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METHANE EMISSION FROM A LANDFILL AND THE METHANE OXIDISING CAPACITY OF ITS COVERING SOIL

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Summary—Methane emission from a small covered landfill site showed, seasonally varying fluxes, ranging from −5.9 to 914.3 mg CH_4 m^{-2} d^{-1}. The moisture content of the CH_4-oxidising cover soil was thought to cause this variation. Comparing gross and net CH_4 emission rates, it was found that the cover soil, due to its CH_4 oxidising capacity, had a large mitigating effect on the CH_4 emission. In laboratory experiments the effects of soil moisture, temperature and different ammonium amendments on CH_4 oxidation were investigated. When the moisture content and temperature were combined, CH_4 oxidation rates between 0.88 and 10.86 ng CH_4 g^{-1} h^{-1} were observed. The optimum moisture content ranged between 15.6 and 18.8% w/w (±1/2 WHC). The optimum incubation temperature (30–20°C) decreased with increasing moisture contents. For the oxidation rates at 10 and 20°C, we found an average Q_{10} value of 1.88 ± 0.14. The activation energy for moisture contents between 5 and 25% was 83.0 ± 4.4 kJ mol^{-1}. Increased ammonium additions reduced the CH_4-oxidising capacity. This reduction decreased with increasing moisture contents. A high correlation ($R^2 > 0.98$) was found between the moisture content and the reduction of the CH_4 uptake rate mg^{-1} NH_4^+–N kg^{-1} added. Because the nitrification rate was also lower at higher moisture contents, it was thought that the CH_4 oxidation rate was more closely connected with the NH_4^+ turnover rate than with its actual concentration. Multiple linear regression analysis of the CH_4 oxidation rates under the different incubation conditions showed the following decreasing effect on the CH_4-oxidising capacity of the soil: amount of NH_4^+ added > moisture content > incubation temperature. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Methane is a radiatively active gas, contributing to about 15% to the potential global warming (OTA, 1991). Over a time span of 100 y CH_4 has as a warming potential 21 times that of CO_2, which is the most significant greenhouse gas. Projections for the year 2000 suggest that, due to an increase in human population and waste generation, landfills could become a major source of atmospheric methane (Kreileman and Bouwman, 1994). The most reliable estimates of methane emission from landfills are situated around 40 (10–70) Tg y^{-1} (Bingemer and Crutzen, 1987; Cicerone and Oremland, 1988; Matthews *et al.*, 1993; Lelieveld and Crutzen, 1993; Kreileman and Bouwman, 1994). This is about 8% of the total CH_4 emission and 11% of the global anthropogenic contribution (WMO, 1995). Europe and North America are responsible for about half of the CH_4 emission from landfills. Although, at this time, important improvements are being made towards landfill management, it is believed that by the year 2050, CH_4 emission from landfills could increase by up to 81 Tg y^{-1} (Kreileman and Bouwman, 1994) or even 93 Tg y^{-1} (van Amstel *et al.*, 1993). Without important mitigating options, landfills could become the third major source of atmospheric CH_4. However, if all potential mitigating options can be achieved by the year 2025 the global CH_4 emission from landfills is estimated at 13 Tg y^{-1} by the year 2100 (van Amstel *et al.*, 1993).

Methods for managing municipal solid waste (MSW) vary widely, ranging from open dumps, burning to sanitary landfills. Two main alternatives exist for managing CH_4 emission from landfill sites (Aitchison, 1993). One option is to undertake landfill gas recovery with associated gas use, and is generally regarded as being the superior choice. The alternative option is that of encouraging CH_4 oxidation in the soil covering the landfill. This is a much cheaper and more effective option for reducing emissions in smaller and older landfills with lower amounts of CH_4 generation, compared with gas extracting, which becomes inefficient at low CH_4 contents. The top soil of a landfill is a dynamic mixing zone for air and landfill gas. Oxygen and nitrogen concentrations decrease with depth, while CH_4 and CO_2 increase with depth. Methane emis-

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sions through the cover soil are greatly reduced by the relative abundance of methanotrophic bacteria within the aerated cover soil (Jones and Nedwell, 1993). High CH_4 oxidation rates in landfill cover soils were reported by Whalen *et al.* (1990) and Kightley *et al.* (1995). These authors found oxidation rates of 45 and 166 mg CH_4 m^{-2} d^{-1}, respectively. It was found that microbial CH_4 oxidation is controlled by several soil properties such as: soil moisture (Adamsen and King, 1993; Whalen *et al.*, 1990), ammonium and nitrite content (King and Schnell, 1994), pH (Hütsch *et al.*, 1994), temperature (Dunfield *et al.*, 1993; Whalen *et al.*, 1990) and nitrogen turnover (Mosier *et al.*, 1991; Steudler *et al.*, 1995).

Relatively little work has been done on CH_4 emission measurements from landfills and the mitigating effect of its covering soils. Landfill CH_4 emission estimates are highly uncertain, because factors influencing gas emission and mitigation are site specific (Meadows, 1996). Landfill CH_4 emissions can range over six orders of magnitude (Bogner and Scott, 1995). These authors observed emissions ranging from 0.003 to more than 1000 g CH_4 m^{-2} d^{-1}. In our work we measured CH_4 emission rates from a small older landfill site. We also looked at the oxidising potential of its covering soil and the role of controlling factors such as the soil moisture content, temperature and ammonium amendments.

MATERIAL AND METHODS

Field experiment

The field experiments were done on a small (±0.5 ha) and old (closed > 5 y) landfill for MSW. The landfill is situated in Schoten near Antwerp (Belgium). It is no longer operational any more and the surface is covered with a soil layer of ±30 cm thick, covered by grass and small trees. Data of CH_4 emission rates as well as of the CH_4 mitigating capacity of the soil covering the landfill were collected. Diffusion chambers (H = 600 mm, dia. = 150 mm) were used to determine the CH_4 flux from the landfill site. The boxes had a removable lid with a rubber septum for gas sampling. After the boxes were closed gas could accumulate in its headspace and gas samples were taken 0, 20 and 40 min after closure. By fitting a linear regression through the calculated headspace concentration, and adjusting for the box volume and the surface covered, the CH_4 flux could be determined. One set of six chambers was placed on top of the soil and another set of six chambers was placed directly on to the buried waste after removal of the cover soil. The walls of the latter covered the surrounding cover soil, to avoid lateral gas migration from the surrounding soil into the chamber. In both cases the same headspace height was used. The chambers were distributed on the landfill in a random way, but chambers placed on top of the cover soil and buried chambers were always placed close to each other to avoid anomalies. The boxes placed directly on the waste were used to measure the CH_4 emission from the refuse (gross emission), while the boxes placed on the surface were used to measure the CH_4 emission after the landfill gas had passed through the cover soil (net emission). The difference between these two emission rates gives information on the potential CH_4-oxidising capacity of the cover soil. During part of 1994, emission data were collected on a monthly basis to obtain a measure of the seasonal variability of the gross and net CH_4 emission. All seasonal measurements were made at the same location.

Laboratory experiments

The CH_4-oxidising capacity of the cover soil was also tested under controlled laboratory conditions. At one location on the landfill a complete layer (±30 cm) of the soil covering the landfill was collected. The soil was air dried, ground, mixed and sieved (2 mm) before use. In an initial experiment, the combined effect of soil temperature and moisture content towards the CH_4-oxidising capacity was determined. In a second experiment, the effect of ammonium and moisture content was tested. Airtight bottles (180 ml), sealed with rubber septa for gas sampling, were filled with 30 g of air dry soil and brought to moisture contents of 5, 10, 15, 20, 25 or 30% w/w (30% = WHC). To study the combined effect of temperature and water content, the soil was incubated at 5, 10, 20, 25 or 30°C at each moisture content. The effect of the ammonium and moisture content was tested with NH_4^+–N amendments of 25, 50 or 75 mg kg^{-1} at 25°C. Before CH_4 was injected into the bottles (10 μl l^{-1}) the soils were conditioned for 7 days at ambient CH_4 concentrations. Gas samples were taken 0, 2, 4, 8 and 24 h after CH_4 injection. Each treatment was triplicated.

Soil properties

The soil covering the landfill had the following granulometric composition: 8.9% clay, 39.0% silt and 52.2% sand. According to the USDA textural classification this soil is situated on the border of a sandy loamy and loamy soil. The total C content was 0.6%, the $CaCO_3$ content was 1.53% and the pH was 7.3. Its mineral N content was as follows: 4.0 mg NO_3^-–N kg^{-1} and 8.6 mg NH_4^+–N kg^{-1}.

Temperature and water content of the landfill cover soil

While the CH_4 emission from the landfill was measured, the soil temperature was measured with a thermometer at 5 cm depth. Samples from the entire soil depth were also removed and dried at 105°C to determine their moisture content.

Gas analysis

The headspace concentration of CH_4 was determined with a Chrompack CP 9000 chromatograph. After injection, part of the gas was led through a 1.8 m × 3 mm NaI deactivated alumina column (100–120 mesh). CH_4 was measured using a flame ionisation detector (FID). Helium was used as carrier gas (36 ml min^{-1}). The analyses were carried out under the following conditions: injector temperature 65°C, oven temperature 55°C and detector temperature 200°C. The chromatograms were registered and analysed using the Thermo Separation System "WOW" software package. Mixtures of $50.3 \pm 1.5\ \mu l\ l^{-1}$ CH_4 in Ar and $513 \pm 15\ \mu l\ l^{-1}$ CH_4 in N_2 (L'air Liquide, Belgium) were used as standard gas.

Statistical analysis

The CH_4 oxidation rates were calculated from the CH_4 mixing ratio at the beginning of the experiment and the mixing ratio after 24 h. The decrease of the CH_4 headspace concentration in the incubation flasks followed first order kinetics ($d[CH_4]/dt = -k[CH_4]$). Plotting the logarithm of the CH_4 concentration against the incubation time a linear curve was found. From the slope of this curve the oxidation rate constants were calculated. Statistical analysis of the data was done with the SPSS for Windows software package. Multiple linear regression was used to fit independent variables in a model explaining a certain percentage of the variance of the CH_4 oxidation rates.

Inorganic N determination

Mineral N was extracted with 60 ml of 1 M KCl 30 g^{-1} dry soil. This suspension was shaken for 1 h. In the filtrate ammonium was determined acidimetrically after distillation and $NO_3^- + NO_2^-$ was determined as NH_4^+, after reduction with Devarda alloy (Keeney and Nelson, 1982). The nitrification rate in the soil was determined at a moisture content of 10 and 30%. After a period of 7 days conditioning, 25 or 100 mg NH_4^+–N kg^{-1} was added to the soil. Zero, 2 and 4 days after ammonium addition, the NO_3^-–N + NO_2^-–N content of the soil was determined. By fitting a linear regression through these data the nitrification rate was calculated.

RESULTS AND DISCUSSION

Field experiment

Gross and net CH_4 emission rates are presented in Table 1. These emissions show a high variability because of the large heterogeneity of landfill sites (Meadows, 1996). The gross CH_4 emission rates give an indication of the CH_4 production rates of the waste. The values we found are of the same order of magnitude as the CH_4 production rates derived from a 20 m deep layer of a landfill (Kightley and Nedwell, 1994). The gross CH_4 emission from the non-covered spots showed lower CH_4 emissions during autumn. At that time, the holes of the non-covered spots were partially filled with rain water. CH_4 transport is about 10^4 times less rapid in water than in air. Therefore, probably lower gross CH_4 emission rates were measured during this part of the year.

The net emission data were much lower and importantly changed seasonally. During summertime (June–September) the net CH_4 emission was lower than in autumn (October–December). Besides external controlling factors such as barometric pressure, wind speed and engineered controls (gas recovery system), the moisture content of the cover soil is the most important internal factor controlling CH_4 emission from landfills (Bogner, 1992; Bogner *et al.*, 1995). When the moisture content of fine-textured cover soils (e.g. clayey soils) rises it can effectively seal the cover soil (Bogner, 1992; Kjeldsen and Fischer, 1995; Tosh *et al.*, 1994). This sealing effect can reduce the vertical gas permeability of the soil layer and increase gas pressure in the upper refuse. The CH_4-oxidising capacity of a landfill cover soil is also importantly influenced by its moisture content (Boeckx and Van Cleemput, 1996; Bogner *et al.*, 1995; Whalen *et al.*, 1990). From Table 1 it can be seen that the CH_4 emission increased with increasing moisture contents until the WHC (30% w/w) is reached. When the moisture content of the cover soil increases its O_2 concentration will drop because of a limited diffusion into the soil. CH_4 diffusion to the cell surface of the methanotrophic bacteria is also slower. As a result of this, less CH_4 will be oxidised and its emission will increase. In December, the cover soil reached a moisture content above its WHC and a decreased

Table 1. Methane emission from covered (net emission) and non-covered (gross emission) landfill spots

Time of the year	Soil temperature °C	Soil moisture %	Net CH_4 flux covered spots mg CH_4 m^{-2} d^{-1}	Coefficient of variance %	Gross CH_4 flux non-covered spots g CH_4 m^{-2} d^{-1}	Coefficient of variance %
June	20.0	8.1	14.2	60.3	156.5	68.1
July	24.5	5.5	−5.9	315.6	176.3	84.2
August	24.0	3.8	50.2	91.4	230.8	86.3
September	18.5	16.0	87.2	132.4	137.4	102.0
October	13.5	29.8	416.0	178.2	21.6	183.2
November	8.0	22.3	914.3	146.5	2.2	124.2
December	10.0	33.1	189.2	127.4	15.1	106.2

CH_4 emission was observed. At this moisture level all air pores are filled up. The sealing of the cover soil is probably responsible for the reduced CH_4 emission. In summer time, with drier soil conditions gas diffusion shifts from aqueous- to gas-phase diffusion. CH_4 transport to the cell surface of the CH_4-oxidising bacteria and oxygen diffusion into the soil is more rapid. This can result in an increased CH_4 oxidising activity and a reduced CH_4 emission. The higher soil temperatures during summertime can also cause physiological changes of the methanotrophs, resulting in higher oxidation rates.

When the net and gross emission rates from Table 1 are compared, and assuming that the gross emissions from October–December were not representative for the actual CH_4 production rates in the landfill, we may conclude that almost all the CH_4 was oxidised before it reached the atmosphere. In addition, during July 1994, the cover soil was even consuming rather than emitting CH_4. This was also observed by Bogner *et al.* (1995), who found negative fluxes ranging from -0.3 to $-5.0\,\mathrm{mg\,m^{-2}\,d^{-1}}$. Soils which have been previously exposed to elevated CH_4 concentrations can develop a large methanotrophic population and consequently a high CH_4-oxidising capacity (Jones and Nedwell, 1993). Bender and Conrad (1992) reported superimposed biphasic saturation curves for CH_4 oxidation. Soils conditioned at high CH_4 mixing ratios (20% CH_4) showed an 11–195-fold higher CH_4 removal rate than soils which were not conditioned. It is supposed that low activity methanotrophic bacteria are responsible for these high CH_4 removal rates. So, soils permanently exposed to high CH_4 concentrations, as is the case in landfill cover soils, can develop a high CH_4 oxidising capacity by which almost all the *in situ* produced CH_4 can be removed. High CH_4-oxidising rates in landfill cover soils were also reported by Whalen *et al.* (1990) and Kightley *et al.* (1995). These authors measured maximum CH_4 oxidation rates of 45 and $166\,\mathrm{g\,CH_4\,m^{-2}\,d^{-1}}$, respectively. The observation of low emission rates, eventually negative fluxes and high CH_4 oxidation rates can have important implications on the estimates for the global CH_4 budgets from landfills.

Laboratory experiments

Effect of moisture content and temperature. The influence of soil moisture and temperature on the CH_4 oxidation rates and the oxidation rate constants are shown in Fig. 1 and Table 2. It is clear that CH_4 oxidation occurred at an optimum soil moisture content and temperature. To estimate these optima, CH_4 oxidation rates were plotted against the incubation temperature as well as against the soil moisture content. In both cases third order polynomials provided the best fit ($R^2 > 0.96$). For each treatment the optima were cal-

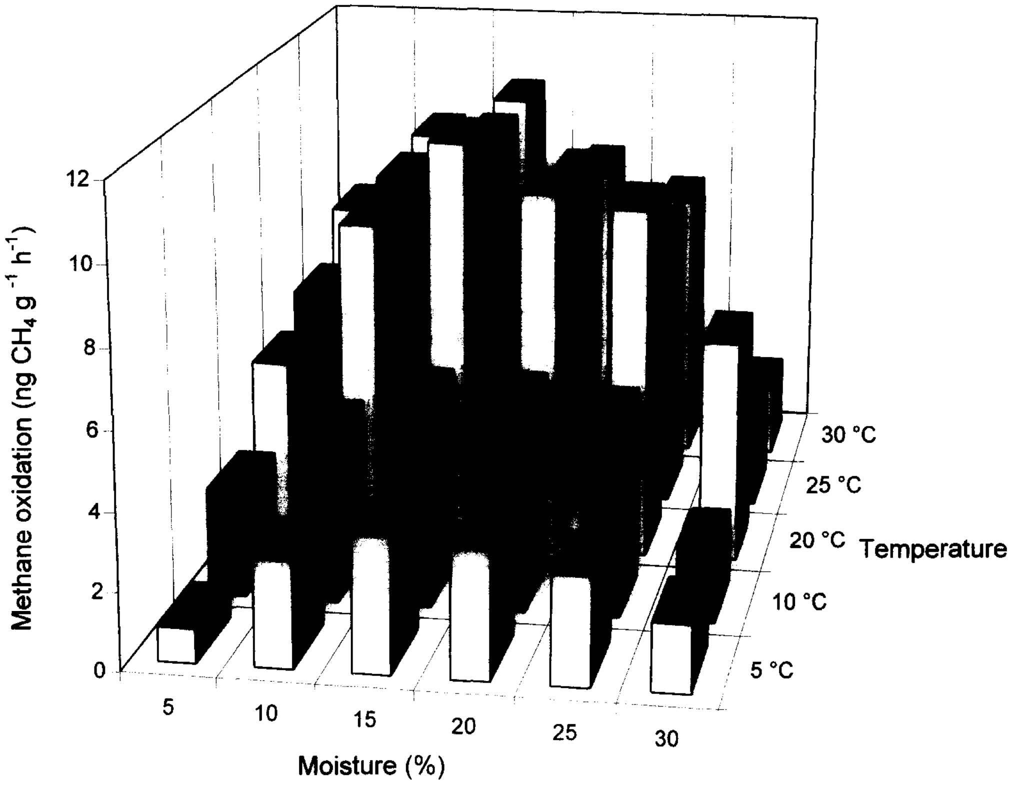

Fig. 1. Methane oxidation rates as a function of soil moisture and temperature.

Table 2. CH_4 oxidation rate constants ($k1$) and standard error (S.E.) as a function of soil moisture and temperature

Moisture content	5°C	10°C	20°C	25°C	30°C
%			$k1$ (h^{-1}) ± SE		
5	0.0064 ± 0.0001	0.0217 ± 0.0052	0.0486 ± 0.0046	0.0495 ± 0.0018	0.0734 ± 0.0004
10	0.0219 ± 0.0018	0.0399 ± 0.0021	0.1265 ± 0.0022	0.0972 ± 0.0067	0.1008 ± 0.0025
15	0.0289 ± 0.0012	0.0522 ± 0.0073	0.2038 ± 0.0015	0.1219 ± 0.0056	0.1271 ± 0.0009
20	0.0252 ± 0.0014	0.0526 ± 0.0005	0.1515 ± 0.0076	0.1113 ± 0.0005	0.0819 ± 0.0050
25	0.0213 ± 0.0002	0.0410 ± 0.0024	0.1289 ± 0.0049	0.0768 ± 0.0047	0.0690 ± 0.0037
30	0.0162 ± 0.0026	0.0151 ± 0.0006	0.0490 ± 0.0018	0.0188 ± 0.0056	0.0146 ± 0.0017

culated from the first derivative ($dy/dx = 0$) of these polynomials. We obtained optimum moisture contents between 15.6 and 18.8% w/w (Table 3). The optimum incubation temperature, however, varied with the soil moisture content. At 5% w/w no optimum temperature was found, which indicates that the methanotrophic activity was not rate limiting. At all other moisture contents an optimum temperature was found which decreased with increasing moisture contents (Table 3). The region between minimum and optimum temperature could be described with an Arrhenius relationship. The Arrhenius plot of the temperature response was linear between 5 and 20°C. In Table 4 the Arrhenius plots are shown together with the activation energy (E_a) calculated from this linear part and the Q_{10} values which were calculated with the oxidation rate constants at 10 and 20°C. For moisture contents between 5 and 25%, the average activation energy was 83.0 ± 4.4 kJ mol^{-1}. The average Q_{10} value was 1.88 ± 0.14. The Q_{10} values are very similar to those measured by Adamsen and King (1993), Crill *et al.* (1994) and Dunfield *et al.* (1993). The values of the activation energy were higher but of the same order of magnitude as those reported by Crill *et al.* (1994) and Nedwell and Watson (1995). At 30% w/w, the E_a and the Q_{10} value were respectively lower and higher than the values found at moisture contents between 5 and 25%. A reason for this was not found.

Biological CH_4 consumption in soils is primarily controlled by the activity of the CH_4 mono-oxygenase (MMO) enzymes, gas-phase and aqueous-phase molecular diffusion of CH_4 and O_2 as well as by physiological stress of the methanotrophs (King and Adamsen, 1992). In drier soils gas diffusion to the cell surface of the bacteria is easier than in wetter soils. Although substrate supply is optimal in dry soils, the CH_4 consumption can still be limited due to a reduced microbial activity. Physiological stress of the methanotrophic population at low moisture contents slows down its enzymatic activity. Therefore, although there is sufficient CH_4 supply, CH_4 consumption could be reduced in dry soils (Whalen *et al.*, 1990). At the optimum moisture contents there is both rapid gas phase molecular diffusion and a sufficient microbial activity to oxidise the delivered CH_4. The reduced CH_4-oxidising capacity at higher moisture contents was caused by a shift of gas-phase molecular diffusion to aqueous-phase molecular diffusion, which is about 10^4 fold less rapid. At each incubation temperature, the optimum moisture content was about 1/2 WHC, obviously supporting optimal CH_4 and O_2 transport as well as microbial activity.

For moisture contents greater than 5%, the third order polynomial relationship between the incubation temperature and the CH_4 uptake rates indicates that the activity of the methanotrophic consortium is rate limiting. However, at a moisture content of 5%, the bacterial activity does not seem to be rate limiting, because no optimum temperature could be detected. In general, we found a decreasing optimum temperature with an increasing moisture content. These decreasing optima can be explained as an equilibrium which exists between the CH_4 diffusion rate at a certain moisture content and the removal rate by the methanotrophic bacteria. At increased moisture contents, there is a reduced gas transport to the methanotrophs. Consequently, it can be possible that the substrate supply is slower than the removal capacity of the CH_4-oxidising bacteria at a certain temperature. So, at higher moisture contents CH_4 transport becomes the rate determining step and not the bacterial activity as is the case at lower moisture contents. Therefore, the optimum incubation temperature at a particular moisture content, resulting in a maximum

Table 3. Optimum moisture content and temperature for methane oxidation

Temperature	Optimum moisture content	Moisture content	Optimum temperature
°C	%	%	°C
5	15.6	5	30.0
10	18.8	10	27.1
		15	24.9
20	16.8	20	23.5
25	16.6	25	21.2
30	15.6	30	20.1

Table 4. Regression and correlation coefficients of the Arrhenius plot of the temperature response of methane oxidation, activation energies (E_a, kJ mol^{-1}) and Q_{10}s (calculated over 10–20°C)

Moisture content (%)	ln $\|k\| = a\,(1/T) + b$				
	a	b	R^2	Q_{10}	E_a (kJ mol^{-1})
5	−10442	32.7	0.914	1.70	86.7
10	−9529	30.5	0.999	1.98	79.1
15	−10697	34.9	0.998	2.05	88.8
20	−9613	30.9	0.994	1.81	79.8
25	−9740	31.2	0.999	1.85	80.8
30	−6502	19.1	0.851	3.05	54.0

CH_4 removal rate, is this temperature where substrate supply and the methanotrophic activity are synchronised. At increased moisture contents, the optimum temperature at each moisture content is a compromise between bacterial activity and CH_4 as well as O_2 supply through diffusion. This observation is an indication that the moisture content is more important in regulating CH_4 oxidation than temperature as was also found by King and Adamsen (1992), Koscherreck and Conrad (1993). The low Q_{10} values (<2) also indicate the weak temperature effect upon CH_4 oxidation (Crill *et al.*, 1994).

Executing a multiple linear regression analysis on the CH_4 oxidation data, using "moisture content" and "temperature" as independent variables, a significant model (F-sign = 0.002) was found. 75% of the variance of CH_4 consumption ($R^2 = 0.75$) could be explained with these variables. Moisture content as well as temperature were significant for the model, but the relative importance of the moisture content ($\beta = 0.098$) was higher than of the temperature ($\beta = 0.063$). This statistical observation again confirms that the moisture content is more important than the soil temperature in controlling CH_4 oxidation.

Effect of ammonium and moisture content. Ammonium is known to have an inhibitory effect on CH_4 oxidation in soils (King and Schnell, 1994). This inhibition is the result of substrate competition between CH_4 and NH_4^+ at the level of the MMO enzyme as well as of a reverse inhibition of the MMO enzyme by the first oxidation product of NH_4^+, hydroxylamine (NH_2OH). It has been suggested that the inhibition by NH_4^+ is not always the direct result of its actual concentration, but rather of its nitrification rate (Sitaula *et al.*, 1995; Steudler *et al.*, 1995) or N-turnover (Hütsch *et al.*, 1994; Goldman *et al.*, 1995). Boeckx and Van Cleemput (1996) have also found evidence that N-dynamics and CH_4 oxidation are related. Ammonium inhibition can also be the result of niche competition between methanotrophs and nitrifiers (Mosier *et al.*, 1991). Upon addition of NH_4^+, nitrifiers can suppress methanotrophs, which can result in a reduced CH_4 oxidation because CH_4 consump-

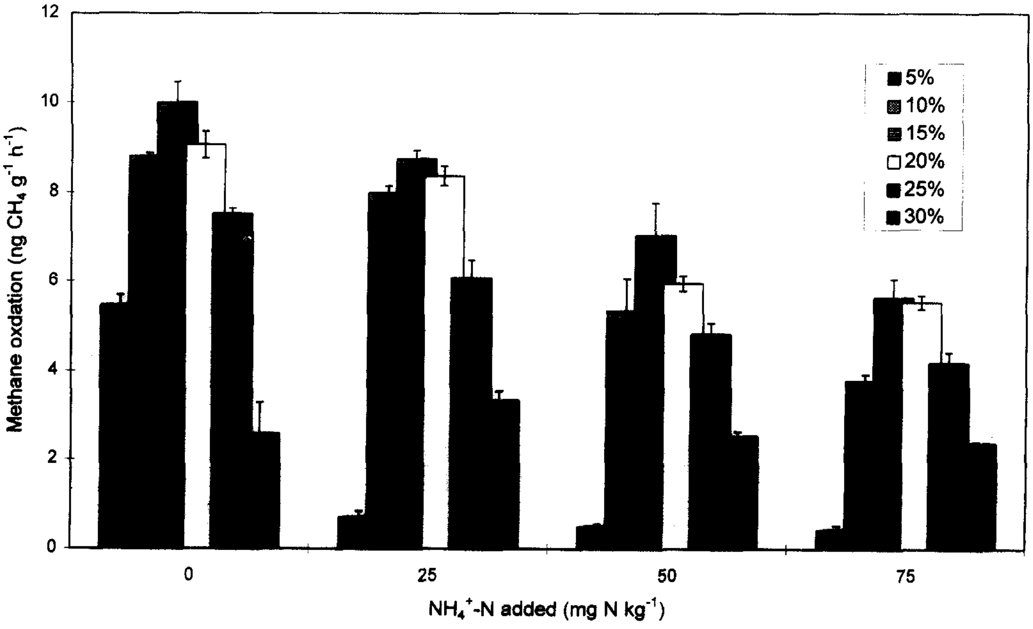

Fig. 2. Methane oxidation rates as a function of soil moisture and the amount of ammonium added (error bars represent +/− 1 S.E.).

Table 5. CH_4 oxidation rate constants ($k1$) and standard error (SE) as a function of soil moisture and the amount of ammonium added to the soil

Moisture content %	0 mg NH_4^+–N kg^{-1}	25 mg NH_4^+–N kg^{-1}	50 mg NH_4^+–N kg^{-1}	75 mg NH_4^+–N kg^{-1}
	$k1$ (h^{-1}) ± SE			
5	0.0495 ± 0.0018	0.0063 ± 0.0012	0.0050 ± 0.0002	0.0048 ± 0.0009
10	0.0972 ± 0.0067	0.1092 ± 0.0016	0.0749 ± 0.0094	0.0550 ± 0.0022
15	0.1219 ± 0.0056	0.1339 ± 0.0047	0.1177 ± 0.0018	0.1009 ± 0.0048
20	0.1113 ± 0.0005	0.1207 ± 0.0032	0.0962 ± 0.0029	0.0919 ± 0.0058
25	0.0768 ± 0.0047	0.0707 ± 0.0056	0.0689 ± 0.0028	0.0624 ± 0.0030
30	0.0188 ± 0.0056	0.0325 ± 0.0027	0.0206 ± 0.0087	0.0306 ± 0.0007

tion by nitrifiers is lower (Bédard and Knowles, 1989). Probably N transformation processes, such as nitrification, better reflect the NH_4^+ availability for the micro-organisms than the actual NH_4^+ concentration. Therefore, inhibition of CH_4 oxidation is probably more related to N-turnover than to the actual NH_4^+ content in the soil.

The effect of increased ammonium amendments at different moisture contents on the CH_4 oxidation rates and rate constants can be seen in Fig. 2 and Table 5. In general, the CH_4 oxidising capacity decreased with increasing ammonium amendments. Only at a moisture content of 30% was an increased CH_4 oxidation observed when 25 mg NH_4^+–N kg^{-1} was applied. However, it was considerably inhibited when the ammonium amendments were increased and the increased CH_4 uptake was also not statistically significant ($P > 0.05$). Bender and Conrad (1995) also observed an increasing CH_4-oxidising capacity when small amounts of ammonium were added. The very low oxidation rates at a moisture content of 5% can be explained by the stability of nitrite at these moisture contents. Upon addition of 25, 50 and 75 mg NH_4^+–N kg^{-1} respectively 31.0, 44.8 and 58.6 ng NO_2^-–N g^{-1} were found in the soil.

Although the mechanism is not clear, nitrite is known to be an important inhibitor of CH_4 oxidation (King and Adamsen, 1992; King and Schnell, 1994; Boeckx and Van Cleemput, 1996). Fitting a linear regression through the CH_4 oxidation rates at the different moisture contents (Fig. 2) and at the initial ammonium amendments (0, 25, 50 and 75 mg N kg^{-1}), the reduction of the CH_4 oxidation rate mg^{-1} NH_4^+–N kg^{-1} added was obtained (Fig. 3). It was clear that this reduction decreased with increasing moisture contents. Ammonium transformation (oxidation) is also slower at higher moisture contents, because O_2 diffusion into the soil is restricted (Focht and Verstraete, 1977; Hutchinson and Davidson, 1993). At a moisture content of 10% w/w and NH_4^+–N additions of 25 and 100 mg kg^{-1}, nitrification rates of 6.9 and 7.6 mg NO_3^-–N h^{-1} g^{-1}, respectively, were found. At a moisture content of 30%, the nitrification rates were respectively 2.1 and 4.6 mg NO_3^-–N h^{-1} g^{-1}. From these observations it may be deduced that the reduction of the CH_4-oxidation rate by ammonium can not be entirely related to the actual ammonium concentration, but rather to its turnover rate. However, more exper-

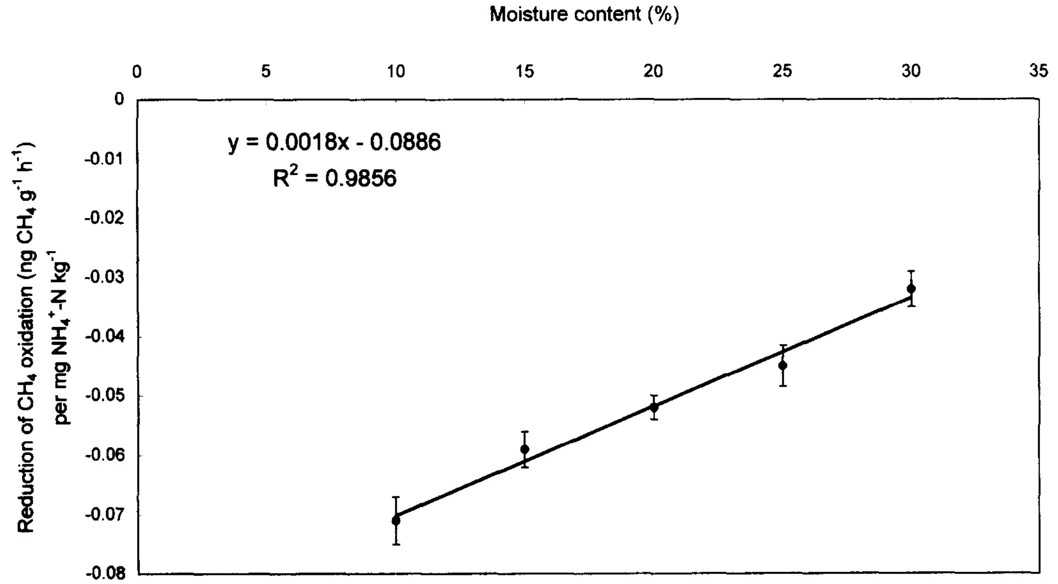

Fig. 3. The reduction of the methane oxidation rate per mg NH_4^+–N kg^{-1} added to the soil as a function of soil moisture (error bars represent + / – 1 SE).

iments with different soil types at different moisture and ammonium contents should be made to obtain a complete relation between the inhibition of CH_4 oxidation and ammonium turnover.

With multiple linear regression analysis a significant model (F-sign = 0.003) was found between the CH_4-oxidation rate and the independent variables "moisture" and "initial ammonium amendment". Moisture and ammonium explained 77% ($R^2 = 0.77$) of the variance of CH_4 oxidation. The relative importance of the ammonium content ($\beta = 0.97$) was higher than of the moisture content ($\beta = 0.31$).

Conclusions

Although the CH_4 emission measurements from the landfill site showed a high variability, a seasonal pattern could be observed. The varying CH_4 emission from this landfill was thought to be related to the moisture content of its covering soil, regulating the methanotrophic activity and gas permeability. The inhibitory effect of ammonium seems to be related to its turnover rate (nitrification), rather than to its actual concentration. The relative importance of ammonium as a controlling factor for CH_4 oxidation is higher than that of the soil moisture content. At low moisture contents, however, the accumulation of small amounts of nitrite could considerably reduce the CH_4 uptake. The optimum moisture content is situated at about 1/2 WHC. CH_4 supply to the CH_4 oxidising bacteria is controlled by the moisture content of the soil. The optimum temperatures decreased with increasing moisture contents. However, from multiple linear regression and Q_{10} values it could be deduced that temperature had only slight effects on CH_4 oxidation.

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