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Microbial methane oxidation processes and technologies for mitigation of landfill gas emissions

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Landfill gas containing methane is produced by anaerobic degradation of organic waste. Methane is a strong greenhouse gas and landfills are one of the major anthropogenic sources of atmospheric methane. Landfill methane may be oxidized by methanotrophic microorganisms in soils or waste materials utilizing oxygen that diffuses into the cover layer from the atmosphere. The methane oxidation process, which is governed by several environmental factors, can be exploited in engineered systems developed for methane emission mitigation. Mathematical models that account for methane oxidation can be used to predict methane emissions from landfills. Additional research and technology development is needed before methane mitigation technologies utilizing microbial methane oxidation processes can become commercially viable and widely deployed.

Keywords: Methane oxidation, methane emission, landfill gas, methanotrophs, landfill covers, biofilters, biocovers, wmr 08–0146

Introduction

Landfill gas (LFG) is produced by microbial anaerobic degradation of the organic fraction in waste disposed in landfills. The biodegradable organic material in waste mostly includes paper, animal and vegetable matter, and garden waste. The main components in LFG are methane (CH_4: 55–60% v/v) and carbon dioxide (CO_2: 40–45% v/v). The production of the principal LFG components occurs through three initial sequential phases followed by a phase characterized by stable CH_4 and CO_2 production (Christensen *et al.* 1996). The production of LFG will continue until the majority of the organic material in the waste has been degraded, which can take several decades.

Both CH_4 and CO_2 are classified as greenhouse gases (i.e. gases that have a high capacity of absorbing infrared radia-

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tion reflected from the earth's surface). CH_4 has the second largest radiative forcing of the long-lived greenhouse gases after CO_2 (Forster *et al.* 2007). CH_4 is however a more powerful greenhouse gas than CO_2. Over a time period of 100 years, the global warming potential for CH_4 is 25 because of its stronger molar absorption coefficient for infrared radiation and its longer residence time in the atmosphere (Solomon *et al.* 2007). The global atmospheric concentration of CH_4 has increased from a pre-industrial value of about 715 to 1732 parts per billion (ppb) in the early 1990s, and was 1774 ppb in 2005 (IPCC 2007). The atmospheric concentration of CH_4 in 2005 far exceeded the natural range of the last 650 000 years (320 to 790 ppb) as determined from ice cores (IPCC 2007). Current atmospheric CH_4 levels are due to continuing anthropogenic CH_4 emissions accounting for more than 60% of the total CH_4 budget (Denman *et al.* 2007). The current contribution of CH_4 to climate change forcing is 18% of the total radiative forcing by all long-lived greenhouse gases (Forster *et al.* 2007).

Landfills, in particular, have been found to be a principal source of CH_4 production. Worldwide, the CH_4 emission from the waste sector is about 18% of the global anthropogenic CH_4 emission (Bogner *et al.* 2007). In the United States, the second largest anthropogenic CH_4 emission originates from landfills, making up 23% of the total anthropogenic CH_4 emission. In 2007, US landfill CH_4 emissions were approximately 6329 Gg (US EPA 2009). In Europe, landfills are reported as the second largest source of anthropogenic CH_4 (22%) with an estimated CH_4 emission of 3373 Gg from waste disposal in 2006 (EEA 2008). Worldwide, landfills have been estimated previously to release between 35 and 69 Tg $year^{-1}$ of CH_4 to the atmosphere, out of an estimated annual global emission of approximately 600 Tg CH_4 (Denman *et al.* 2007, Bogner *et al.* 2007). It is important to note that these projections are based on estimated rates of CH_4 production applied to national statistics for landfilled refuse and not on field emission measurements.

As recognition of global climate change has increased, the contribution of LFG emissions to anthropogenic greenhouse effects has been seriously considered in many countries. LFG extraction and utilization plants have been made mandatory at all new waste disposal sites. At the same time, research has focused increasingly on development of low-cost technologies that limit LFG gas release from existing landfills where gas collection systems have not been implemented and/or are not economically feasible (Barlaz *et al.* 2004, Dever *et al.* 2007, Kjeldsen *et al.* 2007, Stern *et al.* 2007). Much of that research has focused on biocovers designed to optimize and sustain CH_4 oxidation as a cost-effective technology for controlling emissions from waste disposal sites (Bogner *et al.* 2007).

Over the last two decades research has focused on understanding fundamental processes controlling CH_4 oxidation in landfill settings. Laboratory experimental designs have evolved from simple batch experiments for determining CH_4 oxidation rates and short-term responses to environmental factors to more advanced column set-ups that more closely resemble the dynamic behaviour in landfill settings and thereby allow long-term performance to be studied. More recently, research has focused on methods to increase CH_4 oxidation by improving landfill covers by adding organic-rich materials such as sludge and composts. Currently, field investigations on the performance of pilot- and full-scale biocovers or biofilters are ongoing in several countries (Barlaz *et al.* 2004, Abichou *et al.* 2006a, b, Gebert & Gröngröft 2006a, b, Zeiss 2006, Dever *et al.* 2007, Kjeldsen *et al.* 2007, Stern *et al.* 2007). Along with intensive laboratory studies on CH_4 oxidation, field methods for measuring gas emissions from landfill sites have been developed. For example, tracer techniques for whole-site measurements are being developed, as well as stable isotope techniques for determination of *in situ* oxidation rates. Future full-scale implementation of biocovers on landfills requires reliable and readily available emission measurement techniques in order to ensure proper efficiency of the biocover system. Green accounting of whole-site emissions and the expected forthcoming establishment of a cap-and-trade CO_2-credit system in the United States further underscores the need for accurate landfill CH_4 measurement technologies.

In addition to CH_4, LFG contain numerous volatile organic compounds (VOCs) including halogenated and aromatic hydrocarbons, sulfur and oxygen (O_2)-containing compounds (Rettenberger & Stegmann 1996, Allen et al. 1997, Eklund et al. 1998). It has been shown that VOCs disposed in landfills may escape to the atmosphere via diffusion across the landfill cover (Kjeldsen & Christensen 2001). Emission of VOCs from landfills may pose a risk to human health, contribute to global warming, and in the case of chlorofluorocarbons, can contribute to ozone depletion (Wallington et al. 1994, Christensen & Kjeldsen 1995). In addition to mitigating methane emissions, it has been demonstrated that properly designed landfill cover materials can degrade a wide range of VOCs including halogenated hydrocarbons and aromatics (Kjeldsen *et al.* 1997, Scheutz *et al.* 2003, 2004, 2008, 2009, Scheutz & Kjeldsen 2005).

The aim of this paper is to review the state-of-the-science regarding microbial CH_4 oxidation in natural environments and landfills, and focuses on process understanding, case studies, and modelling. The review includes seven sections excluding the introduction. First, a mass balance approach is introduced to illustrate the relative contributions of CH_4 oxidation and other processes governing the fate of CH_4 in landfills. The primary groups of micro-organisms involved in the microbial CH_4 oxidation are described next, followed by a detailed overview of the oxidation process in soils and waste materials including the factors controlling the oxidation rate. Hereafter, experiences with engineered systems for mitigating landfill CH_4 emissions relying on microbial CH_4 oxidation are presented. The next section reviews LFG measurement methods and results. The last two sections describe models; the first section reviews mass balance models used for estimating LFG emissions for national greenhouse gas inventories, while the last section reviews mathematical models that

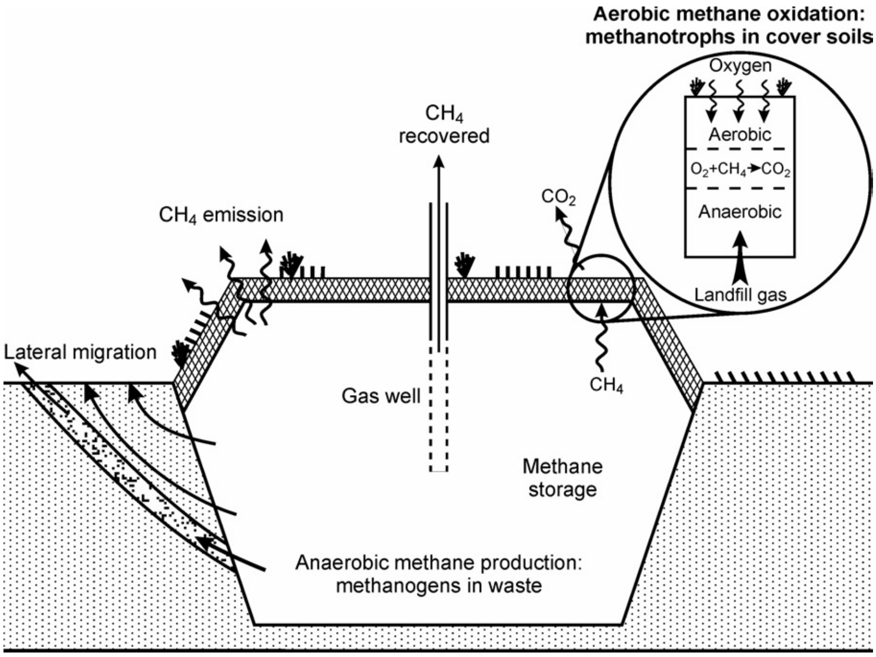

Fig. 1: Landfill methane mass balance.

simulate LFG fate and transport processes in soil covers, including oxidation processes.

Landfill CH_4 mass balance and controlling processes and factors

Many processes other than microbial CH_4 oxidation affect the landfill CH_4 mass balance and the quantities of CH_4 emitted from landfills. To effectively engineer microbial CH_4 oxidation processes at a landfill (see section entitled 'The process of CH_4 oxidation'), it is necessary to understand other processes affecting the CH_4 mass balance. These processes are summarized in Figure 1. The CH_4 mass balance (Bogner & Spokas 1993) is described by the relationship:

$$\begin{aligned} CH_4 \text{ production} = {} & CH_4 \text{ recovered} + CH_4 \text{ emitted} \\ & + \text{Lateral } CH_4 \text{ migration} \\ & + CH_4 \text{ oxidized} + \Delta CH_4 \text{ storage} \end{aligned}$$

(all units = mass t^{-1}; from Bogner & Spokas 1993)

The factors affecting the transport processes of LFG leading to gas emission or migration can be divided into three classes: Meteorological conditions (barometric pressure, precipitation, temperature, wind), soil/cover conditions (cracks, fissures, permeability, diffusivity, porosity, moisture content, organic content, CH_4 oxidation capacity) and waste and landfill conditions (gas production rate, internal barriers, gas vents, lateral migration area) (Kjeldsen 1996). Of particular importance are spatial and temporal variations in soil physical and chemical properties that influence soil gas transport and microbial activity (composition, depth, moisture, temperature, aeration status). Therefore, landfill CH_4 emission and migration is controlled by a combination of engineering design decisions, site-specific management practices, and natural ecological/climatic processes. The following sections present a short description of the most important factors – other than CH_4 oxidation – affecting LFG emission and migration. The CH_4 oxidation process is discussed in the remainder of the paper.

CH_4 production

The production of CH_4 depends on several factors: the landfilled waste volume, content of organic waste fractions and the degradability of these fractions, waste age and environmental factors (temperature, moisture content, nutrients, inhibiting compounds, etc.). LFG generation is modelled based on information on waste volumes, ages, and compositions, and is often based on first-order gas generation equations (Golder Associates 2002, US EPA 2005, Scharff & Jacobs 2006). It is not the aim of this paper to review the science of LFG generation; several reviews give detailed descriptions of this subject (Christensen & Kjeldsen 1989, Barlaz *et al*. 1990, Christensen et al. 1992, 1996).

CH_4 recovery

CH_4 is recovered from many landfills by installing a gas extraction system and utilizing the gas for energy purposes in a combustion engine (Willumsen 1996). In some cases the gas is flared in gas flares where the CH_4 is thermally oxidized into CO_2. The efficiency of gas recovery systems is typically in the range of 50–60% (Börjesson *et al*. 2007, 2009) with the remaining gas escaping to the atmosphere. However, recently it has been shown that a landfill designed with effective, state-of-the-art methane controls including a low-permeability liner, a low-permeability cover, and methane extraction system can achieve LFG recoveries up to 97% (Spokas *et al*. 2006). LFG recoveries in the range of 92 to 97% were demonstrated via CH_4 mass balance for nine landfill cells at three French sites

(Spokas *et al*. 2006). A combination of intensive field measurements, laboratory studies, and modelling was used to demonstrate the high rates of CH_4 recovery at the French sites. For example, it was shown that only about 1–2% of the CH_4 production escapes uncontrolled and about 97% is recovered with an active gas extraction system at Montreuil-sur-Barse in eastern France (near Troyes). At Lapouyade (near Bordeaux, in southwestern France), a minimum of 94% of the CH_4 production was recovered at two cells with engineered gas recovery. On a third cell without gas recovery about 92% of the CH_4 production was emitted (Spokas *et al*. 2006).

CH_4 emission

The major mechanisms for emissions of CH_4 from landfill sources include diffusion, advection via Darcy flow, and wind-induced advection. Diffusive transport is caused by concentration variations in the soil whereas advective transport is caused by pressure gradients. The pressure gradient may be induced by wind (Poulsen 2005), changing barometric pressure (Latham & Young 1993, Kjeldsen & Fischer 1995, Nastev *et al*. 2001, Christophersen & Kjeldsen 2001, Christophersen *et al*. 2001, Franzidis *et al*. 2008, Gebert & Gröngröft 2006a), or by the pressure build up from the gas generation in the waste (Kjeldsen 1996). Czepiel *et al*. (2003) found a robust inverse linear relationship between landfill CH_4 emissions and barometric pressure for landfills in the northeastern US. Similarly, Gebert and Gröngröft (2006a) observed a reciprocal relationship between the gradient of the pressure change (d*P*) and LFG release through the passive gas extraction system that was connected to a biofilter for the mitigation of the landfill emissions. Rising atmospheric pressure not only reduced gas release but frequently caused a complete flux reversal, leading to the influx of atmospheric air through the biofilter and gas extraction system into the landfill (Gebert and Gröngröft 2006a). Continuous field monitoring has indicated that soil gas pressures through the cover materials at an unlined site without gas recovery are consistently in phase and approximately equal to barometric pressure under dry conditions; however, under conditions of surface wetting and drying, small depth-related differences both above and below observed barometric pressure can develop, and the observed pressures may lag behind barometric pressure (Bogner *et al*. 1987).

In landfill settings, the diffusional gas emission is maintained as the concentration of the gas components in the ambient air is low due to dilution. Generally, it has been considered that the diffusive flux dominates soil gas emissions (Bogner *et al* 1997a, b): however, there are several circumstances in landfill settings where pressure gradients can develop – for example, under saturated cover soils (Bogner 1986) or under low-permeability covers (i.e., clay or geomembrane composite). Under saturated conditions, it may also be necessary to consider ebullition (bubbling) flux mechanisms, especially at the edge of the landfill footprint or where there are cover fissures. It can also be shown that in coarse sandy soil covers only very low pressure gradients are needed for advective flux to dominate the diffusion-controlled flux (Kjeldsen 1996).

When cover soils are vegetated, plant-mediated transport mechanisms may also affect observed fluxes (Chanton 2005). The presence of roots and vegetation with hollow stems may increase the gas emissions. However, plant-mediated enhanced O_2 transport has also been observed in wetlands (Ding *et al*. 2005). In general, the effect of vegetation on the CH_4 dynamics of landfill covers has not been studied in great detail.

CH_4 migration

At unlined landfills situated in coarse-sediments or fractured geologic materials, it is well-known that lateral CH_4 migration is facilitated during wet periods when cover soils are saturated, limiting diffusive CH_4 flux to the atmosphere and permitting the development of high internal gas pressures that drive lateral advective flux. Many landfill investigations have demonstrated that advective (pressure driven) transport and diffusion contribute to gas migration (Ghabaee & Rodwell 1989, Williams & Aitkenhead 1991, Hodgson *et al*. 1992, Williams *et al*. 1999, Christophersen & Kjeldsen 2001, Christophersen *et al*. 2001, Franzidis *et al*. 2008). Other processes influencing LFG movement include the sorption of the gas on to solid particles or dissolution in liquid components and the generation or consumption of specific gas compounds through chemical reactions and biological activity (Kjeldsen 1996).

Certainly, short-term daily variations in barometric pressure and longer term changes associated with advancing weather fronts can also affect lateral migration as it affects emissions. It has been proposed from model studies that, for lateral migration, a critical variable is the *d*P, or change in pressure over a given time period (e.g., Lathan & Young 1993). In a recent paper, Poulsen (2005) examined the relative contribution of diffusive, advective, and wind-induced flux to drive gas migration and subsequent emissions of CO_2 at a Danish landfill. As shown in Figure 2, model runs compared with field data indicated that soil moisture was a critical variable, with diffusive flux dominant under drier conditions (higher air-filled porosity). Under more wet conditions

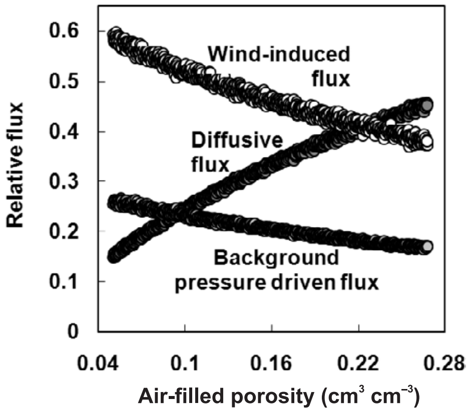

Fig. 2: Relative contribution of various mechanisms to gaseous flux from a Danish landfill. Reproduced from Poulsen, T.G. (2005). Impact of wind turbulence on landfill gas emissions. In: Proceedings Sardinia '05. Tenth International Waste Management and Landfill Symposium, 3–7 October 2005, CISA, Environmental Sanitary Engineering Centre, Cagliari, Italy with permission from CISA.

(lower air-filled porosity), the other two mechanisms were dominant with wind-induced flux responsible for a higher fraction of the emission.

Temporary CH_4 storage

The LFG gas pressure within landfills can vary due to temporal changes of cover gas permeability resulting from variation in precipitation and moisture content within the cover. In general, temporary storage of CH_4 in the landfill can occur during periods of high precipitation, and transient higher emissions can occur during dryer periods. Changes in barometric pressure may lead to similar processes on a much shorter time frame. The mentioned processes are important to consider when planning or interpreting measured CH_4 emissions at landfills, since emissions measurements may be affected by these processes, which can lead to accumulation of CH_4 within the landfill prior to the measurements.

Conclusions on landfill CH_4 mass balances

The primary control on landfill CH_4 emissions is the installation and maintenance of an engineered system that actively extracts LFG for flaring or energy use. Methanotrophic CH_4 oxidation in cover soils provides – at least for larger and new landfills – a secondary biological treatment process to control CH_4 emissions. As described in the section entitled 'The process of CH_4 oxidation', efficiency of methanotrophic CH_4 oxidation is limited by the capacity of cover soils to develop and maintain methanotrophic consortia under field conditions. For older landfills, methanotrophic CH_4 oxidation often is the only control mechanism. Also important are the cover design and maintenance, landfill design and site management practices, and the biodegradable organic carbon content of the buried waste.

Although diffusion is often assumed to be the major mechanism for gaseous emissions from landfill soils, the reality in landfills is more complex due to the internal production of LFG, the degree of isolation of the buried waste from external meteorological influences, temporal and lateral variability in physical properties and CH_4 oxidation capacity of cover materials, and, in some cases, the imposition of an engineered, active gas extraction system that can have an extraction efficiency that varies spatially and temporally. Unfortunately, to date, there have been few intensive field studies that have examined the relative temporal dynamics of these multiple processes in field settings.

In general, there have been few studies that have attempted to elucidate the relative contribution of different emissions mechanisms via integrated analysis of field data, intensive monitoring of temporal pressures, and modelling. Therefore, it is emphasized that understanding of LFG fluxes could be improved through highly instrumented field evaluations that combine continuous monitoring of pressure, moisture contents, gas concentrations, and temperatures along with important field gradients.

In all cases, it must be recognized that measured emissions at or above the landfill surface are the 'net' emissions inclusive of oxidation. More broadly, emissions are only one of several potential pathways for the CH_4 generated in the anaerobic zone; other pathways include recovery by an active gas extraction system, oxidation (and subsequent emission as CO_2), and lateral migration (Bogner & Spokas 1993).

Methanotrophic bacteria

The methanotrophic bacteria

The properties of methanotrophic bacteria have been reviewed extensively by Hanson & Hanson (1996). This section summarizes those aspects most relevant for understanding functional methanotrophic ecology in landfill cover soils and biofilters.

Methanotrophic bacteria (or methanotrophs) are a subset of a physiological group of bacteria known as methylotrophs and are unique in their ability to utilize CH_4 as a carbon and energy source. The use of enzyme CH_4 monooxygenases (MMOs) to catalyse the oxidation of CH_4 to methanol (CH_3OH) is a defining characteristic of methanotrophs. Figure 3 shows the complete pathway for the microbial oxidation of CH_4 to CO_2 by methanotrophs, including intermediate steps for oxidation of CH_4 to methanol, followed by oxidation of methanol to formaldehyde (CHOH) and the subsequent oxidation of formaldehyde to formate (CHOOH).

The first CH_4 oxidizing bacterium was isolated and described by Söhngen in 1906 and named *Bacillus methanicus*. In 1970, Whittenbury *et al*. established the basis of the current classification of the methanotrophs based on morphology, types of resting stages, and the fine structures of intracytoplasmic membranes. More recently Bowman *et al*. (1993, 1994, 1995) made some revisions in this classification, based on a more thorough analysis including numerical taxonomy, DNA-DNA-hybridization, and phospholipid fatty acid (PLFA) composition analysis. Two types of methanotrophs were distinguished, labelled type I and type II. Bowman and his coworkers consistently refer to these types as 'group I' and 'group II'. As of 1995, type I included the genera *Methylococcus*, *Methylomicrobium*, *Methylobacter* and *Methylomonas* and formed the family *Methylococcaceae*. Type II included the genera *Methylosinus* and *Methylocystis*. Type I methanotrophs form a distinct branch within the gamma subdivision of the *Proteobacteria*. They use a particulate MMO (pMMO) to oxidize CH_4. Formaldehyde, a product of CH_4 oxidation (see Figure 3), is assimilated using the ribulose monophosphate pathway (RuMP). Most type I methanotrophs form cysts and are incapable of fixing N_2. Exceptions are some *Methylomonas* and *Methylococcus* species. Type II methanotrophs form a distinct branch within the alpha subdivision of the *Proteobacteria*. They use pMMO, but in the absence of copper a soluble enzyme (sMMO) is produced in most type II methanotrophs and in some type I methanotrophs. This enzyme has broad substrate specificity and enables these micro-organisms to oxidize chlorinated hydrocarbons and aromatic hydrocarbons. Type II methanotrophs assimilate formaldehyde via the serine pathway and are able to fix N_2 (nitrogenase activity).

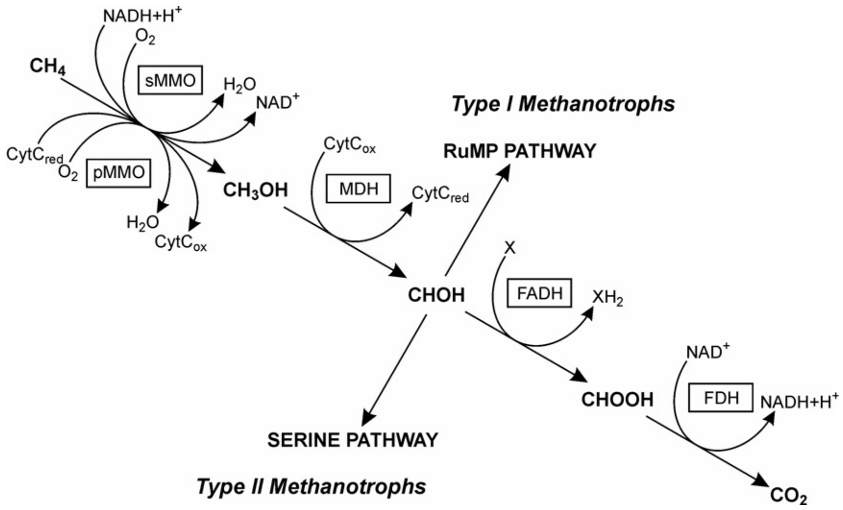

Fig. 3: The pathway for the oxidation of methane and assimilation of formaldehyde by Methanotrophs. Reproduced from Hanson R.S., Hanson, T.E. (1996). Methanotrophic bacteria. Microbiological Reviews. 60:439–471 with permission from the American Society for Microbiology.

In this taxonomy, *Methylococcus* took a special position within the type I genera. Species from this genus are mildly thermophilic, express sMMO and nitrogenase activity, and sometimes use the serine pathway. For these reasons this genus was formerly referred to as type X. This nomenclature became irrelevant with the discovery of other genera with unusual properties, and is no longer in use.

In 1995 more than 136 CH_4-utilizing bacteria had been isolated and characterized (Bowman *et al.* 1993, 1995). However, novel methanotrophic species and genera are continuously being discovered. New type I genera include the psychrophilic *Methylosphaera* (Bowman *et al*. 1997), the thermophilic genera *Methylocaldum* (Bodrossy *et al*. 1997) and *Methylothermus* (Tsubota *et al*. 2005), the strongly clustering *Methylosarcina* (Wise *et al*. 2001), and the halophilic *Methylohalobius* (Heyer *et al*. 2005). A new type II genus is the mildly acidophilic *Methylocella* (Dedysh *et al*. 2000, 2004, Dunfield *et al*. 2003). Dedysh *et al.* (2002) even suggested a ‘type III’ classification for the new genus *Methylocapsa*, which consists of mildly acidophilic bacteria not expressing sMMO, but using the serine pathway. This genus belongs to the α-*Proteobacteria* and its closest relation is *Methylocella*. Wise *et al*. (1999) reported that the result of methanotrophic isolation by enrichment series depends on the strength of the nitrate mineral medium used, indicating that results of enrichments are not necessarily representative for the *in situ* ecology.

To date, a total of eleven methanotrophic genera have been distinguished. Their phylogenetic affiliation and their prominent morphological and physiological properties are summarized in Table 1.

CH_4 oxidation and carbon assimilation

Oxidation of CH_4 by aerobic methanotrophs is initiated by MMO enzymes. MMOs utilize two reducing equivalents to

Table 1: Overview of the characteristics of the eleven methanotrophic genera as known to date.

Genus	Phylogenetic position	ICM-arrangement (type)	Dominant PLFA	C-assimilation	Type of MMO	N_2-fixation
Methylobacter	γ-Proteobact.	stacks (I)	16:ω1	RuMP	pMMO	no
Methylocaldum	γ-Proteobact.	stacks (I)	16:ω1	RuMP	pMMO	no
*Methylocapsa**	α-Proteobact.	Typ III	18:ω1	Serine	pMMO	yes
Methylocella	α-Proteobact.	peripheral (II)	18:ω1	Serine	sMMO	yes
Methylococcus	γ-Proteobact.	stacks (I)	16:ω1	RuMP	pMMO	yes
Methylocystis	α-Proteobact.	peripheral (II)	18:ω1	Serine	sMMO/pMMO	yes
Methylomicrobium	γ-Proteobact.	stacks (I)	16:ω1	RuMP	pMMO	no
Methylomonas	γ-Proteobact.	stacks (I)	16:ω1	RuMP	pMMO	no
Methylosinus	α-Proteobact.	peripheral (II)	18:ω1	Serine	sMMO/pMMO	yes
Methylosphaera	γ-Proteobact.	stacks (I)	16:ω1	RuMP	pMMO	no
*Methylothermus**	γ-Proteobact.	n.d.	n.d.	n.d.	pMMO	n.d.

ICM, intracytoplasmatic membranes; RuMP, ribulose monophosphate path; Serin, serine path; pMMO, particulate methane monooxygenase; sMMO, soluble methane monooxygenase; *genus so far represented by only one species; Proteobact., Proteobacteria; n.d., not determined.

split the O–O bond in O_2. One of the O_2 atoms is reduced to form H_2O, while the other is incorporated into CH_4 to form methanol (Figure 3).Two forms of the enzyme MMO have been found in methanotrophs on the basis of their intracellular localization (Dalton 1991, 1992). All methanotrophs are capable of forming a particulate or membrane-bound MMO (pMMO) when grown in the presence of copper. Methanotrophs classified as types II have been shown to synthesize a soluble MMO (sMMO) under copper limiting growth (Stanley *et al*. 1983, Hanson & Hanson 1996). Cells of methanotrophs that contain pMMO have higher growth yields on CH_4 than cells that contain sMMO (Joergensen & Degn 1987). The synthesis of sMMO by some methanotrophs may be a survival mechanism in the many environments where copper limits the growth of methanotrophs capable of synthesizing only pMMO (Hanson & Hanson 1996).

Methanol is oxidized to formaldehyde by a periplasmic methanol dehydrogenase (MDH) (Figure 3). Most of the reducing power required for the metabolism of CH_4 is produced by oxidation of formaldehyde via formate to CO_2. There are multiple enzyme systems for the oxidation of formaldehyde to formate in methylotrophs. An example is the NAD(P)-linked aldehyde dehydrogenase. Formate is oxidized to CO_2 by a NAD-dependent formate dehydrogenase in most if not in all methanotrophs. Formaldehyde produced from the oxidation of CH_4 and methanol by methanotrophs is assimilated to form intermediates of the central metabolic routes that are subsequently used for biosynthesis of cell material. Two pathways for synthesis of cell materials from formaldehyde are known: the serine and the ribulose monophosphate (RuMP) pathway. In the RuMP pathway (used by Type I methanotrophs) one ATP is used in the formation of one glyceraldehyde-3-P from three formaldehyde molecules whereas in the serine pathway (used by type II methanotrophs) three ATP and two NADH are needed to assimilate two formaldehydes and one CO_2. The RuMP pathway is thus more efficient than the serine pathway. Consequently, type I methanotrophs tend to outgrow their type II counterparts, unless inorganic N or Cu limitation provides an advantage for type II species, expressing sMMO or nitrogenase activity. A 100 % conversion of CH_4 to microbial biomass is not possible since assimilatory pathways lead to a net production of at least 12 % CO_2 (Gommers *et al*. 1988).

Methanotrophs assimilate carbon for growth as formaldehyde. Kightley *et al.* (1995) and Whalen *et al.* (1990) both found that 69% of oxidized CH_4 was assimilated into biomass in soil incubation experiments. Similar findings were obtained by Börjesson *et al.* (1998a) who found CO_2/CH_4-ratios between 0.17 and 0.36 indicating that between 64 and 83% was assimilated. Scheutz *et al*. (2004) found that the incorporation of carbon into biomass was approximately 48 % when the background soil respiration was subtracted. When CH_4 assimilation is occurring, the stoichiometric O_2 consumption per molecule of CH_4 is less than 2, since the conversion of CH_4 to formaldehyde requires only one mole O_2 per mole CH_4.

The process of CH_4 oxidation

Process overview

The aerobic microbial oxidation of CH_4 occurs in the biosphere wherever CH_4 and O_2 are present at the same time. In landfill covers, CH_4 and O_2 counter gradients may appear due to emission of CH_4 from the waste and in-flux of O_2 from the ambient air, which provides the necessary conditions for the development of methanotrophic bacteria. Aerobic CH_4 oxidation proceeds according to the following overall reaction:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat}$$

$$\Delta G° = -780 \text{ kJ mol}^{-1} \text{ CH}_4$$

Most methanotrophic bacteria are obligate methanotrophs and strict aerobes (Hanson & Hanson 1996). Their activity depends on the presence of sufficient concentrations of both CH_4 and O_2, and thus they tend to be confined to fairly narrow horizontal bands within their habitat, limited in their distribution by the downward diffusion of atmospheric O_2 and the upward diffusion of CH_4. In simulated landfill soil covers the greatest CH_4 oxidation potential was found around 20 cm below the surface, in zones where vertical profiles of CH_4 and O_2 overlap (Kightley *et al*. 1995, De Visscher *et al*. 1999, Scheutz *et al*. 2003, 2004). In general, the methanotrophic active zone is located in the upper 30–40 cm of the soil profile, with maximal oxidation activity in a zone that is between 15–20 cm below the surface (Jones & Nedwell 1993, Czepiel *et al*. 1996b, Scheutz *et al*. 2004). Figure 4 shows gas concentration profiles measured at Skellingsted landfill (Zealand, Denmark) and maximal CH_4 oxidation rates obtained in batch incubation experiments versus sampling depth. The

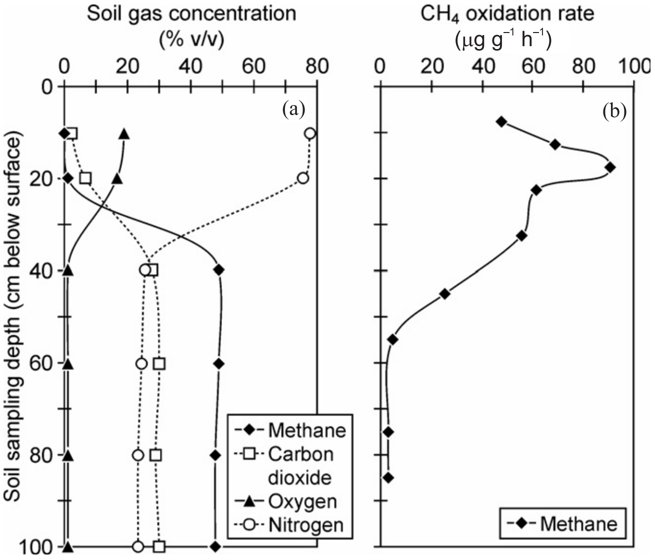

Fig. 4: (a) Soil gas concentration profiles measured at Skellingsted landfill and (b) Maximal methane oxidation rates obtained in batch incubation experiments vs. sampling depth. Reproduced from Scheutz, C.; Pedersen, G.B., Kjeldsen, P. (2009) Biodegradation of methane and halocarbons in simulated landfill biocover systems containing compost materials. Used with permission from the *Journal of Environmental Quality*. 38, 1363–1371.

figure shows that the highest oxidation potential is found in the upper part of the soil profile where both CH_4 and O_2 are present. At depths below 60 cm the methanotrophic activity is limited by low O_2 concentrations. However, at sites with low CH_4 emissions due to, for example, installation of a gas extraction system, the oxidative zone may occur at a greater depth (Scheutz *et al.* 2003). The influence of O_2 on CH_4 oxidation is discussed in the section entitled 'Environmental factors influencing CH_4 oxidation in landfill cover soils'.

In many cases CH_4 oxidation kinetics of soils and methanotrophic cultures can be described by Michaelis–Menten kinetics:

$$r = \frac{V_{\mathrm{max}}[\mathrm{CH_4}]}{K_{\mathrm{m}} + [\mathrm{CH_4}]} \tag{1}$$

where r is the CH_4 oxidation rate, V_{max} the maximum CH_4 oxidation rate, K_m the Michaelis–Menten (or half-saturation) constant, and $[CH_4]$ the CH_4 concentration. K_m is an affinity constant and is given as the CH_4 concentration where the CH_4 oxidation rate is half of the maximum CH_4 oxidation rate, V_{max}.

Previous laboratory studies of CH_4 oxidation kinetics in non-landfill and landfill soils suggest that at least two groups of methanotrophs are active in CH_4 oxidation in soils (Bender & Conrad 1993, 1995, Bogner *et al.* 1997a). The first group of methanotrophs, which has a high CH_4 affinity (low K_m), favours a low CH_4/high O_2 setting near atmospheric concentrations, with low oxidation rates (low V_{max}) limited by available CH_4. The second group, which has a low CH_4 affinity (high K_m), but high oxidation rates (high V_{max}), favours higher CH_4 concentrations and lower O_2 concentrations. The second group is probably limited by O_2 in presence of abundant CH_4. Bender & Conrad (1992) found that CH_4 mixing ratios of 100–1000 ppmv are required to increase the CH_4 oxidizing activity of soils. Schnell & King (1995) found that this threshold is between 170 and 1000 ppmv. The CH_4 concentrations prevalent in landfill cover soils (1–60% v/v) are sufficiently high for induction of low-affinity, high-capacity CH_4 oxidation. In landfill cover soils the value of V_{max} ranges from 2 to 104 $\mu g\ g^{-1}$ soil h^{-1} (dry weight basis) (Kightley *et al.* 1995, Czepiel *et al.* 1996b, De Visscher *et al.* 2001, Scheutz & Kjeldsen 2004, Park *et al.* 2005), whereas K_m typically is around 1000 to 25 000 ppmv (Whalen *et al.* 1990, Bender & Conrad 1992, De Visscher *et al.* 2001, Scheutz & Kjeldsen 2004, Park *et al.* 2005). K_m has been found to increase with temperature (De Visscher *et al.* 2001) and soil moisture (Park *et al.* 2005). In comparison, natural soils exposed to ambient CH_4 concentrations often exhibit kinetics with high affinity (V_{max} values of 0 to 0.1 $\mu g\ g^{-1}$ soil h^{-1}) and low activity (K_m values of 20 to 90 ppmv) (Bender & Conrad 1992, 1994a, Czepiel *et al.* 1994, Whalen & Reeburg 1996).

Type I and type II methanotrophs seem to adapt for survival under different growth conditions. Amaral & Knowles (1995) examined the growth of methanotrophs in CH_4 and O_2 counter gradients and found that type I appeared to be best adapted to growth in low CH_4 concentrations and high O_2 concentrations whereas type II dominated under high CH_4 concentrations and low O_2 concentrations. Their hypothesis has been supported by observations that a type I methanotroph (*Methylomonas albus* BG8) out-competed a type II methanotroph (*Methylosinus trichosporium* OB3b) in continuous cultures under CH_4-limiting conditions (Graham *et al.* 1993). Furthermore, they found that the growth of some type II methanotrophs was favoured when combined nitrogen (N) and O_2 levels were low, and when copper was substantially depleted in the growth media. This can be understood by considering the properties of type I and type II methanotrophs (see section entitled 'Methanotrophic bacteria' above). At low CH_4 concentrations inorganic N is not likely to be limiting, so type I methanotrophs tend to dominate. At high CH_4 concentrations inorganic N is limiting, so only N_2-fixing type II methanotrophs can grow. N_2-fixation (nitrogenase activity) requires low O_2 concentrations (Whittenbury & Dalton 1981), which explains why a combination of high CH_4 concentrations and low O_2 concentrations favour type II methanotrophs (see also the section entitled 'Environmental factors influencing CH_4 oxidation in landfill cover soils' below). This suggests that in a landfill cover system with CH_4 and O_2 counter gradients, type II methanotrophs will dominate in deeper zones with sub-ambient O_2 levels and a continuous supply of CH_4 providing the methanotrophs with high CH_4 concentrations. In the upper soil layers with low CH_4 concentration near atmospheric level (1.7 ppmv) type I will dominate with high CH_4 affinities and capacity for atmospheric uptake. However, the composition of methanotrophic communities and distribution of the methanotrophic bacteria in landfill soil covers and biofilters are only sparsely investigated. Mandernack *et al.* (2000) investigated landfill cover soils from California and Washington and found that the PLFAs extracted from these soils were representative of type II methanotrophs. This was confirmed by a study of the isotope signature of the organic N and the organic C in the microbially most active soil layer. In a comprehensive study, Wise *et al.* (1999) found both type I and type II methanotrophs in a landfill cover soil. Börjesson (1997) found mainly type I methanotrophs in a sewage sludge landfill cover, probably due to the high nutrient content, and mainly type II methanotrophs in a mineral landfill cover soil. Svenning *et al.* (2002) found that type II methanotrophs were dominating in the cover soil (20–25 cm.b.s) of a Danish landfill: 15 isolates of type II (including 10 that carried the genes for sMMO) were identified and only one type I was identified. He *et al.* (2008) showed that type I methanotrophs predominated in a column study containing a landfill clay soil, while the type II methanotrophs were abundant in a column containing waste soil from a landfill reactor. Gebert *et al.* (2004) found that biofilters for CH_4 oxidation consisting of industrial porous clay pellets were dominated by type II methanotrophs.

CH_4 oxidation capacity of landfill cover soils

Landfill cover soils can develop a high capacity for CH_4 oxidation by selection of methanotrophic bacteria. Very high

Table 2: Summary of maximal methane oxidation rates for landfill cover soils obtained from batch studies.

Reference	Soil texture	Content of organic matter	Maximum CH_4 oxidation rate	Initial CH_4 concentration	Investigated temperature range	Optimum temperature	Q_{10}	Investigated soil moisture range	Optimum soil moisture content
		(% w/dw)	(µg CH_4 g^{-1} h^{-1})	(% v/v)	(°C)	(°C)		(% w/dw)	(% w/dw)
Stein & Hettiaratchi (2001)	Loam		16	2.5	4–40	30		0–27	15
Kightley *et al*. (1995)	Coarse sand		16	5	20			40% WHC[c]	
Hilger *et al*. (2000a)	Sandy loam	1.5	2.4	8	22			15	
De Visscher *et al*. (2001)	Sandy loam	3.4	47.2	2	22			14	
De Visscher *et al*. (1999)	Sandy loam	3.4	26	3	22			16.5	
Scheutz & Kjeldsen (2004)	Loamy sand	3.2	118	15	2–50	30	3.4 (2–25 °C)	5–50	25
Scheutz *et al*. (2003)	Silt, sandy	1.81[b]	1.5	15	22				20
Scheutz *et al*. (2007)	Loam	1.86[b]	28	15	22				20
Park *et al*. (2005)	Sandy soil	1.3	25	5–53	4–40	30	2.6–2.7 (20–30 °C)	5–20	10
Figueroa (1993)	Humic soil	7.2	86.4	10	20			0–50	21
	Till	4.4	40	10	10–40	30		0–23	12
	Biowaste compost	31.6	128	10	20				
Jones & Nedwell (1993)	Sandy loam	8.07	0.2	12.5	22				
Whalen *et al*. (1990)	Sandy mixed with clay	4	2.7	7.7	5–46	31	1.9 (5–26 °C)	5–71	11
Boeckx & Van Cleemput (1996)	Sandy loam	1.8	0.0024	0.001	12–35	25–30		5–35	15
Czepiel *et al*. (1996b)	Sand-clay loam	1.8	41.5	1.7-2	5–45	36	2.4 (20–30 °C)	0–40	16
Boeckx *et al*. (1996)	Sandy loam/ loam	1.2	0.01	0.001	5–30	20–30	1.9 (10–20 °C)	5–30	16–19
Christophersen *et al*. (2000)	Sandy loam	1–9	19	18	2–15	15	4.1–7.3 (2–15 °C)	5–35	11–32
Bender & Conrad (1994a)	Loamy clay		0.0096	5		25			22
Börjesson *et al*. (2004)	Sandy loam[a]	25.3	18.8	5	3–20	≥ 20	3.17	66.1	n.m.
Börjesson *et al*. (2004)	Sandy loam[a]	7.5	25.2	5	3–20	≥ 20	4.03	33.5	n.m.
Börjesson (1997) Börjesson *et al* (1998a, b)	Silty loam[a]	22–30	173	5	2–37	31	4.7	22–108	61
Börjesson (1997)	Sandy loam		48	5	25	38	5.2 (2–25 °C)	15–50	35
Börjesson & Svensson (1997b) Börjesson (2001)	Sand[a]	1.3	16	0.2–0.67	20 (2001) 25 (1997)	20–25	n.m.	10–62	16.3
Bogner *et al*. (1997a)			11.8	8.4					
Einola *et al*. (2007)	5-year-old compost cover	7.3	2.5	8-9	1–19	19	6.5–8.4	7–34	21–28
Park *et al*. (2009)			16	10	5–35	25–35		5–30	10–15

[a]According to ISSS (International Society of Soil Science: clay = < 0.002 mm, silt = 0.002–0.02 mm, sand = 0.02–2.0 mm); [b]Total organic carbon, [c]WHC, water holding capacity.

Table 3: Summary of methane oxidation rates obtained in soil column experiments simulating landfill soil covers.

Reference	Soil texture	Moisture content	Organic matter	CH_4 inlet concentration	CH_4 load	Methane oxidation rate			Duration	Gas profiles
						Steady state		Maximum		
		(% w/dw)	(% w/dw)		(g CH_4 m^{-2} day^{-1})	(g CH_4 m^{-2} day^{-1})	(%)	(%)	(days)	yes/no
Stein & Hettiaratchi (2001)	Landfill loam	9.4	3.1	99	Low: 186 High: 319	93 102–120	50 32–38	100 50	260 260	yes yes
Stein & Hettiaratchi (2001)	Rockyview dark soil – agricultural soil	10	4.7	99	310	99	32	40	314	yes
Park *et al*. (2002)	Loamy sand	13	0.4	99	525			83	30	
Kightley *et al*. (1995)	Landfill coarse sand			99	266	166	61		180	yes
	Landfill clay topsoil			99		109	40		180	yes
	Landfill fine sand			99		110	41		180	yes
Hilger *et al*. (2000b)	Landfill sandy loam			50[a]	281	42–56	15–20	45–50	101–172	yes
Hilger *et al*. (2000a)	Landfill sandy loam			50[a]	281	53	19	37	120[c]	yes
De Visscher *et al*. (1999)	Landfill Sandy loam	16.5	3.4	50[a]	368	230	65	79	65	no
	Agricultural loam	16.5	2	50[a]	216	98	45	81	127	no
	Agricultural loam/wheat straw (99 : 1)[b]	16.5	2	50[a]	237	144	61	84	176	no
	Agricultural loam/sugar beet leaves (99 : 1)[b]	16.5	2	50[a]	222	82	37	79	166	no
Scheutz *et al*. (2003)	Landfill loam	9-33	0.6-6.4	50[a]	250	210	81		30	yes
Humer & Lechner (2001a)	Sandy loam	22	5	100	180	75.6	42	47	51	yes
	Sand	21	7	100	94	90	96	100	84	yes
	Sand	21	7	100	216	210	97	100	84	yes
Humer & Lechner (1999a)	Topsoil	17.8	7.4	100	150	55	37	47	51[c]	no
Ahn *et al*. (2002)	Landfill sandy soil	9.7	2.2	50[a]	26-32	22	70–85		95[c]	yes
Pawlowska *et al*. (2003)	fraction of 0.25–0.5 mm	7.57	0.12	99	266.1	134 ± 9.4	50		180	yes
	fraction of 0.5–1.0 mm	5.68	0.12	99	266.1	151.9 ± 7.1	57		180	yes
	fraction of 1.0–2.0 mm	3.15	0.17	99	266.1	135.7 ± 8.1	51		180	yes
	fraction of 2.0–4.0 mm	1.94	0.11	99	266.1	135.2 ± 8.1	51		180	yes
He *et al*. (2008)	Landfill clay soil	14	0.06[d]	70	265	128	48	48	115	no
	Waste soil from a landfill reactor	50	0.3[d]	70	260	26	10[c]	14[c]	115	no

[a] 50%CH_4 : 50%CO_2; [b] per weight, [c] Graphically determined based on figures and graphs in reference; [d] Total organic carbon.

rates of CH_4 oxidation in landfill cover soils (> 100 µg CH_4 g^{-1} h^{-1} and > 200 g CH_4 m^{-2} day^{-1} in batch and column experiments, respectively) have been reported by several authors (Tables 2 and 3). These rates are the highest rates of CH_4 oxidation observed in natural soils (Hanson & Hanson, 1996). The capacity for CH_4 oxidation of soil is often studied in laboratory tests either as incubation experiments (batch tests) or in continuous gas flow systems (packed column test). The batch approach offers several advantages to the column approach, including technical simplicity, lower cost, and less laborious to conduct. As a result batch incubation tests are often chosen when the number of soil samples that need to be incubated is high. The batch approach is also often preferred when the impact of different environmental parameters need to be determined as batch conditions can be manipulated easily. However, unlike continuous flow column tests, batch tests cannot simulate the dynamic gas transport that occurs in landfill soil covers or the effects of long term gas exposure. Due to the system differences, comparison of oxidation rates obtained in batch systems with rates obtained in column tests is not appropriate.

Table 2 summarizes maximal CH_4 oxidation rates for landfill covers soils obtained from batch studies reported in literature, whereas Table 3 shows CH_4 oxidation rates from column studies simulating landfill soil covers. Most of the reported oxidation rates have been obtained with sandy soils with an organic matter content of 2 to 5% w/w incubated with relative high CH_4 concentrations (> 5% v/v). Several authors have studied the influence of environmental factors like soil moisture content and temperature in batch experiment whereas most column experiments have been operated under constant conditions (e.g. room temperature and moisture contents of 10 to 20% w/w). In general, columns were operated with inlet CH_4 concentrations of 50 or 100% v/v and CH_4 loads between 200 to 300 g CH_4 m^{-2} day^{-1}, which is in the middle to high range of reported landfill CH_4 fluxes (Bogner *et al.* 1997b). Assuming a 20-m deep layer of waste, this is equivalent to a generation rate of about 11 to 17 m^3 LFG m^{-3} waste $year^{-1}$, which can be expected within the first 10–15 years after disposal (Willumsen & Bach 1991). Gas fluxes of approximately 85 g CH_4 m^{-2} day^{-1} (0.25 m^3 LFG m^{-2} day^{-1}) are representative for older landfills or sites with gas collection systems, while new and active landfills with high gas production can have gas fluxes of up to 1300 g CH_4 m^{-2} day^{-1} (4 m^3 LFG m^{-2} day^{-1}). Table 3 reports both steady-state and maximum oxidation rates, as long-term laboratory column experiments simulating landfill cover CH_4 oxidation rates often exhibit a peak followed by a decrease to a lower steady state value (Kightley *et al.* 1995, Hilger *et al.* 1999, Scheutz & Kjeldsen 2003, Streese & Stegmann 2003, Wilshusen *et al.* 2004b). In general, steady state CH_4 oxidation rates for landfill cover soils are between 100 to 150 g CH_4 m^{-2} day^{-1} (30 to 60% removal) with maximum rates up to 200 to 250 g CH_4 m^{-2} day^{-1} (80 to 100% removal). It is important to note that only a few column experiments have been run for more than 250 days (e.g., Wilshusen *et al.* 2004b) and the performance over years as well as the seasonal influence of temperature and precipitation remains unknown.

Environmental factors influencing CH_4 oxidation in landfill cover soils

CH_4 oxidation is controlled by a number of environmental factors: soil texture, temperature, soil moisture content, CH_4 and O_2 supply, nutrients, etc. Thus, the climatic conditions are of importance for the actual CH_4 oxidation rate. In landfill soil covers temperature and soil moisture are very important parameters controlling CH_4 oxidation.

Temperature

Temperature has a profound effect on all biological processes, including CH_4 oxidation activity. Most methanotrophs available in pure cultures are mesophiles (Hanson & Hanson 1996). Optimum temperatures are around 25–35 °C for CH_4 oxidation in soil environments (see Table 2), although CH_4 oxidation can occur down to 1–2 °C (Primé & Christensen 1997, Christophersen *et al.* 2000, Scheutz & Kjeldsen 2004, Einola *et al.* 2007). Omel'chenko *et al.* (1993) isolated methanotrophs from acid soils in a bog in the Arctic that had optimum growth at temperatures of 10 °C or lower indicating that some populations of methanotrophs can adapt to lower temperatures in nature. All of the bacteria found in low temperature environments belong to type I methanotrophs (Borjesson *et al.* 2004), indicating that temperature could exhibit a selecting effect that determines which of the two main types of methanotrophs will predominate in a given environmental system. It appears that in landfill conditions type I methanotrophs tend to have a lower temperature optimum than type II methanotrophs (Gebert *et al.* 2003). Consequently, type I methanotrophs are more dominant at 10 °C than at 20 °C (Börjesson *et al.* 2004).

The term Q_{10} is the value for the number of times the oxidation rate increases when temperature is increased 10 °C at temperatures below the optimum temperature. At 10 to 30 °C the temperature response is approximately exponential with Q_{10} values ranging from 1.7 to 4.1 (Boeckx *et al.* 1996, Czepiel *et al.* 1996b, De Visscher *et al.* 2001, Scheutz & Kjeldsen 2004, Börjesson *et al.* 2004, Park *et al.* 2005). King & Adamsen (1992) and De Visscher *et al.* (2001) found that the CH_4 oxidation was more strongly dependent on the temperature giving higher Q_{10}-values at 1–3% v/v CH_4 than at 0.01–0.025% v/v CH_4, which they attributed partly to phase transfer resistances and partly to a decrease of the affinity of the enzyme with increasing temperatures. At low initial CH_4 concentrations mass transfer between the liquid and gas phases might limit the oxidation, resulting in a less pronounced temperature response. In contrast, at high initial CH_4 concentration, the CH_4 oxidation is not phase-transfer limited, but more likely enzymatically limited.

In cold areas or during winter season with temperatures below 5–10 °C the CH_4 oxidation might be significantly reduced or even come to standstill. Börjesson & Svensson (1997b) investigated the seasonal as well as the diurnal variation in CH_4 emissions from a small Swedish landfill and found temperature to be the controlling factor. CH_4 emissions were negatively correlated with soil temperature, indicating that microbial oxidation was an important regulating factor. Christophersen *et al.* (2001) also found higher CH_4 emissions during winter, while no CH_4 was emitted during summer at Skellingsted landfill in Denmark, which was attributed to temperature.

Soil moisture

Moisture is an essential factor for micro-organisms to sustain their activity as it is the transport medium for nutrient supply and also for removal of residual metabolic compounds. However, too much moisture may slow down gaseous transport processes in the soil because molecular diffusion in water is about 10^4 times slower than in the air (Cabral *et al.* 2004). When the soil's degree of saturation (volume of water/volume of voids) reaches a value in the vicinity of 85%, the air-filled voids are no longer interconnected and the gases have to diffuse in the liquid phase (Cabral *et al*. 2004), drastically reducing the availability of CH_4 and O_2, thereby limiting CH_4 oxidation. In contrast, a decrease in moisture content can also reduce the oxidation rates significantly due to microbial water stress resulting from desiccation.

Methanotrophic activity has been reported to require a certain lag period to recover after rewetting (Scheutz & Kjeldsen 2004). At optimum soil moisture content there is both maximum gas phase molecular diffusion and sufficient soil moisture content to achieve microbial activity to oxidize the CH_4 delivered. The specific value is dependent on soil texture and thus on the specific pore size distribution, determining the pore volume available for both water retention and gaseous transport. In general, a high share of pores > 50 µm, also referred to as air capacity, is desired. The air capacity signifies the share of pores available for gaseous transport after a material has drained and the remaining water is bound by capillary forces only. The air capacity may be significantly reduced if the soil is subject to compaction. The optimum soil moisture content for landfill cover soils ranged between 10 and 20% w/w (Table 2 and the references cited therein (Whalen *et al*. 1990, Czepiel *et al*. 1996b, Figueroa 1993, Boeckx *et al*. 1996, Boeckx & Van Cleemput 1996)). However, in some cases higher soil moisture optima have been observed (Börjesson *et al.* 1998a, Christophersen *et al*. 2000, Scheutz & Kjeldsen 2004). The oxidation activity is significantly reduced when soil moisture content decreases below 5% (Whalen *et al*. 1990, Czepiel *et al*. 1996b, Stein & Hettiaratchi 2001, Scheutz & Kjeldsen 2004). De Visscher *et al*. (2007) argue that moisture affects gas diffusion scales; microscale and macroscale, corresponding with liquid phase diffusion and gas phase diffusion, respectively. Gebert *et al*. (2003) have found little influence of moisture content on methanotrophic activity in a biofilter material consisting of industrially produced porous clay pellets. The material had a very favourable pore size distribution with an extremely high air capacity of 78%, minimizing diffusive mass transfer limitation and thus rendering the methanotrophic activity rather independent of the actual moisture content.

Boeckx *et al*. (1996) found that the CH_4 emission was controlled by soil moisture content in a field experiment conducted at a small landfill in Belgium. Likewise, Jones & Nedwell (1990) measured the highest CH_4 emissions from a landfill in England during the warmest and driest periods. In arid areas or during periods with very low precipitation, moisture content can be a critical factor in limiting the oxidation capacity in landfill soil covers. In a combined field and laboratory study, Scheutz *et al*. (2003) found that reduced methanotrophic activity in the upper part of the soil cover was due to moisture limitation rather than substrate limitation.

Water saturation of the soil can, however, lead to increased lateral gas transport causing emissions adjacent to the landfill or to a pressure build-up creating the necessary driving force for advective transport through the soil especially through areas with lower flow resistance. A tragic instance of the former possibility was documented by Kjeldsen & Fischer (1995) at Skellingsted landfill, Denmark, where a heavy rainfall combined with drop in atmospheric pressure resulted in lateral LFG migration leading to a fatal explosion in a nearby house.

Cracks and fissures usually occur in landfill cover soils as a result of waste settlement or due to desiccation of the top soil during dry periods. Several investigations have shown that CH_4 emissions through landfill covers show high spatial variations with 'hot spots' often associated with heterogeneities in the cover soil. Czepiel *et al*. (1996a) found that about 5% of the cover area of a landfill in New Hampshire was responsible for 50% of the CH_4 emission. Bergamaschi *et al*. (1998) found that 70% of CH_4 emissions through cover soils of landfills in Germany and The Netherlands happen through cracks.

The critical factor appears to be the amount of soil pore volume available for gas exchange at different moisture contents. Therefore to promote more uniform methanotrophic distribution and greater possibilities for CH_4 and trace gas removal in wider portions of the soil layer within the cover system, it is recommended to use soils capable of sustaining sufficient moisture content and, concurrently, a high share of coarse pores throughout the depth of the cover. Greater depth penetration is advantageous because it allows oxidation to occur at a depth where the soil layer can maintain more stable moisture and temperature conditions, not being subject to drying from wind and solar radiation as is the case near the surface. Hence, attention has been recently focused on cover materials that can support microbial growth; have a high water holding capacity and a high share of air-filled pores, such as compost materials. This subject is discussed in detail in Section 5.

O_2 supply, porosity and permeability

Methanotrophic bacteria are obligate aerobes that can achieve optimum CH_4 conversion rates even at very low O_2 concentrations. Experiments carried out on paddy fields showed that CH_4 oxidation was insensitive to O_2-mixing ratios greater than 1 to 3%, but decreased rapidly at lower levels. Similar results were found by Czepiel *et al*. (1996b) who found that CH_4 oxidation dropped significantly at O_2-mixing ratios below 3%. Wilshusen *et al*. (2004a) showed that in pure methanotrophic cultures, O_2 concentrations ranging from 0.45 to 20 % could support maximum CH_4 oxidation rates in both type I and II bacteria. For biofilter material, Gebert *et al*. (2003) found that CH_4 oxidation only commenced when O_2-concentrations were above 1.7–2.6%. The half-saturation constant for O_2 was calculated to 58 µmol L^{-1} (5.4%), maximum CH_4 oxidation rates were reached at O_2-concentrations of approximately 9%.

In landfill cover soils, the O_2 penetration depth will often be the limiting factor of the CH_4 oxidation process, making soil composition, particle size, and porosity important controlling parameters. At many landfills, the waste is often covered with a low permeable cover like clay in order to minimize rainfall infiltration and subsequent leachate production. However, clay covers tend to become water saturated during periods with high precipitation or become desiccated creating cracks in the cover during dry seasons, which in both cases will cause preferential gas flows decreasing CH_4 oxidation and increasing emissions.

Inorganic N

Inorganic N (ammonium[NH_4^+]/nitrate[NO_3^-]) might stimulate or inhibit CH_4 oxidation in soils depending on the species of N and its concentrations, CH_4 concentrations, pH, and type of methanotrophs present. Several studies have shown that higher NH_4^+ concentrations in soils tend to inhibit CH_4 oxidation, as NH_4^+ acts as a competitive inhibitor towards MMO enzymes. For example, Boeckx & Van Cleemput (1996) observed inhibition of CH_4 oxidation in landfill cover soil amended with 25 mg-N kg^{-1}, where the CH_4 oxidation rate decreased linearly with the initial NH_4^+ content of the soil. Scheutz & Kjeldsen (2004) found that the oxidation rates for CH_4 were unaltered in NH_4^+-amended LFG exposed soils up to 14 mg-N kg^{-1}, whereas at higher NH_4^+ concentrations the oxidation rates decreased. Similar results were obtained by Hütsch (1998) who found that application of 40 mg-N kg^{-1} (added as NH_4Cl or $(NH_4)_2SO_4$) to an arable soil caused a strong instantaneous inhibition of CH_4 oxidation by up to 96%.

More recently, it has been found that NH_4^+-based fertilization stimulates growth and activity of CH_4 oxidizers. This has been emphasized in the review by Bodelier & Laanbroek (2004), who summarized the observed effects of inorganic N on CH_4 oxidation in experiments reported in the literature. Methanotrophic bacteria have a relatively high N demand: for every mole of assimilated carbon, 0.25 mole of N is required, (Anthony 1982). Hence, especially in environments in which the molar ratio of CH_4 to N is higher than 10 (assuming 40% assimilation of every CH_4 mole consumed), such as in landfill soils, limitation of inorganic N may occur (Bodelier & Laanbroek 2004). Long-term depletion of N reduces bacterial growth and protein synthesis, leading to reduction or cessation of CH_4 consumption. This limitation can nonetheless be potentially overcome by N_2 fixation directly from the atmosphere, as seen for type II methanotrophs. However, this process is energetically less favourable than inorganic N consumption; it is therefore not possible to count on this process to maintain growth of methanotrophs, thus CH_4 oxidation.

N-based stimulation of CH_4 oxidation has been observed in rice fields (Cai & Mosier 2000, Dan *et al.* 2001), forest soils (Sitaula & Bakken 1993, Goldman *et al.* 1995, Börjesson & Nohrstedt 2000, Papen *et al.* 2001), and agricultural soils (Hellebrand *et al.* 2003). N-based stimulation of CH_4 oxidation in landfill cover soils exposed to high CH_4 concentration have been reported by Hilger *et al.* (2000a), De Visscher *et al.* (1999, 2001), and De Visscher and Van Cleemput (2003a).

De Visscher and Van Cleemput (2003a) investigated the influence of exposure time to CH_4 on the immediate effect of adding NH_4Cl and $(NH_4)_2SO_4$ to a soil. From their experiments, the authors concluded that soil exposed to high (> 1%) CH_4 mixing ratios developed methanotrophic activity in three stages. The first stage was a rapid growth of methanotrophs, probably of type I bacteria, which yielded higher growth rates and were dependent on inorganic N for growth. The second stage was a decline of the methanotrophic activity, probably caused by N limitation of type I methanotrophs. After a few weeks of steady-state behaviour, a new growth phase was observed, probably dominated by N_2-fixing type II methanotrophs, now independent from inorganic N. Wilshusen *et al.* (2004a) came to a similar conclusion, based on PLFA analysis of compost samples exposed to different O_2 concentrations.

De Visscher *et al.* (1999) investigated the effect of adding wheat straw and sugar beet leaves on CH_4 oxidation in microcosms imitating landfill cover soils. Adding sugar beet leaves, with a low C/N ratio, led to a net N mineralization, and this extra inorganic N source was used by type I methanotrophs for cell synthesis. This resulted in stimulation of CH_4 oxidation that disappeared after one month, when the mineralization effect subsided. Adding wheat straw, with a high C/N ratio, lead to immobilization of the available inorganic N and immediate N stress of the type I methanotrophs, allowing the type II methanotrophs to gain an immediate advantage as N_2 fixing bacteria. The result was a lasting stimulation of CH_4 oxidation.

NO_3^- has proven to be inhibitory through osmotic effects only at high concentrations that are generally not found in landfill environments, unless a large population of ammonia oxidizing bacteria, which would also exert competitive inhibition, is in place (Bodelier & Laanbroek 2004).

Bodelier & Laanbroek (2004) state that CH_4 oxidation in landfill cover soils will be N-limited due to the high C : N content of soils and therefore stress the need to develop fertilization strategies to ensure optimal CH_4 oxidation. Vegetation on landfills might even intensify N-limitation due to the uptake of N by plants. However, over-fertilization of landfill covers to promote plant growth (e.g., in order to control erosion, or at golf courses built on closed landfills) might cause inhibition of the methanotrophs increasing the CH_4 emissions to the atmosphere.

The inhibition mechanisms of N on methanotrophs are however quite complex and not yet fully understood. Furthermore, present knowledge on N effects on CH_4 oxidation is currently based on laboratory studies and there is obviously a need for more *in situ* studies of the regulatory role of N on CH_4 oxidation in landfill soil covers, as well as in landfill biocovers.

Exopolymeric substances

In long-term laboratory column experiments simulating landfill cover or biofilter environments aimed at measuring CH_4 oxidation outcomes obtainable with different types of substrate, uptake rates have often exhibited a peak followed by a decrease to a lower steady state value (Kightley *et al.*

1995, Hilger *et al.* 1999, Scheutz & Kjeldsen 2003, Streese & Stegmann 2003, Wilshusen *et al.* 2004b). Observations of substantial accumulations of exopolymeric substances (EPS) after prolonged gas exposure has been suggested to cause this efficiency decline either due to clogging of soil pores causing short-circuiting of LFG through the soil material or impeded gas diffusion reducing transfer of substrates into the cells (Hilger *et al.* 2000b, Streese & Stegmann 2003, Wilshusen *et al.* 2004b, Haubrichs & Widmann 2006). Wilshusen *et al.* (2004b) noticed that the highest batch CH_4 oxidation rates (V_{max}) and the highest methanotroph cell counts occurred in areas of EPS formation in column studies. Column areas with EPS also contained a significantly higher proportion of type I methanotrophs than other areas of the column. No problems with EPS have been observed in a passively vented field biofilter packed with porous clay pellets (Gebert *et al.* 2003, Gebert & Gröngröft 2006b). This biofilter is subject to loads as high as 247 g CH_4 m^{-3} h^{-1}, however, the LFG flow is intermittent and highly dependent on atmospheric pressure variations (Gebert & Gröngröft 2006a). Possibly, the intermittent supply of LFG and the regular aeration of the filter prevent a production of EPS as a response to carbon excess.

In contrast, EPS formation has not been observed during the 6 years of operation of a passively vented biofilter consisting of industrially produced porous clay pellets, although the intermittently supplied CH_4 loads were as high as 5928 g CH_4 m^{-2} day^{-1} (Gebert *et al.* 2006b).

EPS are high molecular weight compounds that consist mainly of polysaccharides and are produced by many bacteria, including methanotrophs. They are produced in different forms: primarily as capsules, amorphous slime secretions, or as a biofilm of polymer gel with embedded bacteria (Hou *et al.* 1978, Jensen & Corpe 1991). The main function of EPS is to provide bacteria with a source of anchorage to soil surfaces. However, due to their adsorptive and cation exchange properties, EPS can also immobilize metals, promote nutrient accumulation and offer resistance to desiccation, thereby forming a molecular sieve (biofilm) that acts as a barrier for ions present in the solution, and also provides protection against predators (Fletcher 1992).

The nature and degree of polymer formation vary widely depending on environmental conditions and microbial species. Often, excess production to that strictly necessary for soil attachment has been observed (Hilger *et al.* 1999). Although the mechanisms leading to EPS formation by methanotrophs in soils are yet not well known, EPS are supposed to be produced in order to prevent formaldehyde accumulation in case of carbon excess (Linton *et al.* 1986) or lack of nutrients. Hence surplus secretion production of intracellular and extracellular polymers by methanotrophs and other bacteria has been linked to both nutrient imbalance and O_2 deficiency (Wrangstadh *et al.* 1986, Babel 1992).

Accumulation of EPS cannot generally be regarded as a carbon or energy reserve for methanotrophs outside the cell, because such macromolecular exopolymers usually cannot be re-metabolized by methanotrophic bacteria (Chida *et al.* 1983). However, some methanotrophs (e.g. *Methylococcus NCIB 11083*) can accumulate intracellular polysaccharides under CH_4 excess, which then can later be used as a carbon source for protein and cell synthesis. Such intracellular polysaccharides are usually a strong indication for CH_4 oversupply (Linton & Crips, 1978).

Both type I and type II methanotrophs are known to produce EPS. However, Malashenko *et al.* (2001) found that the amount of EPS produced per carbon substrate was 25–28% higher in methanotrophs using the RuMP pathway (i.e. type I) of carbon assimilation than in those using the serine pathway (i.e. type II). EPS formation by type I methanotrophs is favoured by the fact that in the RuMP pathway C_6 sugar-phosphates are formed from formaldehyde at an early stage, which can readily be used for EPS formation. In contrast, type II methanotrophs produce the C_3 compound acetyl-CoA, from which C_6 sugar-phosphates have to be produced via gluconeogenesis (Babel 1992), which is energetically less favourable. During overflow metabolism (for example, in cases of excess formaldehyde production in CH_4-rich environments) type II methanotrophs use acetyl-CoA as precursor for the synthesis of the internal storage polymer poly-β-hydroxybutyrate (PHB).

The accumulation of EPS leads to O_2 limitation, which in turn may induce favourable conditions for the growth of type II methanotrophs, especially under N-limiting conditions. Type II methanotrophs can fix N_2 from the atmosphere when O_2 concentrations are low ($< 4\%$) (Whittenbury & Dalton 1981).

Wilshusen *et al.* (2004a) observed that more stable and slightly higher CH_4 oxidation rates could be achieved at O_2 concentrations of 1.5% instead of 10.5%, and that EPS production was about 2.5 times greater at higher O_2 concentrations than at the lowest levels. The authors hypothesized that the production of EPS was a mechanism of overflow carbon metabolism by type I methanotrophs due to the limited availability of N restraining cell growth. Furthermore, a shift from type I to type II methanotroph dominance was observed over the 6 months of experimental duration, which was linked to the production of EPS and the subsequent microaerophilic conditions. In another study on biofilter columns, PLFA analyses revealed a predominance of type I methanotrophs in column zones with EPS accumulation (Wilshusen *et al.* 2004b).

Knowledge of the specific pathways and mechanisms for EPS formation may help to mitigate excessive slime production in environments where such EPS hinders CH_4 consumption and is unwanted, like in biofilters and biocovers. In investigations performed by Huber-Humer (2004) the overload on carbon was most probably the reason for excessive EPS formation in engineered substrates, like compost materials. This was observed both under high CH_4 loads in the laboratory tests and in the field, at hot-spots with high LFG emissions. However, the way EPS production influences CH_4 oxidation in landfill settings remains unclear.

pH

The optimum pH values for methanotrophic growth and CH_4 oxidation in soils generally lie between 5.5 and 8.5 (Dunfield *et al.* 1993, Hütsch *et al.* 1994, Bender & Conrad 1995, Scheutz & Kjeldsen 2004) and are generally consistent with those of pure cultures of methanotrophs which are between pH 6.6 and 6.8 (Whittenbury *et al.* 1970, Hanson & Hanson 1996). The pH-value in landfill covers will depend on the characteristics of the soil material used. If decalcified or sand-dominated natural substrates are used, pH- values can be well below 7 (down to 4.5). Owing to their increased cation exchange capacity, loamy substrates in general have a higher buffer capacity and are thus less prone to acidification. However, due to the fairly wide pH-range in which methanotrophs operate and the well-known capability of microbial communities to adapt to the prevailing environmental conditions, pH-limitation of methanotrophy is unlikely to occur in natural soil substrates. Changes in pH were observed in soil columns permeated with CH_4, with a trend toward more acidic conditions near the top of the columns probably due to dissolution of CO_2 generated from the oxidation process in the aqueous phase. Addition of lime raised the pH and enhanced CH_4 oxidation (Hilger *et al.* 2000a). In landfill cover systems it is questionable whether significant pH gradients will develop as the dynamics of the system (infiltrating water – changes in soil gas concentrations) will mitigate the accumulation of acidifying oxidation products (H^+, methanol, formic acid, CO_2).

Inhibition of CH_4 oxidation

Methanotrophy is known to be inhibited by various substances, either due to competition with CH_4 for MMO binding sites (reversible) or due to enzyme toxication (irreversible binding). Inhibitory substances include, for example, difluoromethane (Miller *et al.* 1998), dichloromethane (Byers & Sly 1993), methyl fluoride (Frenzel & Bosse 1996), acetylene and ethylene (Prior & Dalton 1985, Chan & Parkin 2000), and NH_4^+ (Bender & Conrad 1994b, King & Schnell 1994). Boeckx *et al.* (1998) found several pesticides to have a negative impact on CH_4 oxidation in arable soils, including lenacil, Mikado, oxadixyl, atrazine, and dimethenamid (Boeckx *et al.* 1998). They also found that landfill cover soils are at least 10 times less sensitive to pesticides than arable soils not exposed to high CH_4 mixing ratios. Arif *et al.* (1996) found that 5 mg $kg^{-1}_{soil\ DW}$ of 2,4-dichlorophenoxy acetic acid (2,4-D) caused partial inhibition of CH_4 oxidation by soil. Börjesson (2001) found that methanethiol and carbon disulfide inhibit CH_4 oxidation in landfill cover soils.

The extent of inhibition will depend on the concentration of both the inhibitor and CH_4 in the gas supplied to the biofilter, as well as on the methanotrophic community composition. De Visscher & Van Cleemput (2003a), for example, observed different NH_4^+ inhibition patterns over time, including stimulation of methanotrophic activity, depending on the community composition of the methanotrophic population (N-dependent type I vs. N-independent type II methanotrophs) throughout the experiments. It has been shown in some cases that a perceived NH_4^+ inhibition effect is actually the result of inhibition by the counter-ion, especially if the counter-ion is Cl^- (De Visscher & Van Cleemput 2003a, Gulledge & Schimel 1998). This lends support to the finding of Wise *et al.* (1999) that the growth media commonly used to enrich cultures of methanotrophs are too concentrated to yield representative species for landfill cover soils (see section entitled ‘The methanotrophic bacteria’).

Scheutz & Kjeldsen (2004) observed inhibition of CH_4 oxidation in presence of hydrochlorofluorocarbons (HCFCs). The CH_4 oxidation rate decreased by approximately 30% as the total HCFC concentration was increased from zero to 1600 $\mu g\ L^{-1}$. The inhibition of CH_4 oxidation by HCFCs is probably a combination of competition for MMO and of accumulation of toxic intermediates that inhibit the microbial activity. In soil covers the trace gas concentration will be even lower due to dilution in the upper soil with atmospheric air, mitigating the inhibitory effect on CH_4 oxidation. However, other trace components present in LFG like trichloroethylene, chloroform, and 1,1-dichloroethylene might have an inhibitory effect on the methanotrophic bacteria due to the toxicity of the compounds themselves or due to accumulation of toxic degradation products (Alvarez-Cohen & McCarty 1991, Alvarez-Cohen & Speitel 2001).

Engineered systems to optimize CH_4 oxidation

As investigations of microbial CH4 oxidation in landfills progressed, the potential to exploit the process in engineered systems was quickly recognized. Observations that high CH_4 oxidation capacity tended to be associated with materials that were porous, coarse, and in many cases, rich in organic matter (e.g., Croft & Emberton 1989, Bergmann *et al.* 1993, Kightley *et al.* 1995, Figueroa 1993, 1998, Börjesson *et al.* 1998a), led to laboratory investigations of methanotroph performance on low-cost materials such as ceramics and composts (sewage sludge, garden waste, and municipal solid waste (MSW)) that possessed many of these properties (Figueroa 1998, Humer & Lechner 1999a, b, Felske 2003, Wilshusen *et al.* 2004b). Results from successful laboratory systems were subsequently tested in engineered field systems, which have come to be called biocovers or biocaps (Humer & Lechner 2001a, b, c, Huber-Humer 2004, Barlaz *et al.* 2004, Bogner *et al.* 2005, Abichou *et al.* 2006a, b, Cabral *et al.* 2007) and biofilters (Streese & Stegmann 2003, Gebert & Gröngröft 2006b).

CH_4 oxidation in organic-rich biocovers

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 vast bio-filter. The cover typically consists of a basal ‘gas distribution layer’ with high gas permeability to homogenize LFG fluxes, and an overlying ‘oxidation layer’ designed to support the methanotrophic populations that will consume the CH_4 for carbon and energy. Since biocovers are typically spread over an entire landfill area or sector, cost becomes a critical factor in material selection, and often raw or composted waste materials, such as dewatered sewage sludge or yard waste, are used. This chapter presents some of the laboratory and field investigations that contributed to current recommendations for engineered biocover systems.

Laboratory studies

Composted waste materials are so heterogeneous that short-term batch tests are not considered reliable for CH_4 oxidation studies unless they are coupled with continuously charged column tests. Columns allow higher mass and coarser particle size testing and longer test runs that can reveal some of the long-term changes that can occur, such as microbial EPS formation (Huber-Humer 2004, Streese 2005; see section entitled 'The process of CH_4 oxidation).

Table 4 lists CH_4 oxidation rates reported for laboratory scale biocovers. Laboratory studies to assess the factors that influence microbial CH_4 oxidation have been conducted on MSW and sewage sludge composts (Humer & Lechner 1999a, b, Huber-Humer 2004, Wilshusen *et al.* 2004a, b), compost mixtures with soil or sand (Huber-Humer 2004, Scheutz *et al.* 2009), compost mixed with perlite (Melse & Van der Werf 2005), biowaste composts of different ages (Felske 2003), leaf compost, commercially available compost, and unscreened wood-chipscompost (Wilshusen *et al.* 2004b). As shown in Table 4, the best CH_4 uptake occurred in well-decomposed (mature), fairly uniform and coarsely structured compost materials with low C/N-ratios and low ammonium concentrations.

Compost maturity ensures minimum competition for O_2 from heterotrophs. The advantage of mature composts to outperform soils with low organic matter contents, or mineral substrates (Felske 2003, Huber-Humer 2004) – e.g., achieving 100% steady-state CH_4 oxidation compared to the 40–45% uptake seen in the soils and minerals (Huber-Humer 2004) – can be lost if the compost is not initially mature. In addition, amplified O_2 consumption can lead to the formation of EPS. Wilshusen *et al.* (2004b) reported that in columns with media of different chemical and physical properties exposed to 178.6 g CH_4 m^{-2} day^{-1} (250 L CH_4 m^{-2} day^{-1} at normal conditions) for 60 days, varying initial CH_4 uptake performance was observed (max. peak oxidation up to 392.9 g CH_4 m^{-2} day^{-1} (550 L CH_4 m^{-2} day^{-1} at normal conditions)). However, at the end of 220 days of operation, there was an equalization of oxidation rates, and all composts reached an 'EPS-affected' steady-state level of about 100 g CH_4 m^{-2} day^{-1} (140 L CH_4 m^{-2} day^{-1} at normal conditions).

Important influencing factors on CH_4 oxidation such as temperature and moisture content can be controlled by the unique physical properties of the compost. Usually, compost materials have a high water retention capacity due to their high organic content and high specific surface area. While this is a beneficial property in arid climates to preserve moisture for the microbes, under wet conditions, the high water content can block gas transport, reduce CH_4 uptake, and in extreme cases, contribute to CH_4 production (Scheutz *et al.* 2009). Thus, good porosity provided by a balanced grain size distribution is important to ensure sufficient gas permeability at high moisture contents. Huber-Humer (2004) showed that mature sewage sludge compost mixed with roughly shredded wood chips (1 : 1 w/w) offered very favourable conditions for moisture (water retention 120% dry matter) and gas permeability even at high degrees of water saturation (bulk density 0.82 kg L^{-1}; air-filled pore volume 45% v/v; balanced particle size distribution 50% w/w 0.2–6.3 mm, and 50% w/w 6.3–60 mm). Moreover, materials with a high air-filled pore volume have a high insulating effect so that suitable temperature conditions can be maintained. In a laboratory study performed by Kettunen *et al.* (2006), mixtures of sewage sludge compost and de-inking waste amended with either sand (SDS-soil, air filled pore volume equal to 37%) or bark chips (SDB-soil, air-filled pore volume equal to 24%) were tested for their CH_4 oxidation capacity under two different temperatures regimes. As shown in Table 4, the SDS-soil with higher air-filled porosity enabled O_2 to penetrate deeper and provided better temperature isolation, so that the CH_4 consumption rate dropped only by half as ambient temperature declined from 21–23 °C (31.4 g CH_4 m^{-2} day^{-1}) to 4–6 °C (15.7 g CH_4 m^{-2} day^{-1}) over a period of about 17 days following microbial adaptation. In contrast, in the SDB-soil, wet bark chips impeded the soil's air movement and reduced the CH_4 consumption rate at 4–6 °C (6.4 g CH_4 m^{-2} day^{-1}) to one-quarter of that at 21–23 °C (25.7 g CH_4 m^{-2} day^{-1}), even after microbial adaptation.

One study addressing concerns about storm water infiltration through biocovers tested a capillary barrier gas distribution layer overlain by soil and then a layer of a compost and sand mix (Berger *et al.* 2005). The barrier had two layers: a lower 30-cm layer of porous small gravel and an upper 10 cm of sand so that water flow would be impeded from infiltrating above but gas could flow freely from below. While water penetration was successfully prevented, its accumulation on the top of the barrier after rain events prevented atmospheric O_2 from reaching the deeper layers of the media, so that CH_4 removal could not be reliably maintained (Berger *et al.* 2005).

Some studies have suggested that the high water retention capacity of biocover compost materials, particularly when combined with the evapotranspirative capacity of vegetation, will be sufficient to prevent high levels of infiltration and leachate production (Gomiscek *et al.* 2001, Huber-Humer & Lechner 2003, Huber-Humer 2004). Plant growth on biocovers usually flourishes because of the moist nutrient-rich medium that compost provides, and estimates from lysimeter tests and field trials (Huber-Humer & Lechner 2003, Huber-Humer 2004) indicate that about 90% of the annual precipitation may be retained in or evapotranspired by a well-designed vegetated biocover in temperate climates (500 to 1000 mm rainfall). The lysimeter tests revealed that leachate accumulation and water infiltration, respectively, might increase by about 10% when high CH_4 oxidation rates occur in compost biocovers due to: (1) microbially produced water

Table 4: Summary of methane oxidation rates obtained in column experiments simulating landfill bio-covers rich in organic matter.

Reference	Filter material	Moisture content	Organic matter	Temp.	CH_4 inlet concentration	CH_4 load	Methane oxidation rate			Duration	Gas profiles
							Steady state		Maximum		
		(% w/dw)	(% w/dw)	(°C)	(% v/v)	(g CH_4 m^{-2} day^{-1})	(g CH_4 m^{-2} day^{-1})	(%)	(%)	(days)	yes/no
Powelson *et al*. (2006)	Mix of compost and polystyrene pellets				50[a]	250–500	242	69	72	86	
	Coarse sand				53	250–500	203	63	58	86	
Kettunen *et al*. (2006)	Mix of mature sewage sludge compost, de-inking waste, and sand (4 : 2 : 4)	57	14	21–23	50[a]	30.7	31.4	97		10–21	yes
				10–12		35.7	27.9	77		22–41	
				4–6		41.4	9.3	22		42–65	
	Mix of mature sewage sludge compost, de-inking waste, and bark chips (4 : 2 : 4)	164	64	21–23	50[a]	32.9	25.7	74		10–21	yes
				10–12		37.1	6.4	16		22–41	
				4–6		42.1	0.7	>1		42–65	
Stein & Hettiaratchi (2001)	Sedge peat moss	316	79		99	Low: 160	88	55	90[d]	351[d]	yes
						High: 319	93	29	50[d]	351[d]	yes
Humer & Lechner (2001a)	MSW compost (60 weeks old)	85	24		100	400	400	100	100	187	yes
	MSW compost (20 weeks old)	82	29		100	400	212	53	100	187	yes
	MSW compost (36 weeks old)	47	25		100	216	212	98	100	84	yes
	SS compost/ wooden chips well matured	96	26		100	180	180	100	100	53	yes
	SS compost/ wooden chips fresh	85	30		100	94	33	35	70	35	yes
	SS compost/ wooden chips well matured	92	26		100	94	94	100	100	84	yes
	SS compost/ wooden chips well matured	92	26		100	216	184	85	96	84	yes
	SS compost/ wooden chips	75	30	30	100	110	110	100	100	190	yes
				18			110	100	100		
				10			110	100	100		
				4			81	74	78		
Humer & Lechner (1999a)	SS-compost/sand mix (70/30)[c]	45	19		100	180	135	75	100	53	no
Du Plessis *et al*. (2003)	Composted pine bark/perlite mixture (1:3)[c]			22	0.1–2.5	54	38	70		120	
Berger *et al*. (2005)	30 cm of compost/ sand-mix on top of 90 cm of sand	14.2/ 10.7	8.2/1.7	20	50[a]	55	52–54	94–98	98	45	yes
				10			48–54	88–98	98	60	
				10			31–50	57–90	90	49	
				4.8			44	80	80	56	
										Total: 229	
Haubrichs & Widmann (2006)	Yard waste compost	32.2	50.0[g]	19	30[b]	589[e]	583	96	100	369	
	Yard waste compost mixed with wood chips (1 : 1)[c]	92.5	50.0[g]		30[b]	485[e]	476	93	100	369	

Table 4: Summary of methane oxidation rates obtained in column experiments simulating landfill bio-covers rich in organic matter. *(Continued)*

Reference	Filter material	Moisture content	Organic matter	Temp.	CH_4 inlet concentration	CH_4 load	Methane oxidation rate			Duration	Gas profiles
							Steady state		Maximum		
		(% w/dw)	(% w/dw)	(°C)	(% v/v)	(g CH_4 m^{-2} day^{-1})	(g CH_4 m^{-2} day^{-1})	(%)	(%)	(days)	yes/no
Scheutz *et al.* (2009)	Compost/wood chips (1 : 1)[c]	68	56	22	50[a]	229–254	161	58	100	255	yes
	Compost/sand (1 : 1)[c]	30	10	22	50[a]	229–254	–31	–10	48	255	yes
	Compost/sand (1 : 5)[c]	14	3	22	50[a]	229–254	29	12	60	255	yes
	Supermuld®	11	4	22	50[a]	229–254	110	48	84	255	yes
Wilshusen *et al.* (2004b)	Compost – leaves	124	46	r.t.	99	520	100	19	77	600	yes
	Compost – garden	122	78	r.t.	99	520	0	0	10	220	yes
	Compost – wood chips	123	34	r.t.	99	520	100	19	19	220	yes
	Compost – MSW	123	49	r.t.	99	520	100	19	52	220	yes
Einola *et al.* (2008)	MBT residual – 22 weeks stabilization	79	47	22–25	50[a]	30	30	100		5–39	yes
				22–25		60–78	53–82	88–100		39–52	yes
				22–25		78	64–74	82–95		52–77	yes
				9–12		78	56	71		77–87	yes
				2–10		78	39	50		87–124	yes
	MBT residual – 57 weeks stabilization	104	39	22–25	50[a]	30	30	100		5–39	yes
				22–25		60–78	53–82	88–100		39–52	yes
				22–25		78	72–79	92		52–77	yes
				9–12		78	61	78		77–87	yes
				2–10		78	22	28		87–124	yes

[a] 50%CH_4/50%CO_2, [b] 30%CH_4/70%CO_2, [c]per weight, [d]Graphically determined based on figures and graphs in reference [e]The filter load was gradually increased from 104 g CH_4 m^{-2} day^{-1} to the listed maximum load; MSW, municipal solid waste; SS, sewage sludge; [f]Biofilter was irrigated (77 L m^{-2}) for irrigation; [g]per moist mass; r.t., room temperature.

(about 1.6 L cm^{-3} oxidized CH_4); and (2) reduced water uptake by plants when root penetration depths are shortened by shrinking oxygenated zones (a result of high O_2 demand due to CH_4 oxidation). If water addition due to CH_4 oxidation is moderate, as the findings from these lysimeter tests have indicated, they may be a welcome effect and enhance waste degradation, which is often slowed by limited water in conventional landfill designs, particularly in arid climates.

Robust plant growth may also provide a more favourable environment for methanotrophs and thereby contribute to good CH_4 removal. Although the interactions of plants with CH_4 oxidation phenomena are complex, there is evidence that vegetation will likely enhance biotic CH_4 uptake (Hilger *et al.* 2000a, Maurice 2001, Wang *et al.* 2008) as well as control moisture infiltration. As plant roots penetrate the cover, they excrete exudates into the soil and provide a favourable support matrix for micro-organisms so that rhizosphere populations are typically much higher than in soil alone. Some negative effects of plants include their competition for limited O_2 supplies, and the potential for their roots to create preferential channels for localized CH_4 emissions. Recently, it has been demonstrated using stable carbon isotopes that CH_4 is readily formed *in situ* in terrestrial plants under oxic conditions (Keppler *et al.* 2006).

Field trials and experience

In 1999, long-term field trials on two Austrian MSW-landfills were initiated with two main objectives: (a) to find an optimal cover design for middle-European climatic conditions (warm-temperate climate zone, climate classification type Cfb according to Kottek *et al.* 2006), and; (b) assess the interaction between CH_4 oxidation and the water balance (leachate generation) of compost covers to which specific vegetation was planted (Humer & Lechner 2001a, b, c, Huber-Humer 2004). On landfill I (14 ha), which possessed an active gas extraction system, five differently designed test cells were constructed and monitored. On landfill II (3.1 ha), which was a closed MSW-site with no operating gas extraction system, six test cells were installed. Both systems were studied for more than two years. The greatest annual CH_4 emission reduction (89–100%) occurred where a 1.0 m compost layer was placed atop a gravel gas distribution layer (0.3 m). A coarse sewage sludge compost (mixed with big wood chips) exhibited a much better temperature insulating capacity during winter than a fine-sieved MSW-compost (Huber-Humer 2004), and with the proper compost selection, the 1-m deep compost layer was able to maintain suitable temperature conditions during middle-European winter conditions (temperate zone).

A US demonstration site was developed at the Outer Loop Landfill in Louisville, Kentucky, where a biocover system was tested in parallel with a 1 m clay soil cover for CH_4 emissions (Barlaz *et al.* 2004). The biocover included, from bottom up: a 0.15-m base layer of clay, 0.15-m layer of tyre chips that served as gas distribution layer, and a 1-m thick layer of ground yard waste previously windrow-composted for 3 months. Self-seeded vegetation became established on both covers. Flux chamber measurements were performed with and without a gas collection system operating over the course of 1 year. Although emissions were generally low in both covers, the soil cover developed visible cracks, and there was high variability in flux data collected there (compare with Table 6 below). More waste-generated CH_4 passed through the permeable biocover than through the soil, but the biocover data was more uniform and generally showed zero emissions or uptake of atmospheric CH_4 during most measurement campaigns. Of 36 measurements made on the biocover while the gas collection system was off, 22 gave negative values (indicating an uptake of atmospheric CH_4 into the cover) and five had values equal to virtually zero (or below detectable limits). In the soil cover, 25 similar measurements yielded only three negative values and eight with zero flux. The results of the monitoring campaigns conducted for this study (Barlaz *et al.* (2004)) are summarized in Table 6 below.

Isotope methods were used at the Outer Loop site to measure CH_4 oxidation in the covers. However, the high propensity of both covers to consume atmospheric CH_4 made use of this technique challenging because both atmospheric and landfill CH_4 were used simultaneously as substrate by methanotrophs. However, in a few instances where positive emissions were measured, the results showed that an average of 55% of landfill CH_4 was oxidized in the biocover but only 21% in the soil cover. Measurement of trace organics from the two cover types also suggested that trace contaminant emissions were reduced to a greater extent by the biocover than by the soil cover.

Experiments at the Leon County Landfill in Florida assessed biocover effectiveness in subtropical environments and evaluated the suitability of various recycled waste materials for the gas distribution layer (Bogner *et al.* 2005). A base of crushed glass and fluorescent glass light bulbs overlain by composted or ground garden waste comprised the biocover, which is layered atop different existing intermediate soil covers of various thicknesses. The existing intermediate covers serve as control sites (Bogner *et al.* 2005). The results indicate that depending on the design of the biocovers, median positive CH_4 fluxes on the biocovers are one to two orders of magnitude less than the maximum median fluxes on the corresponding control sites. As in the Outer Loop trials, many of the fluxes measured in the biocovered areas were negative because uptake of atmospheric CH_4 was occurring.

The Florida study also compared the CH_4 oxidation and emission mitigation performance of simulated low-dimensioned intermediate/daily covers (15 cm unvegetated sandy clay) against that of a non-engineered cover style (45 cm of sandy clay and sandy loam) of an older closed landfill (Abichou *et al.* 2006a). They found (see Table 6 below) that although CH_4 emissions from the thin intermediate cover (geospatial mean flux 50.0 g CH_4 m^{-2} day^{-1}) were double the emissions from the thicker well-vegetated soil cover (21.6 g CH_4 m^{-2} day^{-1}), isotope measurements showed that CH_4 oxidation was only partly responsible for the lower emissions from the thicker cover. The age and, consequently, the gas generation rate of the underlying waste (1-year-old waste beneath the intermediate cover, 7 years old beneath the thicker cover) had more impact on the emission pattern. Results from Abichou *et al.* (2006a) indicate that low-dimensioned and poorly designed covers do not reach the high CH_4 mitigation potential achieved with properly designed biocovers, as it was also shown by Huber-Humer (2004). Further, these results emphasize the need for site-specific cover designs. Abichou *et al.* (2006a) suggest that one model for intermediate soil cover would be to place a thin compost layer over the entire area, and then place individual compost cells only over high emission zones.

Practical applications and design of compost covers

In Austria, five closed MSW-landfills have been covered with interim compost biocovers (officially approved for a period of about 20 years). These biocovers are serving either as the sole means to mitigate CH_4 emissions or complements an operating gas extraction system. Designed according to recommendations from the Austrian field trials (Huber-Humer 2004), the biocover features are those suitable for temperate climates. The biocovers consist of a coarse gravel gas distribution layer (0.5 m) overlain by a 1.2 m oxidation layer of mature, well-structured sewage sludge/wood chip compost, or a municipal solid waste/sewage sludge/wood chip compost).

The depth of the oxidation layer and the materials used to construct it can vary depending on the climate (precipitation, temperature, frost penetration depth), the expected LFG fluxes, the other functions of the cover (final or temporary), the after-use plans (vegetation, land use), and the local availability and cost of cover materials. A good oxidation layer will possess a long-term nutrient supply (N, P), a high temperature-insulating capacity, and above all, physical properties that provide good porosity and gas permeability even along with a high water holding capacity. To maintain the long-term porosity and gas permeability of an oxidation layer made of compost, it should be placed without any artificial compaction. Based on the Austrian field trials, about 20% settlement is expected on these sites during the first few years after placement, as natural consolidation occurs due to proceeding mineralization processes and subsidence. In three biocovers composed of a mixture of sand and 2-year-old compost sieved to particle size < 12 mm (organic matter content of mixture equal to 25%) constructed at the St-Nicéphore landfill in Quebec, Canada, settlements in the order of 9.4% were observed 1 year after construction (personal com-

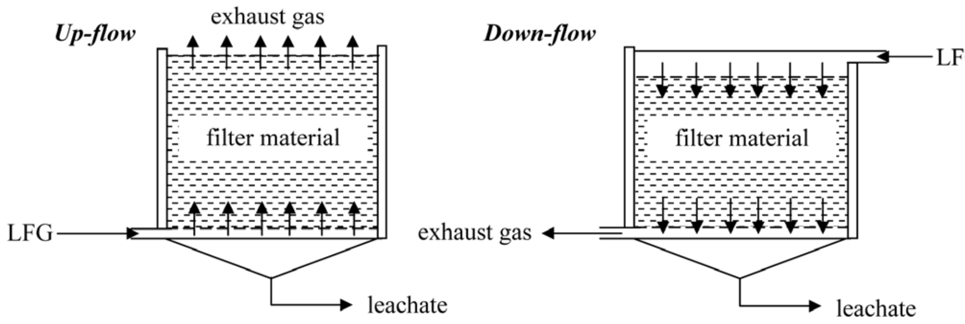

Fig. 5: Standard variants of biofilter design. Modified from Dammann, B., Streese, J., Stegmann, R., (1999). Microbial oxidation of methane from landfills in biofilters. In: Christensen, T. H., Cossu, R., Stegmann, R. (Eds.), Proceedings Sardinia '99. Seventh International Waste Management and Landfill Symposium. CISA, Environmental Sanitary Engineering Centre, Cagliari, Italy, vol. II, pp. 517–524 with permission from CISA.

munication, A. Cabral), despite the fact that the substrate was compacted at the beginning. Furthermore, the Canadian study indicates that compaction and fine-sieving of compost materials may result in bad biocover performance particularly during wet seasons, although their biocovers work reasonably well in dry periods (Cabral *et al*. 2007, Jugnia *et al*. 2008).

CH_4 oxidation in biofilters

Biofilters, like biocovers, exploit CH_4 oxidizing bacteria to mitigate landfill CH_4 emissions. Operated as self-contained fixed bed reactors with a packing material to support and sustain a methanotrophic biofilm, biofilters can accomplish high CH_4 removal rates. Unlike biocovers, biofilters require a steady supply of LFG, which is usually provided by a gas collection or drainage system. This section reviews typical biofilter configurations and packing materials, presents data from both laboratory and field investigations, and describes some operational problems that can arise.

Biofilter design

Typically, biofilters are operated either in an upflow or a downflow mode (Figure 5). The upflow alternative allows for the diffusive ingress of atmospheric O_2, if the biofilter is operated as an open bed.

LFG supply to biofilters may be active or passive. In an active system, gas is extracted from the landfill and supplied to the biofilter at a controlled flow rate. Air can be combined with the LFG flow (e.g. Streese & Stegmann 2003, Du Plessis *et al*. 2003), or it can be introduced into the biofilter through a separate feed line (Haubrichs & Widmann 2006). Alternatively, air may enter by diffusive ingress across the column surface (Wilshusen *et al*. 2004b). Actively fed systems are usually operated at constant temperature and water content and therefore require a power supply. In order to facilitate control over the operational parameters, these systems often are housed.

Passive systems receive LFG when a pressure gradient between the landfill and the atmosphere drives the gas through collection piping and delivers it to the biofilter (Straka *et al*. 1999, Dever *et al*. 2005, Gebert & Gröngröft 2006b). Some passive biofilters currently in use function as up-flow open bed systems that operate at ambient temperature. LFG flow results from pressure gradients, while diffusion may play a role when these pressure gradients are low. O_2 is supplied by diffusion from the atmosphere across the biofilter surface or by advection when the barometric pressure rises (Gebert & Gröngröft 2006a). Another form of passive filter system are 'windows', which are not truly self contained units of media but expanses of biofiltration media integrated into the landfill cover. The porous media offers a preferential pathway for the LFG, and no gas extraction system is employed. (e.g. Swarbrick *et al*. 2005). In 2006, a research project was initiated at Fakse landfill in Denmark under the EU Life Environment programme, implementing a passive full-scale biocover window system into a clay cover in order to optimize CH_4 oxidation and reduce emissions (Kjeldsen *et al*. 2007). While operational conditions are not as manageable in passive systems, the capital and operating costs are considerably lower than for actively vented biofilters.

Filter packing material

Various media have been tested in methanotrophic biofilters such as composts including composted wastes (Mennerich 1986, Figueroa 1996, Straka *et al*. 1999, Streese & Stegmann 2003, Wilshusen *et al*. 2004b, Dever *et al*. 2005, Scheutz *et al*. 2009), wood chips, bark mulch (Mennerich 1986) and peat; inorganic materials such as glass beads (Sly *et al*. 1993, Nikiema *et al*. 2005), bottom ash (Maurice & Lagerkvist 2004) or porous clay pellets (Gebert *et al*. 2003); as well as mixtures of organic and inert materials (Du Plessis *et al*. 2003, Melse & Van der Werf 2005). In general, the filter material should:

- Provide sufficient water-holding capacity at high gas permeability,
- Be homogeneous to prevent preferential flow,
- Be resistant towards microbial degradation, and
- Provide environmental conditions suitable for proliferation of methanotrophs.

High gas permeability is warranted by a high share of pores > 50 µm. Low clay content in natural soil substrates provides for a low shrinking and thus aggregate formation potential and thus minimizes preferential flow. If composts are used, high stability should be ensured to prevent microbial degradation and settlement, thereby avoiding potential reductions in gas permeability. Favourable environmental conditions are provided by materials with circumneutral pH-values and offering an adequate supply of nutrients (see section entitled ‘Environmental factors influencing CH_4 oxidation in landfill cover soils’).

Operational problems

One problem that can occur in biofilters is the accumulation of EPS, which may clog the filter material, thereby reducing gas permeability and impeding mass transfer. The stimuli for its production as well as observations from biofilter operation are discussed in the section entitled ‘Environmental factors influencing CH_4 oxidation in landfill cover soils’. Use of coarse inorganic materials that are less prone to clogging, as well as an intermittent supply of LFG to prevent excess CH_4 charge and provide for regular aeration, may be a solution to prevent EPS formation in biofilters.

Heating biofilters to enhance oxidation rates can lead to partial desiccation of the packing material (Streese & Stegmann 2003, Haubrichs & Widmann 2006) and condensation at the container walls if the surroundings are cooler. Uneven water distribution after irrigation can cause sub-optimum biofilter performance, and especially in organic packing materials, anaerobic conditions can result where CH_4 is produced rather than consumed (Haubrichs & Widmann 2006). If the filter material itself is biodegradable, material settlement can significantly reduce the gas permeability.

Methanotrophy is also subject to a variety of inhibitors (see section entitled ‘Environmental factors influencing CH_4 oxidation in landfill cover soils’), some of which can be contained in the LFG passing through the filter. The extent of inhibition will depend on how much of the compound is present and the community composition of the methanotrophic bacteria. Finally, the performances of systems that rely on the diffusive ingress of O_2 to sustain methanotrophy are sensitive to the magnitude of advective LFG fluxes (Gebert & Gröngröft, 2005).

CH_4 oxidation capacity of biofilters

Table 5 summarizes CH_4 oxidation rates reported for laboratory column experiments intended to test a biofilter application, operated with different filter materials, at different inlet CH_4 concentrations and at different CH_4 flow rates. In many cases, authors have investigated different flow rates or CH_4 concentrations. The table thus only presents a selection of values found in the cited literature. Where applicable, maximum rates observed as well as long-term steady-state oxidation rates were reported. In experiments where different input CH_4 concentrations were tested, oxidation rates increased as inlet CH_4 levels increased according to near first-order reaction kinetics (e.g. Sly *et al*. 1996, Streese &

Table 5: Selected methane oxidation rates reported for column experiments intended to simulate biofilter applications. If the transformation of data on flow and oxidation rates required the conversion of volumetric units into mass units and no information on temperature and pressure was available, standard temperature and pressure were assumed.

Reference	Filter material/ Soil texture	Moisture content	Organic matter	CH_4 inlet conc.	CH_4 flow rate steady state	CH_4 flow rate maximum	CH_4 oxidation rate steady state	CH_4 oxidation rate maximum	Duration	Gas profiles
		(% w/dw)	(% w/dw)	(% v/v)	(g m^{-2} day^{-1})	(g m^{-2} day^{-1})	(g m^{-2} day^{-1})	(g m^{-2} day^{-1})	(days)	yes/no
Sly *et al.* (1993)	glass tubes	0; water trickling system	0	0.25–1	–	2249	–	586	244	no
Park *et al.* (2002)	loamy sand*[1]	13	0.4	100	–	525	–	435	90	yes
Du Plessis *et al.* (2003)	composted pine bark/ perlite mix	n.a.	n.a.	0.1–2.5	–	743	–	87*[2]–49*[3]	n.a.	no
Streese & Stegmann (2003)	compost/ peat/wood fibre mix	85.2	52.1	0.3–32	170	1809	158	341	350	no
Wilshusen *et al.* (2004b)	composts of leaves, wood chips, MSW	123–124	34–49	100	n.a.	n.a.	84–120	276–96	220	yes
Melse & Van der Werf (2005)	compost/ perlite mix	n.a.	n.a.	0.07–0.8**	–	614	–	377	60	no
Haubrichs & Widmann (2006)	compost	100	32.2	30	–	592	–	592	374	yes

*[1]Acccording to United States Department of Agriculture (USDA) texture classification. *[2]Value measured. *[3]Value interpolated.
**Logarithmic mean methane concentration c_M ($c_M = (c_{in} - c_{out})/(\ln c_{in}/c_{out})$), n.a., information not available.

Stegmann 2003, Melse & Van der Werf 2005). In some studies, the mass loading of CH_4 to the biofilter was below the maximum CH_4 oxidation capacity of system. Interestingly, the table shows that in spite of the very different operational conditions with respect to inlet concentration, gas flow rate or filter material, the maximum CH_4 oxidation rates reported are approximately in the same order of magnitude (340–591 g CH_4 m^{-2} day^{-1}), except for the filter investigated by Du Plessis *et al.* (2003) which are a little lower. It has to be noted, however, that frequently the experiments were conducted at inlet CH_4 concentrations yielding first-order kinetics. Increased removal rates are to be expected in systems operated at higher concentrations resulting in zero order kinetics as long as sufficient O_2 supply is warranted.

There are only a few reports of performance data from biofilters actually operated on landfills. Streese (2005) used an actively vented 4 m^3 biofilter (4 × 1 m^3 units) operated in down flow mode and fed with LFG/air mixtures at CH_4 concentrations of approximately 2% v/v (CH_4 flux : approximately 2903 g CH_4 m^{-2} day^{-1}). Tests were conducted at about 20 °C, and of the various filter materials tested, a compost with particle sizes < 10 mm proved the most effective, with stable degradation rates of 258–516 g CH_4 m^{-2} day^{-1}. In many cases, authors have investigated different flow rates or CH_4 concentrations. The table thus only presents a selection of values found in the cited literature. Initial high rates of 1806 g CH_4 m^{-2} day^{-1} could not be maintained, presumably because high temperatures developed in the filter and the media became too dry.

When Gebert & Gröngröft (2006b) analysed a 15 m^3 up flow open bed containing porous clay pellets overtopped by humic topsoil, oxidation rates as high as 1920 g CH_4 m^{-2} day^{-1} were observed. The filter load was 5928 g CH_4 m^{-2} day^{-1} (CH_4 concentrations 0–55% v/v) fed by a passive LFG drainage system. When gas flow rates were higher and constant, the filter capacity was limited by the rate of O_2 diffusion into the bed.

For another passive up flow open bed biofilter that received LFG containing 55–65% v/v CH_4 through a drainage trench from an older landfill, Straka *et al.* (1999) reported CH_4 removal rates of more than 90% at loading rates of 26–60 m^{-3} m^{-3} day^{-1} (Straka *et al.* 1999). The height of the biofilter material varied between 0.8 and 2 m. Data on the chamber emission measurements, however, are not supplied. The biofilter media used were mixtures of compost and bark or wood chips, but few other details are reported.

Powelson *et al.* (2006) evaluated two outdoor biofilters: one made up of a combination of differently textured sands and the other made up of a mixture of chipped yard waste compost and polystyrene pellets, both receiving a synthetic LFG mixture with 53% v/v CH_4. In the sand biofilter, the differently textured sands were installed in such a way to produce a fining-upward gradient of particle size and therefore of soil pores. The intention of this design was to increase the water content near the top as a result of increased matrix potential and the share of gas-filled pore space towards the bottom in order to counteract desiccation in the upper and water-logging in the deeper layers and thereby achieve a more uniform distribution of water. Both biofilters performed similarly well in the longer run, on average oxidizing 63% (sand biofilter) and 69% (compost biofilter) of the input CH_4 flux in the range of close to zero up to 750 g CH_4 m^{-2} day^{-1}. The constancy of the percentage of CH_4 degraded, irrespective of the magnitude of the input flux, indicated that the capacity limit had not been approached. The initially higher CH_4 oxidation rate by the compost material had declined after 63 days of operation to the level of the sand biofilter.

The issue of temperature limitation of methanotrophic activity during winter conditions was addressed by Zeiss (2006) who used a passive heat exchange system to transfer heat from inside the landfill to a compost biofilter bed integrated into the cover of a MSW landfill in Western Canada. The heat exchange raised the filter temperature to 14–18 °C and resulted in an increase in performance from an average of 33% (unheated bed) to 89% oxidation of the inlet CH_4 flux, equalling an oxidation rate of up to 40 g CH_4 m^{-2} day^{-1}.

Several authors have extrapolated their laboratory and pilot scale biofilter data to estimate required biofilter sizes for possible large-scale applications. Streese & Stegmann (2003) calculated that a biofilter operated at 20–25 °C would require a volume of 940 m^3 (area: 2848 m^2) to remove 90% of the CH_4 from LFG entering the system at 9600 m^3 day^{-1} and containing 2.5% v/v CH_4 (i.e. a CH_4 flow rate of 171 360 g day^{-1}). Gebert (2004) estimated that a passively vented system would need to be twice this volume (1920 m^3 = 1920 m^2 at an average height of 1 m) to treat the same CH_4 load. In this system, the CH_4 feed to the biofilter was uncontrolled and the temperature was dominated by the ambient atmospheric conditions. Thus, adverse conditions with respect to both CH_4 load/O_2 supply and temperature, especially during winter necessitated a larger volume to warrant high degradation rates. Melse & Van der Werf (2005) calculated that a biofilter volume of only 47 m^2 would be needed for a passive system to treat 39 600 g CH_4 day^{-1} at 12 °C with 75% efficiency. Just as the biofilter investigated by Streese & Stegmann (2003), this system was operated at optimum conditions of O_2 supply, which entered the filter material with the inlet flow. The reaction rate constant (k-value) reported by Melse & Van der Werf, however, was 2.5 times higher than the more 'conservative' value estimated by Streese & Stegmann. The combination of a higher k-value with the lower CH_4 load and only 75% efficiency accounts for the comparatively small estimated biofilter volume. The calculations by Gebert (2004) and by Streese & Stegmann were derived from long-term experiments (4 years and 350 days, respectively) whereas Melse & Van der Werf (2005) used data from only 60 days of operation. Given the frequent observation that initial high degradation rates decline in the longer term, a conservative estimate of the reaction rate constant k may be applicable to reliably predict long-term performance. Finally, Haubrichs & Widmann (2006) proposed that a 230 m^3 (area = 219 m^2) filter operating at 19 °C would remove 96% of the CH_4 from a 720 m^3 day^{-1} gas flow containing 30% v/v CH_4 (i.e. a CH_4 flow rate of 144 000 g h^{-1}). This system also was housed, well aerated and irrigated. The smaller volume compared to the suggestions made by Streese & Stegmann (2005) for the treatment of a similar CH_4 flow rate is due to the higher oxidation rate observed in the column study (cf. Table 5).

Size and composition of methanotrophic population in biofilters

Information on the size and composition of the methanotrophic population in biofilters is scarce. Dammann *et al.* (1999) and Gebert *et al.* (2003) found very high cell counts both in a compost biofilter column (Most probable number (MPN) = 2×10^{10} to 2×10^{11} g^{-1} dry weight basis (dw)) and in a humic soil and porous clay from a field-scale biofilter (MPN = 1.3×10^8 to 1.2×10^{11} g^{-1} dw). These ranges are up to four orders of magnitude higher than the methanotrophic abundance reported for other CH_4-influenced habitats (6×10^6–6×10^7 g^{-1} dw; Jones & Nedwell 1993, Vecherskaya *et al.* 1993, Joulian *et al.* 1997, Dubey *et al.* 2002, Horz *et al.* 2002).

Wilshusen *et al.* (2004b) found 0.1×10^6 to 7.3×10^6 cells g^{-1} dw in various composts retrieved from biofilter columns. PLFA analyses of media from two field-scale biofilters showed that the filters were strongly dominated by type II methanotrophs (Gebert *et al.* 2004), and that the composition of the type II population was strongly influenced by the presence of trace organics in the LFG fed to one of the filters. Up to 87% of the total methanotrophic PLFA was represented by the fatty acid 18 : 1ω7c. Biofilter columns studied by Wilshusen *et al.* (2004b) showed a mixed type I and type II methanotrophic population, which shifted towards a type I dominance in areas of marked EPS presence. Nikiema *et al.* (2005) used restriction fragment length polymorphism analysis of 16 S rRNA to characterize the structure of the microbial community present in a laboratory-scale biofilter column with an inorganic filter bed and charged with 1.2 g CH_4 h^{-1}. Seventy-five percent of the recovered restriction profiles belonged to the type II methanotroph *Methylocystis parvus*, which was thus judged to be the dominant CH_4 oxidizer resident in the biofilter.

Conclusions on CH_4 oxidation in biocovers and biofilters

Clearly, microbial oxidation of CH_4 in engineered landfill covers and biofilters provides a promising strategy for the cost-effective mitigation of CH_4 emissions. Whether serving as a complement to gas collection systems at large landfills or as a sole removal mechanism at smaller or older landfills with small CH_4 emissions, these biologically based passive treatment systems are appropriate measures. Often the cost of installing energy recovery or flare systems at small landfills is prohibitive, and the same is true of collection system retrofits or repairs at older landfills. Thus, low-cost alternatives are required. In Europe, where the EC landfill directive (1999/31) requires that only material of low biological activity can be disposed, biocovers and biofilters offer an efficient alternative for landfills containing inert solid waste or mechanically and biologically pre-treated (MBP) waste with low CH_4 production potential. Biocovers can also be applied as a temporary cover on operating landfill sites, or to enhance the success of forced in situ aeration measures. The residual CH_4 in the exhaust gas from the *in situ* aeration process can then be treated in biofilters (Scharff *et al.* 2003). Other fields of biofilter application include the treatment of CH_4 emitted from animal husbandry (Melse & Van der Werf 2005), treatment of solution gas associated with the production of fossil fuels (Yang *et al.* 2000) and the treatment of coal mine ventilation (Sly *et al.* 1993, Du Plessis *et al.* 2003).

As 'low technology' systems, biocovers and biofilters offer many economic advantages, including low operation and installation expenses, and low (or no) maintenance requirements, which make them particularly suitable for developing countries. Finally, these systems foster the use of materials like sewage sludge, municipal solid waste, bio-waste or yard waste that would otherwise be disposed off as wastes.

EPS formation, as well as rapid deterioration of the cover material, is amongst the few challenges facing the implementation of biocovers and biofilters. Moreover, such low-tech biobased systems do not allow for much control of the environmental factors that influence CH_4 oxidation or for accurate monitoring of CH_4 removal efficiency.

For biofilters, existing studies have provided data needed for design and dimensioning full-scale systems. However, phenomena impeding successful biofilter operation, such as EPS formation or CH_4 production from organic filter materials reaching high degrees of water saturation, require further investigation, along with continued assessment of the suitability of different filter materials and the loading rates and residence times required for their optimum performance.

Field-scale quantification of landfill CH_4 oxidation and net emissions

CH_4 oxidation at field scale

Landfill cover materials via their gas-filled porosity provide a medium for the bi-directional transport of gases between the landfill and the atmosphere. Stable carbon isotopic methods, which rely on the difference between the $\delta^{13}C$ of emitted CH_4 compared to the $\delta^{13}C$ of unoxidized CH_4 in the anaerobic zone, provide the most robust field approach for the quantification of fractional CH_4 oxidation, that is, the percentage of CH_4 that is oxidized during transport through the landfill cover materials. Since field measurements of emissions quantify 'net' CH_4 emissions inclusive of oxidation, it is then possible to derive the 'gross' rate of CH_4 flux from the waste to the cover using the combined emissions and oxidation data. The isotopic methods have been developed over the last decade and rely on the preference of methanotrophs for the stable carbon isotope of smaller mass, ^{12}C rather than ^{13}C, according to one or more fractionation factor(s) dependent on soil properties and gaseous transport considerations (Liptay *et al.* 1998, Chanton & Liptay 2000). Thus methanotrophic bacteria will oxidize $^{12}CH_4$ at a slightly more rapid rate than $^{13}CH_4$. Using standard isotopic notation, the $\delta^{13}C$ (‰) for CH_4 in a gas sample is calculated by:

$$\delta = 1000\left(\frac{R_{\text{sam}}}{R_{\text{std}}} - 1\right) \tag{2}$$

where R_{sam} is the $^{13}C/^{12}C$ ratio of the sample and R_{std} is the ratio for the standard Vienna Peedee Belemnite (0.01124). As a minimum, calculation of the oxidized fraction requires samples from the anoxic zone gas and the oxidized gas at the location of interest, and knowledge of the isotope fractionation factor due to oxidation, α_{ox} (Liptay *et al.* 1998, Chanton & Liptay 2000). Alternatively, for larger areas, the $\delta^{13}C$ for atmospheric CH_4 can be compared between upwind and downwind transects (Chanton *et al.* 1999). It is highly recommended that controlled field incubations of soils with known CH_4 concentrations is conducted during field campaigns in order to derive site- and time-specific fractionation factors. In general, the isotopic methods are deployed in three ways: (1) at ground level, using static chambers and comparing the $\delta^{13}C$ of CH_4 in the refuse (by sampling at gas recovery wells, gas collection headers, or deep gas probes) to the emitted CH_4 collected in the chamber; (2) in the lower atmosphere, relying on a comparison between the $\delta^{13}C$ of atmospheric CH_4 in an upwind transect to a downwind transect; and (3) below ground level, relying on soil gas profiles for CH_4 and $\delta^{13}C$. These approaches can also be used in combination to derive CH_4 oxidation at various temporal and spatial scales. In general, $\delta^{13}C$ values for unoxidized CH_4 in the anaerobic zone range from about –57 to –60; with oxidation, these values can undergo a positive shift to –35 or more. An additional possibility is to use combined $\delta^{13}C$ and δD methods since the hydrogen isotope has a larger relative fractionation factor than the carbon isotope. Recent literature discusses methods, applications, appropriate isotopic models, and remaining issues with respect to these methods (De Visscher *et al.* 2004, Mahieu *et al.* 2006, Chanton *et al.* 2008a, b). In situations where static chamber measurements yield 'negative' fluxes, indicating that methanotrophs are capable of oxidizing all of the CH_4 transported from the landfill below and also oxidize additional CH_4 out of the atmosphere, the isotopic method discussed above is not applicable. In such cases, the static chamber is quantifying the rate of atmospheric CH_4 oxidation/uptake, and data should be reported accordingly.

Prior to the development of the isotopic methods, field researchers relied on field or laboratory batch incubations of site soils with known CH_4 headspace concentrations, calculating oxidation from CH_4 loss over the incubation period. In the field, cores of cover soil can be incubated in gas-tight bottles under field conditions with individual bottles placed directly in the void space from which a shallow soil core is taken: sets of assays are typically grouped together over a small area with similar cover, slope, aspect, and temperature. If these are completed at field conditions during the same time period as emissions measurements, use a series of headspace CH_4 concentrations which bracket CH_4 concentrations observed in soil gas profiles, and rigorously apply replicates and controls, these techniques provide reasonable field estimates of CH_4 oxidation, albeit via a labour-intensive approach. Where field incubations have been conducted simultaneously with chamber measurements resulting in negative fluxes, the two techniques give comparable results (Bogner *et al.* 1997a).

Older literature ranging back to the 1980s attempted to use mass ratios and mass balances for the CH_4 and CO_2 to derive CH_4 oxidation. However, this is problematical because, in addition to production of CO_2 via methanogenesis and CH_4 oxidation, CO_2 is also produced and consumed by multiple subsurface and near surface processes (soil respiration, organic matter oxidation, photosynthesis) which preclude the use of simple CO_2/CH_4 mass ratios. Moreover, CO_2 is preferentially partitioned to soil moisture because it is more soluble than CH_4. Therefore, unlike in laboratory column studies where inputs and processes can be either controlled or monitored, mass ratio and mass balance methods are not recommended for field settings.

Overall, CH_4 oxidation in landfill cover soils can range from negligible to more than 100% (oxidation of atmospheric CH_4) in field settings. The dynamic coupling between deeper anaerobic landfill CH_4 production zones and near-surface aerobic oxidation zones is similar to wetland ecosystems (Bogner *et al.* 2000). The thickness, physical properties, and moisture content of cover soils all affect CH_4 oxidation, because rates are limited by the transport of CH_4 upward from anaerobic zones and O_2 downward from the atmosphere. In recent French mass balance studies (Spokas *et al.* 2006) the stable carbon isotopic technique of Chanton & Liptay (2000) demonstrated that CH_4 oxidation was negligible at Montreuil-sur-Barse during cold, wet winter conditions. In contrast, at Lapouyade, 15% oxidation was observed during a winter field campaign under warmer Mediterranean conditions. Chanton & Liptay (2000) have previously shown that seasonal variations in fractional CH_4 oxidation at a Florida landfill may range from negligible to > 40%. Figure 6 shows decreased emissions of approximately one order of magnitude resulting from a biocover of 50 cm garden waste compost over 15 cm ground glass (gas distribution layer). For the biocover, note the direct control of emissions by oxidation: where oxidation is high, emissions are low. Figure 7 illustrates some emission trends and the development of high percentages of negative fluxes in a Florida study. The top figure (a) compares a 2-year time series of median positive fluxes for a control area N (15 cm temporary cover), shallow (S) biocover above temporary cover (12 cm glass overlain by 30 cm ground garden waste), and deep (D) biocover above temporary cover (12 cm glass overlain by 60 cm ground garden waste). Each point represents ≥ 8 replicates. Note that the N emissions are roughly an order of magnitude greater than the D fluxes. The lower figure (b) indicates the percentage of negative fluxes (uptake of atmospheric CH_4). There were no negative fluxes for the N area with seasonally variable percentages ranging up to 50 % of measurements for both the S and D areas.

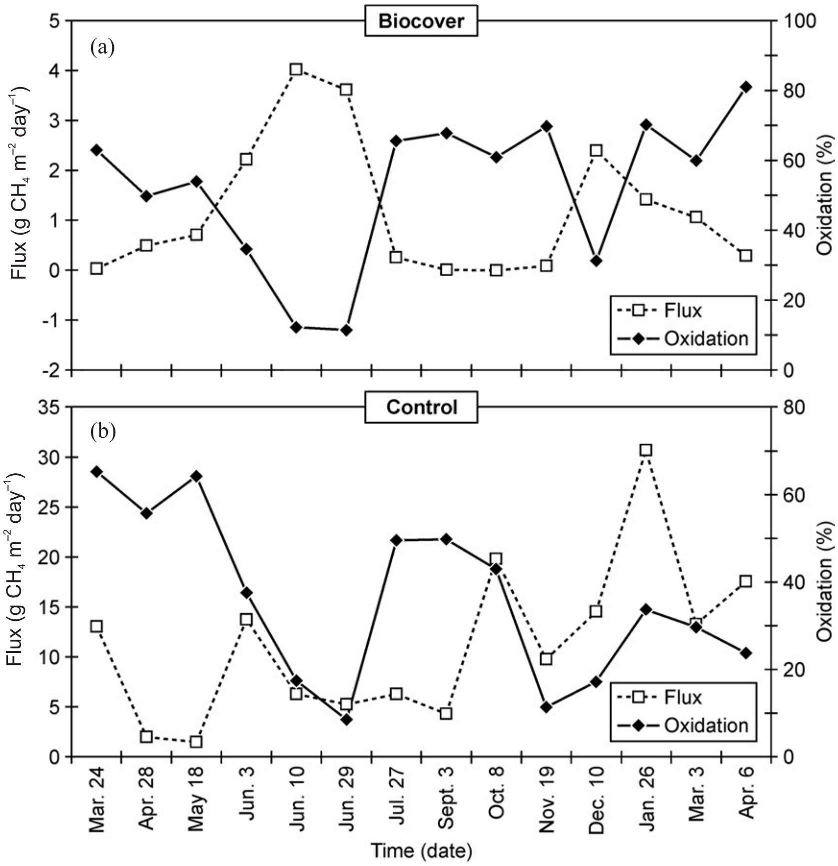

Fig. 6: First year time series showing mean fluxes (g m^{-2} day^{-1}) and percentage oxidation for a biocover area (a): 1 m of clay and 9 cm mulch and topsoil] compared to a control area [(b): 1 m of clay, no mulch or top soil, Leon County, Florida, USA. Fluxes measured using static chambers; oxidation measured using isotopic method. Reproduced from Chanton, J., Liptay, K. (2000). Seasonal variation in methane oxidation in landfill cover soils as determined by an in situ stable isotope technique. Global Biogeochemical Cycles 14, 51–60. Copyright 2000 American Geophysical Union. With permission from American Geophysical Union.

Net CH_4 emissions inclusive of oxidation at field scale: methods and results

During the last decade, field measurement programs on several continents have advanced our technical understanding of 'net' CH_4 emission rates inclusive of methanotrophic oxidation. To a large extent, the discussion below updates a previous review paper (Bogner *et al*. 1997b). In general, compared to terrestrial wetlands and rice production regions, there have been relatively few comprehensive field campaigns documenting seasonal landfill CH_4 emissions over annual cycles at multiple sites. The literature documents landfill CH_4 emissions measured at scales ranging from point measurements to whole sites. Table 6 lists a range of CH_4 emission rates from landfills. Small scale measurements using chamber techniques (areas ≤ 1 m^2) have ranged over more than seven orders of magnitude, from < 0.0001 to > 1000 g CH_4 m^{-2} day^{-1} (Bogner *et al*. 1997b). 'Hot spots' are common at landfills with emissions two to three orders of magnitude higher than the remainder of the landfill area; thus, geostatistical methods must be rigorously applied to chamber results to determine whole landfill fluxes (e.g., Spokas *et al*. 2003). Often, the hot spots are related to leakages at the edge of the landfill footprint, higher emissions associated with piping systems, or elevated emission at locations requiring cover maintenance. Whole landfill CH_4 emissions measurements reported from Europe, the US, and South Africa, also relying predominately on chamber methods, range within about one order of magnitude, from approximately 0.1 to 1.0 t CH_4 ha^{-1} day^{-1} (Nozhevnikova *et al*. 1993, Hovde *et al*. 1995, Borjesson *et al.* 2000, Czepiel *et al*. 1996a, Mosher *et al*. 1999, Tregoures *et al*. 1999, Galle *et al*. 2001, Morris 2001). Field campaigns have indicated that landfill CH_4 emissions are influenced by (1) physical limitations to gaseous transport of CH_4 and O_2 resulting from spatial and dynamic temporal changes in gas-filled porosity, especially by soil moisture; (2) *in situ* CH_4 oxidation rates which are dependent on oxidation capacity, temperature, moisture, competition, and other microbiological factors; and (3) the presence or absence of engineered gas extraction systems. Many of these factors are interrelated.

Several field-validated methods are available to measure landfill CH_4 emissions inclusive of oxidation: these include above-ground micrometeorological and tracer methods, static and dynamic chamber methods deployed at ground level, and below-ground concentration and pressure gradient techniques. Tables 7 and 8 summarize qualitative field reconnaissance methods and quantitative field measurement methods, respectively. The choice of method(s) is dependent upon the desired

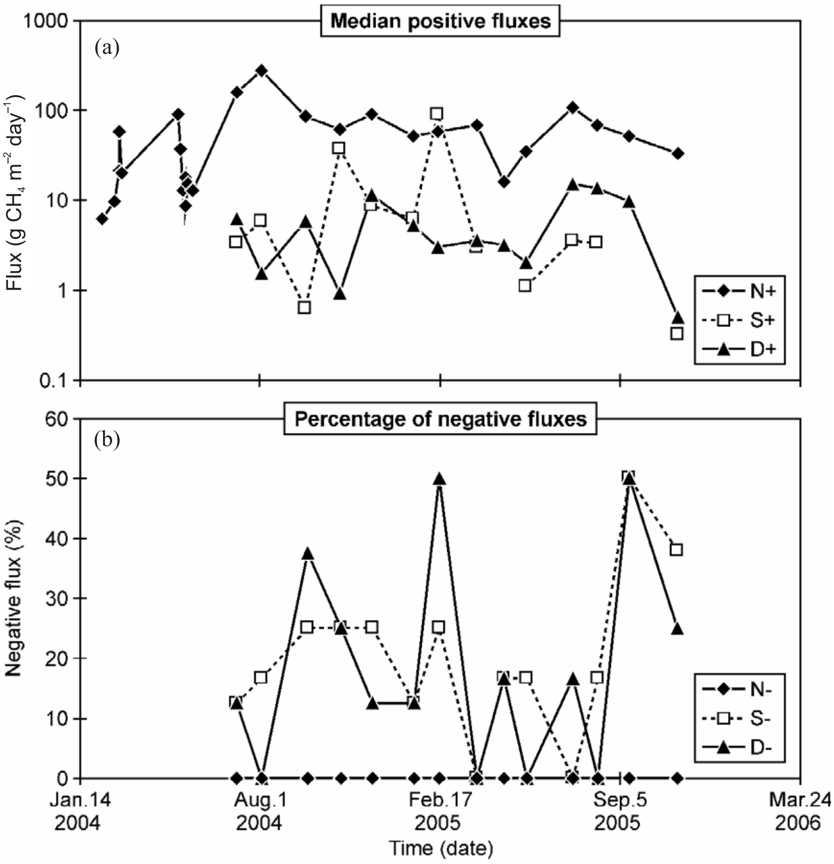

Fig. 7: (a) Two-year time series comparing median positive fluxes for control area (N: 15 cm temporary cover, no biocover), shallow biocover above temporary cover (S: 12 cm glass overlain by 30 cm ground garden waste), and deep biocover above temporary cover (D: 12 cm glass overlain by 60 cm ground garden waste). Each point represents eight or more replicates. (b) Percentage of negative fluxes, same study. S4 area, Leon County, Florida, USA. Modified from Bogner J., Spokas, K., Chanton, J., Powelson, D., Fleiger, J., Abichou, T. (2005). Modeling landfill Methane Emissions from Biocovers: A combined theoretical-empirical Approach. In: Proceedings Sardinia '05. Tenth International Waste Management and Landfill Symposium, 3–7 October 2005, CISA, Environmental Sanitary Engineering Centre, Cagliari, Italy with permission from CISA.

scale and purpose of the measurements. As all methods have some limitations, the parallel use of two or more methods is highly recommended – especially the simultaneous use of static chambers and an above-ground method. With this combination, one can simultaneously determine the lateral variability of emissions (including any edge or piping system leakages), larger area landscape scale fluxes, as well as areas where uptake of atmospheric CH_4 is occurring (using static chambers).

It is often useful to deploy qualitative reconnaissance methods such as a field flame ionization detector (FID) in combination with quantitative methods. The reconnaissance techniques provide useful background information to guide the design of field monitoring campaigns and to detect 'hot spots' of potentially elevated emissions requiring cover maintenance. Some countries such as the USA require surface scans for CH_4 as a regulatory requirement. However, it must be emphasized that none of the reconnaissance techniques provide emissions measurements in standard units for mass flux; for example, mass per area per time. At best, using a field FID, they provide a semi-quantitative determination of atmospheric CH_4 concentration near the ground surface. Where landfill CH_4 emissions are high, it may be possible to combine the field FID with a simple chamber apparatus for rapid direct measurement of fluxes. However, this technique is not appropriate for very low fluxes and is best deployed to provide comparative temporal measurements for mitigation of 'hot spots'.

At some sites and at some locations at sites with optimized gas extraction systems or cover soils with high capacity for CH_4 oxidation, negative CH_4 emissions may be measured using static chambers. Here the cover soils are oxidizing CH_4 out of the atmosphere so that the landfill surface is a sink rather than a source of atmospheric CH_4. Measuring the rate of oxidation of atmospheric CH_4 by surficial soils using static chambers was first validated in arctic wetlands by Whalen & Reeburgh (1990). In such cases, the time series for gas concentrations within the static chamber has a negative rather than a positive slope. Basically, the static chamber functions as a batch incubation experiment measuring the consumption of atmospheric CH_4 within the chamber by methanotrophic consortia in the soil under the chamber. Rates from landfills have ranged from < (–)0.0003 to > (–)3 g CH_4 m^{-2} day^{-1} (Bogner *et al*, 1995, 1997a, Borjesson 1996, Chanton & Liptay 2000, Barlaz *et al*. 2004, Bogner *et al*. 2005). In addition, uptake of atmospheric CH_4 has been quantified in vegetated soils above a surficial geomembrane cover at rates ranging from 0.0002–0.002 g CH_4 m^{-2} day^{-1} (Spokas *et al*. 2006). Limited field data from sites with geomembrane composite covers indicate that these are extremely effective for mitigating

Table 6: Summary of methane emission rates from landfills.

Reference	Location	Texture of cover material	Gas extraction system	Approach	Note	CH_4 emission rate			Soil gas profiles
						Average (*n*)	Min.	Max.	
			yes/no			(g CH_4 m^{-2} day^{-1})			yes/no
Abichou *et al*. (2006a)	Leon County, FL, USA	15-cm thick non-vegetated sandy clay cover		SCT	Feb.–May	54 (*76*)	–4	596	no
		45-cm thick vegetated sandy clay/ loam cover		SCT	Sep.–Feb.	22 (*88*)	–6	330	no
Abichou *et al*. (2006b)	Leon County, FL, USA	30–60 cm cover, flat area		SCT	Jun.–Sep.	167 (*62*)	–14	1755	no
		45 cm cover, slope area		SCT	Jun.–Jul.	9 (*18*)	–2	63	no
		15–30 cm cover, flat area		SCT	Jun.–Nov.	87 (*28*)	0	521	no
		45 cm cover, slope area		SCT	Sep.–Feb.	25 (*112*)	–6	343	no
Ishigaki *et al*. (2005)	Kanto, Japan	10 cm loamy soil	no	SCT	Summer Autumn Winter	26.4 (*45*) 13.7 (*14*) 0.02 (*42*)	–0.3 –1.5 –0.04	384 180 0.36	no
Kallistova *et al*. (2005)	Khmet’evo, Moscow	30–60 cm sand/ clay cover		SCT	April/June	18 (*33*)	–0.6	269	no
Börjesson & Svensson (1997b)	Hökhuvud, Sverige	10–80 cm sand	–	SCT	Seasonal measurements	0.01–7.7 (*72*)	–0.3	18.4	no
Jones & Nedwell (1993)	Martin Farm, UK	40–60 cm sandy loam on top of clay		SCT			< d.l.	225	yes
Maurice & Lagerkvist (2003)	Luleå, Sweden	120 cm silty soil	no	SCT	Seasonal measurements	0.35 (*3–12*)	< 0.04	2	no
Boeckx *et al*. (1996)	Schoten, Belgium	30 cm soil	no	SCT		238.9 (*6*)	–5.9	914.3	no
		no waste	no	SCT		105.7 (*6*)	2.2	230.8	no
Bogner *et al*. (1997a)	Mallard Lake landfill, Illinois, USA	25 cm topsoil on 25–150 cm silty clay	yes	SCT	Proximal	$-6.81\cdot10^{-3}$ (*22*)	$-4.07\cdot10^{-3}$	$-4.33\cdot10^{-2}$	yes
					Distal	$-1.05\cdot10^{-2}$ (*25*)	$-6.67\cdot10^{-4}$	$-9.19\cdot10^{-2}$	yes
Börjesson *et al*. (2000)	Falköpning, Sweden	40 cm topsoil	yes	SCT	May	42.6 (*81*)	–0.17	977	no
				SCT	July	837 (*101*)	–0.33	197	no
				SCT	October	14 (*83*)	–0.36	381	no
Scheutz *et al*. (2003)	Lapouyade, France	80 cm loam on 40 cm coarse sand	yes	SCT	September	2 (*23*)	–0.01	10	yes
		40 cm coarse sand	yes	SCT		37.8		49.9	yes
Scheutz *et al*. (2008)	Grand Landes, France	30 cm top soil on 70 cm clay	yes	SCT	September	–0.001 (*12*)	–2.5	29	yes
		30 cm top soil, 70 cm clay on a HDPE-membrane	yes	SCT		–0.001 (*6*)	–2.2	–0.2	yes
Christophersen *et al*. (2001)	Skellingsted, Denamrk	adjacent to landfill	no	SCT	Seasonal measurements	< 0.2–9.6		72.5	yes
Barlaz *et al*. (2004)	Outer Loop, Louisville, KY, USA	Soil cover	yes	SCT	Apr., Jun, Sept.		< 0	> 15	no

Table 6: Summary of methane emission rates from landfills. *(Continued)*

Reference	Location	Texture of cover material	Gas extraction system	Approach	Note	CH_4 emission rate			Soil gas profiles
						Average (*n*)	Min.	Max.	
			yes/no			(g CH_4 m^{-2} day^{-1})			yes/no
		Compost cover	yes	SCT	Apr., Jun, Sept.		–1.73	1.33	no
Ishigaki *et al.* (2008)	Tay Mo, Hanoi, Vietnam	No daily cover	no	SCT		4.5 (*13*)	–2.9	29.8	no
	Nam Son (phase 1), Hanoi, Vietnam	Daily cover	yes	SCT		23.1 (*14*)	–0.9	154.2	no
	Nam Son (cell 4), Hanoi, Vietnam	Daily cover	yes	SCT		123.4 (*18*)	–5.8	791.5	no
Humer & Lechner (2002, 2001b, c)	MSW-landfill St.Pölten Lower Austria	0.9 m compost cover underlain by 0.3 m gravel	yes	DFT		0–0.3 (*27*)	–0.5	2.1	
		0.9 m compost cover underlain by 0.3 m gravel	yes	DFT		0–1.9 (*27*)	–3.3	5.6	
		0.4 m compost cover	yes	DFT		0–248.9 (*20*)	0	706.8	
		0.6 m cover	yes	DFT		3.9–108.0 (*24*)	0.2	173.9	
		uncovered landfill surface as reference	yes	DFT		27.3–725.2 (*20*)	0.3	1181	

SCT, static chamber technique; DFT, dynamic flux tunnel.

fugitive area emissions from landfill surfaces, provided that any potential edge leakages are monitored and controlled. In recent years, engineered 'biocovers' have also been developed to optimize CH_4 oxidation and thus minimize emissions; these are discussed in detail in the section entitled 'CH_4 oxidation in organic-rich biocovers' within this paper. Biocovers are especially appropriate to mitigate CH_4 emissions at sites with low CH_4 emissions, including older sites.

At the regional level, unlike CH_4 emissions from wetlands or rice production, there have not been extensive field campaigns to quantify the contribution of landfill CH_4 emissions to atmospheric CH_4 over large areas (hundreds of km^2). Therefore, field-validated models for regional landfill CH_4 emissions have not yet been developed which provide more generalized model frameworks for larger scale applications. At the sub-regional level, as more studies are initiated which address urban air and sub-regional atmospheric chemistry, it is expected that the contribution of landfill CH_4 to sub-regional air masses will be better elucidated. For example, a 'top down' study for sources of atmospheric CH_4 in London used stable carbon isotopes to model the relative contribution of several potential sources, including landfill CH_4 (Lowry *et al.* 2001).

Supporting field data: soil gas profiles; soil physical and biochemical properties; isotopic data.

Soil gas concentration profiles measured in parallel with emissions provide valuable information regarding the vertical zonation of transport and biodegradation processes at the time of flux measurement. Soil gas profiles should, as a minimum, include the four major gases in landfill settings: CH_4 and CO_2 from LFG and N_2 and O_2 from the atmosphere. Field techniques must be appropriate for both field conditions (soil physical and chemical properties) and the data quality objectives of the measurements. Soil gas probes should attain a tight fit with soil materials; also, one should minimize internal probe volume so that only minimal purging is required before sampling. If sampling for isotopes or trace components, stainless steel tubing should be used. Often in very wet soils, it is not possible to obtain credible soil gas profiles due to sampling difficulties.

Basic field measurements to be taken in parallel with gaseous emissions include: air temperature, soil temperature, soil moisture, soil texture, and soil organic carbon. For detailed studies of physical transport combined with soil microbiological processes, additional supporting laboratory measurements and modelling of soil properties may be required, including dynamic physical properties such as the gas-filled porosity and relative fracture flow, as well as biochemical parameters such as Q_{10} for microbial processes and CH_4 oxidation kinetics. It is important to point out that the 'apparent' Q_{10} determined from field soils is representative of mixed consortia from specific soils under induced laboratory conditions and is not a 'classic' Q_{10} for a single species.

In addition to the transport of LFG and CH_4 oxidation, additional C and N cycle processes, which influence observed soil gas profiles and measured fluxes, occur in landfill cover

Table 7: Some qualitative reconnaissance techniques which may be useful to locate landfill 'hot spots' with potentially elevated CH_4 emissions. Reconnaissance techniques should be used in combination with quantitative techniques described in Table 8, but can be useful for establishing field experimental designs, checking the integrity of cover materials, and planning site maintenance.

Application	Status	Advantages	Disadvantages and interferences
Field flame ionization detector (FID) or other field gas analyser			
Qualitative or semi-quantitative measurement of atmospheric CH_4 at a point directly above the landfill surface. May be used as a point measurement or as an integrated area measurement using a gridded or random walk design.	Widely used reconnaissance technique. Often deployed as a regulatory tool to determine need for cover remediation and maintenance.	Rapid, simple to deploy in field. Mature technique borrowed from leak detection for natural gas distribution systems. Relatively inexpensive – only requires FID instrument and GPS (global positioining system) capabilities.	Observed CH_4 concentrations affected by many variables, including: (1) non-landfill (interfering) CH_4 sources; (2) other hydrocarbon sources (field FID not specific for CH_4.); (3) meteorological variables (esp. wind speed/direction); (4) soil moisture; and (5) site topography.
Field infrared (IR) survey			
Using thermal infrared techniques, detects point or area where temperature is elevated above background. Assumes high temperatures coincide with warm landfill gas emissions. Deployed either at site or from aircraft at variable scales and with variable sensitivity.	Should be deployed with extreme caution. Must consider multiple causes of observed thermal anomalies.	Rapid, simple to deploy in field. Cost dependent on scale and complexity of field measurement programme.	Many potential causes of elevated surface temperatures in addition to landfill gas emissions, especially dark surface soils and near-surface exothermic chemical and microbial reactions (including aerobic composting). In warm climates, may be no thermal anomalies associated with hot spots. Aircraft applications are expensive, weather-and vegetation-sensitive, and inappropriate for landfills with limited areal extent.
Field inspection without field gas analyser			
Simple visual and olfactory inspection of landfill cover condition, ideally with GPS referenced to site map. Although CH_4 is odorless, landfill gas has a distinctive odor due to its mix of odorous trace components.	A useful first step. Field personnel should be instructed to keep alert for odors indicating landfill gas emissions.	Rapid, simple. Should be part of routine inspection procedures.	Highly subjective with many possible influences, including wind speed and direction, soil moisture, site topography, and landfill cover maintenance.

soils and at the top of the landfill. These include aerobic respiration (resulting in CO_2 production and flux), plant photosynthesis (contributes to observed CO_2 fluxes in transparent static chambers), and, especially where N is abundant, nitrification and denitrification processes which can produce gaseous intermediates of soil N cycling (N_2O, NO, N_2).

These other C and N cycle processes complicate the field measurement and understanding of fluxes and CH_4 oxidation in landfill settings. As discussed above, in all soils the processes for CO_2 production, partitioning to soil moisture, and gaseous flux are complex, especially in soils with vegetative cover and highly functional root zone processes. Thus one cannot assume that observed CO_2 fluxes from landfill cover soils are the result of either the direct emission of LFG (with 40–50% v/v CO_2) or the result of CH_4 oxidation. Especially at sites with an engineered gas recovery system where LFG fluxes are low, the observed CO_2 flux may be dominated by root zone respiration rather than CH_4 oxidation or the direct transport of LFG (Bogner *et al*. 1996, 1999). For field studies where it is important to quantity the various CO_2 fluxes, one must choose among a variety of applicable techniques (for example, see Panikov & Gorbenko 1992). If it is important to determine CO_2 fluxes exclusive of CH_4 oxidation, it may be necessary to apply multiple techniques both at the top of the landfill and at 'control sites' off the landfill footprint with similar soils and vegetation. With respect to N_2O, a more potent greenhouse gas than CH_4, there have been few studies of N_2O production or fluxes in landfill settings. Field studies indicated that the zone of optimum N_2O production at an Illinois site occurred near the base of the cover, where there was restricted aeration but not fully anaerobic conditions (Bogner *et al*. 1999). The N_2O from landfills is considered an insignificant source globally (Bogner *et al*. 1999, Rinne *et al*. 2005) but may need to be considered locally where there is abundant N, high moisture, and restricted aeration; this includes cover soils amended with sewage sludge (Borjesson & Svensson 1997a) or where aerobic or semi-aerobic landfilling practices are implemented (Tsujimoto *et al*. 1994).

Conclusions and remaining issues

Field studies to date have quantified landfill CH_4 emissions at various scales under humid, temperate, semi-arid, and subtropical climatic conditions; however, field emission measurements in tropical zones are lacking. Moreover, there have been relatively few comprehensive field campaigns over complete annual cycles using multiple methods for emissions combined with isotopic measurements of oxidation. Existing data have shown that emission rates vary spatially and temporally

Table 8: Summary of quantitative techniques for field measurement of landfill CH_4 emissions. Arranged in ascending order from small-scale chamber measurements ($\leq m^2$ area) to large-scale techniques ($> km^2$ area).

Application	Status and eferences for method	Advantages	Disadvantages
Static chambers			
Single point measurements for chamber deployed at ground surface for variable time periods (usually less than 1 h). Measures diffusional flux based on change of gas concentration within chamber vs. time.	Most common technique for landfill emissions. Field validated for many terrestrial ecosystems and landfill settings. Rolston (1986)	Good for process level studies of emissions vs. controlling variables (cover soil properties, etc.). Only technique which is appropriate for both positive (+) and negative (–) fluxes (uptake of atmospheric CH_4). Able to quantify very low positive and negative fluxes of CH_4 and non-CH_4 hydrocarbons. Not sensitive to topographic constraints or non-landfill (interfering) CH_4 sources. Simple to deploy with lower limit of detection for fluxes dependent on supporting analytical capability (usually GC/FID for CH=: gas chromatography with flame ionization detector)	Time and labour intensive. Must apply appropriate geostatistical techniques for larger area (landscape scale) fluxes. Temporary disturbance of soil surface.
Dynamic chambers			
Single point measurements at ground surface using a chamber which is continuously flushed with air or a flux gas. Measures flux based on the gas flow and difference between incoming and outgoing chamber CH_4 concentrations.	A common technique which has been field validated for terrestrial ecosystems and landfills. (Rolston 1986)	Same advantages as static chambers except cannot quantify negative CH4 or non-CH_4 hydrocarbon fluxes.	Same disadvantages as static chambers. Not able to quantify very low fluxes because of dilution of chamber gas with flux gas.
Gradient techniques			
Measurement of below-ground gas concentration and pressure gradients with calculation of flux using equations for diffusional and pressure-driven flux.	Limited landfill field measurements but the basis for many transport models. (Glinski & Stepniewski 1985)	Useful for understanding the relative contribution of diffusive and convective flux mechanisms, including the influence of short term barometric pressure changes, passing storm fronts, and wind-driven flux. Gradient measurement helpful as a quantitative basis for hypothesis testing and setting up field measurement programs. Soil gas concentration profiles useful to understand direction of diffusional flux, presence of subsurface sources and sinks, and provide supporting data for other field methods.	Temporal point measurements in field settings are often difficult to interpret within a 3D spatial framework, esp. where there is variable saturation in the waste and cover soils.
Tracer techniques			
Rely on the concurrent measurement of atmospheric CH_4 and a tracer gas (usually SF_6 or N_2O). The tracer is released at a known rate; then the rate of CH_4 release can be determined from the ratio of CH_4 to tracer in the downwind plume.	A common technique which has been field validated for terrestrial ecosystems and landfills. (Czepiel *et al.* 1996; Trégourès *et al.* 1999; Galle *et al.* 2001; Börjesson *et al.* 2007)	Give an integrated measure of whole cell or whole landfill fluxes, including edge leakages.	Cannot quantity negative fluxes (uptake of atmospheric CH4). Difficult or impossible to apply in variable topography with high or variable wind speeds or interfering CH4 sources. The SF6 or N2O tracers are potent greenhouse gases.
Micrometeorological techniques			
A family of techniques which measure the turbulent transfer of gases between the land surface and the lower part of the atmosphere. Rely on tower-mounted fast-response sensors to measure vertical gradients of wind speed and direction, CH_4 concentration, and other variables which are used to determine the surface energy balance. Includes eddy correlation, Bowen ratio, eddy diffusion, mass balance, and other techniques.	Widely used for landscape scale fluxes from terrestrial ecosystems. Has been sparingly used for landfill CH_4 fluxes. (Fowler & Duyzer 1989, Arya 1988, Fowler *et al.* 1995, Hovde 1995, Laurila *et al.* 2005)	Give an integrated measure of landscape scale fluxes. Best for flat terrain. Does not disturb soil surface or vegetation. Useful for short-term temporal studies under changing atmospheric conditions.	Cannot quantity negative fluxes (uptake of atmospheric CH_4). Difficult to apply in variable topography or where other CH_4 sources exist. Footprint of measurement area is determined from experimental data and is not pre-determined. Expensive techniques which require specialized equipment and expertise. Price is declining due to advances in and greater availability of fast-response gas-specific sensors with low detection limits.

Table 8: Summary of quantitative techniques for field measurement of landfill CH_4 emissions. Arranged in ascending order from small-scale chamber measurements (≤ m^2 area) to large-scale techniques (> km^2 area). *(Continued)*

Application	Status and eferences for method	Advantages	Disadvantages
Remote sensing and other regional techniques			
Remote sensing techniques rely on tower- or aircraft-mounted sensors to measure atmospheric CH_4 and other variables. Flux is determined through models and/or scaling up of micrometeorological techniques. Regional techniques encompass both bottom-up and top-down techniques, including inverse modelling to infer fluxes from mixed atmospheric concentrations using isotopic and molecular data.	Used for regional or larger scale atmospheric studies, especially complex regional air quality studies examining spatial and temporal variations. Robust methods and models specific for landfill CH_4 not yet field-validated. (Desjardins & MacPherson 1986, Lowry *et al.* 2001, Modrak *et al.* 2007)	When validated, these techniques have the potential for determining whole landfill fluxes in the context of regional air quality studies.	Cannot quantity negative fluxes (uptake of atmospheric CH_4). Difficult to apply where multiple CH_4 sources. Costly and specialized techniques which require further development to realistically quantify landfill CH_4 contributions to regional atmospheric CH_4.

Also see references and results in Table 6.

over several orders of magnitude, and the emissions may be largely controlled by the efficiency of CH_4 oxidation in a specific setting. Therefore, future data will be key to the improved understanding of process variability and control at field scale, development of a more quantitative guide to the selection of field measurement methodologies, and the fine-tuning of existing field methodologies for emissions and oxidation.

National and global landfill CH_4 emissions and oxidation

At the national level, all countries participating in the United Nations Framework Convention on Climate Change (UNFCCC) are required to periodically compile greenhouse gas inventories which include landfill CH_4 emissions inclusive of oxidation. These estimates are based on national estimates for landfilled waste, the estimated rate of LFG generation, the CH_4 fraction of the LFG, and subtractions for LFG recovery and CH_4 oxidation. For developing countries, an assumption is also made regarding the fraction of landfilled waste which is degrading anaerobically. In general, the national greenhouse gas emissions estimates, especially for developing countries, can be highly uncertain because solid waste data may not be available, and interannual variability is often not well quantified (Bogner & Matthews 2003). For CH_4 oxidation specifically, default values for fractional oxidation are typically applied: 0% for developing countries and 10% for developing countries (the latter based on Czepiel *et al.* 1996b). Annual emissions inventories are prepared for most developed countries, while for many developing countries inventories are available only for 1990 or 1994.

The UNFCCC Tier I default methods in the current 2006 Intergovernmental Panel on Climate Change (IPCC) guidelines for national greenhouse gas inventories are based on a multicomponent First Order Decay (FOD) model with recommended default values for various waste fractions (IPCC 2006). This method takes into account the time delay for CH_4 generation from landfilled waste, and the guidelines include spreadsheet tools to apply the FOD method to all countries. In this method, a first-order kinetic equation is used to partition CH_4 generation over the years after waste placement, based on a chosen kinetic constant (k, with units of t^{-1}) and the gas potential for various waste fractions (L_o, with units of m^3 LFG m^{-3} waste). The use of a first-order kinetic model is similar to what is done at individual sites to predict the CH_4 generation for commercial LFG utilization projects. Previously, under the 1996 IPCC inventory guidelines, the Tier I default method for landfill CH_4 generation consisted of a simplified C mass balance based on national waste data, the degradable organic carbon (DOC) content of the landfilled waste, and an assumption that all of the LFG was produced during the year of disposal – thus the time delay for CH_4 generation was not taken into account. The 1996 guidelines also included a Tier II FOD method which was historically applied in developed but not in developing countries. For the future, however, under the 2006 guidelines, an FOD method will be the default method for all countries. Significantly, the 2006 guidelines also include several higher tier methods which, for the first time in the context of the national inventory process, encourage the application of field measurements to be scaled up to the regional or national level, suggesting that future inventories may be developed with improved modelling tools and reduced uncertainties. Especially, higher tier methods which address CH_4 oxidation as related to seasonal climatic variability and site conditions, could be an important improvement over the current use of default values.

Reported national inventory data through 2003 for developed and developing countries are available from the UNFCCC (UNFCCC 2005). For the waste sector as a whole, greenhouse gas emissions are < 3% of the global anthropogenic greenhouse gas emissions. Waste sector emissions include landfill CH_4 (about 50% of the sector total); wastewater CH_4; N_2O from human sewage; and a small contribution from incinerator CO_2 (fossil carbon only: plastics; synthetic textiles). The CO_2 from landfills, composting, and the incineration of biomass carbon are not included in the national inventories for the waste sector because these are part of the natural carbon cycle and are taken into account in the land use/land use change and forestry (LULUCF) reporting.

Historically, landfills have been implicated as large anthropogenic sources of atmospheric CH_4 in developed countries where landfilling is a dominant waste disposal method. However, these numbers have decreased as LFG recovery rates have increased, the landfilling of biodegradable waste has been restricted in EU countries, and improved databases for national greenhouse gas inventories have been developed. Two recent studies of global landfill CH_4 emissions were compared in the waste management chapter of the IPCC 4th Assessment Report for Working Group III Mitigation (Bogner *et al.* 2007). The first study (US EPA 2006) relied on reported emissions from national inventories and (for non-reporting countries) the 1996 inventory guidelines and extrapolations, resulting in annual emissions for 2005 of 35.7 Tg CH_4 (0.75 Gt CO_2-eq year^{-1}). The second study (Monni *et al.* 2006) used the more recent 2006 inventory guidelines Tier I FOD method for all countries, which resulted in annual emissions of 24.8 Tg CH_4 for 2005 (0.52 Gt CO_2-eq year^{-1}). The sum of all anthropogenic greenhouse gas emissions for 2004 totalled about 49 Gt CO_2-eq year^{-1}, including CO_2, CH_4, N_2O, and F gases from energy supply, industry, buildings, transport, agriculture, forestry, and waste, all normalized to CO_2-eq based on their respective Global Warming Potentials in the IPCC Second Assessment Report (Rogner *et al.* 2007). With respect to landfill CH_4 recovery, this can be conservatively estimated to be > 5 Tg CH_4 year^{-1} in 2003, based on Willumsen's (2003), inventory of known projects, and Bogner and Matthews's (2003) linear projections from previous project compilations. This figure is conservative because (a) it focuses on LFG utilization projects and does not include a large number of projects which only flare the gas; and (b) also does not include a large number of more recent projects in developing countries under the Kyoto Protocol Clean Development Mechanism – as of September 2007, these totalled approximately 0.8 Tg CH_4 year^{-1} (http://cdm.unfccc.int/Projects).

For the future, improved regional and national greenhouse gas inventories will result from the development and use of expanded databases and field methodologies in conjunction with the higher tier methodologies that are currently available. In particular, improved process-based models for CH_4 oxidation, which have been field-validated for seasonal climatic variability and site-specific cover materials could be an important improvement over the current use of default values.

Modelling CH_4 oxidation in landfill cover systems

Introduction

CH_4 oxidation in landfill cover soils is a complex process involving several types of mass transport as well as microbial oxidation operating simultaneously. Getting a conceptual understanding of what happens in a landfill cover soil can be a daunting task. Computer models can improve this understanding in three different ways.

First, simulation models can be used as a measurement tool for CH_4 oxidation (e.g. Czepiel *et al.* 1996b) or CH_4 production (e.g. Perera *et al.* 2002a). In this case, the model is part of a data analysis technique that calculates a property that cannot be measured directly. Second, computer models can be used as a tool for gaining insight in specific processes occurring in a landfill cover. Examples are Hilger *et al.* (1999) and Wilshusen *et al.* (2004a), who used models to understand how EPS formation affects the overall behaviour of landfill covers. Mahieu *et al.* (2005) used models to understand stable isotope fractionation effects in LFG. Rannaud *et al.* (2007) used a model to estimate the depth of CH_4 oxidation. By comparing models with experimental measurements, scientific hypotheses can be tested. Third, computer models can be used for prediction or design (e.g. De Visscher & Van Cleemput 2003b, Park *et al.* 2004, Rannaud *et al.* 2007). Typically, these models are calibrated with laboratory data, and then used to predict field conditions.

Various types of models have been proposed for the description of CH_4 oxidation in landfill cover soils. For the current overview we will divide the existing models into three types: empirical models, process-based models, and the collision model. Empirical models (e.g. Czepiel *et al.* 1996b, Park *et al.* 2004) are assemblies of empirical equations obtained by correlating measurement data. The development of empirical models requires little information on the fundamental processes influencing CH_4 oxidation. However, extrapolation of empirical models should be avoided. Process-based models (e.g. Hilger *et al.* 1999, Stein *et al.* 2001) combine mass transport equations with CH_4 oxidation kinetics in a numerical scheme. Process-based models are potentially the most realistic models, but they generally require a large number of parameters that are difficult to obtain, which limits their usability. The collision model of Bogner *et al.* (1997a) is an attempt to balance theoretical and empirical modelling, by representing the processes occurring in a landfill cover as collisions between gas molecules and the soil.

Empirical models

The first attempt to model CH_4 oxidation in a landfill cover soil was by Czepiel *et al.* (1996b). The purpose of this model was to determine year-round average whole-landfill CH_4 oxidation. The input data are surface CH_4 flux, CH_4 mixing ratio at 7.5 cm depth in the soil, soil temperature, soil moisture content, and soil bulk density. From the CH_4 mixing ratio at 7.5 cm depth an entire CH_4 mixing ratio profile is generated. The estimation of the microbial activity (V_{max}) at each different depth is then computed based on the mixing ratio as well as soil temperature and moisture. This allows the summing of CH_4 oxidation at each depth interval to arrive at the total CH_4 oxidation estimation. Measurements at 139 locations on a New Hampshire landfill in October 1994 led to an average oxidation efficiency of 20%. By combining this result with daily meteorological data from 1 December 1993 to 30 November 1994, which was used to estimate soil temperature and moisture content with the combined heat and moisture transport model BROOK90 (Federer *et al.* 2003), Czepiel *et al.* (1996b) obtained a year-round average whole-landfill CH_4 oxidation of 11%.

Park *et al.* (2004) used empirical relations to estimate landfill CH_4 oxidation efficiencies in the United States, based on

Table 9: Main properties of different process-based models.

Model	Mass transfer mechanism	Dispersion	Dimensions	Limiting substrate	Growth	Implementation
Ishiwata (1998)	Stefan–Maxwell	no	1	O_2, CH_4	no	Dynamic, $\Delta p \neq 0$
Hilger *et al.* (1999)	Stefan–Maxwell	no	1	O_2[d]	no	Steady-state, $\Delta p \neq 0$
Poulsen *et al.* (2001)	Fick	yes[a]	2	CH_4[e]	no	Dynamic, $\Delta p \neq 0$
Stein *et al.* (2001)	Fick + Wilke	no	1	O_2, CH_4	no	Dynamic, $\Delta p \neq 0$
Perera *et al.* (2002a)	Fick + Wilke	yes	1	O_2, CH_4	no	Dynamic, $\Delta p \neq 0$
De Visscher & Van Cleemput (2003)	Stefan–Maxwell	no	1[b]	O_2, CH_4	yes	Dynamic, $\Delta p \neq 0$
Perera *et al.* (2004)	Fick + Wilke	yes	1[c]	O_2, CH_4	no	Dynamic, $\Delta p \neq 0$
Mahieu *et al.* (2005)	Stefan–Maxwell	yes	1	O_2, CH_4	yes	Dynamic, $\Delta p \neq 0$

[a] Longitudinal + lateral dispersion + pressure fluctuation effect; [b] With source strength distribution to model spatial variability; [c] With geostatistics to model spatial variability; [d] Biofilm model; [e] First-order in methane, 'as long as both CH_4 and O_2 were present'.

climatic data in each state. The empirical relations estimate CH_4 oxidation rates from soil temperature, soil moisture content and soil ammonium content and were developed by polynomial regression analysis. The approach is very useful for sophisticated CH_4 budget calculations. However, the results obtained by Park *et al.* (2004) should be considered with great caution, because the model was fitted to the earlier data of Park *et al.* (2002) with open top landfill soil columns, which probably represents an overestimate of the real CH_4 biofilter performance. Park *et al.* (2002) used the change of the CH_4 concentration in the soil as the gas moves up the column as a measure of the CH_4 oxidation. This was an overestimate because the CH_4 concentration also decreases due to dilution by air as it moves up the soil profile.

Process-based models

Process-based models explicitly describe gas transport and microbial oxidation. Some models also include microbial growth. Mass transfer and gas reaction are combined into a set of differential equations by means of a continuity equation, which is solved by means of numerical algorithms.

The first process-based model was developed by Ishiwata (1998). However, the work was published in Japanese, the only English account of the model being published by Yamada *et al.* (1998). Consequently, until recently this contribution was overlooked by the research community. Other models have been developed by Hilger *et al.* (1999), Poulsen *et al.* (2001), Stein *et al.* (2001), Perera *et al.* (2002a), De Visscher and Van Cleemput (2003b), Perera *et al.* (2004), and Mahieu *et al.* (2005, 2008). Rather than discussing the models one by one, this overview shows the most commonly used equations to model mass transfer and CH_4 oxidation in the next two subsections, followed by a few notes on implementation issues. Guidance on recommended input data for the various model components is given in the section entitled 'Input data for process-based models'. Table 9 shows the main characteristics of several process-based models.

Mass transfer

Mass transfer in the gas phase of landfill cover soils is governed by molecular diffusion, mechanical dispersion, and advection. Mathematically, molecular diffusion and mechanical dispersion in a porous medium like a soil can be treated simultaneously by defining the dispersion coefficient D_{ij} (m^3 gas m^{-1} soil s^{-1} or simply m^2 s^{-1}) of a binary gas mixture of components i and j as:

$$D_{ij} = \tau D_{g,ij} + \alpha\,|v| \tag{3}$$

with $D_{g,ij}$ (m^2 gas s^{-1}) the binary diffusion coefficient of component i in a free gas mixture with component j, v (m soil s^{-1}) the interstitial gas velocity, τ (m gas m^{-1} soil) a reduction factor for molecular diffusion due to reduced volume and increased tortuosity of the gas-filled pore space in comparison with the free gas, and α (m^3 gas m^{-2} soil or simply m) the dispersivity of the soil. Recommendations for τ, α and $D_{g,ij}$ are given in the section entitled 'Input data for process-based models'. For the analysis here, we have ignored mechanical dispersivity, since this is important in high flow rates which are not prevalent in soil gas movement. At high gas flow rate O_2 cannot penetrate the soil, and oxidation is very low. In general, the inclusion of dispersion is not critical in CH_4 oxidation modelling, with the one potential exception for modelling isotopic effects.

The basis for quantification of gas transfer is the flux, which is defined as the number of moles that move though a surface unit area perpendicular to the movement of the gas. The total molar flux N (mol m^{-2} soil s^{-1}) of a gas mixture is given by:

$$N = cQ/\Omega = c\,u = c\,v\,\varepsilon, \tag{4}$$

where c is the total gas concentration in the gas phase (mol m^{-3} gas), and Q the volumetric gas flow rate (m^3 gas s^{-1}) through a surface with area Ω (m^2 soil) that is fixed in space and perpendicular to the flow. Q/Ω is equal to the superficial gas velocity, u (m^3 gas m^{-2} soil s^{-1}), which is equal to the interstitial gas velocity, v (m soil s^{-1}) multiplied with the the gas-filled porosity of the soil, ε (m^3 gas m^{-3} soil).

The flux of an individual component i (N_i) relative to a stationary point (frame of reference) comprises two components. The first component is a result of the flux due to total gas flow (N), and the second is a result of molecular dispersion (diffusion) occurring within the flowing gas stream (J_i). Mathematically, these can be represented by the following:

$$N_i = J_i + y_i N, \tag{5}$$

where y_i is the mole fraction of component i in the gas stream. The diffusion flux J_i in a binary gas mixture of components i and j follows Fick's law:

$$J_i = -D_{ij}\frac{\partial c_i}{\partial z}, \tag{6}$$

with c_i (mol m^{-3} gas) the concentration of compound i in the gas phase, and z (m soil) the depth inside the soil. In theory, equation (6) can only be used in the case of binary mixtures, diffusion of a trace component, and in ternary mixtures with one stagnant component (Jaynes & Rogowski 1983). However, Wilke developed an equation for approximate values of the diffusion coefficient $D_{i,\mathrm{m}}$ of component i in a complex gas mixture for use in Fick's law (Froment & Bischoff 1990):

$$D_{i,\mathrm{m}} = \frac{1-y_i}{\sum\limits_{\substack{j=1\\ j\neq i}}^{n}\frac{y_i}{D_{ij}}} \tag{7}$$

This approach was adopted by Stein *et al.* (2001) and Perera *et al.* (2002a). Equation (7) is popular in chemical reactor engineering because it combines good accuracy with ease of implementation (Froment & Bischoff 1990).

A more rigorous approach is the use of the Stefan–Maxwell equations (Jaynes & Rogowski 1983):

$$-\frac{p}{RT}\frac{\partial y_i}{\partial z} = \sum_{\substack{j=1\\ j\neq i}}^{n}\frac{N_i y_j - N_j y_i}{D_{ij}}, \tag{8}$$

where p is the total pressure (Pa), R is the ideal gas constant (8.314472 J mol^{-1} K^{-1}), and T the temperature (K). Equation (8) incorporates both diffusion/dispersion and advection, so it replaces equation (5). This approach was adopted by Ishiwata (1998), Hilger *et al.* (1999), by De Visscher & Van Cleemput (2003b), and by Mahieu *et al.* (2005, 2008).

The Stefan–Maxwell equations were derived from statistical mechanics of free gases. Fick's law is the special case of the Stefan–Maxwell equations for binary gas mixtures. Two differences exist between a free gas and a gas that is confined within a porous medium, however. The first difference is the type of collisions that occur: free gas molecules only collide with each other, whereas gases in porous media also collide with walls. Transport associated with wall collisions is known as Knudsen diffusion. It dominates mass transport when the pore diameter is smaller than the mean free path of the gas molecules. A second difference between free gas and gas in a porous medium can be visualized by considering binary diffusion between a light gas and a heavy gas. The light gas penetrates rapidly into the heavy gas, whereas the heavy gas only slowly penetrates the light gas. Consequently, an overpressure is created in the heavy gas, creating an advective flow towards the lighter gas. In free gas this flow is immediate and no measurable pressure gradient will develop. However, in a porous medium this pressure drop can be substantial. These two processes are strongly interrelated.

To incorporate these two effects of the pore space on mass transport, the Stefan–Maxwell equations can be extended to include the solid particles as an extra compound, the 'dust' (Evans *et al.* 1961, 1962). The dust has a high molecular weight and its flux must be 0. Its mole fraction, y_D, depends on the diffusion regime. When Knudsen diffusion is dominant, y_D approaches 1, whereas when Knudsen diffusion is negligible, y_D approaches 0. This model is known as the dusty gas model. So far it has not yet been applied in models for CH_4 transport and oxidation in landfill cover soils. A detailed discussion of the dusty gas model is given by Thorstenson & Pollock (1989).

The relevance of Knudsen diffusion for gas transport in fine-grained materials has been discussed by Clifford & Hillel (1986) and by Reinecke & Sleep (2002). De Visscher & Van Cleemput (2003b) argued that Knudsen diffusion is negligible under optimal condition for CH_4 oxidation. At atmospheric pressure, Knudsen diffusion is relevant only for pore diameters below 1 μm, and becomes dominant at diameters below 0.1 μm. At ideal conditions for CH_4 oxidation, most of these pores are water-filled.

The effect of the pressure build-up described above can be relevant when studying special issues such as the effect of pressure fluctuations on mass transport in landfill cover soils. When total gas flux entering the soil from underneath is treated as an input parameter, and the pressure gradient is small in comparison with the total pressure, the pressure build-up effect can be ignored.

CH_4 oxidation

An overview of CH_4 oxidation kinetics is given in the section entitled 'CH_4 oxidation capacity of landfill cover soils' above. The depth of the CH_4-oxidizing layer in a landfill cover soil depends on the O_2 penetration. Therefore, a model for CH_4 oxidation in landfill cover soils can only function if O_2 limitation is accounted for. At low CH_4 flux or close to the cover surface, CH_4 concentration can be low enough to be limiting. Therefore, a general-purpose model for CH_4 oxidation in landfill cover soils should include a dual-substrate kinetic model. Ishiwata (1998), Stein *et al.* (2001), Perera *et al.* (2002a), De Visscher & Van Cleemput (2003b), and Mahieu *et al.* (2005, 2008) used a dual-substrate Michaelis–Menten model:

$$r_{\mathrm{CH_4}} = -\frac{V_{\max}\,y_{\mathrm{CH_4}}}{K_{\mathrm{CH_4}}+y_{\mathrm{CH_4}}}\frac{y_{\mathrm{O_2}}}{K_{\mathrm{O_2}}+y_{\mathrm{O_2}}}, \tag{9}$$

with $r_{\mathrm{CH_4}}$ (mol kg^{-1} soil s^{-1}, dw) the CH_4 reaction rate, $V_{\max}$ (mol kg^{-1} soil s^{-1}, dw) the maximum CH_4 uptake rate, and

K_{CH_4} (–) and K_{O_2} (–) the Michaelis–Menten constants for CH_4 and O_2, respectively. In most models, V_{max} is assumed to be constant or a profile is provided by the user. In the models of De Visscher & Van Cleemput (2003b) and Mahieu *et al.* (2005, 2008) a profile of V_{max} is calculated with a growth model combining a logistic model (the Verhulst equation) and Monod kinetics, with a decay term:

$$\frac{dV_{max}}{dt} = \mu V_{max} \tag{10}$$

with

$$\mu = \frac{\mu'_{max}\left(1-\frac{V_{max}}{V_{max,\,max}}\right)y_{CH_4}}{\left(K_{CH_4}+y_{CH_4}\right)} \cdot \frac{y_{O_2}}{K_{O_2}+y_{O_2}} - a, \tag{11}$$

with μ'_{max} (s^{-1}) the maximum specific growth rate, $V_{max,\,max}$ the maximum value of V_{max} that can be supported by the soil, and a (s^{-1}) a decay term.

Other kinetic relations can be used to model specific cases. Hilger et al. (1999) used a biofilm model to evaluate the potential effect of EPS as a diffusion barrier to the limiting substrate. A single substrate model for deep biofilms was used:

$$r_{O_2} = A_b\sqrt{2V_{max,\,b}D_b\left(c_{O_2,\,aq}+K_{O_2,\,aq}\ln\left(\frac{K_{O_2,\,aq}}{K_{O_2,\,aq}+c_{O_2,\,aq}}\right)\right)}, \tag{12}$$

with A_b (m^2 moisture kg^{-1} soil, dw) the biofilm specific area, $V_{max,b}$ (mol m^{-2} moisture s^{-1}) the methanotroph activity in the biofilm, D_b (m^2 moisture s^{-1}) the diffusion coefficient of O_2 in the biofilm, $c_{O_2,\,aq}$ (mol m^{-3} moisture) the dissolved O_2 concentration at the biofilm surface, and $K_{O_2,\,aq}$ (mol m^{-3} moisture) the value of K_{O_2} expressed as aqueous concentration.

Rannaud *et al.* (2007) replaced the reaction rate by a constant CH_4 sink term across a user-defined depth interval. Their model was implemented on the TOUGH2-LGM simulator (Nastev 1998, Nastev *et al.* 2001), which cannot describe chemical kinetics, and which does not distinguish between N_2 and O_2.

The stoichiometry of the reaction in its most general form can be written as:

$$CH_4 + S_{O_2}O_2 \rightarrow S_{CO_2}CO_2 \tag{13}$$

The reaction also produces water, biomass, and EPS. However, these reaction products do not return to the gas phase, and do not need to be considered. Stoichiometric values as used in different models are given in Table 10.

Table 10: Stoichiometric factors used in different process-based models.

	S_{O2}	S_{CO2}
Ishiwata (1998)	2	1
Hilger *et al.* (1999)	1.57	0.593
Poulsen *et al.* (2001)	2	1
Stein *et al.* (2001)	1.8	0.8
Perera *et al.* (2002a)	1.7	0.7
De Visscher & Van Cleemput (2003)	1.5	0.5
Perera *et al.* (2004)	1.7	0.7
Mahieu *et al.* (2005)	1.75	0.75

Implementation

Implementation of a process-based model requires the combination of the mass transfer model and the CH_4 oxidation model by means of a continuity equation. This continuity equation can be derived by considering an infinitesimal soil layer between depths z and z + dz, and assuming that accumulation of a compound in that layer equals the amount of the compound entering the layer, minus the amount of compound leaving it, plus the amount of compound generated by the reaction (negative if the compound is consumed by the reaction). In its most general form, this leads to a partial differential equation for each compound in the gas phase:

$$\varepsilon\frac{\partial c_i}{\partial t} = \rho_{DB}r_i - \frac{\partial N_i}{\partial z}, \tag{14}$$

where ε is the gas-filled porosity of the soil (m^3 gas m^{-3} soil) and ρ_{DB} (kg m^{-3} soil) the dry bulk density of the soil. This equation does not incorporate CO_2 absorption into the soil moisture, but that is a highly transient effect which will not affect long-term trends. The equation is solved numerically, commonly, by a finite-difference approximation.

Equation (14) is one-dimensional, so it only applies to horizontally homogeneous cover soils and horizontally homogeneous gas fluxes. In heterogeneous soils such as landfill covers, horizontal variations need to be addressed separately.

The fluxes in equation (14) are calculated either by equations (5) and (6) for Fick's law, or by equation (8) for the Stefan–Maxwell equations. In the former case, the total flux, N, appears explicitly in the equation. In the latter case, the set of equations (8) is not linearly independent, so one of them must be replaced by an equation of the form:

$$\sum_i N_i = N \tag{15}$$

where N can be calculated using Darcy's law:

$$v = -\frac{k}{\mu}\frac{\partial p}{\partial z}, \tag{16}$$

with k (m^2 soil) the permeability of the soil, and μ (Pa s) the viscosity of the gas mixture. For details on calculating the latter, the reader is referred to the studies that used this method (Stein *et al.* 2001, Perera *et al.* 2002a). The pressure gradient is evaluated by calculating the total gas concentration in each grid point, and calculating the total pressure with the ideal gas law.

Unless the permeability is very low or one wishes to explicitly calculate the effects of pressure fluctuations, the pressure gradient is very small, and the use of Darcy's law can be avoided altogether. To that effect, the ideal gas law is introduced in equation (14) directly:

$$\varepsilon \frac{p}{RT}\frac{\partial y_i}{\partial t} = \rho_{DB} r_i - \frac{\partial N_i}{\partial z} \tag{17}$$

Now the total flux is calculated by integrating the following differential equation (De Visscher & Van Cleemput 2003b):

$$\frac{dN}{dz} = \rho_{DB} r_{\Sigma}, \tag{18}$$

with r_{Σ} the sum of the reaction rates of all gas compounds (negative in case of consumption). Typically, the value of N at the bottom of the cover soil is a model input parameter, so equation (18) is integrated from the bottom up.

When steady-state conditions are assumed, equation (17) can be reduced to:

$$\frac{\partial N_i}{\partial z} = \rho_{DB} r_i \tag{19}$$

If the fluxes of all components are known at one point in the column, together with the concentrations, then integration of equation (19) allows the flux to be calculated at any given point in the column. To that effect, equation (19) is combined with either Fick's law or the Stefan–Maxwell equations. However, the fluxes are usually known or assumed at the bottom of the cover soil, whereas the concentrations are usually known at the top of the cover soil. In that case, the fluxes at the top of the cover soil need to be determined by trial and error. Hilger *et al.* (1999) avoided this problem by using a measured value of the CH_4 flux at the top of the system. Other fluxes were calculated based on reaction stoichiometry. This procedure simplifies the calculations substantially, but experimental errors on the measured flux can propagate through the calculation.

Boundary conditions for the differential equations must be chosen with great care as incorrect or unrealistic boundary conditions invalidate the entire model. At the top boundary the concentrations of the gas components are usually taken equal to atmospheric values. De Visscher & Van Cleemput (2003b) allowed for mass transfer resistance in a boundary layer above the soil. Choosing boundary conditions for the bottom of the cover soil is less straightforward. It is appealing to set the concentrations of the gas components equal to their values inside the landfill mass (e.g., Ishiwata 1998), but this is only realistic if the cover soil is sufficiently deep or if diffusion is sufficiently slow. A more generally applicable boundary condition is obtained by setting the flux and by calculating a relationship between the concentration and its gradient based on the set flux. Most models use such a boundary condition. For future research into the effects of pressure fluctuations, more flexible boundary conditions will have to be selected.

Input data for process-based models

Binary diffusion coefficients in free gas can be calculated with the following equation, which is adapted from Marrero & Mason (1972):

$$D_{g,ij} = \frac{AT^{s}\exp(-S/T)}{p}, \tag{20}$$

where A(m^2 gas s^{-1} Pa K^{-s}), s(–), and S(K) are empirical constants. Recommended values for the most relevant gas pairs are given in Table 11.

As indicated in the section entitled 'Mass transfer' above, gas diffusion in soil is slower than in free air by a factor τ. Several equations have been suggested for the calculation of τ. A convenient overview of early work on τ is given by Collin

Table 11: Recommended values of *A* and *s* for the calculation of binary diffusion coefficients in free gas (Equation (20)). Reproduced form Marrero, T.R., Mason, E.A. (1972). Gaseous diffusion coefficients. Journal of Physical and Chemical Reference Data 1, 3–118, with permission from the American Institute of Physics.

i–	A (10^{-4} m$^2_{gas}$ s^{-1} Pa K^{-s})	s (–)	S (K)	$D_{g,ij}$ (25 °C, 1 atm) (10^{-5} m$^2_{gas}$ s^{-1})
CH_4–CO_2[a)]	0.8496	1.750	0	1.794
CH_4–O_2	1.702	1.695	44.2	2.265
CH_4–N_2	1.013	1.750	0	2.139
CH_4–Ar	0.7944	1.785	0	2.047
CO_2–O_2	1.581	1.661	61.3	1.636
CO_2–N_2	3.192	1.570	113.6	1.651
CO_2–Ar	1.763	1.646	89.1	1.526
O_2–N_2	1.145	1.724	0	2.085
O_2–Ar	0.9899	1.736	0	1.930
N_2–Ar	0.9160	1.752	0	1.956

[a]Calculated from Liley *et al.* (1984).

& Rasmuson (1988), and by Jin & Jury (1996). We will limit our overview to equations that have actually been used in CH_4 oxidation models.

Ishiwata (1998) did not use a factor to correct for the presence of soil, which means that $\tau = 1$ is implicitly assumed. This is a serious overestimation of the actual diffusion coefficient. Hilger *et al.* (1999) found that $\tau = 0.1$ led to a good fit between theory and experiment. Poulsen *et al.* (2001) used an empirical equation which they derived from independent measurements on soil samples from the field site.

Stein *et al.* (2001) used the equation of Millington (1959):

$$\tau = \frac{\varepsilon^2}{\Phi^{2/3}}, \tag{21}$$

where Φ is the total porosity of the soil.

Perera *et al.* (2002a) used the equation of Troeh *et al.* (1982):

$$\tau = \left(\frac{\varepsilon - c}{1 - c}\right)^d, \tag{22}$$

with c and d empirical parameters dependent on the soil. Perera *et al.* (2002a) used 0.05 and 1.4, respectively.

Perera *et al.* (2002b) used the equation of Millington & Quirk (1960):

$$\tau = \frac{\varepsilon^{10/3}}{\Phi^2} \tag{23}$$

De Visscher & Van Cleemput (2003b) used the equation of Moldrup *et al.* (2000a) to describe repacked soils under laboratory conditions:

$$\tau = \frac{\varepsilon^{2.5}}{\Phi} \tag{24}$$

Mahieu *et al.* (2005) used a similar equation, but they found that replacing the value of 2.5 by 2.098 improved the fit between theory and experiment. For extrapolations to field conditions, De Visscher & Van Cleemput (2003) used the equation of Moldrup *et al.* (2000b):

$$\tau = \left(2\varepsilon_{100}^3 + 0.04\varepsilon_{100}\right)\left(\frac{\varepsilon}{\varepsilon_{100}}\right)^{2+3/b}, \tag{25}$$

where ε_{100} is the air-filled pore space at a matric suction of 100 cm and b a soil parameter. Both were obtained from Clapp & Hornberger (1978). For a sandy loam soil the values are 0.2079 and 4.9, respectively.

There is a substantial difference between the predictions of the equations given above. Consequently, it is recommended to test the applicability of an equation before using it. This can be done by comparing model predictions of the gas concentration profiles in the soil by measured values.

Mechanical dispersion was considered by Poulsen *et al.* (2001), by Perera *et al.* (2002a, 2004) and by Mahieu *et al.* (2005). However, there is no agreement on the actual value of the dispersivity (α) yet. Early estimates were on the order of tens of centimetres, and were based on dispersion in soil water (Mendoza & Frind 1990; Massman & Farrier 1992). However, actual measurements have been carried out more recently, showing α values ranging from 1.7 mm to 2.6 cm (Popovicova & Brusseau 1997, Ruiz *et al.* 1999, Garcia-Herruzo *et al.* 2002, Constanza-Robinson & Brusseau 2002).

With a maximum CH_4 flux of 4000 g m^{-2} day^{-1}, and assuming that LFG contains 50% CH_4, the interstitial flow velocity is on the order of 10^{-3} m s^{-1}. Assuming $\alpha = 1$ cm, this leads to a mechanical dispersion coefficient of 10^{-5} m^2 s^{-1}, which is equal to the diffusion coefficient when $D_{g,ij} = 2 \times 10^{-4}$ m^2 s^{-1} and $\tau = 0.05$. However, CH_4 oxidation is not very effective at fluxes above 400 g m^{-2} day^{-1}, so mechanical dispersion is expected to be 10% or less of the total dispersion in those conditions when CH_4 oxidation is important.

At this point there is no clear indication that mechanical dispersion is a key factor in gas movements in landfill cover soils. However, at low flow rates α values up to 7 cm have been observed (Mahieu 2007). This might be due to the occurrence of atmospheric pressure fluctuations. This might necessitate the adoption of a higher value of α, as pointed out in the section entitled 'Remaining issues' below. We conclude that optimum values of α remain an open issue.

The kinetics of CH_4 oxidation in landfill cover soils is discussed in the section entitled 'CH_4 oxidation capacity of landfill cover soils'. In CH_4 oxidation models values of V_{max} ranging from 7×10^{-12} mol kg^{-1} soil s^{-1} to 2.4×10^{-6} mol kg^{-1} soil s^{-1} (dry weight basis) have been used, spanning almost six orders of magnitude. For conditions representative for landfill cover soils the values are usually between 10^{-7} mol kg^{-1} soil s^{-1} and 10^{-6} mol kg^{-1} soil s^{-1} (dry weight basis). It is important to account for the influence of temperature when applying models to field conditions. The values of K_{CH_4} used in models range from 0.12 to 1.25%, which is very similar to the values usually used for K_{O_2} (0.25–1.2%). From physiological experiments (e.g. Joergensen 1985) we expect K_{CH_4} to be in the lower end of the range found in simulation models, whereas K_{O_2} is expected to be about a factor 10 lower than applied in the models. This indicates that simulation models implicitly incorporate micro-scale diffusion limitation effects in their choice of parameters. CH_4 and O_2 have roughly the same solubility in water, but methanotrophs consume more O_2 than CH_4, which explains the more pronounced influence of diffusion limitation on the Michaelis–Menten constant for O_2.

De Visscher & Van Cleemput (2003b) pointed out that process-based model predictions are not very sensitive to K_{CH_4} and K_{O_2}. This is fortunate, given their uncertainty. Nevertheless, the extrapolation of these parameters to new conditions should be treated with caution. One point that has not received any attention to date is the pressure-dependence of these parameters. Kinetically, micro-organisms respond to partial pressures, not mole fractions. When the total pressure is lower than 1 atm, a higher mole fraction is needed to attain the same partial pressure. Therefore, K_{CH_4} and K_{O_2}, when expressed as mole fractions, should be scaled when the total pressure deviates from 1 atm. The most convenient way to do so is to use altitude for this purpose. The following equation should be adequate for practical purposes:

$$K_{CH_4,h} = K_{CH_4,0} \exp(1.2 \times 10^{-4} h) \qquad (26)$$

with $K_{CH_4,h}$ the value of K_{CH_4} at altitude h(m) and $K_{CH_4,0}$ the value at sea-level. The same equation can be used to scale K_{O_2}.

Collision model

In an attempt to produce a better mathematical predictor of CH_4 oxidation in landfill cover soils, a collision model was developed to simulate gas transport as well as CH_4 oxidation in landfill cover soils (Bogner *et al.* 1997a). This model is built on a conceptual framework, rather than theoretical foundation. Nevertheless, the collision model has performed well in a variety of landfill settings and other ecosystems (Bogner *et al.* 2000). In this model, CH_4 could only be oxidized if the CH_4 molecule collides with a bacterial colony that is simulated on the sphere of soil in each node. The size of the soil sphere enclosed within each soil node is controlled by user inputted porosity. The soil sphere surface is divided into three potential areas: dry, wet, or bacteria. The growth of bacteria on the sphere is controlled by a selectable kinetic model: linear, quadratic, or exponential. The surface of the sphere is then mapped to a plane across all six sides of the node using a conformal mapping technique (Wunsch, 2004), which permits the calculations of the probabilities of the CH_4 molecules colliding with the sphere as well as the percentage of CH_4 that passes through the node. CH_4 oxidation occurs if the CH_4 collides with a bacterial colony on the soil sphere, provided there is enough O_2 present in the node to permit oxidation. This technique provides a limit to oxidation in terms of bacterial density as well as oxidation potential based on the O_2 content in the node.

What do we learn from models?

A useful test of a model's reliability is to test it under new conditions. An interesting case was presented by Roeder *et al.* (2004). They added argon to the model formulation of Stein *et al.* (2001), and tested the model's ability to describe the gradual displacement of N by argon in a landfill cover soil column when the headspace flush air is replaced by an O_2–N–argon (20–40–40 by volume) mixture. They found excellent agreement between the model and the experimental data. Apparently models do capture the fundamental processes underlying gas transport and CH_4 oxidation in landfill cover soils.

Hilger *et al.* (1999) used a model to evaluate the potential effect of EPS as a diffusive barrier overlying a methanotrophic biofilm in a landfill cover soil. They found that diffusive barriers do indeed decrease CH_4 oxidation. Wilshusen *et al.* (2004b), on the other hand, fitted the model of Stein *et al.* (2001) to their data, and found that EPS formation by methanotrophs reduced bulk diffusivity in compost-filled columns substantially. It is concluded that EPS can induce both micro-scale (liquid-phase) and macro-scale (gas-phase) diffusion limitation. The former is best described by modifying CH_4 oxidation kinetics; the latter is described by changing τ (De Visscher & Van Cleemput 2003b). Mahieu *et al.* (2005) showed that models coupled with stable isotope measurements can provide insight into the occurrence of mechanical dispersion in landfill cover soils. Despite its present shortcomings, the use of models such as TOUGH2-LGM can provide insight on the depth range of CH_4 oxidation in a biocover (Rannaud *et al.* 2007).

Models for related ecosystems

This section summarizes a number of models that do not strictly describe CH_4 oxidation in landfill cover soils, but that provide useful insights relevant for scientists studying landfill CH_4 oxidation.

Models similar to the ones presented here were developed for CH_4 oxidation in peatlands (Arah & Stephens (1998), based on parameters of Nedwell & Watson (1995)), for gas accumulation in a closed box for flux determination (Jury *et al.* 1981, Healy *et al.* 1996, Conen & Smith 2000, Perera *et al.* 2002b), for CH_4 biofilters treating fugitive emissions from the oil and gas industry (Chandrakanthi & Hettiaratchi 2005), and to describe the effect of pressure fluctuations on CO_2 transport in a landfill (Poulsen 2005).

An ecosystem similar to a landfill cover soil is a biofilter for the removal of CH_4 from a underground mine air (i.e. the air present in the tunnels of the mine). Such system was studied by du Plessis *et al.* (2003). They developed an empirical model for a 1-metre pine bark biofilter. The model consisted of a modified first-order relationship with an empirical fitting constant.

Grant (1999) added CH_4 oxidation to the *ecosys* model based on the kinetics of CH_4 oxidation, as controlled by biomass, and activity of the methanotrophic population as given by soil temperature. Energy gains from CH_4 oxidation are coupled to bacteria growth and kinetics of CH_4 oxidation. Diffusion is simulated accounting for soil moisture.

Remaining issues

An unresolved issue in landfill cover soil CH_4 oxidation modelling is the relevance of the difference between the gas transport models. As the dusty gas model has never been applied to landfill cover CH_4 oxidation modelling, it is unclear to what extent its predictions would differ from predictions of the Stefan–Maxwell equations. However, as Knudsen diffusion is not very important in landfill cover soils under optimal conditions, it is unlikely that the difference would be pronounced. The relevance of the difference between Fick's law and the Stefan–Maxwell equations has not been explored either. However, it is known that the difference is most pronounced when the diffusion coefficients of the gas components are very different. In view of the diffusion coefficients of the most relevant gas pairs (Table 10) it can be expected that the difference will not be very pronounced either. An exception might be the description of stable isotope fractionation, however. Stable isotope fractions can be measured with great precision (< 0.1% relative error), so the use of highly accurate models is recommended here.

The effect of pressure cycles on landfill CH_4 oxidation has not yet been explored. This issue is very complex because atmospheric pressure fluctuates on different time scales. On the time scale of hours to days the atmospheric pressure can fluctuate by up to 3000 Pa (Massmann & Farrier 1992). Pressure cycles on a time scale of minutes are much smaller, but their effect can be readily observed as a fluctuating CH_4 concentration above the landfill. Clearly gas is moving up and down the cover soil, which enhances mass transfer. Poulsen *et al*. (2001) accommodated this effect in their model by assuming increased dispersion near the soil surface. Hence, the dispersivity estimates outlined in the section entitled 'Input data for process-based models' above may well be too low for representative landfill cover soil conditions. However, a more specific investigation is required to put the description of this phenomenon on a more solid footing. The recent work of Poulsen (2005) provides a promising route to such an investigation.

None of the models presented incorporates the influence of moisture on CH_4 oxidation on a physiological level. Nor was micro-scale (liquid-phase) diffusion limitation other than the effect of EPS (Hilger *et al*. 1999) incorporated explicitly in any model. Incorporating these influences would improve the capability of models to describe extreme moisture conditions in landfill cover soils. Suggestions to incorporate these effects at atmospheric CH_4 concentrations have been made by De Visscher & Van Cleemput (2000) and De Visscher (2001), but have never been tested at elevated CH_4 concentrations representative for landfill cover soils.

The process-based models and the collision model are both mechanistic models, but they differ widely from a conceptual perspective. Nevertheless, it can be expected that there are fundamental principles underlying both models. For instance, De Visscher & Van Cleemput (2003b) pointed out that the collision model's emphasis on molecule-soil collisions put it within the realm of Knudsen diffusion. Uncovering such connections in a more quantitative manner would improve our understanding of LFG transport modelling.

Conclusions

This paper reviews our current understanding of microbial CH_4 oxidation in landfill cover soils, biocovers and biofilters, and points out some of the remaining issues. Improving that understanding is important for two reasons. First, in the context of carbon trading, CH_4 mitigation might have a commercial value. For that to be implemented, a reliable method for quantifying microbial CH_4 oxidation is required. Second, for the design and optimization of landfill biocovers and biofilters, the processes leading to CH_4 emission and CH_4 oxidation need to be properly understood.

One of the major obstacles in the measurement of CH_4 oxidation in landfill cover soils is the fact that LFG transport through cover soils is mediated by diffusion and advection simultaneously. Additional research to improve existing measurements techniques is required.

To stimulate CH_4 oxidation for CH_4 emission mitigation an integrated understanding – based on the CH_4 mass balance approach – is needed in which all processes controlling the fate routes of CH_4 at landfills are included. Considerable research has been carried out to understand CH_4 oxidation in soils and lately also in other materials, which may be used in engineered CH_4 oxidation facilities. The CH_4 oxidation rate in soils depends on several environmental factors such as layer properties (porosity, permeability, and diffusivity), moisture content, and temperature, which are some of the most important factors. However, the most poorly understood factors are N limitation and EPS production.

Inorganic N, especially ammonia, usually inhibits CH_4 oxidation. However, many methanotrophs need an external source of inorganic N, and these can be stimulated by inorganic N. The understanding of this as well as other factors would benefit from an improved characterization of the main methanotrophic strains responsible for the CH_4 consumption. However, the proliferation of newly discovered methanotrophs with widely varying properties indicates that we are far from achieving that goal. More research efforts are needed in this area.

There is an increasing awareness of the importance of EPS, which in some cases is produced by the CH_4 oxidizing microbial consortia. The EPS may influence the layer properties and examples of significant reduction in the CH_4 oxidation capacity of the layer due to EPS formation have been observed in laboratory test systems. There is a lack of detailed understanding of which environmental factors control the EPS formation and thus how it is avoided.

Substantial experience is emerging on engineered facilities such as biocovers and biofilters to mitigate the CH_4 emission by the CH_4 oxidation process. However, research on further development on such facilities is still needed. In particular, there is a need for integrated approaches based on controlling the CH_4 mass balance to stimulate CH_4 oxidation for CH_4 emission mitigation in cases where gas recovery is not a cost-effective option. In such integrated approaches mathematical models could play a major role to optimize the CH_4 oxidation process and avoid CH_4 emission through imperfect covers or due to off-site migration. Some of the remaining issues here are the effect of pressure cycles on LFG transport, and a better understanding of the link between the activity of biocover/biofilter materials and environmental factors like moisture content.

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