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Juha Einola

Biotic Oxidation of Methane in Landfills in Boreal Climatic Conditions

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ABSTRACT

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This study focused on the biotic oxidation of methane in landfill covers as a technology for reducing greenhouse gas emissions from landfills, particularly those located in the boreal climatic zone. First, methane oxidation was studied in laboratory batch assays in a landfill cover soil consisting of a composted mixture of sewage sludge and chemical sludge which had been installed on the landfill surface 4-5 years earlier. Second, methane oxidation was studied using mechanically-biologically treated municipal solid waste (MBT residual) as a material for methane-oxidizing landfill covers both in continuously methane-sparged laboratory columns and in an outdoor pilot lysimeter. Finally, methane oxidation was studied at a closed full-scale landfill with a European Union landfill directive-compliant, multilayer final cover system containing a water impermeable layer, passive gas collection and distribution system, and a soil cover consisting of sludge compost and peat. In the four-year old landfill cover, the methane oxidation rates at moisture of ≥33% of water-holding capacity increased along with temperature (Q_{10} values 6.5-8.4 at 1-19 °C) while methane oxidation was suppressed at moisture of 17% of water-holding capacity. Methane oxidation (0.2-4.3 $\mu g\ CH_4\ g_{dw}^{-1}\ h^{-1}$ at 1-6 °C) and increase in oxidation rate over time were observed even at 1 °C. In MBT residual, high methane oxidation rates were observed in laboratory columns (12.2-82.3 $g\ CH_4\ m^{-2}\ d^{-1}$ at 2-25 °C) and in batch assays with samples from the columns (up to 104 $\mu g\ g_{dw}^{-1}\ h^{-1}$ at 5 °C and 581 $\mu g\ g_{dw}^{-1}\ h^{-1}$ at 25 °C). In an outdoor lysimeter filled with MBT residual and containing a cover layer made from the same MBT residual, >96% of the methane produced (<16 $g\ CH_4\ m^{-2}\ d^{-1}$) was oxidized between April and October, while in January oxidation was lower (<0.6 $g\ CH_4\ m^{-2}\ d^{-1}$; this was <22% of the methane produced). In the full-scale landfill, of the mean methane flux (2.92-27.3 $g\ CH_4\ m^{-2}\ d^{-1}$) entering the cover layer at the measuring points at the four measuring times, ≥25% was oxidized in October and February, 0% in November and ≥46% in June. At each time, the high methane fluxes into the soil cover at a few points reduced the mean oxidation rate. To conclude, methane-oxidizing landfill biocovers appear feasible for reducing methane emissions in boreal climatic conditions while reduced oxidation rates are likely to occur in wintertime. To maximize the methane oxidation rate at low ambient temperature, the oxidation layer should have a spatially even gas influx, sufficient thickness and suitable characteristics, particularly those related to oxygen transport and thermal insulation.

Keywords: Greenhouse gases; landfill; methane oxidation; waste management.

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CONTENTS

ABSTRACT
LIST OF ORIGINAL PUBLICATIONS

1 INTRODUCTION 9
  1.1 Production, environmental impact and treatment of landfill gas 9
  1.2 Fundamentals of biotic oxidation of methane 12
  1.3 Factors affecting methane oxidation 15
    1.3.1 General remarks 15
    1.3.2 Temperature 15
    1.3.3 Soil moisture 16
    1.3.4 Methane and oxygen availability and soil properties 17
    1.3.5 Nitrogen compounds 17
    1.3.6 Exopolymeric substances 18
  1.4 Field quantification of methane oxidation in landfill covers 18
  1.5 Optimization of methane oxidation in landfills 20
    1.5.1 Engineered systems to enhance methane oxidation in landfills...20
    1.5.2 Characteristics of the support medium used in the oxidation layer 21
    1.5.3 Distribution of landfill gas into oxidation layer 23
    1.5.4 Thickness and compaction of oxidation layer 23
    1.5.5 Methane oxidation rates in landfill cover layers 24

2 OBJECTIVES 27

3 MATERIALS AND METHODS 28

  3.1 An overview of the conducted studies 28
  3.2 Soil and compost materials studied as support media for methane oxidation 29
  3.3 Batch assays (I-IV) 30
    3.3.1 Methane oxidation potential (I,II, III) and respiration activity (I, II, IV) 30
    3.3.2 Increase in methane consumption rate (I) 32
  3.4 Laboratory column experiment (II) 33
  3.5 Outdoor lysimeter experiment (III) 34
  3.6 Full-scale landfill (IV) 36
  3.7 Chemical and physical analyses and measurements (I-IV) 37
    3.7.1 Analyses of solids (I-IV) 37
    3.7.2 Gas composition in laboratory studies (III, IV) 40
    3.7.3 Gas composition in field studies (III, IV) 40
    3.7.4 Gas emissions in field studies (III, IV) 41
    3.7.5 Measurements of temperature, atmospheric pressure, bulk density, and pH in field studies (III, IV) 42

3.8 Calculations 44
    3.8.1 Estimation of methane production and oxidation in field studies (III, IV)....................44
    3.8.2 Calculation of area-based methane oxidation potential (III).........47
    3.8.3 Calculation of Q_{10} values 48
3.9 Statistical analyses 48

4 RESULTS 49
4.1 Responses of methane oxidation to temperature and moisture in cover soil of a boreal landfill (I) 49
4.2 Methane oxidation in laboratory columns containing mechanically-biologically treated waste (II) 51
    4.2.1 Consumption of methane and oxygen and production of carbon dioxide....................51
    4.2.2 MBT residual properties before and after the column experiment 53
4.3 Methane oxidation in an experimental landfill cover composed from mechanically-biologically treated waste (III)....................53
    4.3.1 Overall methane production and oxidation 53
    4.3.2 Methane, carbon dioxide and oxygen concentrations in pore gas 55
    4.3.3 Methane and carbon dioxide fluxes along the vertical profile of the upper part of the lysimeter....................55
    4.3.4 Methane oxidation potential of the materials in the upper part of the lysimeter....................57
    4.3.5 Gas emissions into the atmosphere....................59
4.4 Methane oxidation at a surface-sealed boreal landfill (IV)....................59
    4.4.1 Gas composition in gas wells....................59
    4.4.2 Gas emissions 59
    4.4.3 Pore gas 62
    4.4.4 Methane flux and oxidation 63

5 DISCUSSION 65
5.1 Response of methane oxidation to temperature (I-IV)....................65
    5.1.1 General remarks....................65
    5.1.2 Responses of methane oxidation to temperature in a four-year-old landfill cover soil....................65
    5.1.3 Methane oxidation at different temperatures in MBT residual in column and batch assays....................68
    5.1.4 Methane oxidation at different temperatures in field studies 68
5.2 Response of methane oxidation to soil moisture (I-IV)....................69
5.3 Methane oxidation in MBT residual 71
    5.3.1 Methane oxidation in MBT residual in laboratory columns (II)...71
    5.3.2 Methane oxidation in MBT residual in outdoor lysimeter (III) 72
5.4 Methane oxidation at a surface-sealed landfill (IV)....................75

5.5 Methane oxidation rates and optimization in landfill covers (III, IV) 77
  5.5.1 Overall performances of the studied landfill cover systems in methane treatment 77
  5.5.2 Field methane oxidation capacity, thickness and temperature of oxidation layers 80
5.6 Field quantification of methane oxidation (III, IV) 82
  5.6.1 Evaluation of gas emissions at the landfill level 82
  5.6.2 Quantifying methane oxidation in situ using the mass balance of methane and carbon dioxide 82

6 CONCLUSIONS 85

Acknowledgements 88

YHTEENVETO (RÉSUMÉ IN FINNISH) 89

REFERENCES 92

LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following original papers, which will be referred to in the text by their Roman numerals I-IV. I am the main author in each paper, and I carried out a large part of the planning of the studies and collecting and analyzing the data in each paper.

I Einola, J.-K. M., Kettunen, R. H. & Rintala, J. A. 2007. Responses of methane oxidation to temperature and water content in cover soil of a boreal landfill. Soil Biology and Biochemistry 39: 1156-1164.

II Einola, J.-K. M., Karhu, A. E. & Rintala, J. A. 2008. Mechanically-biologically treated municipal solid waste as a support medium for microbial methane oxidation to mitigate landfill greenhouse emissions. Waste Management 28: 97-111.

III Einola, J.-K. M., Sormunen, K. M. & Rintala, J. A. 2008. Methane oxidation in a boreal climate in an experimental landfill cover composed from mechanically-biologically treated waste. Science of the Total Environment 407: 67-83.

IV Einola, J., Sormunen, K., Lensu, A., Leiskallio, A., Ettala, M. & Rintala, J. 2009. Methane oxidation at a surface-sealed boreal landfill. Waste Management 29: 2105-2120.

1 INTRODUCTION

1.1 Production, environmental impact and treatment of landfill gas

Biodegradation of organic waste deposited in landfills produces landfill gas, which contains high concentrations of the greenhouse gases methane (CH_4, 35-60%) and carbon dioxide (CO_2, 30-55%) (Jönsson et al. 2003, Rasi et al. 2007). The global warming potential of methane as compared to carbon dioxide (GWP) is significantly higher: 72-fold over a 20-year time period and 25-fold over a 100-year time period (IPCC 2007). The difference in the GWP values for methane calculated for different time periods is due to the rapid degradation of methane in the atmosphere compared to the rate for carbon dioxide. In contrast with methane emissions, carbon dioxide emissions from landfill gas are not accounted as greenhouse gas emissions according to the guidelines of the Intergovernmental Panel on Climate Change (IPCC 2006). This is because carbon dioxide in landfill gas is of biogenic origin and is thus counted for in other sectors of greenhouse gas emission inventories in cases where the amount of carbon dioxide released in biomass harvesting exceeds the amount fixed in the growth of that biomass (IPCC 2006, Bogner et al. 2008).

Methane emissions from landfills are estimated to be 500-800 $MtCO_2$ eq/yr (IPCC 2007), accounting for approximately 7-11% of global anthropogenic methane emissions. The latter in turn account for 14.3% of global anthropogenic greenhouse gas emissions (49 $GtCO_2$ eq/yr) (IPCC 2007). It is important to note that these values have been calculated using CO_2 equivalents based on the GWP values for a 100-year period. It has been argued that the common practice of using GWPs for 100 years, instead of for shorter periods, as the basis of greenhouse gas inventories and mitigation strategies, underestimates the effect of short-lived greenhouse gases such as methane and ozone, and of black carbon (soot), another warming agent, on global warming (Hansen & Sato 2001, Moore & MacCracken 2009). Enhancing reductions in the emissions of short-lived greenhouse gases such as methane could provide a fast and cost-effective way to reduce the radiative forcing of the atmosphere (Hansen & Sato 2001, Kemfert & Schill 2009).

In Europe and the US, landfill methane emissions are estimated to account for 22 and 23%, respectively, of anthropogenic methane emissions (Scheutz et al. 2009a). In addition to its importance to global warming, methane is a flammable gas whose uncontrolled emission or migration has to be prevented because of the risk of explosion and fires (Stearns & Petoyan 1984, Williams & Aitkenhead 1991, Kjeldsen & Fischer 1995, Ettala et al. 1996). Moreover, landfill gas contains substances such as volatile organic compounds (VOC), which may have health and environmental effects and cause odour problems (Allen et al. 1997, Scheutz et al. 2008, Chiriac et al. 2009, Davoli et al. 2009, Rasi 2009). Thus landfill gas has to be treated to minimize its hazards and annoyances on the local and global scale. In the European Union, for example the control of landfill gas is regulated by the European landfill directive (EC 1999) and national regulations (e.g., Finnish Government 1997). The implementation of waste management practices such as composting, waste-to-energy incineration and mechanical-biological treatment are reducing the landfill disposal of organic wastes, and thus the production of landfill gas, in many countries (e.g., Bogner et al. 2008).

Landfill gas generation begins soon after the start of waste disposal and may continue for decades after landfill closure (Fig. 1). Different gas treatment options are suitable for the different phases of the landfill lifespan and different landfill categories and are based on the oxidation of methane to carbon dioxide, thus reducing the global warming potential of the emitted gas. Moreover, in biological oxidation, some of the methane carbon may be stored in soil, thus reducing, at least in the short term, the amount of carbon released into the atmosphere (see 1.2).

Capturing landfill gas through a gas collection system and using it for energy in combined heat and power plants (Haubrichs & Widmann 2006), or as vehicle fuel after upgrading (Rasi 2009), while recommendable, may not be possible in many landfills owing e.g. to the low concentration or amount of methane or lack of market for the gas. Moreover, gas utilization is possible only for a part of the landfill lifespan and, even when gas is being collected, a significant part of the gas is not captured by the collection system (Fig. 1) but is released through the landfill cover layer into the atmosphere. When methane concentrations decrease below 35-40% and total landfill gas production below 30-50 m^3 ha^{-1} h^{-1}, the use of the gas in combined heat and power plants becomes technically and economically unsuitable (Haubrichs & Widmann 2006). In such cases, the gas may be treated using high temperature flares which convert methane to carbon dioxide but do not recover the energy content. When methane concentration and total gas production rate fall below 20-25% and 10-15 m^3 h^{-1}, gas can be treated using fluidized-bed combustion or flameless oxidation systems (Stachowitz 2005), or biofilters (see below). The use of non-biological methods to treat landfill gas with such low methane concentration

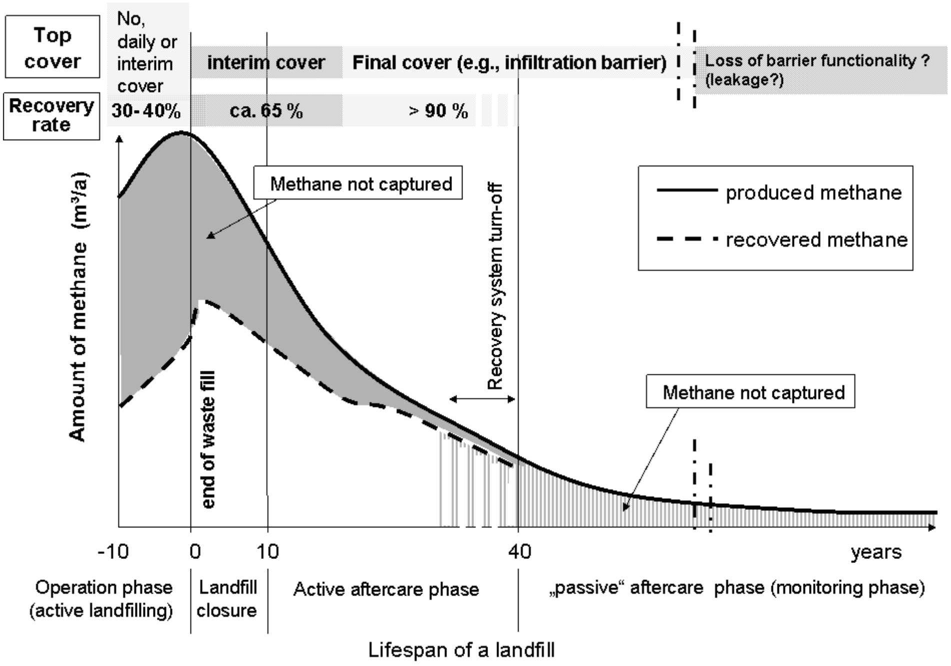

FIGURE 1 Methane production and recovery over a landfill lifetime. The fraction of methane which is not captured is either emitted or oxidized. (Reproduced from Huber-Humer, M., Gebert, J. & Hilger, H. 2008. Biotic systems to mitigate landfill methane emissions. Waste Manage. Res. 26: 33-46 with permission from the International Solid Waste Association.)

may be expensive and complex (Haubrichs & Widmann 2006) and, as with combined heat and power plants or flares, a gas collection system is required.

The biotic oxidation of methane takes place spontaneously in landfill soils and can be enhanced by the implementation of engineered systems, such as biocovers or biofilters (e.g., Czepiel et al. 1996, De Visscher et al. 1999, Börjesson et al. 2001, 2004, Streese & Stegmann 2003, Hilger & Humer 2003, Wilshusen et al. 2004, Gebert & Gröngröft 2006a, Huber-Humer et al. 2008, Scheutz et al. 2009a). Depending on the rate of methane production, biotic oxidation may be suitable either as the sole means of methane treatment, or as a complementary method, i.e., treating the methane escaping from a gas collection system. Biotic oxidation may also be used in landfills with no installed gas collection systems, such as in landfills where the amount of gas is too low for the economical utilization of its energy content. These cases include landfills of waste with a low methane production potential such as small landfills with low amount of waste, or landfills of biologically stabilized (pre-treated) waste. Biotic oxidation can also be promoted in intermediate landfill covers which are installed in parts of the landfill during the active period of the landfill. The fourth assessment report of the Intergovernmental Panel for Climate Change defines methane oxidizing biocovers and biofilters as a key mitigation technology projected for commercialization before 2030 within the waste management sector (IPCC 2007).

1.2 Fundamentals of biotic oxidation of methane

Biotic oxidation of methane in aerobic habitats such as landfill cover soils is based on the activity of aerobic methanotrophic bacteria (methanotrophs) (Hanson & Hanson 1996), which utilize methane as a carbon and energy source, converting methane to carbon dioxide and biomass, thus reducing the global warming potential of the gas emitted into the atmosphere. There are also other microorganisms, including yeasts and nitrifying bacteria, that are capable of oxidizing methane in the presence of oxygen (Hanson & Hanson 1996). In addition, anaerobic microorganisms oxidizing methane using sulphate, nitrate, manganese or iron as electron acceptors, instead of oxygen, have been found in aquatic habitats (Boetius et al. 2000; Raghoebarsing et al. 2006; Beal et al. 2009, Knittel & Boetius 2009). This text focuses on the aerobic methanotrophic bacteria, as these are considered to be the most important group of microorganisms oxidizing methane in landfills.

Aerobic methanotrophs are abundant in various environments and have a high impact on the Earth's atmospheric methane concentration and climate (Hanson & Hanson 1996). Methanotrophs consume a high proportion of the methane produced in biogenic or geologic processes: for example, in ricefields, which are another globally significant source of methane, it has been estimated that 80% of the methane produced (575 Tg yr^{-1}) is microbially oxidized (Hanson & Hanson 1996). In oceans, anaerobic methane oxidation consumes >90% of the estimated rate of methane production (85-300 Tg yr^{-1}) (Knittel & Boetius 2009). Moreover, methanotrophs in soils with no methane production oxidize atmospheric methane, forming a significant methane sink (30 Tg yr^{-1}) (IPCC 2007).

Methanotrophs belong to the methylotrophs, a physiological group of microorganisms with the ability to utilize one-carbon compounds more reduced than formic acid as a carbon and energy source and to assimilate formaldehyde as a major source of cellular carbon (Anthony 1982, Hanson & Hanson 1996). Biotic methane oxidation proceeds via several enzyme reactions (Fig. 2). The net equation of the aerobic biotic oxidation of methane can be formulated as presented in Equation 1 (modified from Chanton et al. 2009):

$$CH_4 + (2 - x)\,O_2 \rightarrow (1 - x)\,CO_2 + (2 - x)\,H_2O + x\,CH_2O + \text{heat} \qquad (1)$$

Methane oxidation is an exothermic reaction ($\Delta G° = 780$ kJ mol^{-1} for the oxidation of methane to carbon dioxide) (Scheutz et al. 2009a). The first step, the oxidation of methane to methanol, is catalyzed by the enzyme methane monooxygenase (MMO), which is a defining characteristic of methanotrophs (Hanson & Hanson 1996). There are two types of MMO: soluble (sMMO) and

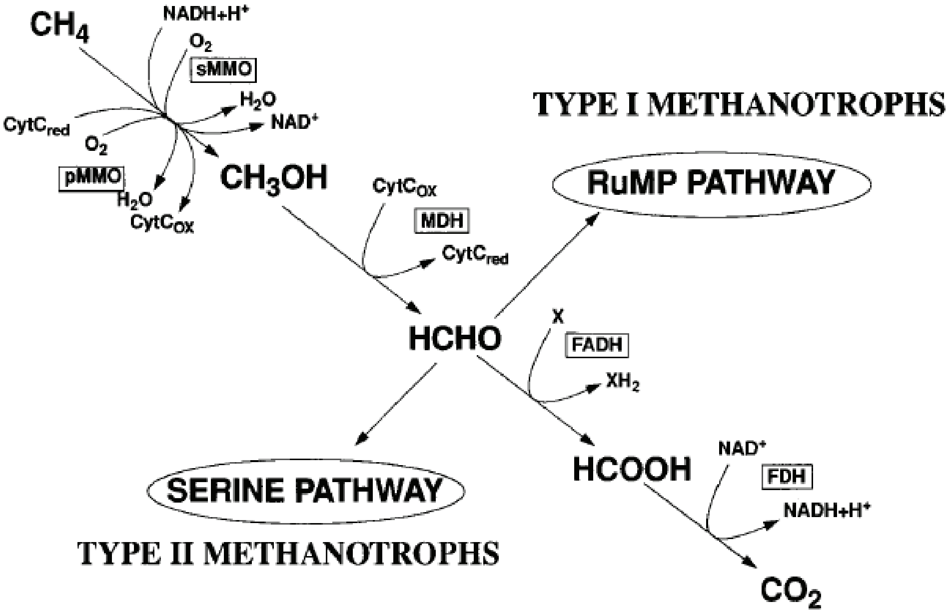

FIGURE 2 Pathways of microbial methane oxidation. (Reproduced from Hanson, R. S. & Hanson, T. E. 1996. Methanotrophic bacteria. Microbiol. Rev. 60: 439-471 with permission from the American Society for Microbiology.)

particulate (pMMO) (described below). Methanol (CH_3OH) is then oxidized further to formaldehyde (CH_2OH) (Anthony 1982, Dalton 2005), which is either dissimilated to carbon dioxide via formic acid to produce metabolic energy, or assimilated to cellular biomass (Fig. 2).

Laboratory experiments have suggested that 8-70% of methane consumed by methane-oxidizers may be incorporated in microbial biomass (reviewed by Huber-Humer 2004). The theoretical maximum proportion converted to biomass is 88%: 100% conversion is not possible because some of the methane is always oxidized to carbon dioxide (Gommers et al. 1988). For greenhouse gas mitigation, for example in landfill cover soils, the retention of methane-derived carbon at the level of any of the intermediate products in the methane oxidation chain is favourable compared to complete oxidation to carbon dioxide, as it reduces the amount of carbon released into the atmosphere. However, field studies on the proportion of methane-derived carbon stored in landfill soils are lacking, as is information on how long carbon can be stored. The carbon assimilated by methanotrophs may be utilized and released as carbon dioxide by other microorganisms (Watzinger et al. 2008).

The consumption of oxygen during methane oxidation is dependent on the proportion of methane converted into biomass (Equation 1). This is due to the fact that the conversion of one mole of methane to formaldehyde, which is then used for the synthesis of biomass, utilizes only one mole of molecular oxygen (O_2) while the further oxidation of formaldehyde to carbon dioxide consumes another mole of molecular oxygen (O_2) (Anthony 1982).

A methane-utilizing microorganism, a bacterium named *Bacillus methanicus,* was isolated for the first time over a century ago (Söhngen 1906 as cited in Dalton 2005). About 100 methanotroph bacterial strains were characterized by Whittenbury et al. (1970), laying the basis for the current classification of methanotrophs (Scheutz et al. 2009a). Methanotrophs are classified into two types, type I and type II, belonging to the *Alfaproteobacteria* and *Gammaproteobacteria*, respectively (Scheutz et al. 2009a). In general, both types utilize particulate methane monooxygenase (pMMO) for methane oxidation, while the ability to produce solube MMO (sMMO) (in the absence of copper) is found in type II, and in only a few type I methanotroph species. Type I methanotrophs use the ribulose monophosphate pathway, which is bioenergetically more efficient, for formaldehyde assimilation, while type II methanotrophs use the serine pathway. In addition, type I methanotrophs are generally not able to fix N_2, in contrast to type II. Novel methanotrophic species and genera continue to be discovered in different environments, including extremophilic strains growing in habitats with low or high temperature or in saline, acidic or alkaline conditions (Dunfield et al. 2007, Scheutz et al. 2009a). It is noteworthy that the novel findings include a methanotroph not belonging to the *Proteobacteria*, but to another phylum, the *Verrucomicrobia* (Dunfield et al. 2007, Conrad 2009).

Methanotrophs show distinct characteristics in their ability to oxidize methane at different concentration ranges and can be divided into high-affinity and low-affinity methanotrophs on this basis. The high-affinity methanotrophs are able to oxidize methane at atmospheric concentration levels (1774 ppb; IPCC 2007) and are common in soils where the main methane source is atmospheric air, forming the above-mentioned soil sink of atmospheric methane (Hanson & Hanson 1996). The low-affinity methanotrophs require a higher methane concentration for methane oxidation to be triggered and have high importance in the oxidation of methane in habitats where methane is emitted into the atmosphere. In many studies, high-affinity methanotrophs have been observed to belong to type I and low affinity methanotrophs to type II, which may in part be connected to their relative ability to fix N_2, as inorganic nitrogen may be more limited in habitats with high methane concentration where the amount of methanotrophs is high (Scheutz et al. 2009a). Since N_2 fixation requires low oxygen concentrations, habitats with a high methane concentration, which often have low oxygen concentrations, may be more suitable for type II methanotrophs. However, recent studies have shown that the commonly cited hypothesis of methane concentration preferences for type I and type II methanotrophs is questionable as the observed trends may be ecosystem-specific (Jugnia et al. 2009).

An important characteristic of methanotrophs is the broad substrate specificity of sMMO which allows these microorganisms to cometabolically oxidize halogenated hydrocarbons and aromatic hydrocarbons (e.g., Hanson &

Hanson 1996). Thus extensive research has been done on the utilization of methanotrophs for the biodegradation of toxic chemicals as well as for the production of chemicals for commercial use (Hanson & Hanson 1996). Methanotrophs, for example in landfill cover, soil are able to cometabolically to oxidize some VOCs such as halogenated hydrocarbons (e.g., Scheutz & Kjeldsen 2003), thus reducing the emissions of these compounds.

1.3 Factors affecting methane oxidation

1.3.1 General remarks

Methane oxidation in landfill cover soils depends on several factors affecting methanotrophic activity, such as the availability of the gaseous substrates (oxygen and methane), and the flux of methane through the landfill cover. Many of these factors are affected by the properties of the cover soil material. Review articles exist on the factors affecting biotic methane oxidation both generally (Hanson & Hanson 1996) and with special reference to landfills (Scheutz et al. 2009a). Selected factors, particularly those relevant to the present study, are described here.

1.3.2 Temperature

The optimum temperatures for methane oxidation in temperate or boreal habats have been within the range 20 to 38 °C, as indicated by batch assays conducted with high methane concentrations (e.g., >1%) (Whalen et al. 1990, Dunfield et al. 1993, Gebert et al. 2003, Scheutz & Kjeldsen 2004). In those studies, methane oxidation has been detected at temperatures as low as 1 °C in landfill cover soils and other environments but at significantly reduced rates. Decreased methane oxidation rates at low temperatures have also been observed in many field studies (e.g., Christophersen et al. 2000, Börjesson et al. 2001, Einola et al. 2003, Maurice & Lagerkvist 2003), as indicated, e.g., by higher methane emissions at low temperatures. In Swedish landfills, the fractional oxidation correlated with the temperature of the landfill cover soil (Börjesson et al. 2007). The response of methane oxidation to temperature in batch studies has depended on the concentration of methane: at low (e.g., 10 μl l^{-1}) concentrations (Boeckx et al. 1996) the response to temperature is low because methane oxidation is limited by the supply of the gaseous substrates to methanotrophs rather than by enzyme activity.

In laboratory column assays with continuous methane load simulating the cover layer of a landfill, the effect of temperature on methane oxidation rate has been significantly lower compared to that in batch assays (Huber-Humer 2004, Kettunen et al. 2006). This low temperature response in columns may be in part be explained by the improved contact between the gaseous substrates (methane and oxygen) and microorganisms in batch assays compared to column experiments or real landfill cover soils. The improved contact between gas and microorganisms is indicated by the higher oxidation rates per gram of soil in batch assays with the same materials (De Visscher et al. 1999, Kettunen et al. 2006) and is explained, e.g., by the conditions and experimental preparations, such as the low amount of sample (e.g., 10-20 g) (Huber-Humer et al. 2009). In column experiments or real landfill covers, oxidation rates at the soil layer level are more limited by other factors than enzyme activity, such as the supply of methane and oxygen. Thus the methane loading, thickness and type of the cover may influence the response of methane oxidation to temperature at the soil layer level. For example, soils with good oxygen transport characteristics may enable a wide distribution of methanotrophs along the soil vertical profile and thus a high methane oxidation rate at low temperatures (Kettunen et al. 2006). Moreover, temperature-dependent changes in the dominant methanotroph species have been reported (Gebert et al. 2003, Börjesson et al. 2004). Psychrophilic methanotrophs with growth optimum at 5-13 °C have been identified in permanently cold habitats (Trotsenko & Khmelenina 2005).

1.3.3 Soil moisture

Soil moisture is important for methane oxidation as an adequate amount of water is needed for microbial metabolism, nutrient uptake and metabolite removal (e.g., Scheutz et al. 2009a). Excessive moisture restricts the diffusion of the gaseous substrates oxygen and methane to microbes and may favour anaerobic instead of aerobic microbial activity. Thus methane oxidation is usually reduced at low and high moisture contents and the optimum rate reached in the middle range (Figueroa 1993, Czepiel et al. 1996, Christophersen et al. 2000). The moisture range suitable or optimal for methane oxidation, as expressed on a weight basis (e.g., % of dry weight), varies among soils, owing to different soil water retention characteristics (Figueroa 1993, Christophersen et al. 2000). When moisture is expressed as a proportion of water-holding capacity (or other measure related to soil water retention characteristics), the optimum moisture for methane oxidation is similar among different soils, when studied in comparable conditions (e.g., methane concentrations) (Figueroa 1993).

Moisture also affects the proportion of air-filled pores and thus the retention time of gas in soil, which may affect the rate of methane oxidation (Huber-Humer 2004). In compost columns Huber-Humer (2004) observed high methane oxidation at a moisture regime 60-100% of water-holding capacity (WHC) (air porosity 30-47%), indicating that in optimized column and field settings where air porosity remains at a suitable level, the upper end of the moisture range suitable for methane oxidation may extend to higher moisture levels than that observed in batch assays.

1.3.4 Methane and oxygen availability and soil properties

The vertical distribution of methanotrophs in soils is determined by the flow of methane from the anaerobic zone and by the transport of oxygen into the soil from the atmosphere (Hanson & Hanson 1996). In landfill cover soils with high methane loadings, methane oxidation is generally restricted by oxygen supply whereas methane supply is abundant and exceeds the threshold concentration needed for the induction of low-affinity (Chapter 1.2) methane oxidation. On the other hand, in landfill covers where all of the methane entering the cover layer is oxidized, the cover soil has been observed also to consume methane from the atmosphere (e.g., Barlaz et al. 2004, Scheutz et al. 2009a), suggesting the existence of high-affinity methane oxidation. The oxidation rate of low-affinity methanotrophs has been relatively non-sensitive to changes in oxygen concentrations above 0.5-3% but decreases when the concentration drops below that level (Czepiel et al. 1996, Ren et al. 1997, Stein & Hettiaratchci 2001, Gebert et al. 2003). Thus, the factors affecting oxygen transport in soil are important for methane oxidation and include soil porosity and particle size (e.g., Scheutz et al. 2009a). Oxygen consumption by other soil organisms may reduce methane oxidation, particularly in materials containing high amounts of biodegradable organic matter (Kettunen et al. 2006).

1.3.5 Nitrogen compounds

Methanotrophs require 0.25 mol of nitrogen per mole of methane assimilated (Anthony 1982) and thus, assuming that 40% of the consumed methane is assimilated, the availability of inorganic nitrogen may be growth-limiting where the molar ratio of methane to N is higher than 10 (Bodelier & Laanbroek 2004, Scheutz et al. 2009a). In landfill soils, such a methane/N molar ratio is likely to occur, due to the abundance of methane. Many methanotrophs are able to fix N_2 (Chapter 1.2), which may enable growth when inorganic nitrogen compounds are scarce. Nitrogen addition to soil has stimulated methane oxidation in landfill soils (De Visscher et al. 1999, Hilger et al. 2000a, De Visscher et al. 2001, De Visscher & Van Cleemput 2003) and in other environments (e.g., Bodelier et al. 2000). However, ammonium nitrogen (NH_4^+) is a competitive inhibitor of MMO and therefore NH_4^+ in high concentrations (e.g., addition of 25 mg N kg^{-1}; Boeckx & Van Cleemput 1996) in soil often inhibit methane oxidation, the degree of inhibition depending on the concentrations of ammonium and methane. In contrast, nitrate (NO_3^-) generally inhibits methane oxidation only at high concentrations which are not typical in landfill covers (Bodelier & Laanbroek 2004). The current knowledge on the effect of nitrogen on methane oxidation in landfills is mostly based on laboratory studies. In a recent study, among several soil parameters, total nitrogen concentration of soil was the variable which correlated most strongly with methane oxidation potential in cover soils sampled from five different landfills, suggesting that the methane oxidation potential of these soils was nitrogen-limited (Gebert et al. 2009).

1.3.6 Exopolymeric substances

Like many other bacteria, methanotrophs are able to produce exopolymeric substances (EPS); these are high molecular weight substances consisting mainly of polysaccharides (Scheutz et al. 2009a). The main function of these substances is to provide anchorage to soil surfaces. The reduction in methane oxidation rates over time observed in laboratory experiments have been attributed to the accumulation of EPS during prolonged exposure to methane (e.g., Hilger et al. 2000b, Wilshusen et al. 2004). Accumulated EPS may clog soil pores causing short-circuiting of LFG, or hamper the diffusion of substrates into the cells, thus decreasing the methane oxidation rate (Scheutz et al. 2009a). The mechanisms causing EPS production by methanotrophs in soils are not yet well known, but it is thought that EPS is produced to prevent the accumulation of formaldehyde in the case of carbon excess or lack of nutrients (Scheutz et al. 2009a).

1.4 Field quantification of methane oxidation in landfill covers

The quantification of the rate of methane oxidation per area unit (e.g., g CH_4 m^{-2} d^{-1}) is important for monitoring the performance of biocovers, biofilters, or other systems to optimize methane oxidation in landfills in different conditions. Information on the field oxidation rates obtainable with different cover types and materials is also important for constructing effective biocovers to eliminate methane (Huber-Humer et al. 2008) (Chapter 1.5). The quantification of methane oxidation per area unit requires the measurement of methane emissions, i.e., “net flux” of methane into the atmosphere and an estimate of the methane loading, i.e., methane flux into the cover layer before any oxidation has taken place. The quantification of gas emissions and methane oxidation at the whole landfill level is complex due to the spatial and temporal variation of gas fluxes and oxidation and because of difficulties in quantifying the methane loading (Czepiel et al. 1996, Chanton et al. 2009, Huber-Humer et al. 2009, Scheutz et al. 2009a). Landfill gas emissions can be measured as point measurements using a flux chamber (area <1 m^2) installed on the landfill surface (Bogner et al. 1997, Scheutz et al. 2009a). Estimates of fluxes for a larger area may be calculated as means from a number of measuring points, or using geostatistical methods (Spokas et al. 2003, Scheutz et al. 2009a). However, obtaining reliable and representative data for a whole landfill using chamber measurements is laborious and time-consuming as a high number of measurements is needed. An alternative is the use of above-ground emission measurement methods, such as tracer or micrometeorological methods (Börjesson et al. 2001, Laurila et al. 2005, Scheutz et al. 2009a), which give an integrated measure of flux over a larger area (such as the entire landfill) (Scheutz et al. 2009a). While the above-ground methods are useful for providing whole-landfill estimates of emission and oxidation less labour intensively than using flux chamber measurements, point measurements are necessary in order to obtain information on the spatial distribution of gas fluxes, or to localize potential high emission areas.

Two methods to quantify methane oxidation in landfills are described in more detail here: the stable carbon isotope method and the methane and carbon dioxide mass balance method. Other methods have also been used, including field or laboratory incubations of soil samples to determine the methane oxidation potential (Bogner et al. 1997, Scheutz et al. 2009a) and removal of the cover from part of the landfill (Boeckx et al. 1996). More recently, gas push-pull tests (Urmann et al. 2005, Streese-Kleeberg et al. 2009) and the use of subsurface chambers (Kjeldsen et al. 2007 as cited in Huber-Humer et al. 2009, Scheutz et al. 2009b) have been introduced.

The stable carbon isotope method, also known as the isotope fractionation method, has been the method most widely used to quantify methane oxidation in landfills (Scheutz et al. 2009a, Chanton et al. 2009). This method is based on determination of fractional methane oxidation, i.e., the proportion of methane oxidized of the total methane produced, using the difference between the ratio of the ^{12}C and ^{13}C isotopes in produced and oxidized gas, and the fractionation factor for methane oxidation as determined in laboratory incubations. When methane is microbially oxidized, e.g., on its passage through the landfill cover, the unoxidized methane becomes enriched in the ^{12}C isotope because methane-oxidizing bacteria consume $^{12}CH_4$ slightly faster than $^{13}CH_4$ (Silverman & Oyama 1968 as cited in Chanton et al. 2009). For the isotope ratio analyses, the produced gas is sampled from the waste layer while the oxidized gas may be sampled from the landfill surface, from cover soil, or from air downwind of the landfill (Chanton et al. 2009). The fractional oxidation value and methane emission value enable the calculation of methane gross flux, and hence also the oxidation rate, on an area basis (e.g., g CH_4 m^{-2} d^{-1}) (Chanton et al. 2009). Another option for quantifying methane oxidation is the mass balance method, which uses methane and carbon dioxide emission measurements and the methane-to-carbon dioxide ratio of the produced gas (obtained from measurements of the pore gas within the waste layer) before any oxidation has taken place. Using this information, the rate of methane flux into the landfill cover is calculated, from which the rate of methane oxidation on an area basis is then obtained by subtracting the rate of methane emission (Christophersen et al. 2001, Laurila et al. 2005, Chanton et al. 2009).

Both the isotope fractionation and the mass balance approaches to the quantification of methane oxidation include sources of error that need to be considered (Chanton et al. 2009, Cabral et al. 2009). With the isotope fractionation method, the fractionation factor for methane oxidation varies among soils and according to environmental conditions, such as temperature, and thus the determination of site and time specific fractionation factors requiring the incubation of soil samples in batch assays in the laboratory is recommended (Scheutz et al. 2009a). Moreover, the fractionation factor for the diffusion of methane in soils is not precisely known and has to be approximated (Chanton et al. 2009). The use of the isotope fractionation method is problematic when methane is completely oxidized, such as in well-performing biocovers, as the ratio of the stable isotopes for methane cannot be determined from the emitting gas.

When using the methane and carbon dioxide mass balance approach for quantifying methane oxidation it should be considered that the carbon dioxide and methane fluxes in soil may be affected, in addition to the anaerobic gas production and methane oxidation, by other factors. These include carbon dioxide production in respiration by soil organisms, carbon dioxide production and consumption by plants, solubility in water and sorption on soil particles of methane and carbon dioxide, and the storage of methane carbon in landfill cover (Huber-Humer et al. 2009). The storage of methane-derived carbon may occur when carbon from oxidized methane is incorporated in methanotrophic biomass, leading to a decrease in the volume of gas on its passage through the oxidizing layer (Equation 1).

1.5 Optimization of methane oxidation in landfills

1.5.1 Engineered systems to enhance methane oxidation in landfills

Engineered systems to optimize methane oxidation in landfills include so called biocovers, biofilters, biowindows, and biotarps. All these applications are based on the optimization of the conditions important for the activity of methane-oxidizing microorganisms. Recent reviews on the optimization of methane oxidation in landfills have been provided by Huber-Humer et al. (2008, 2009) and Scheutz et al. (2009).

A biocover is a “landfill cover system that has been designed to optimize environmental conditions for biotic CH_4 consumption so that the system functions as a fast bio-filter” (Scheutz et al. 2009a). Typically, a biocover consists of a gas distribution layer with a high gas permeability to homogenize gas fluxes, and an oxidation layer designed to promote biotic methane oxidation (Huber-Humer 2004, Barlaz et al. 2004, Stern et al. 2007, Scheutz et al. 2009a). Biocovers are typically used in large areas, e.g., an entire landfill, and thus a high amount of support medium such as compost, is needed.

A biofilter is a bioreactor unit into which gas is collected from a larger landfill area (Maurice & Lagerkvist. 2003, Streese & Stegmann 2003, Gebert & Gröngröft 2006a, 2006b, Philopoulos et al. 2008). Operational parameters such as methane loading, moisture and aeration are more controllable compared to biocovers, and biofilters may thus attain high methane oxidation rates. Biofilters use active or passive venting to direct landfill gas and active or passive aeration. Biowindows are areas in the landfill cover filled with a support medium for methane oxidation, thus forming a specific type of passively vented and passively aerated biofilter. The biowindow functions as a preferential flow path for landfill gas and thus receives gas directly from the waste layer (Scheutz et al. 2009b). A biotarp is a film containing active methanotrophs, which is designed to be used as a daily cover in landfills during the active phase of the landfill lifespan (Fig. 1) for the mitigation of methane emissions before the installation of soil cover (Hilger et al. 2007 as cited in Huber-Humer et al. 2008). Field performance data for biotarps are not yet available (Huber-Humer et al. 2008).

Biocovers are suitable for long-term operation, such as the period after landfill closure in landfills with low methane loading (Scheutz et al. 2009a). The advantages of biocovers include a high surface area and thus high volume of support medium, increasing oxidation capacity and support of vegetation. The high surface area allows low methane loading rates, and thus the formation of exopolymeric substances, which may reduce the oxidation rate, is less likely in biocovers compared to biofilters (Scheutz et al. 2009a). Methane oxidation in landfill biocovers can be optimized by choosing a support medium with favourable properties for methane oxidation, optimizing the thickness and compaction of the cover layer, and arranging an even distribution of landfill gas into the oxidation layer (Table 1).

1.5.2 Characteristics of the support medium used in the oxidation layer

The support medium used in the methane oxidation layer should have properties favourable for the activity of methane oxidizers and for the interaction between methane, oxygen and microorganisms. The important parameters include high porosity, high water-holding capacity, and appropriate nutrient levels (e.g., Kettunen et al. 2006, Huber-Humer et al. 2008, 2009). The medium should be permeable to gas but it should have a fine texture to allow sufficient retention time of gas in order to enable methane oxidation (Stern et al. 2007, Huber-Humer et al. 2008). The medium should also have a sufficient volume of air-filled pores even at high moisture content so that gas flow and air diffusion are maintained (Kettunen et al. 2006, Scheutz et al. 2009a). The organic matter content of the medium should be biologically stable so that oxygen consumption due to heterotrophic microorganisms does not divert oxygen away from methanotrophs (Huber-Humer 2004, Kettunen et al. 2006) and that no methane is produced in the biocover (Barlaz et al. 2004). Different materials have been studied in laboratory experiments and have shown methane oxidation rates similar to or higher than the typical methane loading rates in landfill covers (e.g., De Visscher et al. 1999, Humer & Lechner, 1999, Hilger et al. 2000a, Huber-Humer 2004, Kettunen et al. 2006). Biologically stable compost materials in general have favourable properties for supporting methane oxidation.

The utilization of waste materials in landfill covers instead of natural soils may be favoured for economic and environmental reasons. One potentially suitable support medium for methane oxidation in landfill covers is MBT residual, which is the end-product of the mechanical-biological treatment (MBT) of municipal solid waste (MSW) (Soyez & Plickert 2002). In the European Union, for example, the aim is to reduce the landfilling of biodegradable waste

TABLE 1 Design parameters and structures important for the optimization of methane oxidation in landfill covers.

Parameter/structure	Significance	Examples (based on field studies)
Material of support medium	Should provide favourable conditions for methanotrophic activity, gas flow and oxygen diffusion. Important parameters include porosity, particle size, nutrients concentrations, water-holding capacity and biological stability.	Sludge compost (Huber-Humer 2004), yard waste compost (Stern et al. 2007). Recommended values of the parameters listed by Huber-Humer et al. (2009).
Compaction of oxidation layer	Influences air-filled pore volume and gas permeability.	For compost layers no compaction is recommended (Scheutz et al. 2009a). Recommended bulk density 0.8-1.1. t m^{-3} (Huber-Humer et al. 2009).
Thickness of oxidation layer	Increasing layer thickness may increase oxidation owing to increased oxidation capacity and longer retention time of gas. More stable moisture and higher temperature maintained in deeper layers.	Recommended minimum: 120 cm (Huber-Humer 2004), 40-50 cm (Martikkala & Kettunen 2003). Sufficient thickness depends on required oxidation capacity and climatic conditions.
Gas distribution layer or system	To equalize methane loading rate of the cover layer across the landfill area and to avoid gas shortcuts.	Landfills with no impermeable layer: Gas distribution layer (Huber-Humer 2004, Barlaz et al. 2004, Stern et al. 2007). Landfills with impermeable layer : Vertical gas wells and horizontal gas distribution pipes (Ettala & Väisänen 2002, Martikkala & Kettunen 2003).

so as to mitigate the impact of methane emissions and other environmental hazards associated with landfills (EC 1999). The mechanical-biological treatment of municipal solid waste is one of the ways to achieve this target. In MBT, the mechanically separated fraction of MSW is commonly refined to produce refuse-derived fuel while the residual fraction is further treated biologically, either aerobically or anaerobically, in particular to reduce its methane emission potential, before being landfilled (the biologically stabilised undersized fraction is referred to here as MBT residual). Methane oxidation rates comparable to the areal methane loadings typical of large landfills have been obtained in laboratory column studies with MBT residual at 30 °C (Cossu et al. 2003) and with MSW compost at 20 °C (Huber-Humer 2004), in addition to other compost materials not based on MSW (Hilger & Humer 2003). However, the methane oxidation performance of MBT residual at low temperatures has not been previously reported. Sormunen et al. (2008) reported low methane emissions compared to carbon dioxide emissions from MBT residual placed in an outdoor lysimeter, suggesting that oxidation in MBT residual decreased methane emissions.

1.5.3 Distribution of landfill gas into oxidation layer

The gas flux into the cover layer in landfills typically shows spatial variation owing to the variation in the rate of methane production and methane flux into the cover (Bogner et al. 1997). Preferential gas flow paths are easily formed through, e.g., cracks in the cover soil (e.g., Scheutz et al. 2009a). This may lead to low oxidation and high emissions at the whole landfill level. Thus, arranging for an even distribution of gas into the oxidation layer is crucial to obtain a high methane oxidation rate throughout the landfill. In landfills with no water impermeable cover system (e.g., landfills with temporary covers), a gas distribution layer made from coarse material (Barlaz et al. 2004, Huber-Humer 2004, Stern et al. 2007, Huber-Humer et al. 2008) such as gravel can be installed above the waste layer. Huber-Humer (2004) observed that, in cells with a distribution layer and higher compost cover, the distribution of gas fluxes across the area was more homogeneous and methane oxidation performance was higher compared to cells with no distribution layer and a thinner layer of compost (Chapter 1.5.4).

A water impermeable cover system may be required, as it is, for example, in the EU states by the European Union Landfill Directive (EC 1999), to prevent the infiltration of rainwater on closed landfills, if the authority prescribing the measures for landfill aftercare considers that leachate formation should be prevented. In landfills with a final cover that includes an impermeable layer, gas can be distributed through the impermeable sealing layer using vertical gas wells or openings in that, and then via horizontal pipes into the oxidation layer (Table 1). Methane oxidizing cover layers integrated in landfill cover systems with impermeable layers have been studied in test cells (50x50 m and 10x20 m) constructed in landfills (Ettala & Väisänen 2002, Martikkala & Kettunen 2003). In both studies, the authors concluded on the basis of gas measurements that methane oxidation was promoted in the test cells; however, methane production and oxidation rates were not reported. Furthermore, no earlier publications exist on the full-scale performance of systems distributing landfill gas through the impermeable layer.

1.5.4 Thickness and compaction of oxidation layer

The methane oxidation capacity of an oxidation layer can be expected to increase with increasing thickness of the layer owing to increase in the mass and volume of support medium available for the growth of methanotrophs, providing the methane and oxygen supply (to microorganisms) and other conditions remain favorable throughout the vertical profile. Moreover, a thicker cover generally provides a longer retention time for methane which may increase oxidation (Stern et al. 2007, Albanna et al. 2008). Huber-Humer (2004) obtained a 95-100% reduction in methane emissions with a 120 cm thick compost landfill cover and a gas distribution layer, compared to uncovered control, while lower oxidation (68-74% reduction) was observed with 30-40 cm covers and no gas distribution layer. Higher temperature and more suitable moisture in deeper layers (Maurice & Lagerkvist 2003, Huber-Humer 2004) in the cover may also increase methane oxidation. Increasing the thickness of an oxidation layer increases the costs (material, transportation, construction) and the potential for leachate pollution from cover layers. Thus knowledge of the field methane oxidation capacities obtainable with different layer thicknesses and materials in different climatic conditions is important for designing cost-effective biocovers.

Compaction affects air porosity, and it has been suggested that, to maintain long-term porosity and gas permeability, an oxidation layer made of compost should not be compacted (Scheutz et al. 2009a). The natural settling of compost covers has been 20% during the first few years after biocover installation (Huber-Humer et al. 2008).

1.5.5 Methane oxidation rates in landfill cover layers

Although laboratory studies provide information on the effect of environmental factors and on the suitability of various support media for methane oxidation, the methane oxidation capacities of biocovers cannot be reliably estimated from laboratory results alone (Huber-Humer et al. 2008). Thus, for designing efficient methane oxidizing landfill biocovers, there is a need for information on methane oxidation rates obtained with different biocover design decisions and parameters, such as material and thickness, at ambient conditions in different climates (Chanton et al. 2009). Many field studies have reported fractional oxidation values (percentage of oxidized methane over the total flux into the landfill cover) obtained using the isotope fractionation method (Table 2) (Chanton et al. 2009, Huber-Humer et al. 2008, 2009) while only a few studies have reported methane oxidation rates per areal unit. Chanton et al. (2009) calculated mean values of area-based oxidation rates for many of the earlier studies, using emission and fractional oxidation data. For the 15 studies conducted over the annual cycle, including landfills in Florida (U.S.), New Hampshire (U.S), Germany, Netherlands, Sweden and Denmark, the oxidation rates were 1.7-216 g CH_4 m^{-2} d^{-1} and fractional oxidation values 10-89% (Chanton et al. 2009). In addition, oxidation rates of 111 g CH_4 m^{-2} d^{-1} with a fractional oxidation of 96-100% all year round have been obtained at an Austrian landfill (Huber-Humer 2004). Thus there is considerable variation in methane oxidation between landfills, which may be explained by climatic factors, gas flux rates, cover layer designs and materials. Moreover, a part of the variation is probably explained by differences in the methods used to quantify methane oxidation (Chanton et al. 2009).

Several field studies show that installation of biocovers may notably increase the rate of methane oxidation compared to uncovered landfills or landfills with conventional covers not optimized for methane oxidation (Barlaz et al. 2004, Huber-Humer 2004, Stern et al. 2007, Aït-Benichou et al. 2009). In Austria, several closed landfills have been covered using a gas distribution layer and a compost layer, serving either as the sole means of methane mitigation or in combination with a gas extraction system. The longest monitoring period reported so far for biocovers is 6 years, during which flat, undisturbed areas have consumed nearly 100% of the potentially emitted methane during the entire period (Huber-Humer et al. 2008).

In the European Union countries many small landfills have been closed due to the implementation of the EU landfill directive (EC 1999); such landfills may continue producing methane for decades. Methane oxidation may be a feasible option to mitigate the emissions from these closed landfills. The area-based oxidation rates obtained in the above-mentioned studies appear to be sufficient for treating the methane produced, for example, in old municipal landfills in Finland (e.g., methane production rate 8.5-17 m^3 CH_4 ha^{-1} h^{-1} (14.6-29.2 g CH_4 m^{-2} d^{-1}) (Ettala et al. 2008). However, in several of those studies, fractional oxidation has been relatively low (range 10-89%), i.e., a high proportion of the methane flux into the cover was emitted into the atmosphere. An effective biocover should have a sufficiently high oxidation capacity to oxidize a major part of the methane influx. Studies reporting field methane oxidation rates per area unit obtainable by biocovers in boreal conditions are lacking.

TABLE 2 A summary of field studies with estimates of methane oxidation per area unit. For the references marked with *, the area-based and fractional methane oxidation rates are reported as presented by Chanton et al. (2009).

Country/State	Methods (emissions, oxidation)[a]	Cover material (thickness, cm)	Oxidation (g CH_4 m^{-2} d^{-1})	f_{ox}%[b]	Reference
Austria	C, M	Sludge compost (120)	111	96-100	Huber-Humer (2004)
Denmark	C, M	Sand adjacent to landfill (na)	17.6	89	Christophersen et al. (2001)*
Denmark	C, I	Sand adjacent to landfill (na)	2.4	28	Christophersen et al. (2001)*
Finland	Mi, M	Interim cover soil (nr)	4.6-11.7	4-29	Laurila et al. (2005)
Florida, U.S.	C, I	Yard waste compost (50)	1.7	38	Stern et al. (2007)*
Florida, U.S.	C, I	Mulch and topsoil (109)	26.8	26	Stern et al. (2007)*
Florida, U.S.	C, I	Clay (15)	216.3	14	Chanton & Liptay (2000) *
Florida, U.S.	C, I	Sandy clay (15)	9.0	14	Abichou et al. (2006)*
Florida, U.S.	C, I	Mulch and topsoil (109)	26.8	26	Chanton & Liptay (2000)*
Florida, U.S.	C, I	Sandy loam (45)	7.3	25	Abichou et al. (2006)*
Germany and Netherlands	C, I	Landfill covers (100)	67.8	84	Bergamaschi et al. (1998)*
Kentucky, U.S.	C, I	Clay (100)	19.5	21	Barlaz et al. (2004)*
Kentucky, U.S.	C, I	Compost (115)	0.7	55	Barlaz et al. (2004)*
New Hampshire, U.S.	C, E	Sandy-clay loam (100-200)	14.5	na	Czepiel et al. (1996)*
New Hampshire, U.S.	T, E	Sandy-clay loam (100-200)	16.5	na	Czepiel et al. (1996)*
Sweden	C, I	Sand (30-80)	2.8	42	Börjesson et al. (2001)*
Sweden	C, I	Sandy loam (40-100)	60.7	26	Börjesson et al. (2001)*

na=not applicable; nd= not reported; [a] C= flux chamber, T=plume tracer, Mi=micrometeorological, M=mass balance calculation, I=Isotope fractionation, E=Estimation of fractional oxidation. [b] Fractional oxidation of the methane flux into the cover.

2 OBJECTIVES

The main objectives of the present study were to evaluate the feasibility of methane-oxidizing landfill biocovers as a technology for mitigating methane emissions from boreal landfills and to produce information for the design, operation, and monitoring of methane oxidizing landfill covers in boreal conditions.

The specific objectives were:

- To find out whether methane oxidation occurs at low temperatures in soils exposed to landfill gas with a high methane content and how methane oxidation is regulated by temperature and moisture (I).
- To evaluate the suitability of MBT residual for use as a support medium in the landfill cover layer to mitigate greenhouse gas emissions (II).
- To determine the feasibility of methane oxidation in MBT residual-based cover layers as a method of methane treatment in landfills in field conditions in a boreal climate (III).
- To evaluate the reduction in methane emissions achieved using a gas distribution and methane oxidation system at a boreal landfill sealed with a water impermeable cover system in compliance with the EU landfill directive (IV).

3 MATERIALS AND METHODS

3.1 An overview of the conducted studies

This study evaluated landfill methane oxidation using laboratory batch assays (I-III) and columns (II), and field measurements in outdoor lysimeter (III) and in a full-scale landfill. The studies are summarized in Table 3.

TABLE 3 A summary of the studies of this thesis.

Topic of the study	Scale and type of methane oxidation determinations	Temperature range[a]	Materials studied
Responses of methane oxidation to temperature and moisture (I)	Laboratory batch assays.	1-19 °C	Landfill cover soil (4-5 years old) made from compost materials.
Suitability of MBT residual for biocover (II)	Laboratory column assays and batch assays.	2-23 °C	MBT residual.
Field performance of an MBT residual based biocover (III)	Field methane oxidation rates calculated from measurements of gas emissions and composition of the produced gas. Samples from the lysimeter studied in laboratory batch assays.	−24 to 24 °C (air); −7 to 22 °C (top 80 cm layer)	MBT residual used as a biocover in an outdoor lysimeter. Studied 1-2 years after installation.
Performance of a full-scale methane oxidation system at a sealed landfill (IV)	Field methane oxidation rates calculated from measurements of gas emissions and composition of the produced gas.	−7 to 25 °C (air); <0 °C to 21 °C (top 50 cm layer)	Landfill cover soil composed from sludge compost and peat. Studied 0-1.5 years after installation.

[a] Temperature range applied in laboratory experiments (I, II), or ambient temperatures during the field measurements (III, IV).

3.2 Soil and compost materials studied as support media for methane oxidation

The landfill cover soil (I) was obtained from Tarastenjärvi municipal solid waste landfill, Tampere, Finland. Seven different cover materials used as interim landfill covers from two different landfills were initially screened for their methane oxidation potentials (MOP) in laboratory batch assays (Einola 2002). The soil with the highest MOP was chosen for a further study (I). The material had been spread on the landfill 4-5 years before the present experiment (referred to here as four-year old landfill cover soil). It was originally a composted mixture (1:2 v/v) of municipal sewage sludge, which was anaerobically stabilized prior to composting, and chemical sludge from the treatment of food-board factory effluents. The samples were taken in December 2000 (air temperature 3 °C, soil temperature 5 °C) and combined in the laboratory.

The MBT residual for the present study (II, III) originated from Loimi-Häme Regional Solid Waste Management Ltd (Forssa, Finland). In the Loimi-Häme region metals are source-segregated, and biowaste and papers are source-segregated in residential buildings containing more than five households, while in the case of other buildings, where the segregated wastestreams are >20 kg per week, biowaste, paper, cardboard and glass are source-segregated. Furthermore, a network of local collection points for papers, metals and batteries exists for households. In Loimi-Häme the municipal solid waste fraction which is not source-segregated, i.e., grey waste (see II), is further processed in a mechanical plant in the following steps: pre-shredding, screening (50 mm mesh), removal of non magnetic and magnetic metals, shredding, a second removal of other magnetic metals, and drum screening (50 mm).

For the present study (II, III), the end product from the mechanical treatment of waste (the undersize fraction from the last screening) was transported to Jyväskylä, Finland, where it was aerobically stabilised in seven different batches for 2-3 weeks in aerated tunnels, followed by windrow stabilisation and storage outdoors for 6-14 months (Sormunen et al. 2008). In the tunnel process wood chips or the stabilised oversize fraction (>15 mm) of the windrow material was used as support material (0.5 m^3 $t_{residuals}^{-1}$). The MBT residual used in the laboratory column studies (II) was obtained from two of the seven batches. These two batches, after tunnel composting for 3 weeks, were composted in windrows outdoors for 19 weeks (referred to as MBT residual 22) and 54 weeks (referred as MBT residual 57) in Jyväskylä. MBT residual samples for the laboratory column study (II) were taken in September 2003 at 1 m height from 10-30, 75 and 150 cm horizontal depths from the windrow (volume 45 m^3, width 4.5 m, height 1.3-1.8 m) surface to make up a combined sample for further processing. After sampling, plastics in excess of 30 mm (2-3% of the initial wet weight of the samples) were cut to 30-40 mm particle size, whereas wood chips (21-26%) and other material (1-2%) including stones (>30 mm), glass particles, and batteries, were removed to obtain the processed samples (containing 75% and 70% of the initial wet weight of samples of the MBT residuals 22 and 57, respectively). All of the laboratory experiments and analyses in II were performed using the processed samples.

For the outdoor lysimeter study (III), the materials from the seven windrows were screened (drum, mesh 40 mm) to separate the support material added for the aerobic stabilisation. The undersize materials (MBT residuals) were then combined and mixed, and packed in the outdoor lysimeter (see Chapter 3.5). The characteristics of the MBT residual were: moisture 85% of dry weight (dw), volatile solids (VS) 43% dw, pH 7.0-7.6, and N_{tot} 0.6% (Sormunen et al. 2008) at the time when it was placed in the present landfill lysimeter, i.e., in December 2003.

At the landfill studied in (IV), sludge compost from a local municipal wastewater treatment plant, and peat, were used for the upper part of the top soil cover to promote methane oxidation. The materials were chosen from locally available materials on the basis of laboratory characterization (IV). The mixing of peat and sludge compost in the ratio of 40:60 (v/v) (Table 4) was calculated to yield a medium with balanced characteristics for promoting methane oxidation.

3.3 Batch assays (I-IV)

3.3.1 Methane oxidation potential (I,II, III) and respiration activity (I, II, IV)

In this study, the methane consumption rates of soil and compost materials were determined in batch assays to investigate the activity of methane-oxidizing microorganisms in samples from field sites (I-IV) or from laboratory experiments (II) at adjusted moistures (I) and temperatures (I, II). Oxygen consumption and carbon dioxide production was studied in the assays with added methane (I, II) and in assays with no added substrates (respiratory activity) (I, II, IV) to investigate the overall gas metabolism (I, II) and to evaluate the degree of biological stability of the compost materials (II, IV).

The rates of methane consumption, i.e., methane oxidation potential (MOP), and/or oxygen consumption, and carbon dioxide production of samples from the field study sites (I-IV) or laboratory columns (II) were determined in batch assays with duplicate (I, II) or triplicate (III) 14 g_{dw} (120 ml bottles) (I) or 7 g_{ww} (60 ml bottles) (II-IV) samples in headspace bottles. The bottles were incubated at temperatures of 1-25 °C, and no adjustment of moisture was done, with the exception of (I). In I, at each of the temperatures, the assays were done with soil samples adjusted to the moistures of 7% dw, 14% dw, 21% dw, and 28% dw (for 19 °C 34% dw was also assayed). First, soil aliquots were air-dried at 30 °C to a moisture of 7% dw, and deionised water then added to the dried samples to reach the desired moistures (I). In the methane assays, 10 ml air was removed and 10 ml of methane (99.5%, Aga Ltd.,

TABLE 4 Characteristics of the peat and sludge compost used in the upper part (50 cm) of the top soil cover as determined from samples taken from storage piles before landfill sealing. Values are also presented for a mixture of the materials.

	Peat	Sludge compost	Mixture[a]
Wet bulk density (kg m^{-3})	460	680	
Moisture (% dw)	452	110	161
pH	3.50	5.26	4.3
Conductivity (µS cm^{-1})	26	1430	1200
VS (% dw)	84.4	23.9	33
Water-holding capacity (% dw)	843	143	246
Respiratory O_2 cons. (µg O_2 g_{dw}^{-1} h^{-1}) at 23°C	2.24	18.6	16.2
Respiratory CO_2 prod. (µg CO_2 g_{dw}^{-1} h^{-1}) at 23°C	1.89	16.7	14.5
Leaching test results[b]			
Eluate pH	6.09	5.86	5.9
Eluate conductivity (µS cm^{-1})	42	540	480
Eluate COD_{Cr} (mg l^{-1})	380[c]	130	170
Leachability of total N (mg kg_{dw}^{-1})	180	390	370
Leachability of total NH_4-N (mg kg_{dw}^{-1})	<20	<10	<20
Leachability of total P (mg kg_{dw}^{-1})	2.2	34	30

[a] The values were calculated for a mixture of peat and sludge compost in the ratio of 40:60 on a volume basis which corresponded (as calculated using the moisture and bulk density values of the materials) to a dry weight ratio of 15:85. The dry weight ratio was used to calculate the values of the parameters for the mixture.

[b] Leaching test (EN-12457-4: 2002) and analytical methods described in IV.

[c] The value was obtained by multiplying the COD_{Cr} value determined for the eluate (190 mg l^{-1}) by 2, owing to the higher liquid/solid ratio.

Finland) was added to the bottles (I), or no air was removed and 5 ml 99.5% methane was added (II, III). The initial partial pressures in the methane assays were 8-9% for methane and 18-19% for oxygen (I), or 9% and 20%, respectively (II, III). Respiration activity assays (I, II, IV) were performed in the same way as the MOP assays but no methane was added. In study (I), the samples were pre-incubated for 1 day in assay conditions (temperature, moisture, initial gas phase), i.e., samples for methane assays were pre-incubated with methane while those for respiration assays were pre-incubated without methane. After pre-incubation, the bottles were opened for 30 min for aeration and the actual assays were started as described above. In the other studies (II, III) no pre-incubation was done.

Gas samples (0.1 ml) were taken regularly with a pressure-lock syringe (Vici Precision Sampling Inc., US) and analysed by gas chromatography. Total (gas phase plus liquid phase) molar amounts of gases per sample weight were plotted against time, and linear regressions were fitted to obtain the gas consumption (CH_4, O_2) or production (CO_2) rate (µg g_{dw}^{-1} h^{-1}). Owing to the different reaction rates, different assay durations, measurement intervals, and time periods for the rate calculations were used in each of the studies (see I-III for details). The gas consumption and production rates were calculated over the period when all the rates followed zero-order kinetics and when, in the linear regression analysis (N=4-11), R^2 was >0.95 (I, III) or >0.90 (II). Examples of some of the assays (I) are shown in (Fig. 3). MOP was presented as zero (I, III) or below the estimated detection limit (II) in samples which did not show methane consumption during the experiment. The samples with no methane consumption included the samples adjusted to the lowest moisture tested (I), the samples of MBT residual before the column experiment (II), and some of the outdoor lysimeter samples (III). For the latter, a zero rate was reported if P was >0.05 in the regression analysis (III).

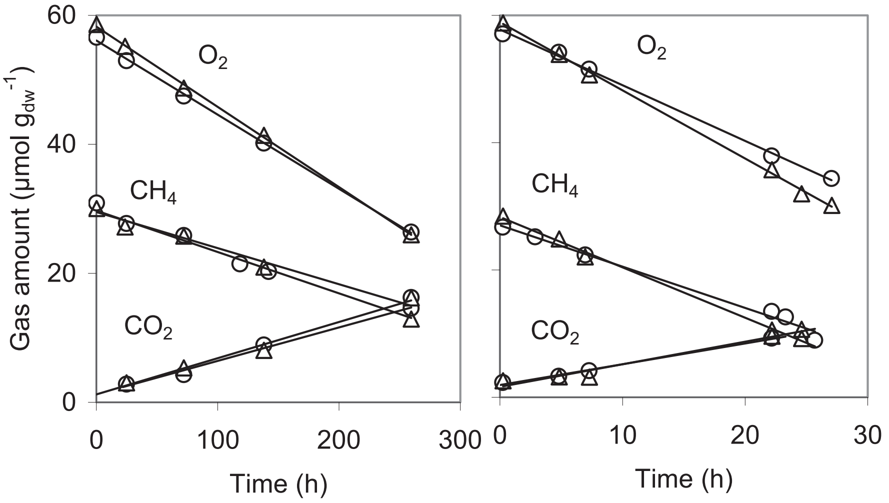

FIGURE 3 An example of changes in total amounts (gas phase+liquid phase) of CH_4, CO_2, and O_2 in bottles over time in batch assays with landfill cover soil at 1 °C (left) and 12 °C (right) with moisture of 21% dw. Initial CH_4 concentration was 9%. Symbols and parallel regression lines show the values obtained for the duplicate samples.

3.3.2 Increase in methane consumption rate (I)

Increase in the methane consumption rate (MOP) was investigated by determining the methane consumption rates in two consecutive methane feeding cycles at 1 and 12 °C with moisture at 21% of dw. When the initial experiment, i.e., the first feeding cycle, was completed, the bottles were opened for 30 min and the second feeding cycle started in the same way as the first one (Chapter 3.3.1). The difference in the rate of methane consumption between the two feeding cycles was divided by the rate in the first cycle to obtain the specific growth of methane consumption rate; this was then divided by the duration of the first feeding cycle (13 d at 1 °C and 1.0 d at 12 °C) to obtain the specific growth rate of methane consumption. The generation time was calculated as the reciprocal of the specific growth rate.

3.4 Laboratory column experiment (II)

The column experiment was performed in two 35-l PVC cylinders (Fig. 4), one column per each of the two MBT residuals used. A 10-cm layer of gravel was installed at the bottom of the cylinders as a methane distribution layer, above which a plastic net was installed to hold the MBT residual. The moisture of the MBT residuals was standardized in relation to their water-holding capacities by air-drying (at 30 °C) MBT residual 22 to the same level as that of MBT residual 57 (55.8% of water-holding capacity). The MBT residuals were packed in 30-cm layers (total volume 21 l) at 700 kg m^{-3} wet bulk density.

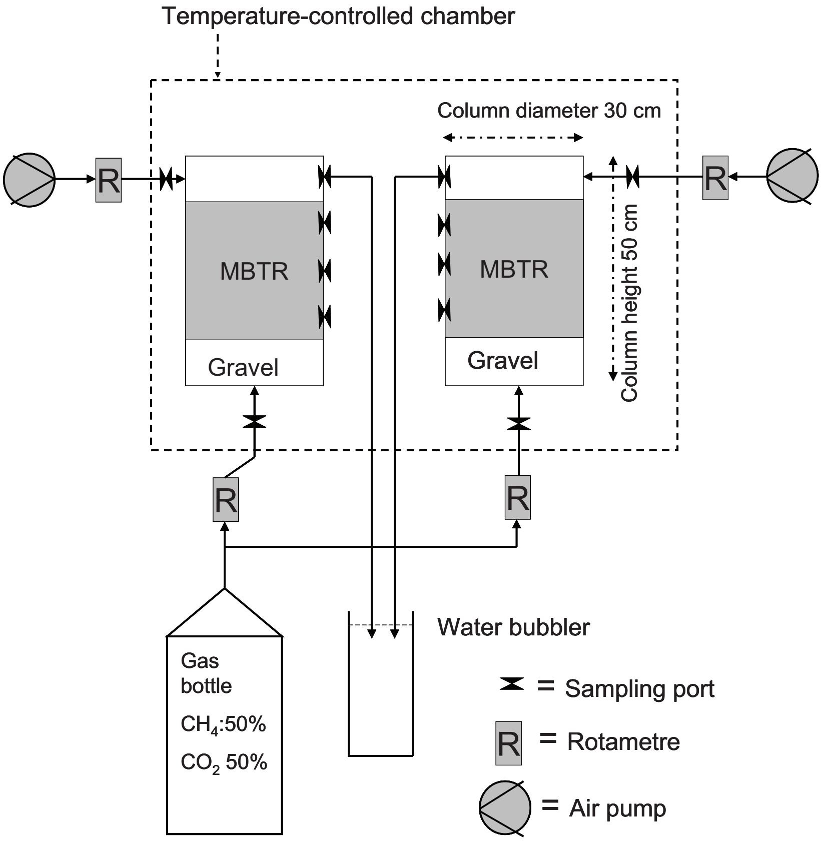

FIGURE 4 The setup and instrumentation of the laboratory column experiment simulating a landfill cover layer.

The columns were placed in a temperature-controlled chamber. Synthetic landfill gas (CH_4 50%:CO_2 50%, Aga Oy, Finland) was fed to the columns from the bottom, while ambient air was fed to the gas space at the top of the columns. Temperature (2-25 °C), synthetic landfill gas flow rates (4.5-12 ml_{gas} min^{-1}, 1.5-5 l CH_4 m^{-2} h^{-1}) and air flow rates (38-140 ml_{air} min^{-1}, 6-22 l O_2 m^{-2} h^{-1}) were adjusted during the experiment as described below. Outlet gas was conducted through a tube equipped with a port for gas sampling, and the tube end was kept 1 cm under the surface of the water in a cylinder to maintain a counter press ure of 1 hPa. Outlet gas and inlet air CH_4, CO_2, and O_2 concentrations and flow rates were measured to calculate the consumption or production of the gases by subtracting the outlet gas volumes from the inlet gas (synthetic landfill gas plus air) volumes. The column inlet air and synthetic landfill gas flow rates were adjusted by rotameters (model P units with FM042-15 and FM032-41 flow tubes, Aalborg Instruments, USA). Outlet gas flow rates were measured and the rotameters calibrated with a soap bubble flow meter. Gas pressure (ambient air pressure) and the temperatures of the temperature controlled chamber and of ambient air were measured by a digital pressure meter (LEO2, Keller, Switzerland) and thermometers (accuracy 0.1 °C), respectively, to convert all the gas data to standard temperature and pressure.

The column experiment was started at 22-25 °C, with a methane loading rate of 21.5 g CH_4 m^{-2} d^{-1}, which corresponds to the area-based methane production of a relatively large landfill. Aeration was initially set to 226 g O_2 m^{-2} d^{-1}, corresponding to an aeration ratio of 3.8 mol O_2 in:1 mol CH_4 in, which is about twice the stoichiometric O_2 need for the complete oxidation of CH_4 (2 mol O_2 per 1 mol CH_4; Anthony 1982). The column inlet flow rates were initially 2.1 ml CH_4 min^{-1} and 7.8 ml O_2 min^{-1}. During the initial period at 22-25 °C, the methane loading rate and aeration were adjusted between days 39 and 52, as described in detail in the results section, and were maintained constant thereafter. After 124 d, the columns were dismantled and 5 cm soil layers with mean depths of 5, 15, and 25 cm were separated for analyses.

3.5 Outdoor lysimeter experiment (III)

The study was performed using a landfill lysimeter (height 3.9 m, width 2.4 m, length 12 m, volume 112 m^3; Fig. 5) placed in Mustankorkea landfill, Jyväskylä, Finland. The purpose of the lysimeter was to evaluate the gas and leachate emissions from the landfilling of MBT residual (Sormunen et al. 2008) and to evaluate methane oxidation in MBT residual in field conditions (III). The lysimeter was made from a steel frame (RHS 60 x 80 mm) and walls (2 mm) and coated with acryl paint (Hempatex Hi-build 46410). The lysimeter was embedded in the ground, the top edge of the frame being ca. 10 cm above the surrounding ground surface. The lysimeter was placed in the ground at an angle of 5° in length direction in order to collect the leachate from the drainage layer (gravel, thickness 30 cm, particle size <25 mm) and collection drain (110 mm) at the bottom of the lysimeter. The lysimeter was filled with the MBT residual in 50 cm horizontal layers, which were compacted by a soil compactor (Bomag 105, 1.6 t) to obtain a wet bulk density of 1.0 t m^{-3}. Gravel (thickness 10-15 cm, particle size <25 mm) was installed to passively deliver the gas produced (from the biodegradation of MBT residual in the waste layer) into the above-lying methane oxidation layer as well as to obtain a leachate distribution layer

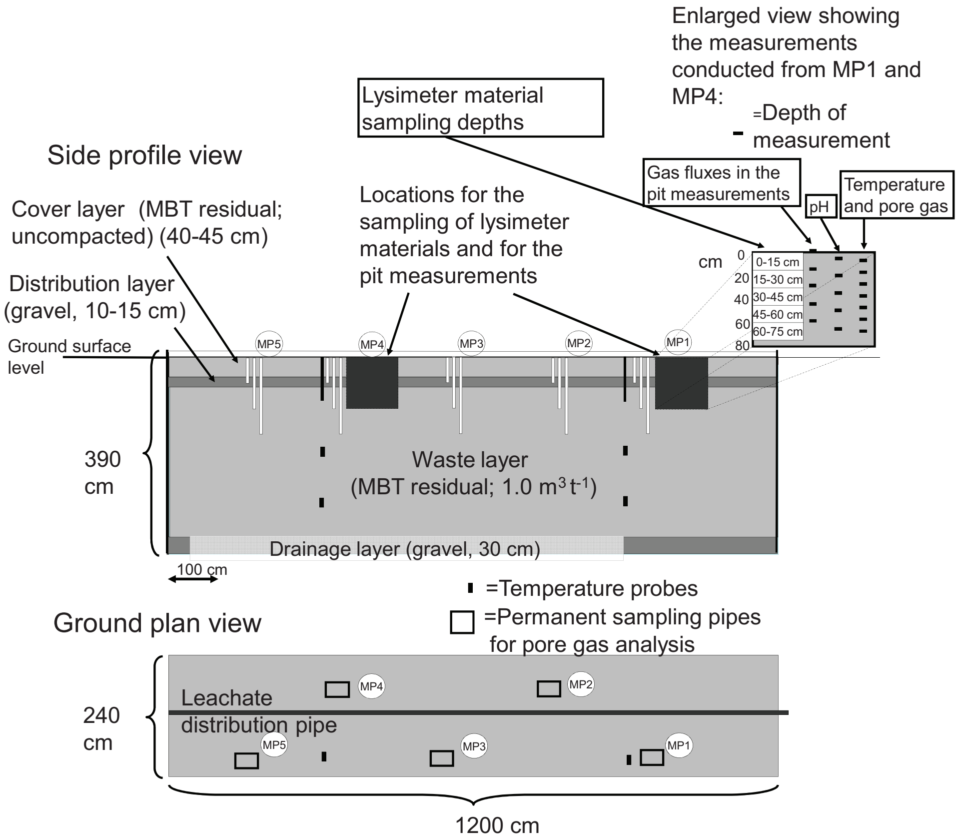

FIGURE 5 Structure and instrumentation of the landfill lysimeter.

during leachate recirculation. Above the gravel gas and leachate distribution layer, a 40-45 cm thick cover layer of MBT residual (slightly compacted, 0.8 t m^{-3}) was installed.

In addition to the seven emission measurement times (Fig. 6; method described in 3.7.4), gas fluxes were also measured twice (4-5 July and 15-16 August 2005) at different depths in the lysimeter (referred to here as pit measurements) down to as low as 60 cm from the top, at MPs 1 and 4. This was done by stepwise removal of the lysimeter materials from an area of approximately 60 × 60 cm in 15 cm layers and measuring the gas flux from the pit formed after removing each layer. Once the flux measurement at 60 cm depth had been taken, the 60 cm deep pit was filled with the removed material so that the material from each of the removed layers was returned to its original depth. The purpose of the pit measurements was to obtain information on methane flux and oxidation along the vertical profile.

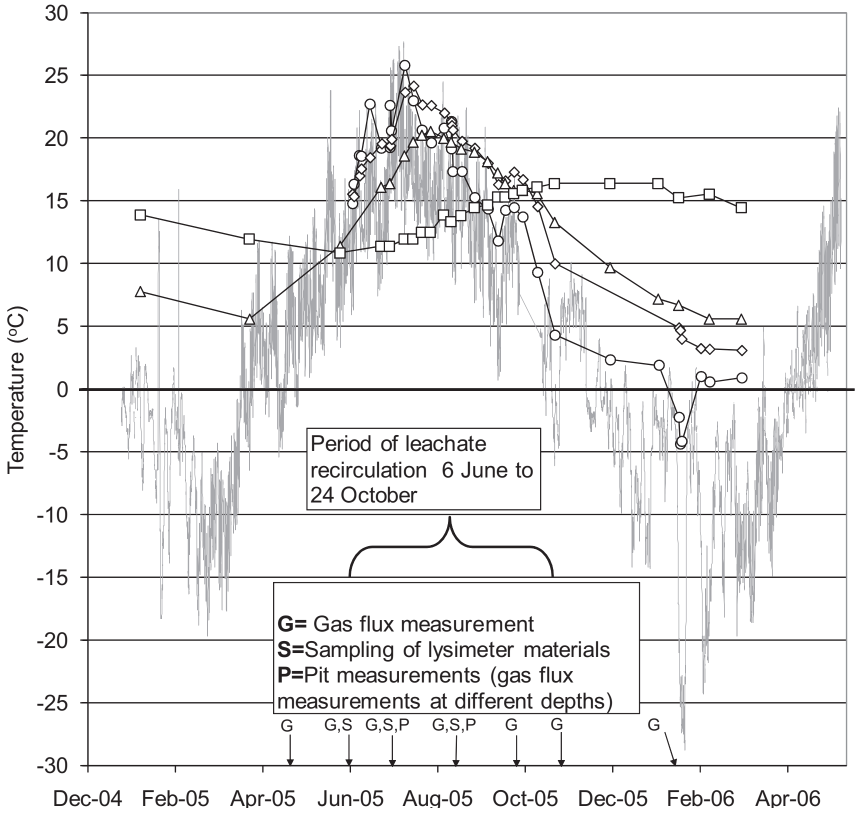

FIGURE 6 Temperatures of ambient air (-) and different depths (○5 cm; ◇35 cm; △ 80 m; □ 320 cm) of the landfill lysimeter, and days of the gas measurements and samplings of the lysimeter materials. Pore gas profiles were measured on the gas emission measurement days (except April 29) and also on 6 June, 20 July, 1 August and 16 September 2005.

3.6 Full-scale landfill (IV)

The field-scale study (IV) was performed at Aikkala landfill, which is located in the municipality of Hollola, Southern Finland. Approximately, 200,000 tonnes of municipal solid waste was deposited in the landfill over the period 1987-2001. The maximum thickness of the waste layer is 10 m. After closure, the landfill surface was sealed by constructing a 2.1-m-thick final cover comprising four layers (Fig. 7). The final cover, including the integrated biological gas treatment system, was installed during the years 2004 and 2005. The final cover was equipped with a passively vented gas collection and distribution system including a network of gas collection canals made from coarse material. The canals, along which the gas was conducted to 14 gas wells (Fig. 7, Fig. 8), were located in the upper part of the waste tip. At each gas well, two or four perforated gas distribution pipes were installed to distribute the gas into the drainage layer and, from there, into the above-lying soil cover. The gas wells were equipped with gas sampling ports and detachable caps. The gas distribution pipes were equipped with valves to enable the adjustment of the gas flow into the pipes. The valves were operable from the top of the gas well by using a metal bar. Within a 2 m radius of each gas well, the sealing layer was thickened and graded to slope towards the drainage layer (Fig. 7); this was done in order to prevent gas flow along the exterior wall of the gas well. The lower 50 cm part of the soil cover was composed of mineral soil with a hydraulic conductivity of approximately $k = 1 \cdot 10^{-6} - 1 \cdot 10^{-7}$ m s^{-1}; its purpose being to enable an even flow of gas into the above-lying oxidation layer across the landfill. The oxidation layer, i.e., upper part of the top soil cover (thickness 50 cm), was made from sludge compost and peat (Chapter 3.2, Table 4).

The performance of the landfill gas treatment system was monitored by gas measurements on four occasions, each lasting for 2-3 days, in October and November 2005, and in February and June 2006 (IV). In addition, one series of measurements was conducted before the sealing of the landfill, in October 2004; at that time approximately one-fourth of the landfill area had a sealing layer but no gas distribution structures had been installed. Each series of measurements included measurements of methane and carbon dioxide emissions and composition of the pore gas in the soil cover, and measurements of the gas composition in the gas wells.

The valves of all the gas wells were fully open and they were not adjusted during the study, except in gas well 12 at two measurement times (November 2005 and February 2006) when the valves were adjusted to test their effect on the gas emissions at two selected points near the gas well (described in detail in IV).

3.7 Chemical and physical analyses and measurements (I-IV)

3.7.1 Analyses of solids (I-IV)

Dry weight was analysed by heating the samples at 105 °C, and organic matter was determined as loss on ignition at 550 °C (Clesceri et al. 1998) (I-IV). Water-holding capacity (I, II, IV) was determined by a pressure-free method adapted from that described by US Composting Council (1997) (I): water was poured slowly to saturate a sample (1.1 kg in (I) and 600 ml in II and IV). The samples were allowed to drain for 30 min through perforations in the bottom of the container. The saturation-draining cycle was repeated four times and the final draining was continued for 4 h. Water-holding capacity was calculated from the moisture per dw after the final 4-h draining. Soil pH was measured with a PHM 210 meter (Radiometer Analytical, France) from suspensions of air-dried (<40 °C) soil in 0.01M $CaCl_2$ (1:5 $v_{soil}/v_{solution}$) after shaking for 5 min in an orbital shaker (200 rev min^{-1}), overnight settling and manual shaking immediately

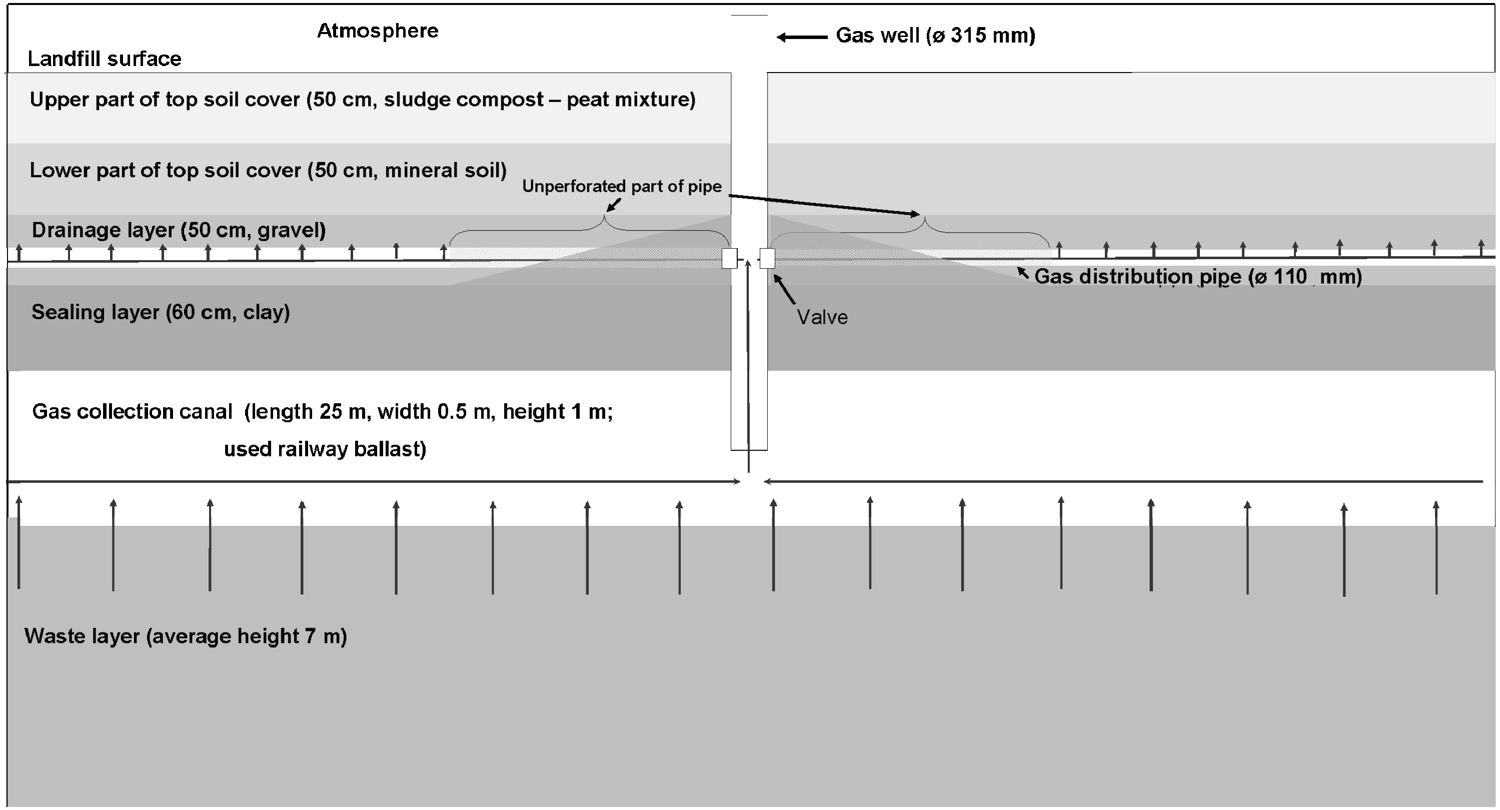

FIGURE 7 Schematic side profile view showing a gas well and an area of approximately four meters around the well. The different layers of the final cover and the gas collection/distribution structures are shown. The arrows indicate the planned directions of the landfill gas flow. Note that for clarity the profile view only shows two gas collection canals and two gas distribution pipes, although, most of the gas wells had four canals and pipes which were installed at different horizontal and vertical angles according to the siting of the gas wells and the landfill topography (see Fig. 8 for map of all wells and distribution pipes)

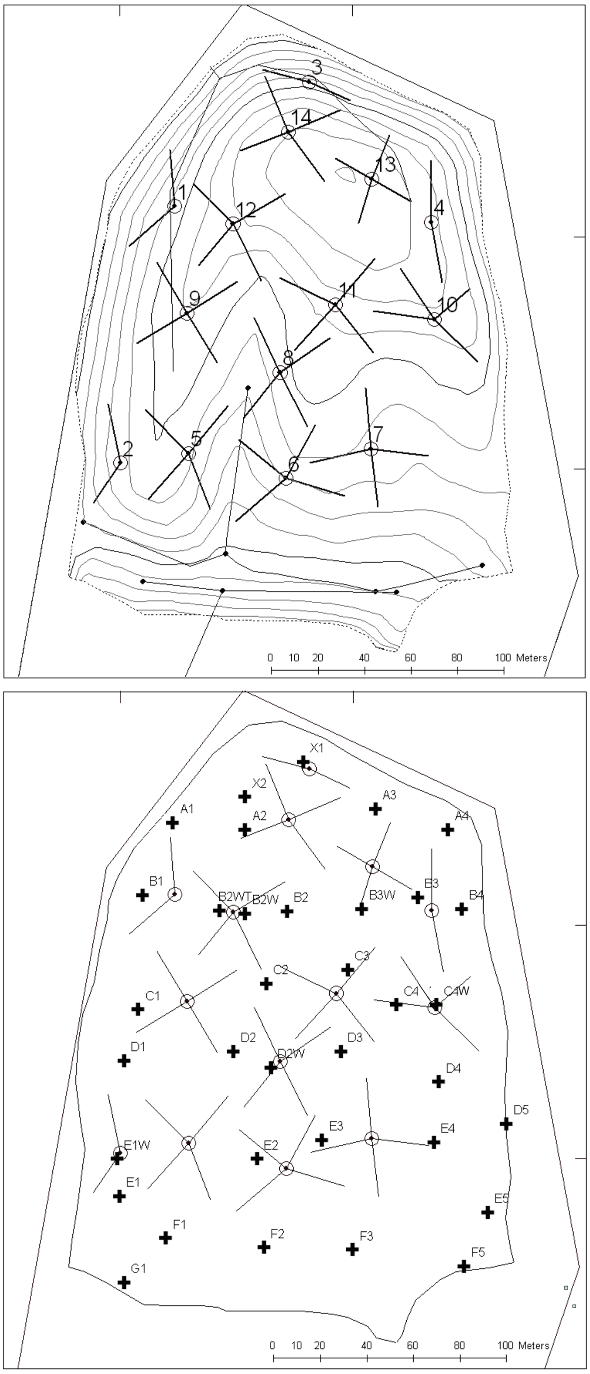

FIGURE 8 The gas wells and distribution pipes installed during the sealing of the landfill, together with elevation lines (above), or with the measuring points used in the measurements after sealing (below). Detailed elevation maps are shown in IV.

prior to measurement (I, II). Electrical conductivity suspensions were prepared and treated similarly, except that distilled water in the ratio 1:2.5 (v/v) was used, and measured with a CDM 210 meter (Radiometer Analytical, France) (I, II). Wet bulk density (IV) was measured from uncompacted samples using 10 l containers.

3.7.2 Gas composition in laboratory studies (III, IV)

The gas phases were sampled by a pressure-lock syringe through a rubber septum and CH_4, CO_2, and O_2 concentrations in the gas samples were analysed using a Perkin Elmer Autosystem XL gas chromatograph. CH_4, CO_2, and O_2 analyses in I and CO_2 and O_2 analyses in (II) were performed using a Carboxen 1010-PLOT column (Supelco, USA) (diameter 0.53 mm, length 30 m) and a thermal conductivity detector (TCD); temperatures: column 35 °C, injector 230 °C and detector 230 °C (I) (carrier (He) and reference gas (He) flow rates were 7 ml min^{-1}). The methane analyses in II and III were done using an Alumina column (PE) (30 m x 0.53 mm) and a flame ionization detector with injector, oven and detector temperatures of 225, 100, and 250 °C, respectively, and with a carrier gas (He) flow of 14 ml min^{-1}. In IV, O_2 and CO_2 were analysed using a Varian Select Permanent Gases column and a TCD (injector, oven and detector temperatures 50, 45, and 160 °C). In the MOP and respiration activity assays (I-IV), gas concentrations in the water phase were calculated from the partial pressures in the gas phase using the Henry's law constants (K_H) $1.4 \cdot 10^{-3}$, $3.4 \cdot 10^{-2}$ and $1.3 \cdot 10^{-3}$ M atm^{-1} (at 298.15 K) converted for each temperature using the temperature dependence coefficients 1600, 2400 and 1500 K for CH_4, CO_2 and O_2, respectively (Sander 1999).

3.7.3 Gas composition in field studies (III, IV)

CH_4, CO_2 and O_2 in pore gas at different depths (up to 75 cm) in the outdoor lysimeter (III), landfill cover (IV) and gas wells (IV) were sampled by a soil gas probe (Eijkelkamp Agrisearch Equipment, Netherlands), gas volume 20 cm^3, which was connected to an infrared gas analyser (GA-94, Geotechnical Instruments, UK). The probe was installed at the measuring depth, or, it was connected to the gas well sampling port (IV). The gas sample was drawn into the analyser until the concentrations stabilised. The pore gas at depths of 100 and 150 cm in the outdoor lysimeter (III) were sampled using permanently installed gas probes (Sormunen et al. 2008) and a GA-94. The pore gas composition of MP2 at the depths of 100 and 150 cm up to October 2005 has been published previously (Sormunen et al. 2008). In the other four MPs permanent sampling probes were installed in August 2005 (first measurements on Aug. 31).

3.7.4 Gas emissions in field studies (III, IV)

Gas emissions were measured by the static flux chamber method, using a Fourier transform infrared spectrometer (Gasmet DX-4000, Gasmet Technologies, Finland) with sample cell volume 1 l, path length 9.8 m and temperature 60 °C. At each measurement point prior to the flux measurement, the flux chamber (round shape, volume 36.7 l, area 0.204 m^2) was first laid on its side on the lysimeter surface and the methane and carbon dioxide concentrations were monitored under a continuous gas flow from the flux chamber into the spectrometer. The gas concentrations were measured until they stabilized, indicating that the sample cell of the spectrometer had been replaced by ambient air, and the flux measurement was then started by installing the flux chamber on the lysimeter surface. Gas was pumped continuously through a sampling tube from the flux chamber into the spectrometer (1.4 l min^{-1}) and the FTIR spectra were recorded in the wavenumber range 900-4200 cm^{-1} with a resolution of 8 cm^{-1} and a scanning rate of 10 scans s^{-1} for 5 min at 0.5 min intervals by a laptop computer connected to the spectrometer. Methane and carbon dioxide concentrations were determined from the wavenumber ranges 2609-2990 and 3400-3800 cm^{-1}, respectively, by Calcmet™ software (Gasmet Technologies, Finland) using the classical least-squares method. The calibration spectra for 11 compounds (e.g., water vapour, CH_4, CO_2, N_2O, NH_3, and NO_2) were obtained by the analysis of pure compounds diluted in nitrogen. The flux chamber was equipped with a balance valve to allow compensation by ambient air for the decrease in pressure induced by sample withdrawal. Because the flow rate of gas from the chamber to the spectrometer was relatively high compared to the volume of the chamber, the measurements of the concentrations were corrected by adding the amounts of gases removed from the chamber and subtracting the amounts of gases entering with the replacement air (ambient air) to obtain the concentrations expected in an undisturbed situation. Gas fluxes were calculated from the rate of change in the gas concentration inside the flux chamber (Equation 2) (Rolston 1986):

$$F = \frac{\Delta C}{\Delta t} \times \left(\frac{V}{A} \right). \tag{2}$$

where F is the flux density of gas (g min^{-1}), V is the volume of air within the chamber (l), A is the area covered by the chamber, and ΔC (mg l^{-1}) is the change in gas concentration during a given time (Δt, min). The $\Delta C/\Delta t$ term was obtained from the slope of the linear regression model fitted between the corrected gas concentration within the chamber and time. A non-zero flux was reported only if the level of significance (P-value) for the regression model was <0.05 (Barlaz et al. 2004). Minimum detectable fluxes for methane and carbon dioxide were approximately 0.03 g CH_4 m^{-2} d^{-1} and 0.12 g CO_2 m^{-2} d^{-1}. The mean gas emissions of the five MPs at the different measuring times up to October 2005 have been published previously (Sormunen et al. 2008). The volumetric gas emissions were converted to standard temperature and pressure

(STP) (1013 hPa and 273 K) by the ideal gas law, using the temperature at the surface of the landfill and the prevailing atmospheric pressure.

The lysimeter surface (III) was covered by vegetation throughout the measurements while the landfill (IV) had vegetation in the June 2006 measurement. Because vegetation may act as a conduit for gas (Schimel 1995, Thomas et al. 1996), the shoots of plants were cut at each measuring point prior to the emission measurement, and the chamber was installed above the cut shoots.

In January 2006, when the lysimeter was covered by approximately 40 cm of snow, gas emissions at each point were first measured above the snow, after which (within 15 min), the snow cover at that point was removed and emissions were measured directly from the surface of the MBT residual cover layer. In the above-snow measurements, long wooden spars were inserted into the snow cover to hold the flux chamber. Only the emissions measured above the snow were used in the calculations and linear regression analyses. At the landfill (IV) in February 2006, when the landfill was covered likewise by approximately 40 cm of snow, the emission measurements were done at the surface of the landfill after removing the snow from the measuring points (IV).

3.7.5 Measurements of temperature, atmospheric pressure, bulk density, and pH in field studies (III, IV)

Ambient air temperature and pressure were continuously measured and recorded at 10 min (IV) or 30 min (III) intervals using weather stations (Davis Vantage Pro) on the landfill area where the outdoor lysimeter was located (III) and 15 km from the studied landfill site (at Kujala landfill, city of Lahti) (IV) (Table 5). The rate of change in atmospheric pressure (hPa h^{-1}) was calculated as the difference between the atmospheric pressures recorded at the time of measurement and one hour before. In the outdoor lysimeter (III), the temperature at the depths of 80-320 cm (Fig. 6, Fig. 9) were monitored by a soil temperature and moisture station (Davis 6343) and temperature probes (Davis 6470) with a wireless Vantage Pro console (Davis 6310) (two parallel four-probe series). In addition, seven digital thermometers (Suomen Lämpömittari Oy, Helsinki, Finland) were installed in the top 65 cm at each of two temperature measurement points (Fig. 6, Fig. 9) as follows: the display units were placed in a plastic box on the lysimeter surface and the wired probes were installed at 5, 15, 25, 35, 45, 55, and 65 cm depths in the lysimeter profile. For each depth, the mean temperatures of the two measurement points are presented. In the full-scale landfill study (IV), soil temperature and moisture (Table 5, Fig. 10) were measured at five points (AB2W, AD2W, AE1W, AE2,AF2; Fig. 8). Soil temperature (IV) was measured once per measurement time at depths of 0 (soil surface), 5, 15, 25, 35, and 45 cm with a HI9025 meter (Hanna Instruments, USA) equipped with a temperature probe (HI 7669/2W). Bulk density (IV) was measured using a metal core (1.2 l) which was hammered in the soil at the landfill surface to obtain an undisturbed soil sample which was then weighed. Mean wet bulk density of eighth points at two measurement times (940 kg m^{-3};

TABLE 5 Meteorological and soil conditions and maximum estimated carbon dioxide production from the landfill top soil material at the different measurement times. Soil conditions refer to the upper (0.5 m) part of the top soil cover as determined from samples taken from storage piles before landfill sealing. Values are also presented for a mixture of the materials.

Dates of gas measurements	Oct 4-5, 2005	Oct 4-5, 2005	Nov 23, 2005	Feb 15, 2005	Jun 21, 2005
Atmospheric pressure (hPa)[a]	1015.1 (1010.7 to 1022.7)	1026.1 (1023.5 to 1028.2)	1026.0 (1024.1 to 1028.4)	1017.3 (1016.4 to 1019.1)	1010.0 (1009.8 to 1010.4)
Rate of change in atm. pressure	−0.35 (−0.9 to 0.1)	0.09 (−0.4 to 0.7)	−0.65 (−0.9 to −0.5)	−0.29 (−0.5 to 0.1)	−0.12 (−0.3 to 0.1)
Air temperature (°C)[a]	10.4 (8.5 to 11.8)	12.8 (8.9 to 15.6)	2.0 (1.3 to 2.6)	−7.4 (−8.2 to −6.7)	25.1 (22.4 to 26.9)
Soil temperature (°C)[b]	12.8	12.8	4.5	1.1[d]	20.9
Soil moisture (% dw)[c]	nd	122±72	137±46	169±82	96±25
Soil VS (% dw)[c]	nd	35.3±4.2	34.1±0.8	38.3±1.4	38.2±2.0
Max. respiratory CO_2 prod. (g CO_2 m^{-2} d^{-1})	nd	23.7	9.52	3.91	37.2

[a] Mean, min., and max. values measured during the gas emission measurements.
[b] Mean of the mean temperatures (at the different depths) from five measuring points the day after the gas emission measurements (except Oct-04 value which is the mean from 22 points at the depth of 10 cm). For June 2006, the mean temperature from four points (16.9°C) was used in calculating respiratory carbon dioxide production (Chapter 3.8.1).
[c] Mean (±standard deviation) of samples from five measuring points.
[d] The result for Feb-15 2006 is the mean of the temperatures measured in the unfrozen part at the depths of 25-45 cm.

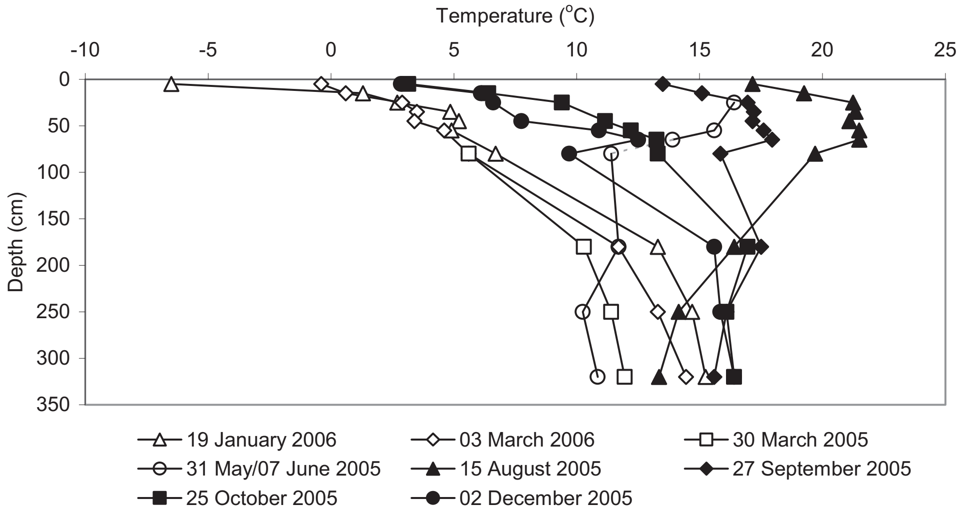

FIGURE 9 Temperature profiles in the lysimeter at selected days. Results for each depth are mean temperatures of the two measuring points. The data for 30 March 2005 are only for 70-320 cm. The data for 31 May (70-320 cm) and 7 June 2005 (0-65 cm) are presented in the same curve.

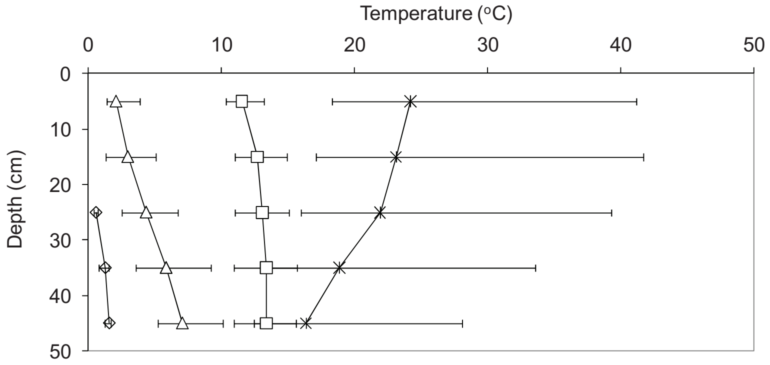

FIGURE 10 Temperature profiles for top soil cover of the landfill (□=Oct-05, Δ=Nov-05, ◊=Feb-06, *=Jun-06). Symbols present the mean temperatures and error bars the minimum and maximum temperatures recorded at the five points. Note that in Feb-06, the 0-15 cm layer was frozen at four of the five points and temperatures for this depth range are not shown.

range 750-1120 kg m^{-3}) and soil moisture was used to calculate mean dry bulk density (360 kg m^{-3}) which was then used in the calculations of respiratory carbon dioxide production (Chapter 3.8.1).

pH profiles in the top 0-75 cm layers of the lysimeter (III) were measured on site using a pH meter (HI 9025, Hanna Instruments, USA) equipped with an 450CD electrode; Sensorex, Stanton, CA, USA). Water was added to saturate the measuring point where the electrode was inserted.

3.8 Calculations

3.8.1 Estimation of methane production and oxidation in field studies (III, IV)

The rates of methane production and oxidation were estimated from the measured emissions into the atmosphere of methane and carbon dioxide, and the concentrations of methane and carbon dioxide in the landfill gas produced in the anaerobic zone. Using this method of estimation, it was assumed that all of the carbon dioxide produced in the anaerobic zone or in methane oxidation would completely escape into the atmosphere (Fig. 11), i.e., that none of the carbon dioxide produced would be consumed, e.g., by microbial activity, on its way to the surface of the lysimeter/landfill. This approach to the quantification of methane oxidation is the same as that used by Christophersen et al. (2001) and Laurila et al. (2005) except that the present calculations include the storage of oxidized methane carbon in the landfill cover and the production of carbon dioxide from aerobic respiration (Fig. 11). The symbol Q is used for the rates for production (III), flux into the cover (IV), oxidation, and emission of methane or carbon dioxide in volume units (e.g., l m^{-2} d^{-1}).

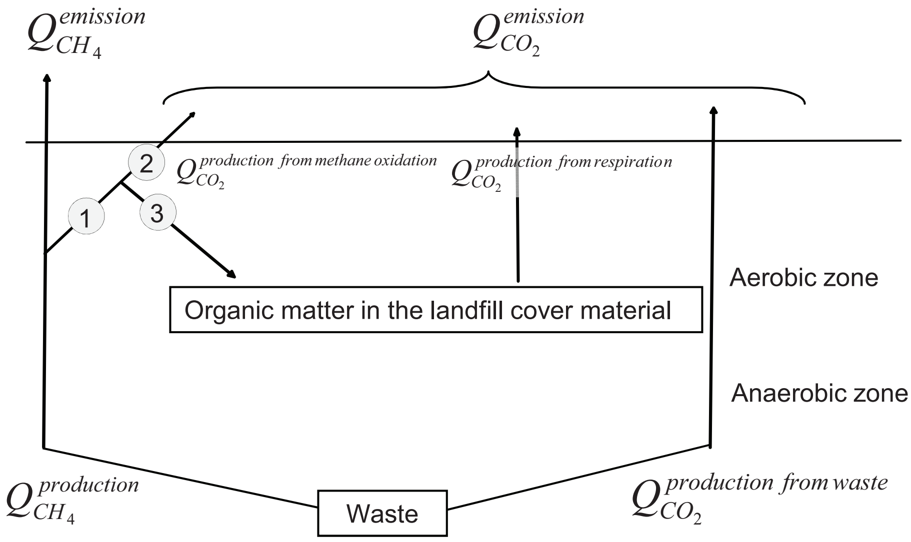

FIGURE 11 Flow chart of methane and carbon dioxide from landfill into the atmosphere. The numbers 1-3 refer to the steps in the methane oxidation chain, which is described, e.g., by Anthony 1982 and Nikiema et al. 2007: 1) conversion of methane, at first to methanol (CH_3OH) by methane monooxygenase; 2) oxidation of the converted methane carbon to carbon dioxide (dissimilation); 3) storage of the converted methane carbon in the landfill cover via microbial synthesis of multicarbon compounds.

In the full-scale study (IV), in Equations 3-12, the term methane flux into the cover is used instead of the term methane production, to indicate the methane flux into the top 100 cm layer, before any methane oxidation has taken place. This is because in the present full-scale landfill, due to the landfill cover and gas distribution systems, the rates of methane flux at a given point and time recorded in short-term measurements may differ from the rates of methane production.

The starting point of the calculation is the assumption that the rate of methane production equals the sum of the rates of methane emission and methane oxidation (Equation 3):

$$Q_{CH_4}^{prod} = Q_{CH_4}^{em} + Q_{CH_4}^{ox}\,. \tag{3}$$

$Q_{CH_4}^{em}$ is obtained from emission measurements and thus $Q_{CH_4}^{ox}$ can be calculated from Equation 3 if $Q_{CH_4}^{prod}$ is known. $Q_{CH_4}^{prod}$ can be calculated from emission and pore gas measurements, if the rate of carbon dioxide production from the anaerobic degradation of the landfilled waste ($Q_{CO_2}^{waste}$) is known. $Q_{CO_2}^{waste}$ in turn can be calculated from the measured carbon dioxide emission if the rates of carbon dioxide production from methane oxidation and from aerobic respiration are known (Fig. 11) (Equation 4):

$$Q_{CO_2}^{waste} = Q_{CO_2}^{em} - Q_{CO_2}^{metox} - Q_{CO_2}^{resp}\,. \tag{4}$$

To calculate $Q_{CO_2}^{metox}$ it is necessary to know the methane oxidation rate ($Q_{CH_4}^{ox}$) and the dissimilation factor (f_{diss}), which is the fraction of the total oxidized methane which is oxidized completely and thus converted to carbon dioxide (Equation 5):

$$Q_{CO_2}^{metox} = Q_{CH_4}^{ox} \times f_{diss} . \tag{5}$$

Assuming that the ratio of the rates of methane and carbon dioxide production (Equation 6),

$$\rho = \frac{Q_{CH_4}^{prod}}{Q_{CO_2}^{waste}} , \tag{6}$$

equals the ratio of methane and carbon dioxide concentrations in the produced landfill gas, this ratio, ρ, can be used in calculating the rate of methane production. In this study the ratios of the mean methane and carbon dioxide concentrations in the pore gas at the depth of 150 cm from the lysimeter surface (III) or in the gas wells (IV) were used as estimates of ρ. Since

$$Q_{CH_4}^{prod} = \rho \times Q_{CO_2}^{waste} , \tag{7}$$

on the basis of Equation 3 it can be written that

$$Q_{CH_4}^{ox} = \rho \times Q_{CO_2}^{waste} - Q_{CH_4}^{em} . \tag{8}$$

By combining Equations 4-8 Equation 9 is obtained:

$$Q_{CO_2}^{waste} = Q_{CO_2}^{em} - \left(\rho \times Q_{CO_2}^{waste} - Q_{CH_4}^{em}\right) \times f_{diss} - Q_{CO_2}^{resp} . \tag{9}$$

By taking into account the relationship of the variables $Q_{CO_2}^{waste}$ and $Q_{CH_4}^{prod}$ (Equation 7), Equation 10 can be formulated:

$$\frac{Q_{CH_4}^{prod}}{\rho} = Q_{CO_2}^{em} - \left(\rho \times \frac{Q_{CH_4}^{prod}}{\rho} - Q_{CH_4}^{em}\right) \times f_{diss} - Q_{CO_2}^{resp} . \tag{10}$$

Then methane production can be solved (Equation 11):

$$Q_{CH_4}^{prod} = \frac{\rho}{\rho \times f_{diss} + 1} \times \left(Q_{CO_2}^{em} + Q_{CH_4}^{em} \times f_{diss} - Q_{CO_2}^{resp}\right). \tag{11}$$

The fractional oxidation, i.e., the proportion of methane oxidized of the total methane produced is calculated as (Equation 12)

$$f_{CH_4}^{ox} = \frac{Q_{CH_4}^{prod} - Q_{CH_4}^{em}}{Q_{CH_4}^{prod}} \times 100\% . \tag{12}$$

In the present study, $Q_{CO_2}^{resp}$ and f_{diss} were approximated whereas all the other parameters were obtained from the measurements. To obtain a maximum estimate of methane production and oxidation, f_{diss} was estimated at 0.3, as maximally 70% of oxidized methane carbon can be stored in soil, as described in the literature (reviewed by Huber-Humer 2004), while $Q_{CO_2}^{resp}$ was estimated as zero. To obtain a minimum estimate of methane production and oxidation for the measurements from April to October, a f_{diss} value of 1.0 was used, thus assuming that none of the oxidized methane was stored in the soil. $Q_{CO_2}^{resp}$ was calculated in III as (Equation 13)

$$Q_{CO_2}^{resp} = Q_{CO_2}^{em} - 3.24\,\mathrm{l\,CO_2\,m^{-2}d^{-1}}. \qquad (13)$$

where 3.24 l CO_2 m^{-2} d^{-1} is a minimum estimate of $Q_{CO_2}^{waste}$, which was calculated using Equation 7 from the January 2006 measurement on the assumption that no methane oxidation occurred ($Q_{CH_4}^{prod} = Q_{CH_4}^{em}$). For the January measurement, the minimum methane production and oxidation estimates were calculated on the assumptions that $f_{diss} = 1.0$ and $Q_{CO_2}^{resp} = 0$. In IV, carbon dioxide production from respiration in the top soil cover material was estimated to be zero for the measurement conducted before the sealing of the landfill, as the cover layer was mostly lacking at that time. For the measurements after the sealing of the landfill, maximum respiratory carbon dioxide production of the top soil material per area unit (Table 5) was calculated on the assumption that the top soil cover consisted only of sludge compost since, due to incomplete mixing, it is possible that at some points the whole 50 cm profile consists only of sludge compost. The calculation was performed using the carbon dioxide production of sludge compost in laboratory assays (Table 4), the amount of dry soil in the top soil cover (calculated from thickness, moisture and bulk density), and soil temperature at each measurement time. The dependence of respiration on temperature was assumed to correspond to a Q_{10} value of 3.0 (I); this value was then used to convert the rates obtained in the laboratory to the prevailing field temperatures, using Equation 14 (Chapter 3.8.3).

For the June 2006 measurement, measuring point AB2W showed temperatures significantly higher (mean 37 °C) than those at the other points (<20 °C) and was excluded from the calculation of mean temperature for the respiration calculations (Table 5) (see IV for details). In many cases, carbon dioxide emission was lower than the maximum estimated respiratory carbon dioxide production. In these points, minimum methane flux into the cover was, instead of being calculated by Equation 11, approximated either to be equal to the observed methane emission or, if no methane emission was observed, the value 0.01 m^3 CH_4 ha^{-1} h^{-1} (0.017 g CH_4 m^{-2} d^{-1}) was used.

3.8.2 Calculation of area-based methane oxidation potential (III)

The area-based oxidation rates for each of the investigated layers of the lysimeter were calculated using the MOP and dry bulk density for each layer. Dry bulk densities of 430 kg m^{-3} and 540 kg m^{-3} were used respectively for MBT residuals above and below the distribution layer, as approximated from the initial wet bulk densities of 800 kg m^{-3} and 1000 kg m^{-3} and initial moisture of 46% of wet weight (Sormunen et al. 2008), while the bulk density of the gravel used in the distribution layer was 1500 kg m^{-3}. To account for the variation in gravel content, for each of the samples the bulk density was approximated on the basis of the proportions of MBT residual and gravel, and the bulk densities of these materials (III). The proportions of gravel and MBT residual in the samples were approximated using the VS concentration of each sample and that of the MBT residual (24.6% dw, approximated as the mean VS concentration of the samples from the layers with no gravel, i.e. 0-15 cm and 60-75 cm), assuming that the VS of gravel is 0% dw. The area-based oxidation rates for each layer were then summed to obtain the area-based MOP for the whole depth range studied.

3.8.3 Calculation of Q_{10} values

The Q_{10} temperature coefficient is often used to compare rates of biological reactions or processes and is defined as "the ratio of the rates of a reaction or process at (T+10)°C and T°C (Hegarty 1973). Q_{10} values of methane oxidation and respiration were calculated using Equation 14 (Kirschbaum 1995)

$$Q_{10} = \frac{R_2}{R_1}^{\left(\frac{10}{T_2 - T_1}\right)} \tag{14}$$

where R_1 and R_2 represent the reaction rates at two observed temperatures, T_1 and T_2. R_1 and R_2 were obtained from linear regressions ($R^2 \geq 0.97$) between the ln-transformed consumption and production rates and temperature (I) or from methane oxidation rates in the column experiment or at the full-scale landfill measured at different time points and at different temperatures.

3.9 Statistical analyses

The statistical analyses were performed using SPSS 12.0.1 (I) or SPSS 14.0 (IV) for Windows, or the Data Analysis Toolpak of Microsoft Excel 2003 (III) software packages. For the statistical analysis (I), natural logarithm transformations for the gas consumption and production rates in the CH oxidation and respiration were performed. The responses of these parameters to temperature within each of the studied moistures, and the responses to moisture within each of the studied temperatures, were analysed using the results from each of the duplicate samples as individual data points (n=6-8 for each regression analysis) (I).

4 RESULTS

4.1 Responses of methane oxidation to temperature and moisture in cover soil of a boreal landfill (I)

On the basis of its MOP, a four-year cover soil from a landfill, selected from seven tested soils, was used to study on whether methane oxidation occurs at low temperatures in landfill soils and, if so, how it is regulated by temperature and moisture. It was also studied whether, as an indication of the ability of methane-oxidizing microorganisms to grow or to increase their activity, the soil methane consumption rate is able to increase at low temperatures.

The effects of temperature (1-19 °C) and moisture (7-28% dw, i.e., 17-67% of WHC) on methane consumption at a percentage-level methane concentration and on the associated oxygen consumption and carbon dioxide production were determined in batch assays. When moisture was between 14% dw and 28% dw (33-67% WHC), methane consumption, oxygen consumption, and carbon dioxide production in the methane assays were detected all the studied temperatures and showed ln-linear increases with temperature (Fig. 12a and c). The Q_{10} values for methane consumption varied between 6.5 and 8.4 (Table 6). When moisture was 7% dw, the rates of gas consumption and production were at their minimum values for all the studied temperatures (Fig. 12 a and b). There was a tendency towards a decrease in the effect of temperature on methane consumption with increasing moisture at 14-28% dw, as shown by the diminishing Q_{10} values (Table 6). At 1-6 °C methane consumption increased up to the highest moisture studied (28% dw) ($p<0.05$ for both linear and quadratic terms in polynomial curves) while at 12 °C methane consumption peaked at 21% dw, and thus the response of methane oxidation to moisture was curvilinear with a maximum ($p<0.05$ for the quadratic term) but no overall trend ($p>0.10$ for linear term) (Fig. 12b and d). At 19 °C a curvilinear response to moisture was apparent in the moisture range 14-34% dw (33-81% WHC) (Fig. 12b and d), although statistically insignificant ($p>0.10$ for linear and quadratic terms).

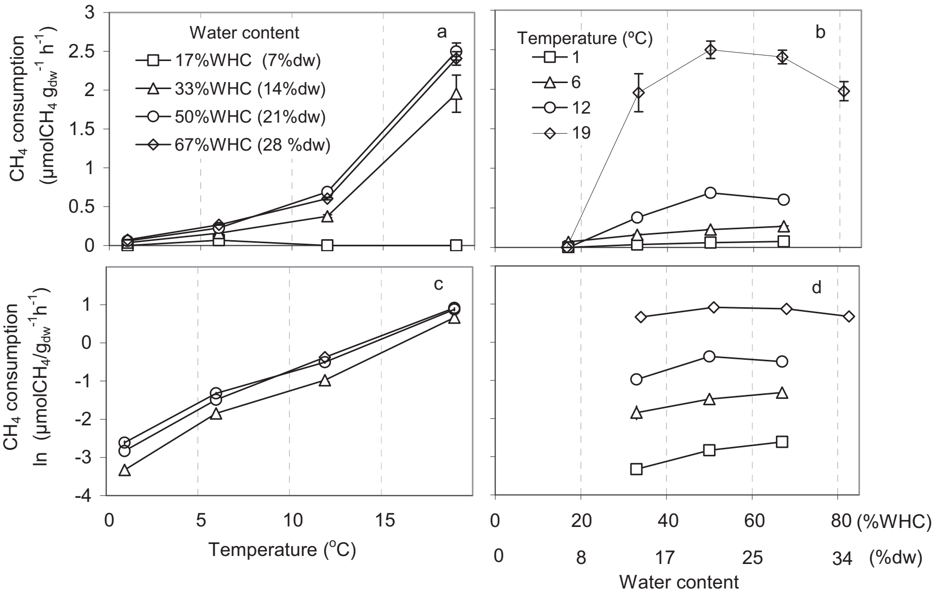

FIGURE 12 Rates (direct and ln-transformed) of methane consumption in the studied landfill cover soil at different moistures as a function of temperature (left) and at different temperatures as a function of moisture (right). Results are mean values of duplicate samples. Error bars present ± standard error of the mean and are smaller than the symbols when not visible. Assays at 34% dw (81% WHC) were only performed for 19 °C.

TABLE 6 Q_{10} values describing the temperature responses of CH_4 consumption rate and CO_2 production and O_2 consumption in the CH_4 assays in landfill cover soil as determined from the CH_4 consumption rates at 1, 6, 12, and 19 °C at different moistures.

Moisture (% dw)	CH_4	CO_2	O_2
14	8.4	5.7	6.6
21	7.7	5.7	6.4
28	6.5	5.8	5.8

The ability of the soil methane oxidizers to be activated or grow in the presence of methane at 1 and 12 °C was studied by determining the specific growth rate of methane consumption from the increase in methane consumption in consecutive methane feeding cycles with moisture at 21% dw. The rates of methane and oxygen consumption, as well as carbon dioxide production recorded in the second feeding cycle (Table 7) were higher than in the first one, corresponding to a specific growth rate (µ) of 0.10±0.001 d^{-1} for methane consumption at 1 °C, which was 15% of the value at 12 °C (0.707±0.006 d^{-1}).

TABLE 7 CH_4 consumption rates and the molar ratios of CO_2 production and O_2 consumption in relation to CH_4 consumption, duration of CH_4 feeding cycles, and specific growth rates (μ) for CH_4 consumption rates in consecutive batch assays with landfill cover soil samples at 1 and 12 °C at moisture of 21% dw; the values are means (±standard error of the mean) of duplicate samples.

	CH_4 feeding cycle			
	1 °C		12 °C	
	1st	2nd	1st	2nd
CH_4 cons. (μmol CH_4 g_{dw}^{-1} h^{-1})	0.059±0.00	0.13±0.01	0.70±0.05	1.49±0.04
CO_2/CH_4 (mol/mol)	0.92±0.04	0.42±0.04	0.49±0.01	0.39±0.07
O_2/CH_4 (mol/mol)	2.04±0.09	1.19±0.20	1.41±0.028	1.17±0.02

	1 °C	12 °C
Duration of 1st feeding cycle (d)	13	1.6
Specific growth rate μ (d^{-1})	0.096±0.001	0.70±0.006
Generation time t_g (d)	10.4	1.43

4.2 Methane oxidation in laboratory columns containing mechanically-biologically treated waste (II)

4.2.1 Consumption of methane and oxygen and production of carbon dioxide

In this study (II), MBT residual was investigated for its suitability for use as a support medium in the landfill cover to promote methane oxidation. The study included the determination of the methane oxidation rate, as well as the changes in and depth distribution of various physical, chemical and microbial parameters in two laboratory columns continuously sparged with methane for 124 d at temperatures ranging between 2 and 25 °C.

Methane consumption was already detected at the first measuring time (day 3) and inlet methane was >99% consumed from day 5 onwards in both columns (MBT residual 22 and MBT residual 57) (Fig. 13a and b). When the methane loading rate was increased from the initial level (30 g CH_4 m^{-2} d^{-1}), first to 2.0-fold (day 39) and further to 2.6-fold (day 45) of that of the initial rate, and aeration increased to provide a similar or higher aeration ratio (>3.8 mol O_2/mol CH_4) (Fig. 13c, Table 8), the methane oxidation rate increased and thus >99% of methane (53-82 g CH_4 m^{-2} d^{-1}) continued to be consumed. The aeration rate was decreased, thereafter, in order to obtain a lower aeration ratio, i.e., more oxygen-limited conditions for methane oxidation and so facilitate the monitoring of the effects of the forthcoming temperature decreases on oxygen concentrations in the pore gas of the columns. When the relative aeration ratio was decreased to 2.5-2.6 mol O_2/mol CH_4 (on day 52), the methane oxidation rate dropped by approximately 20%, i.e., to 66-69 g CH_4 m^{-2} d^{-1} in both MBT residuals, returning to >96% (72-79 g CH_4 m^{-2} d^{-1}) in MBT residual 57 (days 56-

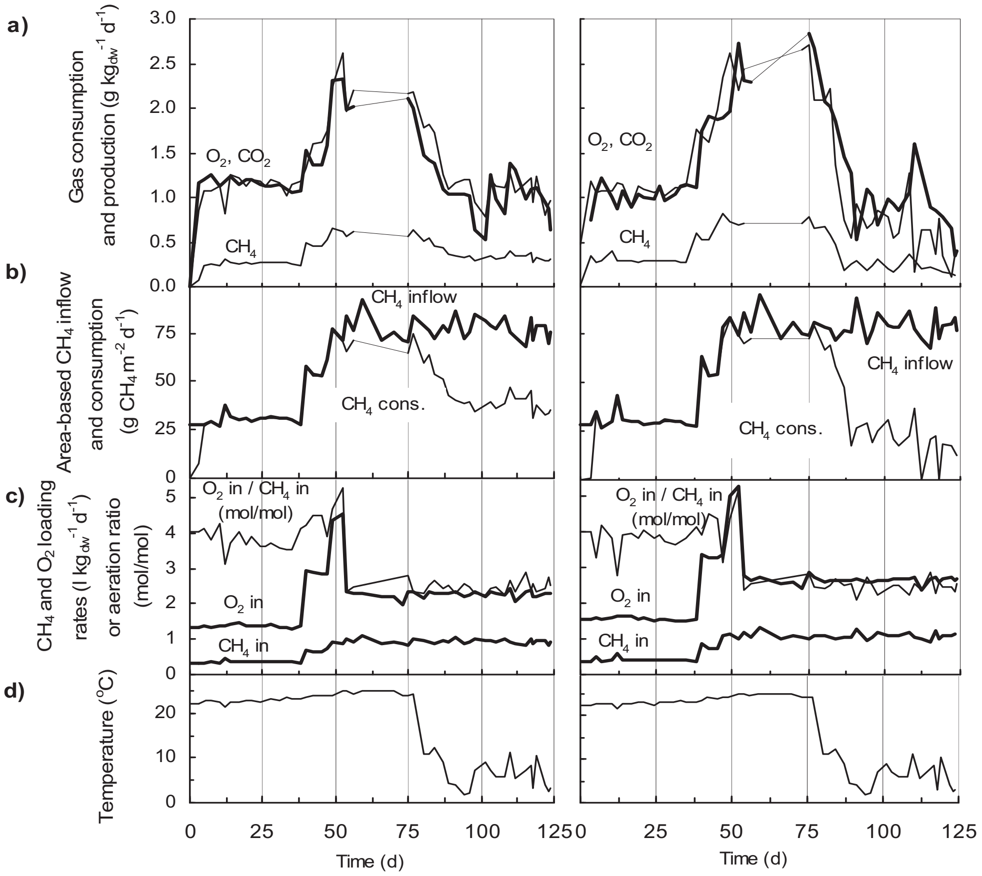

FIGURE 13 The experimental conditions and gas dynamics in the column experiment with MBT residual 22 (left) and MBT residual 57 (right). (a) Mass-based consumption and production of gases (bold line: CO_2; light lines: CH_4 and O_2), (b) area-based CH_4 loading rate and consumption, (c) CH_4 and O_2 loading rates (in litres) and aeration ratio (mol O_2/mol CH_4), and (d) temperature. Lines are based on measurements three times per week. Gas consumption or production was not measured on days 57-74 (thinned lines).

TABLE 8 Operating conditions and average methane oxidation rates of the MBT residual columns during different periods of the experiment.

Days	T (°C)	CH_4 loading rate (g CH_4 m^{-2} d^{-1})	Aeration ratio (mol O_2 in/ mol CH_4 in)	CH_4 oxidation rate (g CH_4 m^{-2} d^{-1})	
				MBT residual 22	MBT residual 57
5-39	22-25	30	3.8	30	30
39-52	22-25	60-78	4.0-4.8	53-82	53-82
52-77	22-25	78	2.6	64-74	72-79
77-87	9-12	78	2.5	56	61
87-124	2-10[a]	78	2.5	39	22

[a] Average temperature was 6 °C

77) while remaining at 89-93% (64-74 g CH_4 m^{-2} d^{-1}) in MBT residual 22. When the temperature was decreased (Fig. 13d), first to 9-12 °C on day 77, methane oxidation rate was on average 56 g CH_4 m^{-2} d^{-1} in MBT residual 22 and 61 g CH_4 m^{-2} d^{-1} in MBT residual 57. After a further decrease (day 87) to 6 °C on average (range 2-10 °C) for the final 34 days, the CH_4 oxidation rate averaged 39 g CH_4 m^{-2} d^{-1} (range 31-47) in MBT residual 22, and 22 g CH_4 m^{-2} d^{-1} (range 12-37) in MBT residual 57.

4.2.2 MBT residual properties before and after the column experiment

The microbial methane oxidation and respiration activities, as well as physical and chemical properties of the MBT residuals, were determined before and after the column experiment (Table 9) to study the changes and depth distribution of these parameters during the column experiment. In batch assays after the column experiment, methane consumption was detected immediately at both temperatures (5 °C and 25 °C) at rates many-fold higher than before the column experiment when, in both of the materials, methane consumption started at 25 °C after a lag of 1-3 d while at 5 °C no methane consumption was observed. MOP was higher in MBT residual 22 compared to MBT residual 57 attaining the highest values in both MBT residuals at 5 cm, medium values at 15 cm, and lowest (25 °C) or negligible values (5 °C) at 25 cm.

The respiration activities in both MBT residuals were higher after the column experiment than before (Table 9) and decreased vertically in the same way as MOP. After the column experiment, respiration activity was higher in MBT residual 57 than in MBT residual 22, in contrast to the initial situation. In samples with methane consumption, the consumption of oxygen and production of carbon dioxide were significantly higher in the methane assays compared to the respiration assays (Table 9).

4.3 Methane oxidation in an experimental landfill cover composed from mechanically-biologically treated waste (III)

4.3.1 Overall methane production and oxidation

As MBT residual showed favorable properties for methane oxidation in the laboratory study (II), a field study of methane oxidation in MBT residual cover layers (III) was implemented using an outdoor lysimeter to assess the methane oxidation performance in actual field conditions. The lysimeter was filled with MBT residual and contained a cover layer made from the same MBT residual. The study was also aimed to determine the vertical location of the methane oxidizing zone by measuring pore gas composition and gas fluxes as well as the MOP of the lysimeter material at different layers.

The rates of methane production and oxidation (g CH_4 m^{-2} d^{-1}) in the lysimeter were estimated by mass balance calculations (Chapter 3.8.1) using the

TABLE 9 Chemical and physical properties of the processed MBT residuals before and after (depths 5, 15, and 25 cm, and their mean value) the column experiment, and their methane consumption, oxygen consumption, and carbon dioxide production rates in batch assays measuring methane oxidation potential and respiratory activity.

	Before column experiment		MBT residual 22 after column exp.				MBT residual 57 after column exp.			
Parameter/Sample	MBT residual 22	MBT residual 57	5 cm	15 cm	25 cm	mean	5 cm	15 cm	25 cm	mean
Moisture (% dw)	79.1[a]	104±9.9	87.4±8.1	91.8±6.2	89.4±15	89.5	111±8.5	125±3.5	112±14	116
VS (% dw)	47.4±0.01	38.9±4.9	37.1±1.3	38.7±2.2	41.1±1.9	39.0	38.2±2.0	38.9±1.2	39.0±3.1	38.7
WHC (% dw)	142	187	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Moisture (% WHC)	55.8[a]	55.8	61.2	64.3	62.6	62.7	59.4	66.8	59.9	62.0
pH	7.39	7.34	6.95	7.18	7.47	7.15	6.77	7.22	7.47	7.06
EC (mS m^{-1})	430	360	560	460	380	470	270	340	390	330
W.b.d.[b] (t m^{-3})	700	700	610	640	660	640	710	770	730	740
Moisture (vol.-%)	31	36	29	31	31	30	38	43	38	40
Air porosity (vol.-%)	49	47	55	52	51	53	46	40	44	53
Methane oxidation potential assays (µg g$_{dw}^{-1}$ h^{-1})										
CH$_4$ cons. (MOP) 5 °C	<0.16	<0.16	104±1.5	65±14	<1.6	56	61±6.1	43±0.23	<1.6	35
O$_2$ cons. 5 °C	4.80±0.23	2.88±0.23	233±20	178±57	<9.6	137	129±29	68±14	<9.6	66
CO$_2$ prod. 5 °C	4.84±0.31	2.20±0.31	129±9	62±12	3.5±0.31	65	95±3	36±8	<4.4	12
CH$_4$ cons. (MOP) 25 °C	<1.6[c] (28±2.4)	<1.6[c] (20±2.8)	581±45	223±42	13±2.6	271	273±2.3	153±2.8	15±0.57	147
O$_2$ cons. 25 °C	37±2.5[c] (97±4.3)	24±3.2[c] (62±11)	1710±109	717±145	98±3.9	842	912±18	477±11	92±3.4	493
CO$_2$. prod. 25 °C	40.4±3.1 [c] (72±2.5)	22±2.5[c] (35±8.1)	986±84	365±69	24±21	458	568±3.1	284±4.7	42±8.7	298
Respiration activity assays (µg g$_{dw}^{-1}$ h^{-1})										
O$_2$ cons. 5 °C	5.1±0.45	2.9±0.23	11±0.45	4.5±0.23	2.2±0.05	6.1	17±0.68	4.8±0.45	2.9±0.45	8.3
CO$_2$ prod. 5 °C	4.4±0.31	2.2±0.28	24±0.93	6.6±0.62	4.0±0.62	11.4	15±0.62	6.2±0.31	3.1±0.06	8.4
O$_2$ cons. 25 °C	36±0.91	20±0.06	133±11	80±3.2	49±4.1	87	191±11	57±14	34±0.43	94
CO$_2$. prod. 25 °C	43±2.2	23±1.2	191±3.4	96±3.4	52±0.6	113	248±3.1	104±3.4	61±3.4	138

The values are means ± standard errors of the mean of duplicate (methane oxidation potential, respiratory activity) or triplicate (moisture, VS) samples. n.d. = not determined. [a] Value after air-drying (original moisture 93.1% dw or 65.6% water-holding capacity). [b] Wet bulk density. [c] Initial value when no CH$_4$ consumption was detected. The rate after 3 d incubation in parentheses.

mean emissions and pore gas concentrations of methane and carbon dioxide during the seven measurement times between April 2005 and January 2006. Between April and October 2005, methane production at the six measuring times was between 1.09 and 16.0 g CH_4 m^{-2} d^{-1}. Fractional oxidation was stable during this period, as more than 96% of the methane produced was oxidized. In January 2006, methane oxidation (<0.55 g CH_4 m^{-2} d^{-1}) was lower than at the other measuring times and only 0-21.9% of the methane produced (<2.51 g CH_4 m^{-2} d^{-1}) was oxidized (Table 10).

4.3.2 Methane, carbon dioxide and oxygen concentrations in pore gas

The vertical distribution of methane oxidation was studied by determining the vertical profiles of the methane, carbon dioxide, and oxygen concentrations, and methane-to-carbon dioxide ratio in the pore gas of the lysimeter. These measurements were conducted at the five MPs on ten occasions between June 2005 and January 2006 (Fig. 6). The results are shown in (III). Methane and carbon dioxide concentrations generally decreased from the depth of 150 cm upwards in the lysimeter; in some cases, however, the concentrations peaked (up to 65% CH_4) in the upper part of the waste layer (depth 50-70 cm). The mean methane concentration at the five MPs fell below the detection limit (of 0.1 vol.%) at the depth of 35-45 cm and remained below that limit all the way up to the surface of the lysimeter at all the measuring times, except for January 2006 when methane was detectable at as low a depth as 15 cm. In the pore gas samples from the deepest layer (150 cm), the mean oxygen concentration at the different measuring times (N=10) was 0.6±0.3% standard deviation (MP2). Oxygen concentration increased from the depth of 150 cm upwards in the vertical profile.

The methane-to-carbon dioxide ratio was typically 0.5-2 at the depths of 100-150 cm at all MPs, although ratios as high as 4 were recorded in MP1 and MP3. Typically, the methane-to carbon dioxide ratio decreased sharply between the depths of 75 and 35 cm, falling to below 0.1, indicating methane oxidation in this depth range. In January 2006, the methane-to-carbon dioxide ratio decreased more gently along the vertical profile compared to the other measuring times, indicating decreased methane oxidation.

4.3.3 Methane and carbon dioxide fluxes along the vertical profile of the upper part of the lysimeter

The methane flux and methane-to-carbon dioxide ratio of the gas flux along the vertical profile of the lysimeter were assessed to obtain flux-based information on methane oxidation at different depths, and thus complement the pore gas profiles as these only give information about changes in the gas composition. Methane and carbon dioxide fluxes at different depths at the uppermost 60 cm were measured in July and August 2005 at MPs 1 and 4 (Table 11) by stepwise removal of the top 60 cm layer of the lysimeter materials. At both MPs at both measuring times, methane flux was >1.8 g CH_4 m^{-2} d^{-1} at 45 and 60 cm, whereas

TABLE 10 Meteorological conditions, methane and carbon dioxide emissions, estimated methane production and oxidation, and the methane-to-carbon dioxide concentration ratios (at depth of 150 cm). Gas emission, production and oxidation data converted from (III) to the unit g CH_4 m^{-2} d^{-1} using the air temperature and pressure values presented.

Date	29 Apr 2005	6 Jun 2005	4 Jul 2005	15 Aug 2005	27 Sep 2005	25 Oct 2005	19 Jan 2006	19 Jan 2006
Air press. (hPa) [a]	1021.4	1000.3	1017.3	1008.4	1020.9	1014.2	1040.1	1040.1
Δ Air press. (hPa h^{-1})[a, b]	0.15	0.50	−0.25	0.13	−0.05	−0.20	0.07	0.07
Air temp. (°C)[a]	7.0	12.6	24.3	17.4	11.7	−0.8	−24.1	−24.1
							Above snow	Below snow
Carbon dioxide emissions (g CO_2 m^{-2} d^{-1})								
MP1	52.9	54.3	36.7	59.3	32.8	8.48	16.4	11.5
MP2	34.9	23.7	38.0	28.8	21.6	6.31	0.00	2.65
MP3	49.4	30.4	45.8	27.9	23.7	11.8	9.51	3.54
MP4	41.3	28.7	32.4	37.7	19.9	17.0	12.2	10.39
MP5	29.3	14.5	48.9	16.2	21.4	13.6	9.95	12.4
Mean	41.6 (24)	30.3 (49)	40.4 (17)	34.3 (47)	23.9 (21)	11.4 (36)	9.6 (62)	8.1 (58)
Methane emissions (g CH_4 m^{-2} d^{-1})								
MP1	0.00	0.00	0.00	0.11	0.00	0.07	6.57	0.87
MP2	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.00
MP3	0.00	0.00	0.00	0.00	0.00	0.04	0.37	0.00
MP4	0.00	0.00	0.00	0.11	0.00	0.00	1.50	0.37
MP5	0.00	0.00	0.00	0.00	0.13	0.00	1.11	2.37
Mean (CVx100)	0.00	0.00	0.00	0.04 (137)	0.03 (224)	0.02 (148)	1.94 (137)	0.72 (136)
ρ (CH_4/CO_2 ratio at 150 cm depth)	1.20	1.20[c]	1.19	1.45	0.93	1.01	0.75	n.d.
Methane production and oxidation rates (g CH_4 m^{-2} d^{-1})								
Min. production	1.39	1.33	1.16	1.31	1.09	1.18	2.34[d]	n.d.
Max. production	16.04	11.70	12.92	12.54	6.33	3.24	2.51	n.d.
Min. oxidation	1.39	1.33	1.16	1.27	1.06	1.16	0.39[d]	n.d.
Max. oxidation.	16.04	11.70	12.92	12.50	6.30	3.22	0.55	n.d.
Fractional oxidation								
Min.	100	100	100	96.6	97.6	98.2	16.4[d]	n.d.
Max.	100	100	100	99.6	99.6	99.3	21.9	n.d.

n.d.= not determined. CV=coefficient of variation. [a] The values are means of the values recorded during the gas emission measurements. [b] Rate of change in atmospheric pressure. [c] Measured on 28 June 2005.

[d] The values presented for 19 January 2006 were calculated based on the assumption that $Q_{CO_2}^{resp} = 0$. If $Q_{CO_2}^{resp} > 0$, methane production and oxidation will be less than reported here (methane oxidation can be as low as zero).

TABLE 11 Methane and carbon dioxide fluxes (in mass units) and the ratios of volumetric methane and carbon dioxide fluxes at the two measuring points in the stepwise layer removal measurements in July and August, 2005. Gas emission data converted from (III) to the unit g CH_4 m^{-2} d^{-1} using the air temperature and pressure values presented in (III).

	MP1 (5-July)			MP1 (16-August)			MP4 (4-July)			MP4 (15-August)		
Depth (cm)	CH_4 g m^{-2} d^{-1}	CO_2 g m^{-2} d^{-1}	CH_4/ CO_2	CH_4 g m^{-2} d^{-1}	CO_2 g m^{-2} d^{-1}	CH_4/ CO_2	CH_4 g m^{-2} d^{-1}	CO_2 g m^{-2} d^{-1}	CH_4/ CO_2	CH_4 g m^{-2} d^{-1}	CO_2 g m^{-2} d^{-1}	CH_4/ CO_2
0	0.00	32.9	0.00	0.00	48.3	0.00	0.00	4.87	0.00	0.00	29.6	0.00
15	0.03	131	0.00	0.26	160	0.00	0.00	0.90	0.00	0.00	142	0.00
30	0.11	161	0.00	0.00	76.7	0.00	4.14	11.4	0.08	0.00	172	0.00
45	4.88	197	0.07	15.8	307	0.14	21.4	93.9	0.21	1.89	67.7	0.08
60	34.8	554	0.17	22.10	351	0.17	12.5	126	0.10	19.0	316	0.16

n.d.= not determined. CV=coefficient of variation.

at 0-30 cm methane flux was low (<0.3 g CH_4 m^{-2} d^{-1}) or below the detection limit, with the exception of July when methane flux at 30 cm was 4.1 g CH_4 m^{-2} d^{-1} at MP4. Although the lower methane flux in the top 30 cm compared with that at 45-60 cm was probably partly explained by methane oxidation, the rate of methane oxidation in each layer could not be determined as the existence of the measuring pit increased the gas flux in the different layers compared to an undisturbed situation (III). However, the methane-to-carbon dioxide ratio in the gas flux, which can be assumed to be less sensitive to the disturbances caused by the pit, indicated methane oxidation at the depth range of 30-60 cm, as the ratio of the volume-based fluxes decreased from 0.08-0.21 at 45-60 cm to 0.00 at 30 cm and above (except in July in MP4 when the ratio was 0.08 at 30 cm).

4.3.4 Methane oxidation potential of the materials in the upper part of the lysimeter

The characteristics of the materials in the top 75 cm of the lysimeter (Fig. 14) were studied to obtain information about the conditions for methane oxidation and about the level, vertical distribution, and temporal changes in microbial methane oxidation activity. The characterization was done for two MPs (MPs 1 and 4) in July and August 2005 on the same days when the gas flux measurements from the different depths were conducted (Chapter 3.5). An additional characterization was performed on samples June 2005.

The total area-based MOP, which is the sum of the MOPs determined for the separate 15-cm layers, in MP1 was 236, 120, and 42 g CH_4 m^{-2} d^{-1} in June, July, and August, respectively, whereas the corresponding values for MP4 were 100, 44, and 28 g CH_4 m^{-2} d^{-1}. Thus in both MPs, the area-based MOPs for the 0-75 cm layer were in July 45-49% and in August only 18-31% of the values observed in June. At both MPs, the total area-based MOP in June and July was 4-13-fold and in August 1.6-1.8-fold compared to the estimated maximum methane production at the same points (III). At MP1, the majority (91-100%) of the total MOP within the 0-75-cm depth range was located in the top 45 cm, i.e.,

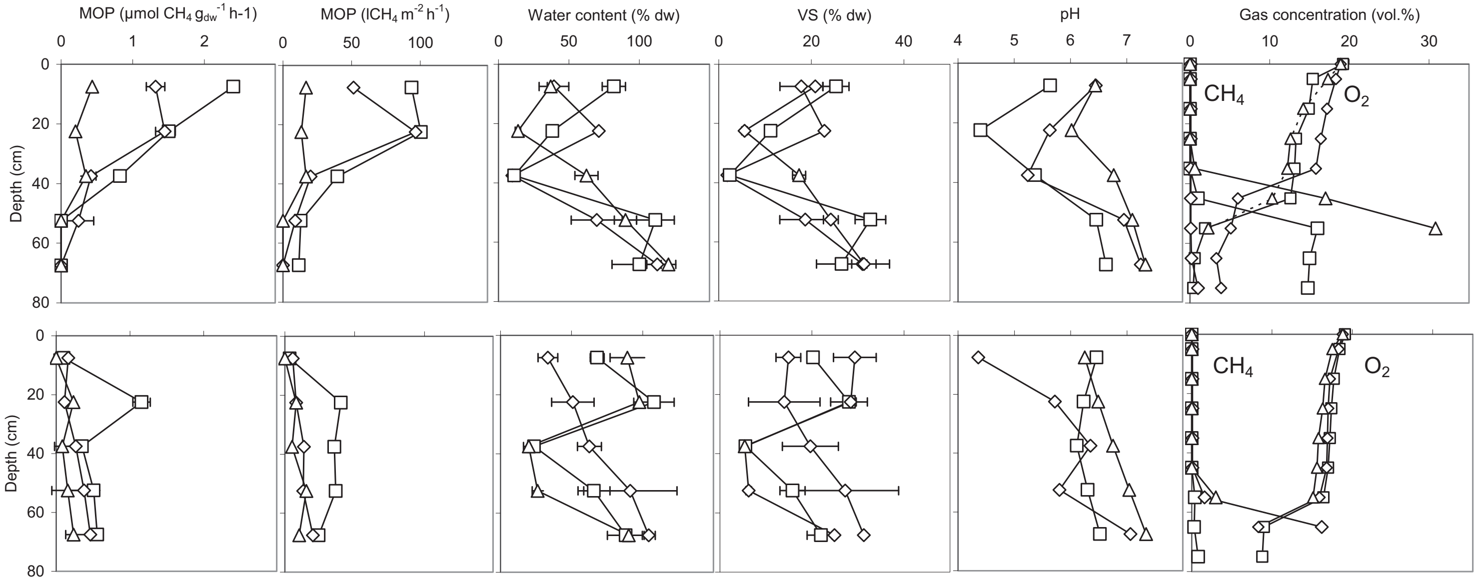

FIGURE 14 Vertical profiles of parameters measured in the top 75 cm of the lysimeter. Results from measuring points 1 (above) and 4 (below) on 6 June (□), 5 (MP1) or 4 (MP4) July (◊) and 16 (MP1) or 15 (MP4) August (Δ) 2005. Horizontal bars (MOP in µmol CH_4 g_{dw}^{-1} h^{-1}, moisture, VS) present standard deviation of triplicate samples and are smaller than the symbols when not apparent.

in the cover layer and distribution layer, while at MP4 only 34-57% was located in those layers, while 43-66% was located in the 45-75-cm range, i.e., mainly in the waste layer (Fig. 14).

4.3.5 Gas emissions into the atmosphere

The emissions of methane and carbon dioxide from the lysimeter into the atmosphere were measured seven times from April 2005 to January 2006 in all five MPs (Table 10). Carbon dioxide emissions were detected at all MPs at all measuring times whereas methane emissions were detected at all MPs in January 2006 (0.37-6.6 g CH_4 m^{-2} d^{-1}) (when the ambient air temperature was −25 °C) and methane emissions 2-3 orders of magnitude lower than carbon dioxide emissions were detected at some MPs from August to October (up to 0.13 g CH_4 m^{-2} d^{-1}).

4.4 Methane oxidation at a surface-sealed boreal landfill (IV)

4.4.1 Gas composition in gas wells

A study (IV) was performed at a closed full-scale landfill which, during the present study period, was equipped with a multilayer cover system including a water impermeable sealing layer, an integrated gas distribution system and a methane oxidizing top soil cover across the whole landfill area. The passive gas distribution system included horizontal collection canals in the waste fill, vertical gas wells, and horizontal distribution pipes in the drainage layer. The methane oxidation performance of the cover system was evaluated once before sealing (October 2004) and four times after sealing (October 2005-June 2006) using gas emission and pore gas measurements.

The composition of the gas in the gas distribution system was studied by measuring the gas concentrations in the 14 gas wells (data shown in (IV)). Methane concentrations in the gas wells ranged from 31% to 72% with the exception of one gas well in which the methane concentration was below this range in three of the measurements (5-29%) (IV). The mean methane concentrations (44-63%) and methane to carbon dioxide ratios (1.47-1.73) in the gas wells were typical for landfill gas. These results showed that the gas generated in the waste layer was seeping into the gas wells.

4.4.2 Gas emissions

Methane and carbon dioxide emissions were measured at 23-34 measuring points using the flux chamber method to study the spatial and temporal variation in emissions. In the pre-sealing measurement (October 2004), methane emission was detected at 52% and carbon dioxide at 90% of the measuring points (N = 21) (Table 12). After sealing, methane was emitted at 16-32% and

TABLE 12 Methane and carbon dioxide emissions (g m^{-2} d^{-1}) from individual measuring points at the different measurement times.

Before landfill sealing			After landfill sealing								
	Oct-04[a]	Oct-04[a]		Oct-05[b]	Nov-05	Feb-06	Jun-06	Oct-05[b]	Nov-05	Feb-06	Jun-06
Point	CH_4	CO_2	Point	CH_4	CH_4	CH_4	CH_4	CO_2	CO_2	CO_2	CO_2
BA1	0.00	5.42	AA1	0.00	0.00	0.00	0.00	35.4	5.14	0.00	14.5
BA2	0.00	3.82	AA2	0.00	10.6	0.15	0.89	35.6	36.9	2.97	55.1
BA3	0.00	4.52	AA3	0.00	0.00	0.00	0.00	15.1	0.00	3.58	21.9
BB4	0.29	1.37	AB2	0.00	0.00	0.00	0.94	32.5	6.22	12.0	82.5
BB1[a]	0.00	1.27	AB2W	0.00	252	38.5	9.81	74.4	369	102	292
BB2	0.19	2.31	AB4	0.00	−0.09	0.00	0.00	9.28	0.00	3.58	24.6
BB3	0.15	5.42	AC1	0.00	−0.05	−0.10	−0.03	18.9	3.44	5.37	33.7
BB4	0.00	2.12	AC2	0.00	0.00	0.00	0.00	17.3	3.49	3.06	34.5
BC2	2.42	4.71	AC3	0.09	0.21	3.52	70.2	24.3	8.06	18.5	232
BC3	0.00	1.41	AC4	0.07	0.00	0.00	27.7	18.3	1.65	17.4	143
BC4	2.70	14.5	AC4W	0.10	0.00	0.00	0.00	24.8	1.60	1.74	56.5
BD1[a]	−0.09	0.00	AD2	−0.09	0.00	0.00	0.00	29.4	5.37	6.03	29.7
BD2	43.8	42.3	AD2W	0.00	0.00	0.00	−0.19	11.5	0.00	2.07	14.2
BD3	3.30	7.16	AD3	0.00	0.00	0.00	−0.07	18.0	2.54	2.83	33.3
BD4	0.07	0.00	AD4	0.00	0.00	5.19	0.00	26.6	0.00	17.43	33.9
BE2	0.14	2.69	AE1	0.00	0.00	0.00	0.00	25.6	1.51	1.60	33.1
BE3	0.19	1.84	AE1W	44.7	0.00	−0.10	0.00	220	2.07	5.28	74.9
BE4	−0.09	4.15	AE2	0.00	0.00	−0.12	0.00	11.6	3.25	3.20	41.6
BF1	0.00	5.23	AE3	5.41	0.26	0.17	0.00	20.9	3.44	7.35	50.4
BF2	0.00	0.00	AE4	0.00	0.00	2.47	0.00	11.8	0.66	15.7	36.5
BF3	0.00	24.1	AF1	0.05	0.00	0.05	0.00	33.1	2.83	6.22	35.2
BF4	0.00	7.02	AF2	0.09	−0.02	0.00	0.00	15.6	0.00	1.13	23.6
BX1	0.26	0.00	AF3	0.07	0.00	0.00	0.00	14.8	0.90	5.98	36.9
BX2	19.0	20.0	AF4	0.00	0.00	0.00	−0.05	6.03	0.00	0.00	24.6
			X1	0.00	0.00	0.00	0.00	24.3	3.53	4.15	7.16
Mean	3.29	7.27		2.02	10.5	1.99	4.37	30.98	18.46	9.97	58.59
St.dev.	9.52	9.73		8.95	50.3	7.71	14.9	41.53	73.36	20.02	67.57

[a] In Oct-04, the points BB1 and BD1 were excluded from calculations because they were located at the part of the landfill covered by sealing layer at that time.

[b] In Oct-05, additional points were measured: AA4 (0.03, 12.8), AB1 (0.05, 16.5), AB3 (0.00, 12.3), AB3W (0.07, 30.5), AD1 (0.00, 16.5), AD5, 0.00, 28.2), AE5, 0.05, 28.4), AG1 (−0.07, 27.4), AX2 (0.00, 28.8); mean, median, and st.dev. presented in the table are for the 25 points shown in the table similarly as for Nov-2005, Feb-2006 and Jun-2006 (the corresponding values for 34 points in Oct-2005 are 1.44, 0.00, and 7.56 g CH_4 m^{-2} d^{-1} for methane and 28.8, 21.1 and 35.3 g CO_2 m^{-2} d^{-1} for carbon dioxide.

carbon dioxide at 76-100% of the measuring points (N = 25) on each measurement occasion (October 2005-June 2006). Before sealing, methane flux was above 1 m^3 CH_4 ha^{-1} h^{-1} (1.7 g CH_4 m^{-2} d^{-1}) at 19% and after sealing at 8-16% of the measuring points.

After the landfill was sealed, the mean methane flux was lower (1.99-2.01 g CH_4 m^{-2} d^{-1}) in October 2005 and February 2006 and higher (4.36-10.5 g CH_4 m^{-2} d^{-1}) in November 2005 and June 2006 compared to the values obtained before sealing in October 2004 (3.29 g CH_4 m^{-2} d^{-1}) (Table 12). Mean carbon dioxide flux after sealing (9.97-58.6 g CO_2 m^{-2} d^{-1}) was higher at all four measurements than before sealing (7.27 g CO_2 m^{-2} d^{-1}).

After landfill sealing the highest methane and carbon dioxide emissions were detected close to the gas wells and gas distribution pipes (Fig. 15). For example, 58-92% of the sum of methane plus carbon dioxide emissions from all the measuring points at the different measurement times occurred within a 15 m radius of the nearest gas well, although this area only covered about 25% of the landfill area and included 32% of the measuring points (data shown in (IV)). Moreover, 73-99% of the emissions were within a 7 m radius or closer from the nearest gas distribution pipe, an area covering approximately 42% of the landfill area and including 52% of the measuring points (IV). Although the measuring points were somewhat clustered around the gas distribution structures, the percentage of the total emissions from within, for example, a 15 m radius of the nearest gas well or a 7 m radius from the nearest gas distribution pipe clearly exceeded the percentage of the number of measuring points within this area (IV). This suggested that the tendency for gas emissions to be higher in the proximity of the gas distribution structures was a real phenomenon and not an artefact due to the siting of the measuring points.

The eight measuring points in which methane plus carbon dioxide emissions exceeded 10 m^3 ha^{-1} h^{-1} at one or several measurement times were located in the northern, central, eastern central, and the southwestern parts of the landfill (Fig. 15). With one exception (AE1W) all the high-emission points were from sites with the highest elevation (139.5-142 m; mean elevation of the landfill 137.4 m) (Fig. 8, Fig. 15, IV). The emissions were also generally aggregated in the areas of highest elevation, as in three of the four measurements 60-90% of total emissions were above 139.5 m, although this area represented less than 20% of the landfill area (IV). Thus, the points with the highest emissions were near the gas wells and distribution pipes, and mainly in the higher areas of the landfill.

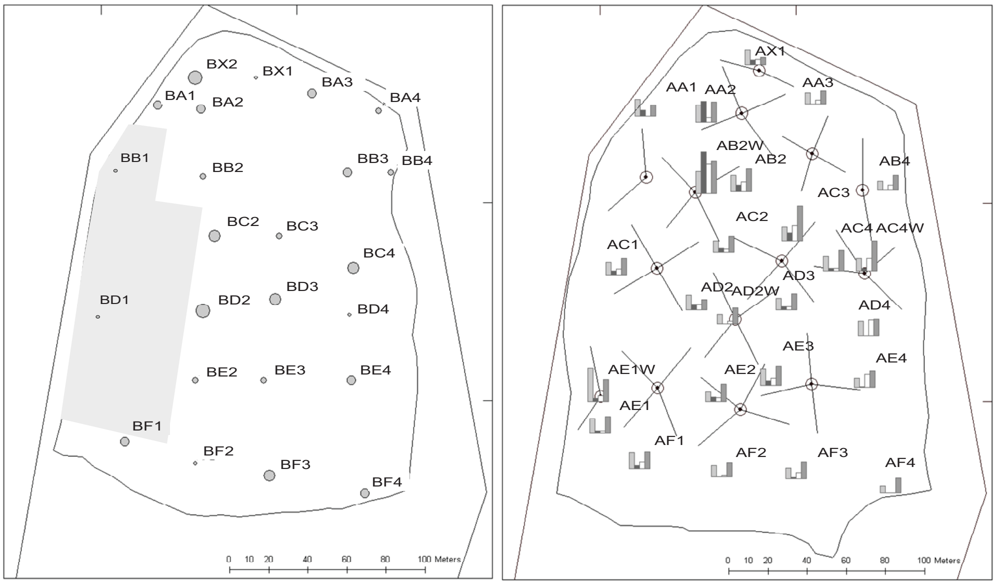

FIGURE 15 Methane plus carbon dioxide emissions at the different measuring points before (left) and after (right) the sealing of the landfill. The radius of the circles (left) and height of the bars (right) are proportional to methane plus carbon dioxide emissions transformed with log(x+1) (untransformed results shown in Table 12). In the map on the right, the measuring points are located in the middle of the lower edges of the bar charts. The bars at each point represent emissions in Oct-05, Nov-05, Feb-06, and Jun-06, from left to right. The shaded area in the map on the left is the area which was covered by the sealing layer at the time of measurement.

4.4.3 Pore gas

Methane, carbon dioxide and oxygen concentrations at different depths of the landfill cover were measured to evaluate the variation in landfill gas input into the cover and the availability of oxygen for methane oxidation (data shown in (IV). Landfill gas appeared to reach the top soil cover across most of the landfill area, as indicated by the fact that in 22 of 25 measuring points methane concentrations above 1% were observed in the pore gas at one or more measurement times, with the sole exception of points AC1, AF1, and AF2, which were located at the edges of the landfill. Methane concentration was above 1% at the depth of 15 cm at two to four points per measurement time (in November 2005 measurements were done only at 45 cm for most of the MPs). Oxygen concentrations at the depth of 15 cm were generally between 10% and 19%. Oxygen concentrations below 10% at the depth of 15 cm were observed at six points (AA2, AB2, AB2W, AC3, AE1W, AF3), on one or several of the measurement times. Methane concentrations above 20% at 45 cm were observed on one or several of the measurement times at five of those six points (but not at point AF3) and at six other points.

Oxygen concentrations decreased downwards and, generally, the steepest decreases in oxygen concentration, in some points down to <1% at the depth of 45 cm, occurred at points with the highest methane concentrations. Oxygen concentration remained above 10% at 45 cm at 33-44% of the points at three of the four different measurement times while in February 2006 this percentage was as high as 86% as oxygen concentration was below 10% at 45 cm at only three of the 25 points.

4.4.4 Methane flux and oxidation

The mean methane fluxes into the cover calculated (Chapter 3.8.1) from the mean emissions at the measuring points were between 2.92 and 27.3 g CH_4 m^{-2} d^{-1} at the different measurement times (Fig. 16). After landfill sealing, mean methane oxidation was 2.06-23.0 g CH_4 m^{-2} d^{-1} (Fig. 16). The mean fractional oxidation (with area-based oxidation in brackets) estimates (minimum and maximum estimates) were 9-14% (0.31-0.55 g CH_4 m^{-2} d^{-1}) before sealing, while after sealing the corresponding values were 29-83% (0.82-9.79 g CH_4 m^{-2} d^{-1}) in October 2005, 25-57% (0.67-2.75 g CH_4 m^{-2} d^{-1}) in February 2006 and 46-84% (3.78-23.0 g CH_4 m^{-2} d^{-1}) in June 2006. In November 2006, the mean fractional oxidation was zero as 90% of the sum of the methane plus carbon dioxide emissions from all points was from a point (AB2W) with very high methane flux into the soil cover and negligible oxidation (Fig. 16).

At the majority (75-96%) of the measuring points at each measurement time, 80-100% of the methane flux into the soil cover was oxidized and methane emissions in these points were less than 10 m^3 CH_4 ha^{-1} h^{-1} (17 g CH_4 m^{-2} d^{-1}) (Fig. 16). In October and November 2005 and June 2006 there were 1−2 points (8% of points) and in February 2006 four points (16% of points) where the mean fractional oxidation was <80% and methane emission >1 m^3 CH_4 ha^{-1} h^{-1} (1.7 g CH_4 m^{-2} d^{-1}) (Fig. 16).

The methane oxidation capacity of the cover layer appeared to be higher in October 2005 and in June 2006 when the soil temperature was 12-17 °C compared to November 2005 and February 2006 when the soil temperature was <5 °C. This is indicated by the fact that fractional oxidation of only 25-75% was observed in November 2005 and February 2006, even at points with a methane flux into the soil cover of <10 m^3 CH_4 ha^{-1} h^{-1} (17 g CH_4 m^{-2} d^{-1}) while in June and October fractional oxidation values of less than 90% were only observed at points with methane flux into the soil cover of >50 g CH_4 m^{-2} d^{-1}, with the exception of one point in October (AE3; Table 12). The highest oxidation rates at individual measuring points were 4.0 g CH_4 m^{-2} d^{-1} in November 2005, 12.8 g CH_4 m^{-2} d^{-1} in February 2006, 40.1 g CH_4 m^{-2} d^{-1} in October 2005 and 90.1 g CH_4 m^{-2} d^{-1} in June 2006.

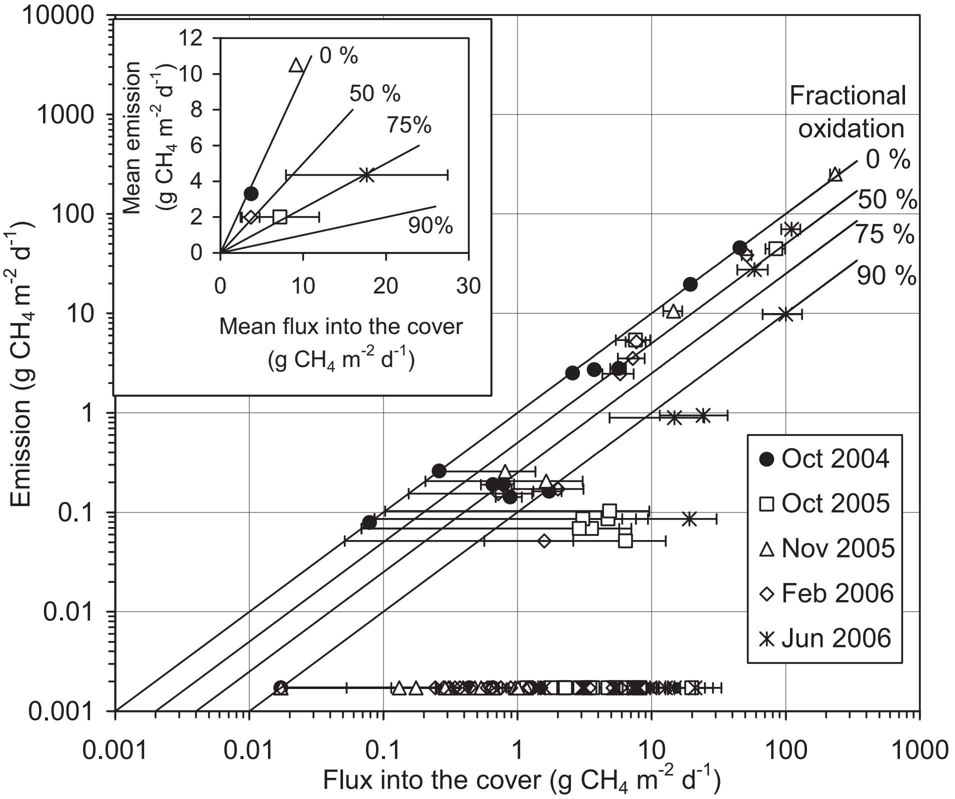

FIGURE 16 The relationship between methane flux into the cover, emission, and oxidation at different measuring points. The symbols represent the mean of the minimum and maximum estimates of methane flux into the cover (error bars present ± difference between minimum and maximum estimates of methane flux into the cover divided by 2 and are smaller than symbols when not apparent). •, October 2004 (before landfill was sealed); □, October 2005; Δ, November 2005; ◊, February 2006; *, June 2006. The insert presents mean methane flux into the cover and mean methane emission at the measuring points. Reference lines for different values of fractional methane oxidation are shown. Methane emissions below the detection limit are approximated with the value 0.017 g CH_4 m^{-2} d^{-1} (0.001 m^3 CH_4 ha^{-1} h^{-1}).

5 DISCUSSION

5.1 Response of methane oxidation to temperature (I-IV)

5.1.1 General remarks

Methane-oxidizers are able to consume methane and increase their activity even at near-freezing temperatures as indicated by the increase in the methane consumption rate in consecutive methane feeding cycles in the landfill cover soil studied in batch assays (I) and by the significant methane oxidation rates at low temperatures in the field studies (III, IV). However, the results also indicate that variation in the ambient temperature and its influence on the temperature and consequently on the rate of methane oxidation in the landfill cover soil have to be taken into account when designing landfill biocovers. In the present field studies (III, IV), the temperature of the landfill covers was strongly influenced by changes in air temperature. For example, at the depth of 45 cm in the outdoor lysimeter, the temperature varied between 3 and 24 °C over the year and was below 10 °C at 0-45 cm for approximately six months of the year. Also, in the full-scale landfill the temperature in the 50-cm thick soil cover was below 10 °C for several months. The relative responses of methane oxidation to temperature observed in the present study are summarized in Table 13 and in Fig. 17.

5.1.2 Responses of methane oxidation to temperature in a four-year-old landfill cover soil

In batch assays with the four-year-old landfill cover soil (I), the response of methane oxidation to temperature was high (Q_{10} values 6.5-8.4; Table 13, Fig. 17) when the soil moisture was within the optimal range for methane oxidation (14-28% dw, 33-67% WHC, Chapter 5.2). These values resemble the responses observed in previous batch assays at temperature ranges typical of temperate or boreal environments, as methane consumption increases along with

TABLE 13 The Q_{10} temperature coefficients of methane oxidation calculated for the different materials/systems investigated in this study. For the outdoor lysimeter study (III), Q_{10} was not calculated owing to the high fractional oxidation and the large range of uncertainty in the estimates of volumetric methane oxidation.

Material	Study scale	Temperatures (°C)[a]	Q_{10}	Paper
Compost	Batch	1, 6, 12, 19	6.5-8.4	I
MBT residual[b]	Column	6, 23.5	1.4-2.0	II
MBT residual (from columns)	Batch	5, 25	1.9-2.4	II
Sludge compost and peat[c, d]	Field	2, 12, 21	2.7	IV
Sludge compost and peat[c, e]	Field	2, 12, 21	2.7	IV

[a] Incubation temperatures (batch and column assays) or mean soil temperatures at 0-50 cm in the landfill cover (field study).

[b] Calculated for the period of the column experiment with stable methane loading rate and with percentage oxidation less than 100% (i.e., the period when methane oxidation at the whole-column level was not methane-limited), and using the average oxidation rates obtained during the periods at the average temperatures of 23.5 °C and 6 °C (Table 8). The values used for the calculation were 39.0 and 69.0 g CH_4 m^{-2} d^{-1} (MBT residual 22) and 22.0 and 75.5 g CH_4 m^{-2} d^{-1} (MBT residual 57) at 6 and 23.5 °C, respectively.

[c] November 2005 measurement excluded from calculations owing to exceptional atmospheric pressure trend compared to the other measuring times.

[d] Q_{10} value calculated from mean oxidation rates of the measuring points at each measuring time (5.17, 1.68, and 13.3 g CH_4 m^{-2} d^{-1} for Oct-05, Feb-06, and Jun-06).

[e] Q_{10} value calculated from the maximum oxidation rate observed at individual points at each measuring time (40.1, 12.8 and 90.1 g CH_4 m^{-2} d^{-1} for Oct-05, Feb-06, and Jun-06).

temperature (Whalen et al. 1990, Czepiel et al. 1996, Gebert et al. 2003, Börjesson et al. 2004, Park et al. 2005) when methane concentration or moisture are not themselves limiting factors. The methane oxidation rate at 1 °C was 2-3% and at 12 °C 20-28% of the rate at 19°C, at moistures 33-67% WHC (Fig. 12, Fig. 17). Such a temperature response suggests that the reaction rate is dependent on enzymatic activity. Methane consumption, defined in batch assays as the rate of methane disappearance—and its response to temperature—are probably regulated by the rate of turnover of the first enzyme reaction in the methane oxidation chain, the hydroxylation of methane to CH_3OH by methane monooxygenase, which removes the dissolved methane from the soil water. As in the present study (9% initial methane conc.), pronounced responses of methane consumption to temperature were observed in soils and methanotroph cultures incubated at methane concentrations of 1000-10,000 µl l^{-1} (0.1-1%), as methane consumption depended on the potential enzyme activity, while less pronounced responses were seen at low initial methane concentrations (2-100 µl l^{-1}) because methane consumption was restricted by the supply of methane (King & Adamsen 1992, Whalen & Reeburgh 1996). Similarly, Boeckx et al. (1996) observed low responses of methane consumption to temperature (average Q_{10} 1.9) in landfill cover soil incubated at 10 µl l^{-1} in contrast to the higher Q_{10} values (1.9-7.26) reported in previous studies at >1% methane concentrations (Czepiel et al. 1996,

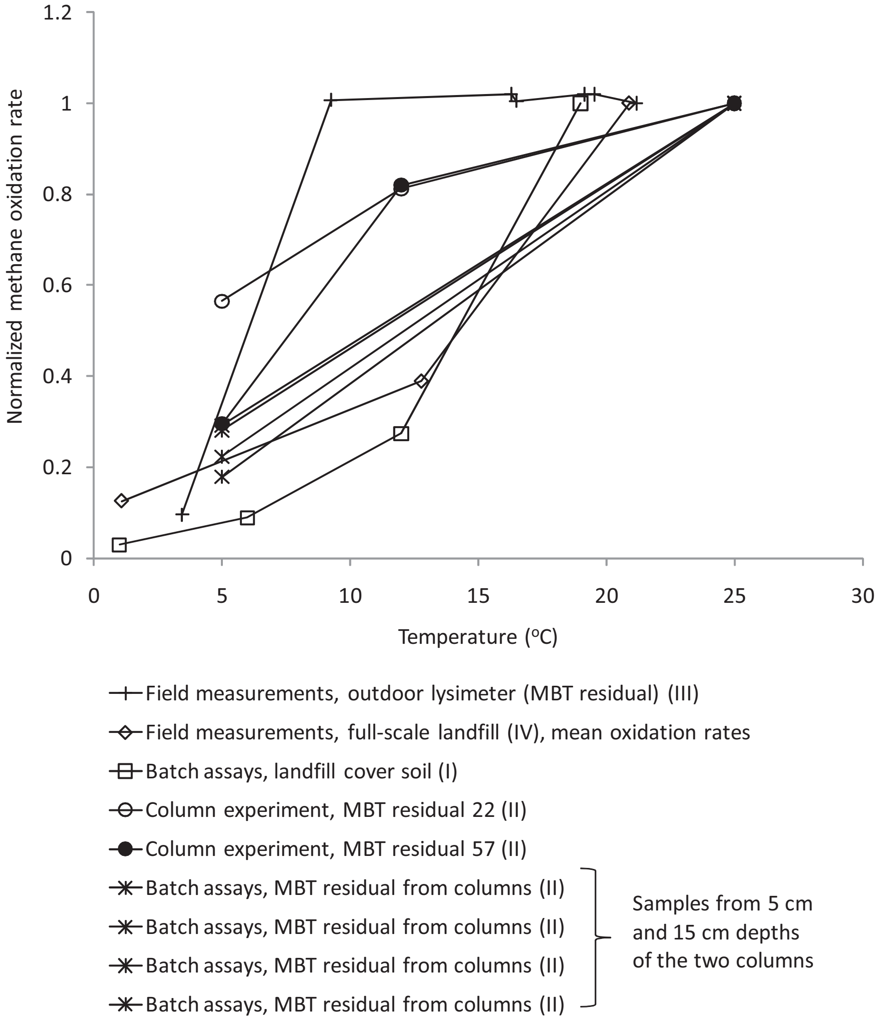

FIGURE 17 The apparent responses of methane oxidation rates to temperature (incubation temperature or temperature in the oxidation layer) in the studied materials and experimental systems. The methane oxidation rates were normalized by dividing the rates obtained at each temperature by the rate observed at the highest temperature (19-25 °C) studied within the same data series. The normalized rates were calculated using the same data as used for the Q_{10} values (Table 13). For the outdoor lysimeter data, mean fractional methane oxidation rates were used. For the four-year old landfill cover soil (I), the results obtained with moisture of 21% dw are presented.

Christophersen et al. 2000, De Visscher et al. 2001, Börjesson et al. 2004) and in the present study (Q_{10} 6.5-8.4).

In the present study, the response of methane oxidation to temperature depended on soil moisture: at the lowest moisture content (16% WHC) methane oxidation was negligible and not dependent on temperature while, at higher moisture levels (33-67% WHC), the response to temperature decreased with increasing moisture (Chapter 5.2). This is due to the decrease in the supply of oxygen and methane (due to the slow diffusion of the gases in the water phase).

5.1.3 Methane oxidation at different temperatures in MBT residual in column and batch assays

In the laboratory column study with MBT residual (II), temperature appeared to have less effect on methane oxidation than in the batch assays with the four-year old landfill cover soil (I) and in other batch assays (see references in Chapter 5.1.2). In the columns, the apparent Q_{10} values were 1.4-2.0 (Table 13) and the methane oxidation rates at 6 °C were 30-57% of the rates at 25 °C (Fig. 17). The effect of temperature on methane oxidation in the present MBT residual columns was similar to that observed in columns filled with organic soil mixtures where the methane oxidation rate at 4-6 °C was 25-50% of the rate at 20-25 °C (Kettunen et al. 2006). Huber-Humer (2004) observed even less temperature-sensitive methane oxidation in compost columns: the oxidation rate at 4 °C was 70% of that at 18 °C (fractional oxidation at 18°C was 100%). The different responses of methane oxidation to temperature between different column studies may be due to differences in the properties of the soils or in the experimental set-ups (discussed in 5.3.1). In column assays methane oxidation is more limited by other factors than enzyme activity, such as the supply of methane and oxygen, which can partly explain the lower response to temperature in columns compared to batch assays (Chapter 1.3.2).

A relatively low response of methane oxidation to temperature was also observed in MBT residuals sampled at the end of the column experiment and studied in batch assays (II): the rates at 5 °C were 20-30% of those at 25 °C and the Q_{10} values were 1.9-2.4, which are at the lower end of the Q_{10} values reported in previous batch assays (Chapter 5.1.2). This suggests that some microbial adaptation to low temperature may have occurred during the column experiment when the columns were run at <10 °C for the last five weeks. Temperature-induced changes in the species composition of methanotrophs have been reported (Gebert et al. 2003, Börjesson et al. 2004).

5.1.4 Methane oxidation at different temperatures in field studies

In the outdoor lysimeter (III), the mean fractional methane oxidation was 96-100% at all measurements between April and October (temperature in the cover layer above 10 °C, Fig. 17), and thus the overall methane oxidation did not depend on temperature but most likely depended on the availability of methane (Fig. 17). The only obvious temperature-associated effect on the level of overall methane oxidation in the outdoor lysimeter was the reduced oxidation at the coldest time of the year. In contrast, in the study at the full-scale landfill (IV), methane fluxes exceeded oxidation capacity at several points at each measuring time. Thus, soil temperature, even when above 10 °C, appeared to have an effect on overall methane oxidation (mean fractional oxidation 0-84%). In the study at the full-scale landfill, methane oxidation at 1 °C was 13-

14% of that at 21 °C and the apparent Q_{10} value was 2.7-2.8 (Fig. 17, Table 13). Thus, at the full-scale landfill, the effect of temperature on methane oxidation appeared to be lower compared to the values obtained in many batch assays (Q_{10} 1.9-7.4) but higher compared to those in laboratory columns with MBT residual (Q_{10} 1.4-2.0; Chapter 5.1.3). It should be noted that the apparent temperature responses for the column and field studies were calculated using data obtained from the same experiments or field sites in the course of time. Therefore, the values obtained may be influenced, in addition to temperature, also changes in other factors such as gas flow into the cover, during the study period.

5.2 Response of methane oxidation to soil moisture (I-IV)

In batch assays, methane oxidation at different moistures depends on the availability to microbes of water and on the "diffusion barrier" caused by high moisture. The batch assays with a four-year old landfill cover soil (I) showed high methane oxidation rates when moisture was between 33 and 67% of WHC, which is in accordance with other batch studies where optimum moisture has ranged from 40% to 80% WHC, when compared on the basis of % WHC (Figueroa 1993, Boeckx et al. 1996, Whalen & Reeburgh 1996). The response of methane consumption to moisture followed the typical curvilinear pattern (Whalen et al. 1990, Boeckx et al. 1996, Czepiel et al. 1996, Whalen & Reeburgh 1996, Christophersen et al. 2000, Scheutz & Kjeldsen 2004, Park et al. 2005) at temperatures of 12-19 °C in the present study (I). The decrease in methane consumption to low levels when soil moisture falls to an unfavourable level, i.e., from 33% WHC to 17% WHC (14-7% dw) in the present study at all temperatures, is apparently due to the decrease in water potential, i.e., increase in water stress (Brown 1976). Correspondingly, the increase in methane consumption that accompanies increasing moisture from dry conditions, e.g. in the present study from 17% WHC to 50% WHC (14-21% dw) (at 12 °C) or up to 67% WHC (28% dw), the highest moisture studied (at 1-6 °C), is apparently due to the increased water potential. Once optimal moisture is reached, any further increase in moisture leads to a decrease in methane consumption, as observed in the present study (12-19 °C), owing to the reduced supply of methane and/or oxygen, as these gases are poorly water soluble and their liquid-phase diffusion is slow. Although in the present study at 1-6 °C methane consumption did not decrease with increasing moisture within the moisture range studied (owing to the temperature-dependent effect of moisture; Chapter 5.1.2), it is likely that a decrease in moistures above this range (67% WHC, i.e., 28% dw) would also occur at 1-6 °C (Whalen & Reeburgh 1996, Christophersen et al. 2000).

While batch assays show the dependence of methane oxidation on moisture as affected by water stress and by the diffusion of methane and oxygen at the soil particle level, changes in soil moisture in columns or in the field may also influence methane oxidation by affecting the proportion of air-filled pores which in turn determines the retention time of gas in soil and thus affects the larger-scale transport of gas in the soil (Chapter 1.3.3). In the column study with MBT residual (II), gravimetric moisture increased in both MBT residuals during the experiment, as also observed in previous column experiments (Hilger et al. 2000a, Huber-Humer 2004); probably due in particular to water produced in methane oxidation. In the present column study (II), in both MBT residuals moisture in relation to WHC (from 56% WHC to up to 67% WHC) remained in the range observed favourable for methane oxidation in batch assays (50-70% WHC, Chapter 5.2). In MBT residual 57, volumetric moisture increased (from 36% to a maximum of 43%) and air porosity decreased (from 47% to a minimum of 40%). The fact that in MBT residual 22 volumetric moisture did not increase was likely due to the loss of solid matter owing to biodegradation (indicated by decrease in VS). The lower air porosity in MBT residual 57 (40-46%) may have contributed to the lower oxidation rate by affecting gas flow properties and/or decreasing thermal insulation, among other factors, such as the macropores in MBT residual 57 made by earthworms, discussed in II. Air porosity is a particularly important factor for methane oxidation at low temperatures (Chapter 5.5.2).

In the outdoor lysimeter (III) there were indications of decreased MOP in the top layer (0-15 cm), where the moisture content fell to 37-39% dw (in July and August), which corresponds to 19-28% of the water-holding capacity for MBT residual (assuming a water-holding capacity of 140-190% dw, Table 9). With such low moisture (% WHC), the methane oxidation rate is reduced compared to the rates achieved with moisture closer to the optimum (I) (Figueroa 1993). However, overall methane oxidation did not decrease in the outdoor lysimeter during this period because of the relatively low methane loading rate and because most of the methane oxidation occurred in deeper layers where a higher moisture content was maintained (Chapter 5.3.2).

In the study at the full-scale landfill (IV), the mean soil moisture was 39-69% WHC (assuming a WHC of 246% dw, Table 4) and thus remained within the appropriate range for methane oxidation. The mean soil moisture content correlated negatively with soil temperature (IV), probably due to seasonal changes in rainfall and evaporation, and was lowest in June 2006. It should be noted that the moisture was analyzed in vertical profile samples for the whole 50-cm layer. It is likely that the top parts of the cover were dryer and thus methane oxidation in the top layer may have been limited by drought, potentially explaining the methane emissions in some of the points with high methane fluxes into the cover in June. Because the present investigation was conducted within one year after the installation of the final cover at the landfill, plant cover was not present at the landfill when three of the four measurements were conducted and was still relatively scarce at the time of the last measurement (June 2006). Thus the landfill cover was exposed to rainwater infiltration and to direct evaporation of water from the soil surface. When plant cover becomes established, a high proportion of rainwater may be retained by vegetation through interception and transpiration (Huber-Humer 2004) while direct evaporation of moisture from soil surface will be smaller. Thus plant cover may stabilize seasonal variation in soil moisture and help to maintain more favourable moisture conditions for methane oxidation.

5.3 Methane oxidation in MBT residual

5.3.1 Methane oxidation in MBT residual in laboratory columns (II)

The present methane oxidation rates in the column experiment suggest that MBT residual is equally or better suited to support microbial methane oxidation than the materials studied previously (Table 14). The present methane oxidation rates at 2-10 °C are higher than those previously reported by Kettunen et al. (2006) but lower than those reported by Huber-Humer (2004). The reason for the lower methane oxidation rates observed by Kettunen et al. (2006) in engineered soil columns could be the more intense heterotrophic microbial activity and low air porosity. The higher area-based rates obtained by Huber-Humer (2004) in compost columns at 4 °C are possibly explained by a thicker layer of support medium. Methane oxidation rates higher than those in the present study have also been obtained at 18-30 °C with various materials, including MBT residual (Cossu et al. 2003), when higher methane loading rates have been used (Table 14).

Methanotrophs in MBT residual proliferated when methane and oxygen were provided, as indicated by the rapid start of methane consumption both in columns and in batch assays at 23 °C, and by the increase in MOP during the column experiment. The MOPs observed at the end (up to 104 µg CH_4 g_{dw}^{-1} h^{-1} at 5 °C) were apparently the highest recorded below 20 °C to date in soils or composts, as the MOPs reported for landfill cover soils at 2-15 °C range from 0.5 to 18 µg CH_4 g_{dw}^{-1} h^{-1} (I, III, Czepiel et al. 1996, Christophersen et al. 2000, Börjesson et al. 2001, 2004, Scheutz & Kjeldsen 2004, Gebert et al. 2009). Also, at 23 °C the present MOPs (up to 581 µg CH_4 g_{dw}^{-1} h^{-1}) were higher than MOPs at 20-25 °C in materials sampled in landfill covers (up to 160 µg CH_4 g_{dw}^{-1} h^{-1}; Czepiel et al. 1996, Christophersen et al. 2000, De Visscher et al. 2001, Einola et al. 2003, Börjesson et al. 2004, Scheutz & Kjeldsen 2004) or in laboratory columns (Visvanathan et al. 1999, De Visscher et al. 1999, Hilger et al. 2000a, Scheutz & Kjeldsen 2003, Wilshusen et al. 2004), the highest value being close to the highest previous value 480 µg CH_4 g_{dw}^{-1} h^{-1} (Wilshusen et al. 2004). Recently, high MOP (up to 441 µg CH_4 g_{dw}^{-1} h^{-1} at 20 °C) have been reported in a landfill biocover (Aït-Benichou et al. 2009)

TABLE 14 Study parameters and CH_4 oxidation rates in published laboratory column studies at different temperatures. nr=not reported.

°C	Material	Thickness (cm)[a]	CH_4 loading rate	CH_4 oxidation rate	Reference
			g CH_4 m^{-2} d^{-1}		
2-10	MBT residual 22	30	77-79	31-47[b] (39)	This study
2-10	MBT residual 57	30	79	12-37[b] (22)	This study
4-6	Sewage sludge compost	60	107	86	Huber-Humer 2004
4-6	SDS mixture[c]	28	42	9-16	Kettunen et al. 2006
5	SDB mixture[c]	30	42	0.7-6.4	Kettunen et al. 2006
9-12	MBT residual 22, MBT residual 57	30	77	56-61	This study
12	SDS mixture[c]	28	36	39	Kettunen et al. 2006
12	SDB mixture[c]	30	37	9	Kettunen et al. 2006
13	Compost	120[d]	52	43	Fornés et al. 2003
10	Compost	120[d]	55	53	Berger et al. 2005
25	MBT residual 22, MBT residual 57	30	70-84	64-79	This study
30	MBT residual	60	653	419	Cossu et al. 2003
22	Agricultural soil	50	215	172	De Visscher et al. 1999
22	Landfill soil	50	369	241	De Visscher et al. 1999
22	Landfill soil	31	141	25-66	Hilger et al. 2000a
18	Sewage sludge compost	60	107	107	Huber- Humer 2004
20	MSW compost	60	250	250	Huber-Humer 2004
23	SDS mixture[c]	28	31	32	Kettunen et al. 2006
23	SDB mixture [c]	30	33	26	Kettunen et al. 2006
22	Landfill soil	95	251	185-211	Scheutz and Kjeldsen 2003
30	Leaf compost	50	nr	100-401	Wilshusen et al. 2004
30	Landfill soil	90	296	164	Visvanathan et al. 1999

[a] Thickness of soil/compost layer.

[b] Minimum and maximum values (mean value in parentheses).

[c] Mixture of sewage sludge, deinking waste, and sand (SDS) or wood bark chips (SDB).

[d] The experimental system included a capillary barrier (30 cm) and a capillary block (10 cm) layer, above which the 120 cm soil layer was installed.

5.3.2 Methane oxidation in MBT residual in outdoor lysimeter (III)

The present results show that MBT residual is a viable material for supporting microbial methane oxidation in landfill covers in field conditions in a boreal climate. The high fractional oxidation (96% of the methane production of 1.06-16.0 g CH_4 m^{-2} d^{-1}) in the present lysimeter from April to October 2005 shows that, at the whole-lysimeter level, methane oxidation was mostly methane-limited during this period. This, in turn, suggests that MBT residual-based covers may attain even higher oxidation rates in landfills with a higher methane loading than in the present lysimeter and may thus be feasible for methane treatment in landfills receiving MBT residuals (discussion in III) as well as in conventional landfills. However, during the coldest time of the year (January 2006, ambient air temperature −25 °C) in the present boreal environment, in contrast with the other measuring times, only 0-22% of the produced methane was oxidized in the present lysimeter (discussed below).

Methane oxidation in the MBT residual in the field lysimeter was indicated by the facts that carbon dioxide emissions were detected at all measuring times and MPs and that methane emissions, much lower than carbon dioxide emissions, were only detected occasionally. From April to October, the vertical distribution of methane oxidation appeared to be mainly governed by the availability of oxygen and methane in the lower and upper parts of the lysimeter, respectively. During this period, methane was oxidized mainly within the depth range of 35-75 cm, i.e., in the uppermost part of the waste layer, in the distribution layer, and in the lower part of the cover layer, as indicated in part by the steep upward decrease in methane concentration within this depth range and, in most cases, undetectable methane (detection limit 0.1%) at the depth of 0-35 cm. The decrease in methane concentrations towards the surface is not explained alone by dilution by air, as there was a concomitant decrease in the methane-to-carbon dioxide ratio, which is considered an indicator of methane oxidation (Visvanathan et al. 1999, Huber-Humer 2004), upwards in the lysimeter in the depth range of 35-75 cm. The pit measurements in July and August also indicated the occurrence of methane oxidation below 35 cm, as negligible methane fluxes entered the top 30-cm layer whereas high methane fluxes were detected at the depths of 45 and 60 cm.

During the period (April to October) when methane emissions were low and the ambient air temperature for the most part varied between 0 and 25 °C, the temperature in the 5-80-cm layers was between 5 and 25 °C, while at the depths where most of the methane oxidation took place (35-75 cm) the temperature ranged from 10 to 25 °C. It is noteworthy that from April and October 2005 no or only minor methane emissions were detected, although the temperature at 35-75 cm was below 10 °C (April) or within the range 10-13 °C (October).

The decreased rate of methane oxidation (0-22% of the methane produced) in January 2006 (ambient air temperature −25 °C) was probably mainly caused by the low temperatures in the depth range of 25-75 cm (2-9 °C). Thus, at that time, methane oxidation appeared to be reaction rate-limited. Therefore, some of the methane produced was reaching the top 0-35 cm of the lysimeter but was not completely oxidized in that layer either due to the low temperatures and freezing of the top 10-15 cm of the lysimeter.

The area-based MOP in the 0-75-cm layer of the present lysimeter in June and July in both MPs was many-fold higher than the estimated maximum methane production at the corresponding measuring times. This is in line with the fact that no methane emissions were detected, indicating that MBT residual was able to support a methane oxidizing microbial community sufficient to treat all of the methane produced.

The present MOP values, calculated on a dry weight basis, were within the range reported for various landfill cover samples (Chapter 5.3.1). In addition to the abundance and activity of methane-oxidizers (Jones & Nedwell 1993, Gebert et al. 2003, Kallistova et al. 2007), MOP is also dependent on other factors, such as moisture and the temperature in the landfill cover (e.g., Czepiel et al. 1996, Scheutz & Kjeldsen 2004). The decrease in MOP from June to July and August may be explained by drying of the cover layer (Chapter 5.2). In addition, the recirculation of leachate may have influenced the reduction in MOP, owing to the apparent alteration in the chemical composition of the materials in the top 75-cm zone of the lysimeter (III).

The occurrence of high MOPs in the zones of the lysimeter with negligible methane, and the low methane emissions recorded in August despite the decreased MOP, show that the MOP values poorly reflected the vertical distribution of, or temporal changes in, overall methane oxidation in the present lysimeter during the sampling period. This may be due to changes in the relative activity of the different methane-oxidizing microorganisms owing to changes in conditions, for instance in the methane and oxygen concentrations, caused by sampling, sample storage, or the experimental set-up of the batch assays. Therefore, MOP, which is a parameter determined in conditions differing from field conditions, should be used cautiously to estimate methane oxidation in the field at the moment of sampling.

Because of the efficient oxidation of methane below the depth of 35 cm between April and October, only a small proportion of the methane produced in the lysimeter appeared to reach the actual cover layer intended for methane oxidation. Nevertheless, the existence of the cover layer and gas distribution layer were likely to promote methane oxidation by acting as a buffer against changes in temperature and moisture and, at the same time, by enabling oxygen entry lower down in the lysimeter where oxidation was observed to take place. Other authors have similarly reported higher temperature (Maurice & Lagerkvist 2003, Huber-Humer 2004) and more stable moisture (Huber-Humer 2004) in the deeper layers of landfill covers (Chapter 5.6).

One potential application of MBT residual is the use of this material in intermediate methane oxidizing cover layers during the active phase of landfilling. Such landfill covers could consist at their simplest of a slightly compacted MBT residual layer. The use of MBT residual-based methane oxidizing cover layers appears to be a feasible method for methane treatment while also reducing the need for external materials for cover layers in MBT residual landfills.

5.4 Methane oxidation at a surface-sealed landfill (IV)

Methane oxidation was studied at a full-scale landfill which was closed and equipped with a European landfill directive compliant final cover system containing a water impermeable layer and an integrated gas distribution and methane oxidation system. The present results show that the investigated landfill gas treatment concept may be a feasible option in seeking to reduce methane emissions in landfills where a water impermeable cover layer is used. Conservative estimates of fractional methane oxidation calculated on the basis of mean methane and carbon dioxide emissions show that, after the sealing of the landfill, at least 29% of the methane entering the measuring points was oxidized in October, at least 46% in June, and at least 25% in February. It is also possible, owing to the uncertainty of the method of calculation (discussed below) that the oxidation rate was higher (maximum fractional oxidation 84%). Thus the results show an improvement on the initial situation as even the minimum values of fractional oxidation after sealing were higher than the maximum value before sealing, which was 14% (October 2004). The mean methane emissions at the same measurements were 2.1-4.3 g CH_4 m^{-2} d^{-1}, thus meeting the maximum acceptable methane emission of 6.0 m^3 CH_4 ha^{-1} h^{-1}, equalling to 10.3 g CH_4 m^{-2} d^{-1} at STP (1013 hPa and 0°C), set for the present landfill by the environmental permit authority (Häme Regional Environment Centre 2003) (IV). However, one of the four measurements performed after the sealing (November 2005) showed higher mean methane emissions (10.5 g CH_4 m^{-2} d^{-1}), while fractional oxidation calculated from mean emissions was zero because of a single high-emission point at which no oxidation occurred, probably partly due to decreasing atmospheric pressure (discussed below).

In some parts of the landfill the methane flux into the soil cover exceeded manifold the mean flux (2.75-27.3 g CH_4 ha^{-1} h^{-1}) at all the measuring points, leading to high methane emissions. On the basis of the mean methane fluxes, the present 50 cm-thick cover layer should be sufficient to oxidize all the methane at the present landfill, provided that the gas is delivered evenly into the cover layer, and that the cover layer remains unfrozen. This is indicated by the fact that oxidation rates up to 4.0-90.1 g CH_4 m^{-2} d^{-1} at different measurement times) were observed at some measuring points. Moreover, the present cover material showed high methane oxidation capacity in the laboratory column experiments (72 g CH_4 m^{-2} d^{-1} at 5 °C; unpublished results). The mean methane flux into the soil cover was also within the range of the methane oxidation rates observed in landfill covers (Table 15) and in laboratory column studies with other materials (at temperatures down to 2 °C; Table 14). Thus, the fractional oxidation values of 80-100% at 75-96% of the measuring points at the present landfill are in accordance with those previous findings.

The occurrence of high-emission points suggests that some unintended preferential gas flow paths were formed within the cover system. Although at each measurement time there were only 1-3 (out of 25) points with methane plus carbon dioxide emissions >20 m^3 ha^{-1} h^{-1}, these points are highly significant for the mean values of the measuring points, as they account for 37-90% of the sum of the methane plus carbon dioxide emissions and 77-98% of the sum of the methane emissions at all points. The fact that all four measuring points (out of 25) in which methane plus carbon dioxide fluxes >20 m^3 ha^{-1} h^{-1} were detected were within a 6 m radius of the nearest distribution pipe or a 12 m radius of the nearest gas well suggests that the gas was flowing through the gas wells and pipes while major gas leakages directly through the sealing layer seem unlikely. This is also supported by the fact that closing the valves of all four of the gas distribution pipes of one gas well appeared effectively to decrease emissions from the high-emission point close by (IV). Moreover, the high-emission points were mainly located in the higher areas of the landfill, where gas production per areal unit is probably the highest. However, the proximity to the pipes or wells, or elevation, statistically explained only a relatively low proportion of the variation in methane or methane plus carbon dioxide emissions across the whole landfill (IV). Therefore, the high-emission areas appear to be localized within a few meters radius of each of the presumed preferential gas flow paths and cover only a relatively small part of the landfill area.

In the present study, the highest methane oxidation rate (90.1 g CH_4 m^{-2} d^{-1}; ≥80% fractional oxidation) was observed in the summer (June 2006) measurements with a soil temperature of 17 °C. The higher oxidation capacity of the top soil cover in October and June compared to November and February is partly explained by the variation in temperature in the top soil cover. At soil temperatures >12 °C, this soil cover type may attain fractional oxidation of 80-100% when methane flux into the soil cover is below 10 m^3 CH_4 ha^{-1} h^{-1} (17 g CH_4 m^{-2} d^{-1}) and maximum methane oxidation rates of 23-53 m^3 CH_4 ha^{-1} h^{-1} (40-90 g CH_4 m^{-2} d^{-1}). In contrast, at soil temperatures of 1-5 °C, fractional oxidation of >80% may be attained only in cases of methane flux into the soil cover of <2 m^3 CH_4 ha^{-1} h^{-1} (3.4 g CH_4 m^{-2} d^{-1}) while maximum oxidation rates may remain below 10 m^3 CH_4 ha^{-1} h^{-1} (17 g CH_4 m^{-2} d^{-1}). In addition to temperature, atmospheric pressure may also have contributed to the different oxidation capacities observed at different measurement times. The highest landfill gas emissions observed in the present study coincided with a period of rapidly decreasing atmospheric pressure (−0.7 hPa h^{-1}) in November 2005. The incidence of an atmospheric pressure decrease of −0.7 hPa h^{-1} or steeper was 8% according to weather station data for 2007. In a passively vented landfill gas biofilter, gas flow and methane oxidation were strongly regulated by atmospheric pressure fluctuations (Gebert & Gröngröft 2006b). Similarly, micrometeorological measurements conducted at the Aikkala landfill have shown methane emissions and oxidation to be dependent on the rate of change in atmospheric pressure (Ettala et al. 2008).

The results show that it may be difficult to distribute the gas evenly across the top soil cover from the gas distribution pipes. However, the decrease in methane plus carbon dioxide emissions and increase in gas well gas concentrations in the valve adjustment test (IV) suggest that adjusting the valves in the gas well is a suitable method for distributing the landfill gas more evenly into the soil cover. Other options to increase overall oxidation would be the use of a thicker layer (e.g. 1 m) of a material suitable for methane oxidation, (Chapter 5.5.2), and to install more gas distribution pipes (Chapter 5.5.1).

5.5 Methane oxidation rates and optimization in landfill covers (III, IV)

5.5.1 Overall performances of the studied landfill cover systems in methane treatment

The estimates of methane oxidation per area unit and as a fraction of the total methane flux in the two biocovers studied provide information of value use in designing such systems. The performance of the studied landfill cover systems in treating methane appears to be similar or higher than that of the landfill covers studied previously. The present mean methane oxidation rates (1.09-23.0 g CH_4 m^{-2} d^{-1}; Table 15, Fig. 18) in the field studies (III, IV), excluding the January (III) and November (IV) measurements when oxidation was reduced, are similar or higher compared to the oxidation rates obtained with similar methane loading rates (1-30 g CH_4 m^{-2} d^{-1}; calculated from data presented by Chanton et al. 2009) in earlier field studies (Christophersen et al. 2000, Börjesson et al. 2001, Barlaz et al. 2004, Abichou et al. 2006, Stern et al. 2007) (Table 2). This indicates that methane oxidizing landfill covers may reduce methane emissions in a boreal climate, despite the possibility of decreased performance during winter. Of the studies included in Table 2 apparently only those by Huber-Humer (2004), Barlaz et al. (2004) and Stern et al. (2007) concern actual biocovers, i.e., landfill covers (test cells) with measures designed to enhance methane oxidation. A high oxidation rate was reported by Huber-Humer (2004) in an Austrian landfill with a 120 cm thick compost cover and a gas distribution layer.

The present results show that distributing the produced landfill gas evenly across the methane oxidation layer is crucial for obtaining high methane oxidation performance, particularly at low temperatures when the oxidation capacity is reduced. The successful oxidation in the outdoor lysimeter (>96% fractional oxidation from April to October) was apparently due to the relatively low gas production (1.1-16.1 g CH_4 m^{-2} d^{-1}), an even distribution of gas throughout the lysimeter surface area, sufficiently high temperatures in the top part of the lysimeter, and the suitability of the cover material for methane oxidation. In the study at the full-scale landfill (IV), mean methane flux into the cover (2.92-27.3 g CH_4 m^{-2} d^{-1}) was somewhat higher than in the outdoor lysimeter whereas a more striking difference between the two sites was observed in the distribution of gas fluxes across the surface area. The occurrence of high-emission points at the full-scale landfill probably explains in

TABLE 15 Selected methane oxidation and flux rates from field studies of landfill covers and biofilters.

Landfill/experimental setup	Cover material or type	Thickness (cm)[a]	Country	Flux[b]	Oxidation	F_{ox}[c] (%)	Reference
				$g\ CH_4\ m^{-2}\ d^{-1}$			
Outdoor landfill lysimeter	MBT residual	40	Finland	1.09-16.4	1.09-16.4	>96%	(II)
Outdoor landfill lysimeter	MBT residual	40	Finland	2.34-2.51	<0.51	<22%	(II)
Aikkala landfill	Sludge compost and peat mixture	50	Finland	100.0	90.1	>80	(IV)[d]
Aikkala landfill	Sludge compost and peat mixture	50	Finland	2.92-27.3	2.06-23.0	0-84	(IV)[e]
Ämmässuo landfill	Interim soil cover	n.r.	Finland	40.0-131	4.64-11.7	4-29	Laurila et al. 2005
Ameis landfill	Compost	120	Austria	111	111	96-100%	Huber-Humer 2004
Leon County landfill	Garden waste	60	Florida, U.S.	501	251	50	Bogner et al. 2005
Outdoor biofilters	Compost and polystyrene pellets; coarse sand	58-92	Florida, U.S.	251-501	203-242	49-80	Powelson et al. 2006
Outdoor biofilter	Leaf compost	35	Alberta, Canada	440	417-440	>95	Hettiarachchi 2005
Outdoor biofilter	Expanded clay pellets	100	Germany	1920	1920	100	Gebert et al. 2006a

n.r.=not reported

[a] Thickness of the layer intended to support methane oxidation.

[b] Methane flux into the cover layer or biofilter before any oxidation has occurred (and after gas extraction, if present).

[c] Fractional oxidation (% of methane flux).

[d] Measurements from April to October

[e] Measurement in January.

[f] Highest oxidation value of single measuring point.

[g] Range of means at different measuring times.

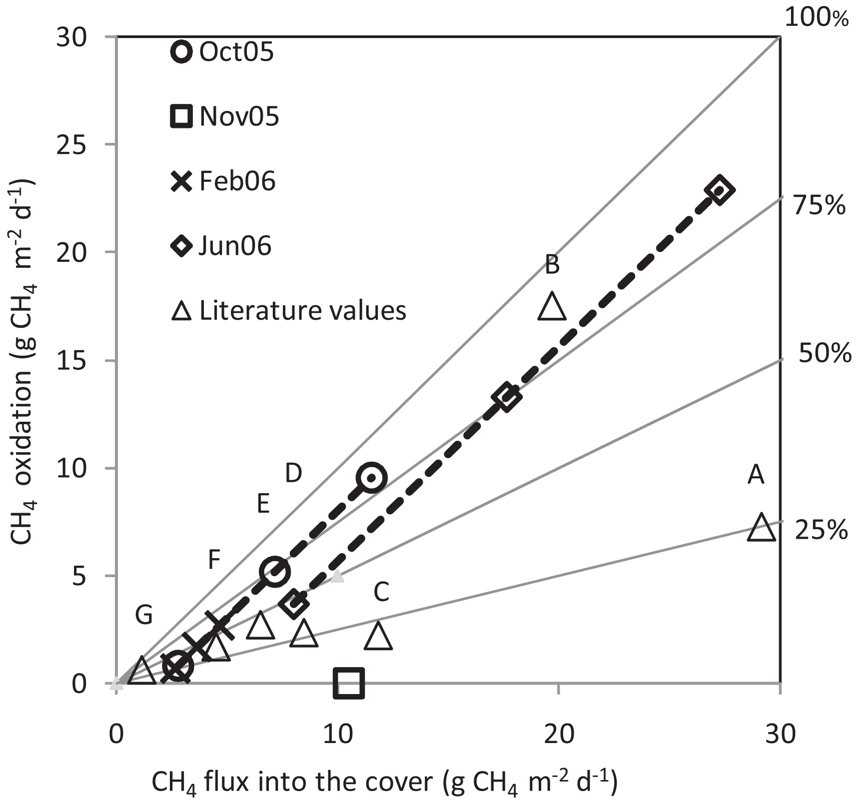

FIGURE 18 Mean methane fluxes and oxidation rates at the full-scale landfill at different measuring times and selected literature values (Table 2). The literature references are: Abichou et al. 2006 (A), Christophersen et al. 2001 (B), Stern et al. 2007 (C); Börjesson et al. 2001 (D); Christophersen et al. 2001 (E); Stern et al. 2007 (F); Barlaz et al. 2004 (G). The methane flux and oxidation rates for the present study are as data series of three points which present the minimum and maximum estimates of methane flux and oxidation, and their mean value. Reference lines for fractional oxidation are shown.

large part the lower mean methane oxidation compared to that observed in the outdoor lysimeter.

In landfills with no impermeable layer, gas can be distributed into the methane oxidation layer using gas distribution layers made from coarse material (Barlaz et al. 2004, Huber-Humer 2004 , Stern et al. 2007). The present results show that in landfills with an impermeable layer, uneven fluxes may occur when gas is distributed through a passive gas distribution system. The distribution of landfill gas and the overall methane treatment performance with the present type of cover system can potentially be improved by adjusting the gas fluxes (Chapter 5.4.) or by increasing the amount of distribution pipes. According to Martikkala & Kettunen (2003), in biocover test cells, successful gas distribution through the sealing layer was achieved using distribution wells and pipes or openings in the sealing layer. Their study area was smaller (test cells 10 x 20 m) and the density of the distribution pipe network (2000-2600 m ha^{-1}; calculated by the author from the data presented) higher than in the present landfill (IV) (300 m ha^{-1}).

5.5.2 Field methane oxidation capacity, thickness and temperature of oxidation layers

The oxidation rates measured at different seasons show that methane oxidation capacity of a 50-cm layer of MBT residual or sludge compost-peat mixture may be sufficient for the treatment of methane where the methane loading rate is ≤1.7 g CH_4 m^{-2} d^{-1} (10 m^3 ha^{-1} h^{-1} at STP) and when the soil temperature is above 10 °C (Chapter 5.4) (Table 16). If the temperature falls below 10 °C throughout a 50-cm thick cover layer, a significant decrease in oxidation rate is likely. At soil temperatures below 10 °C, this type of cover layer would be able to provide >80% fractional oxidation only in landfills with a methane loading of less than 1.7 g CH_4 m^{-2} d^{-1} (1 m^3 ha^{-1} h^{-1} at STP).

TABLE 16 Field methane oxidation capacities observed in the investigated methane oxidation layers at different temperature conditions.

Site/Material (month of measurement)	Air temp.	Temp. in cover layer	CH_4 flux with f_{ox}>80%[a]	Max. oxidation rate[b]
	°C	°C	g CH_4 m^{-2} d^{-1}	
Outdoor lysimeter				
MBT residual (Apr to Oct)	0 to 25	5 to 25	1.4-16.0[c]	1.4-16.0[c]
MBT residual (Jan)	-25	-5 to 9	<2.5[d]	0.6
Full-scale landfill				
Sludge compost/peat (Oct	12.8	12.8	19.9	40.1
Sludge compost/peat (Nov)	2	4.5	1.2	4.0
Sludge compost/peat (Feb)	-7	1.1	5.2	12.8
Sludge compost/peat (Jun)	25	20.9	90.1	90.1

[a] Highest methane flux at which fractional oxidation >80% was detected.

[b] In MBT residual, maximum value of the five-point mean rates at different measuring times; in sludge compost/peat, maximum value of the rates observed at individual measuring points.

[c] 96-100% of methane was oxidized, thus the maximum oxidation capacity may be higher than the methane loading rate in the present lysimeter.

[d] Exact value is not known because fractional oxidation was below 22%.

Thus the present results show that a 50-cm thick cover layer appears to be too shallow to provide a proper methane oxidation performance during the winter in landfills in a boreal climate (Table 16). A thicker cover layer (e.g., 100 cm) would probably maintain higher methane oxidation rates even in the winter. The ability of methane oxidizers to grow or increase their activity even at low temperatures (I) (Chapter 5.1) makes it possible for the distribution of methane-oxidizers to change along the vertical profile of the landfill cover as a response to changes in environmental conditions, such as oxygen concentration. Increased oxygen concentrations at low temperatures were observed in the present study in the laboratory columns (II), outdoor lysimeter (III) and full-scale landfill (IV), and in a previous column study (Kettunen et al. 2006). Increased oxygen concentrations at low temperatures are probably partly due to decreases in the rates of methane oxidation and respiration per soil gram, and thus a decrease in oxygen consumption per soil gram (Kettunen et al. 2006). As soil oxygen concentrations increase the methane-oxidizing layer may become thicker or move downwards as a result of microbial growth or activation in the lower part. Thus, in order to enable methane oxidation to occur deeper in the landfill cover, it is important to ensure oxygen supply to deeper layers by using cover materials with low respiratory oxygen consumption and high porosity, and avoiding excess compaction of the cover layer. High air-filled porosity, and thus low thermal conductivity, reduces the loss of heat from the landfill cover (Huber-Humer 2004).

Temperatures higher than those observed in the present field sites have been reported in other landfill covers and biofilters in boreal climatic conditions. The temperatures in methane oxidation layers (thickness 35-45 cm) in Finnish landfill test cells were 5-12 °C at the depth of 15-23 cm from January to March (Martikkala & Kettunen 2003, Leppänen et al. 2007). In a Canadian landfill gas biofilter (thickness of oxidation layer 1.5 m) with an influent flow of 37 g CH_4 m^{-2} d^{-1}, the temperature at the depth of 20 cm was mostly above 20 °C and the minimum temperature was 9.4 °C (Philopoulos et al. 2008). The higher temperatures compared to those at the present study sites may be explained by higher gas and heat fluxes from the waste fill into the oxidation layer, higher amounts of heat produced in methane oxidation owing to higher methane loading, and/or differences in the materials of the oxidation layers. Although the present results showed low temperatures and limited methane oxidation performance with 50-cm thick covers, such covers may be feasible also in a boreal climate if a higher temperature is maintained.

In both of the present field studies, the landfill covers were at their early stages of development (0-3 years from installation) and, at the full-scale landfill, vegetation was lacking at the time of three measurements. The development of vegetation may support methane oxidation, for example by maintaining a more favourable moisture content (Chapter 5.2) and by producing root exudates which enhance microbial activity (Scheutz et al. 2009a). On the other hand, plants with hollow stems may act as a preferential flow path, thus increasing gas emissions and reducing methane oxidation (Scheutz et al. 2009a). In the outdoor lysimeter, the recirculation of leachate may have decreased oxidation (Chapter 5.3.2). Although fractional oxidation was maintained at a high level (>96%) during the recirculation period, it is possible that leachate affected methane oxidation even after that period and contributed to the decreased oxidation in wintertime.

The utilization of landfill cover for the biotic treatment of landfill gas may bring cost savings if, e.g., the installation of a gas extraction system and flare can be avoided. Although biocovers are often assumed to be suitable for landfills with low gas flux rates (Huber-Humer et al. 2008), the present findings of reduced oxidation capacities of 50-cm thick biocovers at low temperatures in landfills with low gas flux rates, needs to be taken into account. In some cases it may be more advantageous to use biofilters (Zeiss 2006, Gebert & Gröngröft 2006a, Philopoulos et al. 2008) or biowindows (Huber-Humer et al. 2008, Scheutz et al. 2009a, 2009b) where a higher temperature and favourable conditions for methane oxidation can be more easily maintained. Thus, when choosing biological landfill gas treatment applications, the dependence of methane oxidation capacity on temperature, the predicted methane loading and the availability of appropriate landfill cover materials have to be evaluated along with the benefits, drawbacks, and costs of each application.

5.6 Field quantification of methane oxidation (III, IV)

5.6.1 Evaluation of gas emissions at the landfill level

The reliability of estimations of the gas emissions at the level of the whole landfill using flux chamber measurements depends on the temporal and spatial variation of the gas emissions, on the numbers of measuring points and measurement times, and on the prevailing conditions (such as soil temperature and atmospheric pressure trend) during the measurements with respect to the total variation in those conditions. The occurrence of a few high-emission points in the studied landfill (IV) shows that in landfills with this type of gas treatment and cover system, using a higher measurement density across the landfill and/or the use of an above-ground methods of measurement such as plume tracer or micrometeorological methods (see Chapter 1.4), could provide a better estimate of the emissions from the whole landfill. Flux chamber measurements may be necessary, especially if the performance required of the landfill gas treatment system is not achieved, to localize possible high-emission points and to evaluate the need for adjustments of gas distribution. Moreover, the fact that falling atmospheric pressure may increase gas emissions and decrease methane oxidation (IV, Gebert & Gröngröft 2006a, 2006b, Ettala et al. 2008) indicates that frequent measurements are needed to obtain temporally representative data and that the rate of change in atmospheric pressure during each measurement should be recorded to evaluate the representativeness of the measurements.

5.6.2 Quantifying methane oxidation in situ using the mass balance of methane and carbon dioxide

In the present study, the methane flux rate into the landfill cover and oxidation rate in the cover were estimated by using a mass balance calculation method.

The emission and pore gas concentration values of methane and carbon dioxide, and the estimation of minimum and maximum rates of carbon dioxide production from respiration (values from laboratory assays) and from methane oxidation (values from literature) were used to calculate the minimum and maximum rates of methane flux into the cover and of methane oxidation (Chapter 3.8.1). Respiratory carbon dioxide production in the cover adds to the total carbon dioxide emission from a landfill, whereas methane oxidation may reduce the volume of gas flowing through the landfill cover due to the retention of methane-derived carbon in soil (Chapter 1.2). In both studies (III, IV), the minimum values obtained for methane flux into the cover and for methane oxidation, which were based on maximum respiration, are likely to be underestimates of the real level. Correspondingly, the maximum estimates of methane flux into and oxidation in the soil cover, which are based on zero respiration, are likely to exceed the real level. The accuracy of the estimates of methane flux into the soil cover and of methane oxidation obtained by the present method increases, i.e., the difference between minimum and maximum estimates decreases, as the methane-to-carbon dioxide ratio of the gas emission decreases on account of methane oxidation or respiration. The estimates are more accurate when the proportion of estimated respiration over the total emission of carbon dioxide is low compared to the situation when this proportion is high. Thus this method is expected to give more accurate results for landfills with high methane loading into the cover compared to those with low methane loading.

This method enables quantitative information on methane oxidation (oxidation rate per area unit or fractional oxidation over the methane flux into the cover) to be derived from landfill gas emission and pore gas composition measurements, which are often performed in routine monitoring at the different stages of landfill lifespan. In addition, an estimate of respiration is needed. Although the methane and carbon dioxide mass balance approach to the quantification of methane oxidation has been criticized (e.g., Scheutz et al. 2009a) it merits further research, particularly on the comparison of the methane flux and oxidation rates obtained in parallel with the isotope fractionation method, estimation of possible error sources such as the production of carbon dioxide from root respiration, the solubility of gases in soil water and methods to determine respiration in field conditions.

Determination of respiration

In both of the present field sites, the contribution of respiration from organic cover materials to carbon dioxide emission and to total gas emissions appeared to be significant as indicated by the correlation between the temperature in the cover layer and methane plus carbon dioxide emissions (III, IV). Two different ways to estimate respiration were used in the two field studies because of differences in the studied systems (Chapter 3.8.1). In the study at the full-scale landfill, the measurement of carbon dioxide production in laboratory assays was used for the calculation of respiratory carbon dioxide production in the 50-

cm-thick soil. The estimated maximum respiration exceeded actual respiration at many measuring points (Chapter 3.8.1) (IV). This was the case even for the only measurement time (June) with some plant cover present, suggesting that the carbon dioxide produced by root respiration was included in the maximum respiration estimates. In the outdoor lysimeter, aerobic respiration may have occurred over a profile thicker than that in the full-scale landfill (50 cm) and plant root respiration may also have contributed to the carbon dioxide emission. Therefore, in the outdoor lysimeter, maximum respiration was calculated, instead of using laboratory assays, by subtracting the carbon dioxide emission measured in the middle of winter from the carbon dioxide emissions at each measurement time.

Determination of the storage of methane-derived carbon

The storage of carbon derived from methane in biotic oxidation in the cover layer was theoretically estimated for the purpose of calculating methane production and oxidation. The storage of methane-derived carbon is probably influenced by the growth efficiency of methanotrophs, i.e., the efficiency with which methanotrophs incorporate carbon from the consumed methane into their biomass. Growth efficiencies for pure methanotroph cultures were 0.31-0.49 when methane was used as the carbon source (Leak & Dalton 1986). The studies evaluating carbon conversion during methane oxidation in soils (reviewed by Huber-Humer 2004) show that 15-80% of the methane-derived carbon was oxidized to carbon dioxide while 8-70% was retained in soil (apparent growth efficiency 0.08-0.70). For other soil microbes, growth efficiency has varied between 0.14 and 0.77 (reviewed by Herron et al. 2009). For aquatic microbes (Hall & Cotner 2007) and for pure cultures of *E. Coli* (Cotner et al. 2006), growth efficiency has shown a decrease with increasing temperature. Assuming that the same relationship with temperature applies to soil methanotrophs, the fraction of methane-derived carbon stored in the landfill cover soil may increase along with decreasing temperature. Moreover, multicarbon compounds synthesized by methanotrophs from methane-derived carbon can be utilized and mineralized to carbon dioxide by other soil microbes (Watzinger et al. 2007). Thus temporal changes in carbon storage are likely, which means that field studies are needed to evaluate the amount and duration of the net storage of methane-derived carbon in landfill covers in different conditions. Such field data could give a more narrow range for the dissimilation factor (f_{diss}) for the mass balance calculations compared to the range used in the present study (0.3-1.0) and thus result in more accurate estimates of methane flux and oxidation.

6 CONCLUSIONS

This study aimed to evaluate the feasibility of methane-oxidizing landfill biocovers as a technology for mitigating methane emissions from boreal landfills and to produce information for the design, operation, and monitoring of methane-oxidizing landfill covers in boreal conditions. The results show that methane-oxidizing biocovers offer a feasible method to reduce the greenhouse gas emissions in landfills in a boreal climate. This is indicated by the occurrence of methane oxidation at temperatures as low as 1-2 °C in laboratory batch and column assays, in an outdoor lysimeter, and in a landfill cover. However, the influence of low ambient temperatures on the temperature in the landfill cover and consequently on the methane oxidation rate have to be considered in the design of biocovers.

The response of methane oxidation to temperature was high (Q_{10} values 6.5-8.4 in the present study) when studied in batch assays with high initial methane (e.g., >1%) concentrations and with adequate moisture. In such conditions, methane oxidation is mainly dependent on enzyme activity. At the soil layer level the effect of temperature on the methane oxidation rate is generally lower than the effect at the enzyme level (shown in batch assays), as suggested by the methane oxidation rates observed at different temperatures in the laboratory column assays, in the outdoor lysimeter and at a full-scale landfill. This is due to the fact that, at the soil layer level, methane oxidation is limited by other factors than enzymatic activity, such as the availability of methane and oxygen. Moreover, the increase in the oxidation rate in the batch assays over time, including at 1 °C indicates that methane-oxidizers are able to grow or be activated at low temperatures. Thus the vertical distribution or species composition of methane-oxidizers may change along with changes in ambient conditions, such as oxygen concentration, potentially increasing the methane oxidation rate at low temperatures.

The batch assays showed that in dry soil (<33% WHC) methane oxidation is inhibited due to microbial water stress, while at high moisture methane oxidation is reduced due to decreased supply of methane and oxygen to methane-oxidizing microorganisms. The optimal moisture for methane oxidation in the batch assays was higher at lower temperatures. In field conditions, the effect of moisture on methane oxidation is influenced, in addition to water stress and the supply of gases, by air porosity, which affects the transport of gas through the soil.

MBT residual is a suitable material for promoting methane oxidation in landfill covers and showed, in laboratory columns, methane oxidation rates similar to or higher than the methane loading typically found in landfill covers. The methane oxidation potentials determined in the batch assays with samples taken from the columns were among the highest reported in the literature, indicating a high number of methanotrophs. In an outdoor lysimeter filled with MBT residual and containing a cover layer made from the same MBT residual, measurements showed that 96-100% of the methane produced was oxidized between April and October (air temperature 0-25 °C), while reduced oxidation (<22% oxidation) was observed at the coldest time of the year (January, air temperature -25 °C).

A biological gas treatment system including a passive gas distribution system integrated in a multilayer cover may be a feasible option for gas treatment at landfills where a water-impermeable layer is required; however, the occurrence of high methane loading rates at some areas may reduce the methane oxidation performance. Thus arranging an even distribution of gas into the oxidation layer appears to be particularly important at sealed landfills, including those with a low rate of gas production, to obtain a high rate of methane oxidation.

In the field sites studied, the ambient temperature was below 10°C for approximately six months in the top 50 cm layer (temperature range <0 °C to >20 °C over the year), and decreased methane oxidation rates were observed during the wintertime even in places where the methane loading rates were relatively low compared to the methane oxidation rates obtained in laboratory studies with the same materials. Thus, the methane oxidation performance of a 50-cm-thick oxidation layer is likely to decrease in wintertime in boreal conditions. A thicker oxidation layer (e.g., 100 cm) would probably provide a higher methane oxidation performance in wintertime, provided that the oxygen supply is sufficient and other parameters important for methane oxidation are adequate.

The quantification of methane oxidation at a whole landfill level is difficult due to spatial and temporal variation in gas fluxes and due to difficulty in determining the methane loading rate. The differences in gas fluxes measured across the present landfill indicate that above-ground emission measurement methods should be used along with flux chamber measurements to obtain more reliable whole landfill emission and oxidation data. Decreasing atmospheric pressure may increase emissions, and decrease oxidation indicating that frequent measurements are needed to obtain temporally representative data. The in situ methane loading and oxidation in the landfill cover were quantified by a methane and carbon emission mass balance method using the emission measurements by flux chamber, pore gas composition, and an estimated rate of respiratory carbon dioxide production. The storage of methane in the cover layer by biotic oxidation can be theoretically accounted for in the calculations. This method may have a relatively high uncertainty range in landfills with low gas production, since the respiration from organic cover materials may contribute significantly to the total carbon dioxide emission. Despite the uncertainty, this method enables estimation of methane oxidation, both as rate per area unit and as a fraction of the methane flux into the cover, from the emission measurements and landfill gas composition measurements which are often required in routine monitoring at different stages of the landfill lifespan.

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YHTEENVETO (RÉSUMÉ IN FINNISH)

Metaanin biotekninen hapettaminen kaatopaikoilla viileässä ilmastossa

Kaatopaikoilla orgaanisen jätteen biohajoamisessa muodostuva metaani on globaalisti merkittävä kasvihuonekaasupäästöjen lähde. Kaatopaikkametaani vastaa nykyään noin 7 − 11% ihmisen toiminnan aiheuttamista metaanipäästöistä. Kaatopaikoilta aiheutuvia metaanipäästöjä voidaan vähentää rajoittamalla kaatopaikoille sijoitettavan jätteen määrää ja esikäsittelemällä jäte ennen kaatopaikkasijoitusta metaanintuottopotentiaalin pienentämiseksi. Näihin tavoitteisiin pyritään mm. Euroopan Unionin tasolla. Metaanin muodostuminen kaatopaikoilla tulee kuitenkin jatkumaan vanhoilla kaatopaikoilla, uusilla esikäsitellyn jätteen kaatopaikoilla sekä useissa maissa edelleen yleisillä esikäsittelemättömän jätteen kaatopaikoilla. Kaatopaikoilla muodostuvaa metaania voidaan ottaa talteen ja hyödyntää sähkön, lämmön tai liikennepolttoaineen tuotannossa. Kuitenkin vain osa kaatopaikan elinkaaren aikana muodostuvasta metaanista saadaan talteen, koska suuri osa metaanista muodostuu jo kaatopaikan täyttövaiheessa, jolloin kaasun talteenottoa ei ole ja/tai talteenottoaste on alhainen. Lisäksi kaasua talteen ottavalla suljetullakin kaatopaikalla osa metaanista kulkeutuu kaatopaikan pintakerrokseen ja edelleen ilmakehään. Osa kaatopaikan pintakerrokseen kulkeutuvasta metaanista hapettuu mikrobiologisesti hiilidioksidiksi ja biomassaksi, mikä pienentää kaatopaikalta ilmakehään pääsevän kaasun kasvihuonevaikutusta. Metaanin mikrobiologista hapettumista voidaan optimoida kontrolloimalla kaatopaikan pintakerroksen ominaisuuksia ja olosuhteita, mukaan lukien kaasun virtausta pintakerrokseen.

Tämän työn tavoitteena oli arvioida metaania hapettavan pintakerroksen soveltuvuus metaanipäästöjen vähentämiseen kaatopaikoilla viileässä ilmastossa ja tuottaa tietoa metaania hapettavan pintakerroksen suunnittelua, käyttöä ja seurantaa varten. Lämpötilan ja materiaalin kosteuden vaikutusta metaanin hapettumiseen tutkittiin laboratoriokokein ja kenttämittauksin. Mekaanis-biologisesti käsitellyn yhdyskuntajätteen soveltuvuutta käytettäväksi kaatopaikan metaania hapettavassa pintakerroksessa tutkittiin laboratoriokokeissa sekä kenttälysimetrissä. Lisäksi metaanin hapettamista tutkittiin suljetulla täyden mittakaavan kaatopaikalla, jossa oli Euroopan Unionin kaatopaikkadirektiivin mukainen monikerroksinen pintarakenne, johon oli yhdistetty passiivinen kaasun keräys- ja jakojärjestelmä sekä metaanin hapettamiseen suunniteltu pintakerros.

Neljä vuotta kaatopaikalla olleessa pintamaassa metaanin hapettuminen nopeutui lämpötilan kasvaessa (Q_{10}-lämpötilakertoimet olivat 6,5 – 8,4 lämpötilavälillä 1 − 19 °C), kun maankosteus oli ≥33% vedenpidätyskapasiteetista, kun taas metaanin hapettuminen oli hyvin vähäistä, kun kosteus oli 17% vedenpidätyskapasiteetista. Metaania hapettui panoskokeissa alhaisessakin lämpötilassa (0,2 – 4,3 µg CH_4 $g_{\text{kuiva-aine}}^{-1}$ h^{-1} 1 − 6 °C:ssa). Panoskokeissa metaanin lähtöpitoisuuden ollessa korkea (esim. 8 til.-%) ja kosteuden ollessa sopiva, metaanin hapettumisnopeus riippui lähinnä entsyymiaktiivisuudesta. Toisaalta laboratoriolysimetrikokeet sekä kenttälysimetrissä ja kaatopaikalla havaitut metaaninhapetusnopeudet osoittavat, että maakerroksen mittakaavassa metaanin hapettumista rajoittavat tyypillisesti muut tekijät, kuten metaanin ja hapen saatavuus, minkä johdosta metaanin hapettumisen riippuvuus lämpötilasta on maakerroksen mittakaavassa vähäisempää kuin panoskokeissa. Metaaninhapetusnopeuden lisääntyminen panoskokeissa 1°C:ssa osoittaa, että metaania hapettavat mikrobit pystyvät kasvamaan tai aktivoitumaan alhaisessakin lämpötilassa. Tämän johdosta metaania hapettavien mikrobien syvyysjakauma ja/tai lajikoostumus voivat muuttua ympäristöolosuhteiden, esimerkiksi happipitoisuuden, muuttuessa, mikä voi lisätä metaanin hapettumisnopeutta alhaisessa lämpötilassa.

Panoskokeet osoittivat, että kuivassa maassa (kosteus <33% vedenpidätyskapasiteetista) metaanin hapettuminen inhiboituu mikrobien vedenpuutteen johdosta, kun taas maankosteuden ollessa korkea metaanin hapettuminen vähenee metaanin ja hapen saatavuuden mikrobeille huonontuessa. Optimaalinen kosteus metaanin hapettumiselle panoskokeissa oli korkeampi alhaisissa lämpötiloissa. Kenttäolosuhteissa kosteuden vaikutus metaanin hapettumiseen riippuu myös maan ilmatilasta (vedestä vapaa huokostila), joka vaikuttaa kaasujen kulkeutumiseen maassa.

Mekaanis-biologisesti käsitelty yhdyskuntajäte osoittautui metaanin hapettumiselle suotuisaksi materiaaliksi. Mekaanis-biologisesti käsitellyssä yhdyskuntajätteessä laboratoriolysimetrikokeissa metaaninhapetusnopeus (12,2 – 82,3 g CH_4 m^{-2} d^{-1} 2 − 25°C:ssa) oli samaa luokkaa tai korkeampi kuin tyypilliset metaanikuormitukset (pintakerrokseen tuleva metaanivuo) kaatopaikoilla. Laboratoriolysimetreistä otetuilla näytteillä havaittiin panoskokeissa metaaninhapetuspotentiaali (korkeimmillaan 104 µg CH_4 g_{dw}^{-1} h^{-1} 5 °C:ssa ja 581 µg CH_4 g_{dw}^{-1} h^{-1} 25 °C:ssa), joka on suurimpia kirjallisuudessa raportoituja arvoja. Kenttälysimetrissä, jossa sekä jätekerros että pintakerros koostuivat mekaanisbiologisesti käsitellystä yhdyskuntajätteestä, >96% muodostuneesta metaanista (<16 g CH_4 m^{-2} d^{-1}) hapettui huhtikuun ja lokakuun välisenä aikana, kun taas tammikuussa hapettuminen oli vähäistä (<0,6 g CH_4 m^{-2} d^{-1}, <22% muodostuneesta metaanista).

Biologinen kaasunkäsittely- ja passiivinen kaasunjakojärjestelmä integroituna monikerroksiseen pintarakenteeseen voi olla toimiva vaihtoehto kaasun käsittelyyn kaatopaikoilla, joilla on vettä läpäisemätön pintakerros. Tutkitulla kaatopaikalla pintakerrokseen tulevasta keskimääräisestä metaanivuosta (2,92 – 27,3 g CH_4 m^{-2} d^{-1}) neljällä mittauskerralla (8 kk aikavälillä), ≥25% hapettui loka- ja helmikuussa, 0% marraskuussa ja ≥46% kesäkuussa; jokaisella mittauskerralla muutamassa mittauspisteessä suuri metaanivuo heikensi keskimääräistä hapettumista. Tästä syystä kaasun tasainen jakaminen hapetuskerrokseen on erityisen tärkeää metaanin hapettumisen optimoimiseksi kaatopaikoilla, joilla on vettä läpäisemätön pintakerros, silloinkin, kun kaasuntuotto on alhainen.

Tutkituissa kenttäkohteissa ylimmässä 50 cm kerroksessa lämpötila oli alle 10°C noin 6 kk/v (lämpötilan vuosivaihtelu <0 °C:sta >20 °C) ja talvella metaaninhapetusnopeus oli alhainen, vaikka metaanikuormitus oli pienempi kuin samankaltaisilla pintakerrosmateriaaleilla laboratoriokokeissa havaitut metaaninhapetusnopeudet. Metaaninhapetuskerroksen korkeuden ollessa 50 cm metaaninhapetuskapasiteetti pinta-alayksikköä kohden siis pienenee talvella. Korkeampi (esim. 100 cm) metaaninhapetuskerros todennäköisesti hapettaisi enemmän metaania erityisesti talvella edellyttäen, että hapen saatavuus on riittävä ja muut metaanin hapettumiselle tärkeät parametrit ovat soveltuvalla tasolla.

Tulosten perusteella kaatopaikan metaania hapettavat pintakerrokset näyttävät toimivilta metaanipäästöjen vähentämisessä viileässä ilmastossa. Kaatopaikan pintakerroksen lämpötilan vaihtelu ja sen vaikutus metaanin hapettumiseen tulee huomioida pintakerroksen suunnittelussa. Metaanin hapettumisen maksimoimiseksi pintakerroksen metaanikuormituksen tulisi olla alueellisesti tasainen, hapetuskerroksen korkeuden tulisi olla riittävä ja pintakerrosmateriaalin ominaisuuksien metaanin hapettumiselle sopivia; erityisesti hapen saatavuuteen ja lämmön säilyvyyteen tulee kiinnittää huomiota.

Metaanin hapettumisen kvantifiointi koko kaatopaikan tasolla on vaikeaa johtuen kaasuvuon alueellisesta ja ajallisesta vaihtelusta sekä metaanikuormituksen määrittämisen vaikeudesta. Tutkitulla kaatopaikalla havaitut alueelliset vaihtelut kaasuvuossa osoittavat, että kaatopaikkakaasun päästöjä tulisi mitata virtauskammiomenetelmän ohella myös esim. merkkiaine- tai mikrometeorologisin mittauksin, joilla voidaan saada luotettavampi arvio koko kaatopaikan päästöistä ja metaanin hapettumisesta. Nopeasti laskeva ilmanpaine voi lisätä päästöjä ja vähentää hapettumista, mikä osoittaa ajallisesti edustavan tiedon saamiseksi tarvittavan useita mittauksia. Metaanikuormitus ja hapettumisnopeus kaatopaikan pintakerroksessa määritettiin metaani- ja hiilidioksidimittauksiin perustuvalla massatasemenetelmällä metaani- ja hiilidioksidivuon virtauskammiomittausten, huokosilmakoostumuksen, sekä arvioidun pintakerrosmateriaalista aiheutuvan hiilidioksidintuoton perusteella. Metaaniperäisen hiilen säilyminen kaatopaikan pintakerroksessa metaanin hapettumisen vaikutuksesta voidaan teoreettisesti huomioida massataselaskennassa. Tällä metaanin ja hiilidioksidin massataseeseen perustuvalla menetelmällä laskettuna metaanikuormituksen ja hapettumisen arvioiden epävarmuus on suhteellisen suuri kaatopaikoilla, joilla kaasuntuotto on pieni, koska orgaanisten pintakerrosmateriaalien hiilidioksidintuotto voi olla merkittävää suhteessa kaatopaikan kokonaishiilidioksidintuottoon. Tämä menetelmä kuitenkin mahdollistaa metaanin hapettumisen arvioinnin sekä pinta-alayksikköä kohden että suhteellisena osuutena metaanivuosta kaatopaikkojen seurannassa tyypillisesti vaadittavien kaasupäästö- ja pitoisuusmittausten avulla.

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ORIGINAL PAPERS

I

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II

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by

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III

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IV

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