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Limits and dynamics of methane oxidation in landfill cover soils

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ABSTRACT

In order to understand the limits and dynamics of methane (CH_4) oxidation in landfill cover soils, we investigated CH_4 oxidation in daily, intermediate, and final cover soils from two California landfills as a function of temperature, soil moisture and CO_2 concentration. The results indicate a significant difference between the observed soil CH_4 oxidation at field sampled conditions compared to optimum conditions achieved through pre-incubation (60 days) in the presence of CH_4 (50 ml l^{-1}) and soil moisture optimization. This pre-incubation period normalized CH_4 oxidation rates to within the same order of magnitude (112–644 μg CH_4 g^{-1} day^{-1}) for all the cover soils samples examined, as opposed to the four orders of magnitude variation in the soil CH_4 oxidation rates without this pre-incubation (0.9–277 μg CH_4 g^{-1} day^{-1}).

Using pre-incubated soils, a minimum soil moisture potential threshold for CH_4 oxidation activity was estimated at 1500 kPa, which is the soil wilting point. From the laboratory incubations, 50% of the oxidation capacity was inhibited at soil moisture potential drier than 700 kPa and optimum oxidation activity was typical observed at 50 kPa, which is just slightly drier than field capacity (33 kPa). At the extreme temperatures for CH_4 oxidation activity, this minimum moisture potential threshold decreased (300 kPa for temperatures <5 °C and 50 kPa for temperatures >40 °C), indicating the requirement for more easily available soil water. However, oxidation rates at these extreme temperatures were less than 10% of the rate observed at more optimum temperatures (~30 °C). For temperatures from 5 to 40 °C, the rate of CH_4 oxidation was not limited by moisture potentials between 0 (saturated) and 50 kPa. The use of soil moisture potential normalizes soil variability (e.g. soil texture and organic matter content) with respect to the effect of soil moisture on methanotroph activity. The results of this study indicate that the wilting point is the lower moisture threshold for CH_4 oxidation activity and optimum moisture potential is close to field capacity.

No inhibitory effects of elevated CO_2 soil gas concentrations were observed on CH_4 oxidation rates. However, significant differences were observed for diurnal temperature fluctuations compared to thermally equivalent daily isothermal incubations.

1. Introduction

Aerated soils represent the only identified biological sink for atmospheric methane (CH_4). The highest CH_4 oxidation rates have been observed in aerobic soils with elevated levels of CH_4 (Adamse et al., 1972; Le Mer and Roger, 2001). Of particular importance is the attenuating effect that microbial CH_4 oxidation has on reducing fugitive CH_4 emissions from landfill cover soils. Landfill surface emission measurements quantify the net result of CH_4 transport from the anaerobic waste and methanotrophic oxidation through aerobic cover soils. Field data have also documented that point measurements of both CH_4 emissions and oxidation can vary over six orders of magnitude (e.g. Bogner et al., 1997). The potential range of percentage oxidation in landfill soils spans from negligible to more than 100%, with an average value of around 40% estimated with current methodologies (e.g. Bogner et al., 1997; Börjesson and Svensson, 1997; Chanton et al., 2009).

Landfill cover soils experience large temporal variability in soil temperatures, soil moisture, and CH_4 soil gas concentrations (from approximately 500 ml l^{-1} to sub-atmospheric levels of <1.8 μl l^{-1}). All of these environmental factors can drastically affect the oxidation capacity of the soil microbial communities and impact observed landfill CH_4 emission rates. It should be noted that soil properties, such as nutrient availability and pH,

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also impact oxidation rates (e.g. Albanna et al., 2007). The challenge is to develop an improved understanding of the ultimate soil oxidation capacity relative to the temporally-changing environmental conditions.

The literature indicates that fluctuating gradients of soil moisture and temperature are largely responsible for the observed dynamic range in landfill CH_4 oxidation capacities (Kallistova et al., 2005). In addition to other impacts, changes in temperature affect the rate of CH_4 oxidation (e.g. Czepiel et al., 1996) as well as the composition and biodiversity of CH_4-oxidizing consortia (e.g. Mohanty et al., 2007). Temperature is also an important variable when selecting conditions for laboratory oxidation studies (e.g. Schnell and King, 1996; Börjesson et al., 2004). Soil moisture controls on CH_4 oxidation have been suggested as a major controlling factor in numerous studies (e.g. Gebert et al., 2003; Jugnia et al., 2008). In forest soils, soil moisture is a primary variable affecting CH_4 oxidation rates, where 78% of the variability in CH_4 oxidation rates has been correlated to soil moisture variability (Castro et al., 1994).

To date, the majority of studies examining the impact of soil moisture on CH_4 oxidation rates in landfill cover soils are expressed in terms of gravimetric or volumetric moisture contents, thereby further complicating the comparison between soils of differing textures (Zeiss, 2006). Soil texture and structure ultimately control moisture availability (Hillel, 1980). By utilizing soil moisture potential, which expresses soil moisture in terms of the physical force with which water is held in soil, the differences in soil texture and structure can be normalized. At a given soil moisture potential (e.g. 33 kPa; field capacity) the behavior of soil water is equivalent in soils of different texture and structure, even though the gravimetric and volumetric moisture contents of those soils will be different. Thus, soil moisture potential is the preferred measure when examining microbial moisture limitations (Griffin, 1981). However, relationships between soil moisture potential and CH_4 oxidation rates (particularly for landfill cover soils) have not been elucidated (Mancinelli, 1995).

Furthermore, impacts of the CO_2 present in landfill gas and its corresponding effect on CH_4 oxidation rates has not been addressed for landfill settings. Current literature for non-landfill settings reports conflicting results. Phillips et al. (2001) observed a suppression of 16–30% in CH_4 uptake in forest soils continuously enriched with CO_2 at 200 $\mu l\ l^{-1}$ above ambient levels. However, other studies have shown no effect of the enriched levels of CO_2 (up to 700 $\mu l\ l^{-1}$) on microbial CH_4 oxidation rates (e.g. Zak et al., 2000). In general, oxidation rate responses to low levels of CO_2 enrichment have been inconsistent (Sadowsky and Schortemeyer, 1997). On the other hand, elevated CO_2 concentrations (>2 ml l^{-1}) have been linked to significant suppression of microbial respiration rates (e.g. Macfadyen, 1973; Dixon and Kell, 1989; Koizumi et al., 1991). Sierra and Renault (1995) reported that microbial O_2 consumption in soil aggregates was inhibited by CO_2 levels higher than 40 ml l^{-1} (4%). Due to the fact that there are often soil gas CO_2 concentrations higher than 40 ml l^{-1} in landfill cover soils, CH_4 oxidation activity could be suppressed. However, no specific study exists examining the impacts of the elevated CO_2 concentrations (>50 ml l^{-1}) on CH_4 oxidation rates.

The purpose of this manuscript is to document the variability and dependencies observed in CH_4 oxidation rates as a function of soil temperature (including diurnal temperature fluctuations), soil moisture, and CO_2 concentrations. We especially focused on the moisture threshold requirements for CH_4 oxidation using soil moisture potential for six different California landfill cover soils. The study was part of a larger project which is developing improved field-validated inventory methods for landfill CH_4 emissions inclusive of oxidation for the California greenhouse gas (GHG) inventory.

2. Materials and methods

Six different cover soils were collected from two California landfills for laboratory incubation studies. The two landfill sites were the coastal Marina Landfill (Monterey, CA, USA; 36.71°N 121.762°W) and the inland Scholl Canyon Landfill in the Los Angeles area (Glendale, CA; 34.158°N 118.196°W). Soil was collected from each of the cover types typically used at each site: daily, intermediate and final cover areas. Marina uses onsite soils as well as composted sewage sludge and green waste for their cover materials. Both surface and subsurface (profile) samples were collected. Profile samples were collected with a hand auger (AMS Inc.; American Falls, ID) at 10 cm intervals, and surface samples (0–10 cm) were collected using shovels and hand trowels. Sampling depth at the Scholl Canyon site was limited due to the excessive compaction and high density of the cover soils. The intermediate and final covers at Scholl canyon could not be sampled with a soil corer, so these were collected using a pick axe, which limited the sample depths. All soils were stored at collected moisture state and in the dark at 4 °C. Soil was sieved to 2 mm and mixed to ensure homogeneity prior to initiating incubations. Soil pH was measured in a 1:1 soil:deionized water (v:v) slurry. Other soil analyses were completed using reference methods (Black et al., 1965) by A&L Midwest Laboratories (Omaha, NE). Supplemental soil properties are given in Table 1.

For the profile samples, all incubations were conducted at 25 °C at two different moisture contents: as collected and at field capacity. These incubations were used to document the distribution of initial CH_4 oxidation activity through the cover and examine the effect of the pre-incubation conditions on the observed CH_4 oxidation rate.

2.1. Soil moisture retention curves for sieved soils

Soil moisture retention curves were determined using standard pressure plate methods (Soil Moisture Equipment, Santa Barbara, CA; Richards and Fireman, 1943). Since the soil moisture characteristic curve is highly dependent on soil structure, the values acquired here are solely representative of the sieved soils. Briefly, sieved soil was repacked into aluminum cylinders 3.0 cm high and 5.0 cm in diameter. Repacked bulk density was 1.2 ± 0.2 g cm^{-3}. Samples in the cylinders were saturated by soaking them in a plastic tray with the water level just below the top of the cylinders. Samples were soaked for 5 days to saturate and minimize the presence of entrapped air bubbles. After wetting, soil samples were placed in contact with the porous plate inside a pressure chamber and a known air pressure was applied. For this study, the pressures examined were 0, 33, 50, 100, 500, 700, 1000 and 1500 kPa (saturated, 0.33, 0.5, 1, 5, 7, 10 and 15 bar, respectively). All samples were run in triplicate. As mentioned previously, the soil moisture potential allows a normalized expression of soil moisture behavior across soils with various textures.

2.2. CH_4 oxidation incubations

Prior to initiating the oxidation rate incubations, soil was pre-incubated for 60 days in the presence of 50 ml l^{-1} CH_4 at each selected soil moisture potential. This is in agreement with other studies which have utilized 50 ml l^{-1} CH_4 in the headspace for 30–60 days (e.g. Kightley et al., 1995; Amaral et al., 1998). Previous work has observed that a 60 day period is sufficient to induce CH_4 oxidation activity in previously non-CH_4 consuming soils (Amaral et al., 1998). Soils were pre-incubated in 1 l plastic containers (Nalgene; Rochester, NY #2103-0032) with 200 g of soil per container with the 50 ml l^{-1} CH_4 replaced weekly in the headspace. These

Table 1
Chemical and physical properties of the landfill cover soils in this study.

Cover type	Marina			Scholl Canyon		
	Daily	Intermediate	Final	Daily	Intermediate	Final
Total cover thickness (m)	0.3	0.5	2.5	0.3	0.75	2.7
Surface soil properties (0–10 cm)						
Sand (%)	82	74	76	84	60	60
Clay (%)	12	10	10	4	14	14
United States Department of Agriculture Soil Type	S	SL	SL	S	SL	SL
Surface bulk density (g cm^{-3})	1.35	1.6	1.4	1.6	2.0*	2.0*
Field collected gravimetric moisture content (% w/w)	3.5	2.4	13.5	3	1.5	1.5
Organic matter (%)	0.5	2.2	3.9	2.0	0.4	0.9
Nitrogen (%)	0.17	1.53	4.6	0.92	0.58	0.65
pH (1:1)	7.4	7.8	6.7	7.4	8.3	8.2

[*] *Notes:* Excavation method – results may be biased by the high percentage of gravel (>4 mm) present in the cover soil. S represents "sand" and SL represents a "sandy loam" United States Department of Agriculture soil types.

pre-incubations remained aerobic (>180 ml l^{-1} O_2). The soil moisture was modified to the desired soil moisture potential based on the repacked soil moisture retention curves (Fig. 1) and corrected weekly for evaporative loses. In addition, initial oxidation assessments were carried out on soil samples without a pre-incubation period (Table 2A), and assessments with a pre-incubation period of 60 days without soil moisture adjustments in the presence of 50 ml l^{-1} CH_4 were also completed (Table 2B).

For each incubation, 5 g of pre-incubated soil (oven-dry equivalent) were then transferred to a 125 ml serum vial (Wheaton Glass, Milville, NJ) and sealed with red-butyl rubber septa (Grace Davison, Deerfield, IL) and an aluminum crimp. Next, 5 ml of enclosed headspace were removed and 5 ml of 50 ml l^{-1} CH_4 in argon was injected through the septum, bringing headspace CH_4 concentration to approximately 2 ml l^{-1}. This concentration was the average CH_4 concentration observed at 10 cm. The serum vials were then incubated at the desired temperature (with the soil already at the desired soil moisture potential). In all, thirteen temperatures (-5, 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60 and 70 °C) and eight different soil moisture potentials (0, 33, 50, 100, 500, 700, 1000 and 1500 kPa) were chosen for this study. A total of 3744 individual incubations (6 soils × 6 replicates × 8 different moistures × 13 different temperatures) were established to examine the impacts of temperature and moisture on the observed CH_4 oxidation rates. Methane oxidation was determined by monitoring the change in CH_4 concentration in the headspace during periodic sampling (described below). Depending on the observed rates of oxidation, incubations were conducted for 3–75 days. Rates of CH_4 oxidation were quantified by the linear decrease in headspace concentration with time (Fig. 2). These zero-order rate calculations are justified based on the observed linear decreases in CH_4 headspace concentrations (Fig. 2B) as well as other studies which have utilized zero-order reaction rates (e.g. Börjesson et al., 2004; Spokas et al., 2007).

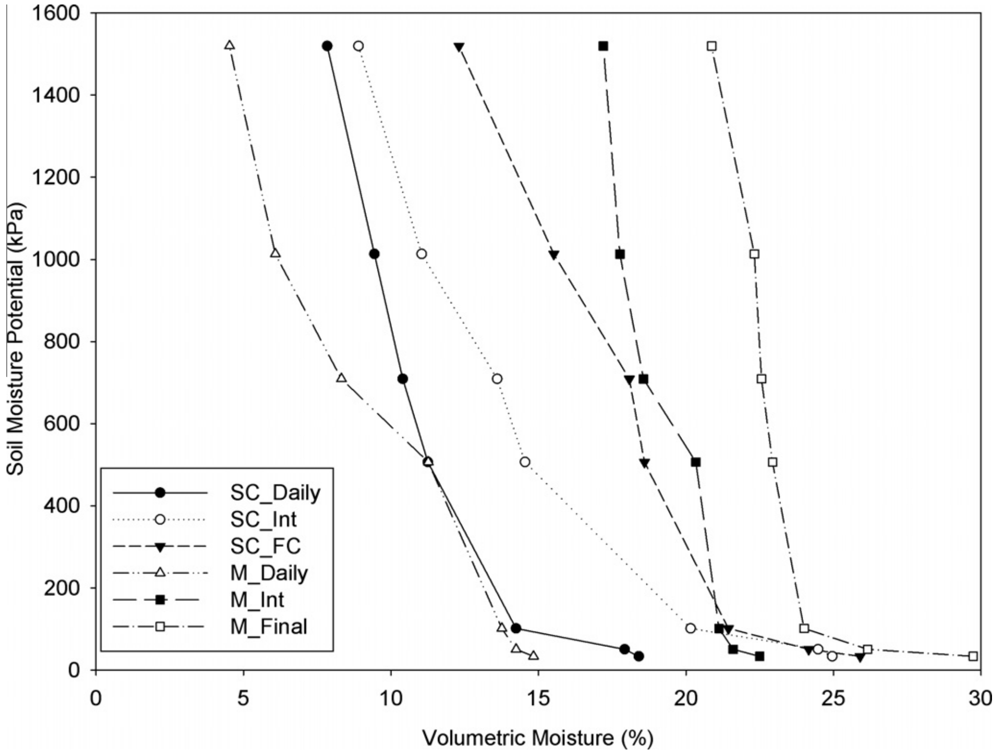

Fig. 1. Soil moisture retention curves for the six California landfill soils. SC represents Scholl Canyon landfill, M represents Marina landfill, Daily is daily cover, Int is intermediate cover, and Final is the final cover.

Table 2
Rates of CH_4 oxidation within the depth profile of the landfill cover soils for three different pre-incubation conditions: (A) no pre-incubation, (B) pre-incubation with CH_4 only and (C) pre-incubation with moisture amendments and CH_4. Rates given are averages of six replicates and standard deviations are given in parentheses.

Depth (cm)	Marina			Scholl Canyon		
	Daily (ug CH_4 g_{soil}^{-1} day^{-1})	Intermediate (ug CH_4 g_{soil}^{-1} day^{-1})	Final (ug CH_4 g_{soil}^{-1} day^{-1})	Daily (ug CH_4 g_{soil}^{-1} day^{-1})	Intermediate (ug CH_4 g_{soil}^{-1} day^{-1})	Final (ug CH_4 g_{soil}^{-1} day^{-1})
(A) Initial Rate – No Pre-incubation at field collected moisture contents						
0–10 cm	0.05 (0.02)	0.4 (0.2)	0.3 (0.1)	0.1 (0.2)	0.2 (0.3)	0.2 (0.1)
10–20 cm	0.04 (0.08)	1.9 (0.4)	0.2 (0.1)	0.1 (0.1)	0.2 (0.1)	0.2 (0.3)
20–30 cm	#	2.5 (0.6)	2.8 (0.5)	#	–	0.1 (0.1)
30–40 cm		171.3 (22)	2.6 (0.2)		–	–
40–50 cm		211.2 (36)	0.5 (0.3)		–	–
50–60 cm		#	1.4 (0.2)		–	–
70–80 cm			0.4 (0.2)		–	–
(B) Pre-incubation with 50 ml l^{-1} CH_4 and 200 ml l^{-1} O_2 at field collected moisture contents						
0–10 cm	0.4 (0.2)	0.1 (0.3)	3.6 (0.5)	1.7 (0.2)	0.2 (0.1)	0.9 (0.2)
10–20 cm	1.8 (0.1)	1.9(0.1)	2.8 (0.4)	3.6 (1.4)	0.2 (0.1)	0.5 (0.1)
20–30 cm	#	8.9 (0.4)	5.6 (10)	#	–	0.2 (0.5)
30–40 cm		384.2 (10.3)	111.3 (12)		–	–
40–50 cm		374.1 (7.1)	199.8 (14)		–	–
50–60 cm		#	219.8 (28)		–	–
70–80 cm			212.7 (23)		–	–
(C) Pre-incubation with 50 ml l^{-1} CH_4 and 200 ml $l^{-1}$$O_2$ (60 d) at field capacity moisture content (33 kPa)						
0–10 cm	142.2 (33)	416.8 (16)	593.8 (31)	112.4 (19)	211.4 (32)	212.9 (22)
10–20 cm	132.6 (20)	412.9 (13)	573.9 (14)	112.1 (13)	212.4 (39)	212.7 (18)
20–30 cm	#	412.7 (15)	613.1 (14)	#	–	212.5 (11)
30–40 cm		412.4 (23)	594.2 (16)		–	–
40–50 cm		452.0 (12)	604.2 (15)		–	–
50–60 cm		#	*ns*		–	–
70–80 cm			644.2 (28)		–	–

Notes: "–" designates a depth interval that was not sampled and "#" designates the base of cover was reached. "*ns*" indicates not sampled due to lack of adequate soil sample for all incubations. Total cover thicknesses are given in Table 1.

In order to compare the impact of temperature on CH_4 oxidation across all six cover soils at the eight different moisture potentials, normalized CH_4 oxidation rates were used. This normalized rate (ranging from 0 to 1) was calculated by dividing all the incubations for a particular soil by the maximum CH_4 oxidation rate observed for that particular soil for each of the respective soil moisture potentials evaluated. By normalizing the soils by soil moisture potentials, the effect of temperature alone could be evaluated. For each particular temperature, 144 incubations (6 soils × 8 soil moisture potentials × 3 replicates) were averaged. By using these normalized rates, the sensitivity to temperature across the various types of cover soils and different soil moisture potentials could be compared.

Similarly, to determine the impact of soil moisture across all six of the various cover soils, normalized CH_4 oxidation rates (rate at a given soil moisture potential divided by the maximum observed CH_4 oxidation rate for that soil at the respective temperature) were used to evaluate the sensitivity to soil moisture potential across the various cover soil types. For each particular soil moisture potential, the resulting normalized rates across various temperatures and soils were averaged. There were three temperature groupings analyzed for the soil moisture potential impacts: <5, 5–40, and >40 °C. These groupings were selected because oxidation rates at the lower (<5 °C) and upper (>40 °C) temperature ranges were very low to negligible. These normalized rates were then used to compare soil moisture effects across the different soils and to evaluate the optimum and minimum threshold soil moisture potentials within the three temperature groupings.

2.3. Examination of cyclic temperatures versus isothermal incubations

In order to ascertain the effect of diurnal temperature cycles on CH_4 oxidation rates, two sets of triplicate incubations for each of the six cover soils were established with equivalent diurnal temperature averages. The first set was placed in a growth chamber (Percival Scientific, Perry, IA; model 35LLV1) with a temperature program from 10 to 40 °C (including 12 h at 10 °C and then 12 h at 40 °C). This particular model growth chamber was limited to two temperature set-points. At 6:00 the incubator temperature was set to 40 °C and then at 18:00 the temperature returned to 10 °C. The temperatures inside the growth chamber were monitored with a temperature data logger at 15 min intervals (Onset Computing, Pocasset, MA; model UA-002-08). This set was compared to a second set of equivalent diurnal temperature incubations at an isothermal temperature of 25 °C. Soil incubations were established at three soil moisture potentials [field capacity (33 kPa), 300 kPa, and 1400 kPa] as described above (5 g soil; 2 ml l^{-1}). The main purpose of these incubations was to assess if there were differences in the observed rates of oxidation as a function of diurnal temperature fluctuations compared to isothermal conditions. CH_4 oxidation rates were calculated as detailed in Section 2.2.

2.4. Impact of elevated CO_2 concentrations

Incubations were also performed to determine the effect of 400 μl l^{-1} (lab ambient), 2 ml l^{-1}, 50 ml l^{-1} and 250 ml l^{-1} CO_2 on rates of CH_4 oxidation. For these incubations, soil moisture was adjusted to 50 kPa, and soils were pre-incubated with 50 ml l^{-1} CH_4 for 60 days (at ambient atmospheric CO_2 levels). Six replicate incubations (5 g soil at each CO_2 concentration) were conducted at 25 °C for each cover soil at field capacity. Specific gas mixtures of CO_2 with 200 ml l^{-1} O_2 (balance N_2; Minneapolis Oxygen) were used to flush the incubation vials after they were sealed with a double needle arrangement for 1 min (one needle for flush gas input ($\sim$10 l min^{-1}) and the other for venting). Following flushing of the headspace with the respective CO_2:O_2 mixture, 5 ml of enclosed headspace were removed and 5 ml of 50 ml l^{-1} CH_4 in argon was injected through the septum, bringing headspace CH_4 concentration to approximately 2 ml l^{-1} (exact initial concentrations were

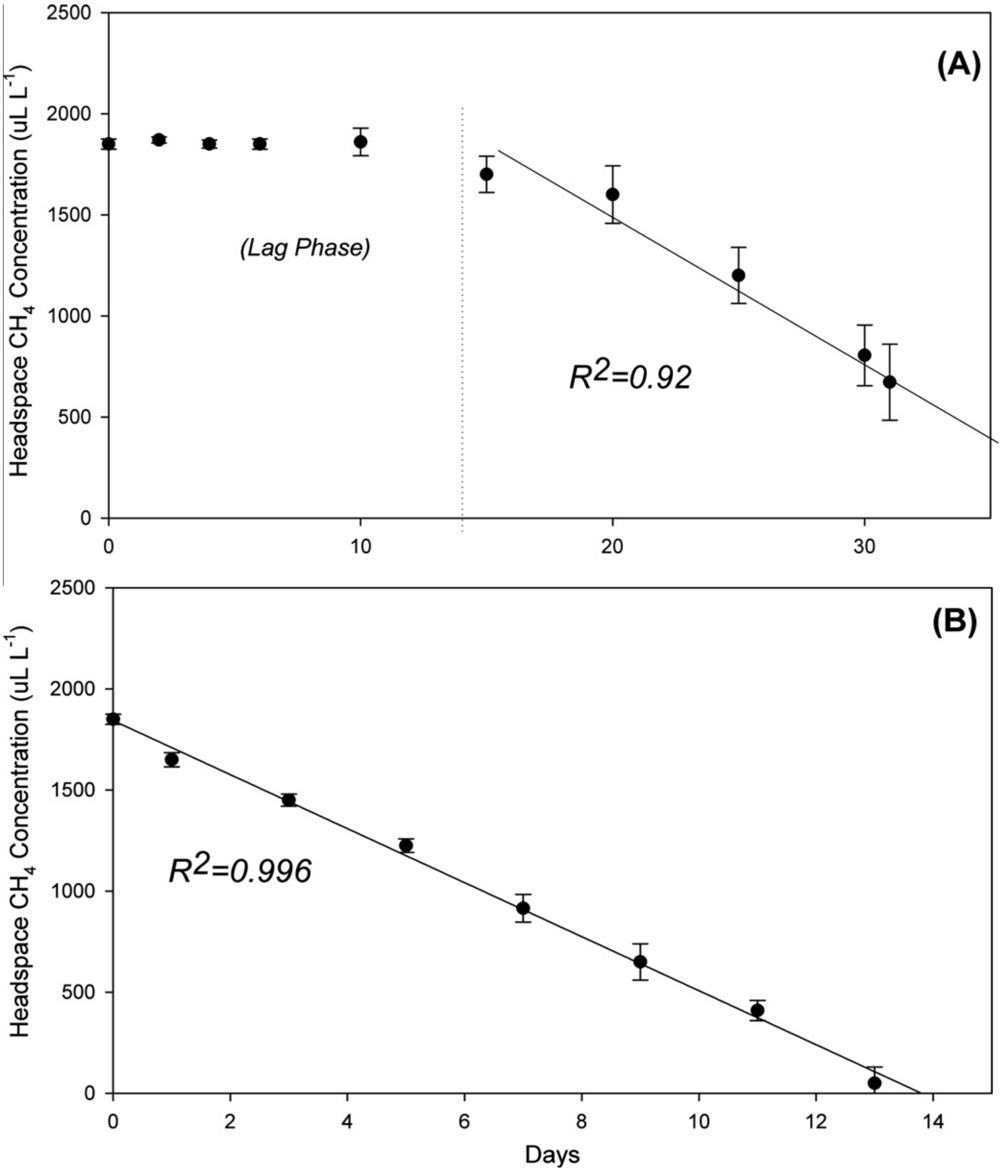

Fig. 2. Comparisons of CH_4 oxidation kinetics of (A) soil sample as collected from field (no pre-incubation period) and (B) soil following 60 d pre-incubation period with 5% CH_4. Data shown is for Scholl Canyon daily cover soil. Average of six replicates shown with standard deviations indicated.

determined by GC below). All incubations remained above 180 ml l^{-1} O_2 (data not shown). The sole variable examined for these incubations was the range of CO_2 concentrations. Differences in N_2 concentration were assumed to have negligible impact on the rates of CH_4 oxidation. CH_4 oxidation rates were calculated as described previously (Section 2.2).

2.5. GC analysis

To sample each incubation, 5 ml of air (known composition) were injected by syringe into each serum bottle. This syringe was flushed three times to allow for adequate mixing with the serum bottle headspace. Then 5 ml of gas was withdrawn and injected into an autosampler vial that had been previously flushed with helium using a dual needle arrangement (as mentioned above for flushing the CO_2 incubations). Concentrations from the GC were corrected for dilution by the 5 ml of air.

There were three gas chromatographic (GC) systems used in this research. All three systems were connected to the same type of headspace sampler (Agilent, Foster City, CA, model 7694) that was modified with additional sample valves to accommodate each analytical system. Details of each GC system are given in Table S1 (Supplementary Material).

3. Results and discussion

3.1. Soil moisture retention curves

The average of the volumetric soil moisture content at each of the respective moisture potentials for the six repacked cover soils are shown in Fig. 1. Note the close clustering in the intermediate and final Scholl Canyon cover soils with lower moisture contents for the daily cover soils and higher moisture contents for the highly organic final cover soil from Marina with the highest moisture-holding capacity. As discussed above, an important aspect about using soil moisture potential is that the soil moisture behavior is normalized across different soil textures (Hillel, 1980). Moreover, the behavior of soil water at the same soil moisture potential is equal in disturbed and undisturbed samples, despite the fact that the resulting water contents of an undisturbed and a repacked sieved sample will be different. Therefore, at the same soil moisture potential, the availability of soil water to microbes is approximately equal regardless of the soil texture.

3.2. Impacts of pre-incubation and soil moisture on CH_4 oxidation rates

Overall, pre-incubating the soil sample with CH_4 for 60 days resulted in higher CH_4 oxidation rates than those observed without the pre-incubation period (Table 2). This increase in CH_4 oxidation rates as a consequence of pre-incubation has been observed by others (e.g. Park et al., 2002; Chanton et al., 2008). Priemé et al. (1996) and Börjesson et al. (1998) described methanotrophs as slow growing (>5 days), which could explain the relatively long pre-incubation periods needed to establish a steady-state condition in the soil (Amaral et al., 1998). These incubation periods for CH_4 oxidation studies are longer than those for typical microbial assessments of 7–10 d (e.g. Franzluebbers et al., 1996). It is interesting to note, that for the California cover soils, steady-state conditions were not reached until 60 days. This could be due to the normally-low soil gas CH_4 values for the majority of cover types sampled (Table 3), which is at least partially attributed to effective gas extraction systems operating at the sites.

We also observed differences in the behavior of oxidation kinetics as a function of the pre-incubation period. Without the CH_4 pre-incubation, we observed a lag phase before CH_4 oxidation was initiated (Fig. 2A). However, with the CH_4 pre-incubation, soils exhibited exceptionally linear decreases in the CH_4 headspace with time (zero-order kinetics, all $R^2 > 0.95$) (Fig. 2B). This behavior was observed in all cover soils examined here and also been observed by Börjesson et al. (2004). This lag phase was most pronounced for the Scholl Canyon daily cover soil, which unlike the Marina daily cover, was not being stored at the landfill site and thus had no prior history of CH_4 exposure.

The use of extended 60 day CH_4 pre-incubations is examining the soil's ultimate CH_4 oxidation potential. This can be contrasted with determinations of CH_4 oxidation activity at selected conditions of soil temperature, moisture availability and exposure to CH_4. There is no consensus in the literature on the optimum pre-incubation period or on the soil moisture content during this period for landfill cover soils. Our results indicate that the 60 day incubation with 50 ml l^{-1} CH_4 (replaced weekly) was adequate to stimulate the dynamics of CH_4 oxidation activity in the cover soils (Table 2C), in order to assess the ultimate potential for CH_4 oxidation.

The data in Table 2A replicate the typical depth distribution for CH_4 oxidation rates in the literature, with the maximum rate occurring slightly below the surface. However, as seen in the subsequent sections of Table 2, this is not a static property. Table 2B indicates elevated CH_4 oxidation rates compared to Table 2A after a 60 d pre-incubation with 50 ml l^{-1} CH_4. Oxidation rates in Table 2B were directly linked to the soil moisture contents. The oxidation rates for those soils with available moisture (wetter than the wilting point) were drastically increased compared to the rates without pre-incubation (typically by an order of magnitude; Table 2A). Thus, soil moisture is a major controlling factor on the CH_4 oxidation capacities at field collected moisture contents, as documented in other studies (e.g. Wahlen and Reeburgh, 1996).

Table 2C presents CH_4 oxidation rates with a 60 day pre-incubation period when the soil was also initially adjusted to 33 kPa (field capacity). This adjustment to field capacity greatly increased the observed rates by about two orders of magnitude compared to Table 2A. In addition, this soil moisture adjustment reduced the variability seen across all soils to within the same order of magnitude (Table 2C; 112–644 μg CH_4 g^{-1} day^{-1}), as opposed to the four orders of magnitude in the non-optimized soil moisture incubations (Table 2B; 0.9–277 μg CH_4 g^{-1} day^{-1}). For all samples, the combined adjustment of soil moisture and the 60 d pre-incubation with CH_4 eliminated the depth differences that were initially seen in the field data. This suggests that oxidation rates as typically measured directly on field collected samples represent their in situ capacity at the time of collection and not their full potential (Table 2A and C). Furthermore, the possibility exists that the ultimate potential rate of CH_4 oxidation could be similar for all the soils examined, but with oxidation rates in situ controlled by soil microclimate (soil temperature and moisture) and historical soil gas CH_4 concentrations.

The pre-incubated rates observed in the California landfill cover soils are within the range observed in other landfill oxidation studies, ranging from 0.06 to 653 μg CH_4 $g_{soil}{}^{-1}d^{-1}$ (e.g. Kightley et al., 1995; Boeckx and van Cleemput, 1996; Gebert et al., 2003; Park et al., 2005). However, without the pre-incubation (Table 2A), the oxidation rates would be at the low end of observed oxidation rates reported in the literature for landfill settings.

3.3. Temperature relationships

Fig. 3 summarizes oxidation rates for all of the temperature incubations at the eight different soil moisture potentials. This type of temperature response for methanotrophic activity has been observed in other studies (e.g. Whalen et al., 1990; Czepiel et al., 1996; Gebert et al., 2003; Börjesson et al., 2004; Jugnia et al., 2006). In general, CH_4 oxidation rates increase with temperature up to a maximum temperature (~30 °C), and then correspondingly decreases up to a temperature maximum threshold of about 55 °C. Optimal oxidation temperatures around 30 °C have been typically reported (e.g. Boeckx and Van Cleemput, 1996; Whalen et al., 1990). The resulting relationship was fitted with a 3-parameter Gaussian peak (Fig. 3; SigmaPlot 11, SysStat; San Jose, CA):

$$\text{Normalized Rate} = 1.05e^{-0.5\left(\frac{T-27.6}{9.59}\right)^2}, \qquad (1)$$

where T is the temperature of the incubation (or soil temperature; $R^2 = 0.981$). From the equation fitting, the optimal temperature across all soil types and soil moistures was 27.6 ± 0.5 °C (Fig. 3).

It is also relevant to note in Fig. 3 that when soils were incubated at >50 °C for 120 d no CH_4 oxidation activity was observed. CH_4 oxidation rates did not immediately recover when the temperature for these same incubations was lowered to 30 °C, and an additional 7–14 d at 30 °C was required before any oxidation activity was observed. This could be directly related to spore formation for survival at the elevated temperatures (e.g. Whittenbury et al., 1970). These lag periods are frequently mentioned in the literature.

Table 3
Corresponding CH_4 soil gas concentrations (μl l^{-1}) at collected depths in the cover materials.

Depth (cm)	Marina			Scholl Canyon		
	Daily	Intermediate	Final	Daily	Intermediate	Final
Methane concentrations (μl l^{-1})						
0–10 cm	120	12,000	5	3	5	3
10–20 cm	350	150,000	2	5	4	2
20–30 cm	#	320,000	2	#	*ns*	3
30–40 cm		390,000	3		*ns*	*ns*
40–50 cm		450,000	8		*ns*	*ns*
50–60 cm		#	5		*ns*	*ns*
70–80 cm			12		*ns*	*ns*

Notes: "*ns*" designates a depth interval that was not sampled and "#" designates the base of cover was reached. Total cover thicknesses are given in Table 1.

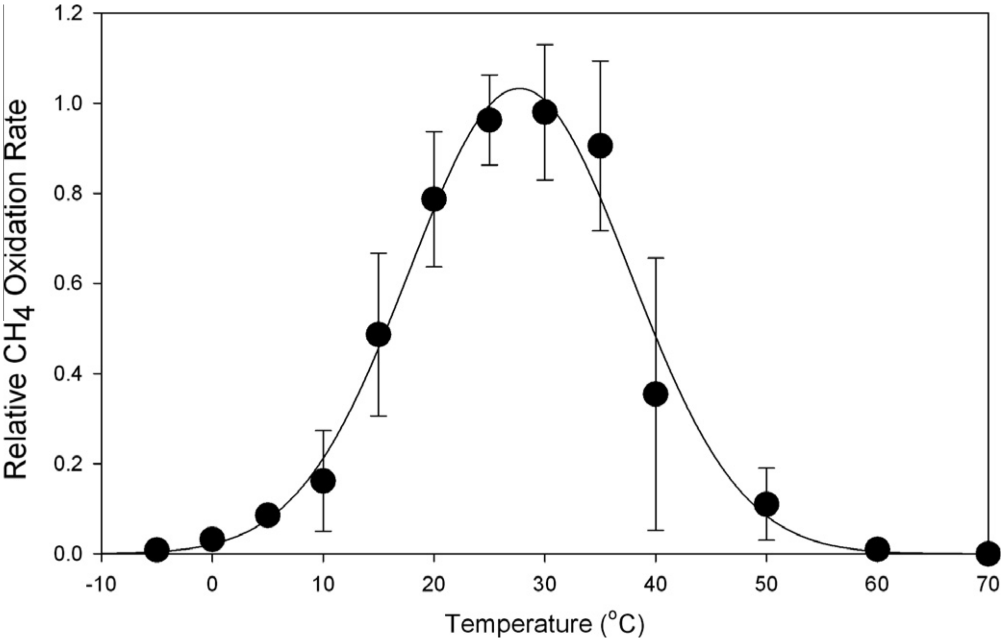

Fig. 3. Effects of temperature on relative rates of CH_4 oxidation (rate at specific temperature divided by maximum rate for the corresponding soil moisture potential for each soil) with associated standard deviations and fit to a 3-parameter Gaussian curve ($n = 3456$).

However, actual quantification of the lag periods as a result of combined temperature and moisture limitations requires further examination.

3.4. Soil moisture potential relationships

Fig. 4 illustrates CH_4 oxidation rates versus soil moisture potential for the six cover soils for three different temperature groupings. For the laboratory incubations at 5–40 °C, a minimum threshold of 1500 kPa was observed (Fig. 4B). This threshold is also referred to as the wilting point (the soil moisture potential at which plants no longer can extract water from the soil). A threshold value of 1500 kPa was maintained if the soil was initially preconditioned at higher soil moisture contents and then allowed to dry. However, if the soils were initially dry and then wetted; a threshold value of 600 kPa was observed. Thus, the threshold value fluctuates depending on the soil wetting history (a hysteresis-type response). These results again illustrate the need to further elucidate the temperature, moisture and pre-incubation relationships, including time lags.

As also seen in Fig. 4, the threshold soil moisture potential for CH_4 oxidation activity shifts to lower soil moisture potentials (higher moisture contents) at the extreme temperatures (<5 °C; Fig. 4A and >40 °C; Fig. 4C). At the low temperature end (<5 °C; Fig. 4A), the minimum soil moisture potential threshold decreases to 300 kPa. At the upper limits of CH_4 oxidation activity (>40 °C; Fig. 4C), the minimum soil moisture potential threshold decreases further to 50 kPa. Thus, these results strongly indicate the coupled interaction of soil moisture and temperature. The impacts of soil moisture on the rates of oxidation can be estimated through the use of a 3-parameter sigmoid function (Fig. 4B; Sigma Plot 11, SysStat; San Jose, CA):

$$\text{Relative rate} = \frac{0.992}{1 + e^{\left(\frac{\text{SMP}-683.8}{171.4}\right)}}, \tag{2}$$

where SMP is the soil moisture potential (+kPa) ($R^2 = 0.994$).

For the majority of soils examined, the optimum soil moisture potential for CH_4 oxidation was approximately 50 kPa, although this value was not statistically significant across all soil types. This 50 kPa is close to field capacity (33 kPa). The results from

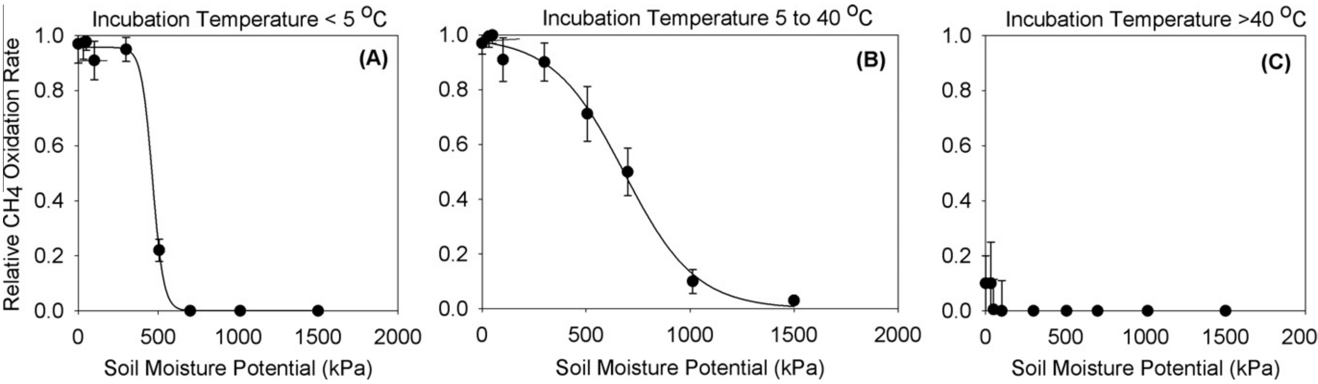

Fig. 4. Effect of soil moisture on relative rates of CH_4 oxidation (rate at soil moisture potential divided by maximum rate for the corresponding temperature of the incubation) for (A) temperatures less than 5 °C ($n = 72$) and (B) temperatures between 5 and 40 °C ($n = 3192$), and (C) for temperatures >40 °C ($n = 192$).

this study suggest that there is no single optimum moisture; rather, an upper soil moisture potential of 50 kPa or wetter does not result in statistical differences in CH_4 oxidation rates. This lack of a distinct optimum moisture content has been observed in other studies (e.g. Einola et al., 2007). However, it should be mentioned that due to the small amount of soil present in the incubation, these laboratory incubations were not exposed to the same diffusion constraints that would exist in a variably-saturated field soil. For comparison with moisture contents in the literature, 50 kPa soil moisture potential corresponds to 8.4–31.7% volumetric moisture for the sieved California cover soils (Fig. 1), which is within the range of optimum soil moisture values that have been reported previously (e.g. Christophersen et al., 2000; Boeckx and Van Cleemput, 1996; Visvanathan et al., 1999). However, volumetric or gravimetric water contents do not provide direct information on soil water availability. From the results presented here, the use of soil moisture potential is highly recommended to normalize soil variability (e.g. soil texture and organic matter content) with respect to the effect of soil moisture on methanotroph activity.

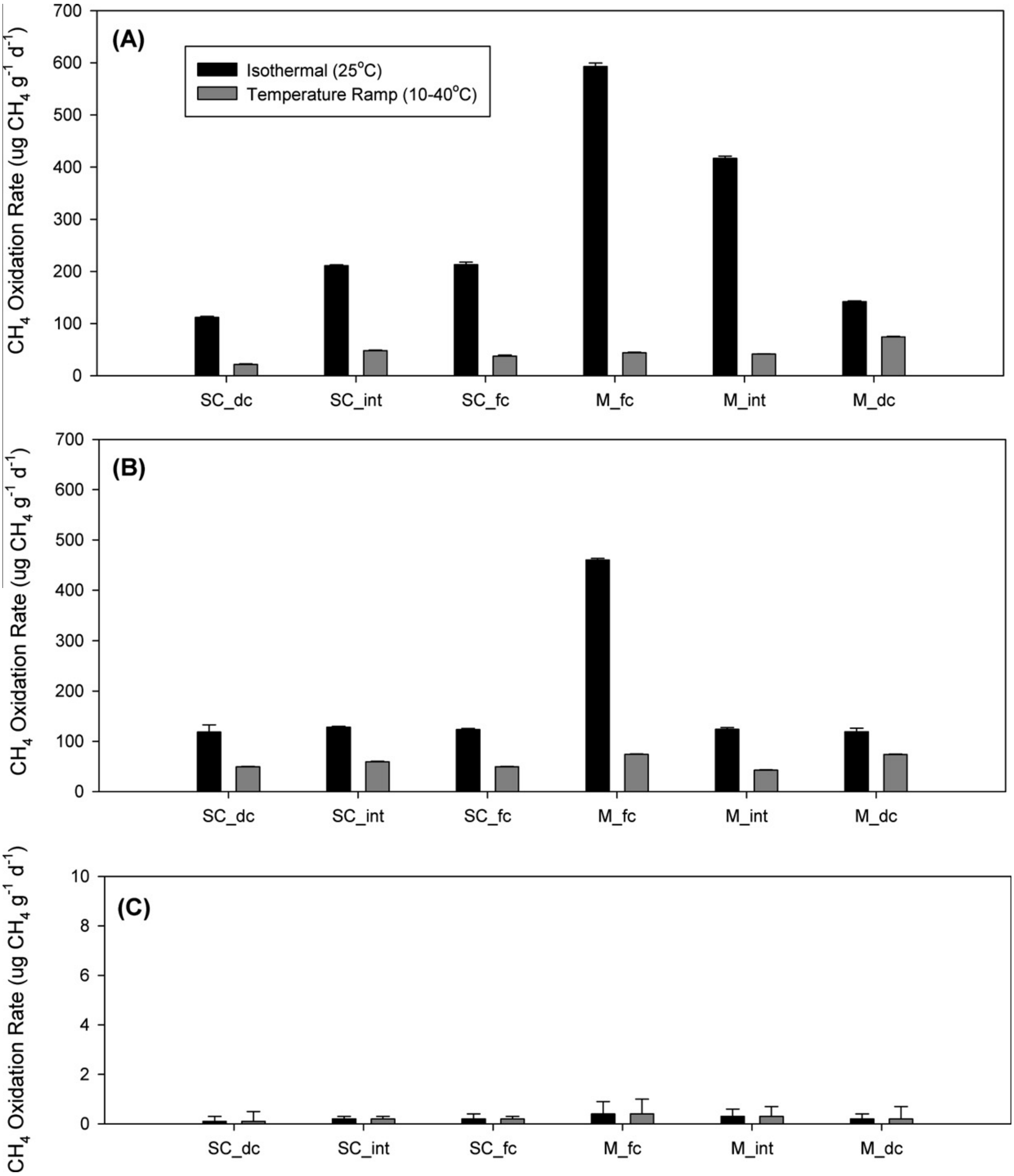

Fig. 5. Illustration of the impacts of a temperature cycle compared to an equivalent isothermal incubation on the methane (CH_4) oxidation rate of various cover soils at (A) −33 kPa, (B) −300 kPa and (C) −1500 kPa. Standard deviations of the replicates are shown. SC represents Scholl Canyon, M represents Marina landfill, fc is final cover, int is intermediate cover and dc is daily cover.

3.5. Cyclic temperature relationships

Fig. 5 indicates CH_4 oxidation rates for three different moisture levels at isothermal conditions compared to fluctuating daily temperatures. The cyclic rates for all soils were significantly lower than the isothermal oxidation rates, despite the fact that the average daily temperature for the two temperature regimes was approximately equal at 25 °C (Fig. 5). Overall, the observed reduction in CH_4 oxidation activity with temperature cycling at the 33 kPa soil moisture potential was 48–93% (average 78%; Fig. 5A). At 300 kPa soil moisture potential, the reductions ranged from 38% to 84% (average 60%; Fig. 5B). This lower average reduction could result from the reduced CH_4 oxidation activity at the 300 kPa soil moisture potential compared to field capacity (33 kPa). The level of reduction was the greatest for the Marina final cover soil (93% at 33 kPa and 84% at 300 kPa). These reductions were directly correlated with the organic matter content, as the Marina final cover soil had the highest reductions and also the highest organic matter content (Table 1). These temperature effects could also be due to the impact of temperature of methanotroph growth (Börjesson et al., 1998). However, the exact cause is unknown. As can be seen in Fig. 5C, the highest soil moisture potential (1500 kPa) resulted in extremely low rates with a majority being non-significantly different than zero, thus confirming the soil moisture potential threshold discussed previously.

When the temperature relationship (Eq. (1)) is applied to the actual recorded incubation temperatures, this relationship predicts an oxidation rate reduction of 81% which is within the range of the observed reductions (Fig. 5). We are not aware of other studies of this type (ramped vs. isothermal temperatures) for landfill cover soils. Despite the fact that we do not know the exact causes behind these reductions, these results suggest that it is imperative to account for diurnal as well as seasonal temperature variability when examining landfill soil CH_4 oxidation.

3.6. Impact of CO_2 concentration on CH_4 oxidation rate

The observed impact of CO_2 concentrations on oxidation rates is shown in Table 4 for the Marina intermediate soil. As seen in the table, the rates of CH_4 oxidation were not significantly different ($P = 0.183$) for the various levels of CO_2 evaluated in the laboratory incubations. Results of the incubations with the other cover soils were similar, in so far as there were no statistically significant impacts observed on the rate of CH_4 oxidation. However, despite the fact that the CH_4 oxidation rates were similar, there was a significant impact on the CO_2 respiration rates as a function of CO_2 concentration ($P < 0.0001$). This is in agreement with other observations of decreasing CO_2 respiration rates with increasing CO_2 concentrations (e.g. Macfadyen, 1973; Dixon and Kell, 1989; Koizumi et al., 1991). These observations indicate that elevated CO_2 concentrations do not alter CH_4 oxidation rates in landfill cover soils, despite decreasing microbial respiration rates.

Table 4

Influence of variable CO_2 concentrations on observed CO_2 respiration and CH_4 oxidation rates over a 25 d incubation with the Marina intermediate cover soil at 25 °C. Data in the table is the average of six replicates with standard deviation given in parentheses. Rates followed by the same letter are not significantly different.

CO_2 Concentration (ml l^{-1})	CO_2 Respiration (mg CO_2 $g_{soil}{}^{-1}d^{-1}$)	CH_4 Oxidation (ug CH_4 $g_{soil}{}^{-1}d^{-1}$)
0.4	25.2 (0.95) a	419.9 (11.7) a
2	23.87 (1.0) a	411.4 (23.2) a
50	18.9 (2.4) b	415.8 (23.4) a
400	14.3 (3.1) c	390.2 (33.6) a

4. Conclusions

Soil moisture potential provides a more robust parameter than gravimetric or volumetric moisture for examining the dependency of landfill CH_4 oxidation rates on soil moisture. The optimal soil moisture potential was very close to field capacity (50 kPa), with the minimum threshold soil moisture potential at approximately 1500 kPa (soil wilting point). Furthermore, these limits for soil moisture potential would be directly applicable to other soils of different textures and structure.

We observed that soil temperature and moisture potential interact to influence CH_4 oxidation rates under field conditions, necessitating the need to evaluate the temporal dynamics of CH_4 oxidation relative to the soil microclimate variability within the soil profile. Simpler assumptions of an average daily temperature, or an average annual temperature and a temperature-dependent rate constant, as illustrated by the results from the cyclic temperature incubations, will lead to significant errors in the quantification of CH_4 oxidation rates. In addition, rates of CH_4 oxidation were not significantly different for the various levels of CO_2 evaluated in the laboratory incubations, despite elevated CO_2 levels suppressing microbial CO_2 respiration rates.

Our results also indicate that many landfill CH_4 oxidation rates previously reported in the literature for field samples actually represent their capacity at field conditions and not their full CH_4 oxidation potential. The pre-incubation period at field capacity moisture normalized CH_4 oxidation rates to high values within the same order of magnitude (112–644 μg CH_4 g^{-1} day^{-1}) for all the cover soils samples examined, as opposed to the four orders of magnitude variation in the soil CH_4 oxidation rates without pre-incubation (0.9–277 μg CH_4 g^{-1} day^{-1}). Therefore, we recommend a 60 day pre-incubation period (with 50 ml l^{-1} CH_4) at field capacity to determine the ultimate potential for CH_4 oxidation in landfill cover soils.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.wasman.2009.12.018.

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