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Radiatively active trace gas emissions from waste management systems

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RADIATIVELY ACTIVE TRACE GAS EMISSIONS FROM WASTE MANAGEMENT SYSTEMS

BY

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DISSERTATION

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PREFACE

The overarching theme of this dissertation is the quantitative assessment of emissions of methane (CH_4) and nitrous oxide (N_2O) 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 N_2O from the liquid treatment processes at a wastewater treatment plant. Chapter 2 describes field measurements of N_2O 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 CH_4 oxidation in temperate zone soils. Chapter 4 describes a comparison study of 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 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 desribes 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 (N_2O) emissions from liquid waste and residuals treatment, emissions of methane (CH_4) from landfills, and the effects of microbial oxidation on landfill CH_4 emissions.

N_2O 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 g N_2O person^{-1} year^{-1} and 1.6×10^{-6} g N_2O (liter wastewater^{-1}). The potential for N_2O 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 g N_2O (dry kg of sludge)$^{-1}$. In addition, potential N_2O 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 g N_2O (dry kg)$^{-1}$ and 0.3 g N_2O (dry kg waste)$^{-1}$ from livestock and yard wastes, respectively. Livestock wastes were determined to present the greatest potential for global N_2O emissions, estimated to contribute 1.2 Tg year^{-1}.

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 CH_4 min^{-1} using the chamber and tracer methods, respectively. The influence of microbial oxidation on landfill CH_4 emissions was also investigated. Soil samples from locations of

CH_4 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_4, 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_4 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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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 g N_2O person^{-1} year^{-1} and flow based emissions of 1.6×10^{-6} g N_2O liter^{-1} 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 % 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^{-1} *(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 Debruyn, 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 4×10^6 liters day^{-1}. The population served during the summer is approximately 6,200 and generates a mean wastewater flow of approximately 2×10^6 liters $days^{-1}$. 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^{-1} with an estimated suspended solids concentration of 220 mg l^{-1}. 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.

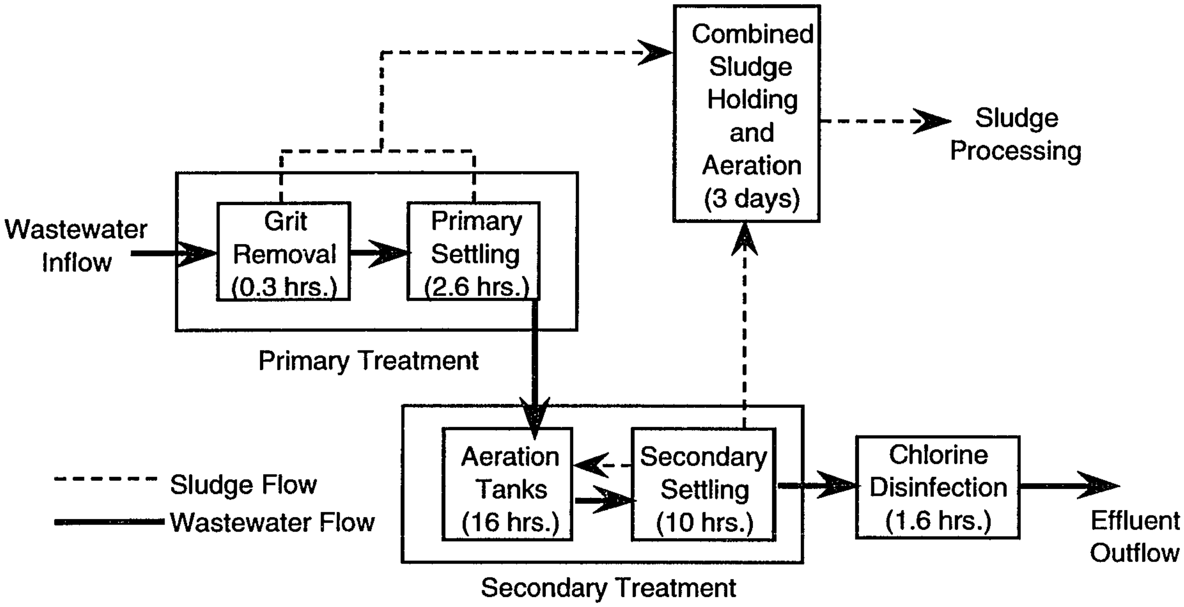

Figure 1-1. Simplified process diagram for the Durham, N. H. wastewater treatment plant. Retention times are given in parentheses.

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_2O 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^{-1} time^{-1}) from the liquid surface in the static chamber was calculated by the equation

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

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 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^2 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 $area^{-1}$ $time^{-1}$) was calculated by the equation

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

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_2O 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_2O 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_2O within 3 to 4 hours after collection. Samples and standards were dried across $CaSO_4$ as they were injected into the gas chromatograph (GC) injection loop. Analyses for N_2O 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_4 mixture. Peaks were quantified with Hewlett Packard Chemstation software on a personal computer. N_2O 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_2O 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_2O 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_2O m^{-2} day^{-1} to a maximum of 1.05 g N_2O m^{-2} day^{-1}. A maximum flux of 2.48 g N_2O m^{-2} day^{-1} 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_2O 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_2O m^{-2} day^{-1} to a maximum of 0.04 g N_2O m^{-2} day^{-1}. 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_2O 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_2O 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_2O fluxes from tank #1 ranged from a minimum of 0.12 g N_2O m^{-2} day^{-1} to a maximum of 1.80 g N_2O m^{-2} day^{-1} (Figure 1-3).

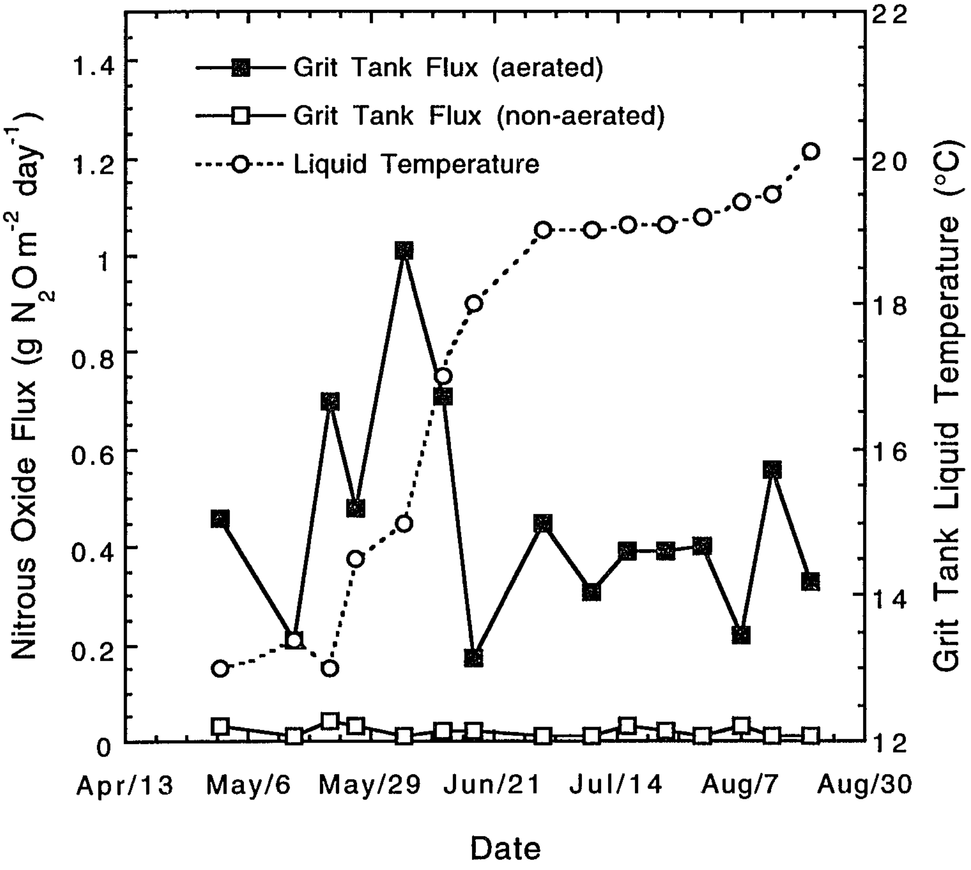

Figure 1-2. Observed N_2O fluxes (g N_2O m^{-2} day^{-1}) and wastewater temperatures (°C) from the aerated and non-aerated areas of the grit tank.

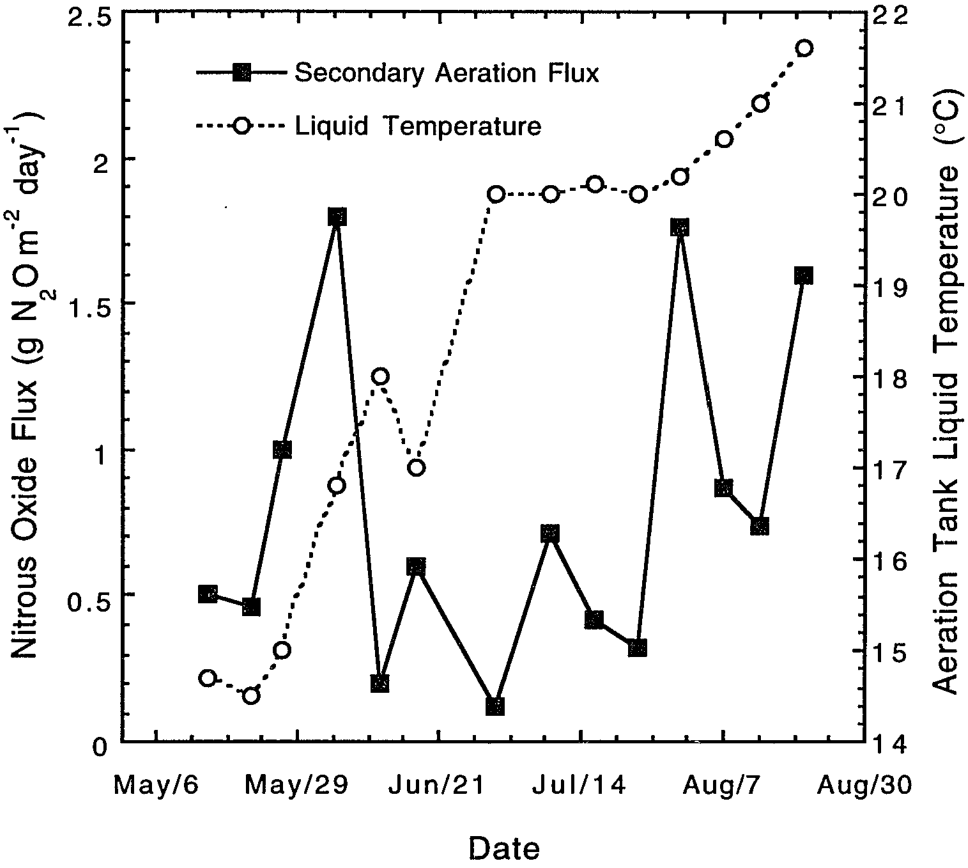

Figure 1-3. Observed N_2O fluxes (g N_2O m^{-2} day^{-1}) and wastewater temperatures (°C) from secondary aeration tank #1.

The aeration tank N_2O 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 x 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 g N_2O m^{-2} day^{-1} were detected immediately after transfer to the holding tanks, while a flux of 0.24 g N_2O m^{-2} 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_2O per unit volume of sludge and was assumed to be fully realized. N_2O concentrations ranged from a minimum of 15.3 μg N_2O $liter^{-1}$ sludge to a maximum of 145 μg N_2O $liter^{-1}$ 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_2O fluxes ranged from a minimum of 0.13 g N_2O m^{-2} day^{-1} to a maximum of 0.28 g N_2O m^{-2} 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 g N_2O m^{-2} 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 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^2. 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^2. The estimated total area weighted annual emissions from the aerated area of the grit tanks were 1.6×10^3 g N_2O $year^{-1}$.

The mean flux measured from the non-aerated area of the grit tanks was 0.02 g N_2O m^{-2} day^{-1}. Total non-aerated surface area was 26 m^2 from September through May and 13 m^2 from June through August yielding a population weighted surface area of 22.8 m^2. The estimated total area weighted annual emission from the non-aerated area of the grit tanks was 158 g N_2O $year^{-1}$.

The mean N_2O flux from secondary aeration tank #1 was 0.61 g N_2O m^{-2} day^{-1} 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^2. The estimated total annual emissions from secondary aeration were 3.2×10^4 g N_2O $year^{-1}$.

The mean sludge sample gas concentrations were 105 μg N_2O $liter^{-1}$ sludge. Approximately 2.4×10^6 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_2O $year^{-1}$.

The mean secondary N_2O flux from the aerated areas of the sludge holding tanks was 0.21 g N_2O m^{-2} day^{-1}. 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^2, yielding annual fluxes from sludge storage due to secondary production of 1.4×10^3 g N_2O $year^{-1}$. Total estimated annual flux from sludge transfer and storage was 1.7×10^3 g N_2O $year^{-1}$.

The estimated total process N_2O flux is summarized in Table 1-1. The total estimated annual N_2O flux from the Durham, N.H. wastewater treatment plant is 3.5×10^4 g N_2O year^{-1}.

Table 1-1. Process and total N_2O fluxes (g N_2O year^{-1}) from the Durham, N. H. wastewater plant.

Process	N_2O Flux
Grit Tank (aerated)	1.6×10^3
Grit Tank (non-aerated)	1.6×10^2
Aeration Tanks	3.2×10^4
Sludge Storage Tank	1.7×10^3
Total	3.5×10^4

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_2O person^{-1} year^{-1} 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 1.1×10^9 liters year^{-1}, annual gas flux is estimated to be 1.6×10^{-6} g N_2O liter^{-1} wastewater for the primary treatment system and 3.1×10^{-5} g N_2O liter^{-1} wastewater for the activated sludge secondary treatment system.

Total annual N_2O 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 4.1×10^{13} liters year^{-1} *(11)*. This study also found return activated sludge to be the most widely used method of secondary treatment with a flow of 3.9×10^{13} liters year^{-1}. Total N_2O emissions from these systems, based on the Durham wastewater treatment plant emission factors, are estimated to be 6.6×10^7 g N_2O year^{-1} from primary treatment and 1.2×10^9 g N_2O year^{-1} from secondary activated sludge treatment.

A recent laboratory investigation of N_2O 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±21 µg N_2O gss^{-1} for raw wastewater and 770±170 µg N_2O gss^{-1} 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^{-1} *(12)*, yields emission factors of 7.3 µg N_2O gss^{-1} for raw wastewater and 132 µg N_2O gss^{-1} for effluent entering the secondary aeration system. These values compare well with the results of Debruyn, et al. Higher observed emission factors from the laboratory incubations of Debruyn, 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_2O 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 x 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.

REFERENCES

(1) Houghton, J. T., Callander, B. A. and Varney, S. K. *The Supplementary Report to the IPCC Scientific Assessment, Climate Change;* Cambridge University Press: New York, 1992.

(2) Crutzen, P. J. *Quat. J. Royal Met. Soc.* **1970**, *96,* 320-325.

(3) Khalil, M. A. K. and Rasmussen, R. A. *J. of Geophys. Res.* **1992**, *97,* 14651-14660.

(4) Bouwman, A. F. "Estimated global source distribution of nitrous oxide" in: *CH4 and N2O: Global Emissions and Controls from Rice Fields and Other Agricultural and Industrial Sources*; 1994 NIAES: Washington, DC, 1994.

(5) Prinn, R., Cunnold, D., Rasmussen, R., Simmonds, P., Alyea, F., Crawford, A., Fraser, P. and Rosen, R. *J. Geophys. Res.* **1990**, *95*, 18369-18385.

(6) Debruyn, W., Lissens, G. and Van Rensbergen, J. *Eviron. Monit. Assess.* **1994**, *31*, 159-165.

(7) Hong, Z., Hanaki, K. and Matsuo, T. *Wat. Sci. Tech.* **1993**, *28,* 203-207.

(8) Crill, P. M., Bartlett, K. B., Wilson, J. O., Sebacher, D. I. and Harriss, R. C. *J. Geophys. Res.* **1988**, *93,* 1564-1570.

(9) Martikainen, P. J., Nykanen, H., Crill, P. and Silvola, J. *Nature* **1993**, *366,* 51-53.

(10) Montgomery, D. C. and Peck, E. A. *Introduction to Linear Regression Analysis;* John Wiley & Sons, Inc.: New York, 1992.

(11) *The 1988 Needs Survey: Conveyance, Treatment, and Control of Municipal Wastewater, Combined Sewer Overflows, and Stormwater Runoff*; U. S. Environmental Protection Agency, U. S. Government Printing Office: Washington, DC, 1989.

(12) Metcalf; Eddy *Wastewater Engineering: Treatment, Disposal, and Reuse;* Water Resources and Environmental Engineering. King, P. H., Eliassen, R. and Linsley, R. K., Eds.; McGraw-Hill, Inc.: New York, 1991.

(13) *International Anthropogenic Methane Emissions: Estimates for 1990*; U. S. Environmental Protection Agency, U. S. Government Printing Office: Washington, DC, 1994; EPA/230/R/93/010.

CHAPTER 2

MEASUREMENTS OF N_2O FROM COMPOSTING AND GLOBAL ESTIMATES OF N_2O FROM ORGANIC WASTES MANAGEMENT

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Summary

Nitrous oxide (N_2O) 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_2O m^{-2} day^{-1}, resulted in a mass based emission rate of 0.7 g N_2O (dry kg sludge)$^{-1}$. The mean flux from the livestock waste compost, 0.5 g N_2O m^{-2} day^{-1}, resulted in a mass based emission rate of 0.5 g N_2O (dry kg waste)$^{-1}$. The mean flux from the yard waste compost, 1.8 g N_2O m^{-2} day^{-1}, resulted in a mass based emission rate of 0.3 g N_2O (dry kg waste)$^{-1}$. Factors effecting N_2O 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_2O emissions from the treatment of wastes. Livestock waste treatment appears to present the greatest N_2O potential with estimated global emissions of 1.2 Tg N_2O annually. Data can be viewed in tabular form in Appendix B.

Introduction

Nitrous oxide (N_2O) 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*). N_2O 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 N_2O is about 310 ppbv and is increasing at a rate of 0.25 to 0.31 % 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 N_2O in the atmosphere, all sources, both natural and anthropogenic, must be identified and quantified. Total global N_2O emissions are estimated to range from 17 to 30 Tg N_2O yr^{-1} (*6*). Significant natural sources, which are estimated to account for about 60 % of total N_2O 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 N_2O increase, but better quantification is necessary to establish a source hierarchy to guide the application of mitigation resources.

The major biogenic processes responsible for N_2O production are nitrification and denitrification (*7, 8*). Nitrification is a two-step process that, under aerobic conditions, oxidizes NH_4^+ to NO_2^- followed by the oxidation of NO_2^- to NO_3^-. N_2O is produced as a byproduct of these reactions. Denitrification, ordinarily associated with anaerobic conditions, is a process in which NO_3^-, NO_2^-, N_2O or NO can be used by bacteria as terminal electron acceptors (*9*). NO, N_2O or N_2 are produced as end-products or by-products of these reactions.

The availability of oxygen (O_2) is a determining factor in N_2O production. During nitrification, the oxidation of NH_4^+ at low O_2 partial pressures results in significant N_2O production, possibly as an intermediate between NH_2OH and NO_2^- (*10*). During denitrification, NO_3^- is reduced to N_2 without appreciable N_2O production in the absence of O_2. But, as O_2 concentration increases, N_2O production increases to a maximum and decreases with additional O_2 (*11*). Therefore, N_2O 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 N_2O 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 N_2O to the atmosphere from the composting of common organic wastes and to derive waste mass based N_2O emission factors from these results. A comprehensive study of N_2O emissions from municipal wastewater sludge composted in aerated static piles was performed from April 1993 through January 1994. Preliminary measurements of N_2O 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 N_2O 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 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^2 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_{N2O} (mass area^{-1} time^{-1}) from the surface was calculated by

$$E_{N2O} = \frac{V}{A} p \left(\frac{\Delta C}{\Delta t}\right) \qquad (1)$$

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^{-2} day^{-1}.

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_2O 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_2O emission factor, E_{N2O} (mass N_2O time^{-1} dry mass compost^{-1}) was calculated by

$$E_{N2O} = \frac{V}{m} p \left(\frac{\Delta C}{\Delta t} \right) \tag{2}$$

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_2O mixing ratio in the jar headspace. $\frac{\Delta C}{\Delta t}$ is calculated by linear regression of the N_2O 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_2O within 3 to 4 hours after collection. Samples and standards were dried across $CaSO_4$ as they were injected into the gas chromatograph injection loop. Analyses for N_2O 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_4 mixture. Peaks were quantified with Hewlett Packard Chemstation software on a personal computer. The ECD was calibrated for N_2O over the range 310 ppb to 100 ppm during each analysis period using N_2O in N_2 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_2O 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_2O m^{-2} day^{-1} while the mean of the fluxes measured with the blowers off was 1.2 g N_2O m^{-2} day^{-1}. The mean value of the entire flux data set was 2.2 g N_2O m^{-2} day^{-1}.

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_2O m^{-2} day^{-1} with a mean value of 0.9 g N_2O m^{-2} day^{-1}.

A mass based N_2O 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_2O m^{-2} day^{-1}. The effective pile emitting surface area is 45 m^2. The resulting mass based emission rate is 0.5 g N_2O (dry kg sludge)$^{-1}$. A similar methodology can be used to estimate emissions from the non-aerated finishing piles. Assuming an emission rate of 0.9 g N_2O m^{-2} day^{-1} and a finishing period of 30 days yields an emission rate of 0.2 g N_2O (dry kg sludge)$^{-1}$. The resulting total mass based N_2O emission rate is 0.7 g N_2O (dry kg sludge)$^{-1}$.

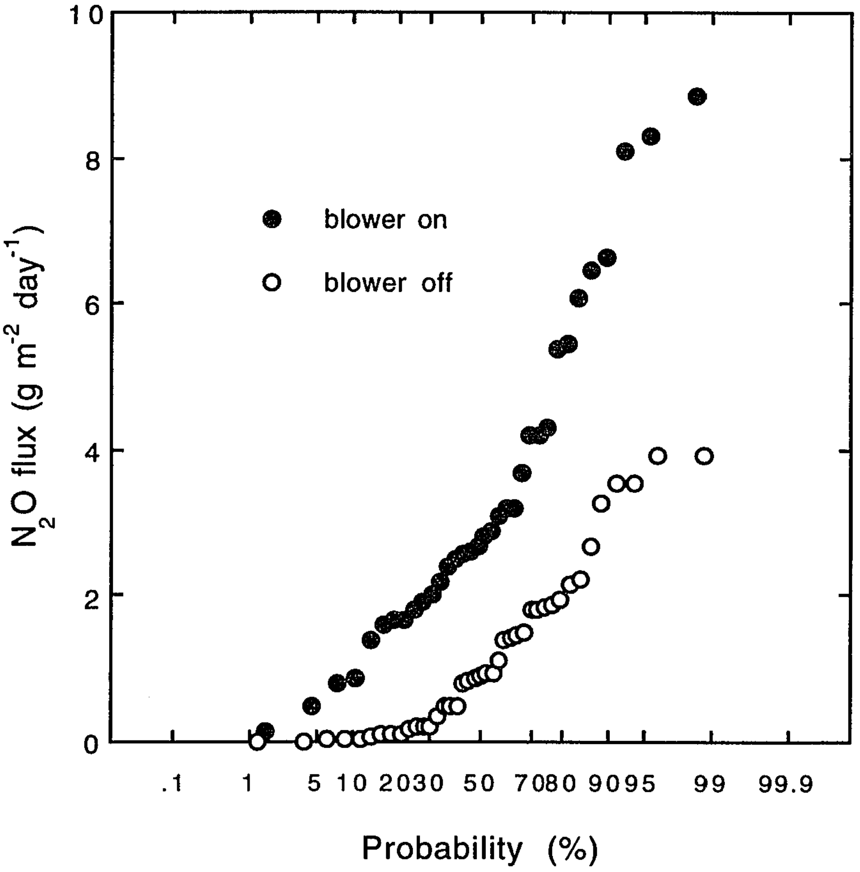

Figure 2-1. Cumulative probability plot of the measured N_2O flux data. Solid circles represent fluxes measured with aeration active and open circles represent fluxes measured with aeration inactive.

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.

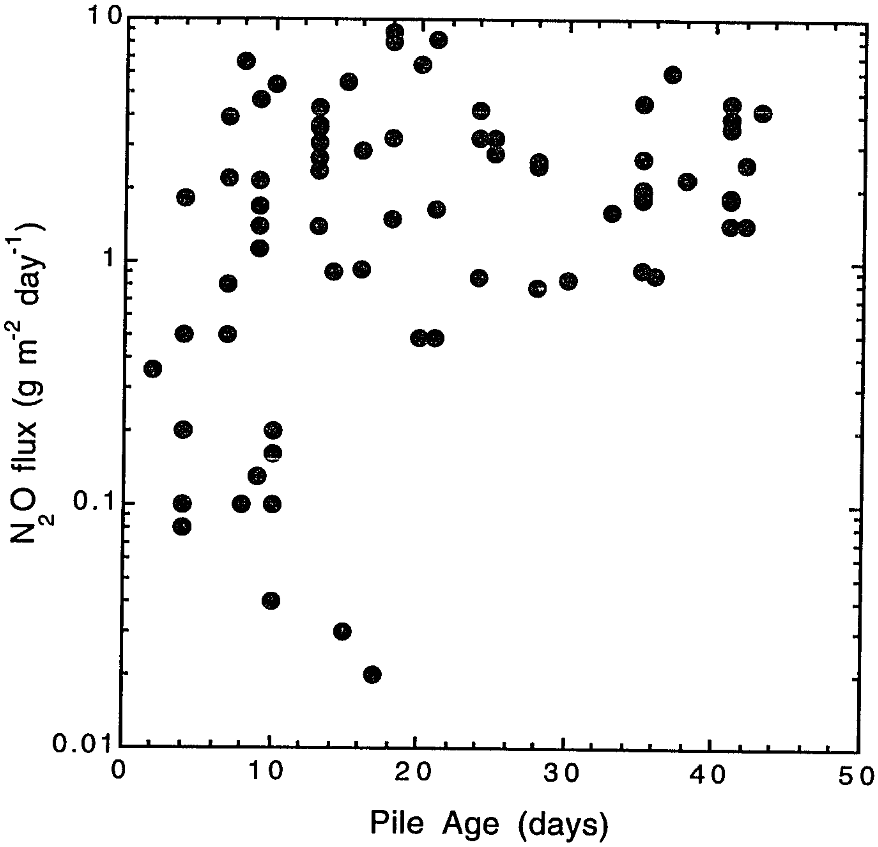

Figure 2-2. Measured N_2O fluxes as a function of compost age.

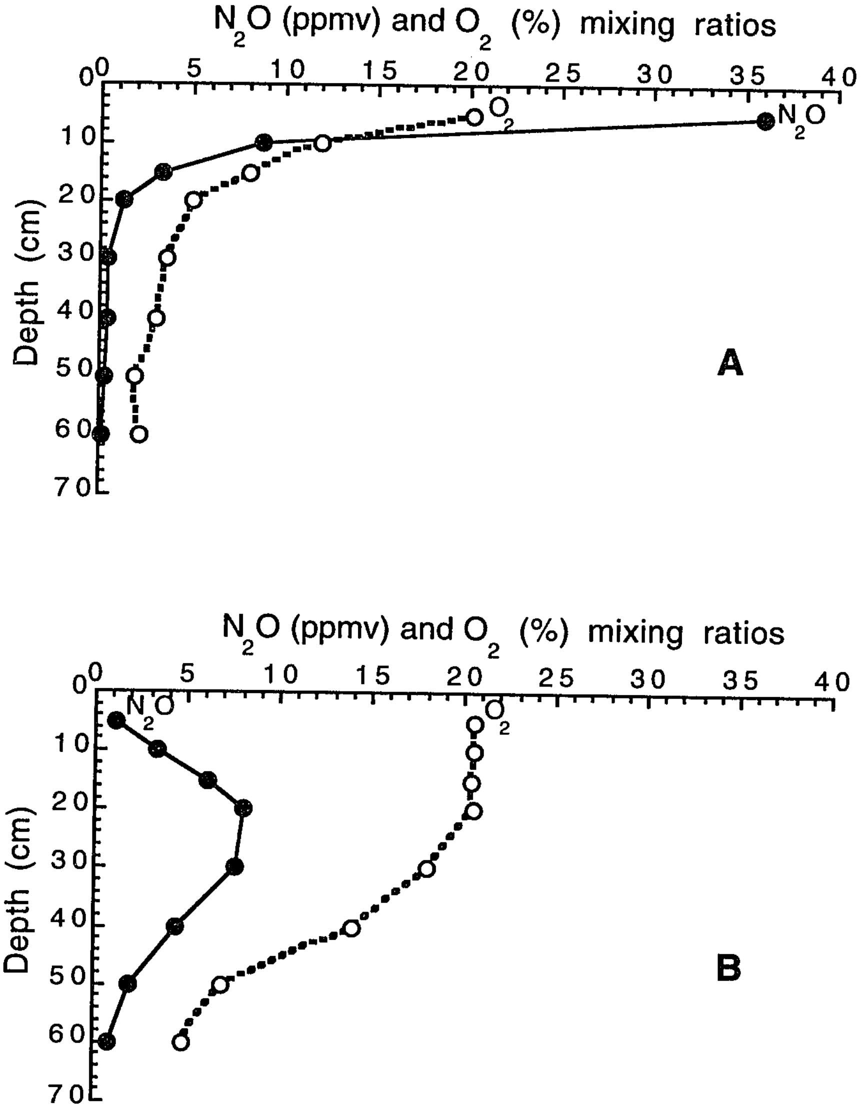

Figure 2-3. Profiles of N_2O (solid circles) and O_2 (open circles) in the oldest and youngest compost piles examined. A) 9 day old compost, B) 38 day old compost.

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 drys, 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 nmol N_2O hr^{-1} g dry compost^{-1} at 33°C to 0.064 nmol N_2O hr^{-1} g dry compost^{-1} at 54°C. The resulting Q_{10} based on the observed relationship was 1.7.

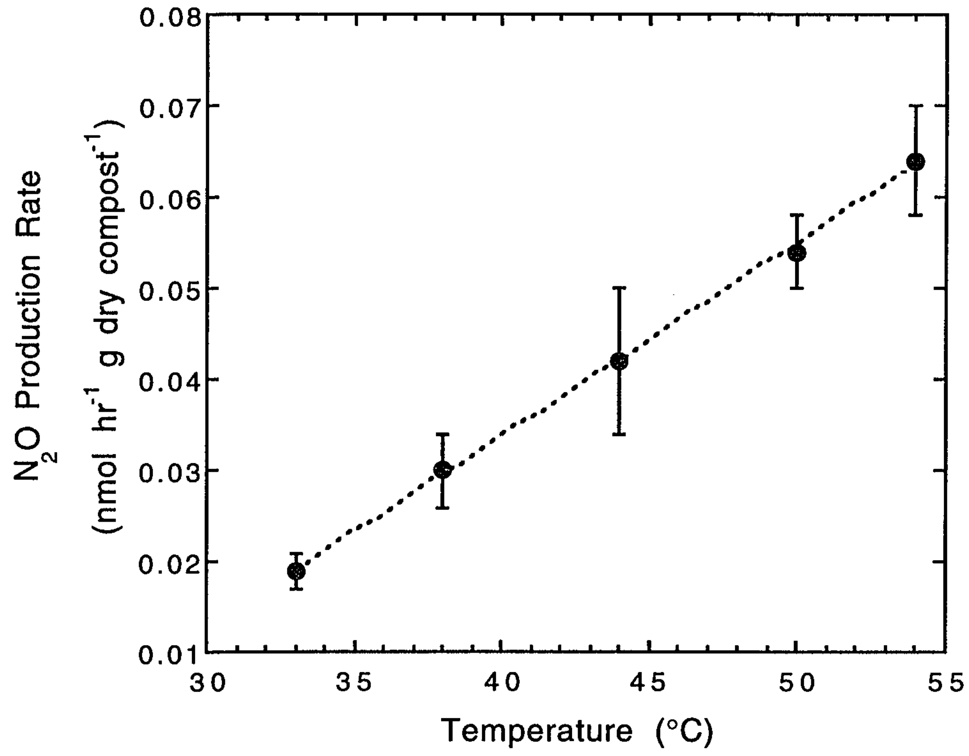

Figure 2-4. N_2O production rates as a function of temperature from jar incubations of 10 composite compost samples. Solid circles represent the mean production rate, error bars represent the standard deviation.

Livestock and Yard Waste Compost

N_2O 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_2O emission rates measured on the livestock waste piles were 1.3 and 0.8 g N_2O m^{-2} day^{-1} from piles 1 and 2, respectively. The average of emissions measured on both piles during the observation period was 0.5 g N_2O m^{-2} day^{-1}.

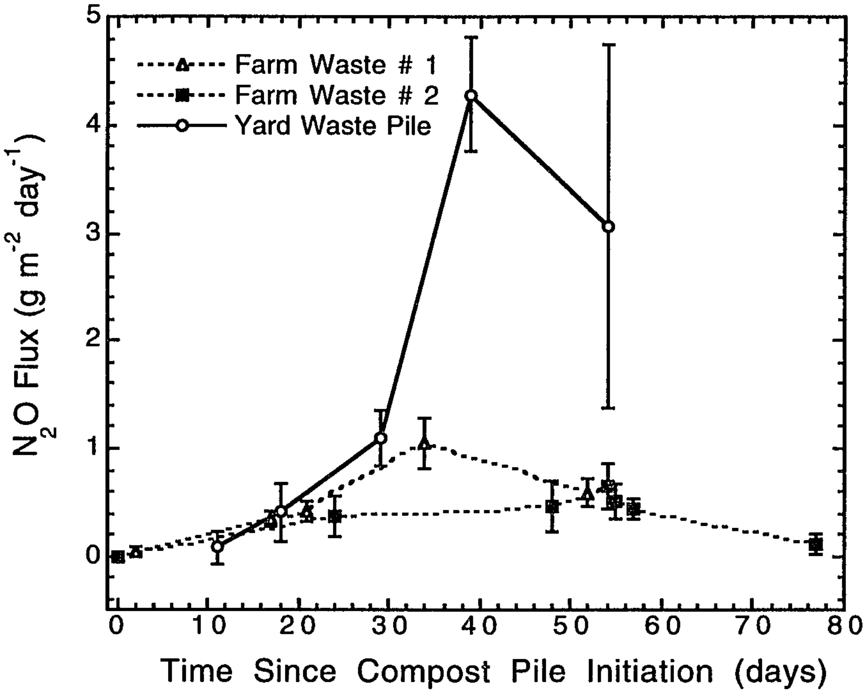

Figure 2-5. N_2O emissions from one yard waste and two livestock waste windrows. Symbols represent flux averages, error bars represent the range of the values.

A mass based N_2O emission factor can be estimated for the livestock waste from the measured emissions. A pile volume of 41.6 m^3 and an initial average dry bulk density of 133 kg m^{-3} yields a total pile dry mass of 5533 kg. Approximately 25 % or 1383 kg of this mass is manure. Total N_2O emissions, E_{N2O} from the compost can be estimated by

$$E_{N2O} = \frac{f\,A\,t}{m} \tag{3}$$

where f is the average emission rate, 0.5 g N_2O m^{-2} day^{-1}, A is the effective emitting surface area, 16 m^2, 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_2O emission factor is 0.5 g N_2O (kg dry waste)$^{-1}$.

N_2O 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_2O m^{-2} day^{-1}, 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_2O m^{-2} day^{-1}.

A mass based N_2O emission factor can be estimated for the yard waste, similarly to that of the livestock waste. A pile volume of 41.6 m^3 and an initial average dry bulk density of 196 kg m^{-3} yields a total pile dry mass of 8154 kg. Total N_2O emissions, E_{N2O} from each pile can be estimated by Equation 3 with an average emission rate, f of 1.8 g N_2O m^{-2} day^{-1}, an effective emitting surface area, A of 16 m^2, 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_2O emission factor is 0.3 g N_2O (kg dry waste)$^{-1}$.

Changes in environmental and operating conditions were observed to effect N_2O emissions from the compost piles. N_2O fluxes were significantly reduced when measured on a windy day. Average N_2O emissions from livestock waste pile 1 measured 35 days after pile initiation were 0.15 g N_2O m^{-2} day^{-1}, compared to 1.3 and 0.7 g N_2O m^{-2} day^{-1} measured 32 and 50 days after pile initiation, respectively. Average wind speed measured during the high wind period was approximately 3.5 m s^{-1}. Emissions under calm conditions are driven by gaseous diffusion of N_2O 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_2O production thereby reduce N_2O emissions.

The mechanical turning of the piles was observed to produce enhanced N_2O emissions. Fluxes from the livestock waste piles ranged from 19 to 39 g N_2O m^{-2} day^{-1} 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_2O 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_2O emissions during this period increased from a pre-rainfall emission rate of 0.4 g N_2O m^{-2} day^{-1} to an average rate of about 1.0 g N_2O m^{-2} day^{-1}. N_2O 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 g N_2O m^{-2} 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 g N_2O m^{-2} day^{-1} and were close to the level of pre-rainfall emissions by 95 hrs.

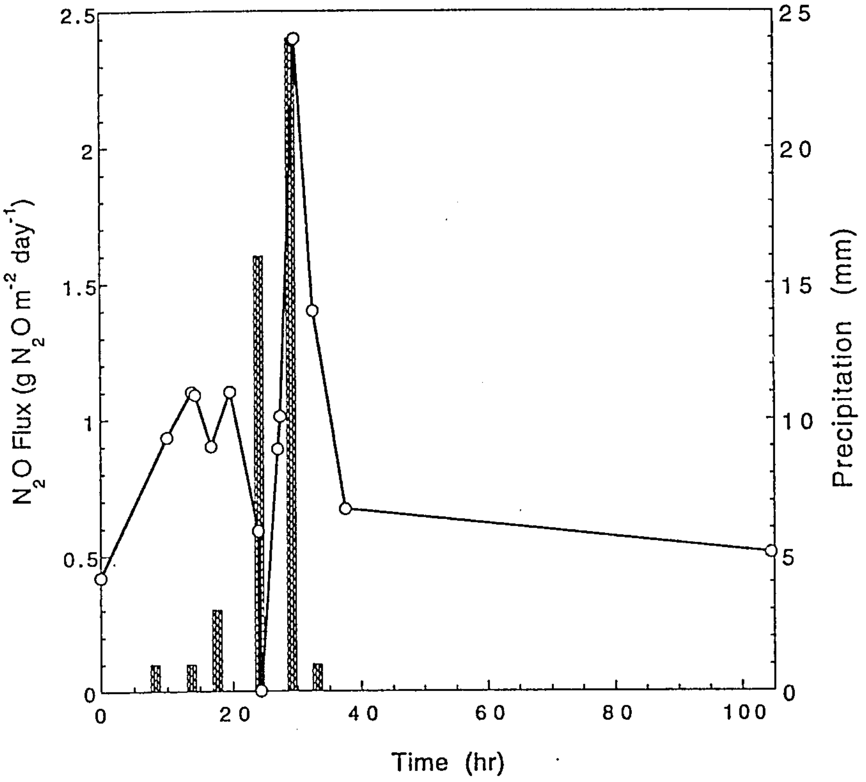

Figure 2-6. N_2O emissions at one location on livestock waste pile 1 during and after a significant precipitation event. Open circles represent measured N_2O fluxes, vertical bars represent precipitation events in half hour increments. Time is presented in hours since experiment initiation.

Discussion

Our results demonstrate the potential for significant emissions of N_2O from the treatment of high organic content wastes. N_2O 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_2O emissions from various waste management systems. Table 2-1 presents our estimates of N_2O emissions from the various waste types and and disposal systems evaluated below.

Table 2-1. Estimated emissions of N_2O from the evaluated waste systems.

Source	(10^{12} g N_2O yr^{-1})
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_2O 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 x 10^9 dry kg yr^{-1}.(*25*). Approximately 50 % was treated by ASP, 25 % by windrowing, and 25 % by in-vessel treatment. If we assume that the ultimate N_2O emission potential calculated from our observations, 0.7 g N_2O (kg dry waste)$^{-1}$, is applicable to all composting systems, albeit with potentially different generation periods, then total N_2O emissions from sludge composting in the U. S. in 1993 were 8.4 x 10^8 g N_2O yr^{-1}.

In Japan, approximately 1.1 x 10^8 dry kg yr^{-1} 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 x 10^7 g N_2O yr^{-1}.

Land disposal or spreading for agriculture and reclamation should also be considered when assessing the N_2O emissions potential of wastewater sludge disposal. Amending soils with wastewater sludge has been observed to substantially increase N_2O emissions (*26*). The observed N_2O 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_2O 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 x 10^9 dry kg yr^{-1} of municipal wastewater sludge was land disposed in 1992 (*24*). Assuming the ultimate N_2O yield from our compost observations, 0.7 g N_2O (kg dry waste)$^{-1}$, yields annual N_2O emissions of 1.7 x 10^9 g N_2O yr^{-1}.

In the U. S., approximately 1.6 x 10^9 dry kg yr^{-1} of municipal wastewater sludge was land disposed in 1988 (*28*). Assuming the ultimate N_2O yield from our compost observations, 0.7 g N_2O (kg dry waste)$^{-1}$, yields annual N_2O emissions of 1.1 x 10^9 g

N_2O yr^{-1}. Land disposal of sludge in Japan is not significant in the sludge disposal budget.

The total N_2O emissions potential from the wastewater sludge treatment and disposal systems considered is estimated to be 3.7×10^9 g N_2O 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 N_2O emissions from the treatment of wastewater sludge.

Yard waste composting also presents significant potential for N_2O 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 7.3×10^9 wet kg yr^{-1} in 1995 or 3.6×10^9 dry kg yr^{-1} assuming a composite moisture content of 50 % by weight (*29*). Assuming the ultimate N_2O yield derived from our observations, 0.3 g N_2O (kg dry waste)$^{-1}$, yields annual N_2O emissions from yard waste composting in the U. S. of 1.1×10^9 g N_2O 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 N_2O emissions from yard waste composting.

The treatment and disposal of livestock wastes appears to hold the greatest potential for N_2O emissions globally. Approximately 13.2×10^{12} wet kg 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 N_2O 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_2O, although disposal of the resulting sludge, which is generally field spread, may hold some potential for N_2O emissions.

Table 2-2. Estimated global livestock and poultry manure generation (10^{11} wet kg yr^{-1}) and waste management systems utilized in 1992 (*30*).

	System types					
Species	Anaerobic lagoons	Liquid systems	Daily spread	Solid storage and drylot	Pasture, range, paddock	Fuel generation[a]
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[b]	none	none	none	minimal	20.0	none
TOTAL	6.5	15.1	9.4	19.1	68.1	11.1

a: anaerobic digestion with gas burned for fuel.
b: includes goats, horses, mules, donkeys, and camels.

The potential N_2O 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_2O potential should be similar. We can estimate potential N_2O emissions using the global manure production numbers presented in Table 2-2. 11.2 x

10^{12} wet kg yr^{-1} of livestock and poultry manure were treated and disposed by the systems previously described that encourage N_2O production. Assuming a composite total solids content as excreted of 20 % (*31*) yields a manure dry mass of 2.3 x 10^{12} kg yr^{-1}. Using the mass based ultimate N_2O yield derived from our livestock waste compost observations, 0.5 g N_2O (kg dry waste)$^{-1}$, yields annual N_2O emissions from livestock waste of 1.2 x 10^{12} g N_2O yr^{-1}.

Khalil and Rasmussen recently observed elevated N_2O mixing ratios around manure piles and feed lots from which they extrapolated a range for N_2O emissions from cattle of 0.3 to 0.8 Tg yr^{-1} based on their observed ratios of methane to N_2O 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 x 10^{12} g N_2O yr^{-1}, very close to the upper end of the previously estimated range.

Conclusion

We have presented the results of N_2O 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_2O emissions from the treatment and disposal of organic wastes. Several further steps must be taken to better characterize this apparently significant N_2O 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_2O production. In addition, comprehensive field measurements must be performed to evaluate N_2O 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_2O emissions.

REFERENCES

(1) Houghton, J.T.; B.A. Callander; Varney S.K. *The Supplementary Report to the IPCC Scientific Assessment, Climate Change*; Cambridge University Press: New York, 1992.

(2) Warneck, P. *Chemistry of the Natural Atmosphere*; Academic Press: San Diego, 1988.

(3) Crutzen, P.J. *Quat. J. Royal Met. Soc.* **1970**, *96*, 320-325.

(4) Khalil, M.A.K. and R.A. Rasmussen, *J. of Geophys. Res.* **1992**, *97*, 14651-14660.

(5) Prinn, R.; Cunnold, D.; Rasmussen, R.; Simmonds, P.; Alyea, F.; Crawford, A.; Fraser, P.; Rosen, R. *J. Geophys. Res.* **1990**, *95*, 18369-18385.

(6) Bouwman, A.F. *Estimated global source distribution of nitrous oxide*, in *CH4 and N2O: Global Emissions and Controls from Rice Fields and Other Agricultural and Industrial Sources*; NIAES: Washington, DC, 1994.

(7) Lipschultz, F.; Zafiriou, O.; Wofsy, S.; McElroy, M.; Valois, F.; Watson, S. *Nature* **1981**, *294*, 641-643.

(8) Payne, W.J., *The status of nitric oxide and nitrous oxide as intermediates in denitrification*, in *Denitrification, nitrification and atmospheric nitrous oxide*, C.C. Delwiche, Editor; John Wiley: New York, NY, 1981.

(9) Cabrera, M.; Chiang, S.; Merka, W.; Pancorbo, O.; Thompson, S. *Plant and Soil* **1994**, *163*, 189-196.

(10) Bandibas, J.; Vermoesen, A.; De Groot, C.; Van Cleemput, O. *Soil Sci* **1994**, *158*, 106-114.

(11) Hochstein, L.; Betlach M.; Kritikos G. *Arch. Microbiol.* **1984**, *137*, 74-78.

(12) Klemedtsson, L.; Svensson B.; Rosswall T. *Biol. Fertil. Soils* **1988**, *6*, 106-111.

(13) Focht, D. *Soil Sci.* **1974**, *118*, 173-179.

(14) Knowles, R. *Microbiol. Rev.* **1982**, *46*, 43-70.

(15) Sikora, L.; Millner P.; Burge W. *Chemical and Microbial Aspects of Sludge Composting and Land Application*; U. S. Environmental Protection Agency, Engineering Research Laboratory: Washington, DC, 1986.

(16) Haug, R., *Compost Engineering: Principles and Practice*; Ann Arbor Science Publishers: Ann Arbor, MI, 1980.

(17) *Composting Yard Trimmings and Municipal Solid Waste*; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response; Washington, DC, 1994.

(18) Douglas, E. *The Transport and Fate of Nitrogen at a Farm and Yard Waste Composting Facility*; Master's Thesis, University of New Hampshire, December 1994.

(19) Livingston, G.; Hutchinson, G. *Enclosure-based measurement of trace gas exchange: applications and sources of error* in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, P.A. Matson and R.C. Harriss, Eds.; Blackwell Science: Cambridge, MA, 1995.

(20) Harriss, R.; Sebacher, D.; Bartlett, K.; Crill, P. *Global Biogeochemical Cycles* **1988**, *2*, 231-243.

(21) Crill, P.; Bartlett, K.; Harriss, R.; Gorham, E.; Verry, E.; Sebacher, D.; Madzar, L.; Sanner, W. *Global Biogeochem. Cycles* **1988**, *2*, 371-384.

(22) Topp, G.C. *Soil water content* in *Soil Sampling and Methods of Analysis*, M.R. Carter, Ed.; Lewis Publishers: Boca Raton, 1993.

(23) Martikainen, P; Nykanen, H.; Crill, P.; Silvola, J. *Nature* **1993**, *366*, 51-53.

(24) Lue-Hing, C.; Zenz D.; Kuchenrither, R. *Municipal Sewage Sludge Management: Processing, Utilization and Disposal*; Water Quality Management Series; Eckenfelder, W., Malina J., Patterson, J., Eds.; Technomic Publishing Co., Inc.: Lancaster, PA, 1992.

(25) Goldstein, N.; Steuteville, R. *1993 Biocycle Biosolids Survey: Biosolids Composting Makes Healthy Progress* in *Biocycle*; December 1993; 48-57.

(26) Benckiser, G.; Gaus, G.; Syring, K.; Haider, K.; Sauerbeck, D. *Zeitschrift Fuer Pflanzenernaehrung Und Bodenkunde* **1987**, *150*, 241-248.

(27) Paul, J.; Beauchamp, E.; Zhang, X. *Can. J. Soil Sci.* **1993**, *73*, 539-553.

(28) *The 1988 Needs Survey: Conveyance, Treatment, and Control of Municipal Wastewater, Combined Sewer Overflows, and Stormwater Runoff*; U. S. Environmental Protection Agency, U. S. Government Printing Office: Washington, DC, 1989.

(29) Kashmanian, R. *Predicting the tonnage of yard trimmings to be composted in 1996* in *Biocycle*; December 1993, 51-53.

(30) Safley, L.; Casada, M.; Woodbury, J.; Roos, K. *Global Methane Emissions from Livestock and Poultry Manure*; U. S. Environmental Protection Agency, U. S. Government Printing Office: Washington, DC, 1992; EPA/400/1-91/048.

(31) Taiganides, E. *Animal waste management and wastewater treatment* in *Animal Production and Environmental Health*, Strauch, D., Ed.; Elsevier: New York, 1987.

CHAPTER 3

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

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

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Summary

The influence of organic matter and soil moisture on the spatial distribution of methane (CH_4) oxidation was examined in temperate zone soils by laboratory incubations. CH_4 oxidation in soil cores exhibited distinct vertical zonation with maxima at 3 to 6 cm. The kinetic parameters of CH_4 oxidation were measured in soil composites. The maximum rate of CH_4 uptake, V_{max}, ranged from 6.8 to 7.4 nmol hr^{-1} g dry $soil^{-1}$ 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^{-1} g dry $soil^{-1}$ 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 (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±0.2 parts per billion by volume (ppbv) yr^{-1} during 1983-1991 to 1.8±1.6 ppbv yr^{-1} in 1992 [*Dlugokencky et al.*, 1994]. This decrease remains unexplained and emphasizes the need for further refinement of our understanding of the CH_4 budget. The removal of CH_4 from the atmosphere by reaction with hydroxyl radicals is estimated to be the largest CH_4 sink, while soil microbial oxidation is estimated to account for 5 to 20% of the total global CH_4 removal [*Bender and Conrad*, 1993; *Cicerone and Oremland*, 1988; *Koschorreck and Conrad*, 1993]. Rates of 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 CH_4 oxidation in soil samples collected within a 300-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 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, *p*H ranged from 4.4 to 4.9, bulk density ranged from 0.83 to 1.10 g cm^{-3}, 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, *p*H ranged from 3.5 to 4.4, bulk density ranged from 0.55 to 0.90 g cm^{-3}, 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 Core Samples			Grassy Area Random Sample Composite	Wooded Area Random Sample Composite
	0 to 6 cm	6 to 12 cm	12 to 18 cm		
Sand/silt/clay, % by wt.	45/35/20	40/43/17	33/43/24	43/37/20	38/42/20
*p*H, 20°C	4.1	4.4	4.7	4.5	3.8
Organic matter, % by wt.	11	6	3	9	14
Total nitrogen, % 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^2 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_2O 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 *p*H, 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 *p*H meter was then used to measure *p*H.

To determine CH_4 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_4 injection and every 2 hours thereafter for 8 to 12 hours. The minimum detectable rate of oxidation at an initial headspace CH_4 concentration of 250 parts per million by volume (ppmv) was 0.1 nmol CH_4 hr^{-1} g dry $soil^{-1}$.

CH_4 oxidation rates were calculated from the resulting time series data. Varying quantities of CH_4 were initially supplied to the jar headspaces, which resulted in first-order or pseudo-zeroth-order oxidation kinetics depending on the initial CH_4 concentration. First-order oxidation kinetics were characterized by exponentially decreasing headspace CH_4 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_4 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_4 oxidation. All oxidation rates were normalized to dry soil sample mass.

Incubation headspace samples were analyzed for CH_4 within 10 min of collection by direct injection into a Shimadzu GC-14A gas chromatograph (GC). All analyses for CH_4 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_4 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_4 oxidation in the soil profile. Core samples were subjected to incubation experiments using headspace CH_4 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_4 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_4 oxidation rates with maximums occurring in the 3 to 6 cm depth interval at all initial CH_4 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_4 concentration of 220 ppmv was 6.1 nmol CH_4 hr^{-1} g dry $soil^{-1}$ in the grassy area core and 7.1 nmol CH_4 hr^{-1} g dry $soil^{-1}$ in the wooded area core. All subsequent soil samples were collected from a depth of 3 to 6 cm.

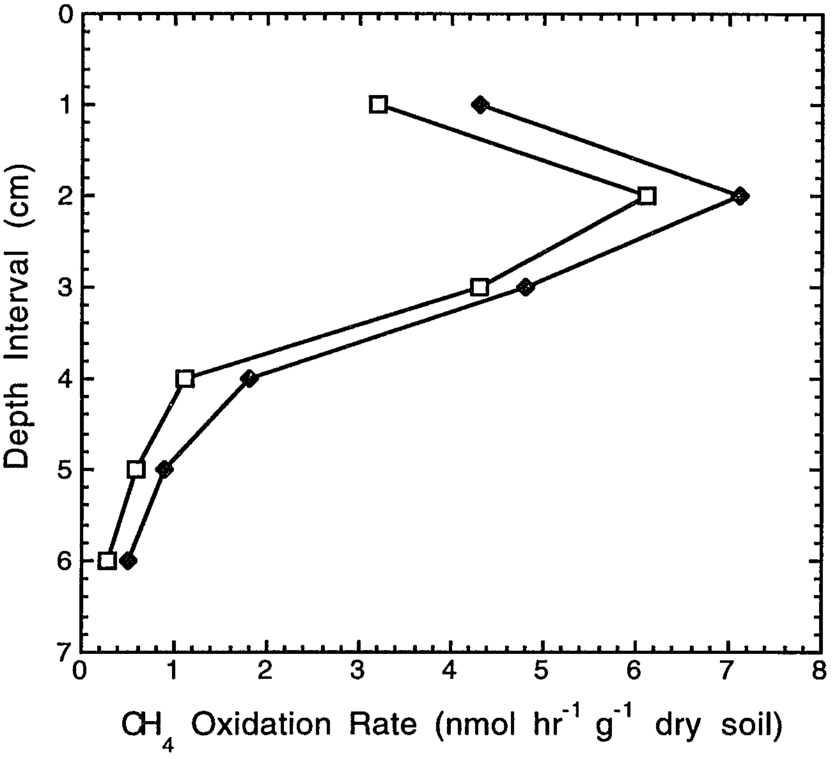

Figure 3-1. Methane oxidation rates for soil core samples from the grassy area (open squares) and the wooded area (solid diamonds). Incubations were performed at initial headspace methane concentrations of 220 to 250 parts per million by volume (ppmv). Samples were collected in 3-cm increments from the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

Kinetic Parameters

An analysis of the CH_4 oxidizing capacity of the soils from the wooded and grassy areas was performed to determine their associated kinetic parameters: the maximum rate of CH_4 oxidation (V_{max}) and the apparent half saturation constant (K_m). Soil samples were collected from the depth of maximum CH_4 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_4 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_4 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

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

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^{-1} g^{-1} and 7.4 nmol hr^{-1} g^{-1} 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.

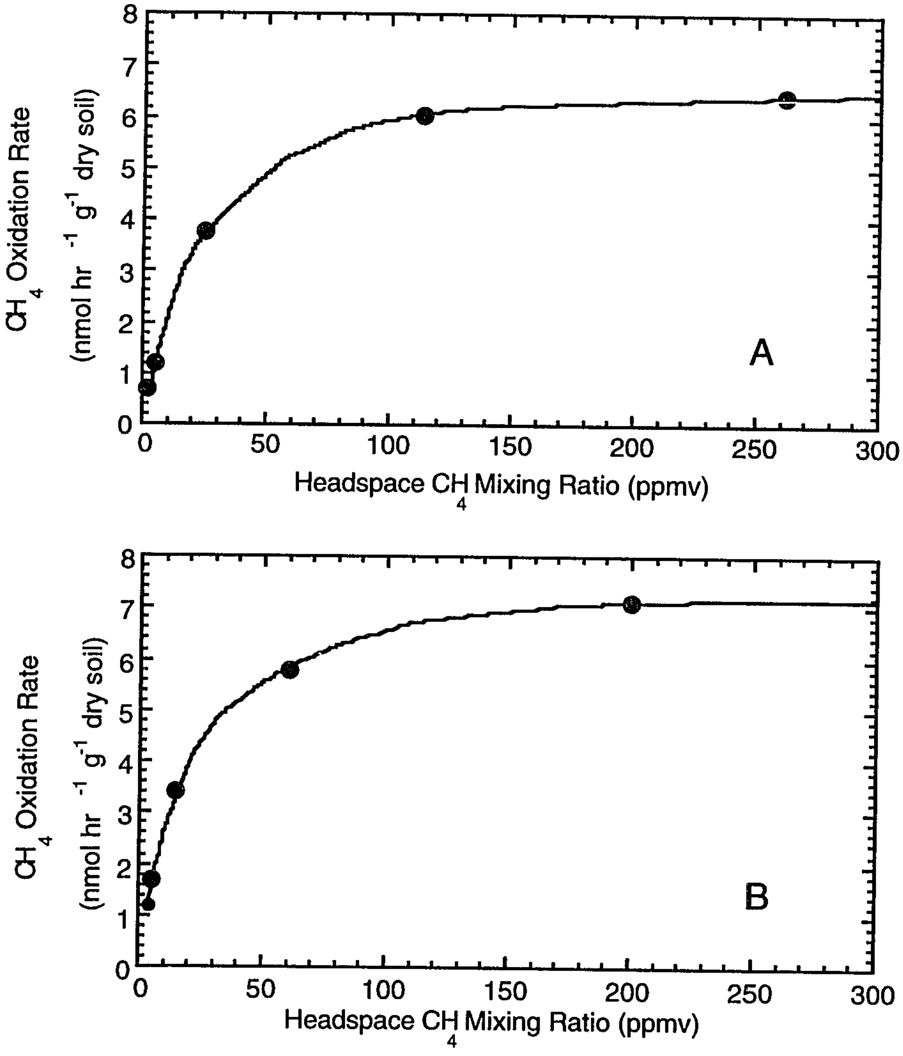

Figure 3-2. Substrate saturation curves of methane oxidation in (A) the grassy area soils and (B) the wooded area soils.

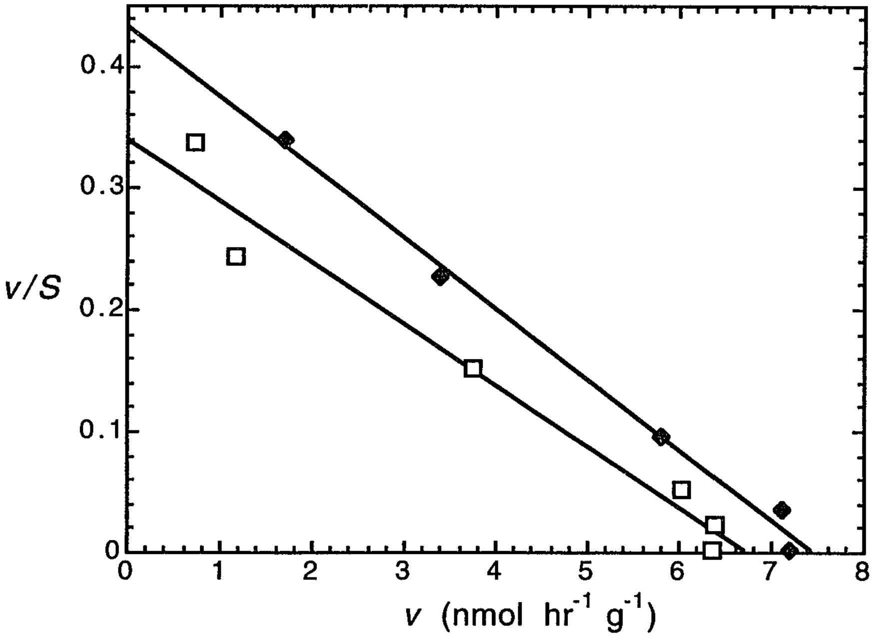

Figure 3-3. Linearization of the grassy area (open squares) and wooded area (solid diamonds) data from Figure 3-2 where *S* is the initial headspace methane concentration and *v* is the oxidation rate per gram of dry soil. The linear fit of the data yields K_m values of 19.9 ppmv for the grassy area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

The calculated kinetic parameters of CH_4 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_4 oxidation in various soils.

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

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_4 oxidizing capacity of the soils in both areas.

The results of the kinetic experiments established the appropriate range of initial headspace CH_4 concentrations used during subsequent moisture manipulation experiments with these soils. An initial concentration range of 250 to 300 ppmv CH_4 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_4 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_4 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^{-1} g dry $soil^{-1}$ in the grassy area soils and from 3.7 to 9.0 nmol hr^{-1} g dry $soil^{-1}$ 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_4 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_4 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_4 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.

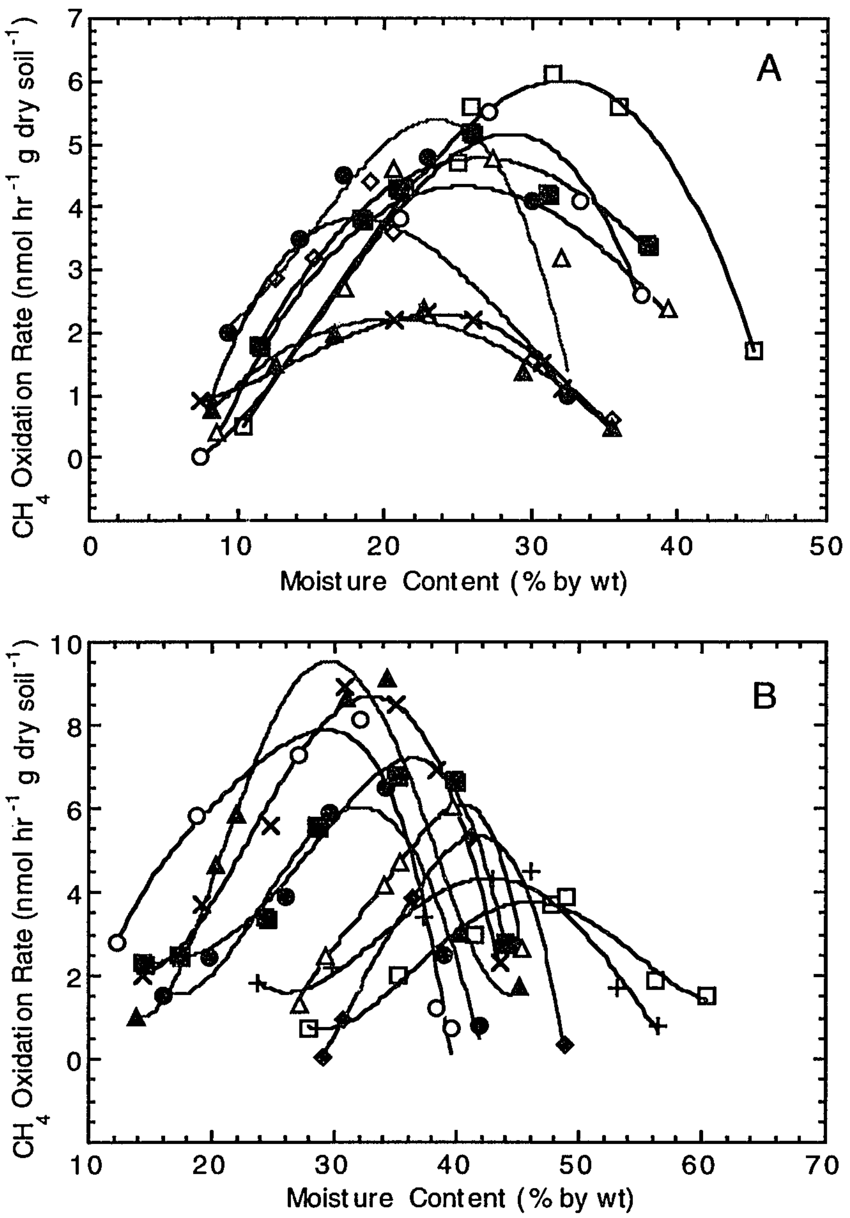

Figure 3-4. Methane oxidation in random samples from (A) the grassy area soils and (B) the wooded area soils as a function of increasing sample moisture contents. The results of individual samples incubations, represented by different symbols, are fit by second-order polynomials.

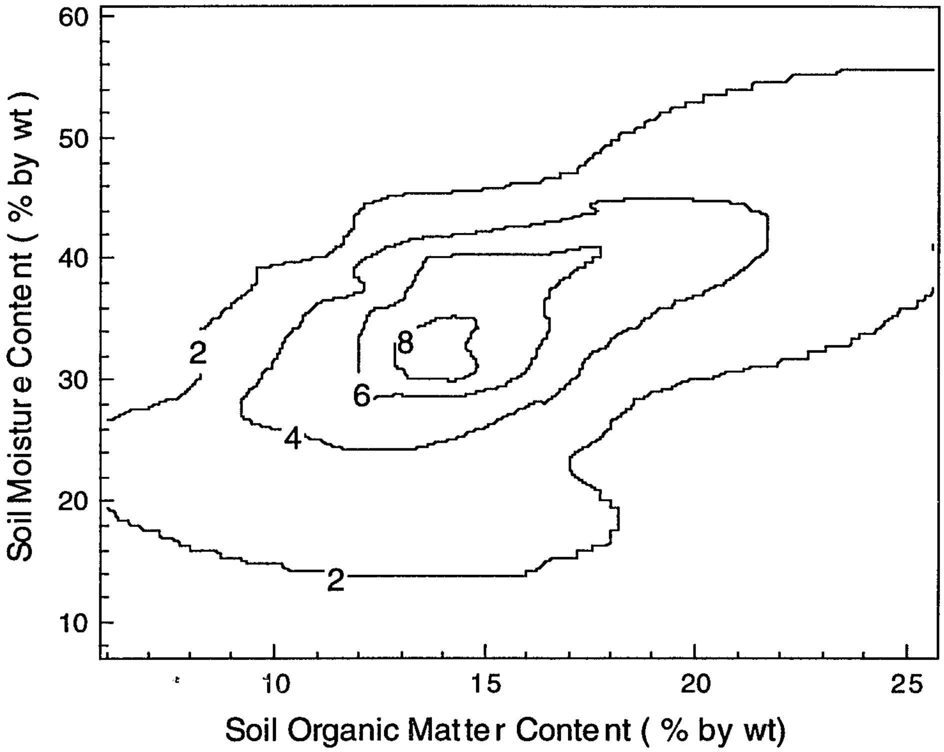

Figure 3-5. Methane oxidation contours in nanomoles per hour per gram of dry soil as a function of both sample moisture and organic matter contents. Plot includes incubation results from all samples.

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.

REFERENCES

Adamsen, A. P. S., and G. M. King, Methane consumption in temperate and subarctic forest soils: Rates, vertical zonation, and responses to water and nitrogen, *Appl. Environ. Microbiol., 59,* 485-490, 1993.

Amaral, J. A., and R. Knowles, Methane metabolism in a temperate swamp, *Appl. Environ. Microbiol., 60,* 3945-3951, 1994.

Armstrong, F. B., *Biochemistry,* Oxford University Press, New York, 1989.

Bender, M. and R. Conrad, Kinetics of methane oxidation in oxic soils, *Chemosphere, 26,* 687-696, 1993.

Cicerone, R. J., and R. S. Oremland, Biogeochemical aspects of atmospheric methane, *Global Biogeochemical Cycles, 2,* 299-327, 1988.

Crill, P. M., Seasonal patterns of methane uptake and carbon dioxide release by a temperate woodland soil, *Global Biogeochemical Cycles, 5,* 319-334, 1991.

Culley, J. L. B., Density and compressibility, in *Soil Sampling and Methods of Analysis,* edited by M. R. Carter, pp. 529-539, Lewis, Boca Raton, Fla., 1993.

Davies, B. E., Loss-on-ignition as an estimate of soil organic matter, *Soil Sci. Soc. Amer. Proc., 38,* 150-151, 1974.

Delmas, R. A., R. Marenco, J. P. Tathy, B. Cros, and J. G. R. Baudet, Sources and sinks of methane in the African savanna. CH_4 emissions from biomass burning, *J. Geophys. Res., 96,* 7287-7299, 1991.

Dlugokencky, E. J., K. A. Masaire, P. M. Lang, P. P. Tans, L. P. Steele, and E. G. Nisbet, A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992, *Geophys. Res. Lett., 21,* 45-48, 1994.

Federer, C. A., D. E. Turcotte, and C. T. Smith, The organic fraction - Bulk density relationship and the expression of nutrient content in forest soils, *Can. J. For. Res., 23,* 1026-1032, 1993.

Harriss, R. C., D. I. Sebacher, and F. P. Day Jr., Methane flux in the Great Dismal Swamp, *Nature, 297,* 673-674, 1982.

Koschorreck, M., and R. Conrad, Oxidation of atmospheric methane in soil: Measurements in the field, in soil cores, and in soil samples, *Global Biogeochemical Cycles, 7,* 109-121, 1993.

Mosier, A., D. Schimel, D. Valentine, K. Bronson, and W. Parton, Methane and nitrous oxide fluxes in native, fertilized and cultivated grasslands, *Nature, 350,* 330-332, 1991.

Seiler, W., R. Conrad, and D. Scharffe, Field studies of methane emission from termite nests into the atmosphere and measurements of methane uptake by tropical soils, *J. Atmos. Chem., 1,* 171-186, 1984.

Steudler, P. A., R. D. Bowden, J. M. Melillo, and J. D. Aber, Influence of nitrogen fertilization on methane uptake in temperate forest soils, *Nature, 341,* 314-316, 1989.

Topp, G. C., Soil water content, in *Soil Sampling and Methods of Analysis*, edited by M. R. Carter, pp. 541-557, Lewis, Boca Raton, Fla., 1993.

Vieira, F. J., and R. W. Bond, Soil survey of Strafford County, New Hampshire, U. S. Dept. of Agriculture, Soil Conservation Service, Washington, D. C., 1971.

Whalen, S. C., W. S. Reeburgh, and K. A. Sandbeck, Rapid methane oxidation in a landfill cover soil, *Appl. Environ. Microbiol., 56,* 3405-3411, 1990.

CHAPTER 4

LANDFILL METHANE EMISSIONS MEASURED BY STATIC ENCLOSURE AND ATMOSPHERIC TRACER METHODS

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LANDFILL METHANE EMISSIONS MEASURED BY STATIC ENCLOSURE AND ATMOSPHERIC TRACER METHODS

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Summary

Methane (CH_4) 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_4 min^{-1}. Omnidirectional variograms displayed spatial correlation among CH_4 fluxes below a separation distance of 7 m. Eleven tracer tests, using SF_6 as a tracer gas, resulted in a mean emissions estimate of 17750 liters CH_4 min^{-1}. The favorable agreement between the emission estimates was further refined using the observed relationship between atmospheric pressure and CH_4 flux. This resulted in a pressure corrected tracer flux estimate of whole landfill emissions of 16740 liters CH_4 min^{-1}. 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_4 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_4 emitted annually to the atmosphere [*IPCC*, 1992]. Landfills have been identified as the largest source of anthropogenic CH_4 emissions in the United States, accounting for approximately 25 % of CH_4 emissions annually [*USEPA*, 1994]. However, there remains significant uncertainty associated with this estimate.

Here we report the results of a comprehensive investigation of CH_4 emissions to the atmosphere from a municipal solid waste (MSW) landfill in the northeastern United States. Two methods for determining CH_4 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_4 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_2) and carbon dioxide (CO_2). The fatty acid substrates such as butyrate and propionate are then available to acetogenic bacteria which convert them to acetate, H_2, and CO_2. Methanogenic bacteria can then utilize acetate and H_2 as energy sources in the final stages of CH_4 formation.

The largest fraction of landfill CH_4 is formed from acetic acid by decarboxylation

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad (1)$$

which also results in the formation of substantial quantities of CO_2. The remaining CH_4 is generated by CO_2 reduction with H_2 or organic molecules (H_2A) as H donors

$$CO_2 + 4H_2A \rightarrow CH_4 + 2H_2O + 4A \qquad (2)$$

The gas formed after the stabilization of anaerobic conditions is approximately composed of 50 % CH_4, 45 % CO_2, 3 % N_2, 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_4. *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_4 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_4 emissions to the atmosphere than currently exists. Relatively few field studies have been performed to quantify landfill CH_4 emissions from singular landfill sites to the atmosphere. *Bogner et al.* [1993] estimated CH_4 emissions from a landfill in Illinois, USA using limited data from static enclosure and pressure flow gas measurements. *Nozhevnikova et al.* [1993] described CH_4 emissions from several landfills around Moscow, Russia using limited static enclosure measurements. *Yasunori and Wakita* [1993] estimate CH_4 emissions from a landfill adjacent to Tokyo Bay, Japan using a continuous CH_4 measuring device and atmospheric dispersion techniques. Our study supplements these results by providing a comprehensive estimate of whole landfill CH_4 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 1.05×10^8 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 1.33×10^8 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_4 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_4 mixing ratio within the chamber while placing it on the soil surface. The screening results indicated significantly higher CH_4 emissions per unit area in the MSW landfill compared to those observed in the C&D landfill. Negligible CH_4 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^2 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 $area^{-1}$ $time^{-1}$) 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 CH_4 mixing ratio in the enclosure headspace. $\frac{\Delta C}{\Delta t}$ is calculated by linear regression of the 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 CH_4 flux was 10 mg m^{-2} 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 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.

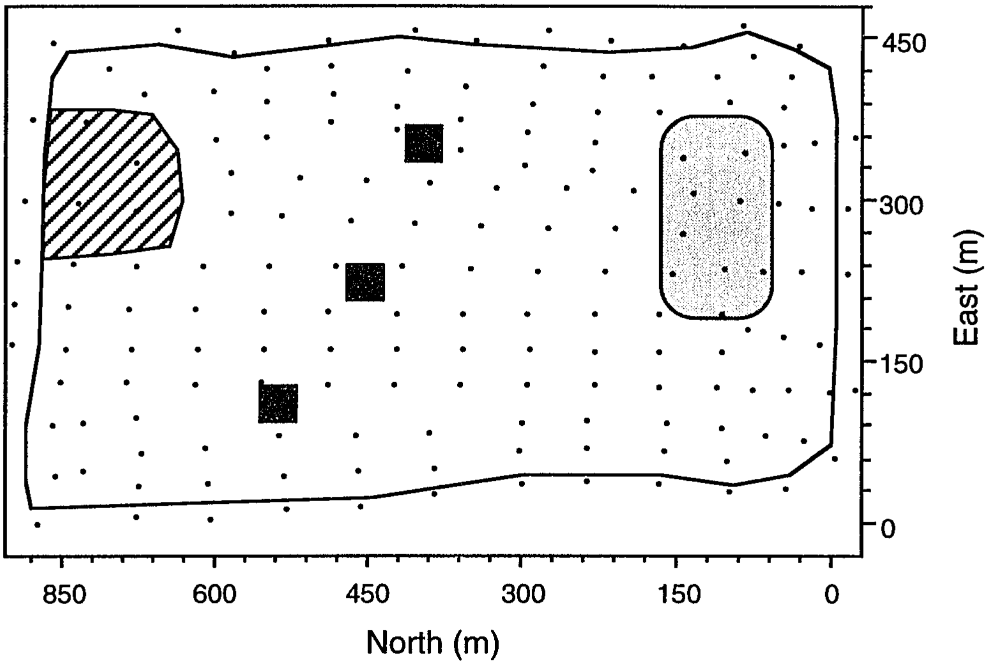

Figure 4-1. Base map of the MSW landfill. Fluxes were collected on an irregular 60 m grid resolution at locations represented by the dots. The black squares represent the areas of finer resolution sampling (6 m and 0.6 m grids). The approximate boundary of the waste is represented by the solid line, 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 CH_4 emission rate from the landfill. Pure sulfur hexafluoride (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 CH_4 emission rate can be obtained directly by the ratio method as

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

where Q_m is the CH_4 flux rate, Q_t is the SF_6 tracer release rate, C_m is the measured CH_4 mixing ratio above background, and C_t is the measured mixing ratio of the 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.

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. CH_4 and SF_6 were measured in the resulting plume 1.2 to 3.5 km from the downwind edge of the landfill.

Both the CH_4 and 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 CH_4 and 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_4 as described by *Crill et al.* [1988]. CH_4 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_4 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_4 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_4 absorption line at 2947.91 cm^{-1} 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_4 mixing ratio. The instrument is sensitive to changes in ambient mixing ratio of about 0.3 % or 5 ppb CH_4 (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_6 tracer concurrent with the Aerodyne RTI measurement of CH_4

[*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_6/air standards from Scott-Marin, Inc. over the range 25 ppt to 10 ppb (±5 % certified accuracy).

A LiCor infrared CO_2/ H_2O analyzer (LI-6262) was used to measure ambient CO_2 mixing ratios. The instrument was calibrated frequently using a CO_2 free gas and a known CO_2 standard gas. The CO_2 instrument was used to identify anomalous CH_4 sources. Significant CH_4 mixing ratios accompanied by high ambient CO_2 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 ±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_4 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_4 at least 4 times to obtain precision of 10 ppb or less. Canister samples were analyzed for SF_6 using a HP5880 electron capture gas chromatograph calibrated with standards from Scott-Marin, 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^{-1} 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_4 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_4 mixing ratio above background typically ranged from 100–200 ppb yielding an uncertainty range of 7–14 %. The 5 % uncertainty in SF_6 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.

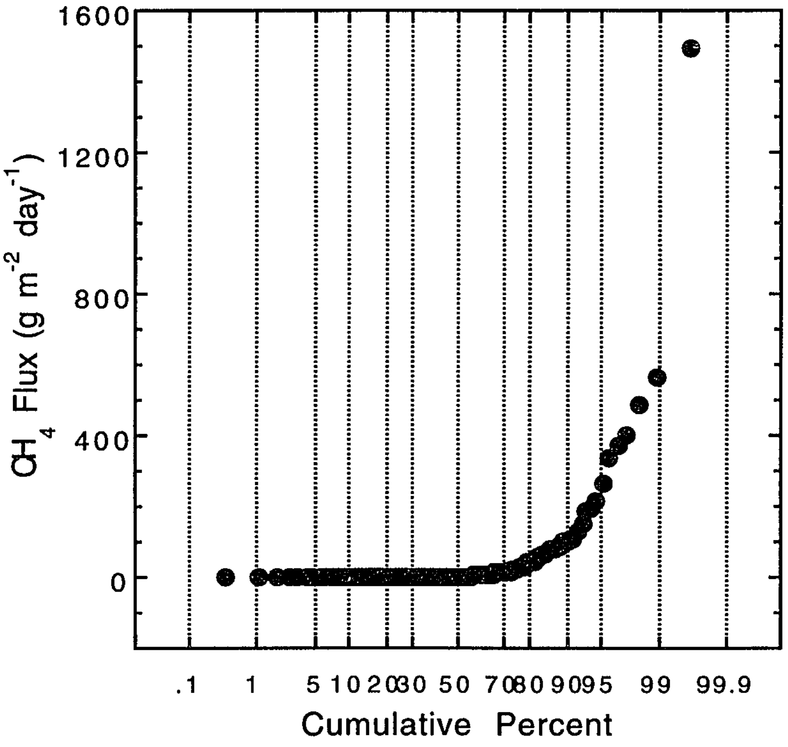

Figure 4-2. Cumulative probability plot of the untransformed coarse grid CH_4 fluxes.

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_4 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.

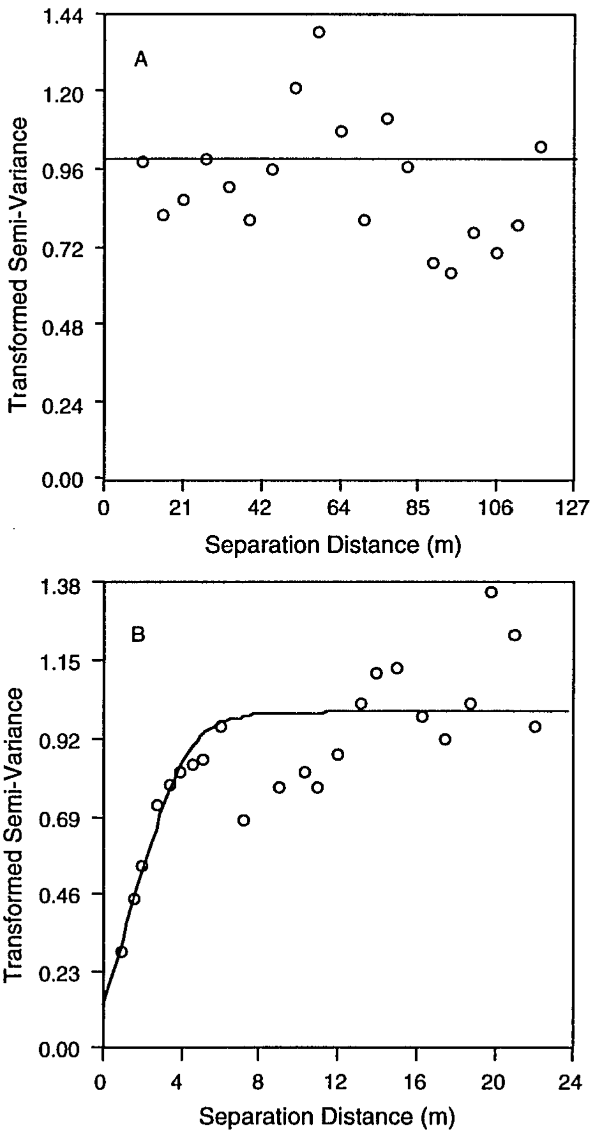

Figure 4-3. Variograms for CH_4 fluxes measured at (A) 6 m, and (B) 0.6 m sampling resolution on square grids. Lines are representative best fit models of the data. The horizontal line in (A) is a linear "pure nugget" model and the line in (B) is a mixed exponential-gaussian model. CH_4 fluxes exhibit 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.

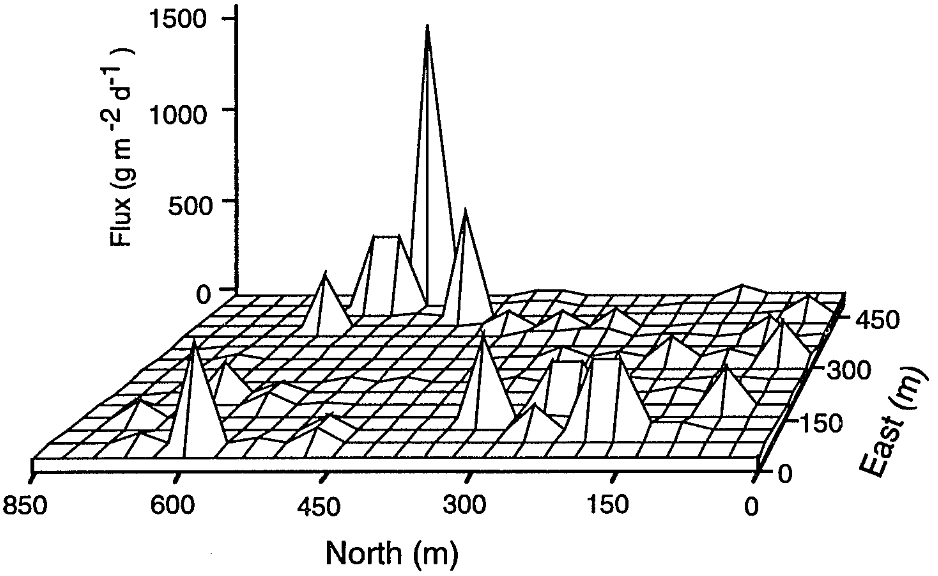

Figure 4-4. Map of CH_4 emissions from the MSW landfill based on linear interpolation of the coarse grid flux data. CH_4 flux is represented on the vertical axis in g CH_4 m^{-2} day^{-1}.

Whole landfill CH_4 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_4 m^{-2} day^{-1} with a mean and coefficient of variation (CV=[standard deviation/mean]x100) of 45±324 g CH_4 m^{-2} day^{-1}.

The estimated total emission from this area based on an emitting surface of 33.5 hectares is 16000 liters CH_4 min^{-1}. Flux values in the C&D landfill were considerably lower, ranging from the detection limit to 144 g CH_4 m^{-2} day^{-1} with a mean and CV of 3.2±95 g CH_4 m^{-2} day^{-1}. The estimated total emission from this area based on an emitting surface of 5.5 hectares is 200 liters CH_4 min^{-1}. The estimated total CH_4 emission from the site based on the enclosure measurements is 16200 liters CH_4 min^{-1}.

Atmospheric Tracer Measurements

CH_4 emissions were measured by atmospheric tracer methods over the course of 5 days of field experiments during October and November, 1994. Initial CH_4 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_4 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_4 min^{-1}.

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.

	Canister samples		Real-time samples	
Test number	CH_4 emission rate (liters min^{-1})	Coefficient of variation (%)	CH_4 emission rate (liters min^{-1})	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_4 emissions and atmospheric pressure consistent with results of other investigators [*Bogner et al.*, 1990; *Young*, 1992].

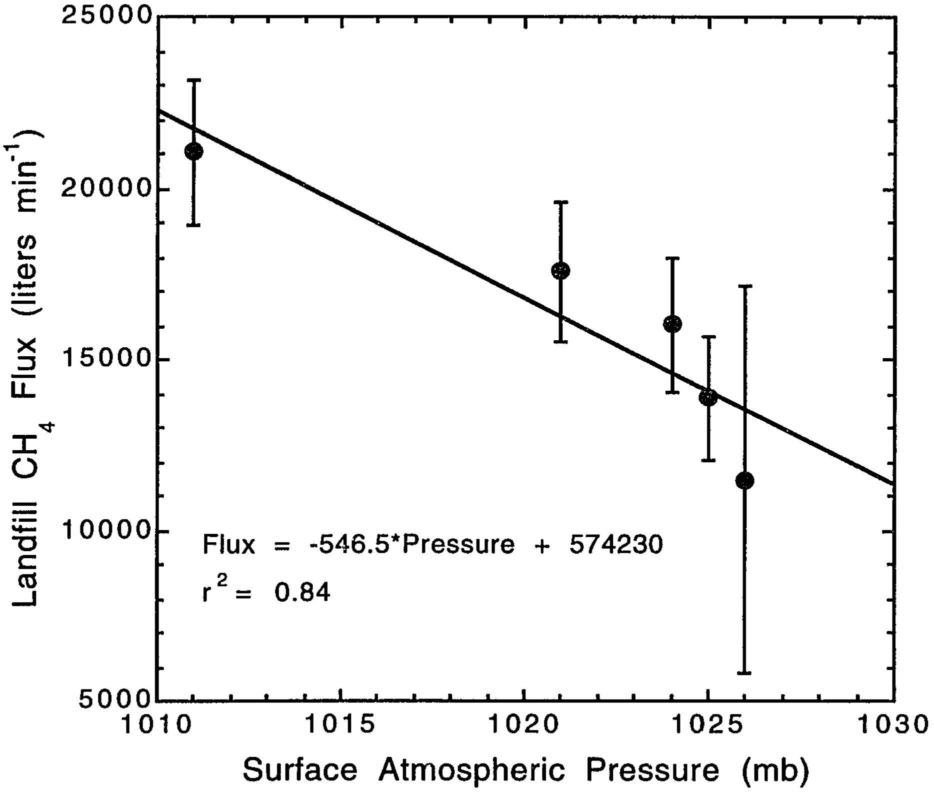

Figure 4-5. Daily average whole landfill CH_4 emissions observed by the tracer method plotted as a function of the average atmospheric pressure observed during each measurement period. Error bars represent the standard deviations of the acceptable values on each day.

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_4 flux predicted at that pressure by the atmospheric pressure versus flux relationship is 16740 liters CH_4 min^{-1}. This value compares even more favorably to the enclosure based estimate of 16200 liters CH_4 min^{-1} than to the uncorrected tracer method mean estimate of 17750 liters CH_4 min^{-1}.

The observed range of CH_4 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_4 m^{-2} day^{-1} to 20 g CH_4 m^{-2} day^{-1} using enclosure methods and calculated fluxes as high as 331 g CH_4 m^{-2} day^{-1} 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_4 m^{-2} day^{-1} 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_4 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 (10^6 wet kg)	Decomposability category[a]	Fraction of total type (%)[b]	Moisture content (%)[a]	Mass in place (10^6 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_4 generation rate, assuming a total waste dry mass of 1.4×10^9 kg and a CH_4 emission rate of 16450 liters CH_4 min^{-1}, calculated as the mean of the enclosure based estimate and the tracer based linear model estimate, is 0.006 m^3 CH_4 (kg dry waste)$^{-1}$ yr^{-1}. The total landfill gas generated, assuming a 50 % CH_4 - 50 % CO_2 composition based on gas samples from onsite test wells, can be calculated by

$$LF = \frac{\left[\dfrac{CH_4}{(1 - OX)}\right]}{Frac_{CH4}} \qquad (3)$$

where LF is the landfill gas emitted, CH_4 is the CH_4 emission estimate, OX is the estimated fractional whole landfill oxidation rate, and $Frac_{CH4}$ is the fractional composition of the landfill gas. Assuming a landfill gas composition of 50 % CH_4 and an estimated 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 m^3 landfill gas (kg dry waste)$^{-1}$ 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 (m^3 dry kg^{-1} yr^{-1})	Comments
this study	0.015	assumes 50 % CH_4 content and 21 % oxidation rate.
[*Rathmell*, 1991]	0.0062	field production estimate Turnkey, landfill Rochester, NH.
[*Augenstein*, 1990]	0.0031-0.011	limits based on field production data.
[*Pacey and Dietz*, 1986]	0.032	field control cell, Mountain View, CA project.
[*EMCON*, 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.

REFERENCES

Augenstein, D.C., Greenhouse Effect Contributions of U. S. Landfill Methane, in *13th Annual Landfill Gas Symposium*, GRCDA, Lincolnshire, Illinois, 1990.

Augenstein, D.C., and J. Pacey, Modeling Landfill Methane Generation, in *Sardinia '91 - Third International Symposium on Landfill Gas*, 1991.

Benner, R.L., and B. Lamb, A fast response continuous analyzer for halogenated atmospheric tracers, *J. Atmos. Ocean. Technol.*, *2* (4), 582-589, 1985.

Bingemer, H.G., and P.J. Crutzen, The production of methane from solid waste, *J. Geophys. Res.*, *92* (D2), 2181-2187, 1987.

Bogner, J., K. Spokas, and J. Jolas, Comparison of measured and calculated methane emissions at mallard lake landfill, Dupage County, Illinois, USA, in *IV International Landfill Symposium*, S. Margherita di Pula, Italy, 1993.

Bogner, J.E., M. Vogt, and R.M. Miller, Studies of soil gas, gas generation, and shallow microbial activity at Mallard North Landfill, Dupage County, Illinois, in *13th Annual Landfill Gas Symposium*, U. S. Dept. of Energy, Lincolnshire, IL, 1990.

Boone, D.R., Ecology of Methanogenesis, in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes*, edited by J.E. Rogers, and W.B. Whitman, pp. 57-70, American Society for Microbiology, Washington, D. C., 1991.

Cicerone, R.J., and R.S. Oremland, Biogeochemical aspects of atmospheric methane, *Glob. Biogeochem. Cycles*, *2* (4), 299-327, 1988.

Crill, P.M., K.B. Bartlett, R.C. Harriss, E. Gorham, E.S. Verry, D.I. Sebacher, L. Madzar, and W. Sanner, Methane flux from minnesota peatlands, *Glob. Biogeochem. Cycles*, *2* (4), 371-384, 1988.

Czepiel, P., B. Mosher, P. Crill, and R. Harriss, Quantifying the effect of oxidation on landfill methane emissions, *J. Geophys. Res.*, this issue.

Deutsch, C.V., and A.G. Journel, *GSLIB: Geostatistical Software Library and User's Guide*, 340 pp., Oxford University Press, New York, 1992.

EMCON, *State of the Art of Methane Gas Enhancement in Landfills*, Argonne National Laboratory, ANL/CNSV-23, 1981.

Farquhar, G.J., and F.A. Rovers, Gas production during refuse decomposition, *Water, Air, Soil Poll.*, *2*, 483-495, 1973.

Franklin Associates, *Characterization of Municipal Solid Waste in the U. S.*, U. S. EPA, WH-565E, 1988.

Ham, R.K., K.K. Hekimian, S.L. Katten, W.J. Lockman, R.J. Lofy, D.E. McFaddin, and E.J. Daley, *Recovery, Processing, and Utilization of Gas from Sanitary Landfills*, Solid and Hazardous Waste Research Division, U.S. Environmental Protection Agency, EPA 68-03-2536, 1979.

Howard, T., B. Lamb, and P. Zimmerman, Measurement of VOC emission fluxes from waste treatment and disposal systems using an atmospheric tracer flux, *J. Air & Waste Manage. Assoc.*, *42*, 1336-1344, 1992.

IPCC, *Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment*, 196 pp., Cambridge University Press, New York, 1992.

Isaaks, E.H., and R.M. Srivastava, *An Introduction to Applied Geostatistics*, 561 pp., Oxford University Press, New York, 1989.

Lamb, B., B. McManus, J. Shorter, C. Kolb, B. Mosher, R. Harriss, E. Allwine, D. Blaha, T. Howard, A. Guenther, R. Lott, R. Siverson, H. Westberg, and P. Zimmerman, Developmentof atmospheric tracer methods to measure methane emissions from natural gas facilities and urban areas, *Environ. Sci. Tech.*, 1995.

Lamb, B., H. Westberg, and E. Allwine, Isoprene emission fluxes determined by atmospheric tracer techniques, *Atmos. Environ.*, *20*, 1-8, 1986.

Livingston, G.P., and G.L. Hutchinson, Enclosure-based measurement of trace gas exchange: applications and sources of error, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P.A. Matson, and R.C. Harriss, pp. 360, Blackwell Science, Cambridge, MA, 1995.

McManus, J.B., P.L. Kebabian, and C.E. Kolb, Atmospheric methane measurement instrument using a Zeeman-split He-Ne laser, *Appl. Opt.*, *28* (23), 5016-5023, 1989.

McManus, J.B., J.H. Shorter, P.L. Kebabian, C.E. Kolb, B. Mosher, R.C. Harriss, B. Lamb, E. Allwine, and T. Howard, Field measurements of atmospheric methane with a HeNe laser-based real-time instrument, *SPIE Proc., Opt. Meth. Atmos. Chem.*, *1715*, 138-150, 1992.

Nozhevnikova, A.N., A.B. Lifshitz, V.S. Lebedev, and G.A. Zavarzin, Emission of methane into the atmosphere from landfills in the former USSR, *Chemosphere*, *26* (1-4), 401-417, 1993.

Pacey, J.G., and A.M. Dietz, Gas Production Enhancement Techniques, in *Energy from Landfill Gas Conference*, Solihull, England, 1986.

Parkin, G., and W. Owen, Fundamentals of anaerobic digestion of wastewater sludges, *J. Environ. Eng.*, *112* (5), 867-920, 1986.

Peer, R.L., D.L. Epperson, D.L. Campbell, and P. von Brook, *Development of an Empirical Model of Methane Emissions from Landfills*, USEPA, Final Report, EPA-600/R-92-037, 1992.

Rasmussen, R.A., and M.A.K. Khalil, Atmospheric methane in the recent and ancient atmospheres: concentrations, trends, and interhemispheric gradient, *J. Geophys. Res.*, *89*, 11599-11605, 1984.

Rathmell, R., Personal Communication. Project manager, Waste Management, Inc. Discussion regarding the production and recovery rate of landfill gas from the Turnkey Landfill in Rochester, N. H., 1991.

Steuteville, R., The State of Garbage in America, *Biocycle, 36* (4), 54-63, 1995.

Straub, W.A., Personal Communication, CMA Engineers, Letter estimating waste in place at the Nashua municipal landfill, 1995.

Tohjima, Y., and H. Wakita, Estimation of methane discharge from a plume: a case of landfill, *Geophys. Res. Lett.*, *20*, 2067-2070, 1993.

Thorneloe, S., M. Barlaz, R. Peer, L. Huff, L. Davis, and J. Mangino, Waste Management, in *Atmospheric Methane: Sources, Sinks and Role in Global Change*, edited by M.A.K. Khalil, Springer-Verlag, Berlin, 1993.

USEPA, *International Anthropogenic Methane Emissions: Estimates for 1990*, U.S. Environmental Protection Agency, Office of Policy, Planning and Evaluation, Report to Congress, EPA 230-R-93-010, 1994.

Young, A., The effects of fluctuations in atmospheric pressure on landfill gas migration and composition,*Water, Air, and Soil Pollution*, *64*, 601-616, 1992.

CHAPTER 5

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_4) in a landfill soil cover at the Nashua, NH municipal landfill. Soil samples from locations of CH_4 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_4 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_4 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_4, 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_4 emissions in the United States and are estimated to account for 3-19% of anthropogenic CH_4 emissions globally [*USEPA*, 1994]. The microbially mediated oxidation of landfill CH_4 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_4 in landfill cover soils has been observed in several laboratory investigations and estimates of total landfill CH_4 oxidation range from 7 to 50 % of CH_4 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_4 in a landfill soil cover. Surface CH_4 fluxes and soil gas CH_4 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_4 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, % sand/silt/clay	53/18/29
Texture coefficient of variation, ±%	11/17/16
Mean pH, 20°C[a]	7.8±14
Mean organic matter content, % by wt[a]	1.8±25

a: ± 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^2 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_4 flux was 10 mg m^{-2} day^{-1}.

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_4. Also, selected gas samples were analyzed for O_2. 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_4 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_4 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_4 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_4 mixing ratio of 2 % was 10 nmol CH_4 hr^{-1} g dry $soil^{-1}$.

Incubations to determine the effect of reduced O_2 mixing ratios on CH_4 oxidation were performed by flushing the jar headspaces with air/N_2 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_4 oxidation rates were calculated from the resulting time series data. Varying quantities of CH_4 were supplied to the jar headspaces which resulted in first order or pseudo-zeroeth order oxidation kinetics depending on the initial CH_4 mixing ratio. First order oxidation kinetics were characterized by exponentially decreasing headspace CH_4 mixing ratios and oxidation rates were calculated from the rate constant of the exponential curve fit. Pseudo-zeroeth order kinetics were characterized by a linear decrease in headspace CH_4 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_4 oxidation. All oxidation rates were normalized to dry soil sample mass.

Analytical Analysis

CH_4 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_2 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_4 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_4 mixing ratios ranging from 1.8 to 2 % during jar incubations at 21°C. The resulting linear drawdown of CH_4 in each jar headspace typified the pseudo-zeroeth 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_4 hr^{-1} g dry $soil^{-1}$. Based on these results, soil samples for use in subsequent incubations were collected from the 5-10 cm depth interval.

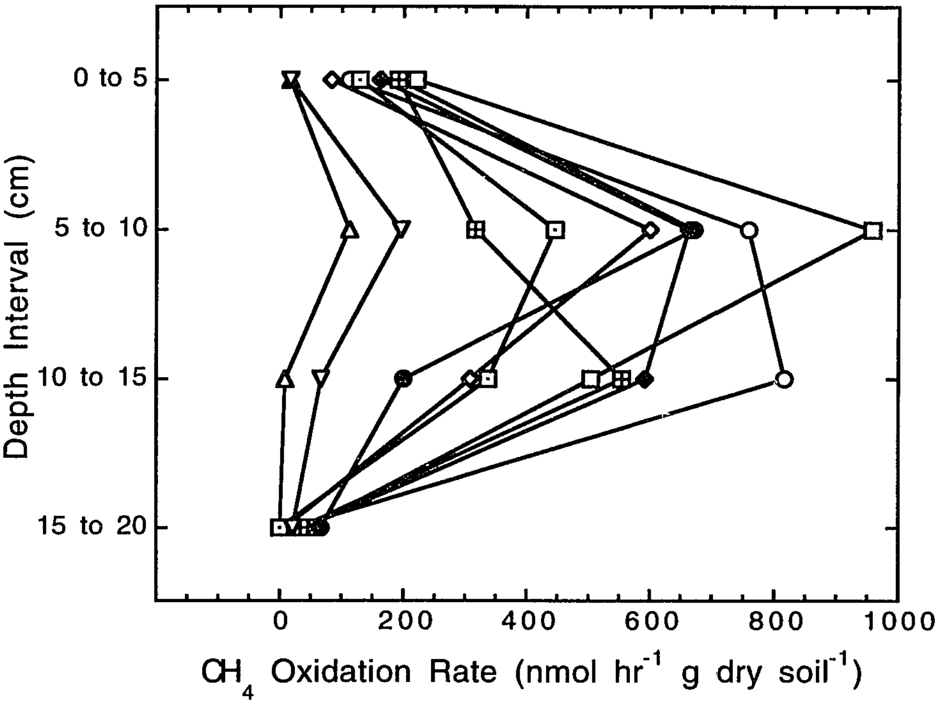

Figure 5-1. CH_4 oxidation rates through the soil profile from samples collected in 9 locations around the MSW landfill. Rates were determined by jar incubations of 5 cm depth integrated samples.

Moisture

The response of soil CH_4 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_2O. 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_4 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^{-1} g dry $soil^{-1}$. 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_4 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 ($r^2 = 0.79$).

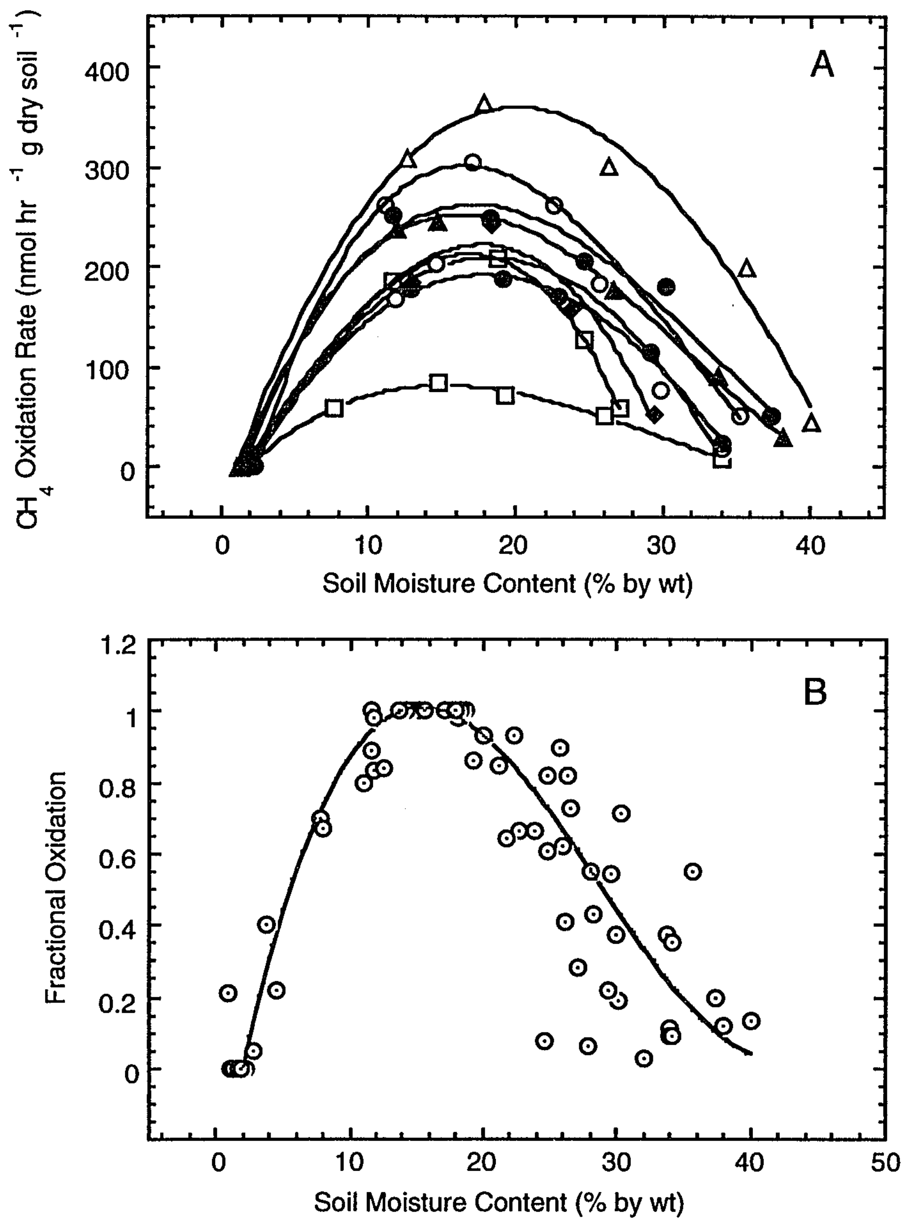

Figure 5-2. (A) Results of the moisture manipulation experiments. Individual samples are represented by different symbols. Solid lines are polynomial curve fits to the data from each sample. (B) A generalized model of the soil moisture response of CH_4 oxidation. Data from 10 samples were pooled after 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_4 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_4 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_{10} values calculated between 20 and 30°C was 2.4±11.

A generalized model of the temperature response of CH_4 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.

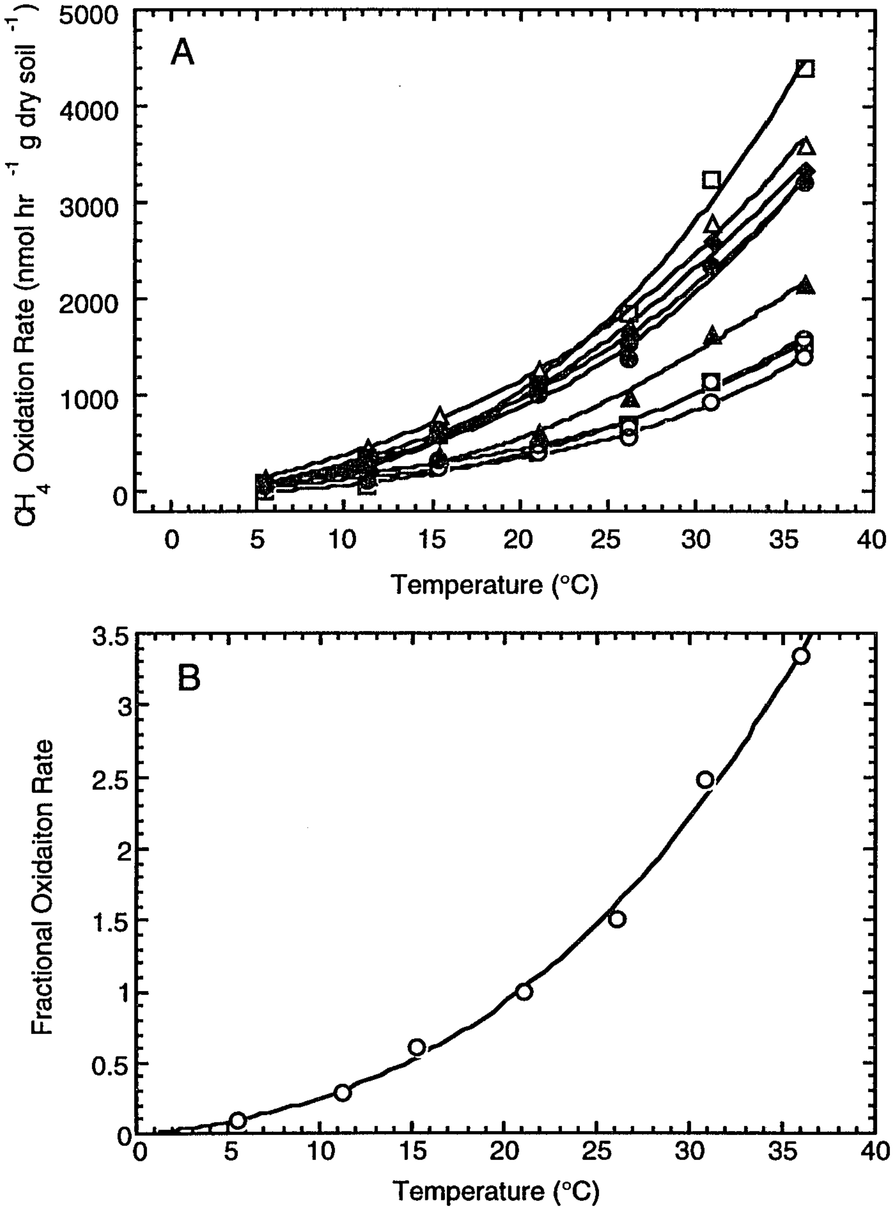

Figure 5-3. (A) Results of the temperature manipulation experiments for temperatures ranging from 5.5 to 36°C. Individual samples are represented by different symbols. Solid lines are polynomial curve fits to the data. (B) A generalized model of the temperature response of CH_4 oxidation. Data from 10 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 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_4 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_4 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_4 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_4 hr^{-1} g dry $soil^{-1}$ and low substrate CH_4 affinity with K_m values ranging from 195 to 5847 ppm.

Oxygen

The effect of variable O_2 mixing ratios on CH_4 oxidation was determined by incubating landfill soils in reduced O_2 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_4 and varying mixing ratios of O_2 in the jar headspaces. Incubation CH_4 mixing ratios ranged from 1.7 to 2.0 %. Figure 5-4 presents the resulting CH_4 oxidation rates as a function of O_2 mixing ratio. CH_4 oxidation rates in the composite subsamples decreased slowly from a peak rate of approximately 930 nmol hr^{-1} g dry $soil^{-1}$ at an O_2 mixing ratio of 20.8 % to 775 nmol hr^{-1} g dry $soil^{-1}$ at an O_2 mixing ratio of 3.0 %. At O_2 mixing ratios below 3.0 %, CH_4 oxidation rates decreased rapidly to zero.

A limited number of soil gas samples were collected to determine the extent of substrate O_2 limitations on CH_4 oxidation. The O_2 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_4 flux. O_2 mixing ratios ranged from 4.0 to 19.2 % with a corresponding CH_4 mixing ratio range of 48 to 0.7 %.

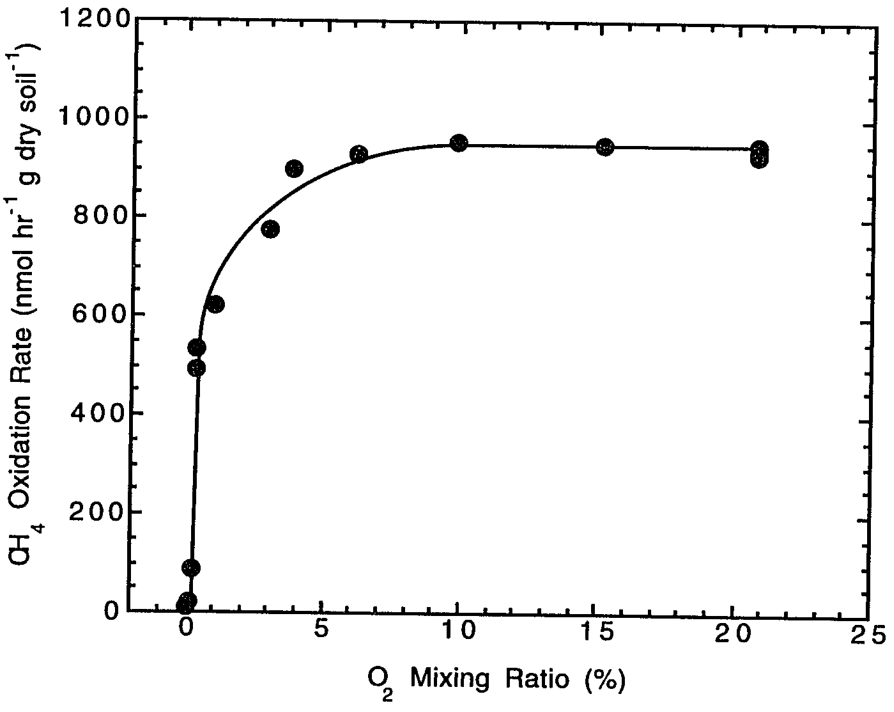

Figure 5-4. CH_4 oxidation rate as a function of O_2 mixing ratio. Rates were determined by jar incubation of soil samples generated from a composite of the temperature and moisture experiment samples.

Oxidation Model

A CH_4 oxidation model was created which incorporates the laboratory incubation results and field measurements of CH_4 emissions. The required model inputs include surface CH_4 flux, soil gas CH_4 mixing ratio at each flux location, and soil physical parameters such as temperature, moisture content, and bulk density. CH_4 fluxes and soil gas CH_4 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_4 flux and to evaluate whole landfill oxidation potential.

The first step in quantifying oxidation was to estimate the soil gas CH_4 mixing ratio in each of the 5 cm soil intervals from the surface to 20 cm. Soil gas CH_4 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_4 mixing ratio of 2 ppm, typical of ambient mixing ratios at the landfill surface. Soil gas CH_4 mixing ratios were computed from this gradient for the center of each of the remaining soil intervals up to a theoretical CH_4 mixing ratio limit of 50 %.

Soil gas O_2 mixing ratio was also considered in the assessment of factors influencing CH_4 oxidation. However, a limited effect was observed in the previously described incubation experiments at O_2 mixing ratios equal to the lowest mixing ratios measured in the field. O_2 was therefore assumed to be a negligible factor in the zone of maximum oxidation and was not included in the calculations.

The estimated CH_4 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_4 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 CH_4 mixing ratio resulting in a significant linear relationship with $r^2=0.68$.

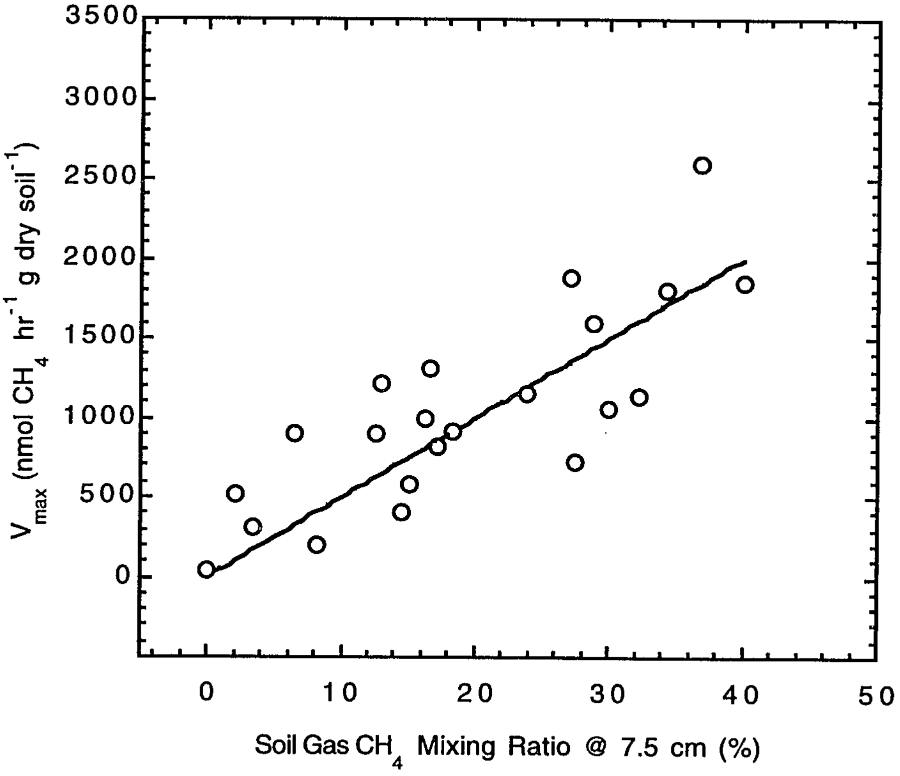

Figure 5-5. The maximum rate of CH_4 oxidation, V_{max}, as a function of the in situ soil gas CH_4 mixing ratio. Soil gas samples were collected from a depth of 7.5 cm, the center of the soil sample depth interval, prior to sample collection.

The previous calculations assume that the oxidation response to the CH_4 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_4 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.

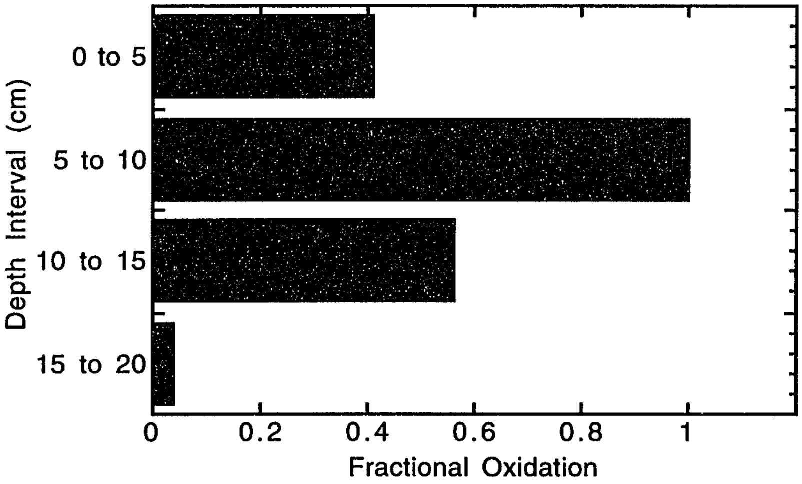

Figure 5-6. The normalized average soil oxidation rate depth profile. Individual oxidation profiles (Figure 5-1) were normalized to the values observed in the 5 to 10 cm intervals and averaged over each depth interval.

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_4 source, or gross CH_4, at each flux location by

$$CH_{4_{Gross}} = CH_{4_{Oxid}} + CH_{4_{Flux}} \qquad (1)$$

where $CH_{4_{Gross}}$ is the gross CH_4 source, $CH_{4_{Oxid}}$ is the total amount of CH_4 oxidized in the soil column, and $CH_{4_{Flux}}$ is the measured surface CH_4 flux, all in g CH_4 m^{-2} day^{-1}. The whole landfill oxidation rate is then calculated from the fractional difference between the oxidized CH_4 and the gross CH_4 source at each flux location by

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

where OX is the oxidation rate in percent and n is the flux location number. The estimated whole landfill CH_4 oxidation rate estimate at the time of the surface flux measurements was 21 %.

The annual rate of CH_4 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_4 fluxes. A significant relationship between whole landfill CH_4 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_4 oxidized and the gross CH_4 source by Equation (1). An annual oxidation estimate was then calculated by summing the resulting daily oxidation estimates over a one year period by

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

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_4 oxidation for the period December 1, 1993 through November 30, 1994. The resulting estimated annual whole landfill oxidation rate was 11 %.

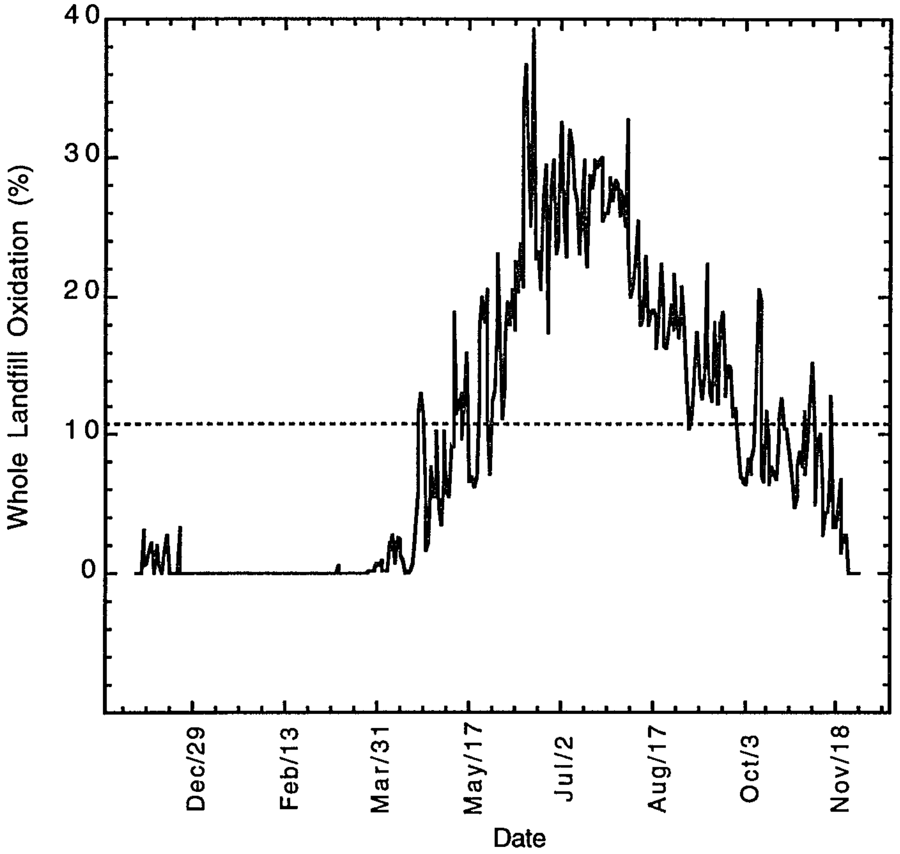

Figure 5-7. Model estimated rate of whole landfill oxidation for each day from 12/1/93 through 11/30/94. The dashed horizontal line indicates the mean annual rate of oxidation of 11 %.

Discussion

The depth distribution of CH_4 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_4^+ 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_4 availability [*Conrad*, 1984]. But, in the landfill environment, CH_4 is unlimited in the soil column. In the landfill soils, O_2 appears to be the limiting substrate below approximately 20 cm. CH_4 oxidation was found in the incubation experiments to be relatively insensitive to O_2 mixing ratios above approximately 3 % but dropped rapidly at O_2 mixing ratios below 3 %. This result is similar to that of Bender and Conrad who observed CH_4 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_2 mixing ratios above 3 % [*Bender and Conrad*, 1994]. Extrapolating the O_2 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_2 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_4 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_4 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_4 into the soils. Whereas, in CH_4 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_{10} of 2.4 for the temperature range 20 to 30°C was also somewhat higher than the Q_{10} 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_4 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_4 diffusional resistance.

Oxidation in our soils was characterized by a high oxidation capacity and a low substrate CH_4 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_4 mixing ratios. Our calculated V_{max} ranged from 40 to 2594 nmol CH_4 hr^{-1} g^{-1} dry soil (1.1 to 70 g CH_4 m^{-2} day^{-1}), 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_4 m^{-2} day^{-1} and a calculated maximum V_{max} of 61 g CH_4 m^{-2} day^{-1}, while *Kightley et al.*, [1995] measured a V_{max} as high as 2342 nmol CH_4 hr^{-1} g^{-1}.

The primary influence of temperature and moisture on CH_4 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^{-1}) and summers with reduced precipitation (-1 mm day^{-1}).

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_4 oxidation (%).

1994 reference scenario	11
2030 soil moisture, 1994 temperature	11
2030 temperature (+4°C), 1994 soil moisture	17
2030 temperature and 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_4 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_4. 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.

REFERENCES

Adamsen, A.P.S., and G.M. King, Methane consumption in temperate and subarctic forest soils: Rates, vertical zonation, and responses to water and nitrogen, *Appl. Environ. Microbiol.,59,* (2), 485-490, 1993.

Armstrong, F.B., *Biochemistry*, Oxford University Press, New York, 1989.

Bender, M., and R. Conrad, Methane oxidation activity in various soils and freshwater sediments: Occurrence, characteristics, vertical profiles, and distribution on grain size fractions, *J. Geophys. Res.,99,* (D8), 16531-16540, 1994.

Bogner, J., and K. Spokas, Landfill methane: rates, fates, and role in global carbon cycle, *Chemosphere,26,* , 369-386, 1993.

Bogner, J., K. Spokas, and J. Jolas, Comparison of Measured and Calculated Methane Emissions at Mallard Lake Landfill, Dupage County, Illinois, USA, in *IV International Landfill Symposium*, S. Margherita di Pula, Italy, 1993.

Clapp, R.B., and G.M. Hornberger, Empirical equations for some soil hydraulic properties, *Water Resources Res.,14,* , 601-604, 1978.

Conrad, R., Capacity of aerobic microorganisms to utilize and grow on atmospheric trace gases (H_2, CO, CH_4), in *Current Perspectives in Microbiol Ecology*, pp. 461-467, American Society for Microbiology, Washington, DC, 1984.

Crill, P., Seasonal patterns of methane uptake and carbon dioxide release by a temperate woodland soil, *Glob. Biogeochem. Cycles,in press,* , 1993.

Crill, P.M., K.B. Bartlett, R.C. Harriss, E. Gorham, E.S. Verry, D.I. Sebacher, L. Madzar, and W. Sanner, Methane Flux From Minnesota Peatlands, *Global Biogeochem. Cycles,2,* (4), 371-384, 1988.

Crill, P.M., J.H. Butler, D.J. Cooper, and P.C. Novelli, Standard analytical methods, for measuring trace gases in the environment, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P. Matson, and H. R., Blackwell Science, Inc., Cambridge, MA, 1995.

Culley, J.L.B., Density and Compressibility, in *Soil Sampling and Methods of Analysis*, edited by M.R. Carter, pp. 529-539, Lewis Publishers, Boca Raton, 1993.

Czepiel, P., P. Crill, and R. Harriss, Environmental influences on methane oxidation in temperate forest soils, *J. Geophys. Res., 100,* 9359-9364, 1995.

Czepiel, P., B. Mosher, J. H. Shorter, J. B. McManus, C. E. Kolb, E. Allwine, B. K. Lamb, and R. C. Harriss, Landfill methane emissions measured by static enclosure and atmospheric tracer methods, *J. Geophys. Res.*, this issue.

Davies, B.E., Loss-on-ignition as an estimate of soil organic matter, *Soil Sci. Soc. Amer. Proc.,38,* , 150-151, 1974.

EMCON, *State of the Art of Methane Gas Enhancement in Landfills*, Argonne National Laboratory, ANL/CNSV-23, 1981.

Frolking, S., Modeling soil climate controls on the exchange of trace gases between the terrestrial biosphere and the atmosphere, Doctoral thesis, University of New Hampshire, 1993.

Gardner, N., and B.J.W. Manley, Gas emissions from landfills and their contributions to global warming, *Applied Energy,44,* , 165-174, 1993a.

Ham, R.K., K.K. Hekimian, S.L. Katten, W.J. Lockman, R.J. Lofy, D.E. McFaddin, and E.J. Daley, *Recovery, Processing, and Utilization of Gas from Sanitary Landfills*, Solid and Hazardous Waste Research Division, USEPA, 68-03-2536, 1979.

Jones, H.A., and D.B. Nedwell, Methane emission and methane oxidation in landfill cover soil, *FEMS Microbiology Ecology,102,* , 185-195, 1993.

Kightley, D., D. Nedwell, and M. Cooper, Capacity for methane oxidation in landfill cover soils measured in laboratory-scale soil microcosms, *Appl. Environ. Microbiol.,61,* (2), 592-601, 1995.

King, G.M., and A.P.S. Adamsen, Effects of temperature on methane consumption in a forest soil and in pure cultures of the methanotroph Methylomonas rubra, *Appl. Environ. Microbiol.,58,* (9), 2758-2763, 1992.

Koschorreck, M., and R. Conrad, Oxidation of atmospheric methane in soil: measurements in the field, in soil cores and in soil samples, *Glob. Biogeochem. Cycles,7,* (1), 109-121, 1993.

Livingston, G.P., and G.L. Hutchinson, Enclosure-based measurement of trace gas exchange: applications and sources of error, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P.A. Matson, and R.C. Harriss, Blackwell Science, Cambridge, MA, 1995.

Mitchell, J., S. Manabe, V. Meleshko, and T. Tokioka, Equilibrium climate change and its implications for the future, in *Climate Change: The IPCC Assessment*, edited by J. Houghton, G. Jenkins, and J. Ephraums, Cambridge University Press, Cambridge, UK, 1990.

Nesbit, S.P., and G.A. Breitenbeck, A laboratory study of factors influencing methane uptake by soils, *Agric. Ecosyst. Environ.,41,* , 39-54, 1992.

Steudler, P.A., R.D. Bowden, J.M. Melillo, and J.D. Aber, Influence of nitrogen fertilization on methane uptake in temperate forest soils, *Nature,341,* , 314-316, 1989.

Thorneloe, S., M. Barlaz, R. Peer, L. Huff, L. Davis, and J. Mangino, Waste Management, in *Atmospheric Methane: Sources, Sinks and Role in Global Change*, edited by M.A.K. Khalil, Springer-Verlag, Berlin, 1993.Topp, G.C., Soil water content, in *Soil Sampling and Methods of Analysis*, edited by M.R. Carter, pp. 541-557, Lewis Publishers, Boca Raton, 1993.

USEPA, *International Anthropogenic Methane Emissions: Estimates for 1990*, U.S. Environmental Protection Agency, Office of Policy, Planning and Evaluation, Report to Congress, EPA 230-R-93-010, 1994.

Whalen, S., and W. Reeburgh, Interannual variation in tundra methane emissions: a 4-year time series at fixed sites, *Global Biogeochem. Cycles,6,* , 139-159, 1992.

Whalen, S.C., W.S. Reeburgh, and K.A. Sandbeck, Rapid Methane Oxidation in a Landfill Cover Soil, *Appl. Environ. Microbiol.,56,* (11), 3405-3411, 1990.

COMPREHENSIVE REFERENCE LIST

CHAPTER 1:

(1) Houghton, J. T., Callander, B. A. and Varney, S. K. *The Supplementary Report to the IPCC Scientific Assessment, Climate Change;* Cambridge University Press: New York, 1992.

(2) Crutzen, P. J. *Quat. J. Royal Met. Soc.* **1970**, *96,* 320-325.

(3) Khalil, M. A. K. and Rasmussen, R. A. *J. of Geophys. Res.* **1992**, *97,* 14651-14660.

(4) Bouwman, A. F. "Estimated global source distribution of nitrous oxide" in: *CH4 and N2O: Global Emissions and Controls from Rice Fields and Other Agricultural and Industrial Sources*; 1994 NIAES: Washington, DC, 1994.

(5) Prinn, R., Cunnold, D., Rasmussen, R., Simmonds, P., Alyea, F., Crawford, A., Fraser, P. and Rosen, R. *J. Geophys. Res.* **1990**, *95*, 18369-18385.

(6) Debruyn, W., Lissens, G. and Van Rensbergen, J. *Eviron. Monit. Assess.* **1994**, *31*, 159-165.

(7) Hong, Z., Hanaki, K. and Matsuo, T. *Wat. Sci. Tech.* **1993**, *28,* 203-207.

(8) Crill, P. M., Bartlett, K. B., Wilson, J. O., Sebacher, D. I. and Harriss, R. C. *J. Geophys. Res.* **1988**, *93,* 1564-1570.

(9) Martikainen, P. J., Nykanen, H., Crill, P. and Silvola, J. *Nature* **1993**, *366,* 51-53.

(10) Montgomery, D. C. and Peck, E. A. *Introduction to Linear Regression Analysis;* John Wiley & Sons, Inc.: New York, 1992.

(11) *The 1988 Needs Survey: Conveyance, Treatment, and Control of Municipal Wastewater, Combined Sewer Overflows, and Stormwater Runoff*; U. S. Environmental Protection Agency, U. S. Government Printing Office: Washington, DC, 1989.

(12) Metcalf; Eddy *Wastewater Engineering: Treatment, Disposal, and Reuse;* Water Resources and Environmental Engineering. King, P. H., Eliassen, R. and Linsley, R. K., Eds.; McGraw-Hill, Inc.: New York, 1991.

(13) *International Anthropogenic Methane Emissions: Estimates for 1990*; U. S. Environmental Protection Agency, U. S. Government Printing Office: Washington, DC, 1994; EPA/230/R/93/010.

CHAPTER 2:

(1) Houghton, J.T.; B.A. Callander; Varney S.K. *The Supplementary Report to the IPCC Scientific Assessment, Climate Change*; Cambridge University Press: New York, 1992.

(2) Warneck, P. *Chemistry of the Natural Atmosphere*; Academic Press: San Diego, 1988.

(3) Crutzen, P.J. *Quat. J. Royal Met. Soc.* **1970**, *96*, 320-325.

(4) Khalil, M.A.K. and R.A. Rasmussen, *J. of Geophys. Res.* **1992**, *97*, 14651-14660.

(5) Prinn, R.; Cunnold, D.; Rasmussen, R.; Simmonds, P.; Alyea, F.; Crawford, A.; Fraser, P.; Rosen, R. *J. Geophys. Res.* **1990**, *95*, 18369-18385.

(6) Bouwman, A.F. *Estimated global source distribution of nitrous oxide*, in *CH4 and N2O: Global Emissions and Controls from Rice Fields and Other Agricultural and Industrial Sources*; NIAES: Washington, DC, 1994.

(7) Lipschultz, F.; Zafiriou, O.; Wofsy, S.; McElroy, M.; Valois, F.; Watson, S. *Nature* **1981**, *294*, 641-643.

(8) Payne, W.J., *The status of nitric oxide and nitrous oxide as intermediates in denitrification*, in *Denitrification, nitrification and atmospheric nitrous oxide*, C.C. Delwiche, Editor; John Wiley: New York, NY, 1981.

(9) Cabrera, M.; Chiang, S.; Merka, W.; Pancorbo, O.; Thompson, S. *Plant and Soil* **1994**, *163*, 189-196.

(10) Bandibas, J.; Vermoesen, A.; De Groot, C.; Van Cleemput, O. *Soil Sci* **1994**, *158*, 106-114.

(11) Hochstein, L.; Betlach M.; Kritikos G. *Arch. Microbiol.* **1984**, *137*, 74-78.

(12) Klemedtsson, L.; Svensson B.; Rosswall T. *Biol. Fertil. Soils* **1988**, *6*, 106-111.

(13) Focht, D. *Soil Sci.* **1974**, *118*, 173-179.

(14) Knowles, R. *Microbiol. Rev.* **1982**, *46*, 43-70.

(15) Sikora, L.; Millner P.; Burge W. *Chemical and Microbial Aspects of Sludge Composting and Land Application*; U. S. Environmental Protection Agency, Engineering Research Laboratory: Washington, DC, 1986.

(16) Haug, R., *Compost Engineering: Principles and Practice*; Ann Arbor Science Publishers: Ann Arbor, MI, 1980.

(17) *Composting Yard Trimmings and Municipal Solid Waste*; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response; Washington, DC, 1994.

(18) Douglas, E. *The Transport and Fate of Nitrogen at a Farm and Yard Waste Composting Facility*; Master's Thesis, University of New Hampshire, December 1994.

(19) Livingston, G.; Hutchinson, G. *Enclosure-based measurement of trace gas exchange: applications and sources of error* in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, P.A. Matson and R.C. Harriss, Eds.; Blackwell Science: Cambridge, MA, 1995.

(20) Harriss, R.; Sebacher, D.; Bartlett, K.; Crill, P. *Global Biogeochemical Cycles* **1988**, *2*, 231-243.

(21) Crill, P.; Bartlett, K.; Harriss, R.; Gorham, E.; Verry, E.; Sebacher, D.; Madzar, L.; Sanner, W. *Global Biogeochem. Cycles* **1988**, *2*, 371-384.

(22) Topp, G.C. *Soil water content* in *Soil Sampling and Methods of Analysis*, M.R. Carter, Ed.; Lewis Publishers: Boca Raton, 1993.

(23) Martikainen, P; Nykanen, H.; Crill, P.; Silvola, J. *Nature* **1993**, *366*, 51-53.

(24) Lue-Hing, C.; Zenz D.; Kuchenrither, R. *Municipal Sewage Sludge Management: Processing, Utilization and Disposal*; Water Quality Management Series; Eckenfelder, W., Malina J., Patterson, J., Eds.; Technomic Publishing Co., Inc.: Lancaster, PA, 1992.

(25) Goldstein, N.; Steuteville, R. *1993 Biocycle Biosolids Survey: Biosolids Composting Makes Healthy Progress* in *Biocycle*; December 1993; 48-57.

(26) Benckiser, G.; Gaus, G.; Syring, K.; Haider, K.; Sauerbeck, D. *Zeitschrift Fuer Pflanzenernaehrung Und Bodenkunde* **1987**, *150*, 241-248.

(27) Paul, J.; Beauchamp, E.; Zhang, X. *Can. J. Soil Sci.* **1993**, *73*, 539-553.

(28) *The 1988 Needs Survey: Conveyance, Treatment, and Control of Municipal Wastewater, Combined Sewer Overflows, and Stormwater Runoff*; U. S. Environmental Protection Agency, U. S. Government Printing Office: Washington, DC, 1989.

(29) Kashmanian, R. *Predicting the tonnage of yard trimmings to be composted in 1996* in *Biocycle*; December 1993, 51-53.

(30) Safley, L.; Casada, M.; Woodbury, J.; Roos, K. *Global Methane Emissions from Livestock and Poultry Manure*; U. S. Environmental Protection Agency, U. S. Government Printing Office: Washington, DC, 1992; EPA/400/1-91/048.

(31) Taiganides, E. *Animal waste management and wastewater treatment* in *Animal Production and Environmental Health*, Strauch, D., Ed.; Elsevier: New York, 1987.

CHAPTER 3:

Adamsen, A. P. S., and G. M. King, Methane consumption in temperate and subarctic forest soils: Rates, vertical zonation, and responses to water and nitrogen, *Appl. Environ. Microbiol., 59,* 485-490, 1993.

Amaral, J. A., and R. Knowles, Methane metabolism in a temperate swamp, *Appl. Environ. Microbiol., 60,* 3945-3951, 1994.

Armstrong, F. B., *Biochemistry,* Oxford University Press, New York, 1989.

Bender, M. and R. Conrad, Kinetics of methane oxidation in oxic soils, *Chemosphere, 26,* 687-696, 1993.

Cicerone, R. J., and R. S. Oremland, Biogeochemical aspects of atmospheric methane, *Global Biogeochemical Cycles, 2,* 299-327, 1988.

Crill, P. M., Seasonal patterns of methane uptake and carbon dioxide release by a temperate woodland soil, *Global Biogeochemical Cycles, 5,* 319-334, 1991.

Culley, J. L. B., Density and compressibility, in *Soil Sampling and Methods of Analysis,* edited by M. R. Carter, pp. 529-539, Lewis, Boca Raton, Fla., 1993.

Davies, B. E., Loss-on-ignition as an estimate of soil organic matter, *Soil Sci. Soc. Amer. Proc., 38,* 150-151, 1974.

Delmas, R. A., R. Marenco, J. P. Tathy, B. Cros, and J. G. R. Baudet, Sources and sinks of methane in the African savanna. CH_4 emissions from biomass burning, *J. Geophys. Res., 96,* 7287-7299, 1991.

Dlugokencky, E. J., K. A. Masaire, P. M. Lang, P. P. Tans, L. P. Steele, and E. G. Nisbet, A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992, *Geophys. Res. Lett., 21,* 45-48, 1994.

Federer, C. A., D. E. Turcotte, and C. T. Smith, The organic fraction - Bulk density relationship and the expression of nutrient content in forest soils, *Can. J. For. Res., 23,* 1026-1032, 1993.

Harriss, R. C., D. I. Sebacher, and F. P. Day Jr., Methane flux in the Great Dismal Swamp, *Nature, 297,* 673-674, 1982.

Koschorreck, M., and R. Conrad, Oxidation of atmospheric methane in soil: Measurements in the field, in soil cores, and in soil samples, *Global Biogeochemical Cycles, 7,* 109-121, 1993.

Mosier, A., D. Schimel, D. Valentine, K. Bronson, and W. Parton, Methane and nitrous oxide fluxes in native, fertilized and cultivated grasslands, *Nature, 350,* 330-332, 1991.

Seiler, W., R. Conrad, and D. Scharffe, Field studies of methane emission from termite nests into the atmosphere and measurements of methane uptake by tropical soils, *J. Atmos. Chem., 1,* 171-186, 1984.

Steudler, P. A., R. D. Bowden, J. M. Melillo, and J. D. Aber, Influence of nitrogen fertilization on methane uptake in temperate forest soils, *Nature, 341,* 314-316, 1989.

Topp, G. C., Soil water content, in *Soil Sampling and Methods of Analysis*, edited by M. R. Carter, pp. 541-557, Lewis, Boca Raton, Fla., 1993.

Vieira, F. J., and R. W. Bond, Soil survey of Strafford County, New Hampshire, U. S. Dept. of Agriculture, Soil Conservation Service, Washington, D. C., 1971.

Whalen, S. C., W. S. Reeburgh, and K. A. Sandbeck, Rapid methane oxidation in a landfill cover soil, *Appl. Environ. Microbiol., 56,* 3405-3411, 1990.

CHAPTER 4:

Augenstein, D.C., Greenhouse Effect Contributions of U. S. Landfill Methane, in *13th Annual Landfill Gas Symposium*, GRCDA, Lincolnshire, Illinois, 1990.

Augenstein, D.C., and J. Pacey, Modeling Landfill Methane Generation, in *Sardinia '91 - Third International Symposium on Landfill Gas*, 1991.

Benner, R.L., and B. Lamb, A fast response continuous analyzer for halogenated atmospheric tracers, *J. Atmos. Ocean. Technol.*, 2 (4), 582-589, 1985.

Bingemer, H.G., and P.J. Crutzen, The production of methane from solid waste, *J. Geophys. Res.*, *92* (D2), 2181-2187, 1987.

Bogner, J., K. Spokas, and J. Jolas, Comparison of measured and calculated methane emissions at mallard lake landfill, Dupage County, Illinois, USA, in *IV International Landfill Symposium*, S. Margherita di Pula, Italy, 1993.

Bogner, J.E., M. Vogt, and R.M. Miller, Studies of soil gas, gas generation, and shallow microbial activity at Mallard North Landfill, Dupage County, Illinois, in *13th Annual Landfill Gas Symposium*, U. S. Dept. of Energy, Lincolnshire, IL, 1990.

Boone, D.R., Ecology of Methanogenesis, in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes*, edited by J.E. Rogers, and W.B. Whitman, pp. 57-70, American Society for Microbiology, Washington, D. C., 1991.

Cicerone, R.J., and R.S. Oremland, Biogeochemical aspects of atmospheric methane, *Glob. Biogeochem. Cycles*, 2 (4), 299-327, 1988.

Crill, P.M., K.B. Bartlett, R.C. Harriss, E. Gorham, E.S. Verry, D.I. Sebacher, L. Madzar, and W. Sanner, Methane flux from minnesota peatlands, *Glob. Biogeochem. Cycles*, *2* (4), 371-384, 1988.

Czepiel, P., B. Mosher, P. Crill, and R. Harriss, Quantifying the effect of oxidation on landfill methane emissions, *J. Geophys. Res.*, this issue.

Deutsch, C.V., and A.G. Journel, *GSLIB: Geostatistical Software Library and User's Guide*, 340 pp., Oxford University Press, New York, 1992.

EMCON, *State of the Art of Methane Gas Enhancement in Landfills*, Argonne National Laboratory, ANL/CNSV-23, 1981.

Farquhar, G.J., and F.A. Rovers, Gas production during refuse decomposition, *Water, Air, Soil Poll.*, *2*, 483-495, 1973.

Franklin Associates, *Characterization of Municipal Solid Waste in the U. S.*, U. S. EPA, WH-565E, 1988.

Ham, R.K., K.K. Hekimian, S.L. Katten, W.J. Lockman, R.J. Lofy, D.E. McFaddin, and E.J. Daley, *Recovery, Processing, and Utilization of Gas from Sanitary Landfills*, Solid and Hazardous Waste Research Division, U.S. Environmental Protection Agency, EPA 68-03-2536, 1979.

Howard, T., B. Lamb, and P. Zimmerman, Measurement of VOC emission fluxes from waste treatment and disposal systems using an atmospheric tracer flux, *J. Air & Waste Manage. Assoc.*, *42*, 1336-1344, 1992.

IPCC, *Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment*, 196 pp., Cambridge University Press, New York, 1992.

Isaaks, E.H., and R.M. Srivastava, *An Introduction to Applied Geostatistics*, 561 pp., Oxford University Press, New York, 1989.

Lamb, B., B. McManus, J. Shorter, C. Kolb, B. Mosher, R. Harriss, E. Allwine, D. Blaha, T. Howard, A. Guenther, R. Lott, R. Siverson, H. Westberg, and P. Zimmerman, Developmentof atmospheric tracer methods to measure methane emissions from natural gas facilities and urban areas, *Environ. Sci. Tech.*, 1995.

Lamb, B., H. Westberg, and E. Allwine, Isoprene emission fluxes determined by atmospheric tracer techniques, *Atmos. Environ.*, *20*, 1-8, 1986.

Livingston, G.P., and G.L. Hutchinson, Enclosure-based measurement of trace gas exchange: applications and sources of error, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P.A. Matson, and R.C. Harriss, pp. 360, Blackwell Science, Cambridge, MA, 1995.

McManus, J.B., P.L. Kebabian, and C.E. Kolb, Atmospheric methane measurement instrument using a Zeeman-split He-Ne laser, *Appl. Opt.*, *28* (23), 5016-5023, 1989.

McManus, J.B., J.H. Shorter, P.L. Kebabian, C.E. Kolb, B. Mosher, R.C. Harriss, B. Lamb, E. Allwine, and T. Howard, Field measurements of atmospheric methane with a HeNe laser-based real-time instrument, *SPIE Proc., Opt. Meth. Atmos. Chem.*, *1715*, 138-150, 1992.

Nozhevnikova, A.N., A.B. Lifshitz, V.S. Lebedev, and G.A. Zavarzin, Emission of methane into the atmosphere from landfills in the former USSR, *Chemosphere, 26* (1-4), 401-417, 1993.

Pacey, J.G., and A.M. Dietz, Gas Production Enhancement Techniques, in *Energy from Landfill Gas Conference*, Solihull, England, 1986.

Parkin, G., and W. Owen, Fundamentals of anaerobic digestion of wastewater sludges, *J. Environ. Eng., 112* (5), 867-920, 1986.

Peer, R.L., D.L. Epperson, D.L. Campbell, and P. von Brook, *Development of an Empirical Model of Methane Emissions from Landfills*, USEPA, Final Report, EPA-600/R-92-037, 1992.

Rasmussen, R.A., and M.A.K. Khalil, Atmospheric methane in the recent and ancient atmospheres: concentrations, trends, and interhemispheric gradient, *J. Geophys. Res., 89*, 11599-11605, 1984.

Rathmell, R., Personal Communication. Project manager, Waste Management, Inc. Discussion regarding the production and recovery rate of landfill gas from the Turnkey Landfill in Rochester, N. H., 1991.

Steuteville, R., The State of Garbage in America, *Biocycle, 36* (4), 54-63, 1995.

Straub, W.A., Personal Communication, CMA Engineers, Letter estimating waste in place at the Nashua municipal landfill, 1995.

Tohjima, Y., and H. Wakita, Estimation of methane discharge from a plume: a case of landfill, *Geophys. Res. Lett., 20*, 2067-2070, 1993.

Thorneloe, S., M. Barlaz, R. Peer, L. Huff, L. Davis, and J. Mangino, Waste Management, in *Atmospheric Methane: Sources, Sinks and Role in Global Change*, edited by M.A.K. Khalil, Springer-Verlag, Berlin, 1993.

USEPA, *International Anthropogenic Methane Emissions: Estimates for 1990*, U.S. Environmental Protection Agency, Office of Policy, Planning and Evaluation, Report to Congress, EPA 230-R-93-010, 1994.

Young, A., The effects of fluctuations in atmospheric pressure on landfill gas migration and composition,*Water, Air, and Soil Pollution*, *64*, 601-616, 1992.

CHAPTER 5:

Adamsen, A.P.S., and G.M. King, Methane consumption in temperate and subarctic forest soils: Rates, vertical zonation, and responses to water and nitrogen, *Appl. Environ. Microbiol.,59,* (2), 485-490, 1993.

Armstrong, F.B., *Biochemistry*, Oxford University Press, New York, 1989.

Bender, M., and R. Conrad, Methane oxidation activity in various soils and freshwater sediments: Occurrence, characteristics, vertical profiles, and distribution on grain size fractions, *J. Geophys. Res.,99,* (D8), 16531-16540, 1994.

Bogner, J., and K. Spokas, Landfill methane: rates, fates, and role in global carbon cycle, *Chemosphere,26,* , 369-386, 1993.

Bogner, J., K. Spokas, and J. Jolas, Comparison of Measured and Calculated Methane Emissions at Mallard Lake Landfill, Dupage County, Illinois, USA, in *IV International Landfill Symposium*, S. Margherita di Pula, Italy, 1993.

Clapp, R.B., and G.M. Hornberger, Empirical equations for some soil hydraulic properties, *Water Resources Res.,14,* , 601-604, 1978.

Conrad, R., Capacity of aerobic microorganisms to utilize and grow on atmospheric trace gases (H_2, CO, CH_4), in *Current Perspectives in Microbiol Ecology*, pp. 461-467, American Society for Microbiology, Washington, DC, 1984.

Crill, P., Seasonal patterns of methane uptake and carbon dioxide release by a temperate woodland soil, *Glob. Biogeochem. Cycles,in press,* , 1993.

Crill, P.M., K.B. Bartlett, R.C. Harriss, E. Gorham, E.S. Verry, D.I. Sebacher, L. Madzar, and W. Sanner, Methane Flux From Minnesota Peatlands, *Global Biogeochem. Cycles,2,* (4), 371-384, 1988.

Crill, P.M., J.H. Butler, D.J. Cooper, and P.C. Novelli, Standard analytical methods, for measuring trace gases in the environment, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P. Matson, and H. R., Blackwell Science, Inc., Cambridge, MA, 1995.

Culley, J.L.B., Density and Compressibility, in *Soil Sampling and Methods of Analysis,* edited by M.R. Carter, pp. 529-539, Lewis Publishers, Boca Raton, 1993.

Czepiel, P., P. Crill, and R. Harriss, Environmental influences on methane oxidation in temperate forest soils, *J. Geophys. Res., 100,* 9359-9364, 1995.

Czepiel, P., B. Mosher, J. H. Shorter, J. B. McManus, C. E. Kolb, E. Allwine, B. K. Lamb, and R. C. Harriss, Landfill methane emissions measured by static enclosure and atmospheric tracer methods, *J. Geophys. Res.*, this issue.

Davies, B.E., Loss-on-ignition as an estimate of soil organic matter, *Soil Sci. Soc. Amer. Proc.,38,* , 150-151, 1974.

EMCON, *State of the Art of Methane Gas Enhancement in Landfills*, Argonne National Laboratory, ANL/CNSV-23, 1981.

Frolking, S., Modeling soil climate controls on the exchange of trace gases between the terrestrial biosphere and the atmosphere, Doctoral thesis, University of New Hampshire, 1993.

Gardner, N., and B.J.W. Manley, Gas emissions from landfills and their contributions to global warming, *Applied Energy,44,* , 165-174, 1993a.

Ham, R.K., K.K. Hekimian, S.L. Katten, W.J. Lockman, R.J. Lofy, D.E. McFaddin, and E.J. Daley, *Recovery, Processing, and Utilization of Gas from Sanitary Landfills*, Solid and Hazardous Waste Research Division, USEPA, 68-03-2536, 1979.

Jones, H.A., and D.B. Nedwell, Methane emission and methane oxidation in landfill cover soil, *FEMS Microbiology Ecology,102,* , 185-195, 1993.

Kightley, D., D. Nedwell, and M. Cooper, Capacity for methane oxidation in landfill cover soils measured in laboratory-scale soil microcosms, *Appl. Environ. Microbiol.,61,* (2), 592-601, 1995.

King, G.M., and A.P.S. Adamsen, Effects of temperature on methane consumption in a forest soil and in pure cultures of the methanotroph Methylomonas rubra, *Appl. Environ. Microbiol.,58,* (9), 2758-2763, 1992.

Koschorreck, M., and R. Conrad, Oxidation of atmospheric methane in soil: measurements in the field, in soil cores and in soil samples, *Glob. Biogeochem. Cycles,7,* (1), 109-121, 1993.

Livingston, G.P., and G.L. Hutchinson, Enclosure-based measurement of trace gas exchange: applications and sources of error, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P.A. Matson, and R.C. Harriss, Blackwell Science, Cambridge, MA, 1995.

Mitchell, J., S. Manabe, V. Meleshko, and T. Tokioka, Equilibrium climate change and its implications for the future, in *Climate Change: The IPCC Assessment*, edited by J. Houghton, G. Jenkins, and J. Ephraums, Cambridge University Press, Cambridge, UK, 1990.

Nesbit, S.P., and G.A. Breitenbeck, A laboratory study of factors influencing methane uptake by soils, *Agric. Ecosyst. Environ.,41,* , 39-54, 1992.

Steudler, P.A., R.D. Bowden, J.M. Melillo, and J.D. Aber, Influence of nitrogen fertilization on methane uptake in temperate forest soils, *Nature,341,* , 314-316, 1989.

Thorneloe, S., M. Barlaz, R. Peer, L. Huff, L. Davis, and J. Mangino, Waste Management, in *Atmospheric Methane: Sources, Sinks and Role in Global Change*, edited by M.A.K. Khalil, Springer-Verlag, Berlin, 1993.Topp, G.C., Soil water content, in *Soil Sampling and Methods of Analysis*, edited by M.R. Carter, pp. 541-557, Lewis Publishers, Boca Raton, 1993.

USEPA, *International Anthropogenic Methane Emissions: Estimates for 1990*, U.S. Environmental Protection Agency, Office of Policy, Planning and Evaluation, Report to Congress, EPA 230-R-93-010, 1994.

Whalen, S., and W. Reeburgh, Interannual variation in tundra methane emissions: a 4-year time series at fixed sites, *Global Biogeochem. Cycles,6,* , 139-159, 1992.

Whalen, S.C., W.S. Reeburgh, and K.A. Sandbeck, Rapid Methane Oxidation in a Landfill Cover Soil, *Appl. Environ. Microbiol.,56,* (11), 3405-3411, 1990.

APPENDIX A

Date	Aerated Grit Tank N2O Flux (g/sq m/day)	Non-Aerated Grit Tank N2O Flux (g/sq m/day)	Secondary Aeration Flux (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 Nitrous Oxide Conc. (ppmv)	9 Day Old Pile Oxygen 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 Nitrous Oxide Conc. (ppmv)	38 Day Old Pile Oxygen 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 (days)	N2O Flux (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 (days)	N2O Flux (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 (days)	N2O Flux (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 (days)	N2O Flux (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 (days)	N2O Flux (g/sq m/day)
21	8.3
21	8.3
18	8.87
18	8.87

FARM WASTE PILE 1

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

APPENDIX C

organic matter (% by wt)	mois. content (% by wt)	oxidation rate (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 (% by wt)	mois. content (% by wt)	oxidation rate (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 (% by wt)	mois. content (% by wt)	oxidation rate (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 (feet)	Y Position (feet)	Methane Flux (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 (feet)	Y Position (feet)	Methane Flux (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 (feet)	Y Position (feet)	Methane Flux (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 (feet)	Y Position (feet)	Methane Flux (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 (feet)	Y Position (feet)	Methane Flux (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 (feet)	Y Position (feet)	Methane Flux (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 (feet)	Y Position (feet)	Methane Flux (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 (feet)	Y Position (feet)	Methane Flux (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 (feet)	Y Position (feet)	Methane Flux (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 (feet)	Y Position (feet)	Methane Flux (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 at 7.5 cm depth (ppmv)	CH4 Oxidation Rate (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 Landfill Oxidation (% 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

Date in 1994	Modeled Whole Landfill Oxidation (% of production)
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

Date in 1994	Modeled Whole Landfill Oxidation (% of production)
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

Date in 1994	Modeled Whole Landfill Oxidation (% of production)
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

Date in 1994	Modeled Whole Landfill Oxidation (% of production)
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

Date in 1994	Modeled Whole Landfill Oxidation (% of production)
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

Date in 1994	Modeled Whole Landfill Oxidation (% of production)
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

Date in 1994	Modeled Whole Landfill Oxidation (% of production)
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

Date in 1994	Modeled Whole Landfill Oxidation (% of production)
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

Date in 1994	Modeled Whole Landfill Oxidation (% of production)
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

Date in 1994	Modeled Whole Landfill Oxidation (% of production)
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 preceeding 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^3) 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.

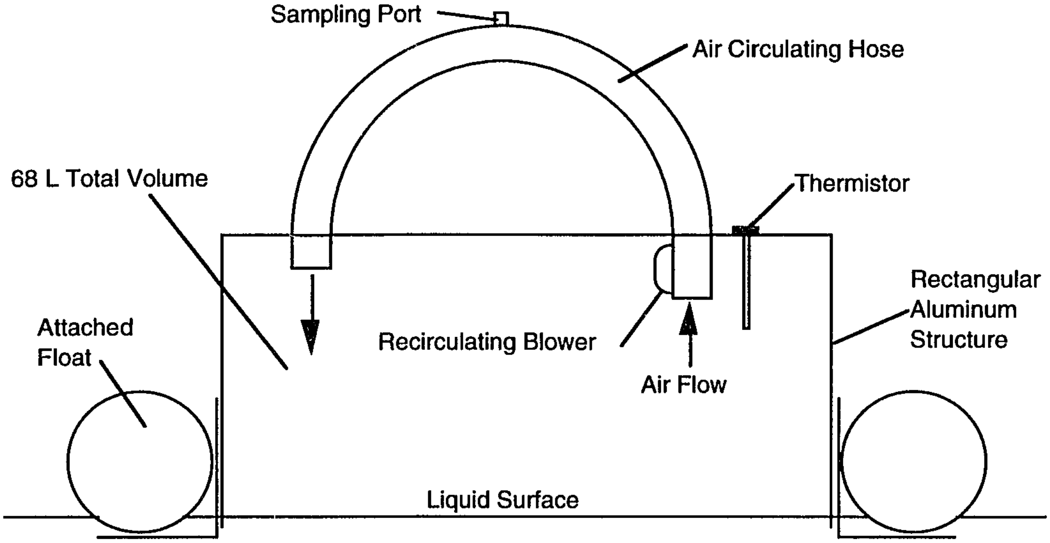

Figure 1 - Enclosure configuration used on non-aerated liquid surfaces.

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^{-1} time^{-1}) from the liquid surface was calculated by the equation

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

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 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.

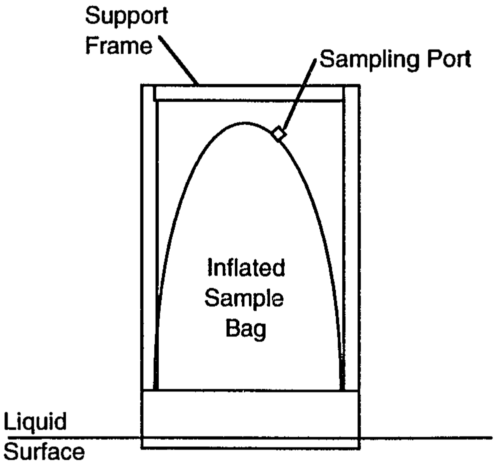

Figure 2 - Configuration of the bag sampler used on aerated liquid surfaces.

The open base of the frame allowed gas to be collected from 0.084 m^2 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 $area^{-1}$ $time^{-1}$) across the entire surface area was calculated by the equation

$$E = p\, c\, Q\, A^{-1} \tag{2}$$

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_2O 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^2 and 93.6 liters respectively.

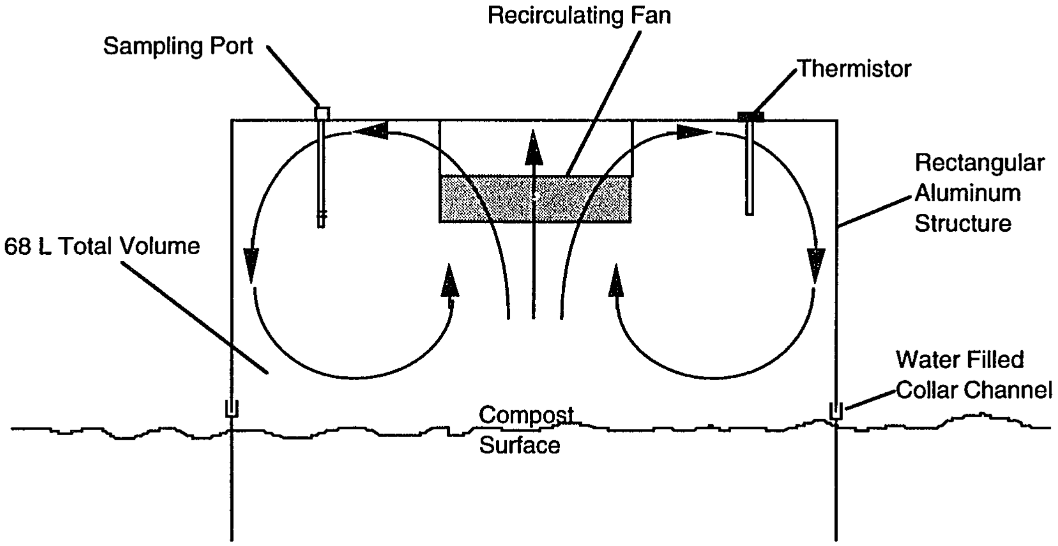

Figure 3 - Enclosure configuration used on compost surfaces.

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^2 and 9.3 liters respectively.

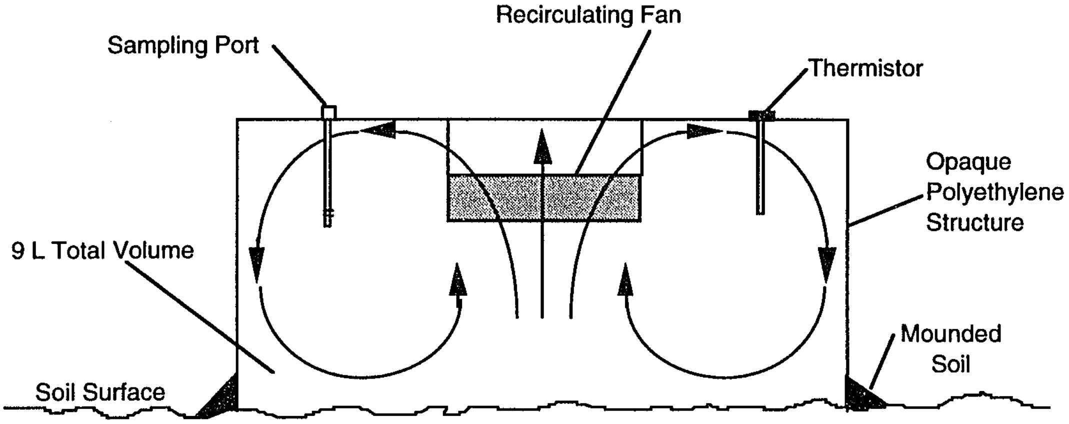

Figure 4 - Enclosure configuration used on landfill soil surfaces.

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^{-1} time^{-1}) from the surface was calculated by

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

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 CH_4 mixing ratio in the enclosure headspace. $\frac{\Delta C}{\Delta t}$ is calculated by linear regression of the 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.