Paper for Luleå 2000, Intercontinental Landfill Research Symposium, 11-13 December 2000, Luleå University of Technology, Luleå, Sweden

FIELD INVESTIGATIONS OF METHANE OXIDATION IN SOIL ADJACENT TO AN OLD LANDFILL

Mette Christophersen & Peter Kjeldsen

Department of Environmental Science and Engineering

Technical University of Denmark, Building 115

DK-2800 Lyngby, Denmark

ABSTRACT

Field investigations of lateral gas transport and subsequent emissions in soil adjacent to an old landfill in Denmark have been conducted during a one-year period. Many indications of methane oxidation were observed. No methane at all emitted during the summer. There was observed elevated soil temperatures in area with methane oxidation. There was a decrease in the CH_4/CO_2 ratio with distance from the landfill and up towards the soil surface, indicating that methane oxidation was taking place. Estimates of the methane oxidation were calculated which showed, as expected, a seasonal variation with higher methane oxidation in the summer. Calculations showed that about 89% of the laterally migrating methane was oxidised on an annual basis at the Skellingsted landfill. Isotope analysis, however, indicated that the calculations overestimated the methane oxidation.

Keywords: methane oxidation, landfill gas, field investigation, seasonal variation, isotope analysis, gas transport model, Denmark

1. INTRODUCTION

Landfills are contributing with about 40 Tg out of the total amount of 600 Tg methane emitted to the atmosphere. Landfill gas (LFG) thereby contributes significantly to the greenhouse effect. Methane is an important greenhouse gas and a more powerful greenhouse gas than carbon dioxide. Over a 100 year span methane has a global warming potential of 21 (kg CH_4/kg CO_2) (Lelieveld, 1998).

There are two main ways to reduce methane emission from landfills. One option is gas recovery with associated gas use, which is very effective at large landfills with high methane generation. At smaller and older landfills with low methane generation it is more effective to encourage methane oxidation in the soil cover of the landfills. In northern Europe there are many small and old landfills with low gas generation. Oxidation of methane in top covers of landfills has been observed at several occasions, and soil exposed to elevated methane concentrations can develop a high capacity for methane oxidation (e.g. Whalen et al., 1990). The methane oxidation is controlled by various environmental factors: temperature, soil water content, nutrients, substrate and oxygen concentrations, etc. (Hanson & Hanson, 1996). Many researchers have investigated methane oxidation in landfill top covers (Kightley et al., 1995; Boeckx et al., 1996; Czepiel et al., 1996; Börjesson & Svensson, 1997; Bogner et al., 1997; Christophersen et al., 2000b). However, only a few investigations have looked at methane oxidation in soils adjacent to a landfill (Kjeldsen & Fischer, 1995; Ward et al., 1996).

Many older landfills, which are placed in abandoned gravel pits are unlined, and compacted waste and impermeable top covers encourage lateral gas migration. However no one has investigated methane oxidation in soils adjacent to landfills, or what influence methane oxidation has on the emissions. The objective of this study was to investigate methane oxidation in soil adjacent to an old municipal landfill, in order to evaluate the importance of methane oxidation on landfill gas emissions.

The field experiments were conducted at Skellingsted landfill, Denmark, which covers an area of 7.5 ha and received waste from 1971-90. The landfill is situated in an abandoned gravel pit located in an area of alluvial sand and gravel sediments. No bottom liner is present. The landfill was covered with a soil layer consisting of approximately 80 cm sand and 20 cm mould at the final closure and the landfill was replanted with grass, trees and bushes. Further information about the landfill is given in Kjeldsen & Fischer (1995) and Christophersen & Kjeldsen (2000a, b).

2. METHODS

Sampling equipment was installed along two transects consisting of nine measuring stations each, at the Skellingsted landfill, in order to measure lateral gas migration and subsequent emissions in the soil adjacent to the landfill (see Figure 1 in Christophersen & Kjeldsen, (2000b)). Transect House was installed close to the only still-existing house at section "C" and transect Field was installed in an area with pronounced crop damage at section "I". The first stations, H1 and M1 were located in the top cover of the landfill. The next stations, H2 and M2, were at the landfill border. The subsequent 7 stations extended in a straight line at increasing distances from the landfill.

Each measuring station consisted of a stationary flux chamber, soil gas probes and probes to measure the water content. Measuring campaigns were conducted every second week from May 97 to May 98. Further information about experimental set-up, materials and methods are given in Christophersen et al. (2000a) and Christophersen & Kjeldsen (2000a,b).

3. RESULTS AND DISCUSSIONS

At the Skellingsted landfill the carbon dioxide flux was higher than the methane flux in almost all situations although the gas composition inside the Skellingsted landfill was about 65% methane and 35% carbon dioxide. The background carbon dioxide flux can not explain the higher flux of carbon dioxide, but a reasonable explanation is methane oxidation. Christophersen & Kjeldsen (2000a) described soil gas profile measurements from Skellingsted landfill and reported several indications of methane oxidation including: (i) changes in the CH_4/CO_2 ratio out through the transect and up through the soil profile at the different stations, (ii) high concentrations/emissions of carbon dioxide associated with methane concentrations/emissions below the detection limit, and (iii) peaks in the nitrogen concentrations in the soil as a result of the volume reduction (Kjeldsen, 1996).

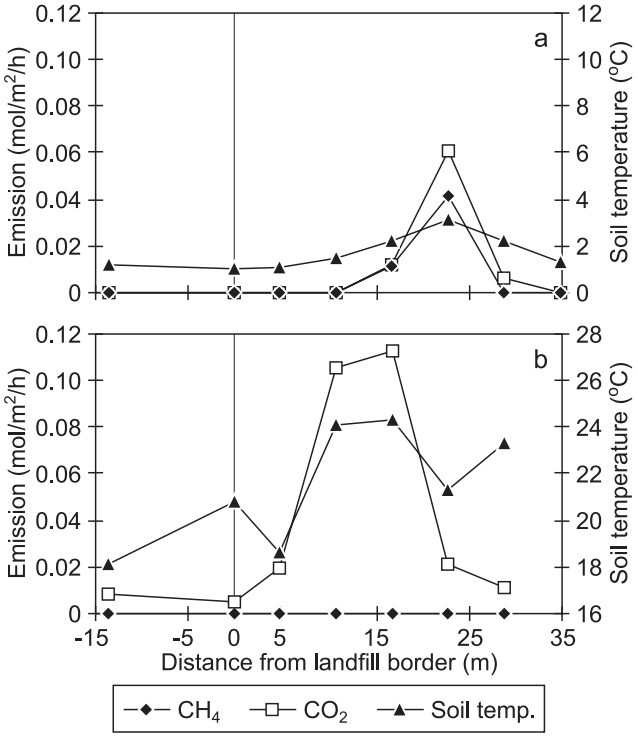

Figure 1. The emissions as a function of distance from the landfill border and the correspondent soil temperature at 10 cm b.s. in transect Field on (a) December 4th and (b) July 16th.

3.1. Soil temperature measurements

Methane oxidation is a biological process and therefore temperature is an important factor. In laboratory experiments an optimum in oxidation rates is observed at 25-35°C (see Christophersen et al. (2000b) for a literature review). Methane oxidation is an exothermal process and the heat produced can cause a desiccation of the soil (Williams & Aitkenhead, 1991).

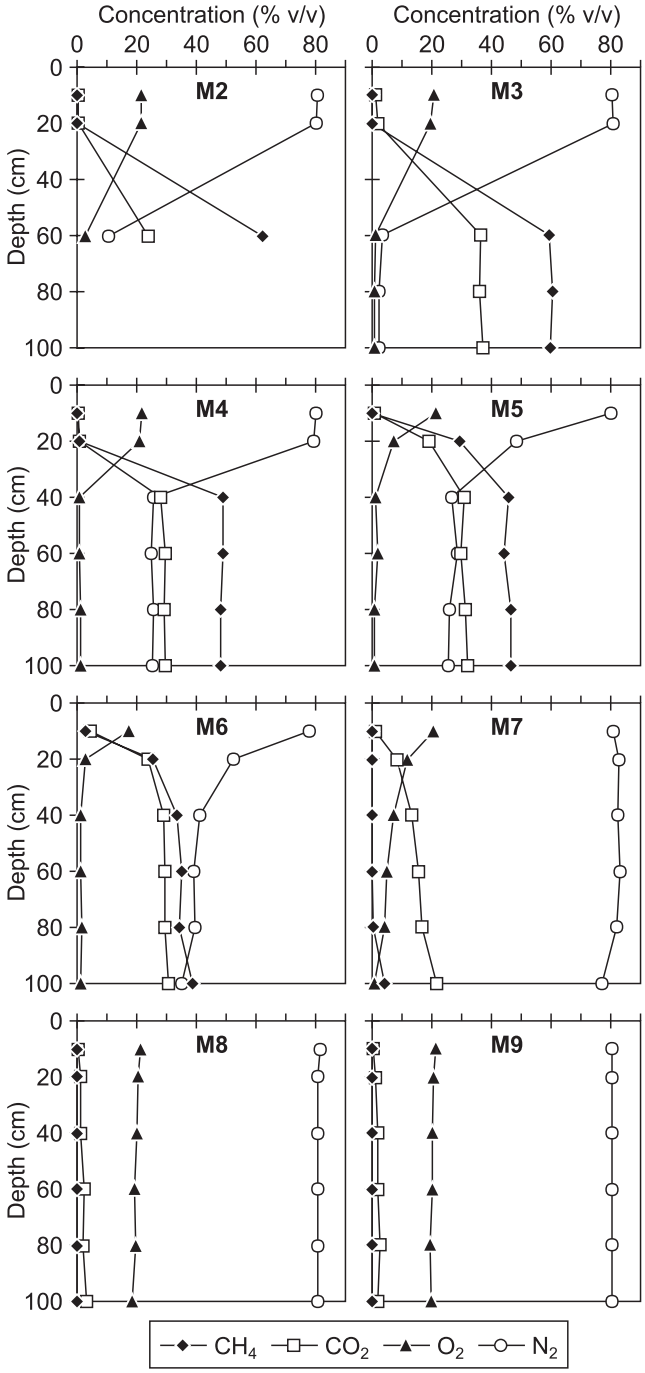

Figure 2. Gas concentration profiles on December 4th 1997 at transect Field. M2 was placed at the landfill border, and stations M3 to M9 was placed respectively 5, 11, 17, 23 29, 35 and 43 m from the landfill border.

Figure 1 shows the emissions as a function of distance from the landfill border and the soil temperature. The air temperature December 4th was –2°C and July 16th it was 25°C. The peak in soil temperature can be caused by heat transported with landfill gas or by methane

oxidation. The temperature inside a landfill can be high due to the anaerobic conversion of the waste. The temperature inside Skellingsted landfill was measured 3 m.b.s. three times in two boreholes in April and May 1998 near transect Field. The temperatures were similar to the soil temperatures measured at station M9 at 1 m b.s. on the same days. The temperatures at station M9 are considered to be the background soil temperature. It does not appear that migrating LFG is the cause of rising temperatures at Skellingsted landfill. On December 4th the soil temperature over depth at station M4, 11 m from the landfill border, was a little warmer but only in the top 40 cm (app. 1°C) compared with station M9, 43 m from the landfill border, which suggests that methane oxidation is taking place in the top 40 cm. The most reasonable explanation of the peak in soil temperature is methane oxidation.

3.2. CH_4/CO_2 ratios

Figure 2 shows the depth-concentration profiles at transect Field on December 4th 1997, where the averaged daily temperature was below zero. Close to the landfill the concentration of methane was higher than the carbon dioxide concentration. Further away from the landfill the concentration of methane decreased, but the concentration of carbon dioxide was almost constant. No methane was detected at station M7 down to 80 cm b.s., but up to 22 % v/v carbon dioxide was measured. At station M7 there was also a rise in the nitrogen concentration compared with the content of atmospheric nitrogen, which is also an indication of methane oxidation (confer Kjeldsen, 1996). Humer & Lechner (1999) also found nitrogen concentrations higher than the atmospheric content in areas with methane oxidation.

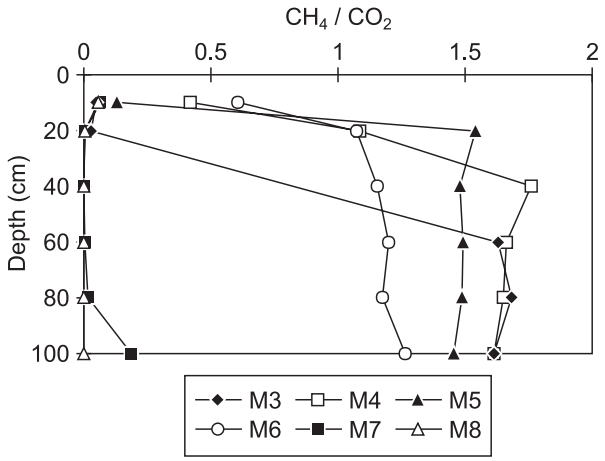

Figure 3. The CH_4/CO_2 ratios on December 4th 1997 at stations M3 to M8 in transect Field (5 to 35 m from the landfill border).

The CH_4/CO_2 ratios on December 4th 1997 are shown in Figure 3. In the deeper probes at station M3 and M4 pure LFG was measured. There was a decrease in the CH_4/CO_2 ratio with distance from the landfill and up towards the soil surface, indicating that methane oxidation was taking place.

3.3. Calculation of in-situ methane oxidation

A combination of flux measurements and soil gas profiles can be used to calculate an estimate of the methane oxidation in the top one meter of a soil profile. It is assumed that no carbon dioxide is dissolved in the infiltrating water and that the production of gas in the soil is negligible. Under stationary conditions the total flux of LFG at the surface is equal to that at the bottom of the profile (at 1 m b.s.). The total flux of landfill gas is:

$$J_{D\,LFG} = J_{D\,CH4\,top} + J_{D\,CO2\,top} = J_{D\,CH4\,bottom} + J_{D\,CO2\,bottom}$$

Where J_D is the flux in mol/m^2/h. Knowing the total flux of landfill gas at the surface and the CH_4/CO_2 ratio at 1 m b.s. the flux of methane at 1 m b.s. (bottom) can be calculated:

$$J_{D\,CH4\,bottom} = \left(J_{D\,CH4\,top} + J_{D\,CO2\,top}\right) \cdot \left(\frac{C_{CH4bottom}}{C_{CH4bottom} + C_{CO2bottom}}\right)$$

The difference between the methane flux at the top and at the bottom is the amount of methane, which is oxidised within the top 1 m of the soil profile:

$$MO = J_{D\,CH4\,bottom} - J_{D\,CH4\,top}$$

Figure 4 shows the calculated methane oxidation in mol CH_4 pr. hour pr. meter of landfill border (interpolation between the stations) and the percentages of methane oxidation when compared with the methane flux at the bottom of the profile at transect Field. As expected there was a seasonal variation with higher methane oxidation in the summer period, which was caused by the higher temperatures and thereby higher methanotrophic activity. On December 4th, which was in a period with air temperatures below zero, a considerable amount of methane was still oxidised. That is in agreement with the results of Christophersen et al. (2000b), who proved that methane oxidation was occurring at 2°C in soils from Skellingsted landfill.

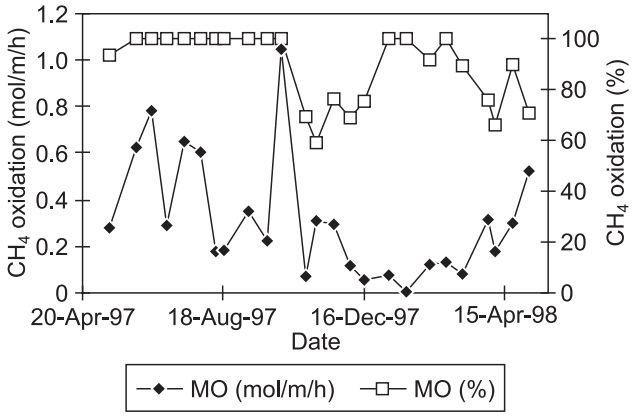

Figure 4. Calculated estimates of methane oxidation in mol CH_4 pr. meter of landfill border pr. hour and percentage of methane oxidation as a function of time in transect Field.

In the summer all the methane was oxidised and also in the winter, high percentages of methane oxidation was found. The lowest percentage of methane oxidation was 60 (November 6th 1998) and on average 89% of the methane was oxidised. Calculations were made where the background carbon dioxide flux was subtracted to investigate whether the background carbon dioxide flux had significant influence on the calculated methane oxidation. The calculations showed that the background carbon dioxide flux had only a slight influence on the methane oxidation. The averaged annual percentage of methane oxidation was 88% when the background carbon dioxide flux was subtracted.

Czepiel et al. (1996) found that 10% of the produced methane was oxidised in the top cover on an annual basis. Chanton et al. (1999) found an annual methane oxidation of 12% in the top cover of a landfill using isotope analysis. The oxidation was greatest in the summer and in the fall. Chanton & Liptay (2000) found an annual methane oxidation of 26% for areas of a landfill with mulch/topsoil and 14% for areas with clay using isotope analysis to quantify methane oxidation in the top cover of a landfill in Florida. A somewhat higher value was found by Bergamaschi et al. (1998), who reported a range of 80-97% oxidation of the methane in landfill cover soils.

3.4. Isotope analysis

Significant isotopic fractionation occurs when methane is oxidised to carbon dioxide. The methanotrophic bacteria preferentially consume lighter isotopes leaving residual methane enriched in both ^{2}H (deuterium) and ^{13}C. On May 6th 1998 samples for methane isotope analysis were taken at stations M4, M5 and M6: the results are shown in Figure 5. At 1 m b.s. $\partial^{13}C$ was very similar (-54.2 to –55.7‰) to what others have reported for landfill gas. See Chanton et al. (1999) for a review of published isotopic values for anoxic zone methane. At station M4, 11 m from the landfill border, the decrease in $\partial^{13}C$ up towards the soil surface was quite small indicating that not much methane had been oxidised, but at station M5 and especially at station M6 larger amounts of methane were oxidised.

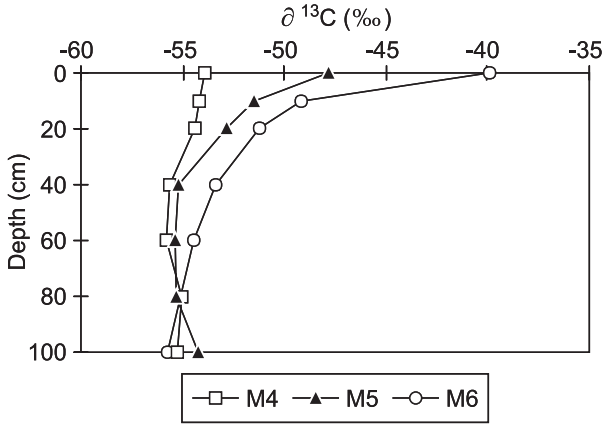

Figure 5. The $\partial^{13}C$-value for methane as a function of depth at stations M4, M5 and M6 11, 17 and 23 m respectively from the landfill border in transect Field.

In these investigations the isotopic fractionating factor α which is defined as the ratio of the rate constants for methane containing the light and the heavy isotope assuming first-order kinetics, was not determined. If α is known the isotopic analysis can be used to quantify the methane oxidation and the results can be compared with the above calculated methane oxidation percentages. Liptay et al. (1998) found at 25°C α=1.022 and in Chanton & Liptay (2000) α is adjusted for a temperature dependency equal to 0.000435/°C. On May 6th the soil temperature at 10 cm b.s. was 12°C and this gives α=1.028. Now the fraction of methane oxidised can be calculated:

$$f_o = \left(\frac{\delta E - \delta A}{(\alpha - 1) \cdot 1000}\right)$$

δE and δA represent the isotopic composition of the emitted zone and the anoxic zone. The $\partial^{13}C$-values at the bottom of the soil profiles were used as δA and the $\partial^{13}C$-values at the different depths were used as δE. In this way f_o was calculated for each depth and for the top 1 m of the soil profile. The largest part of the methane oxidation occurred in the top 10 cm of the soil profile. At stations M4 and M5 methane oxidation was occurring in the top 40 cm, while at station M6 methane oxidation was occurring in the top 1 m of the soil profile. In Table 1 the percentages of methane oxidised in the top 1 m of the soil profile are shown. To evaluate the sensitivity of different α-values on f_o the calculations were repeated with a higher and a lower α (see Table 1), both of which are within the range reported in the literature (Reeburgh, 1996). When the f_o-values found using the isotope analysis is compared with the percentages of methane oxidation calculated in section 3.3 it appears that the box-calculations in section 3.3 overestimate the methane oxidation.

Table 1. Percentages of methane oxidation within the top 1 m of the soil profile on May 6th 1998 calculated using the isotope analysis and with different values for the fractionating factor α. The last column is the results using the concentrations and flux measurements.

Station	α=1.028	α=1.022	α=1.031	Fluxes
M4	5	6	4	19
M5	23	29	21	62
M6	57	72	51	72

3.5. Modelling

The measured gas concentrations and fluxes at the Skellingsted landfill were used as input to a numeric gas transport model (Poulsen et al., 2000). The model was used to evaluate the sensitivity of the concentrations and the fluxes to changes in: methane oxidation, diffusion, gas permeability, barometric pressure and soil moisture content. The results of the sensitivity analysis indicated that landfill gas migration in the field was most sensitive to air permeability and soil moisture content, which is consistent with the statistical analysis of the fluxes (Christophersen et al., 2000a). For the concentrations in the soil, moisture content was the second most important factor followed by methane oxidation however barometric pressure had less influence. Diffusion had no influence at all, which is in agreement with calculations comparing diffusiv and advective flux.

Barometric pressure had larger influence on the fluxes compared with the concentrations in the soil and was the second most important factor for the fluxes. The sensitivity was largest under large changes in barometric pressure. This indicated that changes in barometric pressure were more important than the actual barometric pressure. That was also found by the diurnal measurements during the drop in barometric pressure. The sensitivity for methane oxidation was largest in the summer, and methane oxidation had larger influence on the fluxes compared with the concentrations.

4. CONCLUSIONS

Many indications of methane oxidation were observed at Skellingsted landfill (changes in CH_4/CO_2 ratios, peaks in nitrogen concentrations, temperature rises, high carbon dioxide flux but non-detected methane flux). Methane oxidation was a very important process for the LFG emissions. In the summer no methane at all was emitted at the sampling stations. Estimates of the methane oxidation were calculated which showed, as expected, a seasonal variation with higher methane oxidation in the summer. Calculations showed that about 89% (in relation to the calculated methane flux at 1 m b.s. and summarised out through the transect) of the laterally migrating methane was oxidised on an annual basis at the Skellingsted landfill. Isotope analysis, however, indicated that the calculations overestimated the methane oxidation.

A numeric model was used to evaluate the sensitivity of landfill gas concentration and flux with respect to a set of governing parameters. The results of the sensitivity analysis indicated that landfill gas migration in the field soil was most sensitive to air permeability and soil-water content. Methane oxidation rate and atmospheric pressure variations had some effects, especially on the gas flux, whereas gas diffusion was not important.

5. REFERENCES

Bergamaschi, P., Lubina, C., Konigstedt, R., Fischer, H., Veltkamp, A.C. & Zwaagstra, O. (1998) Stable isotopic signatures (delta C-13, delta D) of methane from European landfill sites. *Journal Of Geophysical Research-Atmospheres* **103** (D7), 8251-8265.

Boeckx, P., Van Cleemput, O. & Villaralvo, I. (1996) Methane emission from a landfill and the methane oxidizing capacity of its covering soil. *Soil Biological Biochemistry* **28,** 1397-1405.

Bogner, J., Spokas, K. & Burton, E.A. (1997) Kinetics of Methane Oxidation in a Landfill Cover Soil: Temporal Variations, a Whole-Landfill Oxidation Experiment, and Modeling of Net CH_4 Emissions. *Environmental Science and Technology* **31**, 2504-2514.

Börjesson, G. & Svensson, B.H. (1997) Seasonal and diurnal methane emissions from a landfill and their regulation by methane oxidation. *Waste Management & Research* **15,** 33-54.

Chanton, J. & Liptay, K. (2000) Seasonal variation in methane oxidation in a landfill cover soil as determined by an in situ stable isotope technique. *Global Biogeochemical Cycles* **14,** 51-60.

Chanton, J.P., Rutkowski, C.M. & Mosher, B. (1999) Quantifying methane oxidation from landfills using stable isotope analysis of downwind plumes. *Environmental Science & Technology* **33**, 3755-3760.

Christophersen, M. & Kjeldsen, P. (2000a) Lateral gas transport in soil adjacent to an old landfill: Factors governing gas migration. Accepted for publication in *Waste Management and Research*.

Christophersen, M. & Kjeldsen, P. (2000b) Factors governing lateral gas migration and subsequent emission in soil adjacent to an old landfill. Paper for Luleå 2000, Intercontinental Landfill Research Symposium, 11-13 December 2000, Luleå University of Technology, Luleå, Sweden

Christophersen, M., Holst, H., Chanton, J. & Kjeldsen, P. (2000a) Lateral Gas Transport in Soil adjacent to an Old Landfill: Factors Governing Emission and Methane Oxidation. Accepted for publication in *Waste Management and Research*.

Christophersen, M., Linderød, L., Jensen, P.E. & Kjeldsen, P. (2000b) Methane Oxidation at Low Temperatures in Soil Exposed to Landfill Gas. *Journal of Environmental Quality*. In press.

Czepiel, P.M., Mosher, B., Crill, P. M. & Harriss, R.C. (1996) Quantifying the effect of oxidation on landfill methane emissions. *Journal of Geophysical Research* **101**, (D11) 16721-16729.

Hanson, R.S. & Hanson, T.E. (1996) Methanotrophic Bacteria. *Microbiological Rewiews* **60,** 439-471.

Humer, M. & Lechner, P. (1999) Methane oxidation in compost cover layers on landfills. In: Christensen, T.H., Cossu, R. & Stegmann, R. (eds), *Proceedings Sardinia 99, Seventh International Waste Management and Landfill Symposium*, S. *Margherita di Pula, Cagliari, Italy, 4-8 October 1999*. Cagliari, Italy: CISA, pp. 403-410.

Kightley, D., Nedwell, D.B. & Cooper, M. (1995) Capacity for Methane Oxidation in Landfill Cover Soils Measured in Laboratory-Scale Soil Microcosms. *Applied and Environmental Microbiology* **61**, 592-601.

Kjeldsen, P. (1996) Landfill gas migration in soil. In: Christensen, T.H., Cossu, R. & Stegmann, R. (eds) *Landfilling of waste: Biogas.* London, GB: E & FN Spon,

Kjeldsen, P. & Fischer, E.V. (1995) Landfill gas migration - Field investigations at Skellingsted landfill, Denmark. *Waste Management & Research* **13,** 467-484.

Lelieveld, J., Crutzen, P. J., & Dentener, F. J. (1998) Changing concentration, lifetime and climate forcing of atmospheric methane. *Tellus* **50B**, 128-150.

Liptay, K., Chanton, J., Czepiel P. & Mosher, B. (1998) Use of stable isotopes to determine methane oxidation in landfill cover soils. *Journal Of Geophysical Research-Atmospheres* **103** (D7), 8243-8250.

Poulsen, T.G., Christophersen, M., Moldrup, P. & Kjeldsen, P. (2000) Modelling lateral gas transport in soil adjacent to an old landfill. Accepted for publication in *Journal of Environmental Engineering.*

Reeburgh. W. S. (1996), "Soft spot" in the global methane budget. In: Lidstrom, M. E. & Tabita, F. R.(eds), *Microbial Growth on C1 Compounds.* Dordrecht, Netherlands: Kluwer Academic Publishers, pp. 334-342.

Ward, R. S., Williams, G. M. & Hills, C. C. (1996) Changes in major and trace components of landfill gas during subsurface migration. *Waste Management & Research,* 14, 243-261.

Whalen, S.C., Reeburgh, W.S. &. Sandbeck. K.A. (1990) Rapid Methane Oxidation in a Landfill Cover Soil. *Applied and Environmental Microbiology* **56**, 3405-3411.

Williams, G.M. & Aitkenhead, N. (1991) Lessons from Loscoe: the uncontrolled migration of landfill gas. *Quarterly Journal of Engineering Geology* **24**, 91-207.