



Column Study for Assessing the Suitability of Different Soil Substrates for CH₄ oxidation in Landfill Covers

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1 Background and study aims

The microbial oxidation of methane in engineered cover soils is considered a potent option for the mitigation of low calorific emissions from landfills. The oxidation efficiency is regulated by the combination of cover material properties, landfill gas source strength and climate conditions. Under given climatic conditions and methane production rates, especially the physical properties of the soil are of eminent importance. Soil texture and compaction determine the pore size distribution effective for both water retention and gaseous transport, thus determining the rate at which methane and atmospheric oxygen become available to the methane oxidising microorganisms. In order to derive design criteria that enable composing an effective methane oxidising recultivation layer from the range of soils that become available to the landfill operator, a laboratory column study was devised to assess the methane oxidation capacity of different soils under simulated landfill conditions. Six potential landfill top cover materials, selected by the client, were investigated with respect to methane oxidation and soil diffusivity over a period of four months.

The column study was carried out by the University of Hamburg, Institute of Soil Science, as a subcontractor of melchior+wittpohl Ingenieurgesellschaft Hamburg. The contract included the technical setup in the laboratory, the filling of columns with the soil material, column operation, data collection, data analysis and interpretation. The material itself was supplied and delivered by NV Afvalzorg, client of melchior+wittpohl Ingenieurgesellschaft, soil chemical and physical analyses were carried out by melchior+wittpohl Ingenieurgesellschaft.

2 Column setup

Six columns were constructed from PVC-pipes (DIN EN 1401-1) with a length of 1070 mm, an inner diameter of 190 mm and a wall thickness of 4.9 mm. They were closed with sealing caps at both ends. At the bottom, an inlet for synthetic landfill gas and at the top an inlet for (synthetic) air and a clean gas outlet were installed. Vertically, gas sampling points were mounted in 10 cm intervals, consisting of a needle penetrating a tightly sealed butyl-rubber stopper and reaching 10 cm into the substrate. The needles were closed with a disposable 1 ml syringe used for sampling the soil gas. At the bottom, a water outlet was installed to provide a drainage in case of leachate build-up. For security reasons the entire setup was placed under a fume hood. The temperature was monitored using a Pt100 temperature sensor placed in the fume hood.

Each column was packed with a gas distribution layer of 17 cm of coarse gravel, topped by 80 cm of one of the six provided substrates. The soil water content was adjusted to field capacity (60-300 hPa suction) and the soil compacted to the densities shown in Table 1. Installation and compaction of the soil was performed in 10 cm intervals. Interface effects between layers were minimized by scraping off the top cm of each layer before placement and compaction of the subsequent layer. A scheme of the setup can be seen in Figure 1, a photograph is given in Figure 2.

Inlet and outlet flow rates were controlled with needle valves and recorded using rotameters operating in the range of 0-19 ml/min (inlet), 0-30 ml/min (outlet) and 0-150 ml/min (outlet), at a total height of 150 mm each (purchased from ANALYT-MTC Messtechnik GmbH).

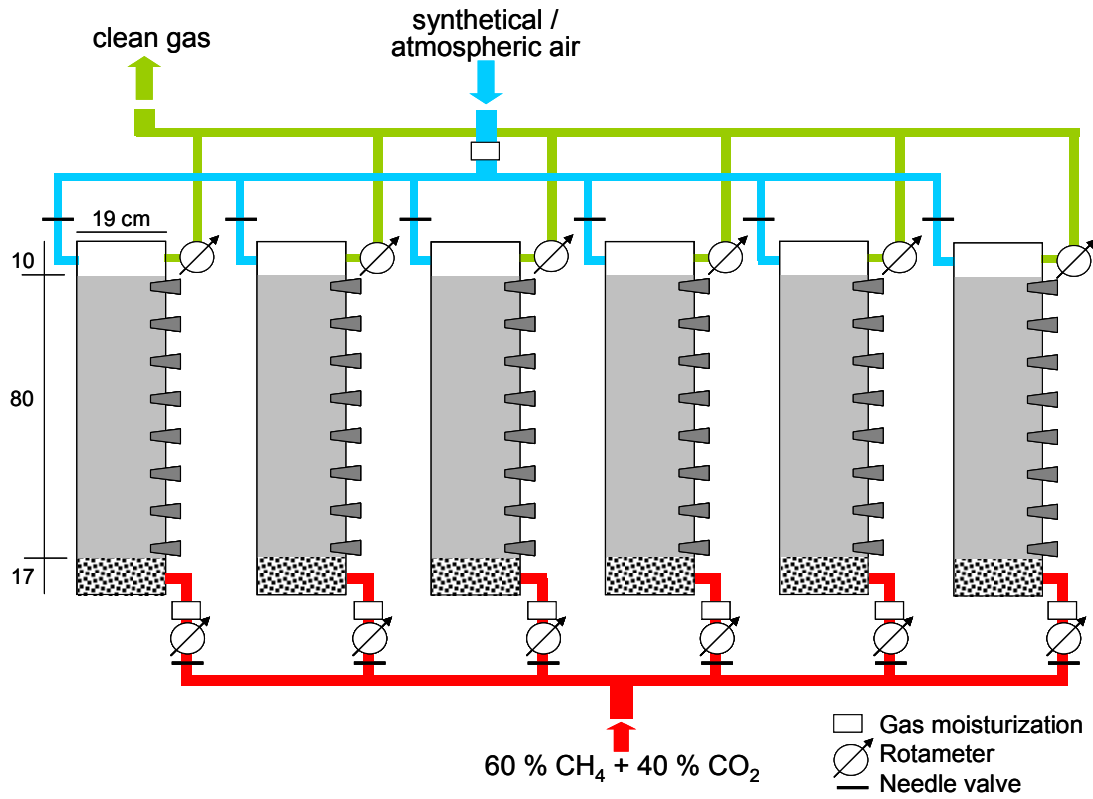


Figure 1: Schematic of column setup, not to scale.

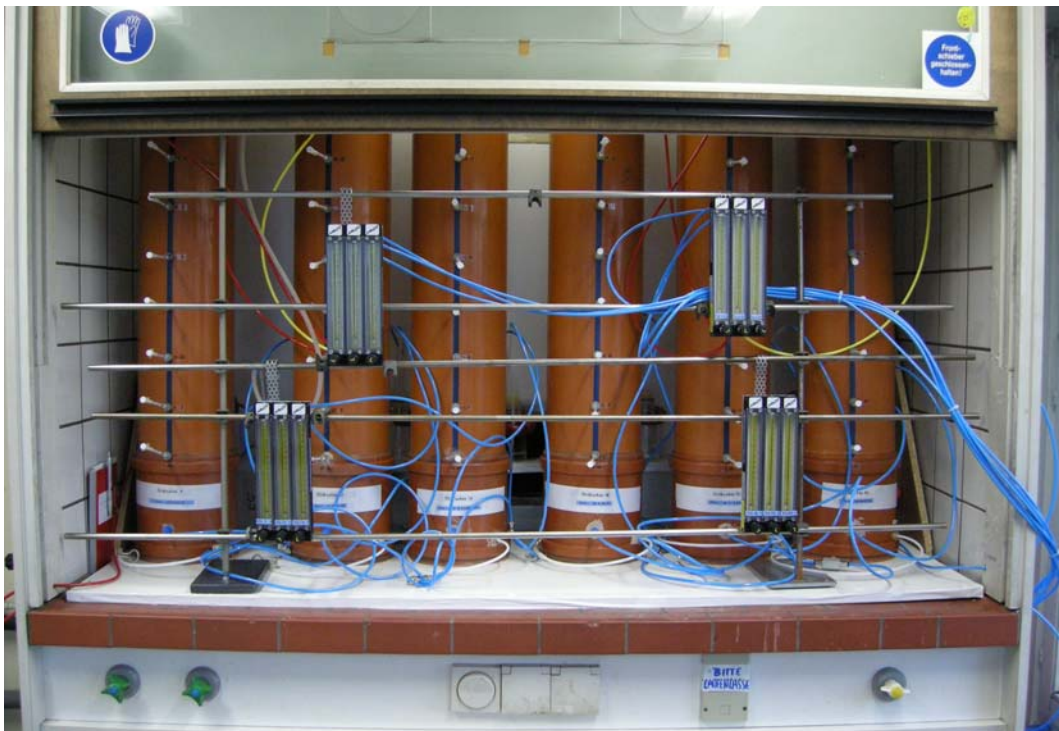


Figure 2: Photograph of column setup.

Table 1: Dimensions of columns; water content, solids and pore volumes, air capacity and water content of column materials. ww = wet weight, dw = dry weight.

Inner diameter [cm]	19					
Base area [m ²]	0.02835					
Column no.	1	2	3	4	5	6
Height (incl. gravel) [cm]	99	97	97	97	97	97
Height (soil) [cm]	82	80	80	80	80	80
Weight (soil) [kg ww]	42.57	36.32	43.81	37.91	39.55	43.15
Bulk density [g dw/cm ³]	1.67	1.38	1.73	1.36	1.26	1.74
Water content [kg]	3.80	5.00	4.54	7.02	10.99	3.67
Solids volume [l]	14.63	11.82	14.82	11.66	10.78	14.90
Pore volume in [l]	8.61	10.86	7.86	11.02	11.90	7.78
Pore volume [vol. %]	37.98	47.90	34.67	48.60	52.48	34.31
Water content [vol. %]	16.75	22.05	20.03	30.95	48.45	16.19
Gas volume [vol. %]	21.23	25.85	14.64	17.65	4.03	18.12

3 Experimental procedures

The columns were continuously charged with synthetical landfill gas (40 vol.% CO₂, 60 vol.% CH₄) derived from a pressurized bottle connected to the gas distribution system (red piping in Figure 1). The gas was passed through a water bottle before entering the columns in order to prevent desiccation of the soil. Flow rates were controlled with needle valves and the inlet rotameter valves. At the top, moisturized air was pumped through the column headspaces at an excess rate compared to the inlet flux. Headspace flux was controlled by needle valves positioned before the air inlet. Total effluent (outlet) gas flux was displayed by rotameters located behind the gas outlet. The flow rates for synthetical landfill gas were run within four different test ranges (Table 3).

Table 2: Phases of column operation.

Phase no.	Date	Inlet CH ₄ flux [l m ⁻² h ⁻¹]	Std. dev.
1	04.10.-09.11.2007	2.44	0.53
2	10.11.-30.11.2007	3.58	0.60
3	01.12.-21.12.2007	4.99	1.15
22.12.2007-01.01.2008: Christmas break, no operation			
4	02.01.-26.02.2008	1.65	0.76

3.1 Gas profiles

The vertical distribution of CH₄, CO₂, O₂ and N₂ within the individual columns was determined weekly for nine depths per column using a GC-FID/TCD (Agilent). 1 ml of sample was withdrawn from the respective depth and directly analysed.

3.2 Calculation of CH₄ oxidation efficiency

Inlet and outlet fluxes were recorded five times per week and combined with the analysis of CH₄- and CO₂-concentrations in the headspace using a GC-FID/TCD (Shimadzu 14A/B) to calculate CH₄ and CO₂ inlet and outlet fluxes. CH₄ oxidation efficiency was calculated as follows:

$$\text{CH}_4\text{ox} = \frac{(\text{flux}_{\text{in}} - \text{flux}_{\text{out}})}{\text{flux}_{\text{in}}} \times 100 \quad \text{Eq. 1}$$

where CH_4ox_i = % of CH₄ inlet flux oxidized at time i
 $\text{flux}_{\text{in}_i}$ = CH₄ flux into the column (ml/min) at time i
 $\text{flux}_{\text{out}_i}$ = CH₄ flux out of the column (ml/min) at time i .

To account for the (residence) time lag between inlet and corresponding outlet fluxes, outlet fluxes were related to inlet fluxes calculated as a moving three day average.

3.3 Batch tests

For the determination of the potential CH₄ oxidation rate of the substrates tested in the columns, standard batch test were performed using a material aliquot. Batch tests are relatively easy to perform and provide a quick means for comparing the potential methane oxidation capacity of different substrates under optimised and standardised conditions.

For each substrate, six standard SCHOTT DURAN® laboratory bottles (100 ml) were filled with 10 g of soil at the same water content as installed in the columns. Three of the parallels were used to prepare a slurry by adding 10 g of sterilized water. Bottles were sealed with butyl rubber stoppers. The headspace composition was adjusted to 10 vol.% CH₄ by addition of an appropriate volume of pure CH₄. Initial gas composition was controlled by analysis of the headspace for CH₄ and CO₂ using a GC-FID/TCD (Shimadzu 14A/B). The bottles were then incubated at 20°C; slurries were agitated on a rotary shaker at 200 rpm. CH₄- and CO₂-concentrations in the headspace were monitored until all CH₄ was oxidised. Oxidation rates were calculated using the linear part of the CH₄ degradation curve as follows:

$$\text{CH}_{4\text{ox_pot}} = \frac{d\text{CH}_4}{dt} \times \frac{\text{Vol}_{\text{bottle}} \times \text{MM}_{\text{CH}_4} \times 10}{\text{MVol} \times \text{dw}_{\text{soil}} \times 24} \quad \text{Eq. 2}$$

where $\text{CH}_{4\text{ox_pot}}$ = potential CH₄ oxidation capacity [$\mu\text{g g}_{\text{dm}}^{-1} \text{h}^{-1}$]
 $d\text{CH}_4/dt$ = slope of change in CH₄-concentration [vol.%] over time [d]
 $\text{Vol}_{\text{bottle}}$ = Gas volume of bottle [ml]
 MM_{CH_4} = molar mass of CH₄ = 16 g/mol
 MVol = molar gas volume at the given temperature [l]
 dw_{soil} = dry weight of soil [g].

3.4 Quality management

The following measures were taken to ensure quality of column operation, GC measurements and data processing:

- All junctions and interfaces were sealed and tested for gas-tightness before and in the course of the experiment by means of a portable FID.
- In a separate experiment it was verified that the disposable syringe and needle setup used to collect gas profile samples did not provide a pathway for diffusive influx of air into the columns.
- Inlet and outlet fluxes were controlled daily and adjusted if necessary.
- The Shimadzu GC-FID/TCD was calibrated daily for CH₄ and CO₂ using 7 standard gas mixtures.
- Stability of the Agilent GC-FID/TCD calibration for CH₄, CO₂, O₂, and N₂ was checked regularly using 3 standard gas mixtures.
- Rotameter calibration supplied by the producer was corrected by triplicate soap film flow meter measurements covering the entire range of flow rates applied.

3.5 Potential for errors

- Under windy weather conditions, outlet rotameter readings sometimes oscillated strongly. In these cases, the average flow rate of the range over which the flow oscillated was selected for outlet CH₄ flux calculations. Calculated CH₄ outlet fluxes could be lower or higher than the actual value.
- For the initial calculation of the amount of material to be used, considering a desired bulk density of 95 % of the Proctor density, the column base area was calculated using a radius of 10 cm. The actual radius, however, was 9.5 cm. Consequently, actual compaction and bulk densities were higher than intended.

4 Soil characteristics

Table 3 summarizes selected soil physical and chemical parameters of the six substrates provided by NV Afvalzorg, Figure 3 shows the water retention curves determined at 95 % of the optimum proctor density. The material selection was intended to cover a broad range of soil physical parameters. However, the analysis of texture showed four of the substrates to be purely sandy (columns 1, 2, 3, 6; see Table 3). The most finely textured material was the 'Saneringsgrond' used to construct column 5, also showing by far the highest humus content of 9 %. The sandy substrates have a similar pH regime, but differ with respect to their humus contents, ranging from 0.7 % (column 6) to 4.9 % (column 2). The increased salt content of the materials in columns 4 and 5, indicated by the elevated electric conductivity values, reflect their marine influence. Further soil analytical data is included in the report by melchior+wittpohl Ingenieurgesellschaft Hamburg.

Table 3: Material characteristics. Soil texture was defined according to the German Soil Classification System (AG Boden 2005), translation given in brackets. EC = Electric conductivity. LOI = loss on ignition.

Parameter	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
Label	Siltig zand 2033	Kleilig zand met veen 7773	Grond voor reining 710880	Baggergut 3181	Saneringsgrond 4110	Siltig zand 9468
Texture	Ss (sand)	Ss (sand)	Ss (sand)	SI2* (loamy sand)	Lt2 (clayey loam)	Ss (sand)
pH	8.4	8.1	8.2	6.8	7.4	8.0
CaCO₃ [%]	4.4	2.4	3.3	7.3	6.1	1.4
EC [mS/m]	10.2	50.1	61.6	196.6	135.4	35.9
LOI [%]	2.0	4.9	3.0	7.5	9.0	0.7

*The texture analysis did not allow for differentiation between the silt and the clay fraction due to flocculation during sedimentation.

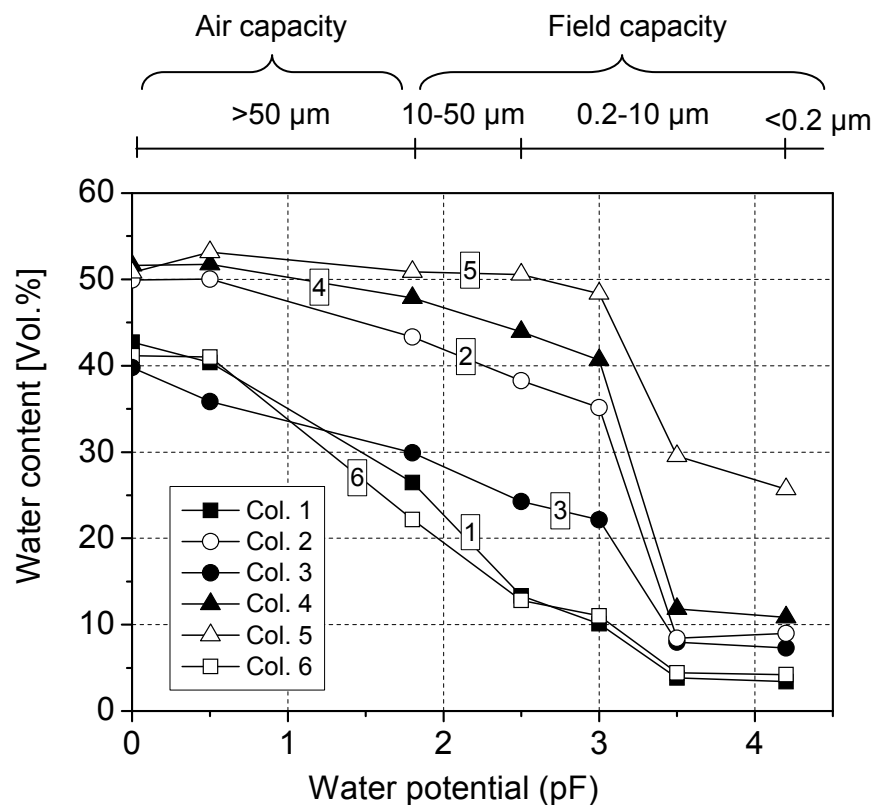


Figure 3: Water retention curves for the six column materials. Water potential is given as $-\log \psi_m$ [hPa], where ψ_m is the matric potential of the material. Top of figure: corresponding pore diameters.

Pore size distribution is the key property for water and gas transport. With respect to this property, derived from the water retention curve (Figure 3), the selected materials belong to two groups:

Materials of columns 1, 3 and 6 are characterized by a (lower) total pore volume of around 40 % ($pF = 0$) and a high air capacity ($pF < 1.8$) of 20-30 vol.%. The air capacity signifies the pore volume available for transport of gases under conditions of field capacity water content, i.e. when all excess water has drained away. Of these substrates, the material used to construct columns 1 and 3 have the highest share of plant available water bound in the medium sized and slowly draining coarse pores (0.2-50 μm ; ~23 vol.%).

The materials belonging to columns 2, 4 and 5 have a higher total pore volume of around 50 %, but a significantly lower air capacity of only close to zero (column 5) – 12 %. Due to its clay fraction, the material in column 5 is characterised by a relatively high share of fine pores (<0.2 μm , ~26 vol.%), generally considered to contain the share of non-plant available water. Column 2 and 4 materials show an elevated share of medium sized and slowly draining coarse pores (0.2-50 μm ; 34 vol.% and 37 vol.%, respectively), providing for a higher share of plant-available water than the other materials.

5 Results of column study

5.1 Course of temperature during the experiment

In the course of the column study, the laboratory temperature averaged around 19.3 °C, with a minimum of 13.7 °C and a maximum of 23.7 °C (Figure 4). Standard deviation was 0.9 °C, indicating relatively stable conditions. With the exception of a short period during the end of October 2007, the figure shows that the general temperature level was similar over the length of the experiment. Daily variations in lab temperature are not expected to affect the temperature within the columns to a significant extent.

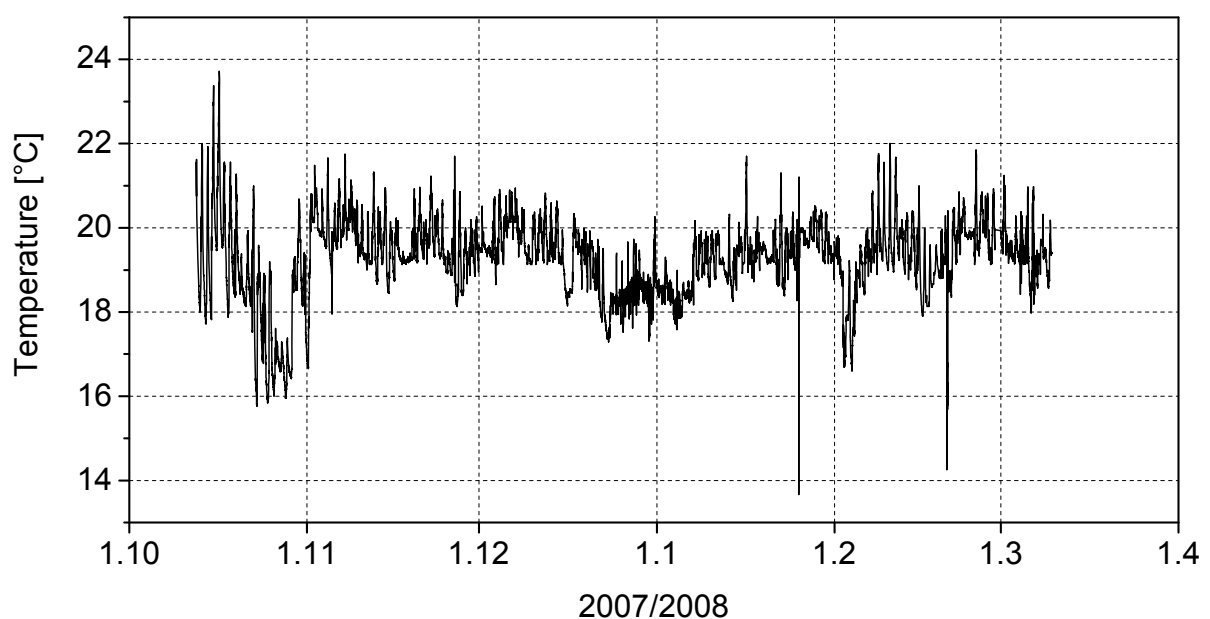


Figure 4: Course of laboratory temperature during the experiment.

5.2 CH₄ oxidation efficiency over time

Methane reduction took part in all investigated columns during the entire period of the experiment (Figure 5). However, the performance of the different substrates varied greatly, both for the same substrate over time and as a result of changing inlet CH₄ fluxes, as well as between columns.

In all cases, the columns were exposed to synthetical landfill gas and air for a week before measurements were started to allow for system equilibration and activation of the methanotrophic community. When monitoring started, oxidation could be observed immediately in all columns, but columns 2, 3 and 6 showed a lag phase of seven to ten days, before reaching a higher level of oxidation efficiency.

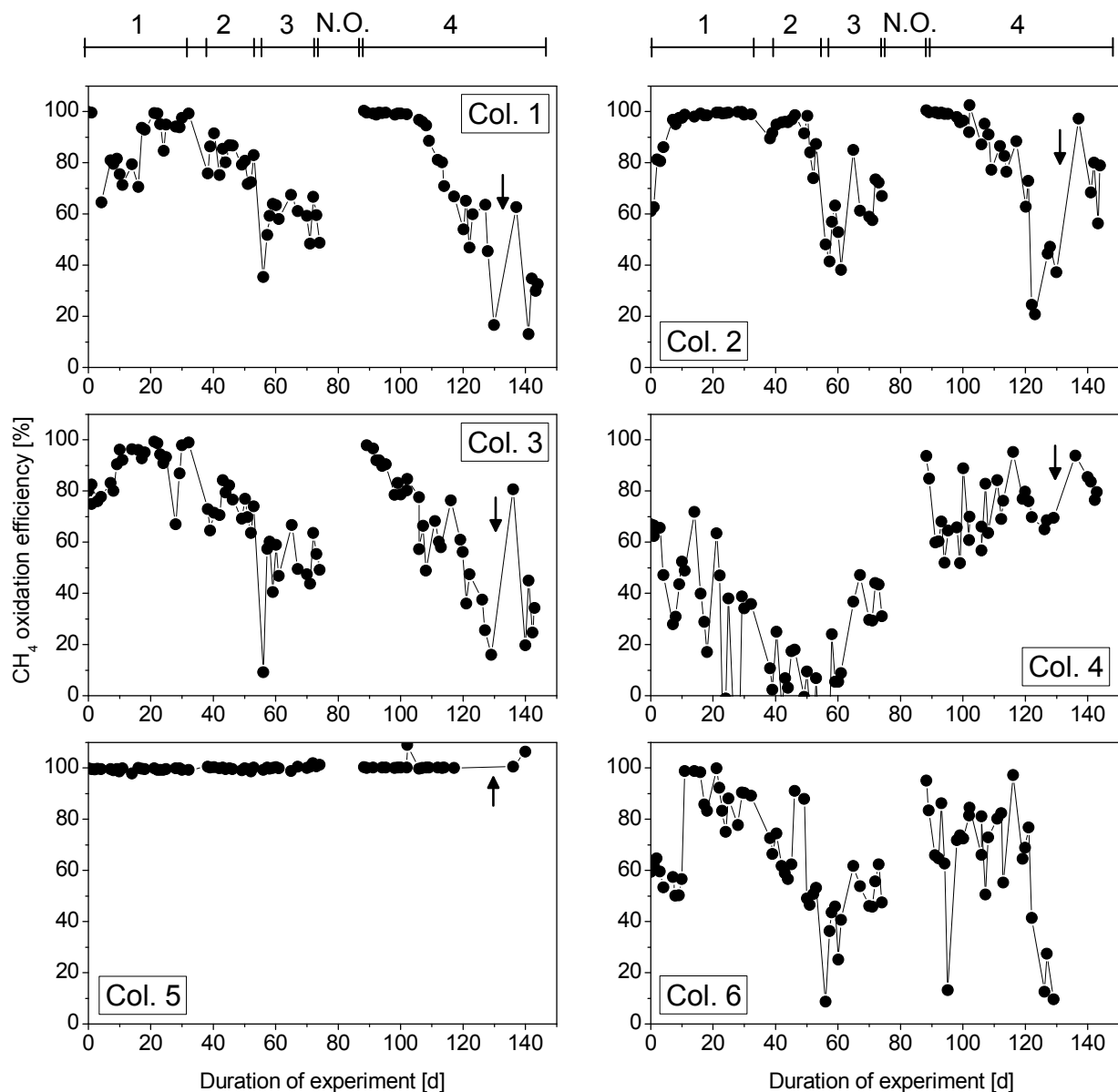


Figure 5: CH₄ oxidation efficiency in the course of the column experiment. Top of figure: indication of the four operational phases. N.O. = no operation (Christmas break). Arrow = aeration of columns.

The initial inlet CH₄ flux of 2.44 l m⁻² h⁻¹ in operational phase no. 1 was almost completely oxidized by all columns except for column 4 at an average efficiency of below 40 % (compare also Figure 7). In general, column performance decreased markedly upon each further increase of inlet CH₄ flux (to 3.58 and 4.99 l m⁻² h⁻¹ in phases 2 and 3, respectively), but recovered to a new optimum within a few days. After the Christmas break, operation was resumed with 1.65 l CH₄ m⁻² h⁻¹, with all columns initially oxidizing 100 % of the feed CH₄. Interestingly, in columns 1 and 2 performance declined dramatically after approximately 20 days of phase 4 operation. Column 3 showed an immediate decline, column 4 performed better than in all phases before and column 6 first stabilized at a higher performance level than during phase 3, but finally also showed a performance decline. In an attempt to recover the soils' methane oxidation capacity, the columns were aerated between day 129 and day 134. Columns one to four responded with a clear increase in oxidation performance, however, which then declined again (due to problems with the inlet rotameter, column 6 was not operated after day 129).

Column 5 is a clear exception: the material showed complete degradation of the supplied CH₄ flux in all phases of the experiment.

5.3 CH₄ oxidation at different inlet fluxes

The relationship between inlet CH₄ fluxes and the absolute CH₄ degradation rates for all measured values is shown in Figure 6. To facilitate estimation of the percentage oxidation efficiency, the graphs include the 100 % oxidation rate as straight line. With the exception of column 4 and 5, all columns show increasing absolute removal rates with increasing influx rates up to a column-specific optimum. The deviation from the 100 % line in the lowest range of inlet fluxes corresponds to the decline in performance observed during phase 4. Especially column 4 occasionally also showed negative methane 'oxidation rates', i.e. higher methane production than oxidation. For these cases it is assumed that the observed outlet CH₄ flux reflects the balance between the processes of methanogenesis and methane oxidation.

The graphs in Figure 6 also contain a red line reflecting an estimate of each column's capacity. According to these estimates, column 2 has the highest capacity of around 4 l CH₄ m⁻² h⁻¹, followed by column 1 at ~3 l CH₄ m⁻² h⁻¹, column 3 with ~2.5 l CH₄ m⁻² h⁻¹ and column 4 with 1-1.5 l CH₄ m⁻² h⁻¹. For column 6, the pattern did not seem clear enough for a capacity estimate. As mentioned above, column 5 behaved exceptionally: the capacity limit was not reached in the course of the experiment.

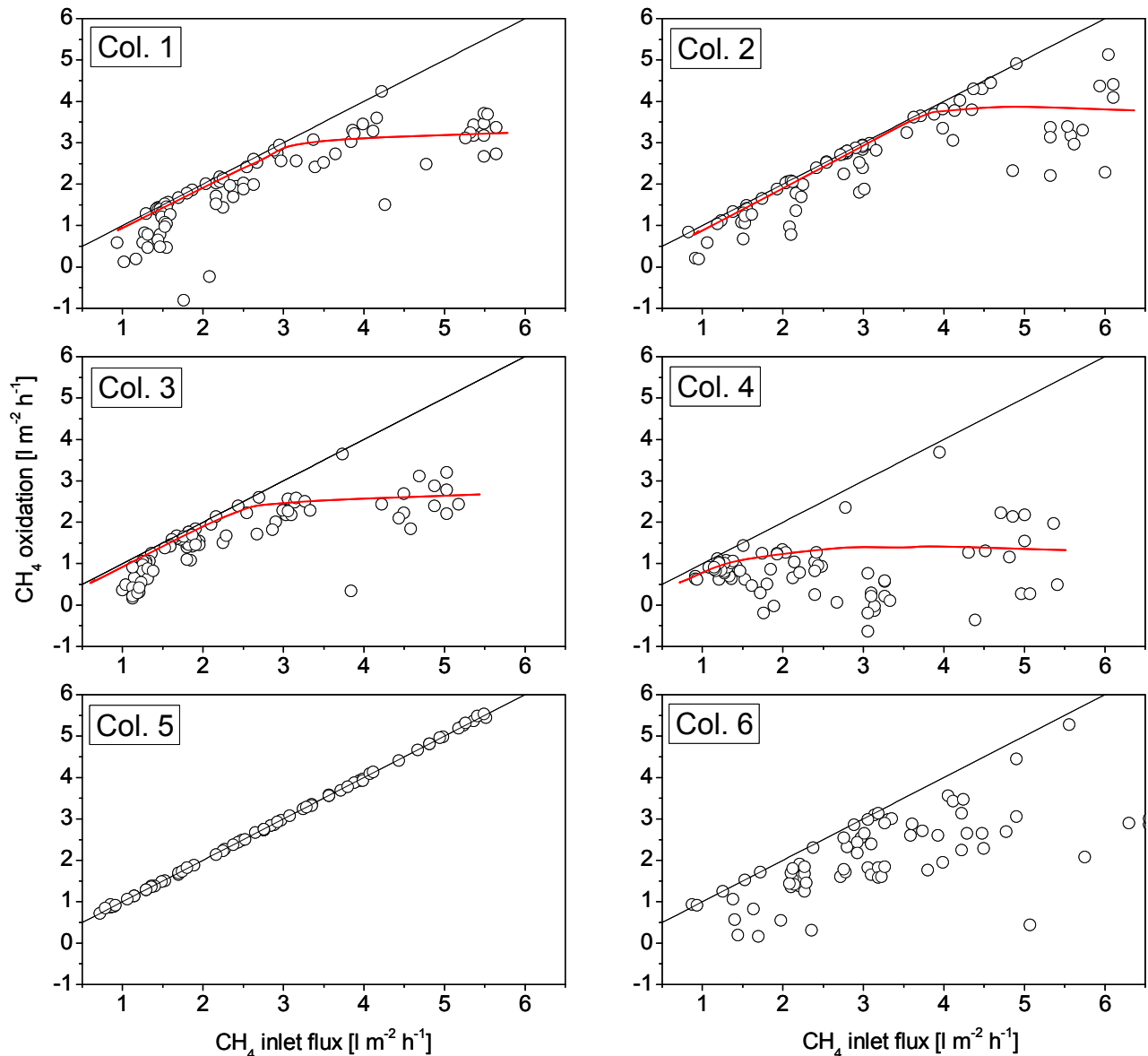


Figure 6: Absolute CH₄ oxidation rates as a function of inlet CH₄ flux. Black line: $x=y$ (100 % oxidation efficiency). Red line = estimated column oxidation capacity curve.

Figure 7 summarizes CH₄ oxidation rates observed for each column for the four phases of operation (compare Table 2) in box plots.

Except for column 5, which showed near total oxidation of the inlet CH₄ at all times, performance decreased with increasing inlet fluxes (phases 1 to 3) and recovered again upon decrease of the inlet flux (phase 4). During the first three phases, columns 1, 2 and 3 clearly performed best, followed by column 6. Column 4 showed the lowest average oxidation rates and even produced methane during phases 1 to 3. Although the performance of all materials recovered after reducing the inlet CH₄ fluxes to the lowest average of 1.65 l m⁻² h⁻¹ (phase 4), the mean CH₄ oxidation efficiency was lower than in phase 1 and showed much greater variation (see also Figure 7). This is due to the decline in efficiency towards the end of the experiment, already mentioned above.

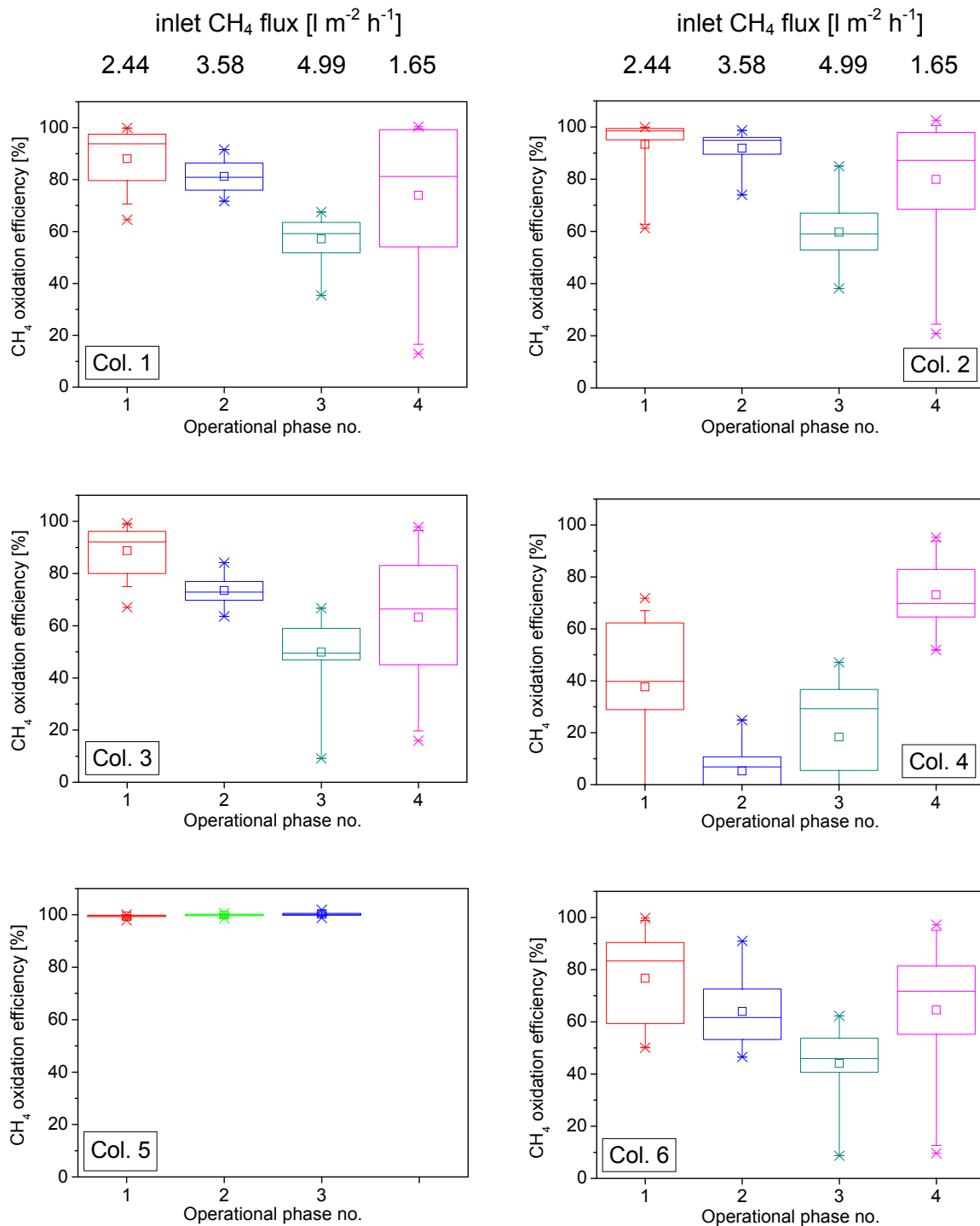


Figure 7: CH₄ oxidation efficiency for all columns during the four operational phases. Box = values within the 25th and the 75th percentile, line = median, symbol = arithmetic mean, whisker = values within the 5th and the 95th percentile, crosses = values between the 1st and the 99th percentile, short horizontal lines = maximum and minimum.

Interestingly, column 4 (# 3181, 'Baggergut') was not affected by this phenomenon; on the contrary, oxidation efficiency steadily increased throughout phase 4, resulting in an average oxidation efficiency of well above 70 %. This is plausible if it is assumed that the observed CH₄ production in phases 1-3 results from the release of easily degradable organic matter in anaerobic

niches of the soil column. Readily degradable organic matter of low humification status is typically present in (dredged) sediments. As shown in a previous study on the CH₄ formation potential of dredged material (Gebert et al. 2006), initial higher CH₄ formation rates observed under completely anaerobic conditions in many cases decline after a period of ~ 80 days. It was also shown that the CH₄ formation rate correlated with the share of easily degradable organic matter present in the light fraction 1.4 g cm^{-3}. It is suspected that after day 88 of the column experiment, i.e. the beginning of phase 4 operation, all easily degradable organic matter still present in the material during construction was released and that after this period, the observed increased efficiency reflects net CH₄ oxidation.

Comparison of column CH₄ oxidation efficiencies with literature values

Table 4 shows the range of CH₄ loads fed to the columns as well as the range of oxidation rates observed.

Table 4: Minimum and maximum values for CH₄ loads and CH₄ oxidation rates in the column experiment. *higher oxidation rates than CH₄ loading rates reflect uncertainties in rotameter readings.

Column no.	CH ₄ load min [g m ⁻² d ⁻¹]	CH ₄ load max [g m ⁻² d ⁻¹]	CH ₄ oxidation min [g m ⁻² d ⁻¹]	CH ₄ oxidation max [g m ⁻² d ⁻¹]
1	14.9	90.2	2.1	67.6
2	13.2	97.3	3.2	82.1
3	15.9	82.7	2.9	58.3
4	14.7	86.5	1.0	59.0
5	11.6	88.0	11.6	88.2*
6	14.0	117.5	2.6	84.5

Table 5 provides a summary of CH₄ loads and oxidation rates as reported from other studies for column experiments simulating landfill covers. Comparison of the values indicates that in the experiment reported here CH₄ loading rates were significantly lower than in the other studies. Only the investigations by Humer and Lechner (2001) and by Ahn et al. (2002) were conducted at comparable CH₄ loading rates. Correspondingly, the absolute CH₄ oxidation rates also were lower than reported for most other studies. However, it has to be noted that to our knowledge, the study presented here is the only one where the soils were deliberately compacted to >95 % of the Proctor density.

Table 5: Summary of CH₄ oxidation rates obtained in soil column experiments simulating landfill soil covers. Extracted from Scheutz et al. (2008).

Reference	Soil texture	CH ₄ inlet conc. [vol.%]	CH ₄ load [g m ⁻² d ⁻¹]	CH ₄ oxidation [g m ⁻² d ⁻¹]
Stein and Hettiaratchi (2001)	Landfill loam	99	Low: 186 High: 319	93 102-120
Stein and Hettiaratchi (2001)	Rockyview dark soil – agricultural soil	99	310	99
Park et al. (2002)	Loamy sand	99	525	
Kightley et al. (1995)	Landfill coarse sand	99	266	166
	Landfill clay topsoil	99		109
	Landfill fine sand	99		110
Hilger et al. (2000b)	Landfill sandy loam	50 ^a	281	42-56
Hilger et al. (2000a)	Landfill sandy loam	50 ^a	281	53
De Visscher et al. (1999)	Landfill sandy loam	50 ^a	368	230
	Agricultural loam	50 ^a	216	98
	Agricultural loam/wheat straw (99:1) ^c	50 ^a	237	144
	Agricultural loam/sugar beet leaves (99:1) ^c	50 ^a	222	82
Scheutz et al. (2003)	Landfill loam	50 ^a	250	210
Humer and Lechner (2001)	Sandy loam	100	180	75.6
	Sand	100	94	90
	Sand	100	216	210
Humer and Lechner (1999)	Topsoil	100	150	55
Ahn et al. (2002)	Landfill sandy soil	50 ^a	26-32	22
Pawlowska et al. (2003)	fraction of 0.25-0.5mm	99	266.1	134 ± 9.4
	fraction of 0.5-1.0mm	99	266.1	151.9 ± 7.1
	fraction of 1.0-2.0mm	99	266.1	135.7 ± 8.1
	fraction of 2.0-4.0mm	99	266.1	135.2 ± 8.1

5.4 Gas profiles

The vertical distribution of CH₄, CO₂, O₂ and N₂ was analysed weekly in order to derive the extent of the ingress of atmospheric air and thus to localize the depth of the active CH₄ oxidation horizon. As O₂ is consumed by both CH₄ oxidation and heterotrophic respiration, N₂ was used for the assessment of the ingress of air.

For each column, figures Figure 8 to Figure 13 show selected gas profiles that are representative for each operational phase. Phase 4 is differentiated into 4a, 4b and 4c, where 4a signifies the initial period shortly after the Christmas break, 4b the situation where a strong performance decline was observed and 4c the situation following aeration of the columns between day 129 and day 134.

Phase 1 (Inlet flux = 2.44 l CH₄ m⁻² h⁻¹)

During the initial phase of the experiment, all columns showed a high degree of aeration down to the column base, as signified by the high concentrations of N₂ across the soil profile. Nevertheless, higher O₂ concentrations were only observed in the top two to three decimetres of the column, below that O₂ concentrations were very low to close to zero. This indicates the (expected) localization of the CH₄ oxidation horizon in the upper soil layers. Consumption of O₂ in these layers prevented O₂ migration into deeper parts of the column.

Particularly in columns 1, 2, 3 and 6, the CH₄ oxidation activity is clearly reflected by the increasing ratio of CO₂ to CH₄ from bottom to top. Column 5 showed an exceptional soil gas composition: N₂ was significantly enriched in the top 35 cm, with concentrations of >90 vol.%, indicating vigorous consumption of headspace O₂. Interestingly, an increase in the ratio of CO₂ to CH₄ was never observed, suggesting relevant precipitation of the produced CO₂ as carbonate.

Phase 2 (Inlet flux = 3.58 l CH₄ m⁻² h⁻¹)

The vertical distribution of N₂ clearly indicates a decreased ingress of air from the column headspace into the soil as a result of the increased inlet flux in all columns. Consequently, the effective CH₄ oxidation horizon moved further upward, also indicated by higher concentrations of CH₄ and lower concentrations of CO₂ in the upper layers as compared to phase 1. Column 4 showed a very low share of atmospheric components across the entire profile and, correspondingly, very high CH₄ and CO₂ concentrations, suggesting that methanotrophic activity was restricted to the top few centimetres for reasons of O₂ deficiency. The phenomenon of N₂ enrichment was still visible in column 5, albeit to a lesser extent than in phase 1.

Phase 3 (Inlet flux = 4.99 l CH₄ m⁻² h⁻¹)

The further increase in inlet fluxes significantly decreased the depth of diffusive air penetration in all materials. Only columns 2 and 5 still showed a clear oxidation horizon below a depth of 5 cm, implying that at this level of inlet flux oxidation for most materials was restricted to the very surface of the soil.

Phase 4 (Inlet flux = 1.65 l CH₄ m⁻² h⁻¹)

In this phase of the experiment, the inlet fluxes were reduced to the lowest level. All columns showed a marked increase in the depth of air ingress, corresponding well with a significant increase in CH₄ oxidation efficiency (phase 4 a, compare also Figure 5). However, after a variable phase of phase 4 operation, the oxidation efficiency steadily declined in columns 1, 2, 3 and 6 (phase 4b). The corresponding gas profile analyses reveal a strong decline in diffusive air ingress compared to the initial phase 4a. Except for column 5, hardly any atmospheric components were detectable below the shallowest sampling point of 5 cm depth. Graphs for phase 4c show the situation after the re-start of operation following a few days of forced aeration of the columns. All columns again showed a high degree of aeration, corresponding to a peak in oxidation efficiency. Column 5 was not operated following the aeration measure.

In summary, columns 1 and 2 showed the highest degree of aeration across the soil profile in phases 1 to 4 of the experiment, corresponding to the highest water-free pore spaces ('gas volume' in Table 1). Ingress of air was comparable for columns 4 and 6 in phase 1 and 3, but clearly better in column 6 during phases 2 and 4a, also corresponding to higher CH₄ oxidation efficiencies. In phase 4b (decline of CH₄ oxidation efficiency), the aeration level was generally very low in all columns with the lowest values in columns 3 and 4.

Column 5 behaved exceptionally with a very high share of atmospheric components, including situations of N₂ enrichment, within the top 45 cm of the column during all operational phases.

Ratio of CO₂:CH₄ in soil gas profiles

As 1 mol of CO₂ is produced for each mol of CH₄ consumed, the ratio of CO₂ to CH₄ in the soil pore space increases during the oxidation process. Table 6 and Table 7 show the ratios in the gas profiles corresponding to the data presented in the figures. The ratio of the artificial landfill gas mixture fed to the columns is 0.67. Thus, values >0.67 indicate methane oxidation, while those <0.67 signify methane formation or a CO₂-consuming process such as precipitation of carbonate. The latter is assumed to be responsible for the low ratios in column 5 in depths 5-75 cm. This hypothesis, however, has not been verified to date. The data show that during phase 4b, when a decline in oxidation efficiency was observed, all columns (col. 5 not considered) had a CO₂:CH₄ ratio <0.67 in depths >5 cm. In some columns (3, 4, and 6), the phenomenon was also observed in the earlier phases. Higher ratios in the column headspaces, clearly indicating oxidation, suggest that under these conditions CH₄ consumption was limited to the upper 5 cm of the material. Conditions for methanogenesis are assumed to be favoured by the high degree of compaction, possibly the formation of extrapolymeric substances (EPS), and the consumption of O₂ in the top layer, all preventing ingress of O₂ deeper into the soil.

Column 1 (# 2033)

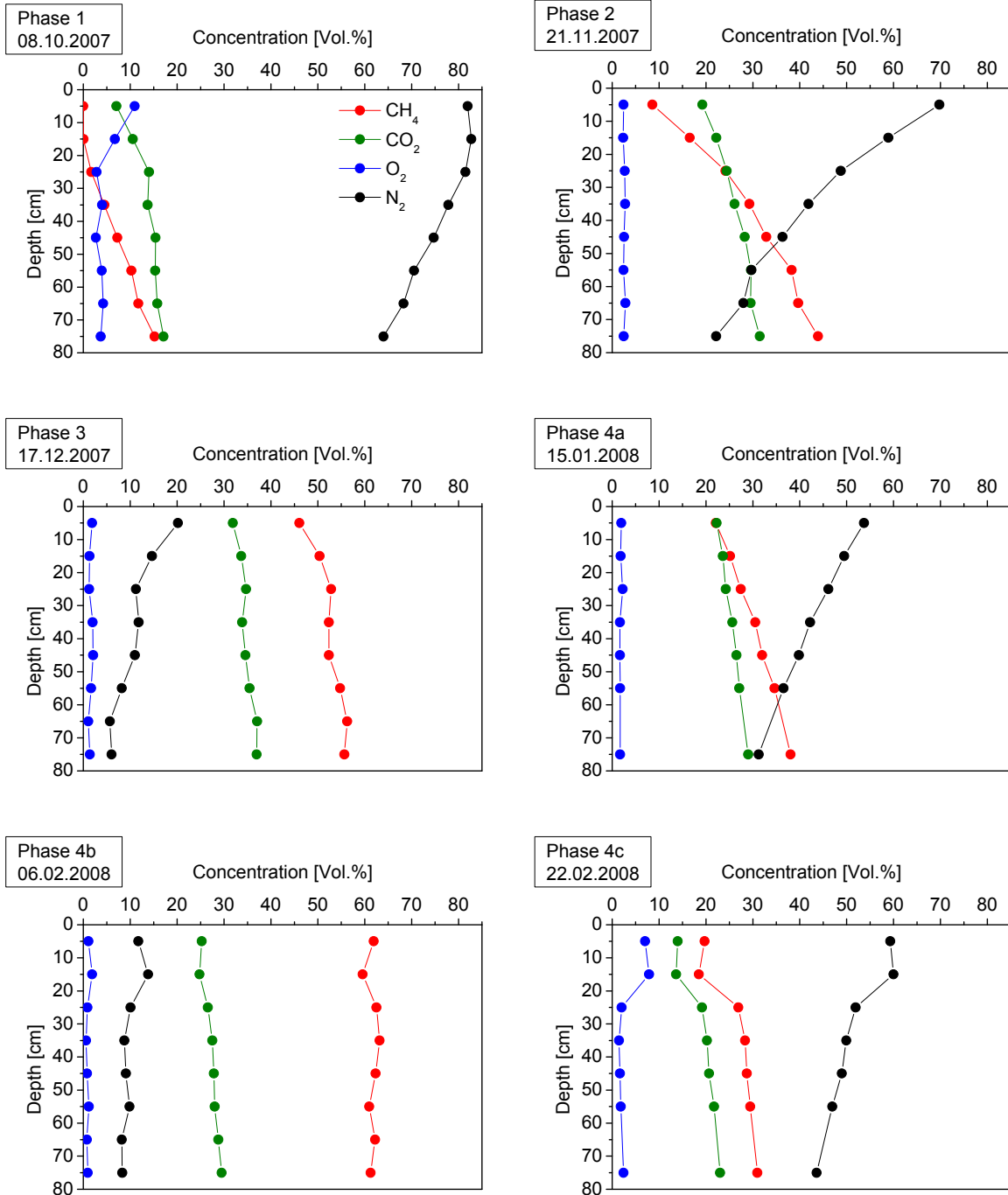


Figure 8: Column 1 gas profiles for the four operational phases.

Column 2 (# 7773)

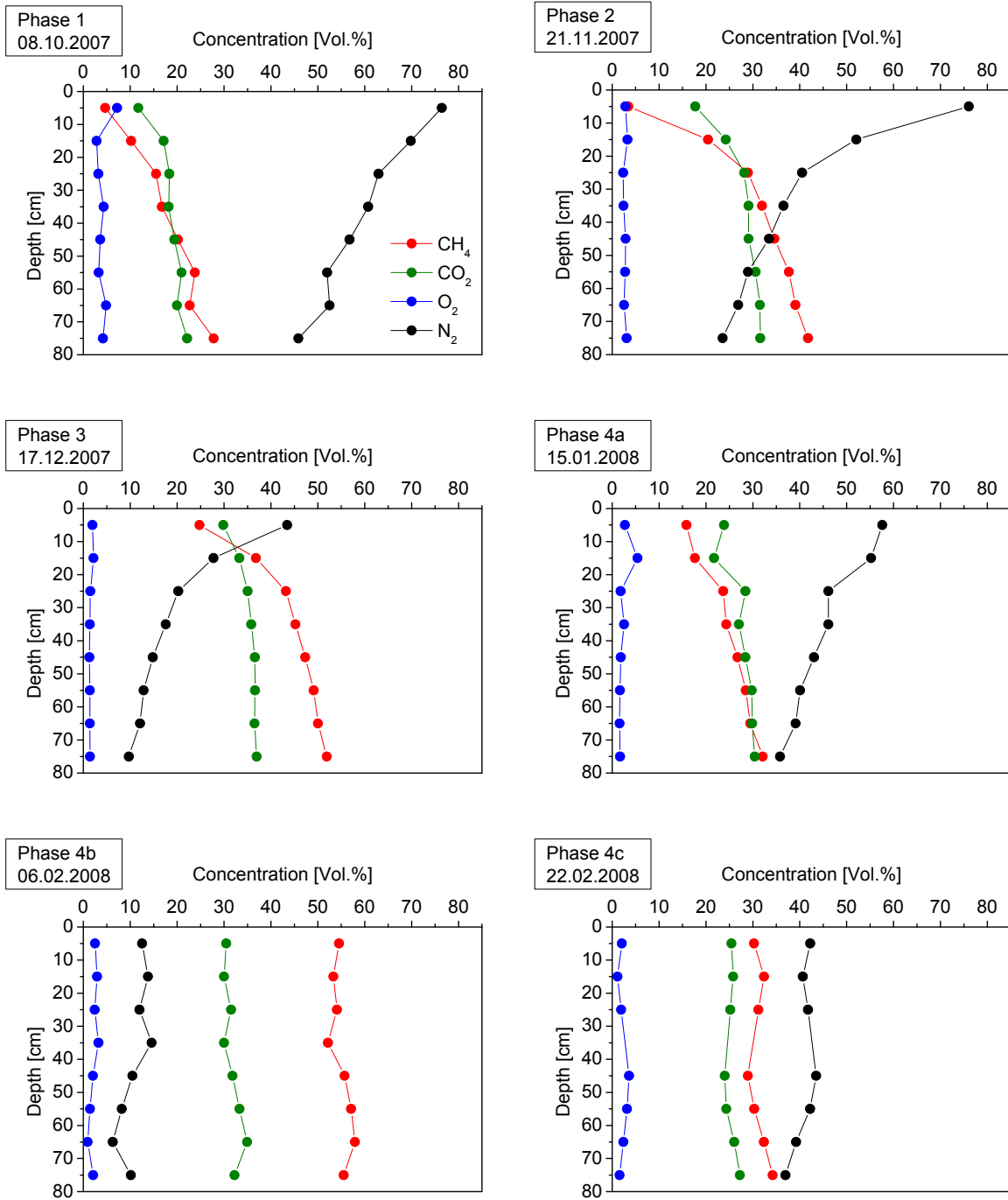


Figure 9: Column 2 gas profiles for the four operational phases.

Column 3 (# 710880)

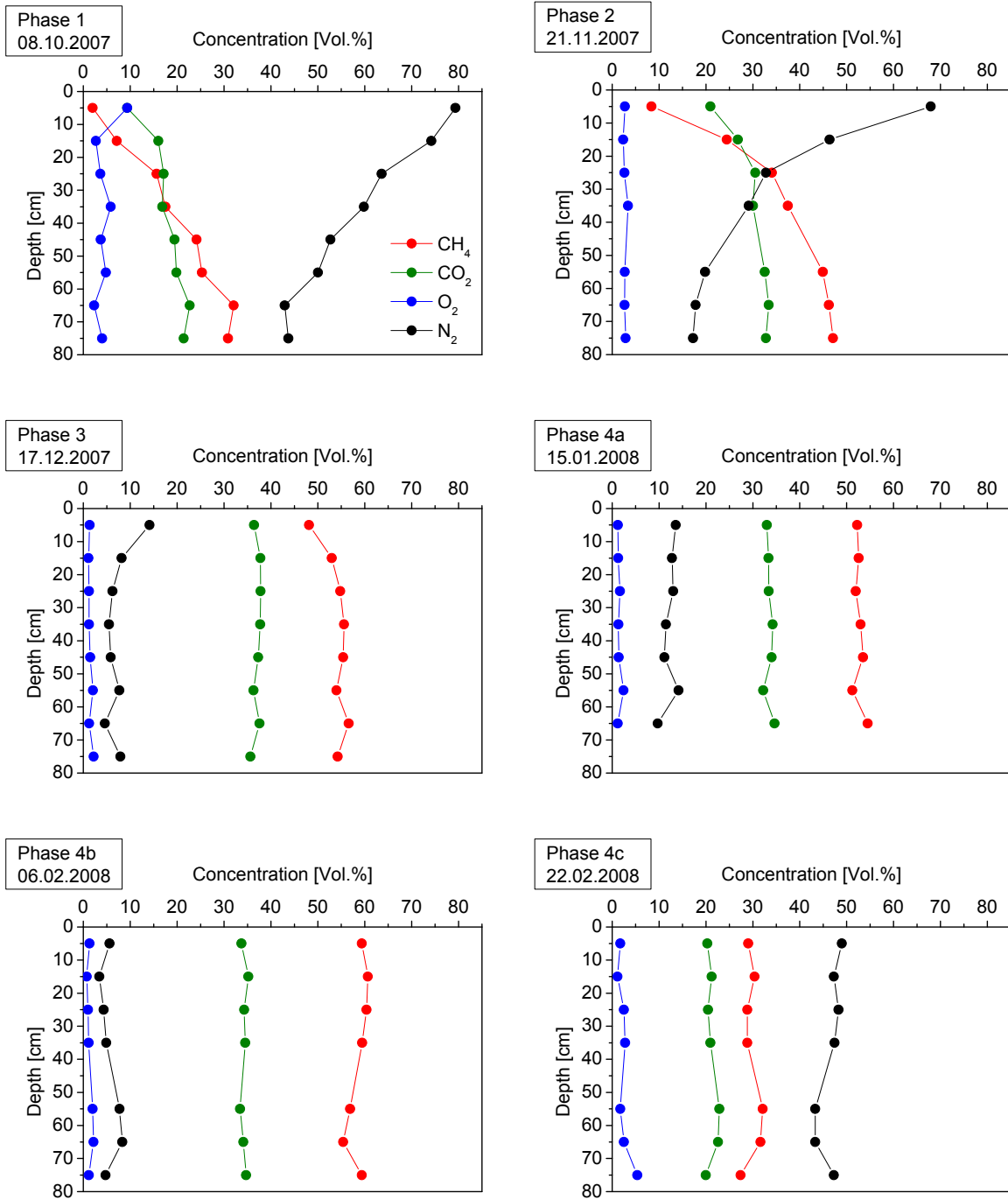


Figure 10: Column 3 gas profiles for the four operational phases.

Column 4 (# 3181)

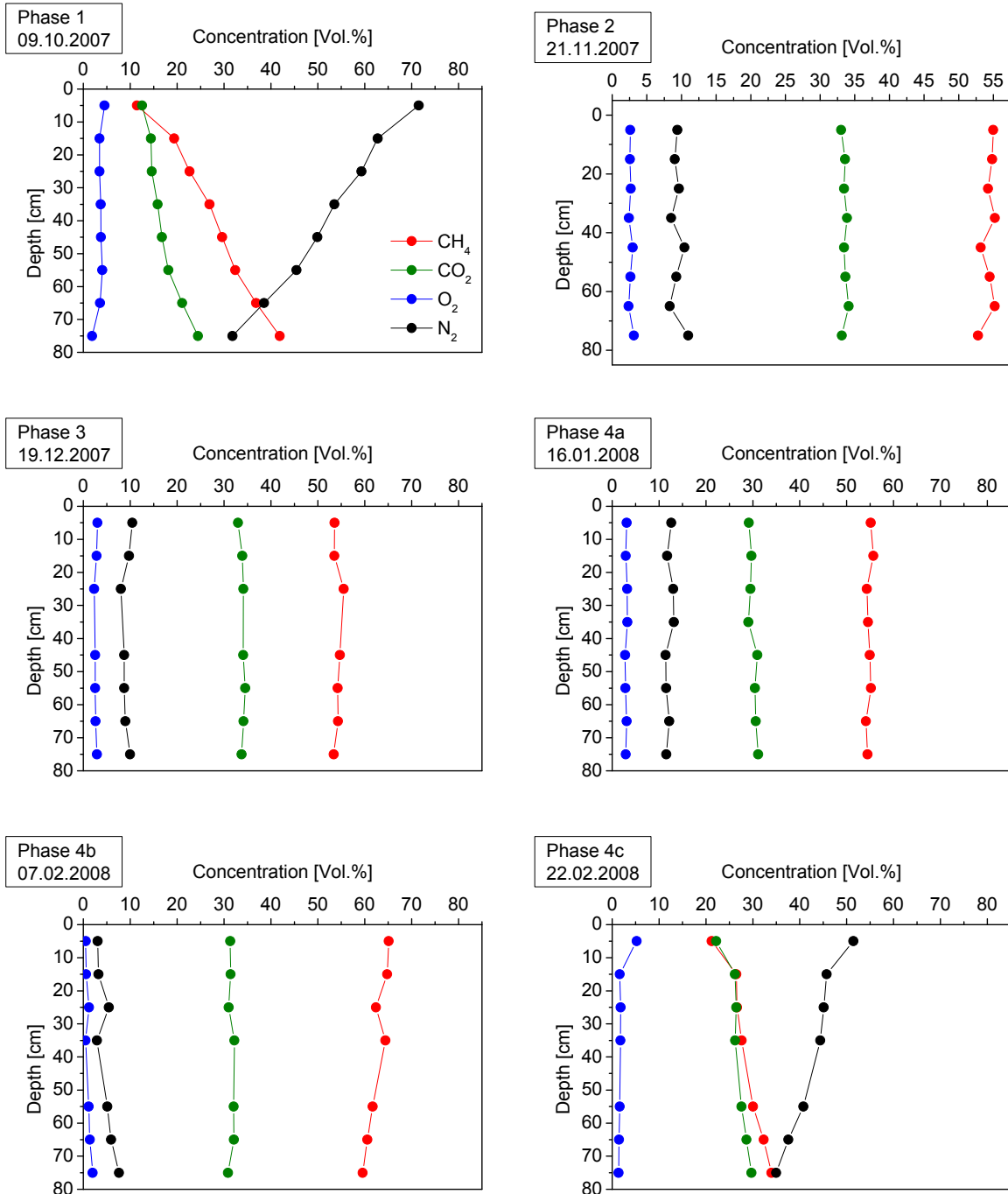


Figure 11: Column 4 gas profiles for the four operational phases.

Column 5 (# 4110)

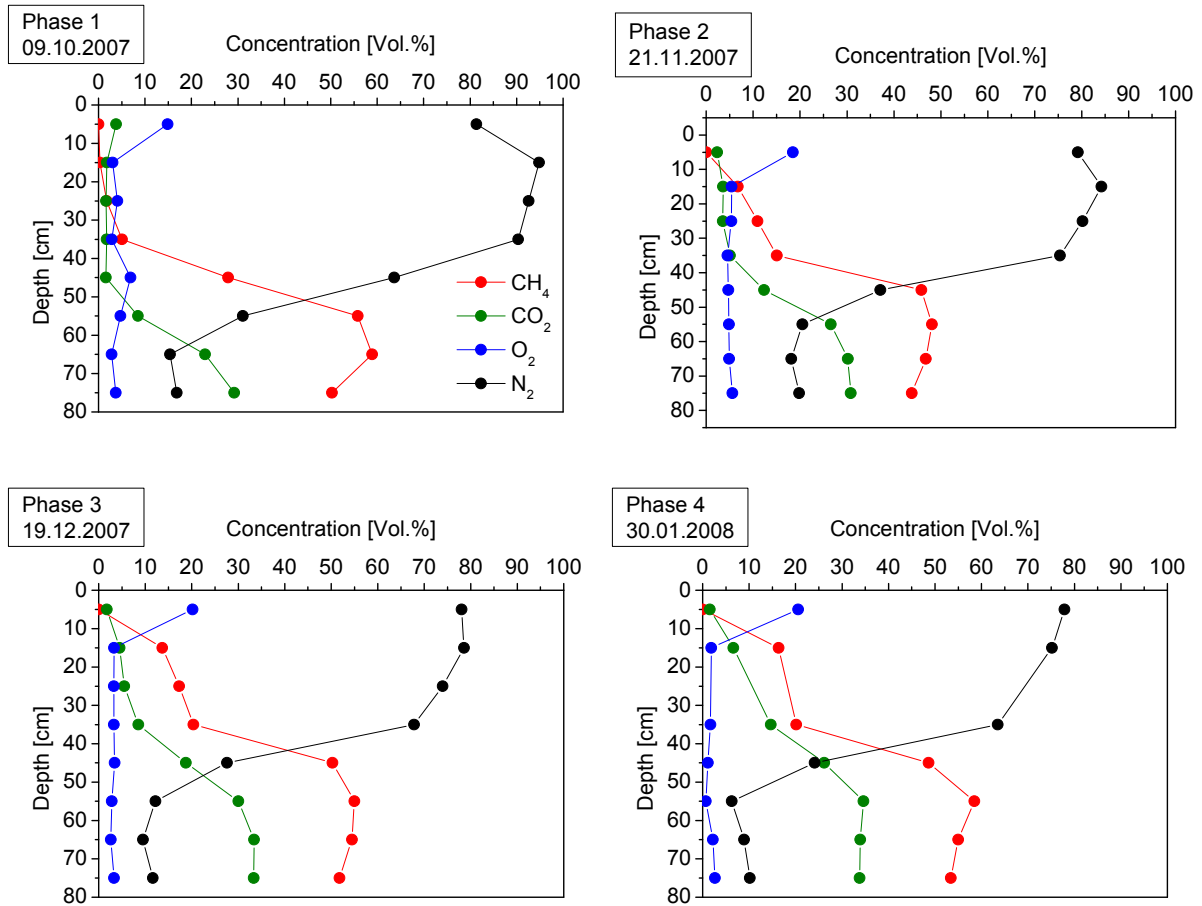


Figure 12: Column 5 gas profiles for the four operational phases.

Column 6 (# 9468)

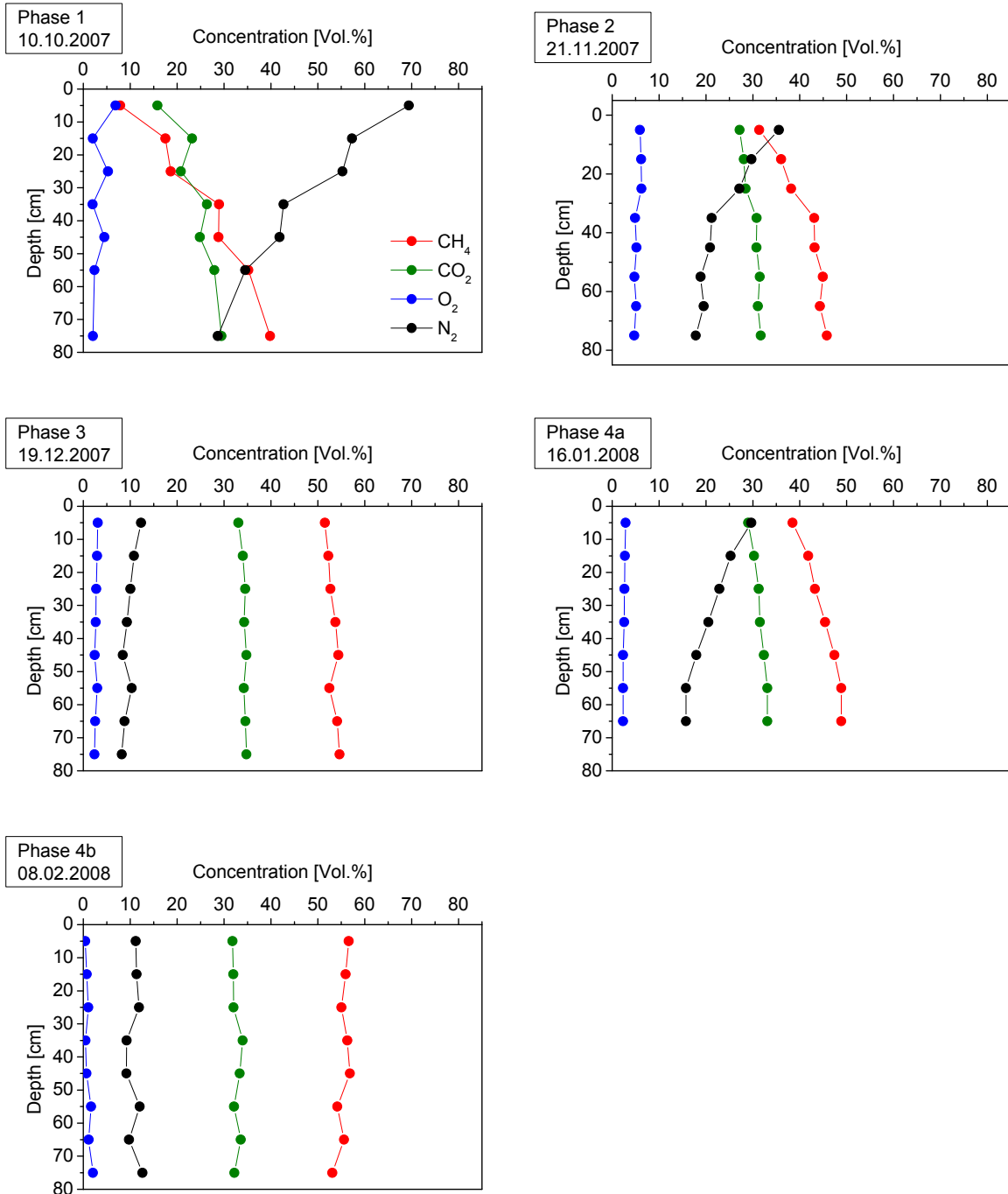


Figure 13: Column 6 gas profiles for the four operational phases.

Table 6: Ratios of CO₂ to CH₄ in the exemplary gas profiles of column 1-3. Shaded cells: ratio indicates CH₄ formation. Depth 0 = headspace.

Depth [cm]	Phase 1	Phase 2	Phase 3	Phase 4a	Phase 4b	Phase 4c
Column 1						
0	4020.0	6.84	1.65	90.08	2.58	1.72
5	1767.5	2.24	0.69	1.01	0.41	0.71
15	263.5	1.34	0.67	0.94	0.42	0.74
25	8.2	1.01	0.66	0.88	0.42	0.71
35	3.1	0.89	0.65	0.84	0.44	0.71
45	2.1	0.86	0.66	0.83	0.45	0.72
55	1.5	0.77	0.65	0.78	0.46	0.74
65	1.3	0.74	0.66	-	0.46	-
75	1.1	0.72	0.66	0.76	0.48	0.74
Column 2						
0	30.86	28.92	1.96	15.01	2.18	2.18
5	31.57	5.19	1.20	1.51	0.56	0.84
15	22.71	1.19	0.90	1.23	0.56	0.80
25	14.20	0.97	0.81	1.20	0.58	0.81
35	12.06	0.91	0.79	1.11	0.58	0.82
45	9.04	0.84	0.77	1.06	0.57	0.83
55	6.86	0.81	0.75	1.05	0.58	0.80
65	6.83	0.81	0.73	1.01	0.60	0.80
75	4.34	0.76	0.71	0.95	0.58	0.80
Column 3						
0	4.51	7.26	1.73	5.00	1.74	1.96
5	4.69	2.50	0.76	0.63	0.57	0.70
15	2.24	1.10	0.71	0.63	0.58	0.70
25	1.10	0.90	0.69	0.64	0.57	0.71
35	0.96	0.80	0.68	0.65	0.58	0.73
45	0.81	-	0.67	0.64	0.58	0.73
55	0.79	0.72	0.67	0.63	0.59	0.71
65	0.71	0.72	0.66	0.64	0.62	0.71
75	0.69	0.70	0.66	0.64	0.58	0.73

Table 7: Ratios of CO₂ to CH₄ in the exemplary gas profiles of column 4-6. Shaded cells: ratio indicates CH₄ formation. Depth 0 = headspace. n.a. = not applicable, columns were not operated.

Depth [cm]	Phase 1	Phase 2	Phase 3	Phase 4a	Phase 4b	Phase 4c
Column 4						
0	1.38	0.82	0.71	0.84	1.32	1.97
5	1.10	0.60	0.62	0.53	0.48	1.04
15	0.74	0.61	0.63	0.53	0.48	0.99
25	0.65	0.62	0.61	0.54	0.50	1.00
35	0.59	0.61	0.63	0.53	0.50	0.95
45	0.57	0.63	0.62	0.56	-	0.96
55	0.56	0.62	0.64	0.55	0.52	0.92
65	0.57	0.62	0.63	0.57	0.53	0.89
75	0.58	0.63	0.63	0.57	0.52	0.88
Column 5						
0	-	-	2.20	7.90	n.a.	n.a.
5	3340.82	3575.02	520.89	281.84	n.a.	n.a.
15	5.76	0.53	0.33	0.41	n.a.	n.a.
25	0.91	0.32	0.32	-	n.a.	n.a.
35	0.34	0.34	0.42	0.73	n.a.	n.a.
45	0.06	0.27	0.37	0.54	n.a.	n.a.
55	0.15	0.55	0.55	0.59	n.a.	n.a.
65	0.39	0.64	0.61	0.62	n.a.	n.a.
75	0.58	0.70	0.64	0.63	n.a.	n.a.
Column 6						
0	1.59	2.04	0.84	1.20	1.02	n.a.
5	2.01	0.87	0.64	0.75	0.56	n.a.
15	1.33	0.78	0.65	0.72	0.57	n.a.
25	1.12	0.75	0.65	0.72	0.58	n.a.
35	0.91	0.72	0.64	0.69	0.60	n.a.
45	0.86	0.71	0.64	0.68	0.59	n.a.
55	0.79	0.70	0.65	0.68	0.59	n.a.
65	0.77	0.70	0.64	0.68	0.60	n.a.
75	0.74	0.69	0.64	0.67	0.61	n.a.

5.5 Batch tests

Figure 14 shows the potential CH₄ oxidation rate of the six investigated materials as determined in a batch assay. A set of three parallels was tested at water contents identical to those used in the column experiment ('adjusted water content') while another set of three parallels were used to prepare a slurry using sterilized tap water.

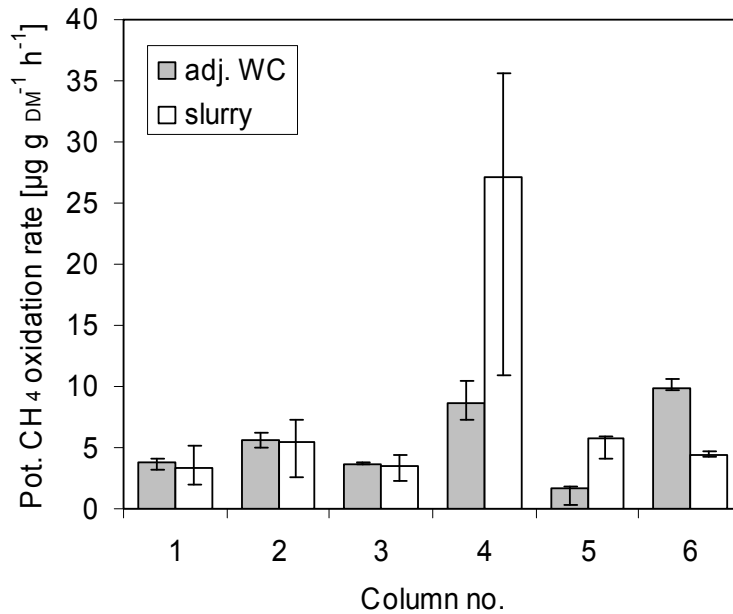


Figure 14: Potential CH₄ oxidation rate as determined in batch tests. Columns = averages of three parallels, whiskers = maximum. minimum. DM = dry matter. Adj. WC = adjusted water content.

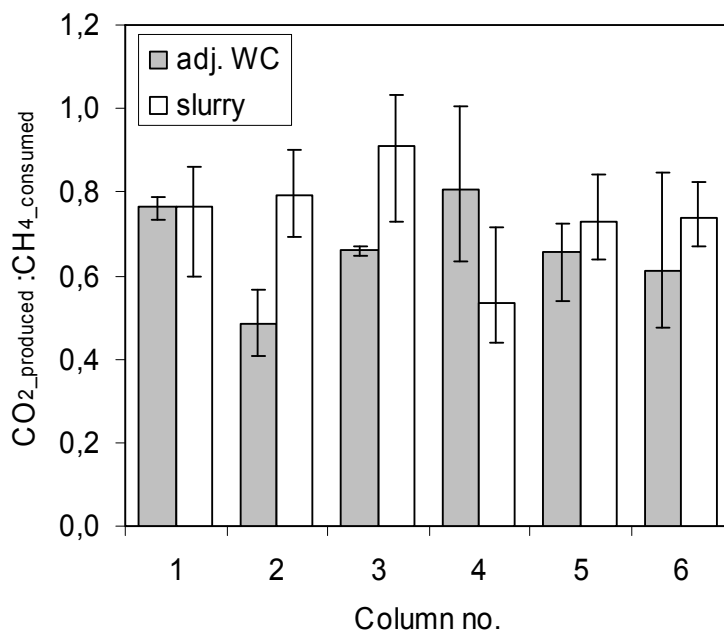


Figure 15: Ratio of CO₂ produced to CH₄ consumed during the batch assay. Columns = averages of three parallels, whiskers = maximum. minimum. DM = dry matter. Adj. WC = adjusted water content.

All investigated substrates were able to completely oxidize the provided methane. Some soils showed a lag phase of up to 12 days before oxidation actually commenced. Underproportional release of CO₂ (ratio of CO₂:CH₄ < 1) indicated growth of the methanotrophic population in almost all samples (Figure 15).

Comparison of samples at adjusted water contents and slurries

The relationship between the activity of solid phase variants and slurries was not uniform. The activity of both variants was similar in the materials corresponding to columns 1, 2 and 3 and therefore did not appear to be influenced by the different water and aeration regimes. Column 4 and 5 materials showed an increased rate in the slurry variant, whereas the potential CH₄ oxidation rate was reduced in the slurry variant for the column 6 material. In general, increased rates are expected in slurries for finely textured materials that tend to form aggregates and thus have a low diffusivity (such as the column 5 material), whereas decreased rates are expected in coarsely textured soils which are characterized by a high diffusivity.

In four out of the six samples the slurry variants were characterized by a higher ratio of CO₂ released to CH₄ consumed. This has been frequently observed before (unpublished data) and indicates increased respiration and thus energy demand of the population in the slurries compared to those at adjusted water contents. The phenomenon is probably related to the radical change in environmental conditions caused by the submersion in water.

Comparison between batch and column experiments

Batch test results did not correspond with column performance (see also Table 8). Contrasting with the results from the column experiment, in both runs column 4 and 6 materials showed higher activities than the materials corresponding to columns 1-3. In the first trial, material no. 5, performing best in the column experiment, showed a lower activity than material no. 4 which performed worst in the first 3 phases of the experiment. In the second trial, material no. 5 had the lowest activity at adjusted water contents.

The following table shows the potential CH₄ oxidation rates for each column extrapolated from the batch tests batch assay results for the adjusted water content variants:

Table 8: Potential CH₄ oxidation rates extrapolated from the batch assays (temperature = 20 °C).

Column/ material no.	Pot. CH ₄ oxidation rate in batch assay [µg g _{DM} ⁻¹ h ⁻¹]	Pot. CH ₄ oxidation rate extrapol. from batch assay [l m ⁻² h ⁻¹]	Max. CH ₄ oxidation efficiency (column) [l m ⁻² h ⁻¹]
1	3.80	7.82	4.2
2	5.56	9.23	5.1
3	3.70	7.70	3.7
4	8.64	14.12	3.7
5	1.62	2.46	5.5
6	9.92	20.75	5.3

In most cases, the batch tests overestimate the CH₄ oxidation actually effected by the columns. Only for column 5, column performance was higher than would have been predicted from the

batch test. Differentiation between the materials is higher in the batch test than in the column test, plausibly suggesting limiting (e.g. O₂ ingress) and thus normalizing conditions of the column operation. In contrast, conditions of substrate supply (CH₄, O₂) are optimized in batch tests, thus allowing for higher methanotrophic activity. Batch results suggested to favour materials 4 and 6 for highest in situ performance, whereas the column experiment clearly indicated the materials 1, 2 and 3 to be the most suitable (apart from the exceptional material no. 5).

Comparison of batch test results with literature values

The potential CH₄ oxidation rates observed for the six investigated materials fit well into the range of values previously reported for landfill cover soils at comparable incubation temperatures (Table 9). The high value reported by Börjesson et al. (1998) corresponds to a landfill cover consisting of sewage sludge and can thus be considered not to be representative for mineral soils.

Table 9: Literature values for potential CH₄ oxidation rates determined in batch assays. dw = dry weight, ww = wet weight. Values for this study: averages for adjusted water contents-

Author	Incubation temperature [°C]	Maximum CH ₄ oxidation rate reported, standardized to $\mu\text{g CH}_4 \text{ h}^{-1}$
Whalen et al. (1990)	25	$2.5 \mu\text{g g}_{\text{ww}}^{-1} \text{ h}^{-1}$
Kightley et al. (1995)	20	$27.2 \mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$
Boeckx et al. (1996)	15	$0.01 \mu\text{g g}_{\text{ww}}^{-1} \text{ h}^{-1}$
Börjesson et al. (1998)	25	$152 \mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$
Kallistova et al. (2005)	20	$1.9 \mu\text{g g}_{\text{ww}}^{-1} \text{ h}^{-1}$
This study	20	$1.6\text{-}9.9 \mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$

6 Discussion

The CH₄ oxidation performance of the six investigated materials varied both as a function of the inlet CH₄ flux and time. Performance also varied between substrates, although the maximum CH₄ oxidation rates were in the same order of magnitude at 58-88 g CH₄ m⁻² d⁻¹. CH₄ oxidation efficiencies and gas profile data imply a strong indication for a link between oxidation capacity and diffusive ingress of air. Increased inlet fluxes resulted in decreased air ingress into all columns, as derived from soil profile N₂-concentrations. The column performing the least also showed the lowest N₂-concentrations across the profile (e. g. column 4 in phases 1-3), signifying little diffusive ingress of air from the top. Higher performance was related to increased depth of air penetration, as for example demonstrated by CH₄ oxidation efficiencies and corresponding gas profiles for columns 1 and 2 both in phases 1 and 2, and for column 6 in phase 4a. The depth of air penetration is a function of both the soil's diffusivity, the magnitude of the ascending landfill gas flux and the intensity of methanotrophy, causing a pressure decrease in the active layers and subsequently invoking advective air ingress near the soil surface. High diffusivity is associated with medium to coarsely textured soils offering a high air capacity and to a low degree of compaction. Compaction of soils provokes a limitation of air ingress and consequently of the methanotrophic activity to the uppermost layers of the soil profile which in turn are prone to desiccation under field conditions.

CH₄ oxidation also varied for the same column over time. Already during phase 1 the gas profiles of consecutive weeks (not all data shown in this report) indicated a decrease in air ingress with time. This became even more apparent during phase 4. Reduced diffusivity may result from clogging of soil pores caused by formation of extrapolymeric substances (EPS), often observed in experiments involving continuous charging of CH₄ to the system. The reasons for EPS-formation are not finally resolved, but the phenomenon is generally interpreted as a product of overflow metabolism as a consequence of excess carbon supply. The columns will be checked for presence of EPS when they are dismantled in the near future.

Column experiments as conducted here do not fully reflect field conditions. While bulk densities, water contents and artificial landfill gas fluxes can be manipulated, climate-driven drying and re-wetting and subsequent soil aggregation, atmospheric pressure fluctuations and the influence of the covering vegetation are difficult to simulate. Intense rootage loosens the soil and subsequently enhances aeration. Atmospheric pressure fluctuations both result in a variation of the landfill gas load to the covering soil and improve oxygen circulation in the soil. The CH₄ oxidation performance of all materials is thus expected to be higher in a field application.

Table 10 summarizes the key characteristics of the investigated materials. Columns 1, 2 and 3 (# 2033, # 7773, # 710880) clearly yielded the highest degradation efficiencies during the first three phases of the experiment. Column 4 (# 3181) not only performed the least, but also showed CH₄ formation across the soil profile in all phases 1 to 4b of the experiment, as indicated by CO₂:CH₄ ratios <0.67. Most of the time, CH₄ was oxidized in the top centimetres but occasionally also a net CH₄ formation was observed, indicated by higher CH₄ fluxes leaving than entering the column. Of the sandy materials, this one had the finest texture with 21 % of particles < 63 µm and the lowest air capacity in combination with the highest amount of organic matter (7.5 %). It is suspected that the combination of these factors with the high extent of compaction resulted in low oxygen supply and consequently in low efficiencies. The formation

of anaerobic niches and the high organic carbon content, probably including easily degradable fractions, invoke conditions favourable for methanogenesis. As the batch assays have shown, the natural potential of the material is actually higher than for materials 1, 2 and 3, presumably due to more favourable soil chemical properties as a result of the share of clay and silt. Interestingly, column 4 performance picked up during phase 4 and stabilised on a rather high level. It is suspected that in this phase the degradation of the sedimentary labile organic matter had been completed and that the high CH₄ oxidation capacity was thus fully tapped.

On the basis of the soil physical properties of the sandy materials (high air capacity of 20 vol.%), column 6 (# 9468) was expected to perform better than column 2. It is assumed that the low organic carbon content (loss on ignition = 0.7 %) reduces this soil's potential for microbial activity.

Column 5 (# 4110) behaved exceptionally and unexpectedly. In spite of its fine texture and the lowest air capacity of all tested substrates, the material showed very good aeration within the top 5 decimetres and, correspondingly, near 100 % CH₄ oxidation efficiency throughout the entire experiment. The vigorous methanotrophic activity was also indicated by the enrichment of N₂ in the upper layers with initial values of > 90 vol.% N₂. Interestingly, almost no CO₂ was released via the headspace. It is suspected that CO₂ was precipitated as carbonate. As the soil chemical analyses show, this material had the highest amount of total Fe, Al, Mn, K and Mg, all potential cations for carbonate precipitation. Also, the material had the highest share of mineral nitrogen available for microbial activity. It is suspected that the volume reduction resulting from methanotrophy and CO₂ precipitation invoked advective O₂ ingress from the surface, fuelling methanotrophic activity.

Table 10: Overview of key material properties and results on CH₄ oxidation.

	Col. 1	Col. 2	Col. 3	Col. 4	Col. 5	Col. 6
Texture	Sand	Sand	Sand	Loamy sand	Clayey loam	Sand
EC [mS/m]	10.2	50.1	61.6	196.6	135.4	35.9
LOI [%]	2.0	4.9	3.0	7.5	9.0	0.7
Bulk density [g/cm ³]	1.67	1.38	1.73	1.36	1.26	1.74
Pore volume [%]	37.98	47.90	34.67	48.60	52.48	34.31
Gas volume [%]	21.23	25.85	14.64	17.65	4.03	18.12
Avg. CH ₄ oxidation in batch test at adj. WC [$\mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$]						
Adj. WC	3.80	5.56	3.70	8.64	1.62	9.92
Slurry	3.30	5.45	3.44	27.08	5.73	4.34
Avg. CH ₄ oxidation efficiency in column test [%]						
Phase 1 2.44 l m ⁻² h ⁻¹	87.7	91.1	88.7	37.4	99.4	76.6
Phase 2 3.65 l m ⁻² h ⁻¹	80.8	91.8	73.4	5.2	99.8	63.8
Phase 3 4.99 l m ⁻² h ⁻¹	56.9	59.6	49.8	18.2	100	43.9
Phase 4 1.65 l m ⁻² h ⁻¹	74.0	79.7	63.0	73.0	-	64.4
Influx at 100 % oxidation efficiency [l m ⁻² h ⁻¹]	3	4	2.5	1-1.5	?	?
Special observations	High gas-filled pore vol.	High gas-filled pore vol.		<ul style="list-style-type: none"> ○ CH₄ formation during ph. 1-3 ○ Good performance in phase 4 	<ul style="list-style-type: none"> ○ Enrichment of N₂ in top layers ○ 100 % oxidation during entire exp. ○ Precipitation of carbonate presumed 	Very low organic carbon content

7 Conclusions

The results of the conducted study emphasize the importance of texture and the corresponding pore size distribution as a criterion for the selection of potential landfill cover materials for the enhancement of microbial CH₄ oxidation. The higher the expected CH₄ load to the soil, the higher the diffusivity necessary to sustain sufficient ingress of atmospheric air and thus the stronger the adverse effects of compaction. While more finely textured soils with a higher organic carbon content harbour a high methanotrophic potential, their pore size distribution renders them more sensitive to effects of compaction and changing water contents. With respect to CH₄ oxidation, a loamy sand with medium organic matter content, neutral pH and low compaction would be the preferred substrate. If compaction cannot be avoided, selection of a more coarsely textured material that retains a higher air capacity while offering sufficient field capacity (e.g. a fine sand) of medium organic matter content and neutral pH is advisable. Favourably, soils intended for enhanced CH₄ oxidation should be compacted to the least possible extent.

Long-term column tests involving continuous charge of CH₄ and excluding vegetation and climate-related effects only allow limited conclusions for field application. The effects of continuous operation and the associated forced landfill flux can invoke effects such as EPS formation. In combination with the exclusion of soil-structuring processes (rootage, desiccation, re-wetting) and pressure-induced oscillations in landfill gas and atmospheric air fluxes, the observed CH₄ oxidations are lower than can be expected in the field. On the other hand, the effects observed for column 4 clearly show that long-term experiments are necessary to cover processes associated to the equilibration of soil conditions. Had the experiment been stopped after phase 3, neither the enhanced performance of column 4 nor the adverse effects of decreasing diffusivity in the other columns would have been observed.

Batch tests are fast and easy to perform, but do not necessarily provide the same information as column tests, mainly because the diffusion-limiting natural or forced bulk soil structure is not warranted. While they are suitable for the pre-selection of potent materials, final selection has to consider additional information on soil physical characteristics and expected or intended soil construction and management practices.

With respect to the low CH₄ fluxes to the covering soil expected for the future Nauerna test cells (0.5-2 l CH₄ m⁻² h⁻¹) and in light under the expected increased performance under field conditions and a lesser extent of compaction, all tested materials are generally suitable for application as CH₄ oxidizing cover soil.

8 References

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