rate of increase of the global  $N_2O$  mixing ratio implies a 40 % excess of sources over sinks (5). Anthropogenic sources present an opportunity to reduce this excess, but better quantification is necessary to establish a source hierarchy to guide the application of mitigation resources.

The purpose of this study was to quantify  $N_2O$  emissions from a municipal wastewater treatment plant consisting of processes typical of those in use in the industrialized world. The transport and management of residential, commercial, and industrial wastewater is known to produce  $N_2O$  (3). The dominant mechanism of  $N_2O$  production in these systems has recently been identified as bacterially mediated denitrification (6, 7). Denitrification occurs under anaerobic conditions which are characterized by low oxygen partial pressure. These conditions typically occur in wastewater when aerobic decomposition processes demand more oxygen than can be supplied by surface diffusion. Therefore, in the absence of mechanical aeration denitrifying bacteria activate the anaerobic conversion of  $NO_3^-$  to  $N_2$  gas and produces  $N_2O$  gas as an intermediate byproduct.

Little quantitative data exists regarding the generation of  $N_2O$  in processes that comprise modern wastewater treatment plants. This lack of data will limit further technical assessments of mitigation options. The field measurements described below were performed to quantify  $N_2O$  emissions from processes in a wastewater treatment plant, and

to compare the field derived  $N_2O$  emission factor to emission factors derived from recent laboratory investigations by Debruyne, et al. (6).

### Field Site

The municipal wastewater treatment plant studied is located in Durham, New Hampshire. The facility serves the town and the main campus of the University of New Hampshire. The population served during the school year is approximately 12,500 and generates a mean wastewater flow of approximately  $4 \times 10^6$  liters day<sup>-1</sup>. The population served during the summer is approximately 6,200 and generates a mean wastewater flow of approximately  $2 \times 10^6$  liters days<sup>-1</sup>. During the summer months plant processing capacity is normally reduced by one half through partial shut down of the grit tanks, primary settling tanks, secondary aeration tanks, and secondary settling tanks.

The facility consists of primary and secondary unit operations and processes (Figure 1.1) that treat a medium strength municipal wastewater with an average influent  $BOD_5$  at 20°C of approximately 250 mg l<sup>-1</sup> with an estimated suspended solids concentration of 220 mg l<sup>-1</sup>. Average removal efficiency is 94%. A set of two grit chambers is the first physical unit operation encountered by the influent where sand, gravel, and other heavy solids are removed from the system. The wastewater then enters the primary settling tanks where it is held in a relatively quiescent state resulting in the removal of solids with a higher specific gravity than the liquid by settlement and solids with a lower specific gravity by flotation and skimming. The liquid then enters secondary treatment, while the solids are removed from the system as primary sludge. The secondary treatment system consists of four aeration tanks and two clarification tanks. In this process the wastewater organic matter that enters the aeration tanks is decomposed by suspended bacterial biomass under aerobic

conditions. This results in the release of gases to the atmosphere and the growth of microbial biomass. The microbial-rich liquid then passes into the secondary clarification tanks where the microbial biomass is separated from the treated wastewater by gravity. A portion of the settled microbes is continuously recycled back to aeration tank #1 as an inoculum to maintain a proper concentration of microorganisms in the aeration tanks. The remaining fraction of the microbial biomass is treated as sludge which is periodically diverted to a holding tank depending on load conditions. The mixed sludge is then transferred to the sludge processing building where it is dewatered and prepared for disposal. The treated effluent moves to the chlorine contact tank for disinfection and is released into the Great Bay estuary.

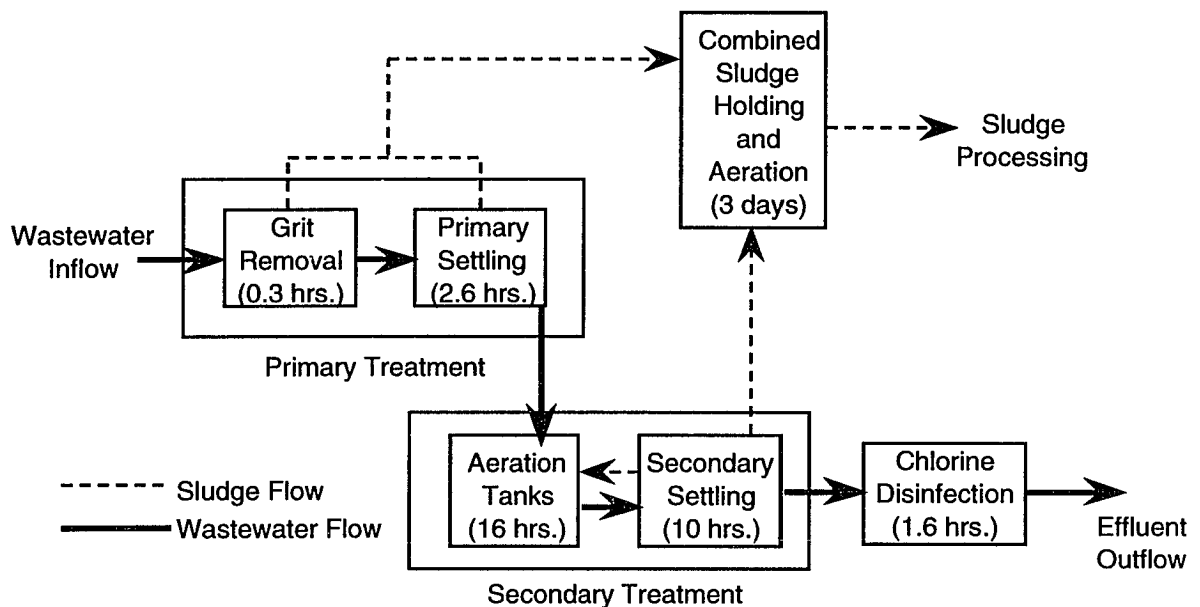


Figure 1-1. Simplified process diagram for the Durham, N. H. wastewater treatment plant. Retention times are given in parentheses.

## Methods

Nitrous oxide fluxes were measured from each tank in the wastewater treatment plant during a preliminary evaluation of plant emissions. The dominant emission sources were determined to be the grit tanks, secondary aeration tanks, and sludge holding tanks. Negligible emissions were measured from surface of the primary settling tanks and secondary clarification tanks. N<sub>2</sub>O fluxes were then measured from the dominant sources at roughly one week intervals at approximately the same time of day. Gas flux measurements were collected from aerated and non-aerated liquid surfaces. The spatial variability of measured methane concentration was examined early in the study in each source tank. The maximum measured spatial variation was found in the aerated area of the grit tank. This variability was determined to be of negligible impact when compared to the expected temporal variability of emissions. The sample collection procedures employed are described below.

### *Non-Aerated Surfaces*

An closed chamber technique was used to measure fluxes from non-aerated liquid surfaces (8). An aluminum enclosure (51 x 51 x 26 cm) was floated on the liquid surface with a thermistor mounted inside the enclosure to measure the enclosed air temperature. Floats were fastened to the enclosure sides and the chamber was manually held in place during sampling to minimize chamber movement due to surface turbulence. A battery operated blower circulated the air within the enclosure and through a closed loop of hose from which headspace air samples were withdrawn. Samples were collected in 20 ml nylon syringes at 2 minute intervals for 10 minutes. The gas flux,  $E$  (mass area<sup>-1</sup> time<sup>-1</sup>) from the liquid surface in the static chamber was calculated by the equation

$$E = (V/A) p (dc/dt) \quad (1)$$

where  $V$  is the volume of the chamber,  $A$  is the enclosed surface area,  $p$  is the density of the gas at the temperature recorded in the chamber, and  $dc/dt$  is the linear increase in the gas concentration in the chamber during the sampling period.

### *Aerated Surfaces*

A bag technique was used to measure fluxes from aerated liquid surfaces. A 40 liter polyethylene sample bag, fastened to the inside of a wood support frame, was used to collect gas samples from the agitated surface of the aerated tanks. The open base of the frame allowed gas to be collected from 0.084 m<sup>2</sup> of the surface. To collect samples the bag was collapsed and emptied of ambient air and the wood support frame was placed several inches into the liquid. Dissolved gases within the liquid, transferred to the mechanically distributed air by diffusion, then filled the collection bag. Samples were withdrawn from the bag in 20 ml nylon syringes. The gas flux,  $E$  (mass area<sup>-1</sup> time<sup>-1</sup>) was calculated by the equation

$$E = p c Q/A \quad (2)$$

where,  $p$  is the density of the gas at the temperature recorded in the sample bag,  $c$  is the sample gas concentration,  $Q$  is the total diffuse air flow, and  $A$  is the total surface area.



### *Sludge Gases*

N<sub>2</sub>O fluxes resulting from sludge storage were determined by two methods. First, gas concentrations in the sludge were determined by sampling the sludge flow, prior to transfer, with a 0.5 liter collection bucket. 30 ml sludge samples were collected immediately after withdrawal from the flow in 60 ml polypropylene syringes. An equal volume of laboratory room air was later introduced into the sludge sample syringe and the syringe was shaken vigorously for 2 minutes. The gases in the syringe headspace were then transferred to a clean 20 ml nylon syringe for analysis. This procedure was repeated five times and stripped greater than 95% of the dissolved N<sub>2</sub>O from the sludge samples. This method estimated the quantities of gases emitted during, and immediately after, transfer of sludge to the holding tanks. Fluxes were calculated under the assumption that the total gas potential of the sludge was realized by aeration stripping during the period of storage prior to final processing.

Second, fluxes resulting from the generation of gases within the sludge holding tanks, and stripped from the liquid during aeration, were determined using the aerated surface collection method described previously. This flux was assumed to be continuously present as a secondary background flux. Emissions from the surface of the non-aerated area of the sludge storage tanks were also evaluated using the closed chamber technique described previously.

### *Gas Analysis*

All samples were analyzed as described by Martikainen, et al. (9). Samples were immediately returned to the lab, allowed to equilibrate to laboratory temperature for 1 to 2 hours, and analyzed for N<sub>2</sub>O within 3 to 4 hours after collection. Samples and standards were dried across CaSO<sub>4</sub> as they were injected into the gas chromatograph (GC) injection loop. Analyses for N<sub>2</sub>O were accomplished using an electron capture detector (ECD-GC)

after constituent separation using a 2 meter x 3.2 mm OD columns packed with Hayesep N. Carrier gas was a 95% Ar - 5% CH<sub>4</sub> mixture. Peaks were quantified with Hewlett Packard Chemstation software on a personal computer. N<sub>2</sub>O standard gases were obtained from Scott Specialty Gases and were calibrated with a National Institute of Standards and Technology certified standard. Precision of analysis for calibration gases was 0.3%.

### *Statistical Analysis*

Emissions data were examined for statistical distribution to determine the appropriate form of statistical analysis. N<sub>2</sub>O flux data from the secondary aeration tank #1 was found to be lognormally distributed, requiring the application of parametric statistics to the data in log transformed form. All other sample data were determined to have been drawn from normally distributed populations, permitting application of parametric statistics. Relationships between emissions and temperature were examined using linear regression techniques (10).

## Results

### *Grit Tanks*

N<sub>2</sub>O fluxes from the aerated area of the grit tanks, measured under normal operating conditions, are presented in Figure 1-2. Fluxes ranged from a minimum of 0.17 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> to a maximum of 1.05 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>. A maximum flux of 2.48 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> was measured in the aerated area of the grit tanks after the disposal of a septic tank load by a local septage hauler. These septage disposal events occur several times during a typical week at which time gas emissions are elevated. However, these events last only a single detention period and do not contribute significantly to total weekly emissions and were disregarded.

N<sub>2</sub>O fluxes from the non-aerated area of the grit tanks, measured under normal operating conditions, are also presented in Figure 1-2. Fluxes ranged from a minimum of 0.01 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> to a maximum of 0.04 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>. Higher fluxes were also measured in this area during the septage disposal events described previously but are not representative of normal plant operations and were disregarded.

The N<sub>2</sub>O emissions data from the grit tanks were examined for temperature dependence by linear regression analyses. No statistically significant correlation was observed in either the aerated areas ( $r^2=0.13$ ) or the non-aerated areas ( $r^2=0.16$ ).

#### *Secondary Treatment Tanks (Aerated)*

Wastewater from the primary settling tanks and return sludge enter the secondary aeration system in tank #1. Preliminary measurements established tank #1 as the significant N<sub>2</sub>O source in the four tank aeration system. Samples collected from tanks #2, 3, and 4 were consistently less than 10% of fluxes measured in tank #1 and were therefore neglected in total plant emission calculations. Gases generated and dissolved in the liquid during primary settling, as well as gases generated in the return sludge during settlement in the secondary clarification tanks, are later stripped from the liquid column by aeration. N<sub>2</sub>O fluxes from tank #1 ranged from a minimum of 0.12 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> to a maximum of 1.80 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> (Figure 1-3).

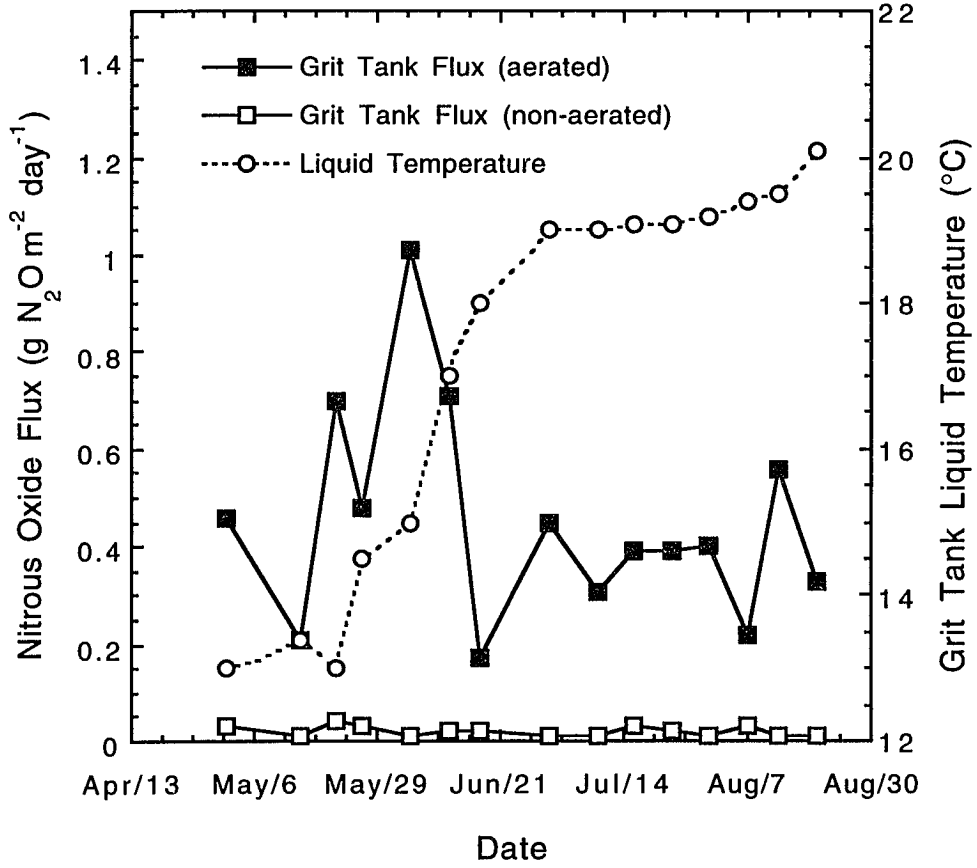


Figure 1-2. Observed  $\text{N}_2\text{O}$  fluxes ( $\text{g N}_2\text{O m}^{-2} \text{ day}^{-1}$ ) and wastewater temperatures ( $^{\circ}\text{C}$ ) from the aerated and non-aerated areas of the grit tank.

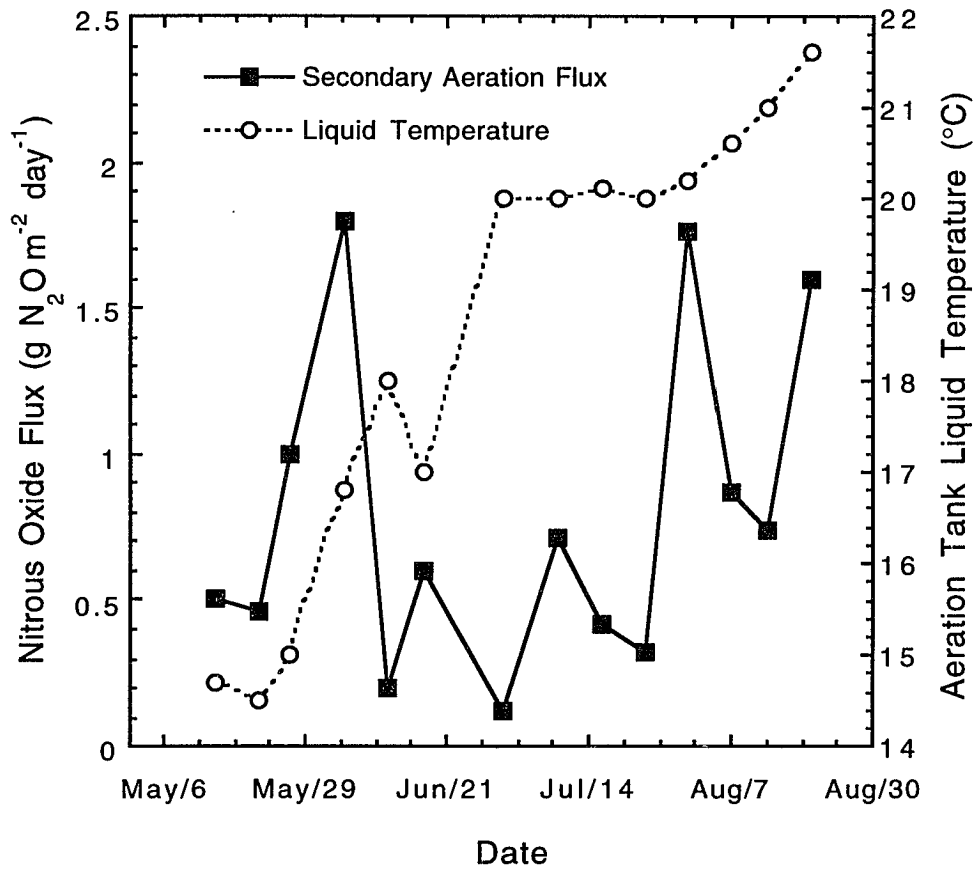


Figure 1-3. Observed  $\text{N}_2\text{O}$  fluxes ( $\text{g N}_2\text{O m}^{-2} \text{ day}^{-1}$ ) and wastewater temperatures ( $^{\circ}\text{C}$ ) from secondary aeration tank #1.

The aeration tank N<sub>2</sub>O emissions data were examined for temperature dependence by linear regression analyses. No statistically significant correlation was observed in either the aerated areas ( $r^2=0.11$ )

### *Sludge Holding Tanks*

Approximately  $2.4 \times 10^6$  liters of sludge from the primary and secondary treatment processes are transferred to the sludge holding tanks annually. The sludge is aerated in the holding tank for several days to reduce the liquid content prior to transfer to the sludge processing facility. Gas samples collected from the aerated surface early in the study indicated highly variable fluxes dependent on the time since sludge transfer. Fluxes from the aerated surface as high as  $3.1 \text{ g N}_2\text{O m}^{-2} \text{ day}^{-1}$  were detected immediately after transfer to the holding tanks, while a flux of  $0.24 \text{ g N}_2\text{O m}^{-2} \text{ day}^{-1}$  was measured from a batch of sludge after one day of aeration.

The flux potential of gases dissolved in the sludge was estimated by determining total dissolved N<sub>2</sub>O per unit volume of sludge and was assumed to be fully realized. N<sub>2</sub>O concentrations ranged from a minimum of  $15.3 \text{ } \mu\text{g N}_2\text{O liter}^{-1}$  sludge to a maximum of  $145 \text{ } \mu\text{g N}_2\text{O liter}^{-1}$  sludge.

Gas fluxes from stored sludge were measured from the aerated areas of the storage tanks to determine the flux of gases due to production during storage. Only samples collected a minimum of one day after sludge transfer were considered appropriate to estimate this secondary flux. A minimum of one day of aeration was considered necessary for the depletion of gases dissolved in the sludge during accumulation and transfer. Data collected on six sampling dates met this criteria. N<sub>2</sub>O fluxes ranged from a minimum of  $0.13 \text{ g N}_2\text{O m}^{-2} \text{ day}^{-1}$  to a maximum of  $0.28 \text{ g N}_2\text{O m}^{-2} \text{ day}^{-1}$ . The non-aerated areas of the storage tanks were also examined as a possible emissions source. Fluxes from the non-aerated areas were found to be less than 10% of the aerated fluxes and were disregarded.

## Discussion

Nitrous oxide is generated by biologically mediated denitrification in wastewater treatment systems in areas of high biological oxygen demand and low oxygen concentration such as the influent lines, primary settling tanks, secondary clarification tanks, sludge holding tanks, and sludge transfer lines. The full potential of dissolved  $N_2O$  is realized in areas of mechanical aeration where gases are stripped from the liquid by diffusion. In the Durham plant,  $N_2O$  generated in the influent lines was emitted in the aerated areas of the grit tanks by aeration and in the non-aerated areas as the result of turbulent liquid flow initiated by aeration.

$N_2O$  generated in the primary settling tanks, and in the returned sludge was stripped by aeration from the liquid in the secondary aeration tanks. The highest emissions of  $N_2O$  from the secondary aeration system were measured in the first tank where the return sludge and wastewater enter the system.  $N_2O$  emissions decreased significantly as the liquid moved sequentially through the four tank process and were negligible after transfer of the liquid to the secondary clarifiers.

$N_2O$  generated in the wasted sludge during storage was emitted during aeration in the holding tanks immediately after transfer. Additional  $N_2O$  was generated in the sludge in the non-aerated areas of these tanks during the three day detention period and was stripped from the liquid column as it flowed into the aerated areas.

The mean flux of  $N_2O$  measured from the aerated area of the grit tanks was  $0.45 \text{ g } N_2O \text{ m}^{-2} \text{ day}^{-1}$ . During the local university school year, from September through May, two grit tanks are operated in parallel with a total aerated surface area of  $11.2 \text{ m}^2$ . During the summer months, from June through August, wastewater flow and organic load is reduced by approximately half due to the local population reduction. Primary treatment

capacity during the summer low flow period is subsequently reduced by the shutdown of one grit tank and the total aerated surface area drops to 5.6 m<sup>2</sup>. These reductions preserve the continuity of emissions from the grit tank, requiring only an area weighting in total annual flux calculations. The population weighted area is 9.8 m<sup>2</sup>. The estimated total area weighted annual emissions from the aerated area of the grit tanks were 1.6 x 10<sup>3</sup> g N<sub>2</sub>O year<sup>-1</sup>.

The mean flux measured from the non-aerated area of the grit tanks was 0.02 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>. Total non-aerated surface area was 26 m<sup>2</sup> from September through May and 13 m<sup>2</sup> from June through August yielding a population weighted surface area of 22.8 m<sup>2</sup>. The estimated total area weighted annual emission from the non-aerated area of the grit tanks was 158 g N<sub>2</sub>O year<sup>-1</sup>.

The mean N<sub>2</sub>O flux from secondary aeration tank #1 was 0.61 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> while emissions from the remaining tanks were negligible. All four secondary aeration tanks remained operational throughout the sample collection period and are normally operational throughout the year with single tank aerated surface areas of approximately 144 m<sup>2</sup>. The estimated total annual emissions from secondary aeration were 3.2 x 10<sup>4</sup> g N<sub>2</sub>O year<sup>-1</sup>.

The mean sludge sample gas concentrations were 105 µg N<sub>2</sub>O liter<sup>-1</sup> sludge. Approximately 2.4 x 10<sup>6</sup> liters of sludge are transferred annually to the sludge holding tanks for aeration. Assuming complete removal of dissolved gases by aeration yields annual fluxes from sludge transfer of 252 g N<sub>2</sub>O year<sup>-1</sup>.

The mean secondary N<sub>2</sub>O flux from the aerated areas of the sludge holding tanks was 0.21 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>. Two of the three holding tanks were typically utilized for sludge storage on a continuous basis. The total aerated surface area was 18.6 m<sup>2</sup>, yielding annual fluxes from sludge storage due to secondary production of 1.4 x 10<sup>3</sup> g N<sub>2</sub>O year<sup>-1</sup>. Total estimated annual flux from sludge transfer and storage was 1.7 x 10<sup>3</sup> g N<sub>2</sub>O year<sup>-1</sup>.



The estimated total process N<sub>2</sub>O flux is summarized in Table 1-1. The total estimated annual N<sub>2</sub>O flux from the Durham, N.H. wastewater treatment plant is 3.5 x 10<sup>4</sup> g N<sub>2</sub>O year<sup>-1</sup>.

Table 1-1. Process and total N<sub>2</sub>O fluxes ( g N<sub>2</sub>O year<sup>-1</sup> ) from the Durham, N. H. wastewater plant.

| Process                 | N <sub>2</sub> O Flux |
|-------------------------|-----------------------|
| Grit Tank (aerated)     | 1.6 x 10 <sup>3</sup> |
| Grit Tank (non-aerated) | 1.6 x 10 <sup>2</sup> |
| Aeration Tanks          | 3.2 x 10 <sup>4</sup> |
| Sludge Storage Tank     | 1.7 x 10 <sup>3</sup> |
| Total                   | 3.5 x 10 <sup>4</sup> |

A weighting must be applied to calculate the population served by the wastewater treatment plant due to annual variations in the number of town residents. Approximately 12,500 people from September through May and approximately 6,200 from June through August generate wastes that are treated at this facility. The time weighted average of this population is 10,925 people which yields a per capita gas flux of 3.2 g N<sub>2</sub>O person<sup>-1</sup> year<sup>-1</sup> from wastewater treatment plants with typical primary and activated sludge treatment processes.

Flow based emission rates can also be determined. Based on an annual wastewater flow of 1.1 x 10<sup>9</sup> liters year<sup>-1</sup>, annual gas flux is estimated to be 1.6 x 10<sup>-6</sup> g N<sub>2</sub>O liter<sup>-1</sup> wastewater for the primary treatment system and 3.1 x 10<sup>-5</sup> g N<sub>2</sub>O liter<sup>-1</sup> wastewater for

the activated sludge secondary treatment system.

Total annual N<sub>2</sub>O emissions from wastewater treatment in the U. S. can be estimated using our emission factors and national wastewater and sludge handling statistics. Wastewater flow through primary treatment in the U. S. in 1988 was estimated to be  $4.1 \times 10^{13}$  liters year<sup>-1</sup> (11). This study also found return activated sludge to be the most widely used method of secondary treatment with a flow of  $3.9 \times 10^{13}$  liters year<sup>-1</sup>. Total N<sub>2</sub>O emissions from these systems, based on the Durham wastewater treatment plant emission factors, are estimated to be  $6.6 \times 10^7$  g N<sub>2</sub>O year<sup>-1</sup> from primary treatment and  $1.2 \times 10^9$  g N<sub>2</sub>O year<sup>-1</sup> from secondary activated sludge treatment.

A recent laboratory investigation of N<sub>2</sub>O generation potential from wastewater has resulted in emission factors for raw wastewater and wastewater after primary sedimentation. Wastewater samples were incubated in the laboratory yielding weighted average temperature emission factors of  $23 \pm 21$  μg N<sub>2</sub>O gss<sup>-1</sup> for raw wastewater and  $770 \pm 170$  μg N<sub>2</sub>O gss<sup>-1</sup> for effluent treated by primary sedimentation, where gss stands for “gram suspended solids” (6). These values can be compared to our results by converting our volume based emission factors to suspended solids based emission factors. Assuming a typical suspended solids concentration for untreated medium strength domestic wastewater of  $220$  mg l<sup>-1</sup> (12), yields emission factors of  $7.3$  μg N<sub>2</sub>O gss<sup>-1</sup> for raw wastewater and  $132$  μg N<sub>2</sub>O gss<sup>-1</sup> for effluent entering the secondary aeration system. These values compare well with the results of Debruyne, et al. Higher observed emission factors from the laboratory incubations of Debruyne, et al. may have resulted from the inclusion of higher strength industrial wastewater samples and ideal incubation conditions.

Our results are a first step to a quantitative national inventory of N<sub>2</sub>O emissions from wastewater treatment and should be viewed as an approximation of the order of magnitude of these emissions. Sampling of a wide variety of wastewater streams, treatment technologies and operating conditions will be necessary to better refine these

estimates. The treatment of industrial wastewater appears to hold the greatest potential for uncertainty in emission estimates. Global industrial sources generated approximately  $4.74 \times 10^{14}$  liters of wastewater in 1990 with organic matter contents, measured as  $BOD_5$ , ranging from 1000 to 35000  $mg\ l^{-1}$  (13). Organic matter of this volume and concentration represents a significant potential for denitrification and  $N_2O$  generation depending on the treatment methods utilized. For example, wastewater and sludge lagoons often operate under facultative or anaerobic conditions creating an ideal environment for denitrification. These systems are used worldwide for the treatment of industrial as well as domestic wastewater. Determining how much of this  $N_2O$  emission potential is actually realized will require continued field measurements and better characterization of global wastewater management practices.

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**CHAPTER 2**  
**MEASUREMENTS OF N<sub>2</sub>O FROM COMPOSTING AND GLOBAL**  
**ESTIMATES OF N<sub>2</sub>O FROM ORGANIC WASTES MANAGEMENT**

## CHAPTER 2

# MEASUREMENTS OF N<sub>2</sub>O FROM COMPOSTING AND GLOBAL ESTIMATES OF N<sub>2</sub>O FROM ORGANIC WASTES MANAGEMENT

To be submitted to Environmental Science & Technology  
with co-authors E. Douglas, P. M. Crill and R. C. Harriss

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### Summary

Nitrous oxide (N<sub>2</sub>O) emissions from the composting of wastewater sludge, livestock waste, and yard waste were measured during 1993 and 1994 in Durham, N. H. The mean flux from the sludge compost, 2.2 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>, resulted in a mass based emission rate of 0.7 g N<sub>2</sub>O (dry kg sludge)<sup>-1</sup>. The mean flux from the livestock waste compost, 0.5 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>, resulted in a mass based emission rate of 0.5 g N<sub>2</sub>O (dry kg waste)<sup>-1</sup>. The mean flux from the yard waste compost, 1.8 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>, resulted in a mass based emission rate of 0.3 g N<sub>2</sub>O (dry kg waste)<sup>-1</sup>. Factors effecting N<sub>2</sub>O emissions including compost age, surface winds, mechanical turning, and precipitation were also studied. Derived emission rates were then used in conjunction with recent global waste statistics to preliminarily determine the potential for N<sub>2</sub>O emissions from the treatment of wastes. Livestock waste treatment appears to present the greatest N<sub>2</sub>O potential with estimated global emissions of 1.2 Tg N<sub>2</sub>O annually. Data can be viewed in tabular form in Appendix B.

### Introduction

Nitrous oxide (N<sub>2</sub>O) is an important trace gas that has been identified as a

significant constituent in several aspects of atmospheric chemistry. Its efficiency in absorbing infrared radiation (about 200 times that of carbon dioxide) makes it important as a greenhouse gas (1, 2).  $\text{N}_2\text{O}$  is also the dominant source of nitrogen oxides to the stratosphere where it plays a catalytic role in ozone destruction (3). The current atmospheric mixing ratio of  $\text{N}_2\text{O}$  is about 310 ppbv and is increasing at a rate of 0.25 to 0.31 %  $\text{yr}^{-1}$  (4). This rate of increase implies a 40 % excess of sources over sinks (5).

To understand and possibly reduce the rate of increase of  $\text{N}_2\text{O}$  in the atmosphere, all sources, both natural and anthropogenic, must be identified and quantified. Total global  $\text{N}_2\text{O}$  emissions are estimated to range from 17 to 30 Tg  $\text{N}_2\text{O}$   $\text{yr}^{-1}$  (6). Significant natural sources, which are estimated to account for about 60 % of total  $\text{N}_2\text{O}$  emissions, include undisturbed soils, oceanic waters and possibly atmospheric formation (4). Numerous anthropogenic sources have also been identified but remain poorly quantified. These sources include cultivated soils, biomass burning, combustion, industrial processes, and the treatment of high organic content wastes (6). Anthropogenic sources present an opportunity to reduce the current rate of  $\text{N}_2\text{O}$  increase, but better quantification is necessary to establish a source hierarchy to guide the application of mitigation resources.

The major biogenic processes responsible for  $\text{N}_2\text{O}$  production are nitrification and denitrification (7, 8). Nitrification is a two-step process that, under aerobic conditions, oxidizes  $\text{NH}_4^+$  to  $\text{NO}_2^-$  followed by the oxidation of  $\text{NO}_2^-$  to  $\text{NO}_3^-$ .  $\text{N}_2\text{O}$  is produced as a byproduct of these reactions. Denitrification, ordinarily associated with anaerobic conditions, is a process in which  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{N}_2\text{O}$  or  $\text{NO}$  can be used by bacteria as terminal electron acceptors (9).  $\text{NO}$ ,  $\text{N}_2\text{O}$  or  $\text{N}_2$  are produced as end-products or by-products of these reactions.

The availability of oxygen ( $\text{O}_2$ ) is a determining factor in  $\text{N}_2\text{O}$  production. During nitrification, the oxidation of  $\text{NH}_4^+$  at low  $\text{O}_2$  partial pressures results in significant  $\text{N}_2\text{O}$  production, possibly as an intermediate between  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$  (10). During

denitrification,  $\text{NO}_3^-$  is reduced to  $\text{N}_2$  without appreciable  $\text{N}_2\text{O}$  production in the absence of  $\text{O}_2$ . But, as  $\text{O}_2$  concentration increases,  $\text{N}_2\text{O}$  production increases to a maximum and decreases with additional  $\text{O}_2$  (11). Therefore,  $\text{N}_2\text{O}$  production by both nitrifiers and denitrifiers is optimized under microaerophilic conditions (12, 13).

A microaerophilic environment, high mineral-N availability, and a high concentration of organic-C substrate have been identified as favorable conditions for  $\text{N}_2\text{O}$  production (9, 14). These conditions are prevalent in several organic waste treatment systems, particularly composting systems. The theory and operation of organic waste composting systems are discussed in detail in several comprehensive reviews (15-17).

The purpose of this study was to quantify and characterize the emissions of  $\text{N}_2\text{O}$  to the atmosphere from the composting of common organic wastes and to derive waste mass based  $\text{N}_2\text{O}$  emission factors from these results. A comprehensive study of  $\text{N}_2\text{O}$  emissions from municipal wastewater sludge composted in aerated static piles was performed from April 1993 through January 1994. Preliminary measurements of  $\text{N}_2\text{O}$  emissions from yard and livestock wastes composted in windrows, performed from September 1992 through December 1993 by Ellen Douglas, were also included in this analysis (18). The resulting emission rate data were then utilized to estimate potential  $\text{N}_2\text{O}$  emissions from composting and other organic waste treatment systems in the U. S. and globally.

### Site Descriptions

The wastewater sludge composting facility is located on the site of the Dover, New Hampshire municipal wastewater treatment (WWT) plant. The WWT plant serves a population of 25,500 and generates approximately  $1800 \text{ dry kg day}^{-1}$  of sludge from primary and secondary WWT processes. The resulting sludge has a typical dry solids content after dewatering of 25 % and a total volatile solids content of 85 %. The sludge is



mixed with wood ash as a bulking agent in a 1:1 mixture by dry weight. The mixture is composted in aerated static piles (ASP) on a concrete slab under a roofed enclosure. Aeration is maintained by introducing air into the base of the piles through perforated polyethylene pipes placed on the concrete slab prior to pile construction. The period of aeration is computer controlled and determined by the feedback of temperature from probes inserted into the center of each pile. The aeration period, which is generally several minutes long, is controlled to maintain optimal temperatures for thermophilic microbial activity in a range from 50 to 60°C. Ten compost piles are maintained on a continuously rotating basis with a new pile started approximately every 4 days. Each pile is 18 m long, 3 m wide at the base, and 2 m high and is actively aerated for approximately 40 days. The composted material is then placed outside in finishing piles for an additional 30 days prior to distribution for use in local ornamental agriculture.

The yard and livestock waste compost piles are located at the Compost Research Center of the Kingman Research Farm at the University of New Hampshire in the town of Madbury, New Hampshire. The site consists of a 1.6 hectare formerly wooded area cleared of vegetation and top soil. Livestock and yard waste is placed uncovered in separate static piles called windrows, approximately 11 m long, 3.7 m wide at the base, and 1.5 m high. The livestock waste consists of about 25 % manure and 75 % seasoned bedding hay by dry weight. The manure consists of approximately equal parts cattle and horse manure. The yard waste consists of about 80 % grass clippings, 15 % leaves, and 5 % woody wastes such as branches and twigs. The windrows are turned regularly with a mechanical windrow turner to ensure nutrient homogeneity and proper aeration. These conditions help to maintain optimal temperatures for thermophilic microbial activity in a range from 50 to 60°C. The composting process continues for approximately 1 year and is considered complete when the internal pile temperature after turning falls to ambient. The finished compost is then bagged and sold as a soil amendment.

## Methods

### *Gas Sampling*

A static enclosure technique was used to measure fluxes from the surface of the compost piles (19, 20). An open aluminum collar was inserted approximately 10 cm into the the compost surface and allowed to stabilize for several minutes prior to each flux measurement to minimize disturbance of the surface at the time of the measurement. An aluminum enclosure (51 x 51 x 26 cm) was then lowered into a water filled channel at the top edge of the collar during each measurement to provide an air-tight seal. The enclosure surface area and volume were 0.26 m<sup>2</sup> and 93.6 liters respectively.

A battery operated blower circulated the air within the enclosure and a thermistor mounted inside measured enclosed air temperature. Enclosure headspace samples were collected at 1 minute intervals in 20 ml nylon syringes and analyzed within 4 hours. The gas flux,  $E_{N_2O}$  (mass area<sup>-1</sup> time<sup>-1</sup>) from the surface was calculated by

$$E_{N_2O} = \frac{V}{A} p \left( \frac{\Delta C}{\Delta t} \right) \quad (1)$$

where  $V$  is the volume of the enclosure,  $A$  is the enclosed surface area,  $p$  is the gas density at the enclosure headspace temperature, and  $\frac{\Delta C}{\Delta t}$  is the change in  $N_2O$  mixing ratio in the enclosure headspace.  $\frac{\Delta C}{\Delta t}$  is calculated by linear regression of the  $N_2O$  mixing ratio in four or five headspace samples with a required correlation coefficient of 0.90 or higher significant to the 95% confidence level for  $n=4$  or 5 (21). The minimum measurable  $N_2O$  flux was 1 mg m<sup>-2</sup> day<sup>-1</sup>.

The sludge compost was sampled approximately bi-monthly from April 1993 to November 1993 using a stratified random sampling approach. Two flux measurements

were performed in random locations on 3 compost piles during each sampling session. The age of the compost was the selection criteria by which each pile was chosen. Piles were chosen at random in each of 3 age categories: 0 to 15 days, 16 to 30 days, and greater than 30 days. No measurements were repeated at the same locations.

In addition, interstitial gas samples were collected at various depths in the profile of several sludge compost piles to determine in-situ  $N_2O$  mixing ratios. Gas samples were collected in 20 mL nylon syringes by inserting an end-perforated 3.175 mm OD stainless steel tube into the compost in 5 to 10 cm increments. Integrated compost samples, in 10 cm depth increments, were collected at the locations of interstitial gas sampling to determine moisture contents. Compost samples were collected from the surface to a depth of 40 cm. Moisture contents were determined in all samples gravimetrically by oven drying at 105°C for 24 h (22).

Two locations were sampled repeatedly on each of the yard and livestock waste windrows. Two livestock waste windrows were sampled approximately bi-monthly, one from its inception in September 1992 through December 1992 and the second from its inception in May 1993 through August 1993. A single windrow of yard waste was sampled approximately weekly from its initiation in October 1993 through December 1993. The effect of precipitation on  $N_2O$  flux was examined during October 1992 when repeated flux measurements were performed during a two day rain event in one location on a livestock waste windrow.

### *Compost Incubations*

Sludge compost samples were incubated in the laboratory to determine the  $N_2O$  generation rate per unit mass of compost as well as the sensitivity of generation to temperature. A composited compost sample was collected from all active piles to guarantee an age averaged generation rate estimate. A trowel was used to gather approximately 50 compost samples from a regular grid over the surface of the active piles. The samples were

placed in a 20 liter bucket and mixed to ensure homogeneity. Samples ranging from 50 to 75 g were then withdrawn from the composite for incubation. Moisture contents were determined in all samples as previously described.

To determine N<sub>2</sub>O generation potential, each compost sample was subjected to time series incubation experiments performed in 1.0 liter air tight glass jars. 3.175 mm Swaglock unions with silicone septa were installed in the jar lids. Jar headspaces were sampled by removing 3 ml of gas in 10 ml glass syringes five times during each experiment. The N<sub>2</sub>O emission factor, E<sub>N<sub>2</sub>O</sub> (mass N<sub>2</sub>O time<sup>-1</sup> dry mass compost<sup>-1</sup>) was calculated by

$$E_{N_2O} = \frac{V}{m} p \left( \frac{\Delta C}{\Delta t} \right) \quad (2)$$

where V is the jar volume, p is the density of the gas at sample temperature, m is the sample dry mass, and  $\frac{\Delta C}{\Delta t}$  is the linear increase in N<sub>2</sub>O mixing ratio in the jar headspace.  $\frac{\Delta C}{\Delta t}$  is calculated by linear regression of the N<sub>2</sub>O mixing ratio in the headspace samples with statistical requirements as described in Equation 1.

### *Gas Analysis*

All samples were analyzed as described by Martikainen (22). Samples were immediately returned to the lab, allowed to equilibrate to laboratory temperature for 1 to 2 hours, and analyzed for N<sub>2</sub>O within 3 to 4 hours after collection. Samples and standards were dried across CaSO<sub>4</sub> as they were injected into the gas chromatograph injection loop. Analyses for N<sub>2</sub>O were accomplished using an electron capture detector (ECD) after constituent separation using a 2 meter x 3.2 mm OD columns packed with Poropak Q. Carrier gas was a 95% Ar - 5% CH<sub>4</sub> mixture. Peaks were quantified with Hewlett Packard Chemstation software on a personal computer. The ECD was calibrated for N<sub>2</sub>O over the

range 310 ppb to 100 ppm during each analysis period using N<sub>2</sub>O in N<sub>2</sub> standard gases obtained from Scott Specialty Gases with ±5% certified accuracy. Precision of analysis for calibration gases was 0.3%.

## Results

### *Sludge Compost*

A total of 74 N<sub>2</sub>O flux measurements were performed on the sludge compost piles. 33 fluxes were measured with the blowers active and 41 were measured with the blowers inactive. Figure 2-1 presents the cumulative probability plot of the measured flux data with aeration active and inactive. A clear difference in the distribution of the fluxes is apparent under different aeration conditions. The mean of the fluxes during active aeration was 3.4 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> while the mean of the fluxes measured with the blowers off was 1.2 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>. The mean value of the entire flux data set was 2.2 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>.

A limited number of flux measurements were also performed on the finishing piles. Twelve fluxes were measured between late winter and early summer which ranged from 0.6 to 1.3 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> with a mean value of 0.9 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>.

A mass based N<sub>2</sub>O emission factor can be calculated for the sludge from the measured emissions. Approximately 1800 dry kg of sludge is generated daily on site and is accumulated for 4 days. 7200 dry kg of sludge per pile is then composted with the added bulking agent under aeration for 40 days with a mean emission rate of 2.2 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>. The effective pile emitting surface area is 45 m<sup>2</sup>. The resulting mass based emission rate is 0.5 g N<sub>2</sub>O (dry kg sludge)<sup>-1</sup>. A similar methodology can be used to estimate emissions from the non-aerated finishing piles. Assuming an emission rate of 0.9 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> and a finishing period of 30 days yields an emission rate of 0.2 g N<sub>2</sub>O (dry kg sludge)<sup>-1</sup>. The resulting total mass based N<sub>2</sub>O emission rate is 0.7 g N<sub>2</sub>O (dry kg sludge)<sup>-1</sup>.

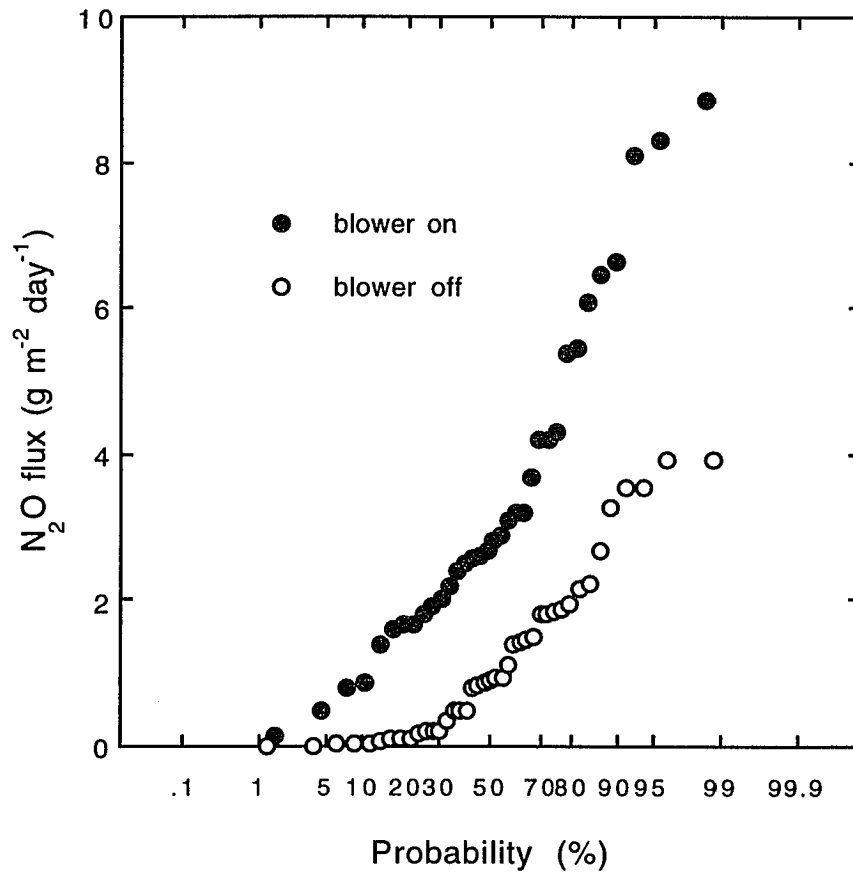


Figure 2-1. Cumulative probability plot of the measured N<sub>2</sub>O flux data. Solid circles represent fluxes measured with aeration active and open circles represent fluxes measured with aeration inactive.

The disparity between fluxes under different aeration conditions is the result of the dominance of different gas transport mechanisms under varying blower conditions. Both thermal convection and gaseous diffusion transport microbially generated trace gases from the compost to the atmosphere when the blowers are inactive. When the blowers are active, advective air movement dominates transport and effectively flushes the trace gases out of the piles and into the atmosphere.

The age of the compost was also recorded at the time of each flux measurement. Figure 2-2 presents the measured fluxes as a function of compost age. No significant statistical correlation was observed between  $N_2O$  flux and compost age. The only significant feature of this relationship is the decreasing variability in measured emissions with compost age. The highest flux variability was observed in compost less than approximately 20 days old. The interstitial gas depth profiles may help explain this variability trend.

Interstitial gas samples were collected from six compost piles of various ages from depths of 5 to 60 cm. Figure 2-3 presents the profiles of  $N_2O$  and  $O_2$  mixing ratios in the oldest and youngest compost piles examined. The mixing ratio of  $N_2O$  in the 9 day old compost is highest in the top 10 cm and is negligible below 20 cm. This decrease in  $N_2O$  is accompanied by a decrease in  $O_2$  mixing ratio from near atmospheric at 5 cm to less than 2 % at 60 cm. The decline of interstitial  $O_2$  is associated with increasing compost water content with depth which limits  $O_2$  diffusion. The measured volumetric water contents in the 0-10 cm, 10-20 cm, 20-30 cm, and 30-40 cm depth intervals were 62 %, 84 %, 103 % and 106 %, respectively.  $N_2O$  production in the 9 day old compost appears to be limited to areas with water content below saturation where  $O_2$  is sufficient to expose the denitrifying microbes to a significant gradient.

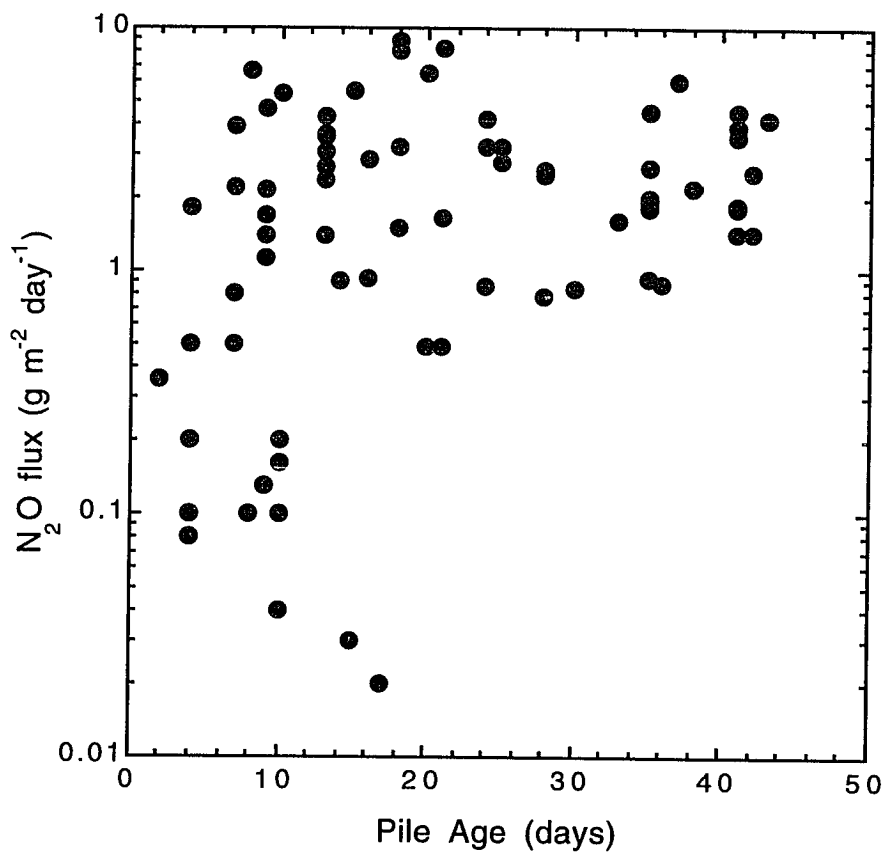


Figure 2-2. Measured N<sub>2</sub>O fluxes as a function of compost age.



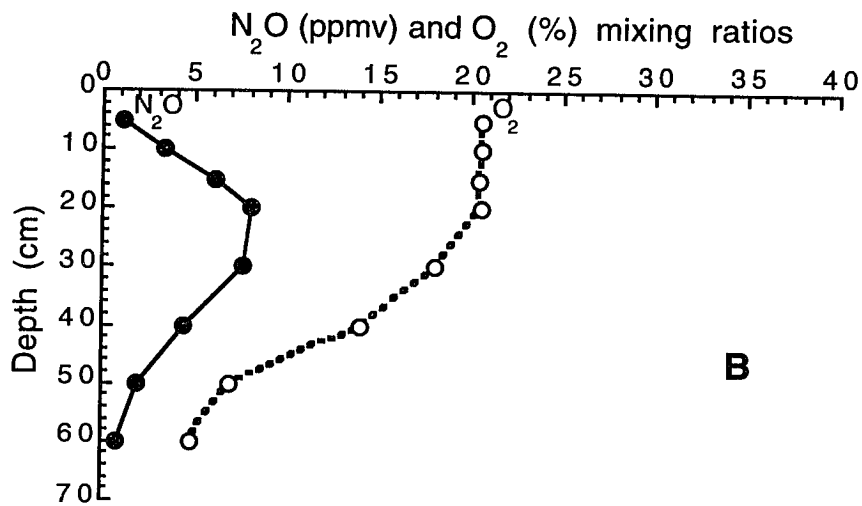
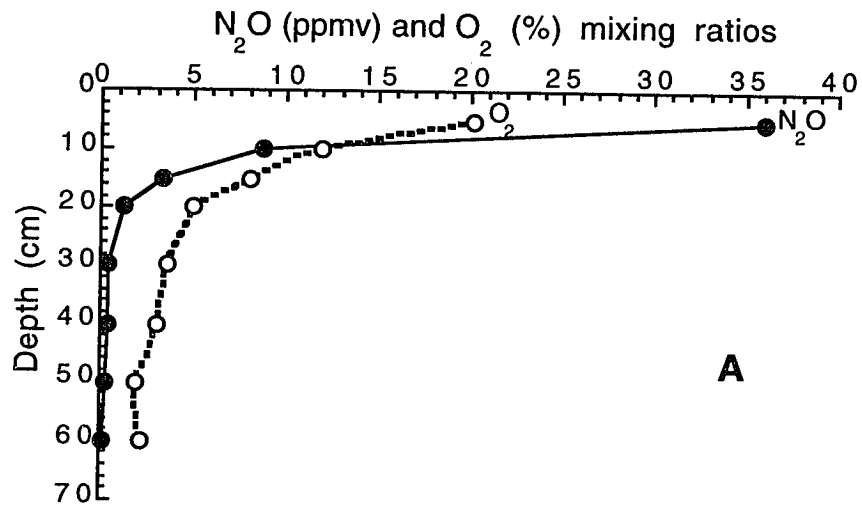


Figure 2-3. Profiles of N<sub>2</sub>O (solid circles) and O<sub>2</sub> (open circles) in the oldest and youngest compost piles examined. A) 9 day old compost, B) 38 day old compost.

In the 38 day old compost, the mixing ratio of  $N_2O$  is minimal in the top 10 cm, gradually increases to a maximum at 20 cm, slowly decreases below 20 cm, and is negligible below 60 cm. The corresponding  $O_2$  mixing ratios are near atmospheric above 20 cm and gradually decrease to 4.5 % at 60 cm.  $N_2O$  production in this pile has been significantly effected by moisture loss due to both diffusion and blower induced advection. The measured volumetric water contents in the 0-10 cm, 10-20 cm, 20-30 cm, and 30-40 cm depth intervals were 29 %, 44 %, 69 % and 89 %, respectively.  $N_2O$  production above 20 cm is inhibited by low moisture contents, maximized between 20 and 30 cm under optimal moisture and  $O_2$  conditions, and decreases with gradually decreasing  $O_2$  and increasing water.

The distribution change of  $N_2O$  production in the compost profile that accompanies drying may account for the decreasing variability of flux with age. Initially, production occurs near the surface where spatial variability is maximized due to the minimal thickness of the production zone. The production zone widens as the pile ages and dries, effectively damping spatial variability by increasing the width of distribution. This effect may also contribute to the lack of correlation between emissions and pile age. Integrating the mixing ratio depth profiles results in similar values implying similar source strengths for emissions.

Incubations of composite sludge compost samples were performed to determine the temperature sensitivity of  $N_2O$  production. Near surface compost temperature surveys were performed prior to incubations to establish the proper experimental temperature range. Temperature was measured on two occasions at a depth of 15 cm over a regular grid including compost of all ages. The temperature on April 16 ranged from 33 to 56°C with a mean of 43°C, while the temperature on August 1 ranged from 32 to 61°C with a mean of 42°C.

Incubation temperatures were chosen to simulate the observed range of field

temperatures. The  $N_2O$  production rate as a function of incubation temperature is shown in Figure 2-4. The resulting rates are presented as the mean and standard deviation at each temperature of ten samples from the original composite.  $N_2O$  production was observed to increase linearly from  $0.019 \text{ nmol } N_2O \text{ hr}^{-1} \text{ g dry compost}^{-1}$  at  $33^\circ\text{C}$  to  $0.064 \text{ nmol } N_2O \text{ hr}^{-1} \text{ g dry compost}^{-1}$  at  $54^\circ\text{C}$ . The resulting  $Q_{10}$  based on the observed relationship was 1.7.

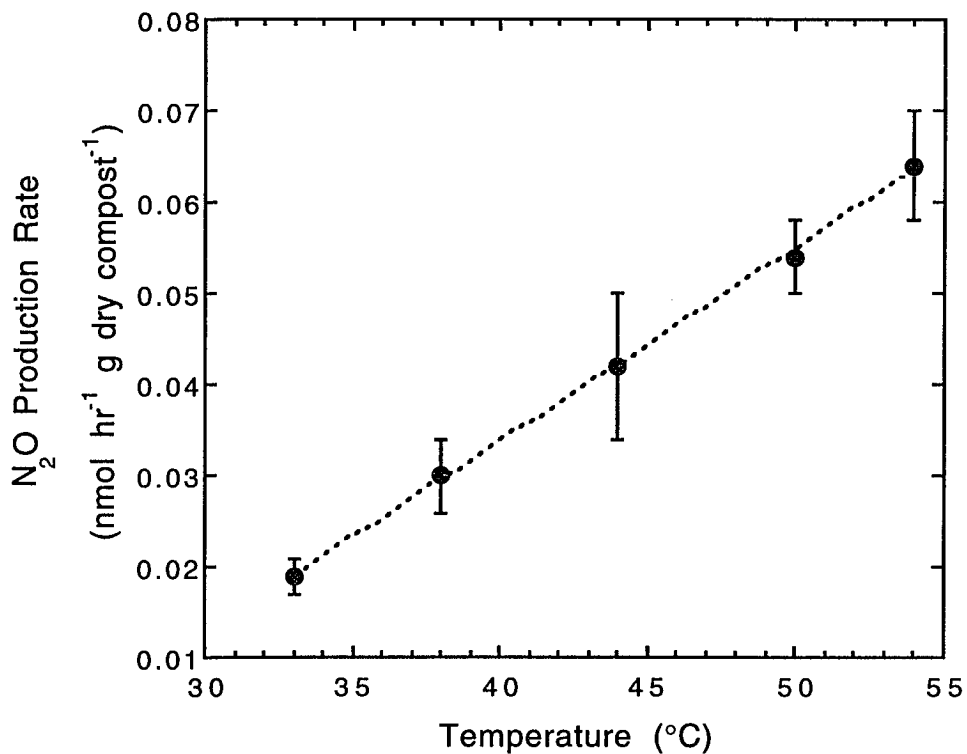


Figure 2-4.  $N_2O$  production rates as a function of temperature from jar incubations of 10 composite compost samples. Solid circles represent the mean production rate, error bars represent the standard deviation.

### Livestock and Yard Waste Compost

N<sub>2</sub>O emissions from one yard waste and two livestock waste windrows are shown in Figure 2-5. Emissions are presented as the average of fluxes measured in two locations on each pile with error bars representing the range of measured fluxes. The presented values are those measured under normal circumstances consisting of calm to low surface winds, no recent or current precipitation, and a static pile condition. Emissions from the livestock waste piles increased during the first 35 to 55 days after inception and decreased thereafter. The peak N<sub>2</sub>O emission rates measured on the livestock waste piles were 1.3 and 0.8 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> from piles 1 and 2, respectively. The average of emissions measured on both piles during the observation period was 0.5 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>.

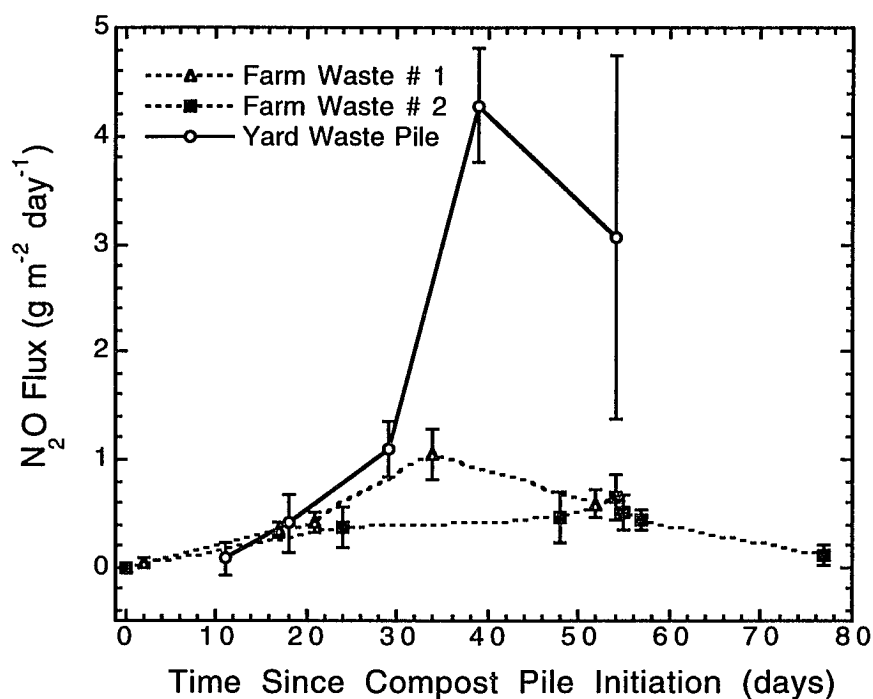


Figure 2-5. N<sub>2</sub>O emissions from one yard waste and two livestock waste windrows. Symbols represent flux averages, error bars represent the range of the values.

A mass based N<sub>2</sub>O emission factor can be estimated for the livestock waste from the measured emissions. A pile volume of 41.6 m<sup>3</sup> and an initial average dry bulk density of 133 kg m<sup>-3</sup> yields a total pile dry mass of 5533 kg. Approximately 25 % or 1383 kg of this mass is manure. Total N<sub>2</sub>O emissions, E<sub>N<sub>2</sub>O</sub> from the compost can be estimated by

$$E_{N_2O} = \frac{f A t}{m} \quad (3)$$

where f is the average emission rate, 0.5 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>, A is the effective emitting surface area, 16 m<sup>2</sup>, and t is the emission period, 90 days, conservatively based on the observed temporal pattern of emissions, and m is the livestock manure mass, 1383 kg. The resulting mass based N<sub>2</sub>O emission factor is 0.5 g N<sub>2</sub>O (kg dry waste)<sup>-1</sup>.

N<sub>2</sub>O emissions from the yard waste pile increased significantly during the 40 day period after pile initiation, approximately the same period of increase observed in the livestock waste. However, the measured peak average yard waste emission rate, 4.3 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>, was considerably higher than emission rates observed on the livestock waste piles. This rate appeared to be decreasing after approximately 40 days of composting, similar to the pattern of emissions observed in the livestock waste. Although, the significant range in the later emissions data limits this observation. The average of measured emissions from the yard waste pile was 1.8 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>.

A mass based N<sub>2</sub>O emission factor can be estimated for the yard waste, similarly to that of the livestock waste. A pile volume of 41.6 m<sup>3</sup> and an initial average dry bulk density of 196 kg m<sup>-3</sup> yields a total pile dry mass of 8154 kg. Total N<sub>2</sub>O emissions, E<sub>N<sub>2</sub>O</sub> from each pile can be estimated by Equation 3 with an average emission rate, f of 1.8 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>, an effective emitting surface area, A of 16 m<sup>2</sup>, an emission period, t of 90 days based on the observed fluxes, and a yard waste dry mass, m of 8154 kg. The resulting mass based N<sub>2</sub>O emission factor is 0.3 g N<sub>2</sub>O (kg dry waste)<sup>-1</sup>.

Changes in environmental and operating conditions were observed to effect N<sub>2</sub>O emissions from the compost piles. N<sub>2</sub>O fluxes were significantly reduced when measured on a windy day. Average N<sub>2</sub>O emissions from livestock waste pile 1 measured 35 days after pile initiation were 0.15 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>, compared to 1.3 and 0.7 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> measured 32 and 50 days after pile initiation, respectively. Average wind speed measured during the high wind period was approximately 3.5 m s<sup>-1</sup>. Emissions under calm conditions are driven by gaseous diffusion of N<sub>2</sub>O from the compost pore spaces to the atmosphere. High wind speeds induce advective movement of interstitial gas due to the pressure differential between the compost and the atmosphere as air moves across the pile surface. The vacillating nature of air movement produces a “pumping effect”, alternately changing the direction of gas flow and infusing the pile with ambient air. This effect may diminish the microaerophilic conditions necessary for optimal N<sub>2</sub>O production thereby reduce N<sub>2</sub>O emissions.

The mechanical turning of the piles was observed to produce enhanced N<sub>2</sub>O emissions. Fluxes from the livestock waste piles ranged from 19 to 39 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> measured within several minutes after pile agitation. This enhancement results from the release of interstitial gases to the atmosphere as the piles are disturbed. Emissions from these areas were observed to return to typical levels within several hours of the event.

Precipitation also appears to significantly effect N<sub>2</sub>O emissions. Figure 2-6 shows the results of high temporal resolution emission measurements at one location on livestock waste pile 1 during and after a significant precipitation event. A gradual increase in emissions was coincident with several hours of light rain. Water from the light rainfall percolated through the compost at a low rate with the probable effect of minimally displacing interstitial gas and enhancing denitrification. N<sub>2</sub>O emissions during this period increased from a pre-rainfall emission rate of 0.4 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup> to an average rate of about 1.0 g N<sub>2</sub>O m<sup>-2</sup> day<sup>-1</sup>. N<sub>2</sub>O emissions then decreased to zero between 14.5 and 15

hrs following a 16 mm rainfall event. The large volume of water infiltrating into the pile as a wetting front appeared to temporarily obstruct gas transport from the pile to the atmosphere.  $N_2O$  emissions rapidly increased shortly after this event and continued to increase to a maximum of  $2.4 \text{ g } N_2O \text{ m}^{-2} \text{ day}^{-1}$  during and after a second significant precipitation event. Interstitial gas initially displaced by the wetting front was released to the atmosphere by the subsequent pore volume reduction. Conditions then returned to the pre-rainfall equilibrium. Emissions decreased during the following 8 hrs to  $0.7 \text{ g } N_2O \text{ m}^{-2} \text{ day}^{-1}$  and were close to the level of pre-rainfall emissions by 95 hrs.

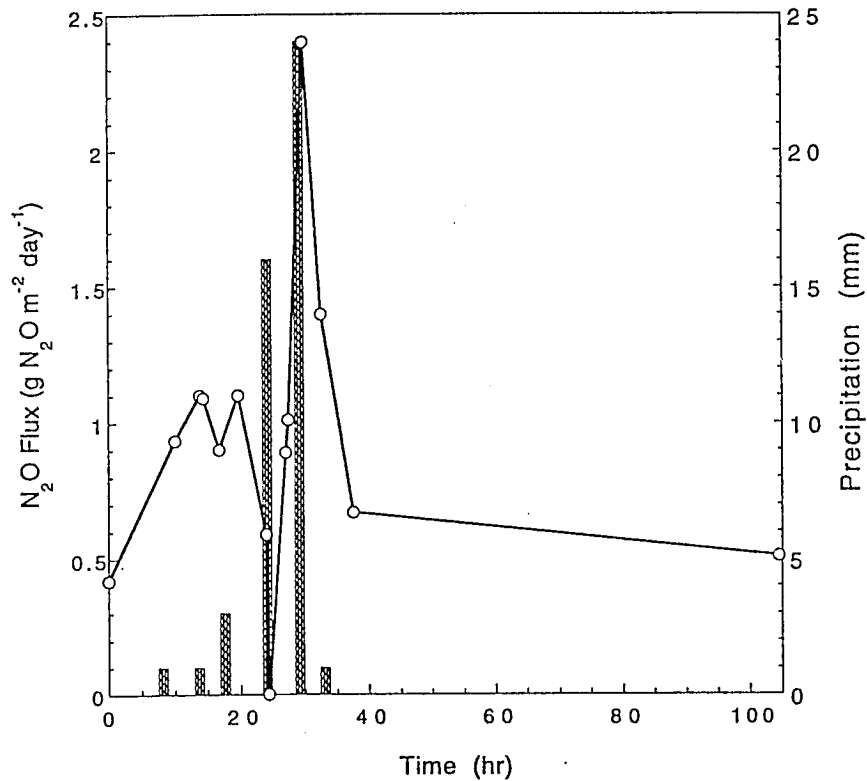


Figure 2-6.  $N_2O$  emissions at one location on livestock waste pile 1 during and after a significant precipitation event. Open circles represent measured  $N_2O$  fluxes, vertical bars represent precipitation events in half hour increments. Time is presented in hours since experiment initiation.

## Discussion

Our results demonstrate the potential for significant emissions of N<sub>2</sub>O from the treatment of high organic content wastes. N<sub>2</sub>O is produced under microaerophilic conditions during the processing of organic wastes with high moisture contents in the presence of adequate oxygen. These conditions are prevalent in the composting systems we observed as well as in other organic waste management systems. This similarity can be utilized to make preliminary estimates of potential N<sub>2</sub>O emissions from various waste management systems. Table 2-1 presents our estimates of N<sub>2</sub>O emissions from the various waste types and disposal systems evaluated below.

Table 2-1. Estimated emissions of N<sub>2</sub>O from the evaluated waste systems.

| Source                              | (10 <sup>12</sup> g N <sub>2</sub> O yr <sup>-1</sup> ) |
|-------------------------------------|---|
| Wastewater sludge:                  |   |
| composting (US, Japan)              | 0.001   |
| land application (US, W. Europe)    | 0.003   |
| Yard waste (US only)                | 0.001   |
| Livestock & poultry wastes (global) | 1.2   |

An estimate of potential global N<sub>2</sub>O emissions from wastewater sludge treatment and disposal can be generated using recent sludge production and disposal statistics from several urbanized regions of the industrialized world. Among the countries that generate



significant quantities of sludge, only the U. S. and Japan compost a significant fraction (24). The amount of municipal sludge treated by composting in the U. S. in 1992 was  $1.2 \times 10^9$  dry kg yr<sup>-1</sup>.(25). Approximately 50 % was treated by ASP, 25 % by windrowing, and 25 % by in-vessel treatment. If we assume that the ultimate N<sub>2</sub>O emission potential calculated from our observations, 0.7 g N<sub>2</sub>O (kg dry waste)<sup>-1</sup>, is applicable to all composting systems, albeit with potentially different generation periods, then total N<sub>2</sub>O emissions from sludge composting in the U. S. in 1993 were  $8.4 \times 10^8$  g N<sub>2</sub>O yr<sup>-1</sup>.

In Japan, approximately  $1.1 \times 10^8$  dry kg yr<sup>-1</sup> of municipal wastewater sludge was composted in 1988 (24). No data was available regarding specific composting methods. Using the assumptions previously presented yields an annual emission rate of  $8.0 \times 10^7$  g N<sub>2</sub>O yr<sup>-1</sup>.

Land disposal or spreading for agriculture and reclamation should also be considered when assessing the N<sub>2</sub>O emissions potential of wastewater sludge disposal. Amending soils with wastewater sludge has been observed to substantially increase N<sub>2</sub>O emissions (26). The observed N<sub>2</sub>O emission rates in amended soils are lower and the generation periods longer than those observed in more concentrated waste environments such as our compost piles (9, 27). This appears to be the result of the influence of lower temperatures on microbially mediated denitrification rates. However, ultimate N<sub>2</sub>O yields appear to fall within a range similar to those observed in our study.

In Western Europe, where sludge composting is minimal, land disposal accounts for about 40 % of sludge disposal. Approximately  $2.4 \times 10^9$  dry kg yr<sup>-1</sup> of municipal wastewater sludge was land disposed in 1992 (24). Assuming the ultimate N<sub>2</sub>O yield from our compost observations, 0.7 g N<sub>2</sub>O (kg dry waste)<sup>-1</sup>, yields annual N<sub>2</sub>O emissions of  $1.7 \times 10^9$  g N<sub>2</sub>O yr<sup>-1</sup>.

In the U. S., approximately  $1.6 \times 10^9$  dry kg yr<sup>-1</sup> of municipal wastewater sludge was land disposed in 1988 (28). Assuming the ultimate N<sub>2</sub>O yield from our compost observations, 0.7 g N<sub>2</sub>O (kg dry waste)<sup>-1</sup>, yields annual N<sub>2</sub>O emissions of  $1.1 \times 10^9$  g

$\text{N}_2\text{O}$   $\text{yr}^{-1}$ . Land disposal of sludge in Japan is not significant in the sludge disposal budget.

The total  $\text{N}_2\text{O}$  emissions potential from the wastewater sludge treatment and disposal systems considered is estimated to be  $3.7 \times 10^9$  g  $\text{N}_2\text{O}$   $\text{yr}^{-1}$ . Unfortunately, few reliable data exist regarding wastewater treatment and sludge generation in the increasingly populated urban regions of Asia, Africa, and Central and South America. The addition of sludge statistics from these areas could be expected to significantly increase estimated  $\text{N}_2\text{O}$  emissions from the treatment of wastewater sludge.

Yard waste composting also presents significant potential for  $\text{N}_2\text{O}$  emissions. However, the absence of reliable statistics regarding yard waste generation and disposal in countries other than the U. S. makes a global emissions estimate impossible. The rate of yard waste composting in the U. S. was recently projected to be  $7.3 \times 10^9$  wet kg  $\text{yr}^{-1}$  in 1995 or  $3.6 \times 10^9$  dry kg  $\text{yr}^{-1}$  assuming a composite moisture content of 50 % by weight (29). Assuming the ultimate  $\text{N}_2\text{O}$  yield derived from our observations,  $0.3$  g  $\text{N}_2\text{O}$  (kg dry waste) $^{-1}$ , yields annual  $\text{N}_2\text{O}$  emissions from yard waste composting in the U. S. of  $1.1 \times 10^9$  g  $\text{N}_2\text{O}$   $\text{yr}^{-1}$ . In this case, as with wastewater sludge, an improvement in the quality of global yard waste statistics could be expected to increase estimated  $\text{N}_2\text{O}$  emissions from yard waste composting.

The treatment and disposal of livestock wastes appears to hold the greatest potential for  $\text{N}_2\text{O}$  emissions globally. Approximately  $13.2 \times 10^{12}$  wet kg  $\text{yr}^{-1}$  of livestock and poultry manure was generated globally in 1992 (30). The distribution of generated wastes by species and the waste management systems utilized are presented in Table 2-2. The microaerophilic conditions necessary for  $\text{N}_2\text{O}$  production are common in several of these systems including daily spread and paddock, where manure is collected daily and spread on fields; pasture and range, where manure is left "as is" on fields; drylot, where manure is dried on feedlots and later spread on fields; solid storage, where manure is collected and

stored for longer than daily periods and ultimately field spread which may include composting. Also, the final disposal of liquid storage is generally field application of the accumulated wastes. Lagoon and digestion systems, where wastes are treated under anaerobic conditions, would not be expected to produce significant quantities of N<sub>2</sub>O, although disposal of the resulting sludge, which is generally field spread, may hold some potential for N<sub>2</sub>O emissions.

Table 2-2. Estimated global livestock and poultry manure generation (10<sup>11</sup> wet kg yr<sup>-1</sup>) and waste management systems utilized in 1992 (30).

| Species            | System types      |                |              |                          |                         |                              |
|--------------------|-------------------|----------------|--------------|--------------------------|-------------------------|------------------------------|
|                    | Anaerobic lagoons | Liquid systems | Daily spread | Solid storage and drylot | Pasture, range, paddock | Fuel generation <sup>a</sup> |
| Beef cattle        | minimal           | 3.9            | 3.9          | 4.5                      | 40.0                    | 9.0                          |
| Dairy cattle       | 5.8               | 5.5            | 5.5          | 8.4                      | 6.6                     | 1.7                          |
| Swine              | 0.7               | 5.7            | minimal      | 6.2                      | none                    | 0.4                          |
| Poultry            | minimal           | minimal        | none         | minimal                  | 1.5                     | minimal                      |
| Other <sup>b</sup> | none              | none           | none         | minimal                  | 20.0                    | none                         |
| <b>TOTAL</b>       | <b>6.5</b>        | <b>15.1</b>    | <b>9.4</b>   | <b>19.1</b>              | <b>68.1</b>             | <b>11.1</b>                  |

a: anaerobic digestion with gas burned for fuel.

b: includes goats, horses, mules, donkeys, and camels.

The potential N<sub>2</sub>O generation rate, as in the case of land spreading of wastewater sludge, will be lower and generation period longer than was observed in the composting systems. But, the ultimate N<sub>2</sub>O potential should be similar. We can estimate potential N<sub>2</sub>O emissions using the global manure production numbers presented in Table 2-2. 11.2 x

$10^{12}$  wet kg yr<sup>-1</sup> of livestock and poultry manure were treated and disposed by the systems previously described that encourage N<sub>2</sub>O production. Assuming a composite total solids content as excreted of 20 % (31) yields a manure dry mass of  $2.3 \times 10^{12}$  kg yr<sup>-1</sup>. Using the mass based ultimate N<sub>2</sub>O yield derived from our livestock waste compost observations, 0.5 g N<sub>2</sub>O (kg dry waste)<sup>-1</sup>, yields annual N<sub>2</sub>O emissions from livestock waste of  $1.2 \times 10^{12}$  g N<sub>2</sub>O yr<sup>-1</sup>.

Khalil and Rasmussen recently observed elevated N<sub>2</sub>O mixing ratios around manure piles and feed lots from which they extrapolated a range for N<sub>2</sub>O emissions from cattle of 0.3 to 0.8 Tg yr<sup>-1</sup> based on their observed ratios of methane to N<sub>2</sub>O in the livestock environment (4). Our estimate compares favorably with this range if the contribution of other livestock wastes are also considered. Cattle wastes account for approximately 75 % of total global livestock wastes. Including only cattle wastes in our estimate would reduce estimated emissions to  $0.9 \times 10^{12}$  g N<sub>2</sub>O yr<sup>-1</sup>, very close to the upper end of the previously estimated range.

### Conclusion

We have presented the results of N<sub>2</sub>O emission measurements from the composting of various organic wastes and applied the resulting emission factors to other organic waste treatment systems where denitrification plays a significant role. These emission estimates are a first step toward a quantitative evaluation of global N<sub>2</sub>O emissions from the treatment and disposal of organic wastes. Several further steps must be taken to better characterize this apparently significant N<sub>2</sub>O source. A more detailed compilation of global waste generation, treatment, and disposal statistics is necessary to determine the quantity of wastes that are exposed to conditions favorable for N<sub>2</sub>O production. In addition, comprehensive field measurements must be performed to evaluate N<sub>2</sub>O emissions from

wastes treated by land application to determine if the predicted potential is actually realized. The influence of several environmental factors including temperature, precipitation, insolation, and waste characteristics must be quantified to more accurately characterize potential N<sub>2</sub>O emissions.

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**CHAPTER 3**

**ENVIRONMENTAL FACTORS INFLUENCING THE VARIABILITY OF**

**METHANE OXIDATION IN TEMPERATE ZONE SOILS**



CHAPTER 3

**ENVIRONMENTAL FACTORS INFLUENCING THE VARIABILITY OF  
METHANE OXIDATION IN TEMPERATE ZONE SOILS**

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with co-authors P. M. Crill and R. C. Harriss

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Summary

The influence of organic matter and soil moisture on the spatial distribution of methane (CH<sub>4</sub>) oxidation was examined in temperate zone soils by laboratory incubations. CH<sub>4</sub> oxidation in soil cores exhibited distinct vertical zonation with maxima at 3 to 6 cm. The kinetic parameters of CH<sub>4</sub> oxidation were measured in soil composites. The maximum rate of CH<sub>4</sub> uptake,  $V_{\max}$ , ranged from 6.8 to 7.4 nmol hr<sup>-1</sup> g dry soil<sup>-1</sup> and the apparent half saturation constant,  $K_m$ , ranged from 17.4 to 19.9 (parts per million by volume) ppmv. Oxidation in random samples was observed to be influenced by both soil moisture and organic matter contents. The rate of oxidation in each sample increased to a maximum with increasing water content and decreased with additional water. Maximum oxidation rates ranged from 2.2 to 9.0 nmol hr<sup>-1</sup> g dry soil<sup>-1</sup> at sample moisture contents of 18 to 51%. Organic matter content appears to explain the spatial variability of methane oxidation at optimal soil moisture contents. The oxidation maximum at this site was coincident with an organic matter content of 14% by weight and a gravimetric moisture content of 33%. Data can be viewed in tabular form in Appendix C.

## Introduction

Methane ( $\text{CH}_4$ ) is a radiatively active atmospheric trace gas whose rate of concentration change in the northern hemisphere has recently decreased from an average of  $11.6 \pm 0.2$  parts per billion by volume (ppbv)  $\text{yr}^{-1}$  during 1983-1991 to  $1.8 \pm 1.6$  ppbv  $\text{yr}^{-1}$  in 1992 [Dlugokencky *et al.*, 1994]. This decrease remains unexplained and emphasizes the need for further refinement of our understanding of the  $\text{CH}_4$  budget. The removal of  $\text{CH}_4$  from the atmosphere by reaction with hydroxyl radicals is estimated to be the largest  $\text{CH}_4$  sink, while soil microbial oxidation is estimated to account for 5 to 20% of the total global  $\text{CH}_4$  removal [Bender and Conrad, 1993; Cicerone and Oremland, 1988; Koschorreck and Conrad, 1993]. Rates of  $\text{CH}_4$  uptake by soils have been determined in a wide range of environments including swamp [Amaral and Knowles, 1994; Harriss *et al.*, 1982], temperate forest [Adamsen and King, 1993; Crill, 1991; Steudler *et al.*, 1989], temperate grassland [Mosier *et al.*, 1991], and tropical savanna [Delmas *et al.*, 1991; Seiler *et al.*, 1984]. The magnitude of the estimated global soil oxidation sink is based on observations which include high intersite as well as intrasite variability in oxidation rate. Intrasite variability as high as 1 order of magnitude has been observed in several of these environments [Crill, 1991; Harriss *et al.*, 1982], but little is known about the source of this variability.

Here we present a comparison of  $\text{CH}_4$  oxidation in soil samples collected within a  $300\text{-m}^2$  site consisting of wooded and grassy areas. Soil samples were randomly collected in both areas and subjected to incubation experiments in the laboratory to determine the response of  $\text{CH}_4$  oxidation to variations in soil physical characteristics and moisture content.

## Site Description

The soils examined were collected between May and October 1993 from a site located in a rural area in east central New England (approximately 43° N, 71° W). The area is generally wooded with small residential clearings and is located in a coastal temperate climate region. The soils in this area are generally classified as spodosols and consist of well-drained soils that formed in thick deposits of stratified sand and gravel after the last glaciation [*Vieira and Bond, 1971*]. A representative profile of these soils has a thin organic layer ranging from 3 to 10 cm, a dark brown loamy layer approximately 25 cm thick overlying a yellow-brown loamy sand, and gravelly loamy sand subsoil that extends to a depth of about 50 cm.

The terrain in the area sampled ranged from shaded lawn with grass and moss ground cover to wooded with mixed hardwoods and conifers. Soil characteristics varied significantly with depth and location as presented in Table 3-1. In the grassy area random samples, *pH* ranged from 4.4 to 4.9, bulk density ranged from 0.83 to 1.10 g cm<sup>-3</sup>, gravimetric moisture content at sample collection ranged from 15.9 to 24.4%, and organic matter content ranged from 6.0 to 11.9% by weight. In the wooded area random samples, *pH* ranged from 3.5 to 4.4, bulk density ranged from 0.55 to 0.90 g cm<sup>-3</sup>, gravimetric moisture content at sample collection ranged from 20.5 to 44.4%, and organic matter content ranged from 9.9 to 25.6% by weight.

Table 3-1. Representative characteristics of the sampled soils.

|                                      | Grassy Area<br>Core Samples |            |             | Grassy Area<br>Random Sample<br>Composite | Wooded Area<br>Random Sample<br>Composite |
|--------------------------------------|-----------------------------|------------|-------------|---|---|
|                                      | 0 to 6 cm                   | 6 to 12 cm | 12 to 18 cm |   |   |
| Sand/silt/clay, 45/35/20<br>% by wt. |                             | 40/43/17   | 33/43/24    | 43/37/20                                  | 38/42/20                                  |
| pH, 20°C                             | 4.1                         | 4.4        | 4.7         | 4.5                                       | 3.8                                       |
| Organic matter,<br>% by wt.          | 11                          | 6          | 3           | 9   | 14  |
| Total nitrogen,<br>% by wt.          | 0.24                        | 0.19       | 0.16        | 0.26                                      | 0.38                                      |

#### Methods and Materials

Soil samples were collected between May and October 1993. All samples were excavated with a trowel and transported immediately to the laboratory in sterile sample bags. Core samples were collected from the grassy and wooded areas in 3-cm intervals from the surface to a depth of 21 cm and split into duplicate 100-g subsamples for incubations. The 0-cm reference surface in the grassy area was the visible soil surface, while the reference surface in the wooded area was the surface exposed after removal of undecomposed leaves and twigs. Samples were collected randomly in both areas from the 3- to 6-cm depth interval, sieved through a 4-mm wire mesh to remove large gravel and roots, and split into duplicate 100- to 150-g subsamples for incubations. Samples collected in the grassy area were located within a 5-m radius, while those collected in the wooded area were collected within the adjacent 200-m<sup>2</sup> area. Composite samples were generated

from random samples combined and mixed in a large bucket.

Soil moisture was measured in each sample at collection and subsequent to each moisture addition. Moisture contents were determined gravimetrically by oven drying at 105°C for 24 hours and are reported as percent H<sub>2</sub>O by weight [Topp, 1993]. Soil bulk density was determined by the coring method [Culley, 1993]. Soil organic matter content was determined by loss on ignition in a muffle furnace at 410°C for 24 hours [Davies, 1974]. To determine soil pH, 10 ml of air-dried soil was mixed in a sterile container with 10 ml of distilled water to form a slurry and repeatedly stirred with a glass rod for 30 min. A Beckman pH meter was then used to measure pH.

To determine CH<sub>4</sub> oxidation potential, each soil sample was subjected to time series incubation experiments performed in 0.5-l air tight glass jars with 1/8 inch Swaglock unions and silicone septa installed in the lids. Each jar headspace was sampled in duplicate a maximum of eight times during each experiment by removing 0.5 ml of gas in 1-ml polyethylene syringes. Headspace sampling typically occurred hourly for the first 4 hours after CH<sub>4</sub> injection and every 2 hours thereafter for 8 to 12 hours. The minimum detectable rate of oxidation at an initial headspace CH<sub>4</sub> concentration of 250 parts per million by volume (ppmv) was 0.1 nmol CH<sub>4</sub> hr<sup>-1</sup> g dry soil<sup>-1</sup>.

CH<sub>4</sub> oxidation rates were calculated from the resulting time series data. Varying quantities of CH<sub>4</sub> were initially supplied to the jar headspaces, which resulted in first-order or pseudo-zeroth-order oxidation kinetics depending on the initial CH<sub>4</sub> concentration. First-order oxidation kinetics were characterized by exponentially decreasing headspace CH<sub>4</sub> concentrations, and oxidation rates were calculated from the rate constant of the exponential curve fit. Pseudo-zeroth-order kinetics were characterized by a linear decrease in headspace CH<sub>4</sub> concentrations. The slope of the linear regression of these data, with a required correlation coefficient greater than 0.95 and significant to the 95% confidence level, defined the rate of CH<sub>4</sub> oxidation. All oxidation rates were normalized to dry soil

sample mass.

Incubation headspace samples were analyzed for CH<sub>4</sub> within 10 min of collection by direct injection into a Shimadzu GC-14A gas chromatograph (GC). All analyses for CH<sub>4</sub> were accomplished using a flame ionization detector after constituent separation using 2 m x 3.2 mm OD columns packed with Poropak Q or HayeSep Q. GC carrier gas was nitrogen and column temperature was 50°C. Peaks were quantified with Hewlett Packard Chemstation integration software on a personal computer. CH<sub>4</sub> concentrations were determined by comparison to standard gases obtained from Scott Specialty Gases calibrated with a National Institute of Standards and Technology certified standards. Precision of analysis for calibration gases was 0.3%.

## Results

### *Depth Profile*

Soil core samples were collected prior to random sampling to determine the distribution of CH<sub>4</sub> oxidation in the soil profile. Core samples were subjected to incubation experiments using headspace CH<sub>4</sub> concentrations covering 3 orders of magnitude: 2.6 ppmv, 25 ppmv, and 220 ppmv. The 2.6-ppmv and 25-ppmv experiments exhibited first-order oxidation kinetics. The 220-ppmv CH<sub>4</sub> experiments resulted in the pseudo-zeroth-order kinetics expected in a maximum oxidation rate or substrate independent environment. Soil cores from both the grassy and wooded areas exhibited similar CH<sub>4</sub> oxidation rates with maximums occurring in the 3 to 6 cm depth interval at all initial CH<sub>4</sub> concentrations (Figure 3-1). This distribution is similar to distributions observed by Whalen et al. in a clayey sand landfill cover soil and Adamsen and King in temperate mixed forest soils [Whalen et al., 1990; Adamsen and King, 1993]. The maximum rate of oxidation at an initial CH<sub>4</sub> concentration of 220 ppmv was 6.1 nmol CH<sub>4</sub> hr<sup>-1</sup> g dry soil<sup>-1</sup> in the grassy area core and 7.1 nmol CH<sub>4</sub> hr<sup>-1</sup> g dry soil<sup>-1</sup> in the wooded

area core. All subsequent soil samples were collected from a depth of 3 to 6 cm.

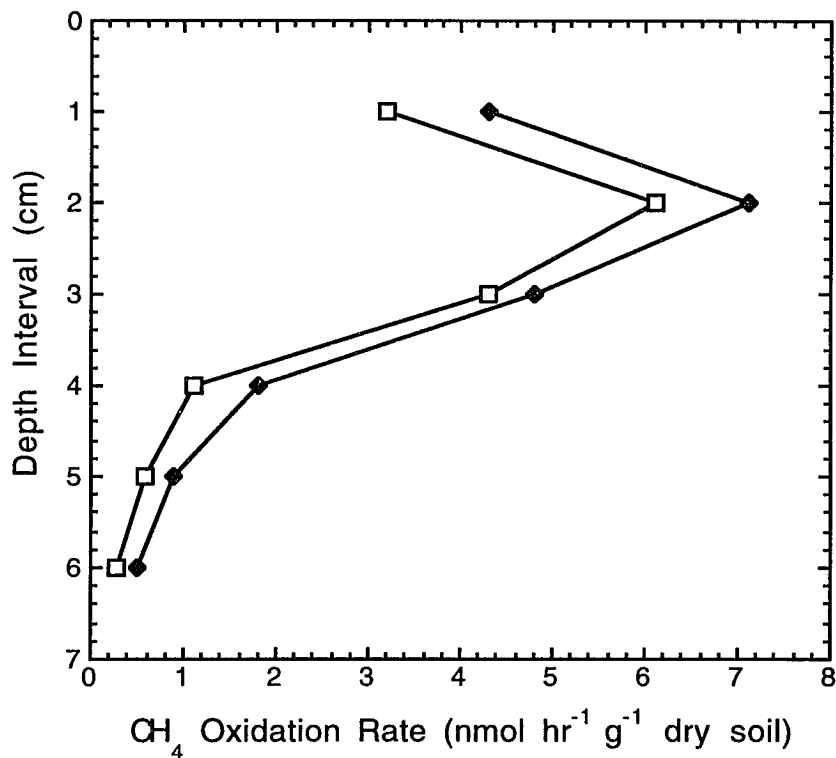


Figure 3-1. Methane oxidation rates for soil core samples from the grassy area (open squares) and the wooded area (solid diamonds). Incubations were performed at initial headspace methane concentrations of 220 to 250 parts per million by volume (ppmv). Samples were collected in 3-cm increments from the surface to 18 cm.

### *Kinetic Parameters*

An analysis of the CH<sub>4</sub> oxidizing capacity of the soils from the wooded and grassy areas was performed to determine their associated kinetic parameters: the maximum rate of CH<sub>4</sub> oxidation ( $V_{max}$ ) and the apparent half saturation constant ( $K_m$ ). Soil samples were collected from the depth of maximum CH<sub>4</sub> oxidation (3 to 6 cm) in 10 random locations in each area and mixed to form separate soil composites. The moisture content of the composite subsamples ranged from 18 to 20% for the grassy area soils and from 21 to 24% for the wooded area soils. The incubation experiments were performed at 25°C with headspace CH<sub>4</sub> concentrations ranging from 2.1 to 2380 ppmv in the grassy area soils and from 5.0 to 4510 ppmv in the wooded area soils. The resulting oxidation rate data were expressed as a function of initial headspace CH<sub>4</sub> concentration and showed typical Michaelis-Menten characteristics as presented in Figure 3-2. Eadie-Hofstee plots [Armstrong, 1989] were then used to linearize the data as presented in Figure 3-3.  $V_{max}$  and  $K_m$  are calculated from the linear fit to the data by

$$\frac{v}{S} = \frac{V_{max}}{K_m} - \frac{1}{K_m} \quad (1)$$

where  $v$  is the oxidation rate per gram of dry soil and  $S$  is the initial headspace methane concentration. The calculated  $V_{max}$  values for these soils were 6.8 nmol hr<sup>-1</sup> g<sup>-1</sup> and 7.4 nmol hr<sup>-1</sup> g<sup>-1</sup> for the grassy area soils and the wooded area soils, respectively. The calculated  $K_m$  values were 17.2 ppmv and 19.9 ppmv for the grassy area soils and the wooded area soils, respectively.



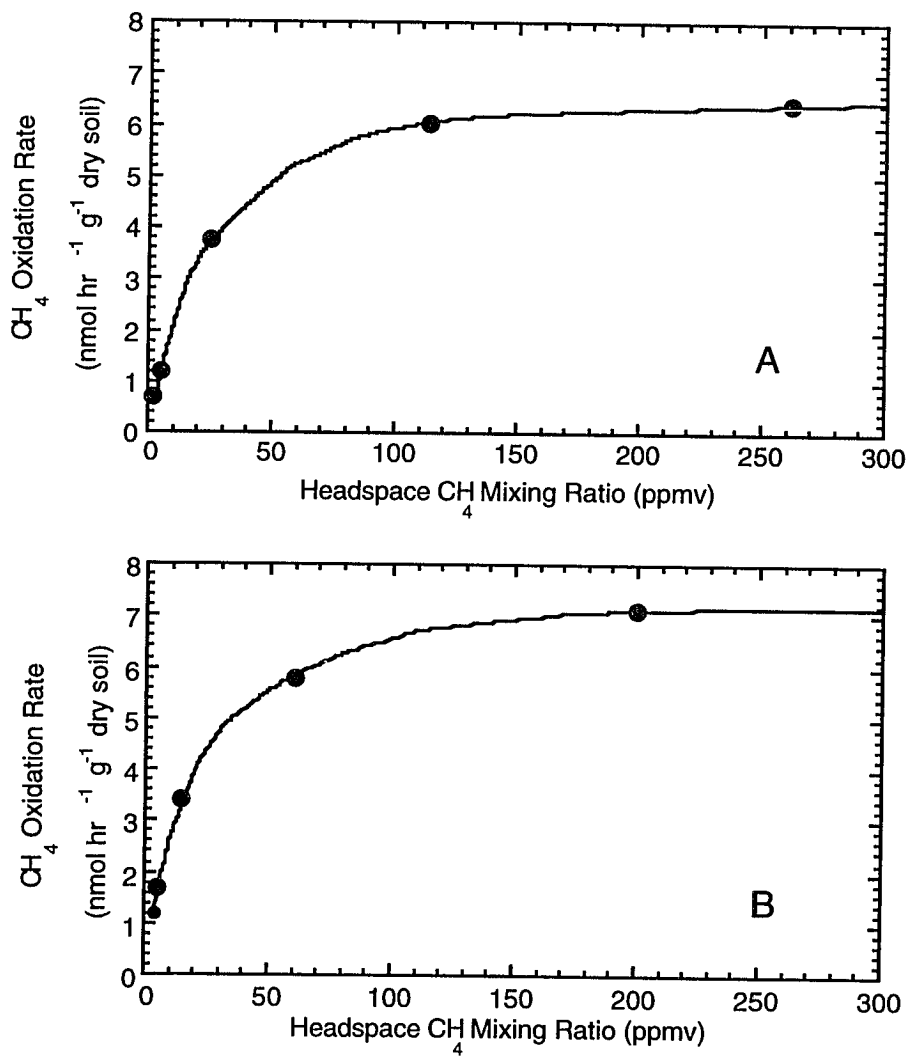


Figure 3-2. Substrate saturation curves of methane oxidation in (A) the grassy area soils and (B) the wooded area soils.

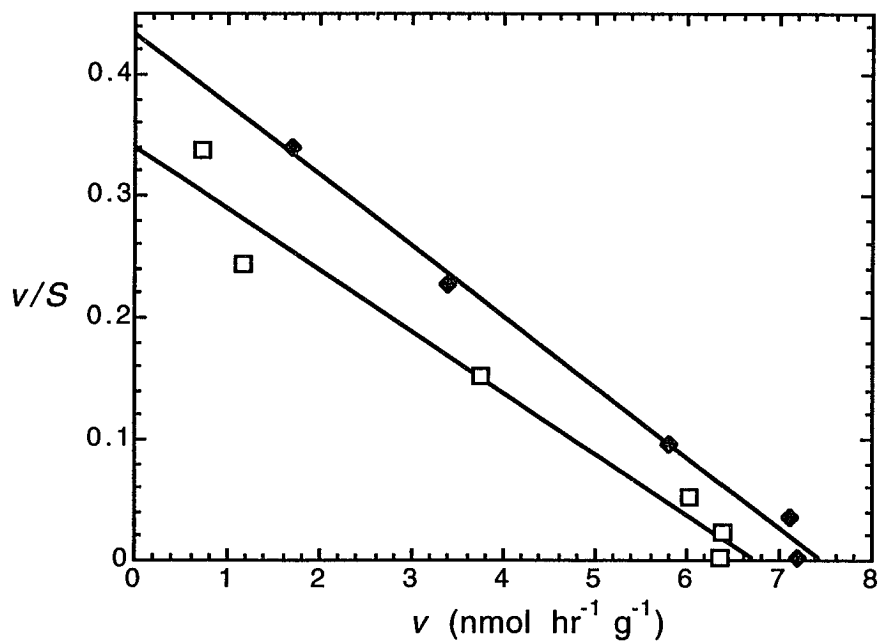


Figure 3-3. Linearization of the grassy area (open squares) and wooded area (solid diamonds) data from Figure 3-2 where  $S$  is the initial headspace methane concentration and  $v$  is the oxidation rate per gram of dry soil. The linear fit of the data yields  $K_m$  values of 19.9 ppmv for the grassy area and 17.4 ppmv for the wooded area and  $V_{\max}$  values of  $6.8 \text{ nmol hr}^{-1} \text{ g}^{-1}$  for the grassy area and  $7.4 \text{ nmol hr}^{-1} \text{ g}^{-1}$  for the wooded area.

The calculated kinetic parameters of CH<sub>4</sub> oxidation for our soils are listed in Table 3-2 together with values from other soils reported in the literature. The  $V_{\max}$  values of our soils were slightly higher but similar in magnitude to fresh soils examined by other investigators.  $K_m$  values were slightly lower than other reported values but similar in magnitude.

Table 3-2. Observed kinetic parameters of CH<sub>4</sub> oxidation in various soils.

|                               | $K_m$<br>(ppmv) | $V_{\max}$<br>(nmol hr <sup>-1</sup> g dry soil <sup>-1</sup> ) | Reference                          |
|-------------------------------|-----------------|---|------------------------------------|
| Grassy area<br>composite soil | 19.9            | 6.8   | this study                         |
| Wooded area<br>composite soil | 17.2            | 7.4   | this study                         |
| Cultivated cambisol           | 32<br>43        | 0.61<br>0.76  | [ <i>Bender and Conrad, 1993</i> ] |
| Meadow cambisol               | 28<br>46        | 0.74<br>1.05  | [ <i>Bender and Conrad, 1993</i> ] |
| Forest cambisol               | 22              | 3.60  | [ <i>Bender and Conrad, 1993</i> ] |
| Landfill soil cover           | 1800            | 156   | [ <i>Whalen et al., 1990</i> ]     |

The kinetic similarity of microbial activity in the grassy and wooded areas was examined by performing an inference test on the regression lines of the Eadie-Hofstee plots, at a 5% significance level, using the  $t$  test statistic. The results of this test indicated that the slopes and intercepts of the regression lines were not significantly different,

implying that no substantial difference exists in the CH<sub>4</sub> oxidizing capacity of the soils in both areas.

The results of the kinetic experiments established the appropriate range of initial headspace CH<sub>4</sub> concentrations used during subsequent moisture manipulation experiments with these soils. An initial concentration range of 250 to 300 ppmv CH<sub>4</sub> was determined to be low enough to resolve concentration changes due to microbial oxidation during an 8-hour incubation but high enough to yield oxidation rates in the range of substrate saturation ( $V_{\max}$ ) where reaction kinetics were pseudo-zeroth order.

### *Soil Moisture*

The effect of soil moisture content on the rate of CH<sub>4</sub> oxidation was examined by moisture content manipulation during incubations of fresh soil samples. Samples were randomly selected at 20 locations in both grassy and wooded areas. Samples were air dried in the laboratory for 72 hours prior to the start of the experiment. The initial sample moisture contents after drying ranged from 7 to 27%. The moisture content of each sample was increased in 3 to 10% increments by the addition of distilled water. Samples were allowed to equilibrate after moisture additions for 12 hours prior to the start of each experiment. The maximum soil moisture contents tested ranged from 33 to 61%. All incubations were performed at 25°C. Incubation headspace methane concentrations ranged from 220 to 250 ppmv resulting in pseudo-zeroth-order oxidation kinetics. The linear regression of time series data was significant at the 95% confidence level for all samples at all moisture contents.

The results indicate a strong dependence of CH<sub>4</sub> oxidation on soil moisture content. Oxidation rates in all samples decreased significantly after drying below field moisture contents, increased to an optimum value as water was added, and decreased with continued water addition. Maximum measured oxidation rates ranged from 2.2 to 6.1 nmol hr<sup>-1</sup> g dry soil<sup>-1</sup> in the grassy area soils and from 3.7 to 9.0 nmol hr<sup>-1</sup> g dry soil<sup>-1</sup> in the

wooded area soils (Figure 3-4). The oxidation rate maxima occurred at different moisture contents for each soil sample and ranged from 18 to 33% for the grassy area soils and from 30 to 51% for the wooded area soils. Whalen et al. suggested that the optimum soil moisture content supports a maximum microbial biomass [Whalen et al., 1990]. Microbial desiccation occurs at lower moisture contents, while aqueous phase diffusion of CH<sub>4</sub> through the increasing water volume limits the rate of substrate delivery to the microbes at higher moisture contents. However, moisture content alone explains only the shape of the data curves in our results. What accounts for the variability in the optimal soil moisture content for methane oxidation in different soil samples?

The interaction of soil water and organic matter appears to explain this variability. Figure 3-5 presents CH<sub>4</sub> oxidation in all soil samples as a function of both moisture content and organic matter content. Maximum oxidation occurs in a narrow range that is centered on a soil moisture content of approximately 33% and a soil organic matter content of approximately 14%. Federer et al. showed that bulk density and pore volume were closely related to organic matter content in soils with similar characteristics to those observed at our site [Federer et al., 1993]. In this relationship, bulk density decreases while pore volume increases with increasing organic matter as soil granules form from the agglomeration of mineral particles and organic matter. Therefore, as soil organic matter increases, the volumetric water content occupying soil pore spaces will decrease to maintain a constant gravimetric water content. For example, consider two soil samples with identical mass, gravimetric moisture contents of 30%, and organic matter contents of 5 and 15%. While both samples have identical gravimetric moisture contents, the sample with more organic matter will have higher porosity, lower bulk density, and less volumetric water than the low organic content sample. As the porosity increases, a decreasing volume of water is distributed in the pore volume, decreasing the water film thickness. This increases the rate of substrate CH<sub>4</sub> delivery to the methanotrophs for oxidation. However, at higher organic contents, more pore space becomes available for a decreasing volume of water which decreases microbial activity due to desiccation.

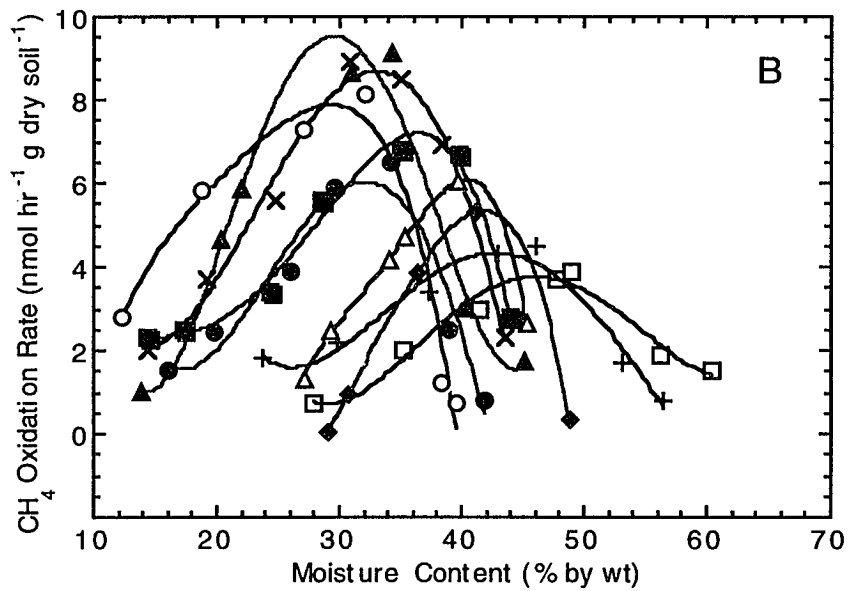
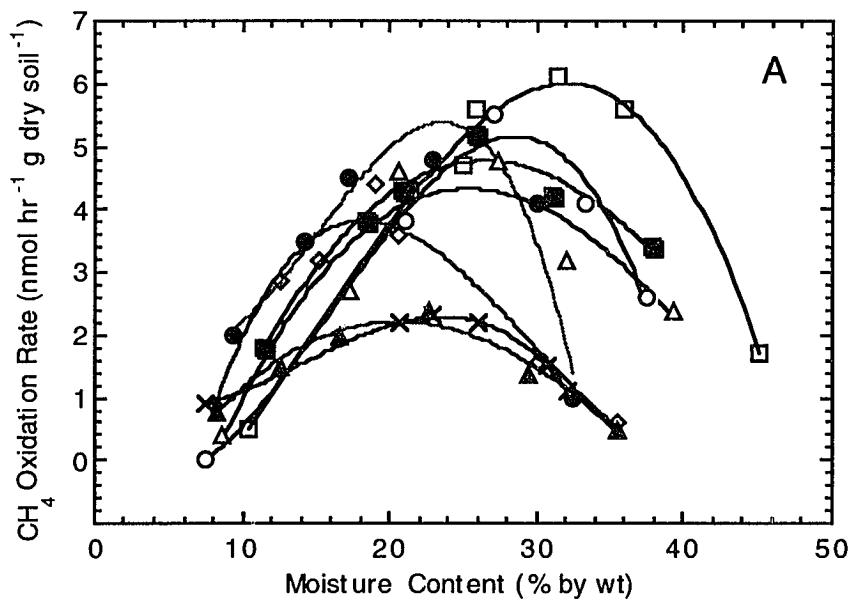


Figure 3-4. Methane oxidation in random samples from (A) the grassy area soils and (B) the wooded area soils as a function of increasing sample moisture contents. The results of individual samples incubations, represented by different symbols, are fit by second-order polynomials.

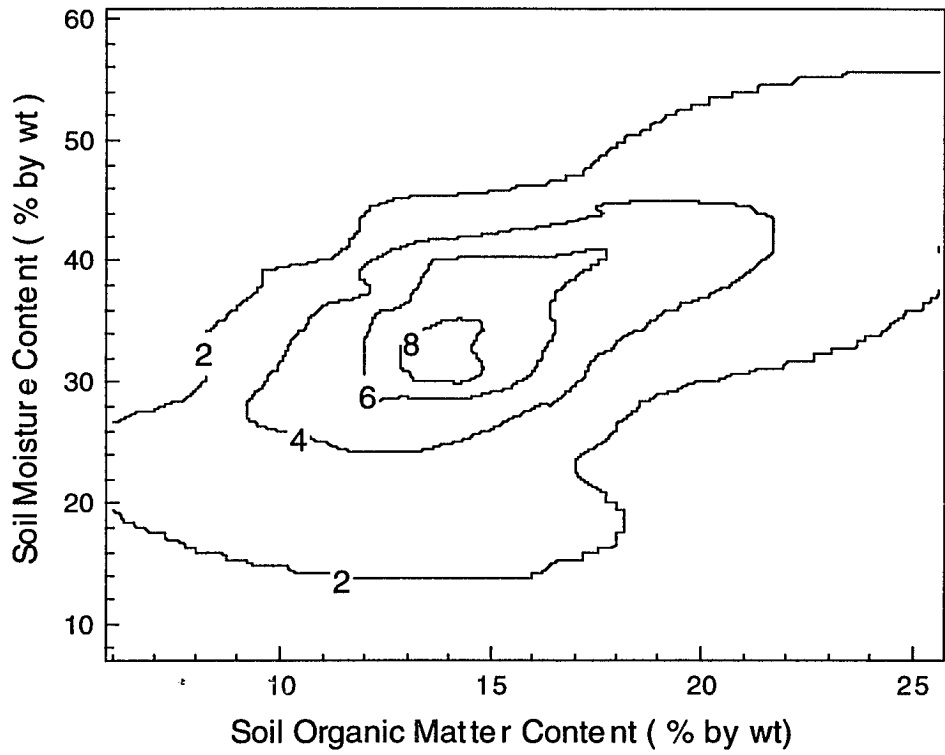


Figure 3-5. Methane oxidation contours in nanomoles per hour per gram of dry soil as a function of both sample moisture and organic matter contents. Plot includes incubation results from all samples.

## Conclusion

The complex, nonlinear response of methane oxidation to the interaction of soil moisture and organic matter documented in this study explains a potentially major source of variability in large-scale biospheric responses to climate change. Expected changes in precipitation patterns and land use will inevitably alter soil climate and composition.

Quantitative information on variables affected by these changes such as soil moisture and organic content will be required to reliably estimate the magnitude of the terrestrial methane sink and its impact on future atmospheric methane mixing ratios.



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**CHAPTER 4**  
**LANDFILL METHANE EMISSIONS MEASURED BY STATIC**  
**ENCLOSURE AND ATMOSPHERIC TRACER METHODS**

## CHAPTER 4

# LANDFILL METHANE EMISSIONS MEASURED BY STATIC ENCLOSURE AND ATMOSPHERIC TRACER METHODS

As submitted to Journal of Geophysical Research-Atmospheres  
with co-authors B. Mosher, J. H. Shorter, J. B. McManus, C. E. Kolb, E. Allwine,  
B. K. Lamb, R. C. Harriss  
August, 1995

### Summary

Methane (CH<sub>4</sub>) emissions were measured from the Nashua, NH municipal landfill using static chamber and atmospheric tracer methods. The spatial variability of emissions was also examined using geostatistical methods. 139 static chamber measurements were performed on a regular grid pattern over the emitting surface of the landfill resulting in an estimate of whole landfill emissions of 16200 liters CH<sub>4</sub> min<sup>-1</sup>. Omnidirectional variograms displayed spatial correlation among CH<sub>4</sub> fluxes below a separation distance of 7 m. Eleven tracer tests, using SF<sub>6</sub> as a tracer gas, resulted in a mean emissions estimate of 17750 liters CH<sub>4</sub> min<sup>-1</sup>. The favorable agreement between the emission estimates was further refined using the observed relationship between atmospheric pressure and CH<sub>4</sub> flux. This resulted in a pressure corrected tracer flux estimate of whole landfill emissions of 16740 liters CH<sub>4</sub> min<sup>-1</sup>. Data can be viewed in tabular form in Appendix D.

### Introduction

Methane is a radiatively active trace gas whose abundance in the atmosphere has

increased significantly during the past several hundred years [*Cicerone and Oremland, 1988*]. This increase appears to be well correlated with increasing human population [*Rasmussen and Khalil, 1984*]. A key to formulating control strategies to reduce the rate of CH<sub>4</sub> increase in the atmosphere is the identification and quantification of all sources. Anthropogenic sources are estimated to contribute approximately 70 % of the estimated 440-640 Tg CH<sub>4</sub> emitted annually to the atmosphere [*IPCC, 1992*]. Landfills have been identified as the largest source of anthropogenic CH<sub>4</sub> emissions in the United States, accounting for approximately 25 % of CH<sub>4</sub> emissions annually [*USEPA, 1994*]. However, there remains significant uncertainty associated with this estimate.

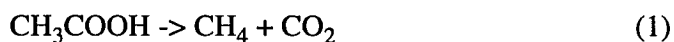
Here we report the results of a comprehensive investigation of CH<sub>4</sub> emissions to the atmosphere from a municipal solid waste (MSW) landfill in the northeastern United States. Two methods for determining CH<sub>4</sub> emissions were compared; static enclosure and inert atmospheric tracer methods. Both have inherent advantages and disadvantages. Static enclosure methods provide simple and low cost techniques for measuring emissions from a small surface area. However, performing multiple measurements over an extended surface to estimate whole area emissions requires a significant time and labor investment. In addition, the spatial heterogeneity ubiquitous in all microbially mediated systems makes extrapolation of enclosure measurements problematic. Atmospheric tracer methods circumvent the problem of spatial heterogeneity by integrating whole area flux. This method is particularly applicable to point sources or distributed area sources with finite boundaries such as landfills. However, the potentially high cost, dependence on micrometeorological conditions, and interfering sources can limit the applicability of tracer methods. This paper presents the results of these measurement methods as applied to the study site as well as a characterization of the spatial heterogeneity associated with landfill CH<sub>4</sub> emissions.

## Background

Modern sanitary landfilling practices, which replaced uncontrolled open dumping and burning in the mid-1960s, limit the content of wastes landfilled, regulate landfilling procedures, manage liquid emissions, and in some cases control gaseous emissions. A result of these practices is the eventual establishment of conditions for the long term decomposition of the organic matter in landfilled wastes by a consortia of heterotrophic, fermentative, acetogenic, and methanogenic bacteria [Boone, 1991; Farquhar and Rovers, 1973; Ham et al., 1979]. The initiation of anaerobic decomposition can require months to years after waste placement depending on several environmental factors including waste density, moisture content, nutrient content, pH, and temperature [Thorneloe et al., 1993].

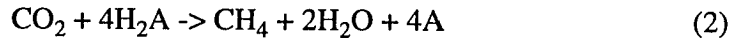
Initially, the presence of entrapped air favors aerobic waste decomposition. Anoxic conditions are established only after the oxygen is consumed by aerobic bacteria. Hydrolytic reactions, catalyzed by bacterial extracellular enzymes, then reduce the complex organic matter to simpler soluble forms, such as amino acids, simple sugars, and fatty acids, that can be utilized by other bacteria. Another group of bacteria, the “acid-formers”, convert these simple organic compounds to long chain fatty acids, as well as acetate, hydrogen (H<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>). The fatty acid substrates such as butyrate and propionate are then available to acetogenic bacteria which convert them to acetate, H<sub>2</sub>, and CO<sub>2</sub>. Methanogenic bacteria can then utilize acetate and H<sub>2</sub> as energy sources in the final stages of CH<sub>4</sub> formation.

The largest fraction of landfill CH<sub>4</sub> is formed from acetic acid by decarboxylation



which also results in the formation of substantial quantities of CO<sub>2</sub>. The remaining CH<sub>4</sub> is

generated by CO<sub>2</sub> reduction with H<sub>2</sub> or organic molecules (H<sub>2</sub>A) as H donors



The gas formed after the stabilization of anaerobic conditions is approximately composed of 50 % CH<sub>4</sub>, 45 % CO<sub>2</sub>, 3 % N<sub>2</sub>, and a small quantity of other trace gases, generally non-methane hydrocarbons [Augenstein and Pacey, 1991; Bogner et al., 1990; Parkin and Owen, 1986].

The quantity of generated landfill gas eventually released to the atmosphere is the subject of some debate. Several models have recently been developed to estimate global emissions of landfill CH<sub>4</sub>. Bingemer and Crutzen, [1987] developed a mass balance approach in which the annual landfill deposit of degradable organic carbon is available for conversion to biogas and emission to the atmosphere that same year. This method appears to overestimate emissions due to its assumption of ideal anaerobic decomposition as well as its neglect of the effects of soil cover oxidation. A model developed by Augenstein and Pacey, [1991] utilizes 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. However, this approach also neglects the effect of oxidation. Finally, the EPA/AEERL model uses an empirical relationship between the average landfill gas recovery rate and the amount of waste in place observed in 21 landfills in the U. S. to predict emissions to the atmosphere [Peer et al., 1992; Thorneloe et al., 1993]. Several factors contribute to significant uncertainties in emission predictions based on this model including estimates of the mass of waste in place, the recovery efficiency of the gas collection systems, and the quantity of CH<sub>4</sub> oxidized in the soil cover.

Reducing the uncertainty associated with these model based estimates will require a

more comprehensive set of field measurements of whole landfill CH<sub>4</sub> emissions to the atmosphere than currently exists. Relatively few field studies have been performed to quantify landfill CH<sub>4</sub> emissions from singular landfill sites to the atmosphere. *Bogner et al.* [1993] estimated CH<sub>4</sub> emissions from a landfill in Illinois, USA using limited data from static enclosure and pressure flow gas measurements. *Nozhevnikova et al.* [1993] described CH<sub>4</sub> emissions from several landfills around Moscow, Russia using limited static enclosure measurements. *Yasunori and Wakita* [1993] estimate CH<sub>4</sub> emissions from a landfill adjacent to Tokyo Bay, Japan using a continuous CH<sub>4</sub> measuring device and atmospheric dispersion techniques. Our study supplements these results by providing a comprehensive estimate of whole landfill CH<sub>4</sub> emissions to the atmosphere utilizing results from two rigorously applied measurement methods.

## Methods

### *Site Description*

The studied landfill is located in south central New Hampshire, USA in the town of Nashua. The site has been accepting waste for disposal since 1971 and is scheduled for closure in 1996. A total of  $1.05 \times 10^8$  kg of waste was accepted for disposal in 1994. The disposed waste consisted of 36 % MSW, 36 % commercial waste, 13 % construction and demolition (C&D) waste, and 13 % wastewater sludge. The disposal rate peaked in 1988 with a total of  $1.33 \times 10^8$  kg of waste accepted.

The site covers approximately 60 hectares and consists of a 33.5 hectare MSW landfill (approximately 3 hectares active), a separate 5.5 hectare C&D waste landfill located directly adjacent to the MSW landfill and approximately 1 hectare of yard waste composting windrows. The inactive areas of both landfills are covered by 1-2 m of sandy-clay loam surface material with limited surface fissuring. However, erosion and slumping of the



cover material along the south edge of the MSW landfill has exposed a section of waste approximately 2 m high and 10 m long. No landfill gas control systems were in place at the time of sampling although exploratory wells were under construction at that time.

Sparse or dead surface vegetation was a reliable visual indicator of significant localized CH<sub>4</sub> emissions. These areas were further examined during the initial site screening using a portable flame ionization detector manufactured by Foxboro Instruments. A 20 cm diameter funnel was attached to the sampling head of the instrument creating a small continuously sampled chamber. A qualitative indication of emissions was acquired by observing the change in CH<sub>4</sub> mixing ratio within the chamber while placing it on the soil surface. The screening results indicated significantly higher CH<sub>4</sub> emissions per unit area in the MSW landfill compared to those observed in the C&D landfill. Negligible CH<sub>4</sub> emissions were observed from the yard waste composting piles.

#### *Enclosure Measurements*

A static enclosed chamber technique, as described by *Livingston and Hutchinson*, [1995], was used to measure fluxes from the surface of the landfills. During each measurement a cylindrical polypropylene sampling enclosure was placed on the ground surface and a small amount of nearby soil was mounded at the soil-chamber interface to provide an adequate seal. Chamber surface area and volume were 510 cm<sup>2</sup> and 9.3 liters respectively. A battery operated blower circulated the air within the enclosure and a thermistor mounted inside measured enclosed air temperature. Enclosure headspace samples were collected at 0.5 or 1 minute intervals in 60 ml polyethylene syringes and analyzed within 24 hours. The gas flux, E (mass area<sup>-1</sup> time<sup>-1</sup>) from the surface was calculated by

$$E = \frac{V}{A} p \left( \frac{\Delta C}{\Delta t} \right) \quad (3)$$

where  $V$  is the volume of the enclosure,  $A$  is the enclosed surface area,  $p$  is the gas density at the enclosure headspace temperature, and  $\frac{\Delta C}{\Delta t}$  is the change in  $\text{CH}_4$  mixing ratio in the enclosure headspace.  $\frac{\Delta C}{\Delta t}$  is calculated by linear regression of the  $\text{CH}_4$  mixing ratio in four or five headspace samples with a required correlation coefficient of 0.90 or higher significant to the 95% confidence level for  $n=4$  or  $5$  [Crill *et al.*, 1988]. The minimum measurable  $\text{CH}_4$  flux was  $10 \text{ mg m}^{-2} \text{ day}^{-1}$ .

Fluxes were measured on a regular grid pattern at three scales of spatial separation during 5 days of similar meteorology and no precipitation. Data for estimates of whole landfill emissions were collected on September 5 and 7 on a quasi-regular grid pattern at an approximate spacing of 60 meters. 139 fluxes were measured over the emitting surface of the MSW landfill (Figure 4-1). Mean barometric pressure during the measurement period on these days was 1019 mb and 1021 mb, respectively. These data are referred to as the coarse grid data. Flux measurements were repeated at 4 locations on each day to quantify data continuity between the two measurement periods. The observed flux variability between days ranged from 5-13 %. The relatively low level of variability is attributable to the low velocity of surface winds during the measurement period. Air movement can alter the localized soil surface gas pressure producing a “pumping” effect on the static enclosure. Wind speed on both days was less than  $1.75 \text{ m s}^{-1}$  which appears to have resulted in negligible short temporal scale surface pressure variations.

Data were also collected in three randomly selected areas of the MSW landfill on September 26, 28, and October 3 on square grid patterns at two spatial resolutions: 6 m and 0.6 m. Mean barometric pressure during the measurement period on each of these days was 1016 mb, 1018 mb, and 1012 mb, respectively. The 0.6 m grids were randomly located within each of the 6 m grids. Each of the 6 m and 0.6 m grids consisted of 30 to 36 nodes and the three areas were each separated by approximately 70 m.

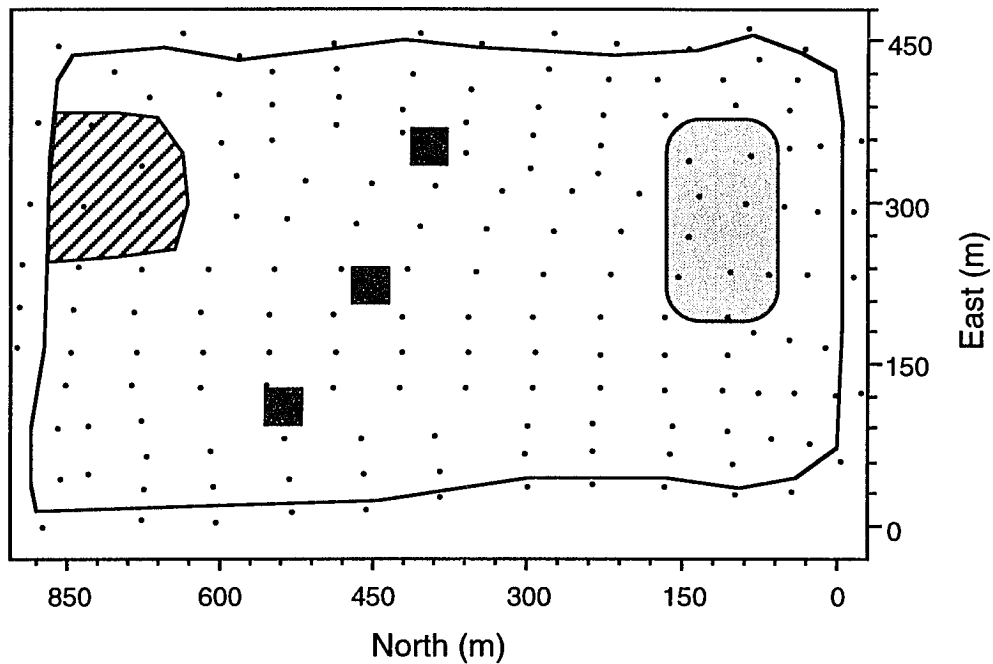


Figure 4-1. Base map of the MSW landfill. Fluxes were collected on an irregular 60 m grid resolution at locations represented by the dots. The black squares represent the areas of finer resolution sampling (6 m and 0.6 m grids). The approximate boundary of the waste is represented by the solid line, the hatched area designates the waste tire dump, and the grey area is the location of the active face.

#### *Atmospheric Tracer Measurements*

An atmospheric tracer method was used to measure the total  $\text{CH}_4$  emission rate from the landfill. Pure sulfur hexafluoride ( $\text{SF}_6$ ) tracer gas was released from the emitting surface to simulate landfill gas emissions [Lamb *et al.*, 1995]. This method has been used successfully to characterize trace gas emissions from a number of natural and anthropogenic sources [Howard *et al.*, 1992; Lamb *et al.*, 1986]. If the released tracer is well mixed in the source plume then the  $\text{CH}_4$  emission rate can be obtained directly by the

ratio method as

$$Q_m = Q_t \left( \frac{C_m}{C_t} \right) \quad (4)$$

where  $Q_m$  is the  $\text{CH}_4$  flux rate,  $Q_t$  is the  $\text{SF}_6$  tracer release rate,  $C_m$  is the measured  $\text{CH}_4$  mixing ratio above background, and  $C_t$  is the measured mixing ratio of the  $\text{SF}_6$  tracer [Howard *et al.*, 1992; Lamb *et al.*, 1986]. This method is restricted to situations with no interfering sources, a sufficient signal to be measured against the background, and a strong enough source to be measured far enough downwind to ensure adequate mixing with the tracer gas under circumstances of stable atmospheric conditions. These requirements were satisfied by the conditions observed at the Nashua landfill under a variety of atmospheric conditions.

$\text{SF}_6$  tracer gas was released from 3 cylinders located along the upwind edge of the landfill on a line perpendicular to the direction of the prevailing wind. The cylinders were placed at locations 0.25, 0.5, and 0.75 times the landfill width.  $\text{CH}_4$  and  $\text{SF}_6$  were measured in the resulting plume 1.2 to 3.5 km from the downwind edge of the landfill.

Both the  $\text{CH}_4$  and  $\text{SF}_6$  plumes were located in real-time by repeated plume traverses using van mounted fast response analyzers. This method allowed field personnel to immediately identify whether the required condition of good  $\text{CH}_4$  and  $\text{SF}_6$  mixing was being satisfied. Having identified an adequately mixed plume, evacuated gas sampling canisters were placed along a perpendicular line within the plume and a canister within the mobile van was used to collect sample along the entire length of the plume. The canister samples, which provide an integrated result over the entire measurement period, were used to independently verify and supplement the “instantaneous” results of the plume traverses using the mobile instruments. Atmospheric background mixing ratios were determined by canister sampling and real-time analyses.

### *Analytical Analysis*

Gas samples from enclosure measurements were analyzed for CH<sub>4</sub> as described by *Crill et al.* [1988]. CH<sub>4</sub> was quantified in syringe samples using a Shimadzu GC-8A gas chromatograph with a flame ionization detector after constituent separation using 2 meter x 3.2 mm OD columns packed with Poropak Q or HayeSep Q. Carrier gas was nitrogen; column temperature was 50°C. All peaks were quantified with Hewlett Packard Chemstation integration software on a personal computer. Mixing ratios were determined by comparison to standard gases obtained from Scott Specialty Gases calibrated with National Institute of Standards and Technology certified standards. Precision of analysis for calibration gases was 0.3%.

Tracer analyses were performed as described by *Lamb et al.* [1995]. A van mounted CH<sub>4</sub> analyzer was used to locate and quantify the landfill gas plume. This real-time instrument (RTI), developed at Aerodyne Research, Inc., is based on the absorption by CH<sub>4</sub> of infrared radiation (3.39 μm wavelength) produced by a HeNe laser [*McManus et al.*, 1989; *McManus et al.*, 1992]. The laser is rapidly tuned on and off a CH<sub>4</sub> absorption line at 2947.91 cm<sup>-1</sup> yielding a high-sensitivity differential absorption measurement. The laser light is directed through a multiple pass optical cell through which the sampled air flows at reduced pressure. Detected changes in light transmission are then detected and processed to yield CH<sub>4</sub> mixing ratio. The instrument is sensitive to changes in ambient mixing ratio of about 0.3 % or 5 ppb CH<sub>4</sub> (RMS at 1 sec averaging). Response time is 6 seconds due to gas flow time through the sampling cell. The instrument is calibrated hourly by comparison to standard gases obtained from Scott Specialty Gases calibrated with National Institute of Standards and Technology certified standards.

The continuous trace gas analyzer, developed by the Laboratory for Atmospheric Research at the Washington State University (WSU), was also van mounted for measurement of the SF<sub>6</sub> tracer concurrent with the Aerodyne RTI measurement of CH<sub>4</sub>

[*Benner and Lamb, 1985*]. The instrument utilizes an electron capture detector and is configured for turbulent fluctuation measurements with a response time of 0.4 sec and a detection limit of less than 10 ppt. The instrument is calibrated hourly using SF<sub>6</sub>/air standards from Scott-Marine, Inc. over the range 25 ppt to 10 ppb ( $\pm 5$  % certified accuracy).

A LiCor infrared CO<sub>2</sub>/ H<sub>2</sub>O analyzer (LI-6262) was used to measure ambient CO<sub>2</sub> mixing ratios. The instrument was calibrated frequently using a CO<sub>2</sub> free gas and a known CO<sub>2</sub> standard gas. The CO<sub>2</sub> instrument was used to identify anomalous CH<sub>4</sub> sources. Significant CH<sub>4</sub> mixing ratios accompanied by high ambient CO<sub>2</sub> are characteristic of combustion processes and can be neglected in the subsequent analysis.

The geographic position of the van is determined using a two-receiver global positioning system (GPS) as manufactured by Trimble, Inc. The GPS portable receiver is mounted in the van while a base station is located at a known, fixed location. Post processing of the data provides van position to an accuracy of 2 to 5 m. The van is also equipped with a drive shaft counter providing driving distances accurate to  $\pm 1$  m.

Whole air samples were collected in evacuated canisters using portable samplers. Ambient air was drawn into each sampler using a battery powered pump fitted with a Teflon-aluminum head. The 6 liter stainless steel electropolished canisters were pressurized with zero air for shipment and evacuated immediately prior to use in the field. The canisters were pressurized to approximately 20 psia at a steady rate by pumping against a stainless steel capillary flow restrictor during a 30 min sampling period. Approximately 4 to 6 canister samples were collected during each tracer test.

Canister samples were analyzed after return to WSU. CH<sub>4</sub> was quantified in samples using a HP5880 gas chromatograph with a fixed sampling loop and a flame ionization detector. Mixing ratios were determined by comparison to standard gases traceable to National Institute of Standards and Technology standards. Samples were

analyzed for CH<sub>4</sub> at least 4 times to obtain precision of 10 ppb or less. Canister samples were analyzed for SF<sub>6</sub> using a HP5880 electron capture gas chromatograph calibrated with standards from Scott-Marine, Inc. with a ±5 % certified accuracy.

Each tracer release system consisted of a gas cylinder pressure regulator and a length of stainless steel capillary restrictor tubing. The length of the tubing was sized to yield approximately 2 l min<sup>-1</sup> flow rate at a second stage pressure setting of 40 psig. Each release system was calibrated using a dry gas meter prior to field deployment, and periodic observation of each release system was made using either a dry gas meter or a calibrated mass flow meter during the tracer release period.

#### *Tracer Method Error*

The systematic error associated with the tracer method can be estimated by quantifying the variability of each step in the process [Lamb *et al.*, 1995]. Three sources of error contributed to the total. Differences noted in the tracer release as measured using both the dry gas meter and the mass flow meter generally ranged from 8–15 %. Upwind and downwind CH<sub>4</sub> mixing ratios had an associated error of ±10 ppb contributing a total error of ±14 ppb calculated as the square root of the sum of the squares (RSS) of the contributing uncertainties. The CH<sub>4</sub> mixing ratio above background typically ranged from 100–200 ppb yielding an uncertainty range of 7–14 %. The 5 % uncertainty in SF<sub>6</sub> calibration standards and the 5 % uncertainty in measurement precision yielded a combined uncertainty in measured tracer mixing ratio of ±10 %. Assuming a 10 % uncertainty for each of the three terms yields an overall RSS uncertainty in the estimate of approximately ±17 %.

The results from individual tests were reported for each of the canister and RTI measurements as an emission rate with a corresponding variability. The mean emission rate and variability were obtained by calculating the emission rate by Equation (4) for each

sampling canister or each plume traverse and averaging the results for each test. The variability is an indication of the agreement of results between the canisters and between traverses during each test. In the absence of interfering sources and with adequate simulation of the source the variability should be low and the canister and RTI mean emission estimates should be similar.

### *Statistical Analysis of Enclosure Measurements*

The extent of spatial correlation among the surface enclosure data was analyzed using a geostatistical method known as semivariogram analysis [Isaaks and Srivastava, 1989]. Semivariograms, or simply variograms, describe the changes in spatial continuity of a value as a function of distance between measurements. A variogram that describes the spatial relationship in all directions is known as omnidirectional. Ordinarily, the average squared difference or variance between data pairs increases with increasing separation distance to a maximum variance known as the sill. Ideally, the variance increases from 0 at the origin to the sill over a distance known as the range. Values separated by distances smaller than the range are autocorrelated while those separated by distances greater than the range are uncorrelated. Often, factors such as sampling and measurement errors result in a discontinuity in the variogram at very small separation distances. This offset in variance from 0 at the origin to a specific value is known as the nugget. Both omnidirectional and directional variograms were utilized during analysis to determine the extent of anisotropy in the data.

## Results

### *Enclosure Measurements*

The 0.6 m, 6 m, and 60 m grid data from the MSW landfill were initially pooled to determine the form of the data distribution. Data from the C&D landfill were excluded



from geostatistical characterizations due to the observed lack of significant emissions from this area. The resulting cumulative probability function (cdf) plot shows a data set that is positively skewed, typical of many variables in the earth sciences (Figure 4-2). A lognormal transformation of the data did not result in the linearly increasing distribution typical of a normal form due to the large number of low values apparent in Figure 4-2.

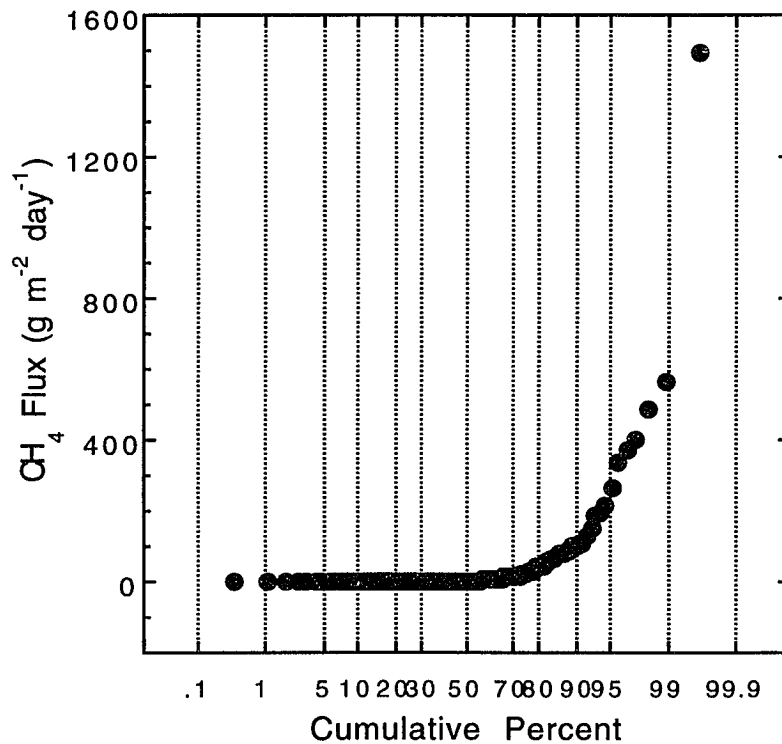


Figure 4-2. Cumulative probability plot of the untransformed coarse grid CH<sub>4</sub> fluxes.

A normal score transformation of the data was performed to circumvent the limitation of a non-normal distribution [Deutsch and Journel, 1992]. In this method, each of the true data values are represented by corresponding values of a Gaussian normal distribution with a mean of 0 and a variance of 1. Operations that assume a Gaussian distribution, such as variogram analysis, can then be performed on the transformed data.

Omnidirectional variograms were generated from the combined 0.6 m, 6 m, and 60 m data set after the normal score transformation to characterize the spatial relationship. Variograms with nodal separation intervals of 60 and 6 m were similar and revealed no significant correlation between data values. However, at node separations of 0.6 m autocorrelation is apparent out to a range of approximately 7 m. Figure 4-3 presents the variograms with nodal separation intervals of 6 and 0.6 m. Beyond a range of 7 m, emissions appear to be spatially independent. The resulting combined exponential/gaussian variogram model implies a minimal nugget value. This was verified by a limited number of sequentially repeated fluxes performed in three locations which yielded a maximum variation of 11 %.

The presence of anisotropy in the data was examined by performing directional variograms in both the vertical (northing) and horizontal (easting) directions. The directional variograms showed similar characteristics in range and nugget and did not indicate significant anisotropy in either direction.

The coarse grid data from the MSW landfill were mapped by linear interpolation and the resulting pattern of CH<sub>4</sub> emissions is presented in Figure 4-4. The small number of high flux values responsible for the significant positive skew in the cdf are readily apparent. Emissions appear to be dominated by a zone of high flux in the northeast section of the site although no extraordinary surface features, such as soil cracks or exposed waste, were observed in the area.

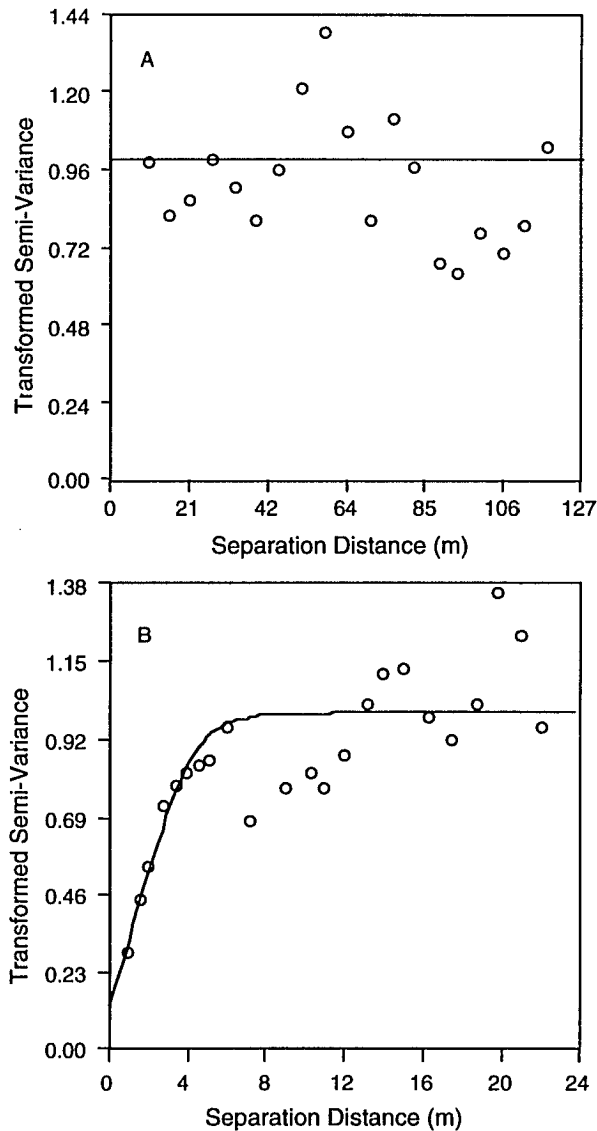


Figure 4-3. Variograms for CH<sub>4</sub> fluxes measured at (A) 6 m, and (B) 0.6 m sampling resolution on square grids. Lines are representative best fit models of the data. The horizontal line in (A) is a linear “pure nugget” model and the line in (B) is a mixed exponential-gaussian model. CH<sub>4</sub> fluxes exhibit spatial autocorrelation only at separation distances less than approximately 6 m as evidenced by the smoothly decreasing variability with decreasing separation distance in (B). The pure nugget model in (A) implies spatial independence in the lower sampling resolution data.

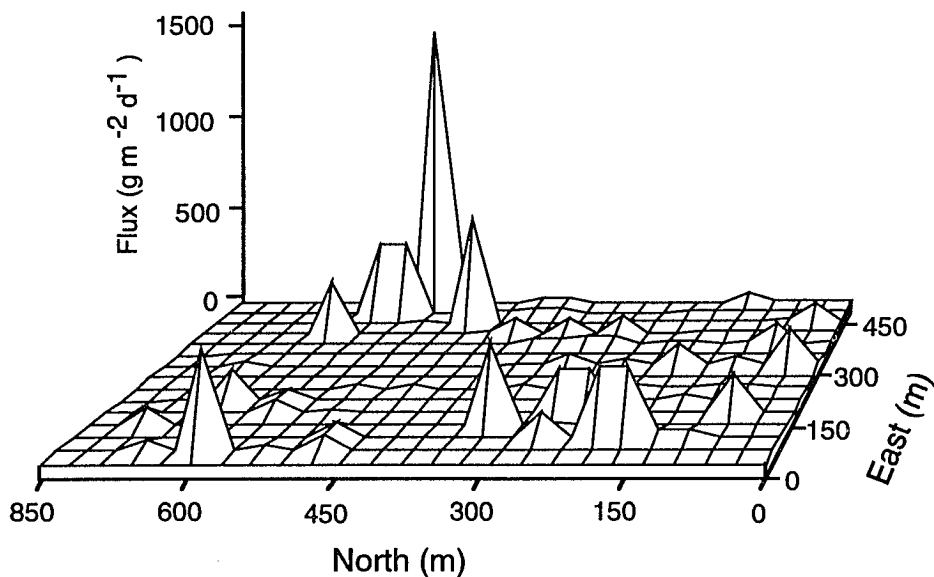


Figure 4-4. Map of CH<sub>4</sub> emissions from the MSW landfill based on linear interpolation of the coarse grid flux data. CH<sub>4</sub> flux is represented on the vertical axis in g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>.

Whole landfill CH<sub>4</sub> emissions were estimated using the mean of the coarse grid flux data from both the MSW and C&D landfills. *Livingston and Hutchinson, [1995]* suggest that descriptive statistics of spatial data based on the arithmetic mean are unbiased regardless of the underlying distribution providing the number of samples is adequately large ( $n > 20-30$ ). Our sample size ( $n$  equals 139 in the MSW landfill and 48 in the C&D landfill) satisfies this criteria.

Calculation of the mean flux included only data collected within the boundary of the solid waste disposal area. Data that were collected outside the waste perimeter implied negligible offsite gas migration and were therefore disregarded. Flux values in the MSW landfill ranged from the detection limit to 1495 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> with a mean and coefficient of variation ( $CV = [\text{standard deviation}/\text{mean}] \times 100$ ) of  $45 \pm 324$  g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>.

The estimated total emission from this area based on an emitting surface of 33.5 hectares is 16000 liters CH<sub>4</sub> min<sup>-1</sup>. Flux values in the C&D landfill were considerably lower, ranging from the detection limit to 144 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> with a mean and CV of 3.2±95 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>. The estimated total emission from this area based on an emitting surface of 5.5 hectares is 200 liters CH<sub>4</sub> min<sup>-1</sup>. The estimated total CH<sub>4</sub> emission from the site based on the enclosure measurements is 16200 liters CH<sub>4</sub> min<sup>-1</sup>.

#### *Atmospheric Tracer Measurements*

CH<sub>4</sub> emissions were measured by atmospheric tracer methods over the course of 5 days of field experiments during October and November, 1994. Initial CH<sub>4</sub> surveys with the RTI identified a significant gas plume ranging approximately 100-500 ppb above background at a range of 1–2 km originating at the landfill site with no significant interfering upwind sources. Eleven tracer tests were subsequently performed to quantify the observed CH<sub>4</sub> emission rate using both canister and RTI methods during each test resulting in 22 emission rate estimates. The resulting whole landfill emission estimates are presented in Table 4-1.

An error threshold was established to reject emission estimates that were determined to retain unacceptable levels of variability. Fifteen flux estimates from 10 tracer tests with variability less than 25 % were accepted based on this criteria. Both canister and RTI flux estimates were accepted in 5 tests. Good correlation was observed between the canister and RTI estimates in these 5 tests with variability ranging from 7-16 %. The resulting overall tracer method mean emission rate and CV was 17750±22 liters CH<sub>4</sub> min<sup>-1</sup>.

Table 4-1. Results of 11 tracer tests performed between 10/7/94 and 11/12/94. Asterisks indicate data values rejected due to coefficients of variation in excess of 25%. Coefficients of variation of the averages represent the variation among the emission estimates in each column.

| Test number | Canister samples  |                              | Real-time samples   |                              |
|-------------|---|------------------------------|---|------------------------------|
|             | CH <sub>4</sub> emission rate (liters min <sup>-1</sup> ) | Coefficient of variation (%) | CH <sub>4</sub> emission rate (liters min <sup>-1</sup> ) | Coefficient of variation (%) |
| 1           | 13860   | 13                           | 41900 *   | 43                           |
| 2           | 20020 *   | 34                           | 24480 *   | 40                           |
| 3           | 18750   | 18                           | 16920   | 11                           |
| 4           | 29700 *   | 27                           | 17030   | 12                           |
| 5           | 10680   | 15                           | 11480   | 23                           |
| 6           | 24450   | 25                           | 9730 *  | 26                           |
| 7           | 20860   | 13                           | 17090 *   | 43                           |
| 8           | 21370   | 15                           | 19670   | 6                            |
| 9           | 23930   | 14                           | 19220   | 16                           |
| 10          | 13950   | 23                           | 16290   | 12                           |
| 11          | 12060 *   | 26                           | 17850   | 18                           |
| Average     | 19060   | 31                           | 19240   | 44                           |

Examining the correlation between emissions and atmospheric pressure revealed a significant relationship. The acceptable emission estimates from each day of measurements were averaged and plotted as a function of the average atmospheric pressure observed during the measurement period (Figure 4-5). The observed trend in the data was then modeled using linear regression techniques. The resulting regression line ( $r^2=0.84$ ) indicated a significant inverse correlation between CH<sub>4</sub> emissions and atmospheric pressure consistent with results of other investigators [Bogner *et al.*, 1990; Young, 1992].

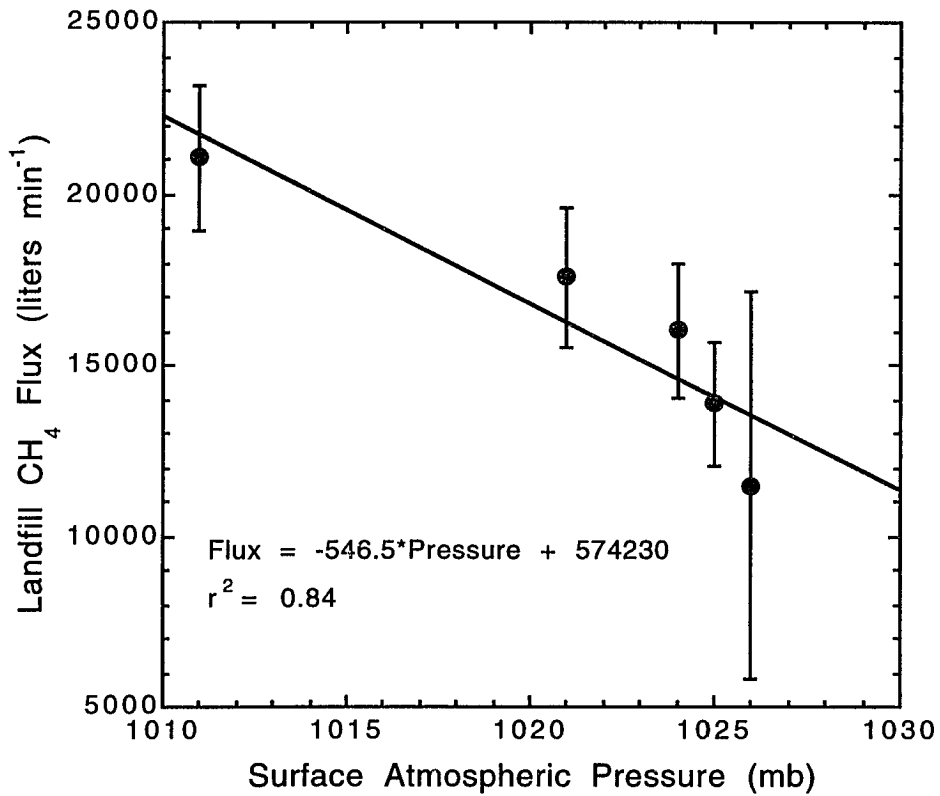


Figure 4-5. Daily average whole landfill CH<sub>4</sub> emissions observed by the tracer method plotted as a function of the average atmospheric pressure observed during each measurement period. Error bars represent the standard deviations of the acceptable values on each day.

## Discussion

The comparison between enclosure and tracer method derived flux estimates can be refined by utilizing the relationship observed between flux and atmospheric pressure as presented in Figure 4-5. Mean atmospheric pressure during the period of enclosure flux measurements was 1020 mb. The whole landfill CH<sub>4</sub> flux predicted at that pressure by the atmospheric pressure versus flux relationship is 16740 liters CH<sub>4</sub> min<sup>-1</sup>. This value compares even more favorably to the enclosure based estimate of 16200 liters CH<sub>4</sub> min<sup>-1</sup> than to the uncorrected tracer method mean estimate of 17750 liters CH<sub>4</sub> min<sup>-1</sup>.

The observed range of CH<sub>4</sub> fluxes at the Nashua landfill are typical of the range observed in other landfills although our maximum values are among the highest reported. Bogner, et al. measured fluxes ranging from 3 mg CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> to 20 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> using enclosure methods and calculated fluxes as high as 331 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> using observed concentration gradients at an Illinois landfill with a gas control system in place [Bogner et al., 1993]. Nozhevnikova, et al. observed fluxes as high as 32 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> at several uncontrolled landfills around Moscow [Nozhevnikova et al., 1993]. Both studies observed a pattern of emissions with spatial heterogeneity similar to that observed in our coarse grid data. The localized nature of these emissions, as evidenced by the low range of autocorrelation in the variogram analysis, is probably ubiquitous in all landfills as a result of the heterogeneity of both landfill disposal methods and the solid waste disposed. The interbedded mix of waste and daily cover soil appears to induce preferred subsurface pathways for gas movement which may produce limited areas of high emissions as opposed to distributed areas of diffuse emissions.

An estimate of the CH<sub>4</sub> generation rate can be calculated from the emission estimates and the quantity of waste in place as reported by *Straub*, [1995]. The refuse types, their associated wet masses, estimated moisture contents, and the total estimated dry mass are presented in Table 4-2.



Table 4-2. Categorical breakdown of estimated waste disposed in the Nashua, NH municipal landfill from 1971 -1994. Dry weights are calculated from the estimated original moisture content of each waste fraction before disposal.

| Waste type | Mass in place (10 <sup>6</sup> wet kg) | Decomposability category <sup>a</sup> | Fraction of total type (%) <sup>b</sup> | Moisture content (%) <sup>a</sup> | Mass in place (10 <sup>6</sup> dry kg) |
|------------|--|---------------------------------------|---|-----------------------------------|--|
| MSW        | 819                                    | readily                               | 20                                      | 55                                | 73.7                                   |
|            |  | moderately                            | 45                                      | 20                                | 294.8                                  |
|            |  | slowly                                | 10                                      | 15                                | 69.9                                   |
|            |  | non                                   | 20                                      | 0                                 | 163.9                                  |
| Commercial | 922                                    | readily                               | 10                                      | 55                                | 41.5                                   |
|            |  | moderately                            | 70                                      | 20                                | 516.1                                  |
|            |  | slowly                                | 10                                      | 15                                | 78.3                                   |
|            |  | non                                   | 10                                      | 0                                 | 92.2                                   |
| C&D        | 75                                     | readily                               | 0                                       | 55                                | 0                                      |
|            |  | moderately                            | 10                                      | 20                                | 6.0                                    |
|            |  | slowly                                | 50                                      | 15                                | 31.7                                   |
|            |  | non                                   | 40                                      | 0                                 | 29.8                                   |
| Sludge     | 212                                    | readily                               | 100                                     | 80                                | 42.3                                   |
| Total      | 2027                                   |                                       |   |                                   | 1440                                   |

a: [Augenstein and Pacey, 1991]

b: [Franklin Associates, 1988]

The resulting CH<sub>4</sub> generation rate, assuming a total waste dry mass of 1.4 x 10<sup>9</sup> kg and a CH<sub>4</sub> emission rate of 16450 liters CH<sub>4</sub> min<sup>-1</sup>, calculated as the mean of the enclosure based estimate and the tracer based linear model estimate, is 0.006 m<sup>3</sup> CH<sub>4</sub> (kg dry waste)<sup>-1</sup> yr<sup>-1</sup>. The total landfill gas generated, assuming a 50 % CH<sub>4</sub> - 50 % CO<sub>2</sub> composition based on gas samples from onsite test wells, can be calculated by

$$LF = \frac{\left[ \frac{CH_4}{(1 - OX)} \right]}{Frac_{CH_4}} \quad (3)$$

where LF is the landfill gas emitted, CH<sub>4</sub> is the CH<sub>4</sub> emission estimate, OX is the

estimated fractional whole landfill oxidation rate, and  $\text{Frac}_{\text{CH}_4}$  is the fractional composition of the landfill gas. Assuming a landfill gas composition of 50 %  $\text{CH}_4$  and an estimated  $\text{CH}_4$  oxidation rate during the measurement period of 21 % as described by *Czepiel et al.* [this issue], yields a generation rate of  $0.015 \text{ m}^3 \text{ landfill gas (kg dry waste)}^{-1} \text{ yr}^{-1}$ .

Table 4-3 presents a range of recently observed landfill gas generation rates from various field investigations. Our estimate compares favorably with the upper range of estimates based on field measured data. The range of observed generation rates may be a result of several factors including differences in waste composition, regional climate variability, and physical differences in physical landfill characteristics such as site geometry and cover material. The cover condition at the Nashua landfill is probably the most significant factor contributing to the observed rate of gas generation. The absence of an impermeable barrier on the landfill surface allows significant water to percolate through the body of the landfill enhancing degradation thereby increasing gas flow.

Table 4-3. Comparison of recent estimates of landfill gas generation rates calculated from data collected under field conditions.

| Source                           | Landfill gas generation rate<br>( $\text{m}^3 \text{ dry kg}^{-1} \text{ yr}^{-1}$ ) | Comments  |
|----------------------------------|--|---|
| this study                       | 0.015  | assumes 50 % $\text{CH}_4$ content and 21 % oxidation rate.             |
| [ <i>Rathmell</i> , 1991]        | 0.0062   | field production estimate   |
| [ <i>Augenstein</i> , 1990]      | 0.0031-0.011   | Turnkey, landfill Rochester, NH. limits based on field production data. |
| [ <i>Pacey and Dietz</i> , 1986] | 0.032  | field control cell, Mountain View, CA project.                          |
| [ <i>EMCON</i> , 1981]           | 0.0075   | maximum from field pumping tests, no location given.                    |

## Conclusion

We have presented a unique intercomparison of two methods of estimating trace gas emissions. During the course of this study we observed very favorable agreement between the enclosure and tracer method based estimates. The tracer method, in this case, was preferable due to its speed and logistic simplicity. The absence of interfering sources and the substantial local road network made this an ideal tracer site. However, interfering sources and limited access to downwind areas can often restrict its applicability. Under those circumstances, enclosure methods become a viable alternative, particularly when funding is limited. A properly executed enclosure method survey appears to provide an adequate estimate of large area emissions with the added benefit of characterizing the spatial distribution of those emissions.

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**CHAPTER 5**  
**QUANTIFYING THE EFFECT OF OXIDATION ON LANDFILL**  
**METHANE EMISSIONS**

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QUANTIFYING THE EFFECT OF OXIDATION ON LANDFILL  
METHANE EMISSIONS

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Summary

Field, laboratory, and computer modeling methods were utilized to quantitatively assess the whole landfill capability of aerobic microorganisms to oxidize methane (CH<sub>4</sub>) in a landfill soil cover at the Nashua, NH municipal landfill. Soil samples from locations of CH<sub>4</sub> flux to the atmosphere were returned to the laboratory and subjected to incubation experiments to quantify the response of oxidation in these soils to temperature, soil moisture, in-situ CH<sub>4</sub> mixing ratio, soil depth, and oxygen. The mathematical representations of the observed oxidation responses were combined with measured and predicted soil characteristics in a computer model to predict the rate of CH<sub>4</sub> oxidation in the soils at the locations of the measured fluxes described by *Czepiel*, [this issue]. The estimated whole landfill oxidation rate at the time of the flux measurements in October, 1994 was 21 %. Local air temperature and precipitation data were then used in conjunction with an existing soil climate model to estimate an annual whole landfill oxidation rate in 1994 of 11 %. Data can be viewed in tabular form in Appendix E.



## Introduction

The primary product of the degradation of landfilled solid waste organic matter is a gas composed of approximately 50 % CH<sub>4</sub>, 45 % carbon dioxide, 3 % nitrogen and a small quantity of other trace gases [EMCON, 1981; Ham *et al.*, 1979]. Much of this landfill gas eventually makes its way to the atmosphere. Landfills comprise the largest source of anthropogenic CH<sub>4</sub> emissions in the United States and are estimated to account for 3-19% of anthropogenic CH<sub>4</sub> emissions globally [USEPA, 1994]. The microbially mediated oxidation of landfill CH<sub>4</sub> in the overlying soil cover contributes significantly to the uncertainty of this estimate [Bogner and Spokas, 1993; Thorneloe *et al.*, 1993]. The oxidation of CH<sub>4</sub> in landfill cover soils has been observed in several laboratory investigations and estimates of total landfill CH<sub>4</sub> oxidation range from 7 to 50 % of CH<sub>4</sub> production [Gardner and Manley, 1993; Jones and Nedwell, 1993; Kightley *et al.*, 1995; Whalen *et al.*, 1990]. However, few field data exist with which to verify the quantitative significance of oxidation in assessments of landfill emissions.

A field and laboratory investigation was performed during autumn 1994 to quantitatively assess the whole landfill capability of aerobic microorganisms to oxidize CH<sub>4</sub> in a landfill soil cover. Surface CH<sub>4</sub> fluxes and soil gas CH<sub>4</sub> mixing ratios were measured in the field while soil samples were collected and returned to the laboratory to determine the response of oxidation to several soil environmental variables in a series of jar incubations. The results were then incorporated into a site specific empirical computer model to estimate the total fraction of landfill CH<sub>4</sub> oxidized in the cover soils at both the time of flux measurements and annually.

## Methods

### *Site Description*

The field data were collected from the surface of the Nashua Municipal Landfill. The landfill is located at a site in south central New Hampshire, USA in the town of Nashua. The site covers approximately 60 hectares and consists of a 33.5 hectare MSW landfill (approximately 3 hectares active), a separate 5.5 hectare construction and demolition (C&D) waste landfill and approximately 4 hectares of yard waste composting windrows. The landfills are covered by 1-2 m of sandy-clay loam surface material with intermittent low shrubs and grasses in the older sections. A summary of the soil physical characteristics is presented in Table 5-1. All soil samples were collected from locations outside of the active dumping area in cover materials with placement ages ranging from 3 to 10 years.

Table 5-1. Representative Characteristics of the Soil Samples Collected at the Nashua Site (n=29).

|  |              |
|--|--------------|
| Mean texture,<br>% sand/silt/clay                    | 53/18/29     |
| Texture coefficient<br>of variation, $\pm\%$         | 11/17/16     |
| Mean pH, 20°C <sup>a</sup>                           | 7.8 $\pm$ 14 |
| Mean organic matter<br>content, % by wt <sup>a</sup> | 1.8 $\pm$ 25 |

a:  $\pm$  coefficient of variation

### *Flux and Soil Gas Measurements*

Surface fluxes were measured on a quasi-regular grid pattern over the entire landfill surface during two days in September, 1994 and at the locations of soil sample collection in October, 1994 [Czepiel *et al.*, this issue]. An enclosed chamber technique was used to measure fluxes [Crill *et al.*, 1988; Livingston and Hutchinson, 1995]. During each measurement, a polypropylene sampling enclosure was placed on the ground surface and a small amount of nearby soil was mounded at the soil-chamber interface to provide an adequate seal. Chamber surface area and volume were 510 cm<sup>2</sup> and 9.3 liters respectively. A battery operated blower circulated the air within the enclosure and a thermistor mounted inside measured enclosed air temperature. Four or five enclosure headspace samples were collected at 0.5 or 1 minute intervals in 60 ml polyethylene syringes and analyzed within 24 hours. Fluxes were calculated by linear regression of the mixing ratio changes in four or five samples with a required correlation coefficient significant to the 95% confidence level for n=4 or 5 [Crill *et al.*, 1988]. The minimum measurable CH<sub>4</sub> flux was 10 mg m<sup>-2</sup> day<sup>-1</sup>.

Soil gas samples were collected prior to each flux measurement by inserting an end-perforated 3.175 mm OD stainless steel tube into the soil to a depth of 7.5 cm. Gas samples were collected in 60 mL polypropylene syringes and analyzed for CH<sub>4</sub>. Also, selected gas samples were analyzed for O<sub>2</sub>. All gas samples were returned to the laboratory and analyzed within 24 hours.

### *Soil Sampling and Incubations*

Soil samples were collected during October, 1994 at locations on the landfill surface after performing flux measurements. The entire soil volume in each 5 cm depth interval of interest (approximately 2500 ml) directly below the flux enclosure was collected after the measurement of in situ temperature. Soils were excavated with a trowel and transported immediately to the laboratory in sterile sample bags. Soil bulk density was determined by

the coring method within 5 cm of the sampling location [Culley, 1993]. Each soil sample was homogenized by mixing in a bucket and large gravel was removed. Subsamples were then withdrawn in 100-150 g increments for incubation. Approximately 100 g was also withdrawn for moisture, organic matter, and pH measurement.

Soil samples from 9 random locations around the emitting surface of the landfill were collected initially, to a depth of 25 cm, to determine the zone of maximum oxidation in the soil column. Samples for the moisture, temperature, oxygen, and kinetic experiments were subsequently collected from the identified interval of maximum oxidation in 10 random locations. Samples were also collected for the kinetic experiments from 12 additional locations selected to maximize the range of CH<sub>4</sub> exposure. All soil moisture contents are reported by weight.

Soil sample moisture contents were determined gravimetrically by oven drying at 105°C for 24 h [Topp, 1993]. Soil organic matter content was determined by loss on ignition in a muffle furnace at 410°C for 24 hours [Davies, 1974]. To determine soil pH, 10 ml of air dried soil was mixed in a sterile container with 10 ml of distilled water to form a slurry and repeatedly stirred with a glass rod for 30 minutes. A Beckman pH meter was then used to measure pH.

To determine CH<sub>4</sub> oxidation potential, each soil sample was subjected to time series incubation experiments performed in 1.0 liter air tight glass jars. 3.175 mm Swaglock unions with silicone septa were installed in the jar lids. Jar headspaces were sampled a maximum of six times during each experiment by removing 3 ml of gas in 10 ml polyethylene syringes. Headspace sampling typically occurred every half hour for the first two hours after CH<sub>4</sub> injection and every hour thereafter. All incubations were performed at 21°C except during the temperature manipulation experiments where temperatures ranged from 5 to 45°C. The minimum detectable rate of oxidation at an initial headspace CH<sub>4</sub> mixing ratio of 2 % was 10 nmol CH<sub>4</sub> hr<sup>-1</sup> g dry soil<sup>-1</sup>.

Incubations to determine the effect of reduced O<sub>2</sub> mixing ratios on CH<sub>4</sub> oxidation were performed by flushing the jar headspaces with air/N<sub>2</sub> gas mixtures of varying ratios for approximately 15 min prior to incubation. Samples were allowed to equilibrate to amended headspace atmospheres for approximately 2 hours. Time series incubations were then performed as previously described.

CH<sub>4</sub> oxidation rates were calculated from the resulting time series data. Varying quantities of CH<sub>4</sub> were supplied to the jar headspaces which resulted in first order or pseudo-zeroth order oxidation kinetics depending on the initial CH<sub>4</sub> mixing ratio. First order oxidation kinetics were characterized by exponentially decreasing headspace CH<sub>4</sub> mixing ratios and oxidation rates were calculated from the rate constant of the exponential curve fit. Pseudo-zeroth order kinetics were characterized by a linear decrease in headspace CH<sub>4</sub> mixing ratios. The slope of the linear regression of these data, with a required correlation coefficient greater than 0.95 and significant to the 95% confidence level, defined the rate of CH<sub>4</sub> oxidation. All oxidation rates were normalized to dry soil sample mass.

#### *Analytical Analysis*

CH<sub>4</sub> was quantified using a Shimadzu GC-8A gas chromatograph with a flame ionization detector (GC-FID) after constituent separation using 2 meter x 3.2 mm OD columns packed with Poropak Q or HayeSep Q [Crill *et al.*, 1995]. Carrier gas was nitrogen, column temperature was 50°C.

O<sub>2</sub> was quantified using a Shimadzu GC-8A gas chromatograph with a thermal conductivity detector (GC-TCD) after constituent separation using 2 meter x 3.2 mm OD columns packed with molecular sieve 5A (80/100 mesh) Carrier gas was helium, column temperature was 70°C.

All peaks were quantified with Hewlett Packard Chemstation integration software

on a personal computer. Mixing ratios were determined by comparison to standard gases obtained from Scott Specialty Gases calibrated with National Institute of Standards and Technology certified standards. Precision of analysis for calibration gases was 0.2%.

### *Soil Climate Model*

A one-dimensional soil heat flux and moisture flow model (SCM) was used to calculate daily average soil temperature and moisture profiles [Frolking, 1993]. The SCM heat fluxes and moisture flows are modeled by gradient-driven diffusion utilizing meteorological data (air temperature and precipitation) recorded in the city of Nashua. The gradient driven equations are numerically modeled by explicit finite difference equations for a multi-layered soil profile.

The SCM model characterizes soil physical properties based on texture as described by Clapp and Hornberger [Clapp and Hornberger, 1978]. The modeled soil is divided into a series of 5 cm thick horizontal layers. Each layer is assumed to have a uniform temperature and moisture content which is assigned to the center of the layer. Water fluxes and heat flows for each soil layer are determined by the gradients of soil water head potential and soil temperature, respectively. All values are determined per unit area in the horizontal plane.

## Results

### Laboratory Incubations

#### *Depth Profile*

Soil samples from successive depth intervals were collected initially to determine the distribution of CH<sub>4</sub> oxidation in the soil profile. The soils at each location were sampled in

5 cm intervals from the surface to a depth of 25 cm. Each depth interval sample was subjected to headspace CH<sub>4</sub> mixing ratios ranging from 1.8 to 2 % during jar incubations at 21°C. The resulting linear drawdown of CH<sub>4</sub> in each jar headspace typified the pseudo-zeroth order kinetics expected in a maximum oxidation rate or substrate independent environment. The distribution of oxidation in the soil column was similar in each profile with maximums occurring in the 5-10 cm depth interval in 7 of the 9 profiles (Figure 5-1). The observed maximum rates of oxidation ranged from 110 to 955 nmol CH<sub>4</sub> hr<sup>-1</sup> g dry soil<sup>-1</sup>. Based on these results, soil samples for use in subsequent incubations were collected from the 5-10 cm depth interval.

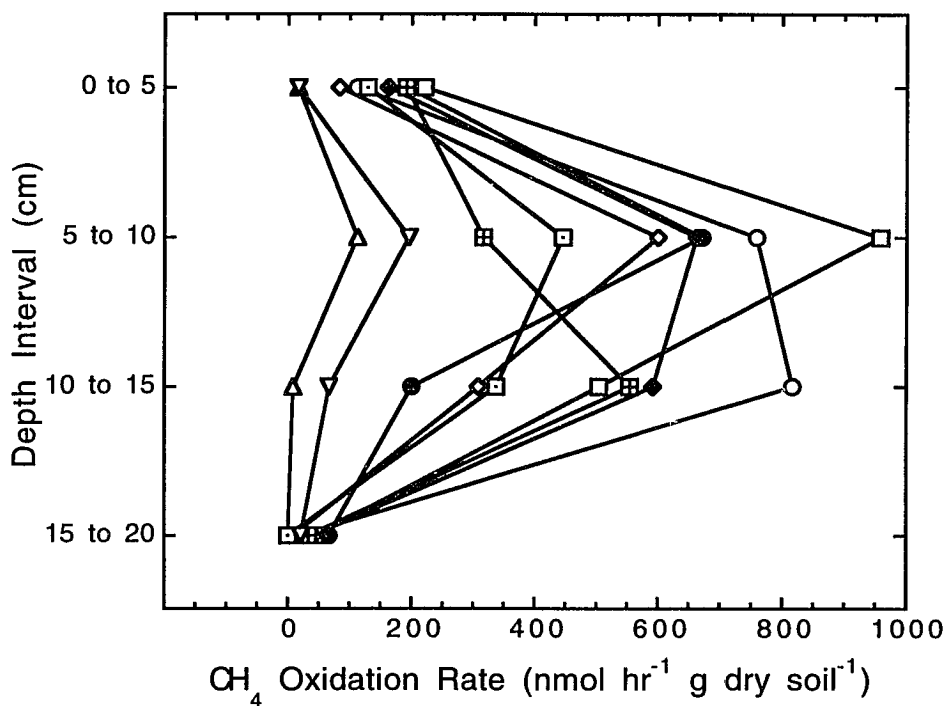


Figure 5-1. CH<sub>4</sub> oxidation rates through the soil profile from samples collected in 9 locations around the MSW landfill. Rates were determined by jar incubations of 5 cm depth integrated samples.

### *Moisture*

The response of soil CH<sub>4</sub> oxidation to varying moisture content was determined by manipulating soil moisture during soil sample incubations. 100 g subsamples were prepared from the samples as previously described and incubated in a constant temperature water bath. Subsamples were air dried in the laboratory for 72 hours before the start of each incubation. The initial sample moisture contents after drying ranged from 0 to 3 % H<sub>2</sub>O. The moisture content of each sample was increased in 5 to 10 % increments by the addition of distilled water. Samples were allowed to equilibrate to adjusted moisture for 12 hours prior to the start of each experiment. Initial headspace CH<sub>4</sub> mixing ratios ranged from 1.7 to 2.0 %, yielding pseudo-zeroth order drawdown characteristics. The linear regression of time series data was significant at the 95 % confidence level for all samples at all moisture contents. The resulting data and third order polynomial curve fits are presented in Figure 5-2A. Oxidation rates in all samples decreased significantly after drying below field moisture contents, increased to an optimum value as water was added, and decreased with continued water addition. Maximum measured oxidation rates ranged from 252 to 1390 nmol hr<sup>-1</sup> g dry soil<sup>-1</sup>. The oxidation rate maxima occurred in a relatively narrow range of moisture contents with a mean and coefficient of variation (CV) of 15.7±13.

A generalized model of the soil moisture response of CH<sub>4</sub> oxidation was generated from the incubation results and is presented in Figure 5-2B. The oxidation values in each sample curve were normalized to the maximum observed oxidation rate for that sample. The resulting fractional oxidation rates were then pooled and the entire data set fit by a third order polynomial function ( $r^2 = 0.79$ ).



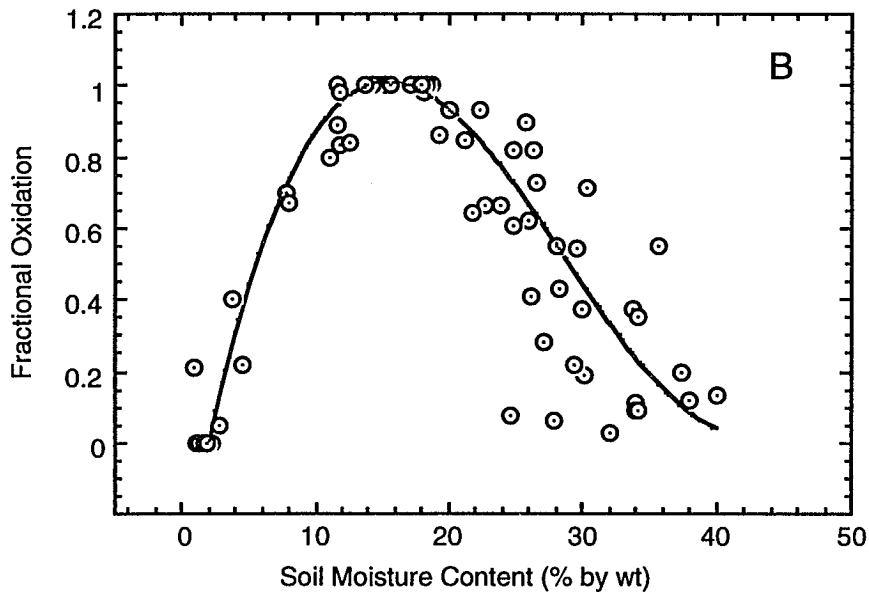
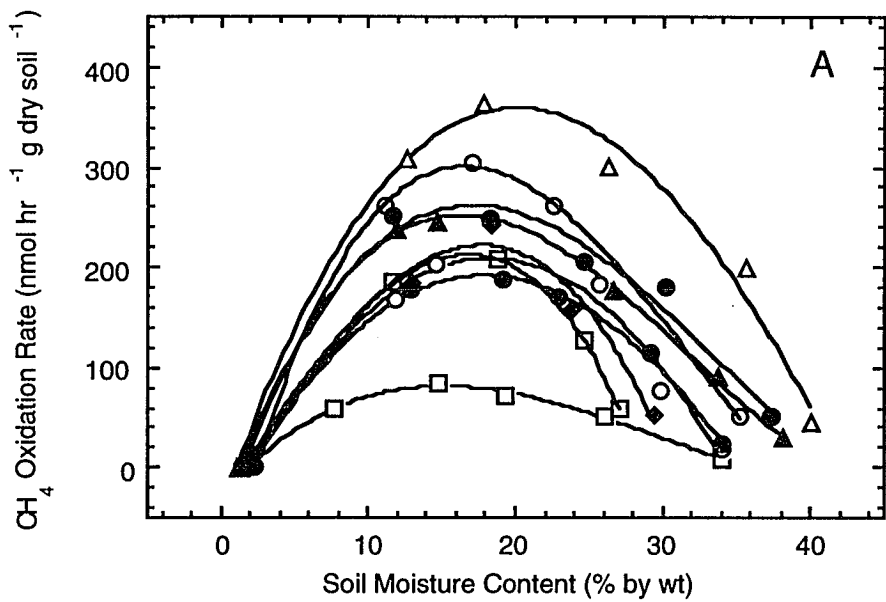


Figure 5-2. (A) Results of the moisture manipulation experiments. Individual samples are represented by different symbols. Solid lines are polynomial curve fits to the data from each sample. (B) A generalized model of the soil moisture response of  $\text{CH}_4$  oxidation. Data from 10 samples were pooled after normalization of the oxidation values to the maximum observed oxidation rate in each sample. The resulting values were best fit with a third order polynomial curve.

### *Temperature*

The response of soil CH<sub>4</sub> oxidation to varying temperatures was determined by manipulating temperature during soil sample incubations. 100 g subsamples were prepared from the samples as previously described and incubated in a constant temperature water bath. Soils were allowed to equilibrate to adjusted temperatures for 12 hr prior to the start of each experiment. Initial headspace CH<sub>4</sub> mixing ratios ranged from 1.5 to 1.8 %, yielding pseudo-zeroth order drawdown characteristics at incubation temperatures of 5, 11, 15, 21, 26, 30, and 36°C. A composite sample generated from the 10 random samples was also incubated in triplicate at 45°C. The linear regression of the time series data was significant at the 95% confidence level for all samples at all temperatures except 45°C where the slope was not statistically different from zero. The data were fit by third order polynomial curves without the inclusion of the value at 45°C (Figure 5-3A). All of the samples exhibited similar non-linearly increasing oxidation rates with increasing temperatures up to 36°C with no oxidation activity noted in the composite at 45°C. The mean and CV of linear Q<sub>10</sub> values calculated between 20 and 30°C was 2.4±11.

A generalized model of the temperature response of CH<sub>4</sub> oxidation was generated from the 5 to 36°C oxidation data. The oxidation values in each sample curve were first normalized to the oxidation rates observed at 21°C. The resulting fractional rate data were then pooled by averaging the response of each sample at each incubation temperature. The average normalized oxidation temperature response is presented in Figure 5-3B.

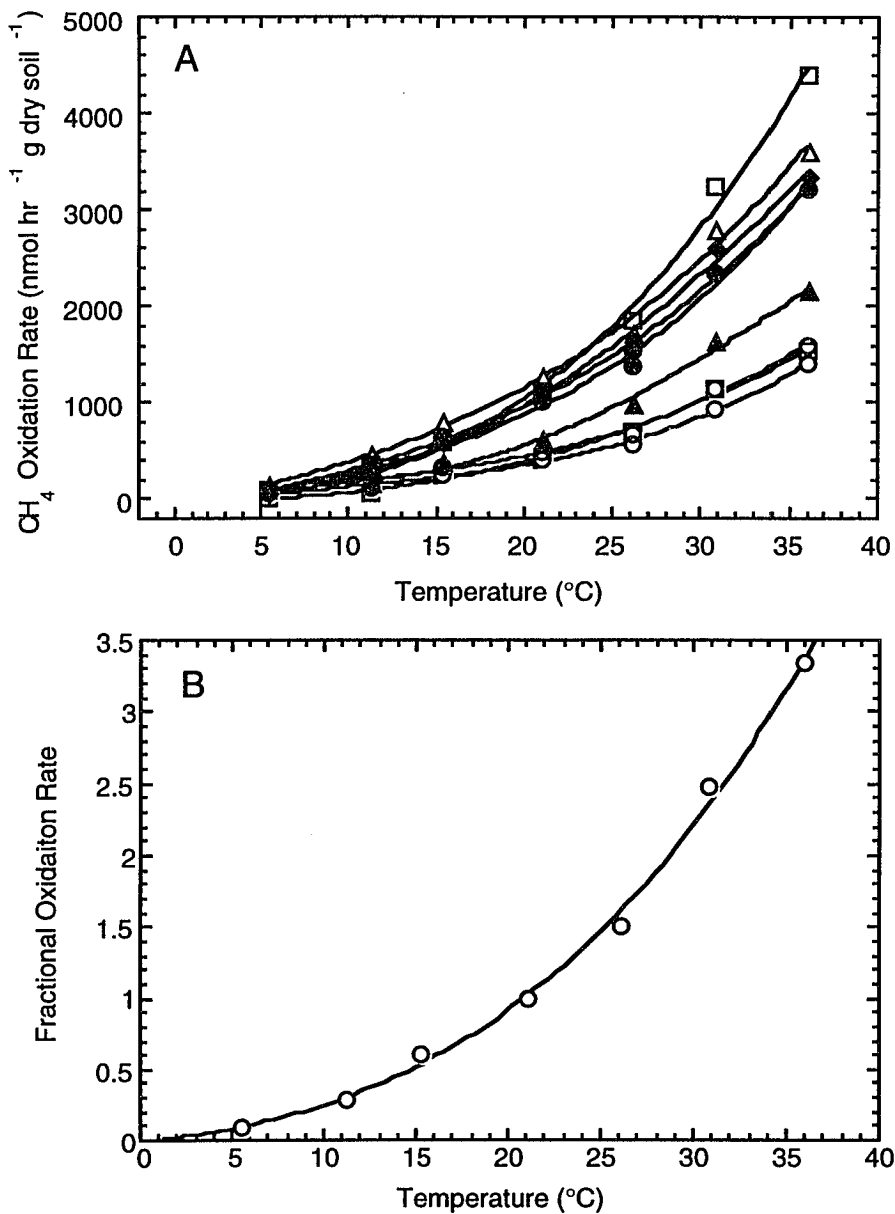


Figure 5-3. (A) Results of the temperature manipulation experiments for temperatures ranging from 5.5 to 36°C. Individual samples are represented by different symbols. Solid lines are polynomial curve fits to the data. (B) A generalized model of the temperature response of CH<sub>4</sub> oxidation. Data from 10 samples were averaged at each temperature after normalization of the oxidation values to the values observed at 21°C in each sample. The resulting values were best fit with a third order polynomial curve.

### *Kinetic Parameters*

An analysis of the methane oxidizing capacity of the soil samples was performed to determine their associated kinetic parameters. Each sample was exposed to six different initial headspace CH<sub>4</sub> mixing ratios ranging from 2 ppm to approximately 2 %. The resulting pseudo-zeroth order or first order drawdown characteristics were used to calculate the maximum rate of CH<sub>4</sub> oxidation ( $V_{\max}$ ) and the apparent half saturation constant ( $K_m$ ) for each sample.

The resulting oxidation rate data were expressed in substrate saturation curves as a function of initial headspace CH<sub>4</sub> mixing ratio and showed typical Michaelis-Menten characteristics. Eadie-Hofstee plots were then used to linearize the data from which  $V_{\max}$  and  $K_m$  were then calculated [Armstrong, 1989]. Examples of this technique are presented in detail in recent publications [Czepiel *et al.*, 1995; Koschorreck and Conrad, 1993] as well as Chapter 3 of this dissertation.

The landfill soils were characterized by a high activity with  $V_{\max}$  values that ranged from 40 to 2594 nmol CH<sub>4</sub> hr<sup>-1</sup> g dry soil<sup>-1</sup> and low substrate CH<sub>4</sub> affinity with  $K_m$  values ranging from 195 to 5847 ppm.

### *Oxygen*

The effect of variable O<sub>2</sub> mixing ratios on CH<sub>4</sub> oxidation was determined by incubating landfill soils in reduced O<sub>2</sub> atmospheres. A soil composite was formed from the 10 random samples previously described. The composite was then subsampled and the subsamples incubated in excess CH<sub>4</sub> and varying mixing ratios of O<sub>2</sub> in the jar headspaces. Incubation CH<sub>4</sub> mixing ratios ranged from 1.7 to 2.0 %. Figure 5-4 presents the resulting CH<sub>4</sub> oxidation rates as a function of O<sub>2</sub> mixing ratio. CH<sub>4</sub> oxidation rates in the composite subsamples decreased slowly from a peak rate of approximately 930 nmol hr<sup>-1</sup> g dry soil<sup>-1</sup> at an O<sub>2</sub> mixing ratio of 20.8 % to 775 nmol hr<sup>-1</sup> g dry soil<sup>-1</sup> at an O<sub>2</sub> mixing ratio of 3.0 %. At O<sub>2</sub> mixing ratios below 3.0 %, CH<sub>4</sub> oxidation rates decreased rapidly to zero.

A limited number of soil gas samples were collected to determine the extent of

substrate O<sub>2</sub> limitations on CH<sub>4</sub> oxidation. The O<sub>2</sub> mixing ratio was determined in 7 soil gas samples, from a depth of 7.5 cm, collected in various locations selected for evidence of high surface CH<sub>4</sub> flux. O<sub>2</sub> mixing ratios ranged from 4.0 to 19.2 % with a corresponding CH<sub>4</sub> mixing ratio range of 48 to 0.7 %.

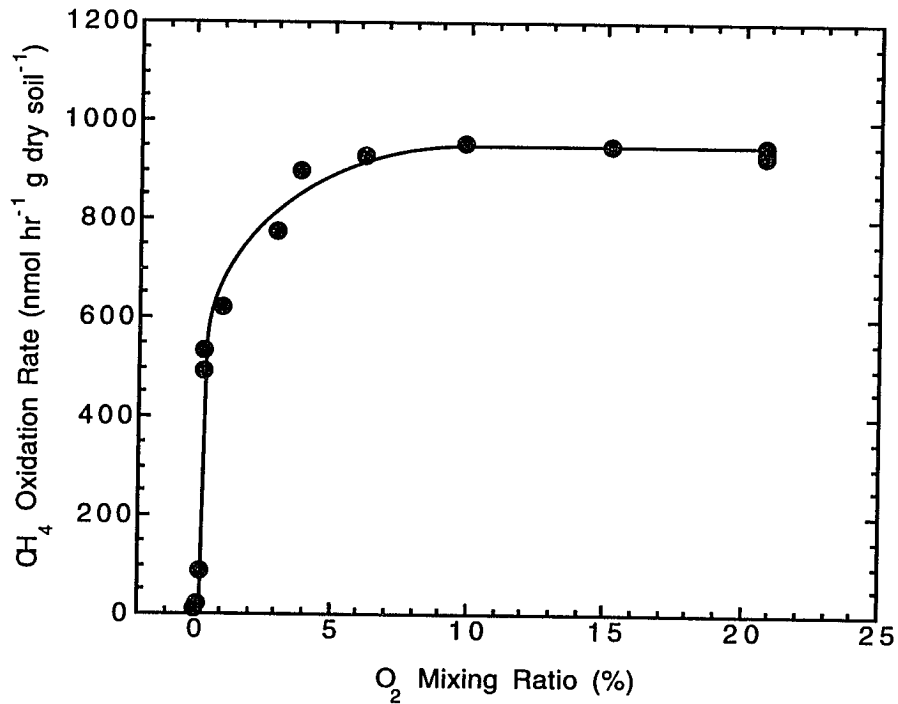


Figure 5-4. CH<sub>4</sub> oxidation rate as a function of O<sub>2</sub> mixing ratio. Rates were determined by jar incubation of soil samples generated from a composite of the temperature and moisture experiment samples.

## Oxidation Model

A CH<sub>4</sub> oxidation model was created which incorporates the laboratory incubation results and field measurements of CH<sub>4</sub> emissions. The required model inputs include surface CH<sub>4</sub> flux, soil gas CH<sub>4</sub> mixing ratio at each flux location, and soil physical parameters such as temperature, moisture content, and bulk density. CH<sub>4</sub> fluxes and soil gas CH<sub>4</sub> mixing ratios were measured in at 139 locations on a regular gridded sampling pattern [Czepiel *et al.*, this issue]. These data were used to quantitatively estimate oxidation at each location of measured CH<sub>4</sub> flux and to evaluate whole landfill oxidation potential.

The first step in quantifying oxidation was to estimate the soil gas CH<sub>4</sub> mixing ratio in each of the 5 cm soil intervals from the surface to 20 cm. Soil gas CH<sub>4</sub> was measured at a depth of 7.5 cm (the center of the observed maximum oxidizing interval) at each flux location. A linear mixing ratio gradient was calculated at each location using the 7.5 cm value and assuming an ambient air CH<sub>4</sub> mixing ratio of 2 ppm, typical of ambient mixing ratios at the landfill surface. Soil gas CH<sub>4</sub> mixing ratios were computed from this gradient for the center of each of the remaining soil intervals up to a theoretical CH<sub>4</sub> mixing ratio limit of 50 %.

Soil gas O<sub>2</sub> mixing ratio was also considered in the assessment of factors influencing CH<sub>4</sub> oxidation. However, a limited effect was observed in the previously described incubation experiments at O<sub>2</sub> mixing ratios equal to the lowest mixing ratios measured in the field. O<sub>2</sub> was therefore assumed to be a negligible factor in the zone of maximum oxidation and was not included in the calculations.

The estimated CH<sub>4</sub> mixing ratio values were used to predict the rate of oxidation expected in each soil interval from the observed relationship between  $V_{\max}$  and the mixing ratio of CH<sub>4</sub> measured in the soil gas prior to soil sample collection. Figure 5-5 presents this relationship after the transformation of the  $V_{\max}$  data to values expected under optimal moisture conditions. Each  $V_{\max}$  value was adjusted by the fractional difference between

the rate associated with the sample moisture content and the rate associated with the optimal moisture content as presented in Figure 5-2B. Linear regression techniques were then used to represent the dependence of the  $V_{\max}$  values on in situ  $\text{CH}_4$  mixing ratio resulting in a significant linear relationship with  $r^2=0.68$ .

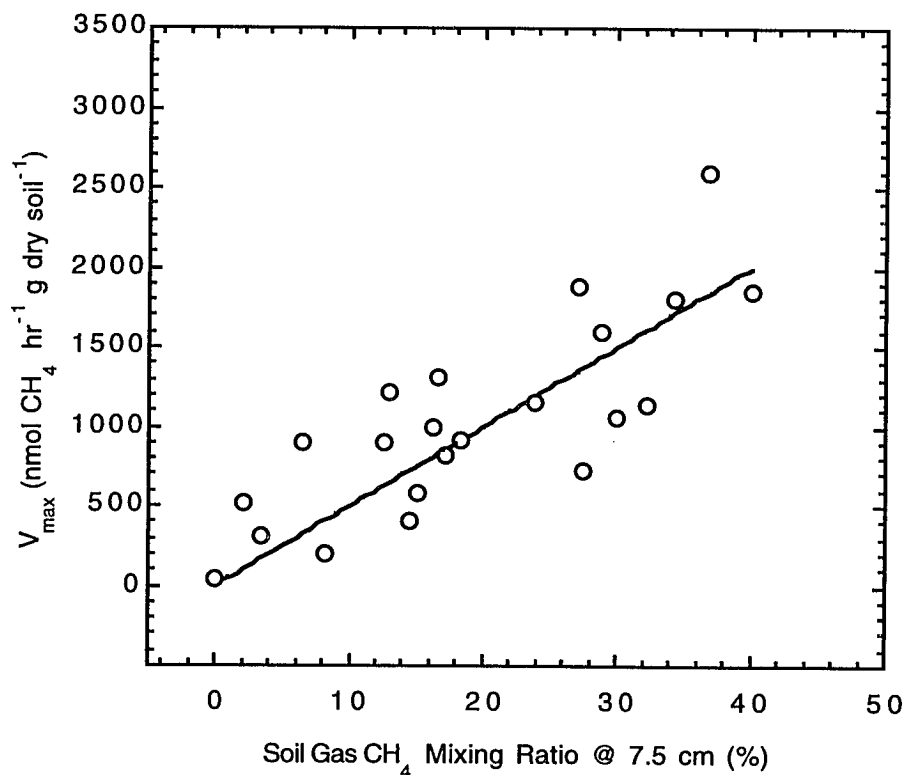


Figure 5-5. The maximum rate of  $\text{CH}_4$  oxidation,  $V_{\max}$ , as a function of the in situ soil gas  $\text{CH}_4$  mixing ratio. Soil gas samples were collected from a depth of 7.5 cm, the center of the soil sample depth interval, prior to sample collection.

The previous calculations assume that the oxidation response to the CH<sub>4</sub> mixing ratio in each soil interval is identical to the response of the maximum oxidation interval. A fractional model of the depth distribution of CH<sub>4</sub> oxidation in the soil profile, based on the incubation results presented in Figure 5-1, was used to adjust this response.

In each of the 9 soil profiles, the actual interval oxidation rates were first transformed to reflect the oxidation behavior expected under optimal moisture conditions as previously described. The moisture adjusted oxidation rates in each profile were then normalized by dividing each rate by the maximum observed rate in the profile. The profile data were pooled by averaging the normalized rates from each depth interval. The resulting average normalized soil oxidation rate profile is presented in Figure 5-6. This relationship was used to adjust the oxidation rates predicted in each soil interval by the mixing ratio- $V_{\max}$  relationship.

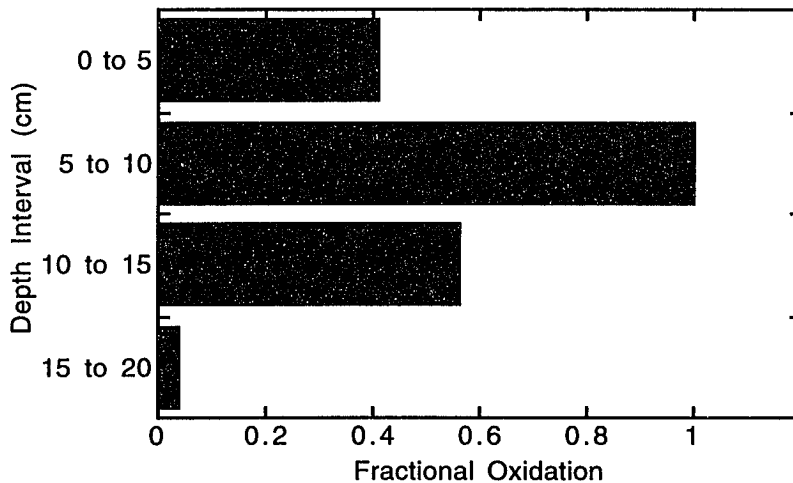


Figure 5-6. The normalized average soil oxidation rate depth profile. Individual oxidation profiles (Figure 5-1) were normalized to the values observed in the 5 to 10 cm intervals and averaged over each depth interval.



The calculated oxidation rates were adjusted for in situ soil temperature and moisture content using the previously described relationships presented in Figures 2B and 3B. Soil temperatures were estimated from values measured at 6 locations in the 0–5 cm and 5–10 cm soil intervals during the period of whole landfill flux measurements. The resulting average temperatures were 19.2°C in the 0–5 cm interval and 18.4°C in the 5–10 cm interval. Deeper soil interval temperatures were estimated by linearly extrapolating the measured mean temperatures resulting in estimates of 17.6°C for the 10–15 cm interval and 16.8°C for the 15–20 cm interval.

Average soil moisture conditions in each depth interval at the time of the flux measurements were estimated using the SCM model. The modeled average soil moisture contents were 14.8 % in the 0–5 cm interval, 15.9 % in the 5–10 cm interval, 16.5 % in the 10–15 cm interval, and 16.9 % in the 15–20 cm interval.

The oxidation model estimates the CH<sub>4</sub> source, or gross CH<sub>4</sub>, at each flux location by

$$\text{CH}_{4\text{Gross}} = \text{CH}_{4\text{Oxid}} + \text{CH}_{4\text{Flux}} \quad (1)$$

where CH<sub>4Gross</sub> is the gross CH<sub>4</sub> source, CH<sub>4Oxid</sub> is the total amount of CH<sub>4</sub> oxidized in the soil column, and CH<sub>4Flux</sub> is the measured surface CH<sub>4</sub> flux, all in g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>. The whole landfill oxidation rate is then calculated from the fractional difference between the oxidized CH<sub>4</sub> and the gross CH<sub>4</sub> source at each flux location by

$$\text{OX} = \frac{\sum_{n=1}^{139} \text{CH}_{4\text{Oxid}}}{\sum_{n=1}^{139} \text{CH}_{4\text{Gross}}} \times 100 \quad (2)$$

where OX is the oxidation rate in percent and n is the flux location number. The estimated

whole landfill CH<sub>4</sub> oxidation rate estimate at the time of the surface flux measurements was 21 %.

The annual rate of CH<sub>4</sub> oxidation was estimated by extrapolating the previously described relationships over a one year period in daily increments. An estimate of daily average oxidation was calculated using regional daily average meteorological data. Average daily air temperatures and precipitation were input to the SCM model to calculate average daily soil profile temperatures and moisture contents. In addition, daily average atmospheric pressure was utilized to predict variability in CH<sub>4</sub> fluxes. A significant relationship between whole landfill CH<sub>4</sub> flux and atmospheric pressure was observed at this site as described by *Czepiel et al.* [this issue]. This linear relationship was normalized to the value of whole landfill flux predicted at 1020 mb, the average pressure observed during the period of flux measurements. The measured fluxes were then adjusted by the fractional difference between the flux predicted at the daily average atmospheric pressure and the flux at 1020 mb.

Soil temperatures, moisture contents, and atmospheric pressure were input to the soil oxidation model which calculated daily values of CH<sub>4</sub> oxidized and the gross CH<sub>4</sub> source by Equation (1). An annual oxidation estimate was then calculated by summing the resulting daily oxidation estimates over a one year period by

$$OX_{Year} = \frac{\sum_{m=1}^{365} \sum_{n=1}^{139} CH_{4Oxid}}{\sum_{m=1}^{365} \sum_{n=1}^{139} CH_{4Gross}} \times 100 \quad (3)$$

where  $OX_{Year}$  is the annual whole landfill oxidation rate in percent and  $m$  is the number of days in the estimate. Figure 5-7 presents daily estimates of whole landfill CH<sub>4</sub> oxidation for the period December 1, 1993 through November 30, 1994. The resulting estimated annual whole landfill oxidation rate was 11 %.

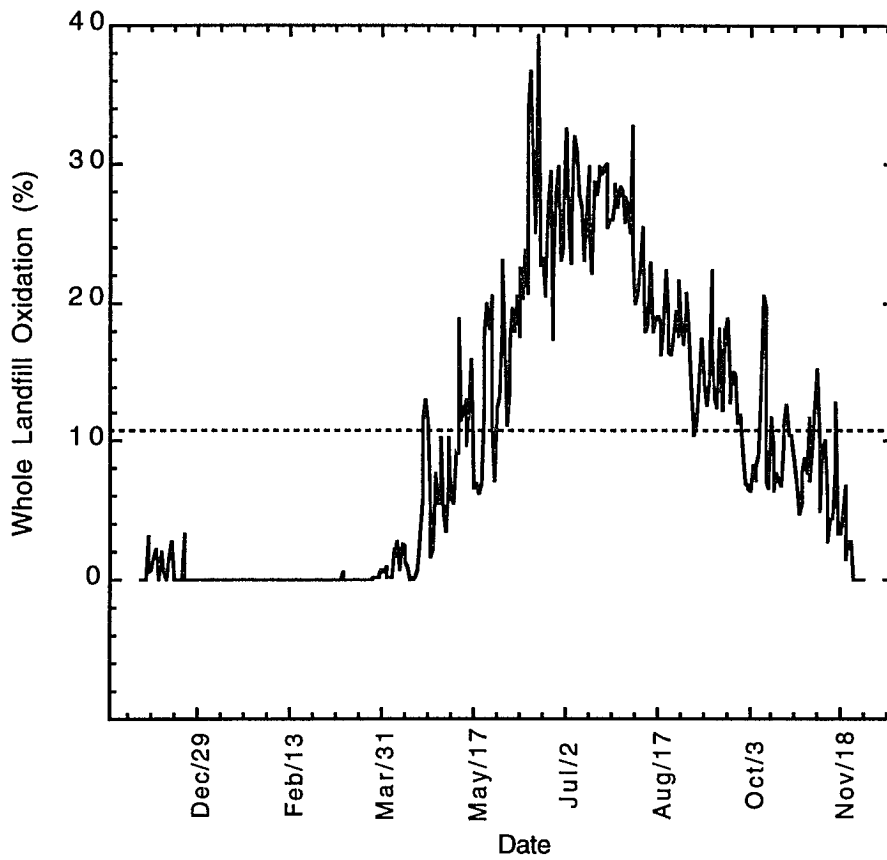


Figure 5-7. Model estimated rate of whole landfill oxidation for each day from 12/1/93 through 11/30/94. The dashed horizontal line indicates the mean annual rate of oxidation of 11 %.

## Discussion

The depth distribution of CH<sub>4</sub> oxidation and the peak rates observed in the 5–10 and 10–15 cm soil intervals are consistent with results observed in other natural and landfill cover soils. Oxidation peaks were found in temperate forest soils in the 3–6 cm depth interval by *Czepiel et al.*, [1995] and in the 3–9 cm interval by *Adamsen and King*, [1993]. *Whalen, et al.* [1990] observed peak oxidation in landfill cover soils in the 3–6 cm depth interval with significant oxidation also observed in the 6–9 cm and 9–12 cm intervals, while *Kightley et al.*, [1995] observed peak oxidation in incubated landfill soil cores at a depth of approximately 20 cm. The soils both above and below the oxidation maxima at our site and those described above showed significantly reduced oxidation activity. Reduced methanotrophic activity in upper soil layers has been suggested by some investigators to result from microbial competition for mineral nutrients [*Bender and Conrad*, 1994; *Koschorreck and Conrad*, 1993], inhibition by NH<sub>4</sub><sup>+</sup> released by decomposing organic matter [*Adamsen and King*, 1993; *Nesbit and Breitenbeck*, 1992], or a less than optimal moisture environment [*Whalen and Reeburgh*, 1992]. The latter mechanism is most consistent with observations at our site. The physical characteristics of the surface soils appear to promote rapid moisture cycling while the general lack of surface vegetation and the minimal organic layer would tend to minimize microbial competition and organic decomposition.

Reduced activity below the maxima in natural soils appears to be the result of limited substrate CH<sub>4</sub> availability [*Conrad*, 1984]. But, in the landfill environment, CH<sub>4</sub> is unlimited in the soil column. In the landfill soils, O<sub>2</sub> appears to be the limiting substrate below approximately 20 cm. CH<sub>4</sub> oxidation was found in the incubation experiments to be relatively insensitive to O<sub>2</sub> mixing ratios above approximately 3 % but dropped rapidly at O<sub>2</sub> mixing ratios below 3 %. This result is similar to that of *Bender and Conrad* who

observed CH<sub>4</sub> oxidation in a preincubated paddy soil to also drop off rapidly to zero below 3 % and to be even less sensitive than our soils to O<sub>2</sub> mixing ratios above 3 % [Bender and Conrad, 1994]. Extrapolating the O<sub>2</sub> mixing ratios observed in the field samples to depths below the maximum oxidation zone yields mixing ratios below the 3 % threshold. Intersite differences in the lower boundary of the oxidation zone are probably due to the effect of soil spatial heterogeneity on the depth of O<sub>2</sub> diffusion.

The rapid increase in oxidation rates observed over the 5–36°C temperature range is consistent with the temperature responses of oxidation under unlimited CH<sub>4</sub> conditions reported by others [King and Adamsen, 1992; Whalen *et al.*, 1990]. This is in contrast to the limited effect of temperature on oxidation observed at atmospheric CH<sub>4</sub> mixing ratios [Crill, 1993; King and Adamsen, 1992; Steudler *et al.*, 1989]. King and Adamsen, [1992] explain this discrepancy as a difference in the rate limiting factor in the oxidation reaction. Oxidation in natural soils has been shown to be limited by the rate of gaseous diffusion of atmospheric CH<sub>4</sub> into the soils. Whereas, in CH<sub>4</sub> saturated environments, such as in landfill cover soils or around natural gas leaks, the enzymatic activity of the methanotrophs becomes the rate limiting factor. This activity can be described by the Arrhenius relationship in which oxidation exhibits an approximately parabolic behavior; increasing with increasing temperature to a distinct maximum and decreasing with continued temperature increase. This behavior was observed in our samples with an optimum temperature in excess of 36°C. This result is similar to the 38°C optimum observed by King and Adamsen, [1992] and somewhat higher than the 31°C optimum observed by Whalen *et al.*, [1990]. Our average Q<sub>10</sub> of 2.4 for the temperature range 20 to 30°C was also somewhat higher than the Q<sub>10</sub> of 1.9 for the temperature range 5 to 26°C reported by Whalen *et al.*, [1990].

The effects of soil moisture are clearly evident in our results. Two factors appear to be responsible; soil water gas exchange and microbial water stress [Adamsen and King,

1993]. *Whalen et al.*, [1990] suggested that the optimum soil moisture content supports a maximum microbial biomass. Low soil water content results in microbial desiccation and activity reduction, while aqueous phase diffusion of CH<sub>4</sub> through the increasing water volume limits the rate of substrate delivery to the microbes at higher moisture contents. Oxidation activity peaks when balance is achieved. The microbial mass is fully hydrated while pore water film thickness is low enough to minimize CH<sub>4</sub> diffusional resistance.

Oxidation in our soils was characterized by a high oxidation capacity and a low substrate CH<sub>4</sub> affinity. The observed range of the kinetic parameters compared favorably with the results of other recent investigations of oxidation in soils exposed to high CH<sub>4</sub> mixing ratios. Our calculated  $V_{\max}$  ranged from 40 to 2594 nmol CH<sub>4</sub> hr<sup>-1</sup> g<sup>-1</sup> dry soil (1.1 to 70 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>), the maximum being among the highest values reported in landfill cover soils. *Whalen et al.*, [1990] observed a maximum oxidation rate of 45 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> and a calculated maximum  $V_{\max}$  of 61 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>, while *Kightley et al.*, [1995] measured a  $V_{\max}$  as high as 2342 nmol CH<sub>4</sub> hr<sup>-1</sup> g<sup>-1</sup>.

The primary influence of temperature and moisture on CH<sub>4</sub> oxidation in this environment makes it particularly susceptible to climate variability. An analysis of the sensitivity of the oxidation model to temperature and moisture changes was performed by comparing the annual oxidation estimate for 1994 to oxidation estimates that reflect predicted changes in regional climate as described by *Mitchell et al.*, [1990]. Global climate models predict an average annual increase in surface air temperatures of approximately 4°C by 2030 for the New England region. Changes in average precipitation are also expected resulting in winters with increased precipitation (+1 mm day<sup>-1</sup>) and summers with reduced precipitation (-1 mm day<sup>-1</sup>).

Changes in the average soil environment expected to accompany these climate changes were estimated by modifying the 1994 temperature and precipitation data for use with the SCM model to estimate soil temperatures and moisture contents. Air temperature

values were increased by 4°C, winter precipitation values were increased 15 %, and summer precipitation values were reduced 25 %. The magnitudes of the precipitation changes are the result of the differences between the actual 1994 seasonal precipitation and the predicted changes integrated seasonally. Extrapolating the winter and summer precipitation changes resulted in spring and autumn precipitation values reduced 5 % from 1994 values.

The resulting predictions of annual whole landfill oxidation rate indicate a significantly stronger dependence on temperature than on soil moisture (Table 5-2). Changing precipitation alone resulted in an oxidation rate that was not significantly different than the 1994 reference scenario. Increasing temperature alone resulted in an oxidation rate of 17 %, a 59 % oxidation increase. Combining temperature and precipitation changes resulted in an oxidation rate of 18 %, a 64 % oxidation increase.

Table 5-2. Model estimated whole landfill CH<sub>4</sub> oxidation (%).

|  |    |
|--|----|
| 1994 reference scenario                        | 11 |
| 2030 soil moisture,<br>1994 temperature        | 11 |
| 2030 temperature (+4°C),<br>1994 soil moisture | 17 |
| 2030 temperature and<br>soil moisture          | 18 |

The negligible influence of modified precipitation is the result of the parabolic shape of the observed oxidation response to soil moisture content (Figure 5-2B). In spring, early summer, and late autumn soil moisture is generally higher than optimal for oxidation. Reducing precipitation during those periods reduces soil moisture and increases oxidation. In late summer and early autumn soil moisture is less than optimal for oxidation and a reduction in precipitation reduces oxidation. The net result is a small increase in the annual oxidation estimate. The significant influence of increased temperature is a result of the observed oxidation response to temperature (Figure 5-3B). A uniform 4°C increase in temperatures results in a substantial increase in oxidation. This effect is most significant during the warmer weather due to the non-linearly increasing nature of the response.

### Conclusion

We have presented the results of a quantitative study of the primary factors influencing the microbial oxidation of CH<sub>4</sub> in the surface soils of a municipal solid waste landfill. The whole landfill rates presented here are probably upper limits on oxidation. Calculations based on the laboratory incubations assume optimal exposure of soil microorganisms to substrate CH<sub>4</sub>. Actual field conditions complicate this assumption. Uncontrolled landfill soil covers are notoriously unstable environments. Waste settlement and surface erosion promotes significant surface cracking. These cracks may provide paths of minimal resistance for gas flow, effectively bypassing microbial influence. Soil macropores created by plant roots and insect and animal activity may also supply a low resistance path for gas flow. These surface features as well as the influence of different soil types must be addressed in future studies of oxidation in the landfill environment.



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## APPENDIX A

| Date    | Aerated Grit<br>Tank N2O Flux<br>(g/sq m/day) | Non-Aerated Grit<br>Tank N2O Flux<br>(g/sq m/day) | Secondary<br>Aeration Flux<br>(g/sq m/day) |
|---------|---|---|--|
| 5/8/92  | 0.46  | 0.03  |  |
| 5/15/92 | 0.21  | 0.01  | 0.5  |
| 5/22/92 | 0.7   | 0.04  | 0.46                                       |
| 5/27/92 | 0.48  | 0.03  | 1  |
| 6/5/92  | 1.01  | 0.01  | 1.8  |
| 6/12/92 | 0.71  | 0.02  | 0.2  |
| 6/18/92 | 0.17  | 0.02  | 0.6  |
| 7/1/92  | 0.45  | 0.01  | 0.12                                       |
| 7/10/92 | 0.31  | 0.01  | 0.71                                       |
| 7/17/92 | 0.39  | 0.03  | 0.42                                       |
| 7/24/92 | 0.39  | 0.02  | 0.32                                       |
| 7/31/92 | 0.4   | 0.01  | 1.76                                       |
| 8/7/92  | 0.22  | 0.03  | 0.87                                       |
| 8/13/92 | 0.56  | 0.01  | 0.74                                       |
| 8/20/92 | 0.33  | 0.01  | 1.6  |

## APPENDIX B



| Depth (cm) | 9 Day Old Pile<br>Nitrous Oxide<br>Conc. (ppmv) | 9 Day Old Pile<br>Oxygen<br>Conc. (%) |
|------------|---|---------------------------------------|
| 5          | 36  | 20.1                                  |
| 10         | 8.7   | 12                                    |
| 15         | 3.3   | 8                                     |
| 20         | 1.2   | 5                                     |
| 30         | 0.4   | 3.6                                   |
| 40         | 0.37  | 3.1                                   |
| 50         | 0.29  | 2                                     |
| 60         | 0.2   | 2.2                                   |

| Depth (cm) | 38 Day Old Pile<br>Nitrous Oxide<br>Conc. (ppmv) | 38 Day Old Pile<br>Oxygen<br>Conc. (%) |
|------------|--|--|
| 5          | 1.1  | 20.6                                   |
| 10         | 3.3  | 20.6                                   |
| 15         | 6.1  | 20.4                                   |
| 20         | 8.1  | 20.5                                   |
| 30         | 7.6  | 18                                     |
| 40         | 4.4  | 14                                     |
| 50         | 2  | 7                                      |
| 60         | 0.9  | 4.8                                    |

| Compost Age<br>(days) | N2O Flux<br>(g/sq m/day) |
|-----------------------|--------------------------|
| 17                    | 0.02                     |
| 15                    | 0.03                     |
| 10                    | 0.04                     |
| 4                     | 0.08                     |
| 10                    | 0.1                      |
| 4                     | 0.1                      |
| 8                     | 0.1                      |
| 8                     | 0.1                      |
| 10                    | 0.1                      |
| 10                    | 0.1                      |
| 10                    | 0.1                      |
| 4                     | 0.1                      |
| 9                     | 0.13                     |
| 9                     | 0.13                     |
| 10                    | 0.16                     |
| 10                    | 0.16                     |
| 10                    | 0.2                      |
| 10                    | 0.2                      |
| 4                     | 0.2                      |
| 4                     | 0.2                      |
| 4                     | 0.2                      |
| 4                     | 0.2                      |
| 2                     | 0.36                     |
| 2                     | 0.36                     |
| 20                    | 0.49                     |
| 21                    | 0.49                     |
| 20                    | 0.49                     |
| 21                    | 0.49                     |
| 4                     | 0.5                      |
| 4                     | 0.5                      |
| 7                     | 0.5                      |
| 7                     | 0.5                      |
| 28                    | 0.79                     |
| 28                    | 0.79                     |
| 7                     | 0.81                     |
| 7                     | 0.81                     |

| Compost Age<br>(days) | N2O Flux<br>(g/sq m/day) |
|-----------------------|--------------------------|
| 30                    | 0.85                     |
| 30                    | 0.85                     |
| 24                    | 0.87                     |
| 24                    | 0.87                     |
| 36                    | 0.88                     |
| 36                    | 0.88                     |
| 14                    | 0.9                      |
| 14                    | 0.9                      |
| 35                    | 0.94                     |
| 16                    | 0.94                     |
| 35                    | 0.94                     |
| 16                    | 0.94                     |
| 9                     | 1.13                     |
| 9                     | 1.13                     |
| 9                     | 1.4                      |
| 9                     | 1.4                      |
| 13                    | 1.4                      |
| 13                    | 1.4                      |
| 41                    | 1.43                     |
| 41                    | 1.43                     |
| 42                    | 1.45                     |
| 42                    | 1.45                     |
| 18                    | 1.5                      |
| 18                    | 1.5                      |
| 33                    | 1.6                      |
| 33                    | 1.6                      |
| 21                    | 1.66                     |
| 21                    | 1.66                     |
| 9                     | 1.68                     |
| 9                     | 1.68                     |
| 41                    | 1.81                     |
| 41                    | 1.81                     |
| 4                     | 1.81                     |
| 4                     | 1.81                     |
| 35                    | 1.82                     |
| 35                    | 1.82                     |

| Compost Age<br>(days) | N2O Flux<br>(g/sq m/day) |
|-----------------------|--------------------------|
| 35                    | 1.84                     |
| 35                    | 1.84                     |
| 41                    | 1.87                     |
| 41                    | 1.87                     |
| 35                    | 1.91                     |
| 35                    | 1.91                     |
| 35                    | 1.95                     |
| 35                    | 1.95                     |
| 35                    | 2.03                     |
| 35                    | 2.03                     |
| 9                     | 2.14                     |
| 9                     | 2.14                     |
| 38                    | 2.19                     |
| 38                    | 2.19                     |
| 7                     | 2.23                     |
| 7                     | 2.23                     |
| 13                    | 2.39                     |
| 13                    | 2.39                     |
| 28                    | 2.5                      |
| 28                    | 2.5                      |
| 42                    | 2.58                     |
| 42                    | 2.58                     |
| 28                    | 2.6                      |
| 28                    | 2.6                      |
| 13                    | 2.67                     |
| 13                    | 2.67                     |
| 35                    | 2.69                     |
| 35                    | 2.69                     |
| 25                    | 2.82                     |
| 25                    | 2.82                     |
| 16                    | 2.9                      |
| 16                    | 2.9                      |
| 13                    | 3.08                     |
| 13                    | 3.08                     |
| 24                    | 3.21                     |
| 25                    | 3.21                     |

| Compost Age<br>(days) | N2O Flux<br>(g/sq m/day) |
|-----------------------|--------------------------|
| 25                    | 3.21                     |
| 24                    | 3.21                     |
| 18                    | 3.28                     |
| 18                    | 3.28                     |
| 41                    | 3.55                     |
| 41                    | 3.55                     |
| 13                    | 3.56                     |
| 13                    | 3.56                     |
| 13                    | 3.7                      |
| 13                    | 3.7                      |
| 41                    | 3.91                     |
| 41                    | 3.91                     |
| 7                     | 3.94                     |
| 7                     | 3.94                     |
| 43                    | 4.2                      |
| 43                    | 4.2                      |
| 24                    | 4.21                     |
| 24                    | 4.21                     |
| 13                    | 4.31                     |
| 13                    | 4.31                     |
| 35                    | 4.55                     |
| 35                    | 4.55                     |
| 41                    | 4.59                     |
| 41                    | 4.59                     |
| 9                     | 4.61                     |
| 9                     | 4.61                     |
| 10                    | 5.4                      |
| 10                    | 5.4                      |
| 15                    | 5.46                     |
| 15                    | 5.46                     |
| 37                    | 6.07                     |
| 37                    | 6.07                     |
| 20                    | 6.45                     |
| 20                    | 6.45                     |
| 8                     | 6.64                     |
| 8                     | 6.64                     |

| Compost Age<br>(days) | N2O Flux<br>(g/sq m/day) |
|-----------------------|--------------------------|
| 21                    | 8.3                      |
| 21                    | 8.3                      |
| 18                    | 8.87                     |
| 18                    | 8.87                     |

#### FARM WASTE PILE 1

| Time Since Compost<br>Pile Inception<br>(days) | Mean N2O<br>Emissions<br>(g/sq m/day) |
|--|---------------------------------------|
| 2  | 0.048                                 |
| 17   | 0.342                                 |
| 21   | 0.42                                  |
| 34   | 1.05                                  |
| 52   | 0.589                                 |

#### FARM WASTE PILE 2

| Time Since Compost<br>Pile Inception<br>(days) | Mean N2O<br>Emissions<br>(g/sq m/day) |
|--|---------------------------------------|
| 0  | 0                                     |
| 24   | 0.356                                 |
| 48   | 0.459                                 |
| 54   | 0.656                                 |
| 55   | 0.504                                 |
| 57   | 0.439                                 |
| 77   | 0.101                                 |

#### YARD WASTE PILE

| Time Since Compost<br>Pile Inception<br>(days) | Mean N2O<br>Emissions<br>(g/sq m/day) |
|--|---------------------------------------|
| 11   | 0.076                                 |
| 18   | 0.404                                 |
| 29   | 1.095                                 |
| 39   | 4.286                                 |
| 54   | 3.056                                 |

## APPENDIX C



| organic matter<br>(% by wt) | mois. content<br>(% by wt) | oxidation rate<br>(nmol/hr/g) |
|-----------------------------|----------------------------|-------------------------------|
| 10.6                        | 7.4                        | 0                             |
| 10.6                        | 21.1                       | 3.8                           |
| 10.6                        | 27.1                       | 5.5                           |
| 10.6                        | 33.3                       | 4.1                           |
| 10.6                        | 37.5                       | 2.6                           |
| 6                           | 7.5                        | 0.9                           |
| 6                           | 20.7                       | 2.2                           |
| 6                           | 23                         | 2.3                           |
| 6                           | 26                         | 2.2                           |
| 6                           | 30.8                       | 1.5                           |
| 6                           | 32.1                       | 1.1                           |
| 11.9                        | 11.4                       | 1.8                           |
| 11.9                        | 18.4                       | 3.8                           |
| 11.9                        | 20.9                       | 4.3                           |
| 11.9                        | 25.9                       | 5.2                           |
| 11.9                        | 31.1                       | 4.2                           |
| 11.9                        | 37.8                       | 3.4                           |
| 9.9                         | 8.6                        | 0.4                           |
| 9.9                         | 17.2                       | 2.7                           |
| 9.9                         | 20.5                       | 4.6                           |
| 9.9                         | 27.3                       | 4.8                           |
| 9.9                         | 31.9                       | 3.2                           |
| 9.9                         | 39.3                       | 2.4                           |
| 7.4                         | 8.2                        | 0.8                           |
| 7.4                         | 12.5                       | 1.5                           |
| 7.4                         | 16.5                       | 2                             |
| 7.4                         | 22.6                       | 2.4                           |
| 7.4                         | 29.3                       | 1.4                           |
| 7.4                         | 35.5                       | 0.5                           |
| 7.7                         | 8                          | 0.9                           |
| 7.7                         | 12.5                       | 2.9                           |
| 7.7                         | 15.2                       | 3.2                           |
| 7.7                         | 19                         | 4.4                           |
| 7.7                         | 20.5                       | 3.6                           |
| 7.7                         | 30                         | 1.6                           |
| 7.7                         | 35.5                       | 0.6                           |

| organic matter<br>(% by wt) | mois. content<br>(% by wt) | oxidation rate<br>(nmol/hr/g) |
|-----------------------------|----------------------------|-------------------------------|
| 12                          | 10.4                       | 0.5                           |
| 12                          | 21.4                       | 4.3                           |
| 12                          | 25                         | 4.7                           |
| 12                          | 25.8                       | 5.6                           |
| 12                          | 31.4                       | 6.1                           |
| 12                          | 36                         | 5.6                           |
| 12                          | 45.1                       | 1.7                           |
| 14.3                        | 14.3                       | 2                             |
| 14.3                        | 19.2                       | 3.7                           |
| 14.3                        | 24.7                       | 5.6                           |
| 14.3                        | 30.9                       | 8.9                           |
| 14.3                        | 35.1                       | 8.5                           |
| 14.3                        | 38.4                       | 6.9                           |
| 14.3                        | 43.5                       | 2.3                           |
| 12.8                        | 14.3                       | 2.3                           |
| 12.8                        | 17.4                       | 2.5                           |
| 12.8                        | 24.3                       | 3.4                           |
| 12.8                        | 28.6                       | 5.6                           |
| 12.8                        | 35.1                       | 6.8                           |
| 12.8                        | 39.7                       | 6.7                           |
| 12.8                        | 43.9                       | 2.8                           |
| 10.5                        | 16                         | 1.5                           |
| 10.5                        | 19.7                       | 2.4                           |
| 10.5                        | 26.1                       | 3.9                           |
| 10.5                        | 29.6                       | 5.9                           |
| 10.5                        | 34.2                       | 6.5                           |
| 10.5                        | 39                         | 2.5                           |
| 10.5                        | 41.8                       | 0.8                           |
| 11.8                        | 13.8                       | 2.8                           |
| 11.8                        | 20.3                       | 4.6                           |
| 11.8                        | 21.9                       | 5.8                           |
| 11.8                        | 30.9                       | 8.6                           |
| 11.8                        | 34.1                       | 9.1                           |
| 11.8                        | 40.2                       | 3                             |
| 11.8                        | 45                         | 1.7                           |
| 10.8                        | 11.6                       | 1.3                           |

| organic matter<br>(% by wt) | mois. content<br>(% by wt) | oxidation rate<br>(nmol/hr/g) |
|-----------------------------|----------------------------|-------------------------------|
| 10.8                        | 17.6                       | 1.7                           |
| 10.8                        | 25                         | 2.9                           |
| 10.8                        | 30.8                       | 3.8                           |
| 10.8                        | 33.8                       | 4                             |
| 10.8                        | 40.9                       | 1                             |
| 10.8                        | 44.3                       | 0.8                           |
| 25.6                        | 27.9                       | 1.7                           |
| 25.6                        | 35.3                       | 1.8                           |
| 25.6                        | 41.4                       | 2                             |
| 25.6                        | 47.7                       | 3.7                           |
| 25.6                        | 48.9                       | 3.9                           |
| 25.6                        | 56.3                       | 1.9                           |
| 25.6                        | 60.5                       | 1.5                           |
| 17.9                        | 23.7                       | 1.3                           |
| 17.9                        | 29.2                       | 2.4                           |
| 17.9                        | 34                         | 4.1                           |
| 17.9                        | 35.2                       | 4.7                           |
| 17.9                        | 44.4                       | 6                             |
| 17.9                        | 45.3                       | 2.6                           |
| 17.6                        | 23.4                       | 1.3                           |
| 17.6                        | 27.1                       | 2.3                           |
| 17.6                        | 31.8                       | 3.7                           |
| 17.6                        | 36                         | 4.5                           |
| 17.6                        | 41                         | 6.1                           |
| 17.6                        | 43.9                       | 3.8                           |

## APPENDIX D

| X Position<br>(feet) | Y Position<br>(feet) | Methane Flux<br>(g/sq m/day) |
|----------------------|----------------------|------------------------------|
| 694                  | 1406                 | 105.90                       |
| 890                  | 1418                 | 1,497.00                     |
| 1121                 | 1398                 | 1.00                         |
| 1303                 | 1360                 | 28.00                        |
| 1503                 | 1302                 | 0.00                         |
| 1699                 | 1272                 | 0.00                         |
| 1888                 | 1272                 | 0.00                         |
| 2053                 | 1386                 | 47.00                        |
| 2306                 | 1485                 | 0.00                         |
| 2469                 | 1200                 | 0.00                         |
| 2451                 | 985                  | 0.70                         |
| 2446                 | 774                  | 11.00                        |
| 2367                 | 558                  | 0.00                         |
| 2308                 | 369                  | 0.00                         |
| 2098                 | 98                   | 0.00                         |
| 1889                 | 130                  | 0.00                         |
| 1667                 | 136                  | 0.00                         |
| 1469                 | 127                  | 0.00                         |
| 1206                 | 91                   | 0.23                         |
| 982                  | 61                   | 0.00                         |
| 755                  | 41                   | 0.04                         |
| 528                  | 15                   | 0.00                         |
| 303                  | 20                   | 0.00                         |
| 51                   | 150                  | 0.00                         |
| 49                   | 309                  | 0.00                         |
| 694                  | 1305                 | 375.50                       |
| 895                  | 1332                 | 0.35                         |
| 1094                 | 1293                 | 8.20                         |
| 1285                 | 1254                 | 2.20                         |
| 1485                 | 1211                 | 0.70                         |
| 1683                 | 1184                 | 10.90                        |
| 1916                 | 1202                 | 0.00                         |
| 2092                 | 1305                 | 2.80                         |
| 2283                 | 1382                 | 0.00                         |
| 2342                 | 1183                 | 101.40                       |
| 2341                 | 984                  | 0.00                         |

| X Position<br>(feet) | Y Position<br>(feet) | Methane Flux<br>(g/sq m/day) |
|----------------------|----------------------|------------------------------|
| 2312                 | 779                  | 184.20                       |
| 2258                 | 581                  | 18.40                        |
| 2215                 | 379                  | 190.60                       |
| 2094                 | 180                  | 42.50                        |
| 1899                 | 222                  | 337.10                       |
| 1667                 | 236                  | 127.50                       |
| 1465                 | 226                  | 0.00                         |
| 1205                 | 178                  | 0.00                         |
| 975                  | 160                  | 71.50                        |
| 750                  | 150                  | 22.70                        |
| 522                  | 128                  | 483.60                       |
| 308                  | 121                  | 51.80                        |
| 135                  | 161                  | 0.00                         |
| 135                  | 312                  | 0.00                         |
| 692                  | 1197                 | 4.90                         |
| 889                  | 1247                 | 13.70                        |
| 1088                 | 1221                 | 564.40                       |
| 1283                 | 1152                 | 81.00                        |
| 1479                 | 1117                 | 76.00                        |
| 1677                 | 1103                 | 85.80                        |
| 1949                 | 1131                 | 12.60                        |
| 2137                 | 1236                 | 0.00                         |
| 2254                 | 1292                 | 1.70                         |
| 2256                 | 1179                 | 20.90                        |
| 2240                 | 1000                 | 101.50                       |
| 2191                 | 783                  | 43.40                        |
| 2146                 | 604                  | 15.60                        |
| 2102                 | 406                  | 0.00                         |
| 2095                 | 287                  | 0.16                         |
| 1909                 | 318                  | 0.00                         |
| 1665                 | 324                  | 10.30                        |
| 1467                 | 314                  | 398.40                       |
| 1189                 | 280                  | 6.30                         |
| 967                  | 275                  | 0.00                         |
| 733                  | 275                  | 0.00                         |
| 514                  | 233                  | 1.52                         |

| X Position<br>(feet) | Y Position<br>(feet) | Methane Flux<br>(g/sq m/day) |
|----------------------|----------------------|------------------------------|
| 317                  | 216                  | 0.00                         |
| 227                  | 203                  | 0.00                         |
| 224                  | 323                  | 86.40                        |
| 68                   | 441                  | 0.00                         |
| 478                  | 435                  | 1.12                         |
| 677                  | 439                  | 62.10                        |
| 880                  | 433                  | 8.60                         |
| 1081                 | 436                  | 0.00                         |
| 1282                 | 436                  | 0.00                         |
| 1481                 | 431                  | 0.00                         |
| 1695                 | 434                  | 213.00                       |
| 1881                 | 427                  | 0.70                         |
| 2052                 | 429                  | 0.00                         |
| 302                  | 1124                 | 0.00                         |
| 591                  | 1083                 | 267.90                       |
| 796                  | 1075                 | 0.00                         |
| 998                  | 1063                 | 0.00                         |
| 1192                 | 1057                 | 5.90                         |
| 1397                 | 1047                 | 29.90                        |
| 1600                 | 1037                 | 43.20                        |
| 1805                 | 1028                 | 8.60                         |
| 1984                 | 1024                 | 12.80                        |
| 2124                 | 1023                 | 5.80                         |
| 81                   | 547                  | 0.00                         |
| 284                  | 543                  | 0.61                         |
| 483                  | 541                  | 152.90                       |
| 685                  | 539                  | 56.00                        |
| 889                  | 540                  | 0.80                         |
| 1093                 | 539                  | 0.50                         |
| 1295                 | 535                  | 5.33                         |
| 1499                 | 534                  | 0.32                         |
| 1694                 | 532                  | 66.50                        |
| 1879                 | 530                  | 0.00                         |
| 2066                 | 529                  | 28.90                        |
| 121                  | 996                  | 0.00                         |
| 306                  | 969                  | 0.00                         |

| X Position<br>(feet) | Y Position<br>(feet) | Methane Flux<br>(g/sq m/day) |
|----------------------|----------------------|------------------------------|
| 587                  | 960                  | 0.00                         |
| 742                  | 953                  | 0.35                         |
| 946                  | 940                  | 0.10                         |
| 1146                 | 935                  | 0.15                         |
| 1347                 | 924                  | 0.32                         |
| 1548                 | 916                  | 3.50                         |
| 1753                 | 910                  | 0.14                         |
| 1957                 | 900                  | 1.60                         |
| 89                   | 675                  | 0.00                         |
| 274                  | 661                  | 0.00                         |
| 476                  | 661                  | 0.00                         |
| 684                  | 656                  | 0.00                         |
| 882                  | 655                  | 18.10                        |
| 1085                 | 651                  | 18.30                        |
| 1288                 | 650                  | 0.00                         |
| 1487                 | 650                  | 13.40                        |
| 1685                 | 648                  | 15.50                        |
| 1889                 | 647                  | 16.95                        |
| 2067                 | 646                  | 10.80                        |
| 99                   | 806                  | 0.00                         |
| 306                  | 804                  | 19.20                        |
| 508                  | 803                  | 2.70                         |
| 706                  | 798                  | 0.34                         |
| 910                  | 798                  | 0.06                         |
| 1111                 | 798                  | 0.14                         |
| 1316                 | 786                  | 0.14                         |
| 1517                 | 781                  | 55.10                        |
| 1718                 | 780                  | 30.90                        |
| 1919                 | 772                  | 110.70                       |



| X Position<br>(feet) | Y Position<br>(feet) | Methane Flux<br>(g/sq m/day) |
|----------------------|----------------------|------------------------------|
| 1048                 | 1113                 | 0.00                         |
| 1048                 | 1093                 | 15.60                        |
| 1048                 | 1073                 | 5.50                         |
| 1048                 | 1053                 | 45.00                        |
| 1048                 | 1033                 | 5.40                         |
| 1068                 | 1113                 | 2.50                         |
| 1068                 | 1093                 | 116.50                       |
| 1068                 | 1073                 | 422.70                       |
| 1068                 | 1053                 | 64.30                        |
| 1068                 | 1033                 | 0.00                         |
| 1088                 | 1113                 | 0.60                         |
| 1088                 | 1093                 | 0.00                         |
| 1088                 | 1073                 | 1.60                         |
| 1088                 | 1053                 | 13.00                        |
| 1088                 | 1033                 | 60.60                        |
| 1108                 | 1113                 | 535.20                       |
| 1108                 | 1093                 | 0.00                         |
| 1108                 | 1073                 | 0.80                         |
| 1108                 | 1053                 | 0.20                         |
| 1108                 | 1033                 | 6.20                         |
| 1128                 | 1113                 | 1.00                         |
| 1128                 | 1093                 | 9.40                         |
| 1128                 | 1073                 | 44.50                        |
| 1128                 | 1053                 | 233.20                       |
| 1128                 | 1033                 | 0.30                         |
| 1148                 | 1113                 | 36.60                        |
| 1148                 | 1093                 | 333.90                       |
| 1148                 | 1073                 | 3.60                         |
| 1148                 | 1053                 | 5.40                         |
| 1148                 | 1033                 | 1.10                         |
| 1049                 | 1052                 | 3.50                         |
| 1049                 | 1049                 | 5.40                         |
| 1049                 | 1046                 | 15.70                        |
| 1049                 | 1043                 | 56.40                        |
| 1049                 | 1040                 | 24.40                        |
| 1049                 | 1037                 | 7.20                         |

| X Position<br>(feet) | Y Position<br>(feet) | Methane Flux<br>(g/sq m/day) |
|----------------------|----------------------|------------------------------|
| 1049                 | 1034                 | 1.20                         |
| 1052                 | 1052                 | 1.90                         |
| 1052                 | 1049                 | 1.10                         |
| 1052                 | 1046                 | 0.00                         |
| 1052                 | 1043                 | 5.40                         |
| 1052                 | 1040                 | 2.00                         |
| 1052                 | 1037                 | 1.90                         |
| 1052                 | 1034                 | 1.90                         |
| 1055                 | 1052                 | 65.30                        |
| 1055                 | 1049                 | 378.00                       |
| 1055                 | 1046                 | 35.00                        |
| 1055                 | 1043                 | 2.50                         |
| 1055                 | 1040                 | 0.60                         |
| 1055                 | 1037                 | 0.60                         |
| 1055                 | 1034                 | 2.40                         |
| 1058                 | 1052                 | 143.00                       |
| 1058                 | 1049                 | 833.00                       |
| 1058                 | 1046                 | 98.00                        |
| 1058                 | 1043                 | 20.00                        |
| 1058                 | 1040                 | 6.00                         |
| 1058                 | 1037                 | 1.20                         |
| 1058                 | 1034                 | 10.40                        |
| 1061                 | 1052                 | 279.00                       |
| 1061                 | 1049                 | 662.00                       |
| 1061                 | 1046                 | 15.40                        |
| 1061                 | 1043                 | 0.70                         |
| 1061                 | 1040                 | 23.70                        |
| 1061                 | 1037                 | 130.60                       |
| 1061                 | 1034                 | 60.70                        |
| 960                  | 748                  | 10.90                        |
| 960                  | 728                  | 26.10                        |
| 960                  | 708                  | 63.30                        |
| 960                  | 688                  | 18.20                        |
| 960                  | 668                  | 0.00                         |
| 980                  | 748                  | 0.10                         |
| 980                  | 728                  | 2.20                         |

| X Position<br>(feet) | Y Position<br>(feet) | Methane Flux<br>(g/sq m/day) |
|----------------------|----------------------|------------------------------|
| 980                  | 708                  | 4.80                         |
| 980                  | 688                  | 0.00                         |
| 980                  | 668                  | 19.80                        |
| 1000                 | 748                  | 30.10                        |
| 1000                 | 728                  | 0.20                         |
| 1000                 | 708                  | 0.07                         |
| 1000                 | 688                  | 4.00                         |
| 1000                 | 668                  | 48.80                        |
| 1020                 | 748                  | 0.75                         |
| 1020                 | 728                  | 2.80                         |
| 1020                 | 708                  | 0.00                         |
| 1020                 | 688                  | 25.30                        |
| 1020                 | 668                  | 17.70                        |
| 1040                 | 748                  | 0.20                         |
| 1040                 | 728                  | 0.00                         |
| 1040                 | 708                  | 0.00                         |
| 1040                 | 688                  | 0.00                         |
| 1040                 | 668                  | 5.00                         |
| 1060                 | 748                  | 0.14                         |
| 1060                 | 728                  | 0.00                         |
| 1060                 | 708                  | 0.00                         |
| 1060                 | 688                  | 2.40                         |
| 1060                 | 668                  | 0.00                         |
| 990                  | 748                  | 14.70                        |
| 990                  | 745                  | 28.20                        |
| 990                  | 742                  | 55.10                        |
| 990                  | 739                  | 97.40                        |
| 990                  | 736                  | 132.60                       |
| 990                  | 733                  | 11.00                        |
| 993                  | 748                  | 124.90                       |
| 993                  | 745                  | 73.40                        |
| 993                  | 742                  | 83.90                        |
| 993                  | 739                  | 71.70                        |
| 993                  | 736                  | 112.60                       |
| 993                  | 733                  | 8.20                         |
| 996                  | 748                  | 62.70                        |

| X Position<br>(feet) | Y Position<br>(feet) | Methane Flux<br>(g/sq m/day) |
|----------------------|----------------------|------------------------------|
| 996                  | 745                  | 41.70                        |
| 996                  | 742                  | 223.00                       |
| 996                  | 739                  | 5.60                         |
| 996                  | 736                  | 13.70                        |
| 996                  | 733                  | 43.10                        |
| 999                  | 748                  | 39.60                        |
| 999                  | 745                  | 20.70                        |
| 999                  | 742                  | 13.50                        |
| 999                  | 739                  | 1.00                         |
| 999                  | 736                  | 2.90                         |
| 999                  | 733                  | 0.10                         |
| 1002                 | 748                  | 70.50                        |
| 1002                 | 745                  | 11.50                        |
| 1002                 | 742                  | 0.70                         |
| 1002                 | 739                  | 0.60                         |
| 1002                 | 736                  | 1.50                         |
| 1002                 | 733                  | 2.80                         |
| 1005                 | 748                  | 12.90                        |
| 1005                 | 745                  | 68.10                        |
| 1005                 | 742                  | 18.90                        |
| 1005                 | 739                  | 2.00                         |
| 1005                 | 736                  | 1.70                         |
| 1005                 | 733                  | 6.10                         |
| 730                  | 530                  | 9.40                         |
| 730                  | 510                  | 24.30                        |
| 730                  | 490                  | 13.40                        |
| 730                  | 470                  | 30.60                        |
| 730                  | 450                  | 0.00                         |
| 730                  | 430                  | 0.00                         |
| 750                  | 530                  | 0.00                         |
| 750                  | 510                  | 447.00                       |
| 750                  | 490                  | 17.40                        |
| 750                  | 470                  | 0.00                         |
| 750                  | 450                  | 506.00                       |
| 750                  | 430                  | 0.00                         |
| 770                  | 530                  | 44.50                        |

| X Position<br>(feet) | Y Position<br>(feet) | Methane Flux<br>(g/sq m/day) |
|----------------------|----------------------|------------------------------|
| 770                  | 510                  | 40.70                        |
| 770                  | 490                  | 47.10                        |
| 770                  | 470                  | 322.00                       |
| 770                  | 450                  | 41.00                        |
| 770                  | 430                  | 751.00                       |
| 790                  | 530                  | 2.50                         |
| 790                  | 510                  | 2.90                         |
| 790                  | 490                  | 63.30                        |
| 790                  | 470                  | 0.30                         |
| 790                  | 450                  | 47.80                        |
| 790                  | 430                  | 0.10                         |
| 810                  | 530                  | 1.80                         |
| 810                  | 510                  | 103.40                       |
| 810                  | 490                  | 9.70                         |
| 810                  | 470                  | 4.80                         |
| 810                  | 450                  | 5.30                         |
| 810                  | 430                  | 0.13                         |
| 830                  | 530                  | 3.80                         |
| 830                  | 510                  | 427.00                       |
| 830                  | 490                  | 0.90                         |
| 830                  | 470                  | 112.80                       |
| 830                  | 450                  | 338.00                       |
| 830                  | 430                  | 1.20                         |
| 793                  | 527                  | 212.50                       |
| 793                  | 524                  | 133.30                       |
| 793                  | 521                  | 13.20                        |
| 793                  | 518                  | 2.00                         |
| 793                  | 515                  | 20.40                        |
| 793                  | 512                  | 8.50                         |
| 796                  | 527                  | 72.80                        |
| 796                  | 524                  | 192.00                       |
| 796                  | 521                  | 259.00                       |
| 796                  | 518                  | 51.20                        |
| 796                  | 515                  | 41.90                        |
| 796                  | 512                  | 390.00                       |
| 799                  | 527                  | 1.70                         |

| X Position<br>(feet) | Y Position<br>(feet) | Methane Flux<br>(g/sq m/day) |
|----------------------|----------------------|------------------------------|
| 799                  | 524                  | 14.30                        |
| 799                  | 521                  | 16.10                        |
| 799                  | 518                  | 83.90                        |
| 799                  | 515                  | 827.00                       |
| 799                  | 512                  | 50.50                        |
| 802                  | 527                  | 0.24                         |
| 802                  | 524                  | 0.16                         |
| 802                  | 521                  | 8.90                         |
| 802                  | 518                  | 37.70                        |
| 802                  | 515                  | 241.00                       |
| 802                  | 512                  | 195.80                       |
| 805                  | 527                  | 0.16                         |
| 805                  | 524                  | 0.20                         |
| 805                  | 521                  | 9.60                         |
| 805                  | 518                  | 11.50                        |
| 805                  | 515                  | 120.90                       |
| 805                  | 512                  | 506.00                       |
| 808                  | 527                  | 0.26                         |
| 808                  | 524                  | 0.29                         |
| 808                  | 521                  | 1.00                         |
| 808                  | 518                  | 2.80                         |
| 808                  | 515                  | 24.00                        |

## APPENDIX E

| Soil Gas CH4<br>at 7.5 cm depth<br>(ppmv) | CH4 Oxidation<br>Rate<br>(nmol/hr/g soil) |
|---|---|
| 1.26E+05                                  | 895                                       |
| 318                                       | 41  |
| 64950                                     | 898                                       |
| 2.88E+05                                  | 1593                                      |
| 1.65E+05                                  | 1317                                      |
| 1.29E+05                                  | 1215                                      |
| 2.70E+05                                  | 1877                                      |
| 21580                                     | 517                                       |
| 1.63E+05                                  | 986                                       |
| 3.69E+05                                  | 2594                                      |
| 1.84E+05                                  | 918                                       |
| 1.72E+05                                  | 825                                       |
| 1.45E+05                                  | 409                                       |
| 2.38E+05                                  | 1160                                      |
| 4.49E+05                                  | 4999                                      |
| 3.22E+05                                  | 1133                                      |
| 2.75E+05                                  | 720                                       |
| 2.99E+05                                  | 1065                                      |
| 3.43E+05                                  | 1798                                      |
| 33420                                     | 318                                       |
| 1.50E+05                                  | 575                                       |
| 4.00E+05                                  | 1850                                      |
| 81000                                     | 200                                       |



| Date in 1994 | Modeled Whole<br>Landfill Oxidation<br>(% of production) |
|--------------|--|
| 12/1/93      | 0  |
| 12/2/93      | 0  |
| 12/3/93      | 0  |
| 12/4/93      | 2  |
| 12/5/93      | 0.8  |
| 12/6/93      | 1  |
| 12/7/93      | 2  |
| 12/8/93      | 2.1  |
| 12/9/93      | 0.1  |
| 12/10/93     | 0  |
| 12/11/93     | 2.1  |
| 12/12/93     | 0.6  |
| 12/13/93     | 0  |
| 12/14/93     | 0  |
| 12/15/93     | 1.8  |
| 12/16/93     | 3  |
| 12/17/93     | 0  |
| 12/18/93     | 0  |
| 12/19/93     | 0  |
| 12/20/93     | 0  |
| 12/21/93     | 0  |
| 12/22/93     | 3.3  |
| 12/23/93     | 0  |
| 12/24/93     | 0  |
| 12/25/93     | 0  |
| 12/26/93     | 0  |
| 12/27/93     | 0  |
| 12/28/93     | 0  |
| 12/29/93     | 0  |
| 12/30/93     | 0  |
| 12/31/93     | 0  |
| 1/1/94       | 0  |
| 1/2/94       | 0  |
| 1/3/94       | 0  |
| 1/4/94       | 0  |

| <u>Date in 1994</u> | <u>Modeled Whole<br/>Landfill Oxidation<br/>(% of production)</u> |
|---------------------|---|
| 1/5/94              | 0   |
| 1/6/94              | 0   |
| 1/7/94              | 0   |
| 1/8/94              | 0   |
| 1/9/94              | 0   |
| 1/10/94             | 0   |
| 1/11/94             | 0   |
| 1/12/94             | 0   |
| 1/13/94             | 0   |
| 1/14/94             | 0   |
| 1/15/94             | 0   |
| 1/16/94             | 0   |
| 1/17/94             | 0   |
| 1/18/94             | 0   |
| 1/19/94             | 0   |
| 1/20/94             | 0   |
| 1/21/94             | 0   |
| 1/22/94             | 0   |
| 1/23/94             | 0   |
| 1/24/94             | 0   |
| 1/25/94             | 0   |
| 1/26/94             | 0   |
| 1/27/94             | 0   |
| 1/28/94             | 0   |
| 1/29/94             | 0   |
| 1/30/94             | 0   |
| 1/31/94             | 0   |
| 2/1/94              | 0   |
| 2/2/94              | 0   |
| 2/3/94              | 0   |
| 2/4/94              | 0   |
| 2/5/94              | 0   |
| 2/6/94              | 0   |
| 2/7/94              | 0   |
| 2/8/94              | 0   |

| <u>Date in 1994</u> | <u>Modeled Whole<br/>Landfill Oxidation<br/>(% of production)</u> |
|---------------------|---|
| 2/9/94              | 0   |
| 2/10/94             | 0   |
| 2/11/94             | 0   |
| 2/12/94             | 0   |
| 2/13/94             | 0   |
| 2/14/94             | 0   |
| 2/15/94             | 0   |
| 2/16/94             | 0   |
| 2/17/94             | 0   |
| 2/18/94             | 0   |
| 2/19/94             | 0   |
| 2/20/94             | 0   |
| 2/21/94             | 0   |
| 2/22/94             | 0   |
| 2/23/94             | 0   |
| 2/24/94             | 0   |
| 2/25/94             | 0   |
| 2/26/94             | 0   |
| 2/27/94             | 0   |
| 2/28/94             | 0   |
| 3/1/94              | 0   |
| 3/2/94              | 0   |
| 3/3/94              | 0   |
| 3/4/94              | 0   |
| 3/5/94              | 0   |
| 3/6/94              | 0   |
| 3/7/94              | 0   |
| 3/8/94              | 0   |
| 3/9/94              | 0   |
| 3/10/94             | 0.1   |
| 3/11/94             | 0.1   |
| 3/12/94             | 0.8   |
| 3/13/94             | 0   |
| 3/14/94             | 0   |
| 3/15/94             | 0   |

| <u>Date in 1994</u> | <u>Modeled Whole<br/>Landfill Oxidation<br/>(% of production)</u> |
|---------------------|---|
| 3/16/94             | 0   |
| 3/17/94             | 0   |
| 3/18/94             | 0   |
| 3/19/94             | 0   |
| 3/20/94             | 0   |
| 3/21/94             | 0   |
| 3/22/94             | 0   |
| 3/23/94             | 0   |
| 3/24/94             | 0   |
| 3/25/94             | 0   |
| 3/26/94             | 0   |
| 3/27/94             | 0.1   |
| 3/28/94             | 0.4   |
| 3/29/94             | 0.2   |
| 3/30/94             | 0.2   |
| 3/31/94             | 0.5   |
| 4/1/94              | 0.7   |
| 4/2/94              | 0.5   |
| 4/3/94              | 1.1   |
| 4/4/94              | 0.4   |
| 4/5/94              | 0.4   |
| 4/6/94              | 0.4   |
| 4/7/94              | 2.6   |
| 4/8/94              | 2   |
| 4/9/94              | 3.2   |
| 4/10/94             | 1   |
| 4/11/94             | 3.3   |
| 4/12/94             | 3   |
| 4/13/94             | 1.3   |
| 4/14/94             | 0.9   |
| 4/15/94             | 0.1   |
| 4/16/94             | 0.4   |
| 4/17/94             | 0   |
| 4/18/94             | 0.3   |
| 4/19/94             | 0.7   |

| <u>Date in 1994</u> | <u>Modeled Whole<br/>Landfill Oxidation<br/>(% of production)</u> |
|---------------------|---|
| 4/20/94             | 2.7   |
| 4/21/94             | 5.8   |
| 4/22/94             | 12.5  |
| 4/23/94             | 14.8  |
| 4/24/94             | 12.6  |
| 4/25/94             | 6.5   |
| 4/26/94             | 2.4   |
| 4/27/94             | 2.9   |
| 4/28/94             | 11.2  |
| 4/29/94             | 7.4   |
| 4/30/94             | 7.6   |
| 5/1/94              | 12.9  |
| 5/2/94              | 6.3   |
| 5/3/94              | 4.6   |
| 5/4/94              | 7.6   |
| 5/5/94              | 9.4   |
| 5/6/94              | 5.7   |
| 5/7/94              | 6.8   |
| 5/8/94              | 11  |
| 5/9/94              | 7.7   |
| 5/10/94             | 13  |
| 5/11/94             | 9.6   |
| 5/12/94             | 11.2  |
| 5/13/94             | 10.7  |
| 5/14/94             | 9.2   |
| 5/15/94             | 11.8  |
| 5/16/94             | 17.3  |
| 5/17/94             | 7.9   |
| 5/18/94             | 8.2   |
| 5/19/94             | 9.3   |
| 5/20/94             | 8.3   |
| 5/21/94             | 9.1   |
| 5/22/94             | 15.8  |
| 5/23/94             | 21.8  |
| 5/24/94             | 22.5  |

| <u>Date in 1994</u> | <u>Modeled Whole<br/>Landfill Oxidation<br/>(% of production)</u> |
|---------------------|---|
| 5/25/94             | 20.1  |
| 5/26/94             | 21  |
| 5/27/94             | 12.4  |
| 5/28/94             | 8   |
| 5/29/94             | 13.8  |
| 5/30/94             | 19  |
| 5/31/94             | 22.6  |
| 6/1/94              | 26.3  |
| 6/2/94              | 19.4  |
| 6/3/94              | 13.4  |
| 6/4/94              | 17.8  |
| 6/5/94              | 21  |
| 6/6/94              | 23.1  |
| 6/7/94              | 23.8  |
| 6/8/94              | 24.4  |
| 6/9/94              | 17.9  |
| 6/10/94             | 21.3  |
| 6/11/94             | 20.8  |
| 6/12/94             | 22.6  |
| 6/13/94             | 22.8  |
| 6/14/94             | 29.8  |
| 6/15/94             | 29.1  |
| 6/16/94             | 27.7  |
| 6/17/94             | 29.6  |
| 6/18/94             | 35.1  |
| 6/19/94             | 36.7  |
| 6/20/94             | 30.9  |
| 6/21/94             | 30.7  |
| 6/22/94             | 24.4  |
| 6/23/94             | 26.4  |
| 6/24/94             | 28.3  |
| 6/25/94             | 21.1  |
| 6/26/94             | 21.2  |
| 6/27/94             | 28.1  |
| 6/28/94             | 31  |

| <u>Date in 1994</u> | <u>Modeled Whole<br/>Landfill Oxidation<br/>(% of production)</u> |
|---------------------|---|
| 6/29/94             | 28.3  |
| 6/30/94             | 26.9  |
| 7/1/94              | 27.5  |
| 7/2/94              | 28  |
| 7/3/94              | 30.3  |
| 7/4/94              | 25.3  |
| 7/5/94              | 26.2  |
| 7/6/94              | 28.6  |
| 7/7/94              | 33.3  |
| 7/8/94              | 33.6  |
| 7/9/94              | 32.7  |
| 7/10/94             | 29.8  |
| 7/11/94             | 30.6  |
| 7/12/94             | 26.9  |
| 7/13/94             | 26.9  |
| 7/14/94             | 31.1  |
| 7/15/94             | 27.7  |
| 7/16/94             | 22.1  |
| 7/17/94             | 29.4  |
| 7/18/94             | 29.6  |
| 7/19/94             | 29.3  |
| 7/20/94             | 31.8  |
| 7/21/94             | 33.8  |
| 7/22/94             | 34.9  |
| 7/23/94             | 34.9  |
| 7/24/94             | 30.5  |
| 7/25/94             | 32.2  |
| 7/26/94             | 31.8  |
| 7/27/94             | 32.2  |
| 7/28/94             | 30.5  |
| 7/29/94             | 26.8  |
| 7/30/94             | 27.7  |
| 7/31/94             | 28.6  |
| 8/1/94              | 28.1  |
| 8/2/94              | 30.1  |

| <u>Date in 1994</u> | <u>Modeled Whole<br/>Landfill Oxidation<br/>(% of production)</u> |
|---------------------|---|
| 8/3/94              | 31.3  |
| 8/4/94              | 31.3  |
| 8/5/94              | 33.6  |
| 8/6/94              | 23.3  |
| 8/7/94              | 20  |
| 8/8/94              | 21.6  |
| 8/9/94              | 23.6  |
| 8/10/94             | 25.4  |
| 8/11/94             | 23.5  |
| 8/12/94             | 20.2  |
| 8/13/94             | 24.9  |
| 8/14/94             | 27.8  |
| 8/15/94             | 23.4  |
| 8/16/94             | 17.5  |
| 8/17/94             | 20.9  |
| 8/18/94             | 21  |
| 8/19/94             | 21.3  |
| 8/20/94             | 21.7  |
| 8/21/94             | 24  |
| 8/22/94             | 24.6  |
| 8/23/94             | 16.7  |
| 8/24/94             | 16.5  |
| 8/25/94             | 17.6  |
| 8/26/94             | 20.2  |
| 8/27/94             | 24.1  |
| 8/28/94             | 23.6  |
| 8/29/94             | 25.2  |
| 8/30/94             | 21.4  |
| 8/31/94             | 20.1  |
| 9/1/94              | 18.9  |
| 9/2/94              | 17.3  |
| 9/3/94              | 14.9  |
| 9/4/94              | 15.9  |
| 9/5/94              | 14.9  |
| 9/6/94              | 13.7  |



| <u>Date in 1994</u> | <u>Modeled Whole<br/>Landfill Oxidation<br/>(% of production)</u> |
|---------------------|---|
| 10/12/94            | 5.9   |
| 10/13/94            | 6.1   |
| 10/14/94            | 9.6   |
| 10/15/94            | 9   |
| 10/16/94            | 6.2   |
| 10/17/94            | 8.4   |
| 10/18/94            | 8.5   |
| 10/19/94            | 8.4   |
| 10/20/94            | 13  |
| 10/21/94            | 14.4  |
| 10/22/94            | 16.5  |
| 10/23/94            | 13.1  |
| 10/24/94            | 13.1  |
| 10/25/94            | 11.4  |
| 10/26/94            | 9.6   |
| 10/27/94            | 7.3   |
| 10/28/94            | 5.2   |
| 10/29/94            | 6.2   |
| 10/30/94            | 8.7   |
| 10/31/94            | 13  |
| 11/1/94             | 13.3  |
| 11/2/94             | 13.7  |
| 11/3/94             | 8   |
| 11/4/94             | 11.3  |
| 11/5/94             | 16.3  |
| 11/6/94             | 19.2  |
| 11/7/94             | 11.5  |
| 11/8/94             | 6.8   |
| 11/9/94             | 11.5  |
| 11/10/94            | 10.4  |
| 11/11/94            | 5.7   |
| 11/12/94            | 2.8   |
| 11/13/94            | 4.1   |
| 11/14/94            | 4.9   |
| 11/15/94            | 6.8   |

| <u>Date in 1994</u> | <u>Modeled Whole<br/>Landfill Oxidation<br/>(% of production)</u> |
|---------------------|---|
| 9/7/94              | 13.9  |
| 9/8/94              | 16.6  |
| 9/9/94              | 19.6  |
| 9/10/94             | 15.9  |
| 9/11/94             | 16.3  |
| 9/12/94             | 15.4  |
| 9/13/94             | 17.4  |
| 9/14/94             | 23.5  |
| 9/15/94             | 17.9  |
| 9/16/94             | 17.6  |
| 9/17/94             | 16.5  |
| 9/18/94             | 21.5  |
| 9/19/94             | 13.1  |
| 9/20/94             | 12  |
| 9/21/94             | 14.9  |
| 9/22/94             | 18.8  |
| 9/23/94             | 15.7  |
| 9/24/94             | 14.5  |
| 9/25/94             | 16.6  |
| 9/26/94             | 17.6  |
| 9/27/94             | 15.4  |
| 9/28/94             | 15  |
| 9/29/94             | 16.8  |
| 9/30/94             | 12.4  |
| 10/1/94             | 9.4   |
| 10/2/94             | 8.6   |
| 10/3/94             | 8.4   |
| 10/4/94             | 8.3   |
| 10/5/94             | 8.9   |
| 10/6/94             | 6.4   |
| 10/7/94             | 8   |
| 10/8/94             | 10.7  |
| 10/9/94             | 15.9  |
| 10/10/94            | 17.6  |
| 10/11/94            | 13.5  |

| <u>Date in 1994</u> | <u>Modeled Whole<br/>Landfill Oxidation<br/>(% of production)</u> |
|---------------------|---|
| 11/16/94            | 9.5   |
| 11/17/94            | 3   |
| 11/18/94            | 4.2   |
| 11/19/94            | 4.1   |
| 11/20/94            | 6.2   |
| 11/21/94            | 2.2   |
| 11/22/94            | 4   |
| 11/23/94            | 3.5   |
| 11/24/94            | 0.2   |
| 11/25/94            | 0   |
| 11/26/94            | 0   |
| 11/27/94            | 0   |
| 11/28/94            | 0   |
| 11/29/94            | 0   |
| 11/30/94            | 0   |

## APPENDIX F

## SUMMARY OF TRACE GAS FLUX MEASUREMENT METHODS

Several methods were utilized to determine trace gas fluxes to the atmosphere from the environments presented in the preceding chapters. This appendix summarizes these methods as applied to the various surface conditions encountered.

### *Non-Aerated Liquid Surfaces*

An enclosed chamber technique was used to measure fluxes from non-aerated liquid surfaces as shown in Figure 1. An aluminum enclosure (0.068 m<sup>3</sup>) was suspended on the liquid surface by floats fastened to opposite sides of the enclosure. A thermistor was mounted inside the enclosure to measure the enclosed air temperature. The enclosure was manually held in place during sampling to minimize movement due to surface turbulence. A battery operated blower circulated the air within the enclosure and through a closed loop of 5 cm diameter hose.

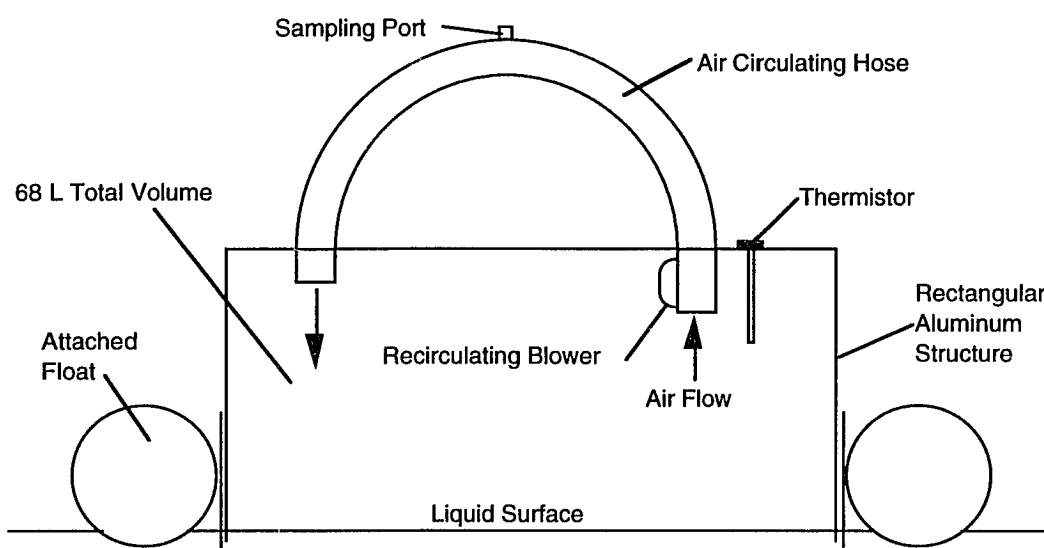


Figure 1 - Enclosure configuration used on non-aerated liquid surfaces.

Headspace air samples were withdrawn from the hose. Gas samples were collected in 20 mL nylon syringes at 2 minute intervals for 10 minutes. The gas flux,  $E$  (mass area<sup>-1</sup> time<sup>-1</sup>) from the liquid surface was calculated by the equation

$$E = \frac{V}{A} p \left( \frac{\Delta C}{\Delta t} \right) \quad (1)$$

where  $V$  is the volume of the chamber,  $A$  is the enclosed surface area,  $p$  is the density of the gas at the measured temperature, and  $\frac{\Delta C}{\Delta t}$  is the linear increase in the gas concentration in the enclosure headspace during the sampling period.  $\frac{\Delta C}{\Delta t}$  is calculated by linear regression of the gas concentration in four or five headspace samples with a required correlation coefficient of 0.90 or higher significant to the 95% confidence level for  $n=5$ .

#### *Aerated Liquid Surfaces*

A bag technique was used to measure fluxes from aerated liquid surfaces. A 40 liter polyethylene sample bag, fastened to the inside of a wood support frame, was used to collect gas samples from the agitated surface of aerated tanks as shown in Figure 2.

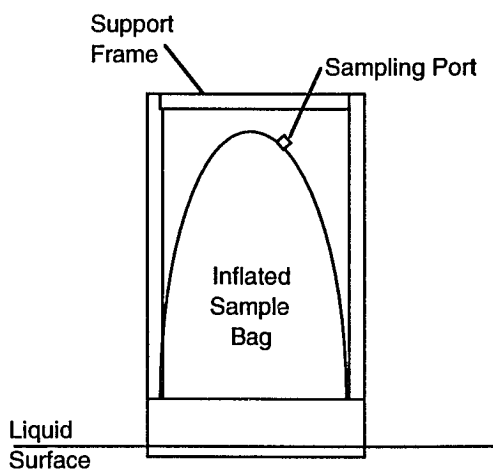


Figure 2 - Configuration of the bag sampler used on aerated liquid surfaces.

The open base of the frame allowed gas to be collected from 0.084 m<sup>2</sup> of the surface. To collect samples, the bag was initially collapsed and emptied of ambient air. The wood support frame was then placed several inches into the liquid. Dissolved gases within the liquid, transferred to the mechanically distributed air by diffusion, filled the collection bag. Samples were withdrawn from the bag in 20 mL nylon syringes. The gas flux, E (mass area<sup>-1</sup> time<sup>-1</sup>) across the entire surface area was calculated by the equation

$$E = p c Q A^{-1} \quad (2)$$

where, p is the density of the gas at the temperature recorded in the sample bag, c is the sample gas concentration, Q is the total diffuse air flow, and A is the total surface area.

### *Sludge Gases*

Trace gas fluxes resulting from sludge storage were determined by two methods. First, gas concentrations in the sludge were determined by sampling the sludge flow, prior to transfer, with a 0.5 liter collection bucket. 30 mL sludge samples were collected immediately after withdrawal from the flow in 60 mL polypropylene syringes. An equal volume of laboratory room air was later introduced into the sludge sample syringe and the syringe was shaken vigorously for 2 minutes. The gases in the syringe headspace were then transferred to a clean 20 mL nylon syringe for analysis. This procedure was repeated five times and was found to have stripped greater than 95% of the dissolved N<sub>2</sub>O from the sludge samples. This method estimated the quantities of gases emitted during, and immediately after, transfer of sludge to the holding tanks. Fluxes were calculated under the assumption that the total gas potential of the sludge was realized by aeration stripping during the period of storage prior to final processing. Second, fluxes resulting from the generation of gases within the sludge holding tanks, and stripped from the liquid during

aeration, were determined using the aerated surface collection method described previously.

### *Solid Surfaces*

A static enclosure technique was used to measure fluxes from both landfill cover soils and compost surfaces. Compost fluxes were measured by initially inserting an open aluminum collar approximately 10 cm into the the compost surface which was allowed to stabilize for several minutes prior to each flux measurement to minimize disturbance of the surface at the time of the measurement (Figure 3). An aluminum enclosure was then lowered into a water filled channel at the top edge of the collar during each measurement to provide an air-tight seal. The enclosure surface area and volume were 0.26 m<sup>2</sup> and 93.6 liters respectively.

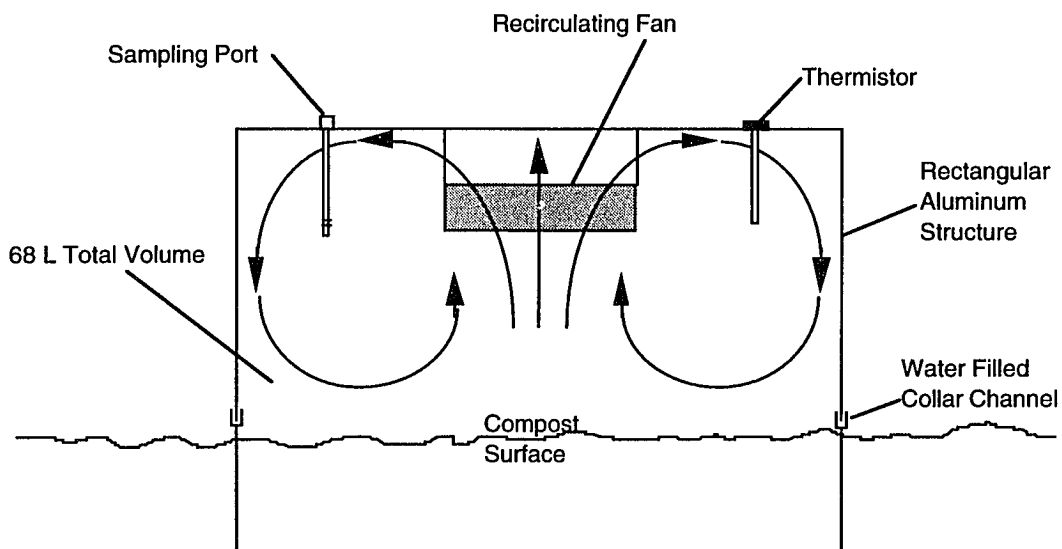


Figure 3 - Enclosure configuration used on compost surfaces.



Landfill surface fluxes were measured by placing a polyethylene enclosure directly on the ground surface as shown in Figure 4. A small amount of nearby soil was mounded at the soil-chamber interface to provide an adequate seal. Chamber surface area and volume were 510 cm<sup>2</sup> and 9.3 liters respectively.

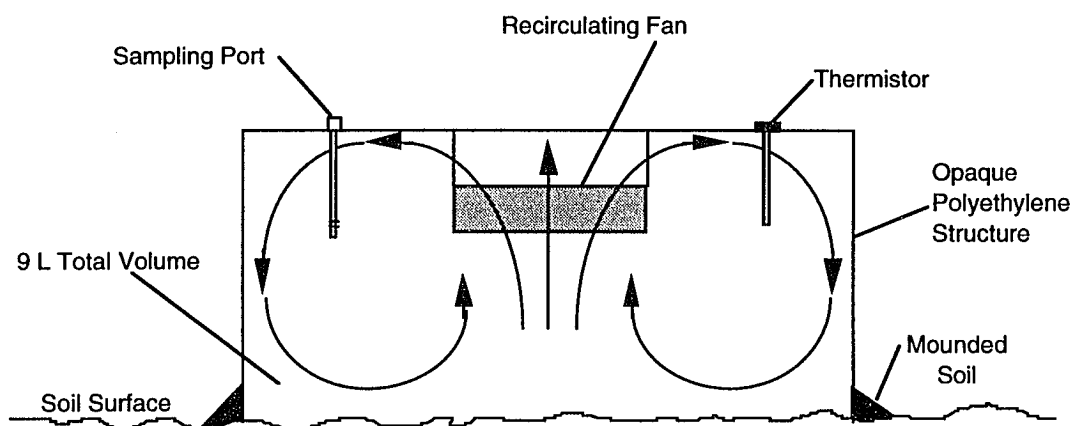


Figure 4 - Enclosure configuration used on landfill soil surfaces.

A battery operated blower circulated the air within both enclosure types and a thermistor mounted inside measured enclosed air temperatures. Enclosure headspace samples were collected at 0.5 or 1 minute intervals in 60 ml polyethylene or 20 ml nylon syringes and analyzed within 24 hours. The gas flux,  $E$  (mass area<sup>-1</sup> time<sup>-1</sup>) from the surface was calculated by

$$E = \frac{V}{A} p \left( \frac{\Delta C}{\Delta t} \right) \quad (3)$$

where  $V$  is the volume of the enclosure,  $A$  is the enclosed surface area,  $p$  is the gas density at the enclosure headspace temperature, and  $\frac{\Delta C}{\Delta t}$  is the change in  $\text{CH}_4$  mixing ratio in the enclosure headspace.  $\frac{\Delta C}{\Delta t}$  is calculated by linear regression of the  $\text{CH}_4$  mixing ratio in four or five headspace samples with a required correlation coefficient of 0.90 or higher significant to the 95% confidence level for  $n=4$  or 5.

### *Interstitial Gases*

Interstitial gas samples were collected at various depths in the profile of the landfill cover soils as well as in the profile of several sludge compost piles to determine in-situ gas concentrations. Gas samples were collected in 60 ml polyethylene or 20 mL nylon syringes by inserting an end-perforated 3.175 mm OD stainless steel tube into the subsurface in 5 to 10 cm increments. Gas samples were withdrawn slowly to prevent the intrusion of surface air into the subsurface.