

Methane Oxidation Tool

An approach to estimate methane oxidation on landfills

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Background

It is the intention of this Methane Oxidation Tool to replace the IPCC Tier 1 default values (0% and 10% default methane oxidation) by a more meaningful estimate for the purpose of individual landfill emission reporting. The IPCC default value is intended for national reporting. Insufficient, reliable full-scale oxidation measurements were available to justify better estimates at the moment the guidelines were made. IPCC deliberately kept the value low, to prevent an overestimation of oxidation and underestimation of methane emissions. For country comparability the default value may be appropriate, it is however inadequate to describe the situation on individual landfills. The 10% default describes that oxidation in a cover increases (without any ceiling) with increased methane load to the cover. This assumes that oxidation is a function of gas production, whereas research has shown that oxidation is a function of the properties of the cover. Oxidation can be described as a function of the methane load as long as the maximum oxidation capacity of the cover, window or filter is not exceeded. An incentive for operators is required to pay more attention to oxidation and to invest in research and improvements. Operators thus need an absolute value for the methane oxidation rate achieved by their covers, windows or filters, which then can be improved by management practices. It should be a conservative approach in order not to compromise acceptance by regulators. The majority of currently available oxidation data is based on laboratory studies and box measurements. Both lab and box measurements cannot provide an adequate indication of how much of the gas flow diffuses through the cover and how much emits through hot-spots or preferential pathways. Applying these results to entire landfills, without allowing for emission through hot-spots and preferential pathways, would result in an overestimation of oxidation. It is therefore inevitable to make assumptions for the emission through hot-spots and/or preferential pathways. These assumptions can be based on educated guesses and are therefore at least of equal quality as the 10% default value. Preferential pathways, porosity, temperature and moisture are considered the most important factors determining oxidation. Monitoring regulations and protocols such as UN-PRTR and E-PRTR (European Commission, 2006a & 2006b) allow application of alternative methods for quantification of emission of individual landfills. The Methane Oxidation Tool proposes to determine the methane emission of individual landfills based on the following formulas:

- (1) Potential Emission = Production – Recovery
- (2) Load to Cover = Potential Emission * (1-DE)
- (3) Potential Oxidation = Standard Oxidation * P * T * WP
- (4) Load to Cover < Potential Oxidation => Oxidation = Load to Cover
Load to Cover > Potential Oxidation => Oxidation = Potential Oxidation
- (5) Emission = Potential Emission - Oxidation

Where:

- DE correction factor for direct emission through hot-spots and preferential pathways
 P correction factor for porosity of the cover or filter material
 T correction factor for monthly average temperature at 20 cm depth in the cover or filter
 WP correction factor for the annual average water potential in the cover or filter

The following definitions are used for this approach:

Potential Emission	The remaining amount of methane after subtracting methane recovery from the calculated methane production. The amount that could potentially emit.
Load to Cover	The amount of methane diffusely and/or advectively flowing through the cover material. This is the potential emission minus the amount of methane that flows through hot-spots/preferential pathways.
Direct Emission	The contribution of preferential pathways and hot spots to the total emission. Methane emitting through preferential pathways and hot-spots is as conservative approach considered not to be oxidised at all. This is a simplification as methane oxidation has been found in hot-spots, but is very difficult to quantify over the entire year.
Standard Oxidation	For the MOT 6.2 kg CH ₄ m ⁻² a ⁻¹ at 14% porosity and 20 °C in a loamy sand was selected as 'standard oxidation' (see Approach).
Potential Oxidation	'Standard' oxidation multiplied with the appropriate correction factors for porosity (P), temperature (T) and water potential (WP).
Oxidation	The actual oxidation by the specific landfill cover. The actual oxidation rate can be higher than the load of methane to cover. At low loading rates covers, windows and filters can take up methane from the atmosphere. For the purpose of reporting the emission due to production of landfill gas in the landfill this is irrelevant. Therefore the Methane Oxidation Tool considers that the actual oxidation cannot be higher than the methane load to the cover or filter.
Porosity	Water free pore volume left at field capacity. The value needs to be determined based on undisturbed as built in-situ samples.
Temperature	Average monthly temperature in the active methane oxidation horizon. The active oxidation horizon is assumed to be at 20 cm depth on average. This can be situated deeper (e.g. in coarse substrates). In future versions it will be considered to make this factor more flexible in order to adapt to the specific situation.
Water Potential	Not moisture is considered, but the water potential as this is the physiologically effective parameter. Excess moisture (water logging) is (or should be) accounted for by reduced porosity. Only the limiting effect of increased water potentials (increased drought) is considered. Water potential = Matric potential * (-1)

Disclaimer

This approach is based on recent scientific findings. It has however not been validated in the field, nor has it been peer reviewed. Nevertheless for reasons explained above it is a better and more realistic approach towards methane oxidation for the purpose of emission reporting of individual landfills than the IPCC default values. Comments, recommendations and additional data and experience are welcomed by the authors and will be included in future versions of this Methane Oxidation Tool. The authors consider preferential pathways, porosity, temperature and moisture the determining and therefore most relevant aspects for methane oxidation. Consequently this approach has limited its considerations to these four aspects. The conservative approach could be made more realistic once more research data on entire landfill covers, windows or filters become available. The approach is a simplification and only applies to materials like natural soils and mature compost (i.e. with a stable organic fraction). Industrially produced materials often show extreme pH values, salinity or nutrient deficiency. For these materials the Methane Oxidation Tool cannot automatically be considered appropriate. The approach is considered to be valid for soils and cover materials that can sustain vegetation, i.e. in the sense of a recultivation layer. If conditions and nutrient supply suffice to support healthy vegetation then it can be assumed the conditions will also support a

population of methane oxidising microorganisms. In addition, the effect of possible adverse chemical properties (e.g. low pH in pure sand, salinity in sea clays, nutrient deficiency in very poor soils) has to be accounted for separately.

Approach

The Methane Oxidation Tool follows a stepwise approach. Since emission reporting has to be done in $\text{kg CH}_4 \text{ a}^{-1}$, the approach starts with definition of a 'standard' methane oxidation unit in $\text{kg CH}_4 \text{ m}^{-2} \text{ a}^{-1}$. Literature studies have indicated that oxidation of $1 \text{ dm}^3 \text{ CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ ($17.1 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ or $6.2 \text{ kg CH}_4 \text{ m}^{-2} \text{ a}^{-1}$) in conventional landfill covers seems realistic. This has led to a value of $0.5 \text{ dm}^3 \text{ CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ ($8.5 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ or $3.1 \text{ kg CH}_4 \text{ m}^{-2} \text{ a}^{-1}$) entering the cover being considered suitable for relying completely on covers for methane mitigation in German and Austrian guidelines (Stegmann, 2006; Fellner, 2008). The 'typical' landfill cover is applied with a bulldozer. A 'standard' bulldozer (e.g. Caterpillar D6) has a soil pressure of 36 kPa. In loamy sand at Nauerna landfill (Netherlands) this has resulted in a cover with a 92% Proctor density. The same soil (Gebert et al., 2010) at 95% Proctor density and 14% porosity showed oxidation of $1 \text{ dm}^3 \text{ CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ ($17.1 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ or $6.2 \text{ kg CH}_4 \text{ m}^{-2} \text{ a}^{-1}$) at 20 °C in the laboratory. The $6.2 \text{ kg CH}_4 \text{ m}^{-2} \text{ a}^{-1}$ at 14% porosity and 20 °C seems a suitable 'standard' unit for methane not passing through a hot-spot or preferential pathway. In specifically designed and operated oxidation systems higher oxidation rates have been found. These systems invariably have better characteristics in terms of hot-spots, porosity, moisture and/or temperature. The Methane Oxidation Tool aims to allow for that by means of correction factors. A separate spreadsheet (110429 Methane Oxidation Tool.xls) clarifies how the different correction factors to the standard methane oxidation unit were derived.

Step 1

Diffusive flux could in theory dominate the total flux (see spreadsheet file tab 'Diffusive flux'). Covers however often are heterogeneous or without gas distribution layers. Covers with a large amount of clay are more prone to crack formation due to desiccation than cover materials containing coarser particles. This causes direct emission through hot-spots and preferential pathways. The presence and importance of hot-spots/preferential pathways depends on material properties (porosity) and the level of engineering of the cover. For the level of engineering the most important aspects are the presence of a gas distribution layer and the level of homogenisation of the material. The level of compaction of the engineered cover is (or should be) accounted for in the porosity. More clay (at the same compaction rate) also results in a lower porosity of the cover. It can thus be assumed that direct emission is related to porosity. In the Methane Oxidation Tool direct emission and the other important porosity related aspect oxygen diffusion are separated. In step 1 (file tab 'Direct emission' in the spreadsheet model) the user chooses the appropriate factor (for the specific landfill) for direct emission. One minus the factor for direct emission is the factor by which to multiply the potential emission to account for preferential pathways. Direct emission in the framework of the Methane Oxidation Tool is defined as the contribution of preferential pathways and hot spots to the total emission. As conservative approach methane emitting through preferential pathways and hot-spots is for the purpose of this approach considered not to be oxidised at all. The factors presented in Table 1 (file tab 'Direct emission') are based on an educated guess and related to cover porosity and the presence of a gas distribution layer. For the sake of simplicity it is assumed that daily and temporary (shorter than one year) covers do not have a gas distribution layer and are not homogenised. More permanent covers (longer than one year) are assumed to have a gas distribution layer and are homogenised. If more permanent covers are not homogenised and do not have a gas distribution layer they should (for the purpose of determination of oxidation with this approach) be considered as temporary cover. On operational landfills various cover types can be present. In such cases the surface for each landfill section with a specific cover type needs to be determined. For each particular section gas production, gas recovery, oxidation and emission need to be determined separately.

Table 1: Correction factors for direct emission (DE) and methane load to cover (1-DE).

Cover type	(DE) [-]	(1-DE) [-]
No cover or daily cover <30 cm, no gas distribution layer	0.90	0.10
“Temporary” cover >30 cm, porosity <0.10 , no gas distribution layer	0.80	0.20
“Temporary” cover >30 cm, porosity 0.10-0.20 , no gas distribution layer	0.70	0.30
“Temporary” cover >30 cm, porosity >0.20 , no gas distribution layer	0.60	0.40
“Permanent” cover >100 cm, porosity <0.10 , gas distribution layer	0.50	0.50
“Permanent” cover >100 cm, porosity 0.10-0.20 , gas distribution layer	0.30	0.70
“Permanent” cover >100 cm, porosity >0.20 , gas distribution layer	0.10	0.90

In reality DE might also be related to the methane flux through the top-layer. At higher fluxes larger part (expressed in % of total methane flux) might be released through hot-spots and short cuts, compared to low methane fluxes. At low fluxes diffusion might become the predominant pathway of methane pathway of migration of methane through the top-layer. If this is the case, DE will decrease with decreasing methane flux and might even get close to 0 at low fluxes. However, this is highly speculative and hasn't received much attention until now.

TNO measurement data (Figure 1) from 1994-1995 and 2001-2002 indicate that in the Netherlands oxidation on landfills rarely exceeds $1 \text{ g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ or $8.7 \text{ kg CH}_4 \text{ m}^{-2} \text{ a}^{-1}$. In this study, both methane and carbon dioxide emissions from an entire landfill were measured, using a 1D-mass balance method. Comparison of ratio of methane and carbon dioxide emissions to the ratio of methane and carbon dioxide in the extracted landfill gas yields an estimation of methane oxidation. This supports the hypothesis that there is a 'ceiling' for methane oxidation in covers. The data further indicate that below a methane load of $5 \text{ g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ oxidation can be anywhere between 10% and 90% of the methane load. The data can unfortunately not be related to cover properties. In some cases they were derived from landfills with an operational tip face. The data do show that even at very low methane loads oxidation does not reach 100% of the load. This may be mainly attributed to preferential pathways, but also other factors (not investigated in this study) could hamper methane oxidation such as toxic compounds in the landfill gas or cover material as well as high ammonium concentrations and nitrogen turnover rates in the cover.

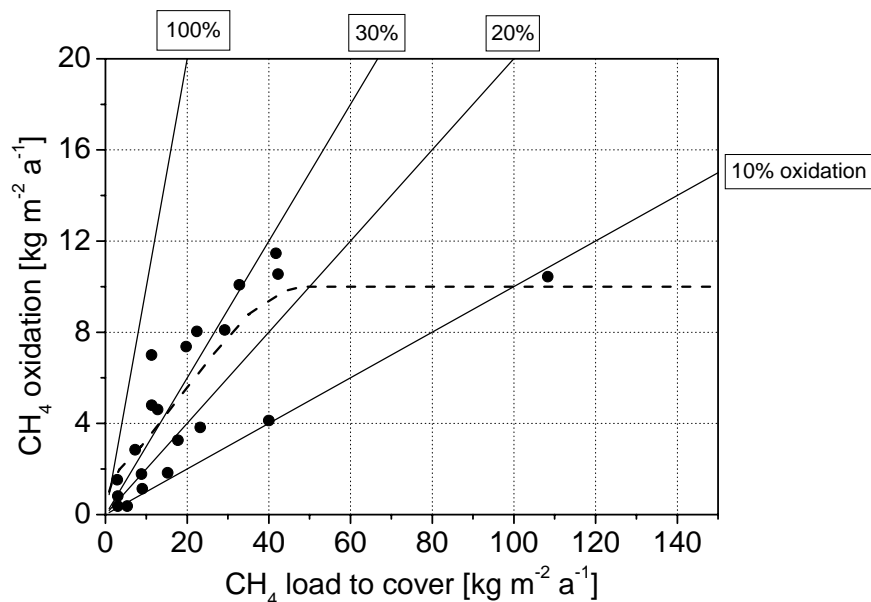


Figure 1: TNO measurement data from 1994-1995 and 2001-2002 (reprocessed data from Oonk & Boom, 1995 and Scharff et al, 2003). Dashed line: proposed 'ceiling' of methane oxidation.

Step 2

For the Methane Oxidation Tool porosity impact has been based on the relationship between porosity and oxygen diffusivity (spreadsheet file tab 'Porosity'). By stoichiometry 2 mol of O₂ are required to oxidize 1 mol of CH₄. Diffusion follows Fick's first law: $J = -D \cdot dc/dx$ with J = flux, D = diffusion coefficient, dc/dx concentration gradient. The estimate is currently based on the assumption that all oxygen has to diffuse into a depth of 20 cm. Overcoming advection with the diffusive flux was neglected because diffusive flux is much larger than advective flux a couple of years after closure (Rannaud et al, 2009). The separate spreadsheet (110429 Methane Oxidation Tool.xls) provides a calculation example illustrating this. Below 10 % porosity there is hardly any diffusion due to decreased connectivity (Gebert et al., 2010). Gebert et al. (2010) experimentally determined the relationship between porosity and diffusivity. Møldrup et al. (2000 & 2001) found similar results.

Table 2: Correction factors for porosity: P (Table 4 in spreadsheet file tab 'Porosity').

Porosity [v/v]	Porosity correction factor (a) [-]
no cover or <0.10	0,05
0.10-0.12	0,16
0.12-0.14	0,52
0.14-0.16	0,90
0.16-0.18	1,32
0.18-0.20	1,77
0.20-0.22	2,29
0.22-0.24	2,87
0.24-0.26	3,55
0.26-0.28	4,19
0.28-0.30	5,16
>0.30	6,13

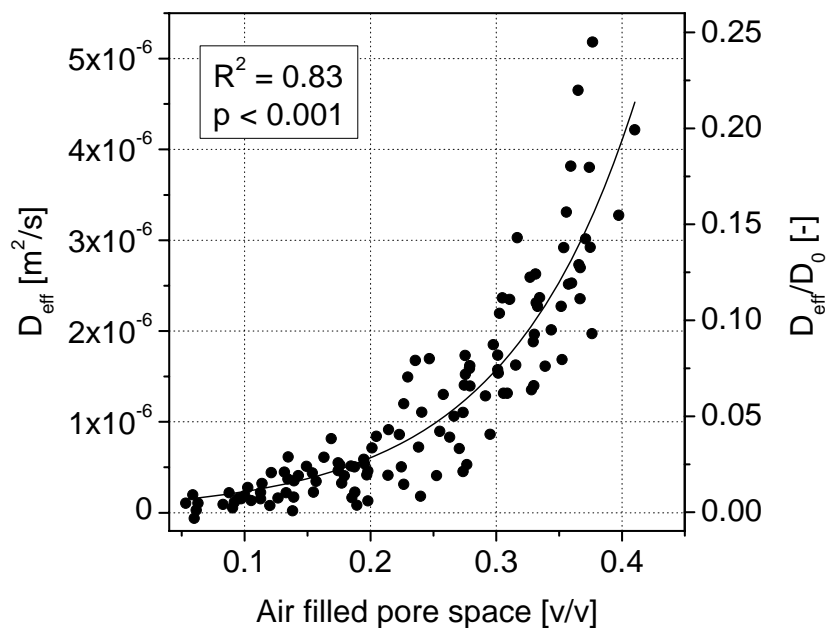


Figure 2: Relation between porosity and diffusivity (Gebert et al., 2011). Line: exponential fit.

Step 3

Temperature impact has been based on the 'Q10-rule' and available laboratory data (Figure 4). At 20 cm depth, an average annual temperature of 10 °C was assumed. This is a reasonable assumption for the humid oceanic European climate zone but needs to be verified for all climate regions in Europe and be applied on the basis of monthly rather than annual averages. In the spreadsheet an example calculation (spreadsheet file tab 'Temperature', Table 6) illustrates that a monthly average of a situation with a large amplitude in annual temperatures results in a different weighed correction factor than based on an annual average. The difference between activity based on average temperature versus temperature amplitude has also been demonstrated by Spokas & Bogner (2011). Spokas & Bogner (2011), Gebert et al. (2003) and Huber-Humer (2004) have found that oxidation activity 'peaks' at 30-38 °C and strongly decreases at higher temperatures. In the Methane Oxidation Tool, the 'Q10-rule' was hence applied to derive correction factors for a temperature range of 0-35 °C only. For higher temperatures, the user should check the literature (e.g. by the abovementioned authors) for factors to downscale the activity. Please note that since laboratory data at 20°C were used as the reference, the temperature correction factor should be 1 at 20°C. Please also note that the function might overestimate the activity at 0°C.



Figure 3: Climate zones in Europe. Source: <http://img526.imageshack.us/img526/261/euroclimateym3.gif>

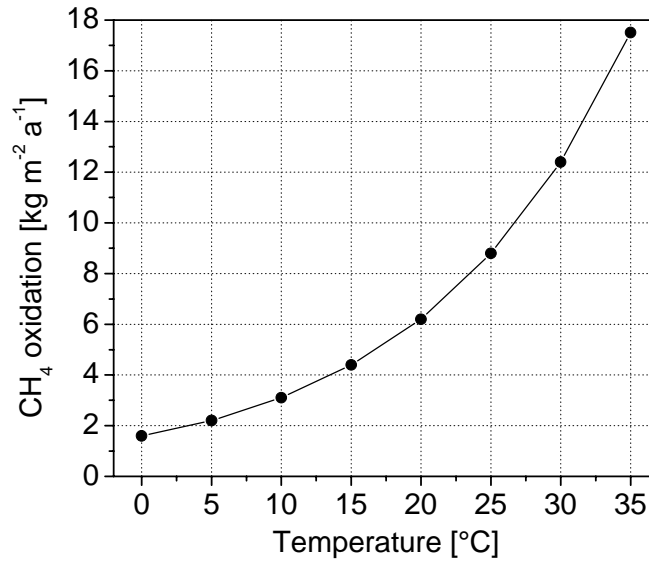


Figure 4: Relationship between temperature and biological activity based on the 'Q10-rule'.

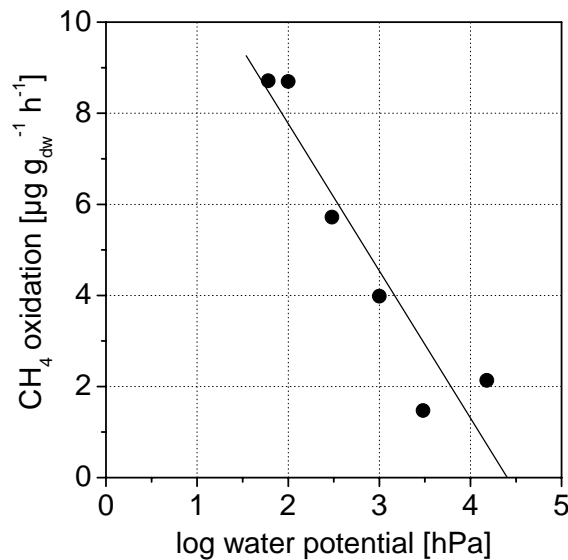


Figure 5: Relation between water potential and methane oxidation (Adapted from Gebert, 2004). Line: linear fit.

Step 4

Microbial activity can be limited both by a lack and an excess of moisture. Moisture limitation has been based on available laboratory data. The pF value is the logarithm of the water potential in the unit hPa. Field capacity is at pF 1.8 (= 60 hPa water potential). If the water potential is lower, then the soil cannot drain freely and is waterlogged. The relationship between water potential and methane oxidation was derived from Gebert et al. (2003). Spokas and Bogner (2011) confirmed that activity is highest around field capacity and declines with dryer conditions. Further elaboration and comparison with more data would be beneficial.

Table 3: Water potential correction factors (Table 7 in spreadsheet file tab 'Water potential').

pF	Water potential correction factor
[-]	(c) [-]
<1.8	1.00
1.8-2.0	0.92
2.0-2.5	0.73
2.5-3.0	0.53
3.0-3.5	0.35
3.5-4.2	0.08
>4.2	0.00

Step 5

Prior to step 5 the user has determined (by means of modelling) the methane production and has measured the amount of methane recovered. Please note that in the IPCC guidelines measuring methane recovered (and correction for measured temperature and pressure) is the standard for determining recovery. The Methane Oxidation Tool intends to offer a more sophisticated approach for determination of methane oxidation than the IPCC methane oxidation default values. Such an approach based on actual landfill data is incompatible with an estimated methane recovery based on assumed recovery efficiency rates. In steps 1 to 4 the user has chosen the appropriate factors (for the specific landfill) for direct emission, porosity, temperature and moisture from the various tables to the 'standard' methane oxidation unit in order to determine oxidation.

In step 5 the user first determines the potential emission by subtracting the measured recovery from the modelled production:

$$(1) \quad \text{Potential Emission} = \text{Production} - \text{Recovery}$$

Then the user determines the actual methane load to the cover material by correcting for direct emission through preferential pathways and hot-spots. The potential emission is multiplied with one minus the correction factor for direct emission (DE):

$$(2) \quad \text{Load to Cover} = \text{Potential Emission} * (1-DE)$$

Then the user determines the potential oxidation by multiplying the 'standard' oxidation unit (see section 'approach') with the correction factors for porosity (P), temperature (T) and water potential (WP):

$$(3) \quad \text{Potential Oxidation} = \text{Standard Oxidation} * P * T * WP$$

Then the user determines the oxidation by checking if the potential oxidation is smaller or larger than the methane load to the cover:

$$(4) \quad \begin{aligned} \text{Load to Cover} < \text{Potential Oxidation} &\Rightarrow \text{Oxidation} = \text{Load to Cover} \\ \text{Load to Cover} > \text{Potential Oxidation} &\Rightarrow \text{Oxidation} = \text{Potential Oxidation} \end{aligned}$$

Finally the user determines the landfill methane emission by subtracting the oxidation from the potential emission:

$$(5) \quad \text{Emission} = \text{Potential Emission} - \text{Oxidation}$$

Final remarks

Research data on the relation between cover type and hot-spots/preferential pathways would be helpful to in the future replace the educated guess with respect to direct emission. More work on the temperature and moisture aspects is required. It would be better if the approach could account for the gradient between air temperature and soil temperature in 20 cm depth and for a methane oxidation horizon deeper than 20 cm. For the sake of simplicity the landfill operator should preferably be able to select annual average temperature and moisture data from a database. For the estimation of annual values for water potential and, possibly, of soil temperature, at least monthly values typical for each region have to be considered. It is serious task beyond the resources of the authors to compile such data for entire Europe and/or other regions in the world. For the time being this approach allows operators and regulators to use a more sophisticated approach for individual landfill for cases where the necessary data are compiled. However, gathering individual temperature data from different depths in landfill covers could be easily done on each site with simple, low-cost and readily available equipment (e.g., pt100 temperature probes). Thus, reliable year-round temperature profiles of the individual covers can be gained, accounting for distinct cover material properties (thermal conductivity), specific heat production due to occurring microbial exothermic reactions, and the local climatic situation.

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