Sampling method for the determination of methane emissions from landfill surfaces

FEDERICO LUCERNONI[a], MATTEO RIZZOTTO[a], LAURA CAPELLI[a*], VALENTINA BUSINI[a], RENATO DEL ROSSO[a] & SELENA SIRONI[a]

[a] *Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "Giulio Natta" - Piazza L. da Vinci 32, 20133 Milano, Italy*

[*]**Corresponding author:** Laura Capelli. Address: Piazza L. da Vinci 32, 20133 Milano, Italy. E-mail: laura.capelli@polimi.it

Abstract

The first aim of this work is the definition and the study of a suitable sampling method for the measurement of landfill gas (LFG) emissions from landfill surfaces, since, up to now, there are no codified nor universally accepted sampling methods for this specific task. The studied sampling method is based on the use of a static hood. The research work involves a preliminary theoretical study for the hood design, experimental tests for the definition of the optimal sampling procedures, and simulations of the hood fluid-dynamics for the system validation. The second aim of this study is the investigation of the correlations between LFG emissions and meteorological conditions, whose identification would be very useful in terms of effective landfill management and pollution control. This involved a wide literature study for the selection of those parameters that seem to have an influence on LFG emission, and the collection of a great number of experimental data on a target site, which led to the conclusion that atmospheric pressure and soil humidity are the parameters that mostly affect LFG emissions.

Keywords: landfill, sampling, passive area sources, static hood, flux chamber, CFD, surface emissions.

Introduction

Landfills are significant sources of pollution (Kumar *et al.*, 2004). Disposal of waste in such sites leads to the generation of a leachate, which may pollute the land and the aquifer (Renou *et al.*, 2008), and a biogas, a mixture of carbon dioxide (CO_2) and methane (CH_4), greenhouse gases and pollutants (Young & Parker, 1983). Landfills are typically also an important source of odour pollution (Palmiotto *et al.*, 2014), because of the presence in landfill biogas (LFG) of traces of compounds characterized by very low odour detection thresholds (Davoli *et al.*, 2003; Capelli *et al.*, 2008), giving that LFG emissions can be related to odour emissions from a landfill (Lucernoni *et al.*, 2016a).

Even though modern landfills are always equipped with a gas capture system, a portion of the gas escapes and is emitted into the atmosphere through the surface. Thus, the possibility of quantifying the LFG surface emissions and monitoring them over time may represent an important aspect for the landfill operation and management (Mosher *et al.*, 1999). Quantification of LFG emissions, and their possible correlation to odour emissions, requires the periodical execution of specific measurement campaigns, which should be carried out by means of a suitable sampling method that should be repeatable, reproducible and accurate. This is a complicated task: to date, there are no codified nor universally accepted sampling methods.

Despite in literature several studies hypothesize the existence of some sort of correlations between meteorological conditions and emissions, such correlations are undemonstrated, mostly contrasting, and never quantified. For this reason, it is not known how to account for the effect of the changing meteorological conditions on the LFG emissions.

The first aim of this work is the definition of a sampling method that allows for reproducible and repeatable measurements. As already mentioned, to date the best way for LFG sampling on landfill surfaces is still debated in the scientific community.

On a regulatory level, there are two different approaches, both based on so called “hood methods”, involving the use of a specific sampling hood that isolates a portion of the surface to be sampled. The oldest – and more consolidated – is the EPA method (EPA, 1986), which entails the use of a flux chamber (FC) flushed with a neutral gas flow (N_2 or air) (Reinhart *et al.*, 1992; Park & Shin, 2001; Gebert *et al.*, 2011; Di Trapani *et al.*, 2013). The other one, adopted by the UK-EA (EA, 2010), entails the use of a static hood (SH), in which the increase of methane concentration is measured over time. The static chamber measurement approach, for methane and LFG emission determination from landfill surfaces, is the most often used in Italy and it is also commonly applied in many cases outside of the UK because it is relatively inexpensive, simple, and highly sensitive at detecting even small fluxes (Abichou *et al.*, 2006; Bogner *et al.*, 1995; Cardellini *et al.*, 2003; Schroth *et al.*, 2012); thus new and optimized designs for static chambers have been recently proposed (Rachor *et al.*, 2013; Lucernoni *et al.*, 2016b).

Moreover, hood methods, and especially fluxed hoods, are by far the preferred method for the assessment of odour emissions from passive area sources (Hudson & Ayoko, 2008; Capelli *et al.*, 2013; Parker *et al.*, 2013), and also from landfill surfaces (Sarkar & Hobbs, 2002; Frechen *et al.*, 2004; Sironi *et al.*, 2005; Romain *et al.*, 2008).

However, as far as the assessment of CH_4 and LFG emissions from landfills are concerned, several alternatives to hood sampling methodologies exist, which are worth to be mentioned.

- The main alternative is the tracer gas (TG) method entailing the controlled release on the emission surface of a given traceable gas (*e.g.* SF_6), used to simulate the landfill gaseous emissions (Börjesson *et al.*, 2000; Spokas *et al.*, 2003). There are different options depending on the tracer gas used and on the kind of measurement performed. The main two possibilities are mobile or static measurement. The mobile plume measurement (MPM) consists in driving with a tuneable diode laser spectrometer (TDL) along a downwind transect perpendicular to the wind direction around 200 m from the site to measure tracer gas concentrations in the plume’s cross

71 section. An inlet tube is located at the front of the van above the cabin to let the outside air come
72 into the TDL system; this avoids additional mixing. A tracer gas (*e.g.* N_2O) is released with a
73 known constant flow-rate from the source and used as a reference compound to calibrate the
74 model. The released gas flow is controlled; before and after the experiments the tracer bottles are
75 weighted to know the exact volume of tracer gas lost within the release period. The emission is
76 calculated from the measured/modelled concentration levels above the background (Babilotte *et*
77 *al.*, 2010). The static plume measurement (SPM) entails using vacuum gas bottles installed at a
78 road downwind of the source. The bottles are evacuated before the measurements with a vacuum
79 pump and will fill themselves to approximately 0.5 bar, requiring a defined time. After, the
80 bottles are closed and analysed with a TDL system. One of the bottles is used for the assessment
81 of the background concentration of CH_4 and tracer gas; this one needs to be located upwind of
82 the landfill. The emission from the source is calculated from the measured/modelled
83 concentration levels above the background (Simpson et al., 1995; Babilotte *et al.*, 2010).

84 • The radial plume mapping (RPM) entails the use of optical remote sensing (ORS) for the
85 collection of path-integrated concentration (PIC) data over multiple, non-overlapping beam paths
86 (Babilotte *et al.*, 2010).

87 • The differential absorption LiDAR – or Light Detection And Ranging - (DiAL) technique is a
88 laser-based remote monitoring, enabling range-resolved concentration measures of a large
89 variety of atmospheric chemical compounds both in the infra-red (*e.g.* CH_4, C_2H6, etc.) and
90 ultra-violet wave-length spectrum (*e.g.* NO_x, SO_x, etc.) with a ppm sensitivity at ranges higher
91 than 500 m. The system consists of an accessorized self-powered truck. In the DiAL, the laser is
92 operated alternately at two adjacent wavelengths. The on-resonant wavelength is chosen to be at
93 a wavelength that is absorbed by the target species. The off-resonant wavelength is chosen to be
94 at a wavelength that is not absorbed by the target species in order to avoid interferences.

Emission fluxes are measured scanning the DiAL measurement beam in a vertical plane downwind of the target sources and determining the total concentration of CH_4 above the background in that plane. Vertical planes are typically 600 m x 600 m with a range resolution of 25 m vertically and 5 m horizontally. To determine the emission flux of CH_4 due to the landfill site itself, the background CH_4 needs to be subtracted from the concentration profiles before the flux is calculated (Babilotte *et al.*, 2010).

- The inverse modelling (IM) entails the use of a concentration analyser that provides real-time CH_4 concentration measures. Concentration measures are performed at discrete receptors downwind of the landfill. CH_4 concentrations and associated Global Positioning System (GPS) coordinates are then used in an atmospheric dispersion modelling software (*e.g.* ADMS3, CALPUFF, etc.). The software performs an inverse modelling analysis according to the geo-referenced CH_4 concentrations. The output is a CH_4 emission factor for each landfill cell (Babilotte *et al.*, 2010).

As previously mentioned, there are several literature works describing the possibility to use hood methods for measuring both LFG (Reinhart *et al.*, 1992; Bogner *et al.*, 1995; Park & Shin, 2001; Cardellini *et al.*, 2003; Abichou *et al.*, 2006; Gebert *et al.*, 2011; Schroth *et al.*, 2012; Di Trapani *et al.*, 2013; Liu *et al.*, 2015) and odour (Sarkar & Hobbs, 2002; Frechen *et al.*, 2004; Sironi *et al.*, 2005; Romain *et al.*, 2008) emissions from landfills. As demonstrated in other previous works, odour emissions from landfill surfaces can be determined either by means of direct odour sampling, or indirectly, i.e. by measuring the LFG emissions and then multiplying the LFG flux by the LFG odour concentration (Lucernoni *et al.*, 2016a, 2017). In this second case, the odour concentration of the LFG emitted through the landfill surface needs to be estimated by relating the CH_4 and the odour concentration of samples collected over the landfill surface (Lucernoni *et al.*, 2016a, 2017). Even though odour measurement is not the primary objective of this work, because of the above mentioned possibility to relate CH_4 and odour concentration data, hood

methods were preferred as the investigated method for the development of a sampling methodology that allows both the measurement of LFG fluxes and of odour emissions.

The development of the sampling methodology involved: a preliminary theoretical study for the hood design, experimental tests for the definition of optimal sampling procedures and operative conditions and a fluid-dynamic study exploiting computational fluid dynamics (CFD) simulations for the system validation.

The second goal of the study is the investigation of the correlations between LFG emissions and meteorological parameters. This involved a wide literature study for the selection of those parameters that seem to have an influence on the LFG emission. The identification of such a correlation would be useful in terms of effective landfill management and pollution control.

Materials and methods

Experimental campaigns

The site is a landfill in Northern Italy operative since 1993, it has an extension of 250 000 m^2 subdivided in 6 allotments of which only one still is operational. The landfill waste storage capacity amounts to roughly 6 200 000 m^3. The LFG collection system sucks 2200 m^3 h^{-1} of gas, which is burnt in four co-generators for the production of electric energy. The campaigns were planned with a frequency of two times per week on average, for a total of 40: from December 2014 to November 2015 in allotments 1 and 2, both closed and covered with a clay layer, without waterproofing seal. Four different points were identified for LFG sampling from December 2014 to March 2015, since two of these points resulted scarcely emissive (not measurable), these points were discarded and replaced with three new points for the measurements from March 2015 to November 2015. Measures were carried out always at the same time, around 11 a.m., in order to prevent additional variability.

Materials

142 The device developed at the Politecnico di Milano for CH_4 sampling over landfill surfaces is a hood (Fig.
143 1), which was designed based on the one described in the UK-EA (EA, 2010) and by the modified version
144 proposed by Rachor *et al.* (2013). The hood has a squared base, 50 cm x 50 cm, with a height of 10 cm
145 and it is connected to the outside by means of a 3 m long Teflon tube that allows keeping the internal
146 pressure equal to the atmospheric pressure in order to avoid over-pressures that may affect the emission.
147 The device is made of steel. A 10 cm long tube on the top of the hood allows the CH_4 concentration
148 measurement by attaching a Flame Ionization Detector (FID), which has a suction flow of 1.06 l min^{-1}, to
149 the outlet tube for 2 min. The CH_4 concentration analyser used is a Crowcon GasTec portable FID, with a
150 detection range of 0-10000 ppm and an accuracy of 1 ppm.


151

152 **Figure 1.** *The sampling hood designed at the Politecnico di Milano operated as a FC (left) and as a SH*
153 *(right).*

154 One particular feature of this newly designed hood is that it can be operated both as a FC or as a SH, i.e.
155 with or without the introduction of a neutral sweep air flow, respectively. This gives the advantage of
156 allowing both the direct and indirect measurement of odour emissions from landfill area sources. Direct
157 odour measurement needs to be performed using the hood as a FC, since the withdrawal of the

158 olfactometric sample volume would perturb the internal SH too much; this is less true for a FC whose
159 internal volume is continuously flushed by a neutral gas flow. On the other hand, indirect odour emission
160 measurement can be carried out with both hoods, since this method relies primarily on the evaluation of
161 the LFG flux through the measurement of the CH_4 concentration over the landfill surface, and the
162 subsequent estimation of the odour emission rate by multiplication with the LFG odour concentration
163 (Lucernoni *et al.*, 2016a, 2017).
164 In order to evaluate the possibility to use the designed hood in both modes (fluxed or static), in the period
165 from December to March the hood was operated both as a FC and a SH to compare the two sampling
166 methods.
167 The procedure defined for the FC mode (Fig. 1, left) provides that the hood is fluxed with a neutral air
168 flow of 200 l h^{-1} for a period of 12 min by connecting an air bottle to the tube on the top of the hood.
169 The SH mode procedure provides that the hood is positioned on the landfill surface for a period of 10 min
170 before measuring the CH_4 concentration. From the CH_4 concentration, it is possible to calculate the
171 specific emissive LFG flow, in l m^{-2} h^{-1}. The presence of the lateral tube connecting the interior of the
172 hood with the external ambient assuring isobaric conditions during sampling also guarantees that a higher
173 CH_4 concentration inside the hood is avoided without continuously sweeping the air out of the hood
174 (Rachor *et al.*, 2013; Lucernoni *et al.*, 2016b).
175 For the fluxed mode, it is possible to write the CH_4 mass balance as:

176 $$\dot{Q}_{out} \cdot c_{CH_4,mis} = \dot{Q}_{in} \cdot c_{CH_4,in} + \dot{Q}_{LFG} \cdot c_{CH_4,LFG} \quad (1)$$

177 In Eq.1 ($\dot{Q}_{out}$) is the total flow [$l\ h^{-1}$] equal to the inlet air flow ($\dot{Q}_{in} = 200\ l\ h^{-1}$) plus the emitted LFG
178 flow ($\dot{Q}_{LFG}$), ($c_{CH_4,mis}$) is the measured CH_4 concentration [$\mu mol\ mol^{-1}$], ($c_{CH_4,in}$) is the CH_4
179 concentration in the neutral air equal to zero [$\mu mol\ mol^{-1}$] and ($c_{CH_4,LFG}$) is the concentration in the pure
180 LFG equal to 500 000 [$\mu mol\ mol^{-1}$], that is 50% molar fraction. The CH_4 concentration of 50% in the
181 pure LFG is a datum obtained from the operational information regarding the LFG collection and

combustion system of the landfill. Since the emitted LFG flow rate is much lower than the fluxed neutral air, it is possible to assume that ($\dot{Q}_{out}$) and ($\dot{Q}_{in}$) are equal. The specific LFG flow ($\hat{Q}_{LFG}$) [$l\ m^{-2}\ h^{-1}$] is obtained by dividing by the base area of the hood (S_h), which is 0.25 m^2:

$$\hat{Q}_{LFG} = \frac{Q_{in} \cdot c_{CH_4,mis}}{c_{CH_4,LFG} \cdot S_h} \quad (2)$$

When operating the hood as a SH (Fig. 1, right), it is possible to write the mass balance for CH_4 as shown:

$$V \cdot \frac{d\bar{c}_{CH_4}}{dt} = \dot{Q}_{LFG} \cdot c_{CH_4,LFG} \quad (3)$$

In Eq. 3, (V) is the volume of the hood equal to 25 [l], $\left(\frac{d\bar{c}_{CH_4}}{dt}\right)$ is the average CH_4 concentration variation inside the hood over time, ($\dot{Q}_{LFG}$) is the emitted LFG flow [$l\ h^{-1}$] and ($c_{CH_4,LFG}$) is the concentration in the pure LFG equal to 500 000 [$\mu mol\ mol^{-1}$]. The specific LFG flow may be obtained by making two assumptions:

I. the CH_4 concentration inside the hood has a linear growth over time;
II. the CH_4 concentration that is measured by means of the FID is equal to the average CH_4 concentration inside the hood $\bar{c}_{CH_4}$.

The specific LFG flow can be computed by using Eq.4:

$$\hat{Q}_{LFG} = \frac{c_{CH_4,mis} \cdot V}{c_{CH_4,LFG} \cdot \Delta t \cdot S_h} \quad (4)$$

CFD simulations

Computational Fluid Dynamics (CFD) was applied to study the static sampling procedure, since the understanding of the fluid-dynamic behaviour of the sampling hood is fundamental for the correct interpretation of the sampled data (Prata Jr. *et al.*, 2016). CFD simulations with the software ANSYS Fluent were performed with the aim of verifying the assumptions of linear growth of the CH_4 concentration inside the hood and of equivalence of measured CH_4 concentration and average CH_4

204 concentration inside the hood, on which the method (Eq.4) is based. This fluid-dynamic study is
205 fundamental to verify the appropriateness of the developed sampling method, thereby involving the
206 verification of the pertinence of the choice of the sampling point and of the sampling time, thus proving
207 the representativeness of the adopted procedure for the determination of the emitted LFG flow rate. The
208 advantage of this approach is to avoid the perturbation in the concentration inside the chamber induced by
209 the flow of the FID, which would make it very difficult experimentally to evaluate the concentration in a
210 precise point and impossible during a single test.
211 In order to apply CFD, it was first necessary to generate a suitable mesh that provides the software with a
212 discrete representation of the hood geometry. The adopted mesh is non-structured with a refinement of 14
213 layers of structured mesh at the inlet boundary (as shown in Fig. 4) and a total number of cells of 3 000
214 000. Then the simulation settings have to be defined: the source term was set equal to 0.25 [$l\ m^{-2}\ h^{-1}$],
215 which is the mean specific LFG flow emitted from the landfill surface, deriving from the experimental
216 campaigns on site. This value is not the final datum, but it is a value obtained during the first campaigns,
217 in order to perform the CFD study assessing the appropriateness of the adopted sampling method in the
218 early stages of the project. The model also requires setting the values of pressure, temperature, and
219 diffusivity coefficients. The simulations were run considering a total time of 12 min: 10 min of static
220 hood positioning + 2 min for the FID analysis.
221 *Correlation between meteorological data and LFG emissions*
222 In order to investigate the existence of a correlation between LFG emissions from the landfill surface and
223 meteorological conditions, a great number of emission and meteorological data are required. Before
224 starting the analysis of the experimental data acquired from the measurement campaigns on site, a
225 thorough review of the scientific literature on the subject was performed to identify the meteorological
226 parameters that other authors had investigated as possibly affecting the LFG emissions. As a first result of
227 this first literature review step, Tab. 1 tries to resume a bibliographic overview of what has been written

by other researchers on this matter by summarizing their statements and observations about the influence of atmospheric parameters on LFG emissions.

Finally, the meteorological data considered for the study were rainfall, temperature, atmospheric pressure, wind speed, relative humidity and solar radiation. In addition, the soil humidity was considered as well, which was determined experimentally by collecting soil samples and weighting them before and after drying, thus assessing the humidity as the removed water fraction.

Table 1. *Bibliographic overview of the statements and observations about the influence of atmospheric parameters on LFG emissions made by other researchers.*

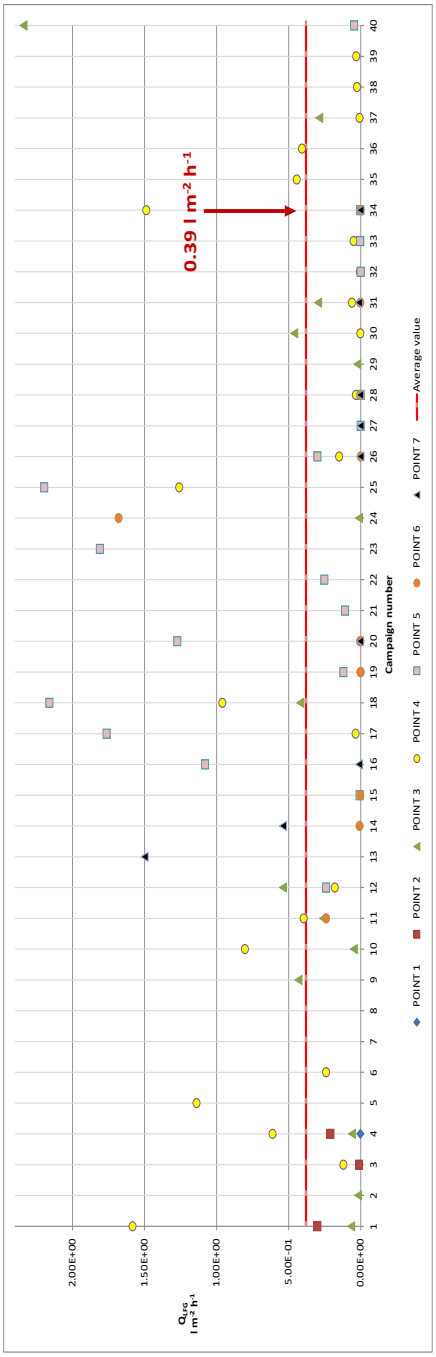
Atmospheric Parameter	**Source(s)**	**Correlation Type**	**Author's Hypothesis**
Atmospheric Pressure (P)	Reinhart *et al.*, 1992; McBain *et al.*, 2005	Negative Correlation (-): P increases and LFG flow decreases	Landfill "respiration"
Temperature (T)	Park & Shin, 2001	Positive Correlation (+): T increases and LFG flow increases	Waste decomposition process is enhanced
Temperature (T)	Rachor *et al.*, 2013	Negative Correlation (-): T increases and LFG flow decreases	Temperature governs microbial CH_4 oxidation because chemical processes in the cells are faster at greater energy supplies (i.e during the warm season)
Soil Humidity (U)	Rachor *et al.*, 2013	Positive Correlation (+): U increases and LFG	CH_4 production is enhanced in a moist environment and CH_4

		flow increases	oxidation is disadvantaged by lack of O_2 (pores occupied by H_2O)
Soil Humidity (U)	Rachor *et al.*, 2013	Negative Correlation (-): U increases and LFG flow decreases	CH_4 oxidation is favoured, more favourable environment for metanotroph bacteria
Wind Velocity (v)	McBain *et al.*, 2005	Positive Correlation (+): v increases and LFG flow increases	Diffusive resistance is lowered, the boundary layer thickness decreases
Wind Velocity (v)	Rachor *et al.*, 2013; Reinhart *et al.*, 1992	Negative Correlation (-): v increases and LFG flow decreases	Wind velocity influences the pressure value on soil surface, P increases
Rainfalls (p)	Rachor *et al.*, 2013	Negative Correlation (-): p increases and LFG flow decreases	Cork effect, water prevents LFG from going into the atmosphere

Results and discussion

Definition of the sampling method

Fig. 2 shows LFG specific flow data obtained in the different sampling points for all experimental campaigns. In order to define the most suitable sampling method, emission data obtained with the SH have been compared with those obtained with the FC until March: the comparison showed no dramatic differences between the two methods (Fig. 3).



243

244 **Figure 2.** *Results of the experimental campaigns (specific LFG flow rates in l m^{-2} h^{-1}).*

The average flux highlighted in Fig. 2 is obtained computing the arithmetic mean, in accordance with the criteria in the guideline of the UK Environment Agency (UK-EA, 2010).

The mean specific LFG flux value turned out to be 0.39 l m^{-2} h^{-1}. There is a significant variability of the experimental data (Fig. 2), which is the case in environmental measurement campaigns, since the measurement is highly affected by different factors. In Fig. 2, the majority of the flux values are rather low while the high ones represent a smaller share. The method adopted to assess the LFG flux has been used in a recent publication to assess odour emissions from landfill surfaces (Lucernoni *et al.*, 2016a).

By plotting the LFG flux data (Fig. 3) with the SH data on the x-axis and the FC data on the y-axis, it is possible to see how the resulting points are very close to the line representing perfect equivalence between the two methods (*i.e.* x=y). Once verified that both methods provide similar results in terms of CH_4 – and thus also in terms of related odour – emission fluxes, it was decided to prefer the SH method, since it is less demanding especially as far as logistics is concerned, as it does not involve the need to provide a neutral sweep air flow (*i.e.* no need to transport and consume air bottles, or to use a rotameter).

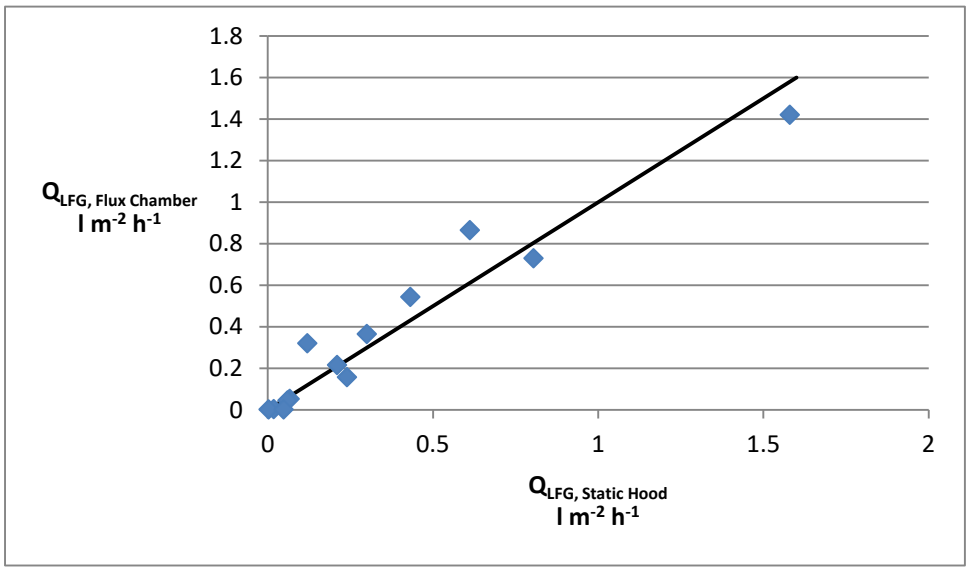


Figure 3. *Comparison between LFG emission data obtained with FC and SH ‘*

(December 2014 – March 2015).

The mean specific LFG flow rate derived from the experimental measurements turned out to be equal to 0.39 l m^{-2} h^{-1}. This value is similar to that found in literature in a study by Palmiotto *et al.* (2014), in a MSW landfill located also in Northern Italy, which is likely to have both landfilled waste quality and landfill management operations similar to those of the landfill considered for this study. In that case, the obtained surface LFG flux is equal to 0.2 l m^{-2} h^{-1} (Palmiotto *et al.*, 2014). In parallel, a CFD simulation of the sampling with the hood was performed to see if the sampling system adopted was proper for the study.

CFD simulation of the sampling procedure with SH

In order to verify the assumptions of linear growth of the CH_4 concentration inside the SH and of equivalence of measured CH_4 concentration and average CH_4 concentration inside the hood, which the adopted sampling method relies on, it was decided to evaluate the CH_4 concentration at some specific points inside the hood with a CFD simulation. The LFG specific flux imposed as source term for the CFD simulations is not 0.39 l m^{-2} h^{-1}, as finally resulting from the experimental campaigns, but 0.25 l m^{-2} h^{-1}. This discrepancy is because it was necessary to run the preliminary simulations by means of CFD to describe the fluid-dynamic behaviour of the hood before completing the experimental campaigns in the field to validate the sampling system. For this reason, the specific LFG flux of 0.25 l m^{-2} h^{-1} used for the simulations is a partial result that was obtained after the first campaigns. The fact that the “true” value resulting after completion of the experimental data collection turned out to be 0.39 l m^{-2} h^{-1}, does not affect the significance and validity of the CFD simulations, since the two values do not differ substantially. In order to confirm this assumptions other simulations were run subsequently changing the LFG specific flux in a range from 0.05 l m^{-2} h^{-1} to 1 l m^{-2} h^{-1}, as described in the paper by Lucernoni *et al.* (2016b).

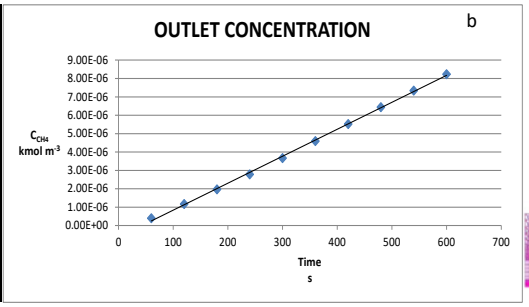
Fig. 4 shows the results of the simulation relevant to the point at the outlet orifice on top of the hood, where the shorter tube is attached and where the FID is inserted for the concentration measurement. The

values at each minute from 0 to 10 in kmol m^{-3} and the resulting plot over time are reported. It is possible to observe that the concentration points are linearly interpolated, with a correlation index R^2 of 0.9991, confirming the first hypothesis of linear increase of the CH_4 concentration inside the hood. This linear growth for short horizon times is observed for all the points on the central axis of the hood.

a

OUTLET CONCENTRATION	
t [s]	C_{CH4} [kmol m^{-3}]
60	3.98E-07
120	1.17E-06
180	1.97E-06
240	2.78E-06
300	3.67E-06
360	4.59E-06
420	5.52E-06
480	6.44E-06
540	7.34E-06
600	8.23E-06

b



c

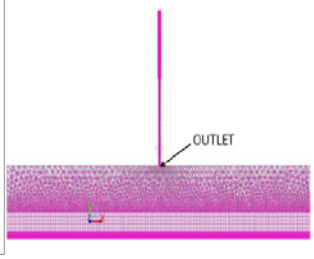


Figure 4. *Methane concentration values over time (a), concentration trend over time at the hood outlet (b) and mesh representation for the device highlighting the outlet (c).*

The CFD simulation also allowed to verify the second assumption - that the CH_4 concentration read by the FID is representative of the average CH_4 concentration inside the hood - by analysing the CH_4 concentration contours inside the hood over time, i.e. during the first 10 min in which the SH is positioned over the landfill surface and during the following 2 min of the FID measurement duration.

The LFG flow rate considered as source term (*i.e.* 0.25 $l\ m^{-2}\ h^{-1}$) is rather low, so no mixing is foreseen inside the hood; this was confirmed by the simulation showing that the CH_4 concentration distribution inside the SH after 10 min is not homogeneous, but stratified (Fig. 5a). The simulation results sketched in Fig. 5a show also that the stratification is bell shaped, the typical concentration distribution in case of plug flow with axial diffusion: this is corroborated by the order of magnitude of the diffusive velocity, 10^{-4} m s^{-1}, higher than the convective velocity inside the hood, order of magnitude of 10^{-7} m s^{-1}. Thus, after the established "deposition" time of 10 min, the CH_4 concentration at the sampling point (the outlet), is

equal to 196 μmol mol^{-1}, a value very close to the average CH_4 concentration inside the hood after 10 min (which contour is highlighted with the dashed line in Fig. 5a), equal to 208 μmol mol^{-1}, which can also be calculated as shown in Eq. 5:

$$\bar{c}_{CH_4} = \frac{\hat{Q}_{LFG} * \bar{c}_{CH_4,LFG} * \Delta t * S_h}{V} \quad (5)$$

After the FID operation time of 2 min (Fig. 5b), the system is perturbed with respect to the static deposition period (Fig. 5a), giving a fairly mixed system. The simulation results show that the CH_4 concentration at the sampling point after this time (10 + 2 min) is 260 μmol mol^{-1}, compared to an average CH_4 concentration in the chamber of 248 μmol mol^{-1}. These results confirm both the appropriateness of the choice of the sampling point and consequently the legitimacy of the assumption of considering the CH_4 concentration value measured with the FID at the sampling point as representative of the average CH_4 concentration inside the hood. A more detailed study of the trend of concentration inside the hood and the validation of the CFD results with the experimental data has been presented elsewhere (Lucernoni *et al.*, 2016b).

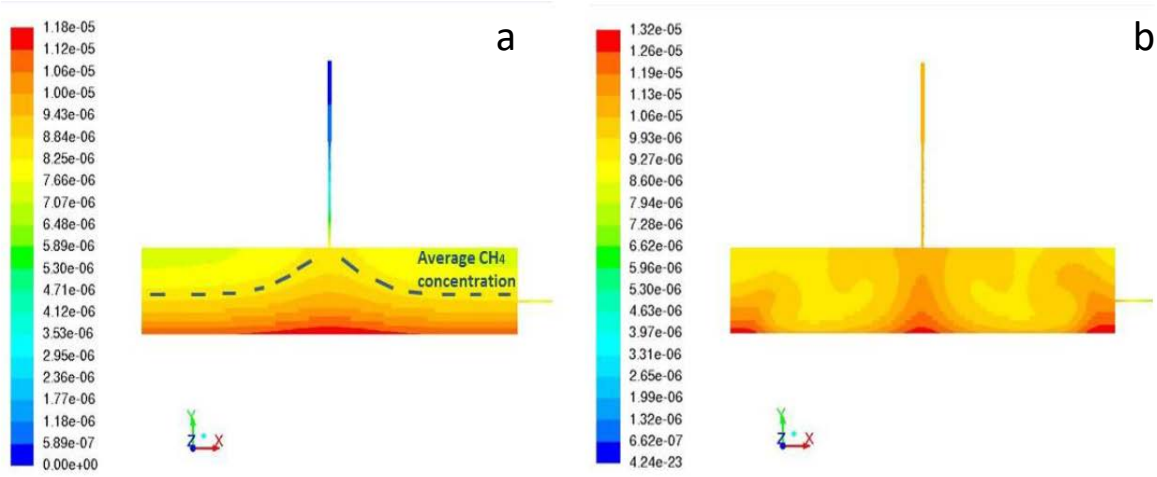


Figure 5. *CH_4 concentration distribution after 10 min (a) and after 10+2 min (b).*

LFG emissions and meteorological parameters

The first step of this part of the work was the selection of the meteorological parameters deemed as the most influential on the LFG emissions. The wind velocity and the wind direction were excluded since the sampling method adopted is a hood isolating the sampling area, making the action of the wind uninfluential, especially for the present study where the source is located in a region characterized by weak winds. Air temperature proved to have a small influence on emissions, probably because the waste decomposition process is in an advanced stage and external air temperature has a minimal influence on the phenomenon. There could be also an alternative explanation: considering that the air temperature only has an influence on soil temperature up to a certain depth (1-2 m below the surface), the temperature in the landfill body is typically constant. As most of the waste is located deeper than that, it is possible that the air temperature will not affect LFG generation.

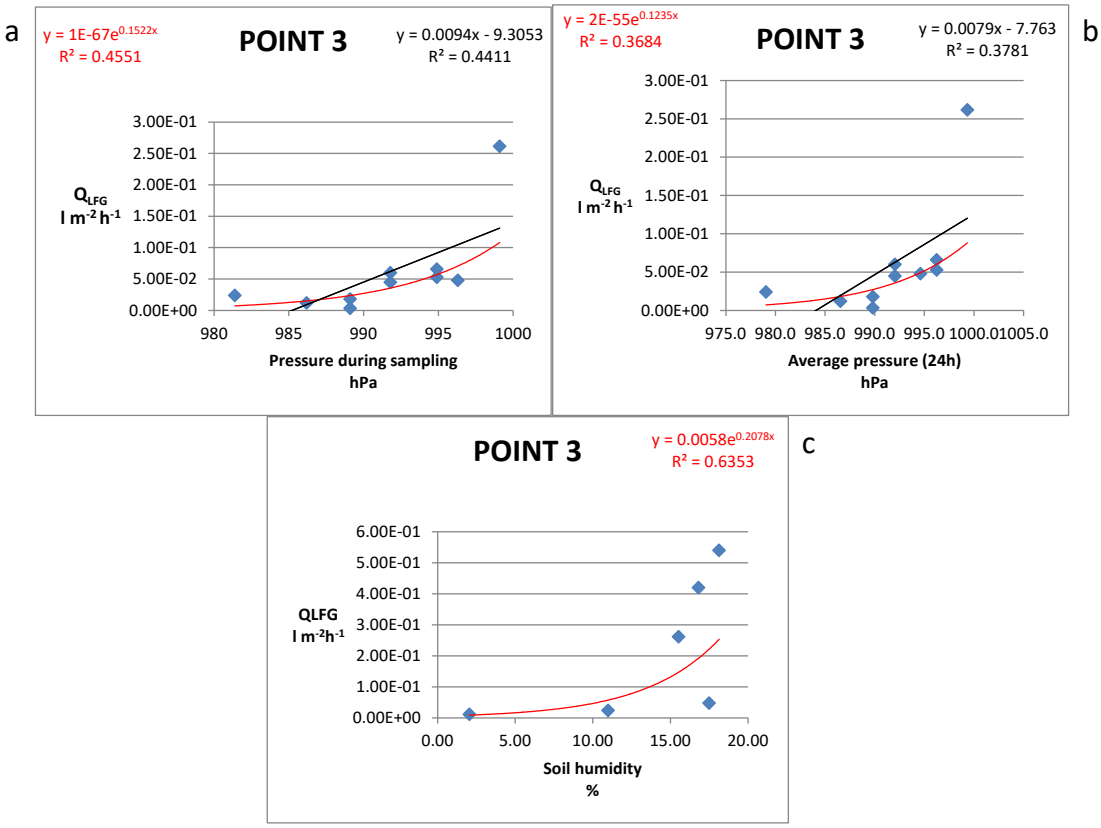
On the other hand, there are some studies in literature investigating the effects of temperature on microbial methane oxidation in landfill cover soils, which might thus have measurable consequences on methane emissions from the landfill surface to the atmosphere (e.g., Börjesson *et al.*, 2004; Einola *et al.*, 2007; Spokas & Bogner, 2011). However, most of these studies have been performed on a laboratory-scale or by isolating a portion of the cover soil to be tested, and in general, up to now, there have been very few field studies that have attempted to investigate the relative contribution of the effective temporal dynamics and the relative contribution of such environmental parameters directly on landfill surfaces (Scheutz *et al*., 2009). For this reason it is very difficult to make accurate and quantitative considerations about the possibility that temperature is negatively correlated to CH_4 emissions from landfill surfaces. Moreover, in those laboratory studies, significant variations of CH_4 emissions were observed only for considerable temperature differences by controlling other parameters. For this study, samples were collected always in the morning, giving that the temperature differences were significant only when comparing measurements carried out in different seasons, and in such a long time frame and with other

parameters affecting the CH_4 emissions more than temperature, it is unlikely that such effects of temperature on the potential of methane oxidation are observed.

Air humidity seems to not have a significant influence on LFG emissions, which was hypothesized a priori since the there is no theoretical justification for that and no mention of a possible influence of air humidity on the emissions was found in literature neither. Up to now, there are no conclusive evidences that solar radiation directly affects the emissions, even if several undergoing researches are trying to study a possible cross-correlation between radiation and atmospheric pressure, since both parameters are indicative of the weather conditions. Rainfalls were not investigated directly as a parameter, it was preferred to consider the soil humidity. Therefore, the variables considered for the study were atmospheric pressure and soil humidity. As explained in the scientific literature, it is possible to ascribe the negative influence of pressure increase on LFG emissions to a phenomenon called landfill "respiration": in some cases, a weak negative correlation was found between the two variables. According to this explanation, a pressure increase "pushes" the biogas into the soil, obstructing the emission. In order to investigate the effectiveness of this hypothesis, the daily and monthly pressure trends were analysed as well as the pressure gradients during the 3 and 6 hours preceding each campaign. The only correlations that were identified are those between emissions and instantaneous pressure at the time of the sampling, and the average pressure in the preceding 24 hours and 48 hours. The preliminary analysis of the data shows a correlation that – differently from what has been found in some other studies – is positive; even though weak, the correlation seems to indicate an increase of the LFG emission with atmospheric pressure. This observed correlation might be partially explained based on some considerations found in the manual "Solid Waste Engineering" by Sirini et al. (2010), which in Chapter 15 discusses the migration of trace gases across the landfill surface (Eq. 6).

$$J_i = \frac{\mathfrak{D}_i * \alpha^{4/3} * (C_{i,atm} - C_{i,s} * W_i)}{L} \quad (6)$$

368 The authors indicate that the emission flux of the specific gas (J_i) is a function of several parameters, such
369 as molecular diffusivity (D_i), soil porosity (α), atmospheric gas concentration ($C_{i,atm}$), saturation gas
370 concentration ($C_{i,s}$), scaling factor (W_i) and landfill covering thickness (L). It is possible to assume that all
371 the parameters contained in the equation are not affected by atmospheric pressure, except the diffusivity,
372 which is related to the soil porosity. Therefore, it is possible that, since high pressure indicates a "no-rain
373 condition", the soil porosity will be higher and thus emission will be higher as well.
374 As an example, the correlation between specific LFG flow rate and atmospheric pressure (instantaneous
375 and average of the preceding 24 hours) relevant to sampling point #3 is shown in Fig. 6a and 6b.
376
377



378

Figure 6. *Landfill gas emission vs. environmental parameters. LFG emission vs. atmospheric pressure at the time of sampling (a) and vs. average atmospheric pressure in the 24 h preceding the sampling (b) and vs. soil humidity (c).*

Concerning the correlation between LFG emissions and soil humidity, a positive correlation was found and the LFG emission seems to increase with the soil humidity (*e.g.* Fig. 6c shows the correlation between LFG emission and soil humidity relevant to sampling point #3). This only is true in the case of no-rain, since during rainfall a sort of "cork" effect is observed due to the obstruction of the pores and thus reduced diffusivity, and measured emissions from the landfill surface are 0. In order to give an explanation to this experimental evidence, some considerations about the operation of the studied landfill should be made. In the examined landfill the common practice of "leachate recirculation" inside the waste mass is not performed, the leachate formed during waste fermentation is compelled by gravity to move downwards, giving that the upper levels of waste will be typically dry and thus generate less biogas due to slower fermentation kinetics. Moreover, given that the closed allotments of the studied landfill are not fully waterproofed, during rainfall, water trickles across the soil wetting those wastes stored in the upper levels, which are normally dry: this might speed up the LFG production kinetics and cause higher emissions. However, there may be an alternative reason as well: the hotspots can be assumed to contain wider pores than the soil around these hotspots. Therefore, if it starts raining the pores in the soil may be obstructed more and earlier than the pores in the hotspot. This may drive a larger portion of the emission through the hotspot without affecting the overall landfill emission.

The correlation observed in Fig. 6c looks more exponential than linear. This observation would be coherent with the influence of the humidity found in most expressions for the CH_4 production kinetics via waste fermentation. As an example, the equation used by the US-EPA software LandGEM (Alexander *et al.*, 2005) describes an exponential trend whereby the exponent contains the kinetic constant (k), which depends mainly on the soil humidity:

$$Q_{CH_4} = \sum_{i=1}^{n} \sum_{j=0,1}^{1} kL_0 \left(\frac{M_i}{10}\right) e^{-kt_{ij}} \quad (7)$$

Conclusions

The first aim of the work was the definition of a reliable and reproducible sampling procedure. The optimal procedure defined is based on the use of a SH, with a static sampling time of 10 min followed by 2 min required by the FID for the CH_4 concentration measurement. The CFD simulations confirmed the basic assumptions for the definition of this sampling method: linear CH_4 concentration growth during the established sampling time and equivalence between measured CH_4 concentration and average CH_4 concentration inside the hood, as well as the appropriateness of the chosen sampling point.

The second aim was a preliminary study of the correlation between LFG emissions and meteorological parameters; the most influential parameters were identified, these being atmospheric pressure and soil humidity. Some preliminary positive correlations were observed between those parameters and the LFG emission from the landfill surface.

415 **References**

416 Abichou T., Chanton J., Powelson D., Fleiger J., Escoriaza S., Lei Y. & Stern J. (2006). Methane flux and
417 oxidation at two types of intermediate landfill covers. *Waste Management* 26, 1305-1312.

418 Alexander A., Burklin C. & Singleton A. (2005). Landfill Gas Emissions Model (LandGEM) Version
419 3.02 User's Guide, US-EPA-600/R-05/047.

420 Babilotte A., Lagier T., Fiani E. & Taramini V. (2010). Fugitive Methane Emissions from Landfills: Field
421 Comparison of Five Methods on a French Landfill. *Journal of Environmental Management* 136, 777-784.

422 Bogner J., Spokas K., Burton E., Sweeney R. & Corona V. (1995). Landfills as atmospheric methane
423 sources and sinks. *Chemosphere* 9, 4119-4130.

424 Börjesson G., Danielsson Ä. & Svensson B.H. (2000). Methane Fluxes from a Swedish landfill
425 Determined by Geostatistical Treatment of Static Chamber Measurements. *Environmental Science &*
426 *Technology* 34, 4044-4050.

427 Börjesson G., Sundh I. & Svensson B.H. (2004). Microbial oxidation of CH4 at different temperatures in
428 landfill cover soils. *FEMS Microbiology Ecology* 48, 305-312.

429 Capelli L., Sironi S., Del Rosso R., Céntola P. & Il Grande M. (2008). A comparative and critical
430 evaluation of odour assessment methods on a landfill site. *Atmospheric Environment* 42, 7050-7058. DOI:
431 10.1016/j.atmosenv.2008.06.009.

432 Capelli L., Sironi S. $ Del Rosso R. (2013). Odor Sampling: Techniques and Strategies for the Estimation
433 of Odor Emission Rates from Different Source Types. *Sensors* 13, 938-955.

434 Cardellini C., Chiodini G., Frondini F., Granieri D., Lewicki J. & Peruzzi L. (2003). Accumulation
435 chamber measurements of methane fluxes: application to volcanic-geothermal areas and landfills. *Applied*
436 *Geochemistry* 18, 45-54.

437 Davoli E., Gangai M.L., Morselli L. & Tonelli D. (2003). Characterization of odorants emissions from
438 landfills by SPME and GC/MS. *Chemosphere* 51, 357-368. DOI: 10.1016/S0045-6535(02)00845-7.

439 Di Trapani D., Di Bella G. & Viviani G. (2013). Uncontrolled methane emissions from a MSW landfill
440 surface: Influence of landfill features and side slopes. *Waste Management* 33, 2108-2115.

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

443 Frechen F.B., Frey M., Wett M. & Löser C. (2004). Aerodynamic performance of a low-speed wind
444 tunnel. *Water Science and Technology* 50, 57-64.

445 Gebert J., Rachor I., Gröngröft A. & Pfeiffer E.M. (2011). Temporal variability of soil gas composition in
446 landfill covers. *Waste Management* 31, 935-945.

447 Hudson N. & Ayoko G.A. (2008). Odour sampling 2. Comparison of physical and aerodynamic
448 characteristics of sampling devices: A review. *Bioresource Technology* 99, 3993-4007.

449 Klenbusch M.R. (1986). Measurement of gaseous emission rates from land surfaces using an emission
450 isolation flux chamber. Radian Corporation. US-EPA.

451 Kumar S., Gaikwad S.A., Shekdar A.V., Kshirsagar P.S. & Singh R.N. (2004). Estimation method for
452 national methane emission from solid waste landfills. *Atmospheric Environment* 38, 3481–3487.

453 Liu, Y., Lu, W., Li, D., Guo, H., Caicedo, L., Wang, C., Xu S. & Wang, H. (2015). Estimation of volatile
454 compounds emission rates from the working face of a large anaerobic landfill in China using a wind
455 tunnel system. *Atmospheric Environment* 111, 213-221.

456 Lucernoni F., Tapparo F., Capelli L. & Sironi S. (2016a). Evaluation of an Odour Emission Factor (OEF)
457 to Estimate Odour Emissions from Landfill Surfaces. *Atmospheric Environment* 144, 87-99.

458 Lucernoni F., Rizzotto M., Tapparo F., Capelli L., Sironi S. & Busini V. (2016b). Use of CFD for static
459 sampling hood design: An example for methane flux assessment on landfill surfaces. *Chemosphere* 163,
460 259-269.

461 Lucernoni F., Capelli L. & Sironi S. (2017). Comparison of different approaches for the estimation of
462 odour emissions from landfill surfaces. *Waste Management 63, 345-353*.

463 McBain M., Warland J., McBride R. & Wagner-Riddle C. (2005). Micrometeorological measurements of
464 N_2O and CH_4 emissions from a municipal solid waste landfill. *Waste Management & Research* 23, 409-
465 419.

466 Mosher B., Czepiel P. & Harriss R. (1999). Methane emissions at nine landfill sites in the northeastern
467 United States. *Environmental Science & Technology* 33, 2088-2094.

468 Palmiotto M., Fattore E., Paiano V., Celeste G., Colombo A. & Davoli E. (2014). Influence of a
469 municipal solid waste landfill in the surrounding environment: Toxicological risk and odor nuisance
470 effects. *Environment International* 68, 16-24. DOI: 10.1016/j.envint.2014.03.004.

471 Park J.W. & Shin H.C. (2001). Surface emissions of landfill gas from solid waste landfill. *Atmospheric*
472 *Environment* 35, 3445–3451.

473 Parker D., Ham J., Woodbury B., Cai L., Spiehs M., Rhoades M., Trabue S., Casey K., Todd R. & Cole
474 A. (2013). Standardization of flux chamber and wind tunnel flux measurements for quantifying volatile
475 organic compound and ammonia emissions from area sources at animal feeding operations. *Atmospheric*
476 *Environment* 66, 72-83.

477 Prata Jr. A.A., Santos J.M., Beghi S.P., Fernandes I.F., Vom Marttens L.L.C., Pereira Neto L.I., Martins
478 R.S., Reis Jr. N.C. & Stuetz R.M. (2016). Dynamic flux chamber measurements of hydrogen sulphide
479 emission rate from a quiescent surface – A computational evaluation. Chemosphere 146, 426-434.

480 Rachor I.M., Gebert J., Grongroft A. & E. & Pfeiffer M. (2013). Variability of methane emissions from
481 an old landfill over different time-scales. *European Journal of Soil Science* 64, 16–26.

482 Reinhart D.R., Cooper D.C. & Walker B.L. (1992). Flux Chamber Design and Operation for the
483 Measurement of Municipal Solid Waste Landfill Gas Emission Rates. *Journal of the Air & Waste*
484 *Management Association* 42, 1067-1070.

485 Renou S., Givaudan J.G., Poulain S., Dirassouyan F. & Moulin P. (2008). Landfill leachate treatment:
486 Review and opportunity. *Journal of Hazardous Materials* 150, 468–493.

487 Romain A.C., Delva J. & Nicolas J. (2008). Complementary approaches to measure environmental odours
488 emitted by landfill areas. *Sensors and Actuators B: Chemical* 131, 18-23.

489 Sarkar U. & Hobbs S.H. (2002). Odour from municipal waste (MSW) landfills: a study of the analysis of
490 perception. *Environment International* 27, 655–662.

491 Scheutz C., Kjeldsen P., Bogner J.E., De Visscher A., Hilger H.A., Huber-Humer M. & Spokas K.
492 (2009). Microbial methane oxidation processes and technologies for mitigation of landfill gas emissions.
493 *Waste Management & Research* 27, 409-455.

494 Schroth M.H., Eugster W., Gómez K.E., Gonzalez-Gil G., Niklaus P.A. & Oester P. (2012). Above- and
495 below-ground methane fluxes and methanotrophic activity in a landfill-cover soil. *Waste Management* 32,
496 879-889.

497 Simpson I.J., Thurtell G.W., Kidd G.E., Lin M., Demetriades-Shah T.H., Flitcroft I.D., Kanemasu E.T.,
498 Nie D., Bronson K.F. & Neue H.U. (1995). Tunable diode laser measurements of methane fluxes from an
499 irrigated rice paddy field in the Philippines. *Journal of Geophysical Research* 100, 7283–7290.

500 Sirini P., Tchobanoglous G. & Noto La Diega R.C. (2010). Ingegneria dei Rifiuti Solidi. P. Roncoroni
501 (ed.), The McGraw-Hill Companies, Chapter 15.

502 Sironi, S., Capelli, L., Centola, P., Del Rosso, R. & Il Grande, M. (2005). Odour emission factors for
503 assessment and prediction of Italian MSW landfills odour impact. *Atmospheric Environment* 39, 5387–
504 5394.

505 Spokas K., Graff C., Morcet M. & Aran C. (2003). Implications of the spatial variability of landfill
506 emission rates on geospatial analyses. *Waste Management* 23, 599–607.

507 Spokas K.A. & Bogner J.E. (2010). Limits and dynamics of methane oxidation in landfill cover soils.
508 *Waste Management* 31, 823-832.

509 United Kingdom Environment Agency, (2010). Guidance on monitoring landfill gas surface emissions.
510 UK-EA.

511 Young P.J. & Parker A. (1983). The identification and possible environmental impact of trace gases and
512 vapours in landfill gas. *Waste Management and Research* 1, 213-226.

513