

1 Methodology to determine the extent of anaerobic
2 digestion, composting and CH₄ oxidation in a
3 landfill environment

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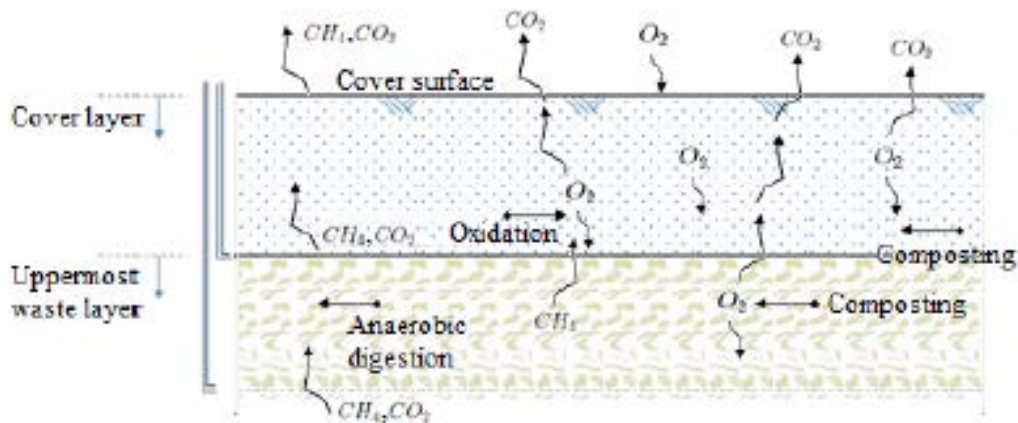
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1 **Highlights:**

- 2 • Composting, digestion and CH₄ oxidation rates were measured in the top 1.6m of two
3 soil capped landfill profiles.
- 4 • Anaerobic and aerobic activity observed simultaneously in a lift of waste for 18 months
5 after placement of interim cover.
- 6 • Composting accounts for 30% of waste degradation for an extended period.
- 7 • Carbon mass balance is improved with stable isotopes ($\delta^{13}\text{C-CO}_2$, $\delta^{13}\text{C-CH}_4$).



23 **Abstract:**

24 An examination of the processes contributing to the production of landfill greenhouse gas
 25 (GHG) emissions is required, as the actual level to which waste degrades anaerobically and
 26 aerobically beneath covers has not been differentiated. This paper presents a methodology to
 27 distinguish between the rate of anaerobic digestion (r_{AD}), composting (r_{COM}) and CH_4 oxidation
 28 (r_{OX}) in a landfill environment, by means of a system of mass balances developed for molecular
 29 species (CH_4 , CO_2) and stable carbon isotopes ($\delta^{13}C-CO_2$ and $\delta^{13}C-CH_4$). The technique was
 30 applied at two sampling locations on a sloped area of landfill. Four sampling rounds were
 31 performed over an 18 month period after a 1.0m layer of fresh waste and 30-50 cm of silty clay
 32 loam had been placed over the area. Static chambers were used to measure the flux of the
 33 molecular and isotope species at the surface and soil gas probes were used to collect gas samples
 34 at depths of approximately 0.5, 1.0 and 1.5m. Mass balances were based on the surface flux and
 35 the concentration of the molecular and isotopic species at the deepest sampling depth. The
 36 sensitivity of calculated rates was considered by randomly varying stoichiometric and isotopic
 37 parameters by $\pm 5\%$ to generate at least 500 calculations of r_{OX} , r_{AD} and r_{COM} for each location in
 38 each sampling round. The resulting average value of r_{AD} and r_{COM} indicated anaerobic digestion

39 and composting were equally dominant at both locations. Average values of r_{COM} ranged from
40 9.8 to 44.5 g CO₂ m⁻² d⁻¹ over the four sampling rounds, declining monotonically at one site and
41 rising then falling at the other. Average values of r_{AD} ranged from 10.6 to 45.3 g CO₂ m⁻² d⁻¹.
42 Although the highest average r_{AD} value occurred in the initial sampling round, all subsequent r_{AD}
43 values fell between 10 and 20 g CO₂ m⁻² d⁻¹. r_{OX} had the smallest activity contribution at both
44 sites, with averages ranging from 1.6 to 8.6 g CO₂ m⁻² d⁻¹. This study has demonstrated that for
45 an interim cover, composting and anaerobic digestion of shallow landfill waste can occur
46 simultaneously.

47 **Keywords:** Aerobic degradation; methane oxidation; composting; anaerobic digestion; mass and
48 isotope balances; landfill.

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51 capped landfill profiles.
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53 placement of interim cover.
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56 **1. INTRODUCTION**

57 Composting in landfilled waste is known to occur at least to the extent supported by O₂ that is
58 entrained with waste as it is placed in a landfill (Bookter and Ham, 1982, Komilis et al., 1999) .
59 However, the actual level to which waste composts beneath covers has not been measured. All
60 waste in a landfill lies at some stage directly beneath a soil cover. As this study demonstrates,
61 neglecting aerobic activity can lead to inflated predictions of CH₄ production and greenhouse
62 emissions, particularly in cases where interim soil covers, which minimises odour, eliminates
63 access to vermin and prevents windblown debris, but cannot eliminate atmospheric O₂ diffusion
64 to the waste layer; thus, supporting aerobic processes for an extended period of time.

65 In a column study by Kallel et al. (2006) using municipal solid waste there was diffusion of
66 O₂ observed through the waste bed. There is further evidence in landfill field trials that O₂ can
67 reach the waste mass, due to natural gas transport. For example, in a landfill constructed on an
68 old quarry site in the United Kingdom, O₂ levels at 10 v/v% were observed at depths of 20 m
69 (Barry et al., 2004). At the Fíflholt landfill, in Iceland, where a final cover of 1-1.2 m (15-25 cm
70 mulch under 1 m of sandy soil) for mature cells spanning 6-10 years, atmospheric O₂ and N₂
71 were observed 80 cm in the waste (Kjeld et al., 2014), with O₂ concentrations reaching 0.75 –
72 16.25 v/v% (average of 8.14 v/v%) and, for N₂, 5.85 – 73.40 v/v% (average of 46.1
73 v/v%).1v/v%) 80 cm into the waste layer (Kjeld et al., 2014).

74 In fact, continuous O₂ migration through the surface may sustain aerobic degradation of both
75 the organic fraction of the cover soil and within shallow waste materials. Aerobic degradation
76 might occur at a uniform depth in a homogeneous fine medium, but given the heterogeneity of
77 buried waste (i.e. bagged waste or large objects) zones of aerobic and anaerobic activity will

78 likely be highly variable. This gives rise to mixed regions of composting and anaerobic digestion
79 within the uppermost layers of the waste mass.

80 Previous studies have developed carbon mass balances to define methane oxidation behaviour
81 in landfill soil covers (Christophersen et al., 2001, Einola et al., 2009, Pedersen et al., 2011).
82 These calculations require an estimation of gas fluxes exiting the surface (CH_4 , CO_2), and
83 upward fluxes from the underlying waste mass that migrates into the cover (CH_4 and CO_2)
84 (Bogner and Spokas, 1993, Gebert et al., 2011, Scheutz et al., 2011). However, gas fluxes at the
85 base of the control volume cannot be measured physically without disturbing the system. This
86 can be overcome by assuming the fluxes of CH_4 and CO_2 are proportional to the concentration of
87 these gases at the base of the cover and that total carbon flux is conserved through the soil cover.

88 The carbon flux is not conserved however if composting is significant. For the purposes of
89 distinguishing composting and methane oxidation others have proposed measuring the rate of
90 composting in separate aerobic incubations of the soil (Scheutz et al., 2011). Instead, the same
91 mass balance approach can be extended to incorporate both composting and anaerobic reactions
92 within the landfill. The determination of the simultaneous rates of anaerobic digestion, CH_4
93 oxidation, and composting in landfill has not been presented in the literature. The logical
94 extension of the carbon balance method would be to develop a method based on mass balances
95 of O_2 , CO_2 and CH_4 (Rafiee et al., 2017). In practice however, it is problematic to measure the O_2
96 flux into the landfill cover with conventional methods.

97 Preliminary findings by Bogner et al. (1996) highlighted the potential use of stable isotopes to
98 characterise aerobic and anaerobic mechanisms in landfills. Bogner et al. (1996) concluded that
99 CH_4 oxidation was the most significant aerobic process, but that it was still plausible for the
100 composting of organic matter to occur in parallel. Stable isotopes have since been applied

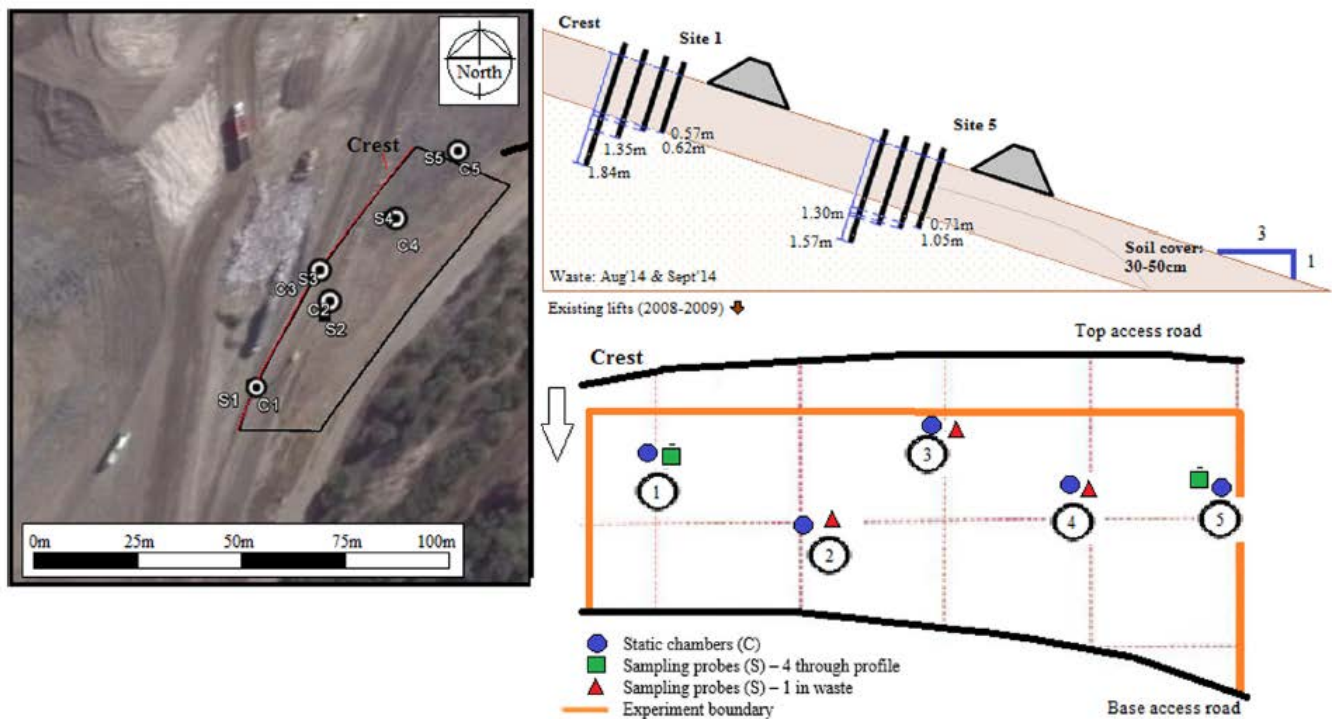
101 extensively in landfills to analyse CH₄ oxidation (Cabral et al., 2010, Cabral and Capanema,
102 2012), with different soil types (Chanton and Liptay, 2000), climatic zones (Chanton et al.,
103 2010), soil texture and porosity (Gebert et al., 2013) and modes of gas transport (De Visscher et
104 al., 2004).

105 It is hypothesised that the rate and extent of anaerobic digestion, CH₄ oxidation and
106 composting within the soil cover and the fresh waste immediately below the cover can be
107 determined by the combination of stable isotope and mass balances for carbon species (CH₄ and
108 CO₂). This is readily obtained from surface flux measurements and sampling of gas and isotope
109 composition through the soil and waste profile to a nominated depth in the field environment.
110 This paper documents the rates of activity derived 4 to 18 months after a layer of fresh waste was
111 placed, compacted and subsequently covered with an interim soil layer of thickness (30 - 50 cm).
112 The calculated rates are lumped values for the combined soil layer and shallow waste zone.
113 Whether this measured activity occurs in the soil or the shallow waste is not distinguished.

114 **2. MATERIALS AND METHODS**

115 **2.1 Description of field site**

116 The experimental site was located on a sloped edge (3:1 vertical to horizontal) of a municipal
117 solid waste landfill in Ipswich, Queensland, Australia (27°39'32.18"S, 152°49'39.77"E). A fresh
118 waste lift was placed over this area in August-September 2014 and was progressively covered
119 with 30-50 cm of silty clay loam (interim cover) as the waste was placed. The lift was placed
120 above pre-existing landfill lifts deposited from 2008 to 2009. Five sampling locations were
121 selected at varying distances from the crest of the slope (Figure 1).



122
123 **Figure 1.** Plan and elevation schematic of field site and installed equipment

124 **2.2 Field sampling and gas analysis**

125 At each selected site, gas samples were collected from a static chamber and nest of soil gas
126 probes. Gas fluxes (CH_4 and CO_2), gas composition profiles (CH_4 , CO_2 , N_2 , O_2) and isotopic
127 abundance profiles ($\delta^{13}\text{C}$ for CH_4 , CO_2 and $\delta^2\text{H} - \text{CH}_4$) were monitored in four sampling
128 campaigns, performed 4 to 18 months after the waste and interim cover were placed. One
129 sampling campaign was performed in each of the four climatic seasons.

130 Gas sampling probes were constructed of stainless steel (SS) 12 mm internal diameter tubes.
131 The top of each spear was fitted with a septa and aluminium crimp and a conical tip at the base.
132 Samples were drawn through four perforated holes at the tip of the spear. Probes were installed
133 at four depths at site 1 (0.57, 0.62, 1.35, and 1.84 m) and site 5 (0.71, 1.05, 1.30, and 1.57 m). At
134 sites 2, 3 and 4 only one probe was installed to track gas composition within the waste (1.65 m at
135 site 2; 1.33 m at site 3 and 1.51 m at site 4).

136 A short-circuiting test was performed using helium as a tracer gas with a Laco Technologies
137 Gas Check G3 leak detector and 3L aluminium shroud placed as a collar over each probe ,
138 sealing a radius of 150mm ground surface around the probe (*see Supplementary materials,*
139 *section A.1*). The dilution factor due to short-circuiting was calculated by the concentration of
140 helium detected in the gas probe sample divided by the helium concentration in the shroud.
141 Based on soil probe guidelines, dilution values less than 5-10% indicate negligible short-
142 circuiting (Ma et al., 2012).

143 The static chambers were fabricated with SS 316 and had a conical geometry (15L, height of
144 0.2m, cross-sectional area of 0.28m²) designed to prevent the formation of stagnant headspace
145 zones (Dever, 2006). Each static chamber was seated on a circular anchor plate that was
146 hammered into the cover soil, which ensured samples were collected from the same locations
147 throughout the study period. A CO₂ infrared gas analyser (EGM-4, PP Systems) system was used
148 to measure CO₂ concentrations on site during static chamber experiments. To avoid creating a
149 vacuum in the chamber, gas that was drawn through the EGM-4 was circulated back into the
150 chamber. The flux of the gas species was calculated from the concentration data (C in ppmv)
151 plotted versus sampling time (t in minutes). The CH₄ and CO₂ data typically observed a linear
152 relationship, with the rate of accumulation of each species (dC/dt) in the chamber expressed as
153 the slope of the fitted line. The gas fluxes were calculated as:

$$154 \quad F \text{ [g/m}^2\text{d]} = PVMU/ATR \text{ (dC/dt)} \quad (1)$$

155 where P = chamber pressure [atm]; V = chamber volume [L]; M = molar mass [g/mol]; U =
156 0.00144 [L min/ μ L d]; A = chamber area [m²]; R = 0.08205 [atm L/mol K]; T = chamber
157 temperature [K]; dC/dt = concentration of gas [ppmv] per unit time [min].

158 The slope of the fitted line (dC/dt) was determined by linear regression of the measured
159 concentrations versus time sampled. Gas fluxes were considered to be reportable if there was a
160 95% confidence ($p < 0.05$) in the correlation between the gas concentrations and time, in a similar
161 fashion to other studies (Barlaz et al., 2004, Abichou et al., 2006, Bogner et al., 2011).

162 All gas samples were collected using gas-tight syringes (SGE Australia) and stored in serum
163 bottles (30mL and 50mL sizes) sealed with 20 mm butyl rubber septa (Rubber BV) and
164 aluminium crimps rather than the commonly used evacuated vials. Gas samples were large
165 enough to first flush the bottle before filling with the sample based on recommendations by
166 Sturm et al. (2015) (*see Supplementary materials section A.2, Table S.2* for flush and injection
167 ratios for each sampling type). Eby et al. (2015) identified that serum bottles provide the best
168 reliability for isotope sampling, with minimal fractionation effects during storage and transport.

169 Molecular gas composition was analysed by gas chromatography (GC) using three replicate
170 injections into a Shimadzu GC-8A FID with 100/120 mesh ShinCarbon ST micropacked column
171 for CO_2 and CH_4 analysis and three replicate injections into a Shimadzu GC-8A TCD with
172 80/100 mesh Mole Sieve 5A column for O_2 and N_2 analysis. Calibration for both GCs was
173 performed using external gas standards obtained from British Oxygen Company (BOC).

174 The isotopic abundances for all samples were determined in the Stable Isotope Geochemistry
175 Laboratory, University of Queensland, using an Isoprime/Agilent Gas Chromatograph-
176 combustion-isotope ratio mass spectrometer (GC-c-IRMS). The $\delta^{13}C$ and δ^2H values (per
177 mil, ‰) were normalised to the Vienna Pee Dee Belemnite (VPDB) and VSMOW scales
178 respectively, following a 2-point normalisation for $\delta^{13}C$ and δ^2H using a combination of
179 international reference gases (Oztech: $\delta^{13}CO_2$: -40.75‰, -3.59‰ and δ^2H : -125‰, -365‰) and
180 laboratory CH_4 and CO_2 standards. The reproducibility for $\delta^{13}C$ is ± 0.3 ‰ and for δ^2H ± 4.0 ‰

181 at one standard deviation. Additional details on the analytical equipment, procedure and
182 calibration can be found in (Baublys et al., 2015).

183 **2.3 Determination of isotopic parameters for key processes**

184 Microorganisms typically metabolise the lighter isotopic forms of key substrates, which gives
185 rise to preferential effects called isotopic fractionation. The degree to which lighter isotopic
186 forms are preferentially metabolised is characteristic for each biochemical process (Kendall and
187 McDonnell, 2012). The characterisation of fractionation factors is usually performed via the
188 Rayleigh approach by closed system incubations with samples at field conditions (Coleman et
189 al., 1981, Liptay et al., 1998).

190 The fractionation factor for CH₄ oxidation has been shown to be dependent on temperature
191 (Scheutz et al., 2009). A correlation for the effect of temperature on the degree of fractionation
192 for CH₄ oxidation in a clay soil was developed by Chanton and Liptay (2000):

$$193 \quad \alpha \quad (2)$$

194 where α_{OX} is the adjusted fractionation factor, T is the temperature of the cover[°C].

195 In anaerobic digestion, this process is described by two parameters: the apparent fractionation
196 factors for stable carbon and hydrogen isotopes (Whiticar, 1999) . The isotopic composition of
197 the biogas produced will depend on the isotopic composition of the organic solids and the
198 preferential uptake by the dominating methanogenesis pathway. The fractionation factor for the
199 anaerobic digestion reaction in terms of the carbon system is:

$$200 \quad \text{—————} \quad (3)$$

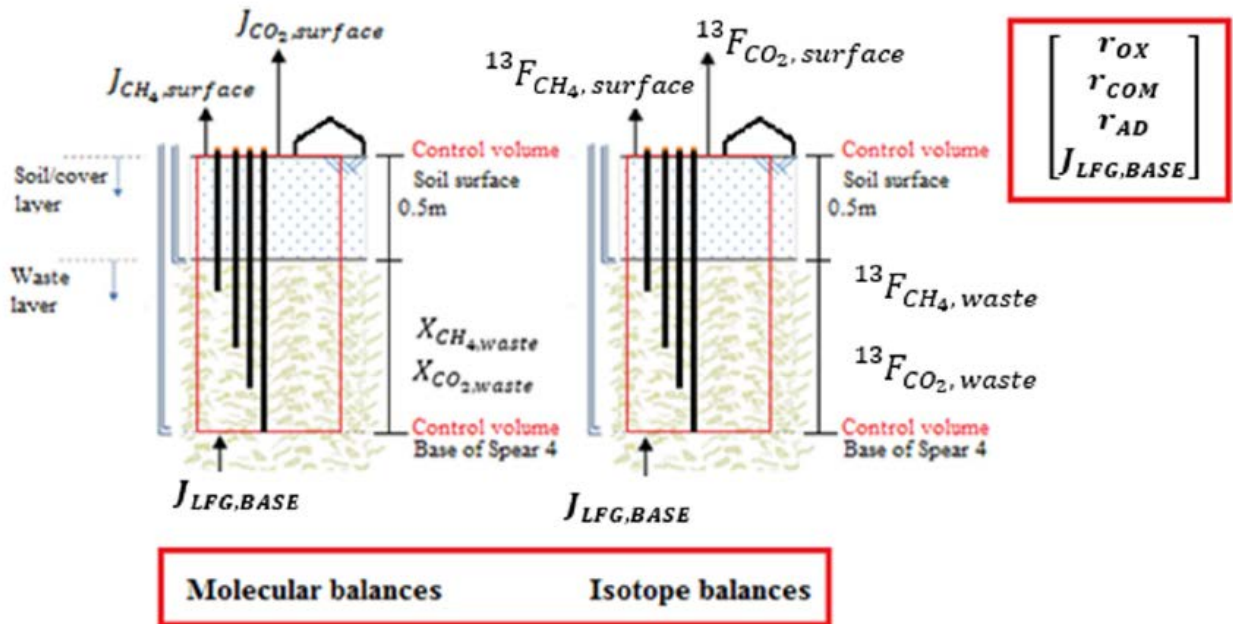
201 where $\delta^{13}C_{CO_2}$ and $\delta^{13}C_{CH_4}$ are the stable isotopes of ^{13}C in CO_2 and CH_4 produced by the
202 anaerobic region of the ecosystem. In this study, gas sampled at the deepest depth, which marked
203 the base of the control volume were used to calculate α_{AD} .

204 In contrast, composting organisms have no preferential bias towards ^{12}C or ^{13}C (O'Leary, 1981,
205 Corbett et al., 2013). Therefore, the ratio of $^{13}C-CO_2$ and $^{12}C-CO_2$ in the gas produced from
206 composting reflects the ratio of these isotopes in the organic carbon substrate (O'Leary, 1981,
207 Corbett et al., 2013). It is difficult to determine the direct measurement of the organic carbon
208 signature in waste due to heterogeneity. Instead, waste was sampled from the fresh lift at the
209 field site and incubated under composting assay conditions, with the carbon isotopic composition
210 of headspace gas CO_2 sampled from three incubations (33) as described by Rafiee et al. (2017).

211 **2.4 Mass and isotope balances**

212 The control volume for the mass balance includes the soil cover and the top 1.6 m of waste
213 beneath the cover as presented in Figure 2. Despite the landfill being a complex system with an
214 array of biochemical processes, to gain an insight into aerobic and anaerobic degradation, this
215 was simplified. Three different reactions are proposed to occur in these layers, namely anaerobic
216 digestion (r_{AD}), CH_4 oxidation (r_{OX}) and composting (r_{COM}). Anaerobic digestion was treated as
217 a lumped process, rather than a combination of by acetoclastic and hydrogenotrophic
218 methanogenesis mechanisms, as it was desired to identify the overall rate of anaerobic activity.
219 In addition, the composting activity described by the mass balance is predominately related to
220 the aerobic degradation of the waste, with the contribution of soil respiration considered to be
221 minimal. At this particular landfill, the interim soil cover was composed of relatively sterile and
222 coarse material. Furthermore, CO_2 uptake by photosynthesis was not addressed in this
223 formulation because the interim cover at this landfill site had no to limited vegetation present.

224 The described rates (r_{AD} , r_{OX} and r_{COM}) have been previously estimated in laboratory reactors
 225 that contained packed beds of waste overlain with soil sourced from the same landfill (Rafiee et
 226 al., 2018). These rates were determined from the measurement of the net fluxes of CH₄, CO₂, O₂
 227 and ¹³C-CO₂ with mass balances for each of these four components. The mass balance equations
 228 comprised an overdetermined system for the 3 unknowns, r_{AD} , r_{OX} and r_{COM} . Therefore, the rates
 229 were estimated as fitting parameters, optimised by Excel Solver ® with the Generalised
 230 Reduction Gradient nonlinear algorithm to minimise the Root Mean Square Error, with the
 231 constraint that all rates were positive.



232
 233 **Figure 2.** Required data to estimate r_{AD} , r_{OX} and r_{COM} over control volume

234 O₂ uptake cannot be measured in the field, because drawdown in O₂ cannot be measured
 235 within static chambers. Instead, balances were developed for the molecular (CH₄ and CO₂) and
 236 isotope species (¹³C-CO₂ and ¹³C-CH₄). The surface fluxes measured by the static chamber
 237 method were assumed to be steady over the 15-minute measurement period, implying that the

238 measured gas fluxes reflect reaction rates at the time, with negligible mass transfer delays.
 239 Therefore, the steady state condition was assumed for the mass balances. The general mass
 240 balance equation is (Eq. 4):

241 (4)

242 where J_i is the flux of species i into the fresh lift base of waste [$\text{g m}^{-2} \text{d}^{-1}$], $J_{i,s}$ is the flux of
 243 species i at the surface of the cover [$\text{g m}^{-2} \text{d}^{-1}$] and R_i is the net generation rate of species
 244 i as a result of n reaction processes, rate [$\text{g m}^{-2} \text{d}^{-1}$] describes the n reactions that species i is
 245 either produced or consumed in, with $\nu_{i,n}$ referring to the stoichiometric coefficient of species
 246 affiliated with the specific reaction.

247 Reaction rates were expressed in terms of CO_2 [$\text{g CO}_2 \text{ m}^{-2} \text{d}^{-1}$] as it is a common product in the
 248 three reaction processes. The dissolution of CO_2 due to moisture was not an effect as at steady
 249 state conditions the water would be saturated with CO_2 . The normalised stoichiometric
 250 coefficient Ψ_i can be expressed on a mass basis (Eq 5):

251 (5)

252 where a_i is the stoichiometric coefficient of species i [mol]; a_{CO_2} is the stoichiometric
 253 coefficient of CO_2 [mol]; MW_i is the molecular weight of species i [g]; MW_{CO_2} is the molecular
 254 weight of CO_2 [g]. The normalised stoichiometric equations for the three reactions are:



257 **Composting:** (8)

258 For the development of isotope balances, the fractional abundance (F) notation was used (Fry,
259 2003). For example, ^{13}F designates the fractional abundance of $^{13}C = ^{13}C / (^{13}C + ^{12}C)$. This can
260 also be defined in terms of the δ notation and isotopic ratios (R), as follows (Eq. 9):

261 _____ (9)

262 Carbon isotopic balances (eq. 10) were developed in a similar way to standard mass balances
263 (Eq 4), with isotopic flows in ($^{13}F_{in,i}$) and out ($^{13}F_{out,i}$) of the system defined by gas samples
264 collected at these points. An additional consideration for each biochemical reaction (r_j) is
265 whether there is an associated isotopic value ($^{13}F_{reaction}$) or fractionation factor ($\alpha_{reaction}$) to
266 account for the consumption or production terms.

267 (10)

268 The flux into the base of the control volume cannot be measured directly. Conservation of
269 carbon flux through the control volume cannot be assumed, as in calculation for CH₄ oxidation in
270 soil covers, because gaseous carbon is generated from the composting and anaerobic digestion
271 reactions. The carbon flux at the base of the control volume could be calculated as a complex
272 function of the total carbon flux at the base, and the rates of reaction that yield gaseous carbon
273 within the control volume, r_{AD} and r_{COM} .

274 Instead, a formulation is proposed which considers that the flux of each component at the base
275 of the control volume expressed as a mass fraction (X) and a total mass flow of landfill gas, ($J_{LFG,$
276 $BASE}$). $J_{LFG, BASE}$ becomes an additional variable and a unique solution can be found for r_{AD} , r_{OX} ,

277 r_{COM} and $J_{LFG, BASE}$ from the four mass balances. Solutions are considered only when r_{AD} , r_{OX} and
 278 $r_{COM} > 0$. The full set of equations is:

$$\begin{bmatrix}
 1 & 1 & 1 & X_{CO_2, waste} \\
 -\Psi_{CH_4, OD} & 0 & \Psi_{CH_4, AD} & X_{CH_4, waste} \\
 F_{solid} \alpha_{AD} \alpha_{OX} & F_{solid} & F_{solid} \alpha_{AD} & X_{CO_2, waste} {}^{13}F_{CO_2, waste} \\
 -F_{solid} \alpha_{AD} \alpha_{OX} \Psi_{CH_4, OX} & 0 & F_{solid} \alpha_{AD} \Psi_{CH_4, AD} & X_{CH_4, waste} {}^{13}F_{CH_4, waste}
 \end{bmatrix} \cdot \begin{bmatrix} r_{OX} \\ r_{COM} \\ r_{AD} \\ J_{LFG, BASE} \end{bmatrix}$$

$$= \begin{bmatrix} J_{CO_2, surface} \\ J_{CH_4, surface} \\ {}^{13}F_{CO_2, surface} J_{CO_2, surface} \\ {}^{13}F_{CH_4, surface} J_{CH_4, surface} \end{bmatrix} \quad (11)$$

279

280 where all terms have been previously defined.

281 2.5 Model application

282 The field observations and input parameters required to apply mass balances are summarised
 283 in Tables 1 and 2. It is difficult to obtain precise stoichiometries of biochemical processes in a
 284 dynamic and heterogeneous environment like a landfill. For the reaction stoichiometries of
 285 composting, anaerobic digestion and CH₄ oxidation, averages were adopted from the proof of
 286 concept laboratory study by Rafiee et al. (2017). The average stoichiometries and F_{solid} applied in
 287 the model are shown in Table 2. For the application of the model, the field data obtained from
 288 Sites 1 and 5 was utilised.

289 To determine the uncertainty in the calculated rates and test the robustness of the model, a
 290 $\pm 5\%$ perturbation was applied to the all model parameters (reaction stoichiometries $\varphi_{CH_4, OD}$,
 291 $\varphi_{CH_4, AD}$ and isotopic terms of F_{solid} for composting, and fractionation factors α_{AD} and α_{OX}). In
 292 particular, with the sensitivity analysis conducted, the two pathways of methanogenesis were

293 considered by performing mass balances with a range of isotopic fractionation factors for
 294 anaerobic digestion that covered both the hydrogenotrophic and acetoclastic pathways.

295 A uniform distribution population for each parameter was generated using SIMLAB® with
 296 500 entries per parameter (*Supplementary materials, section A.3*). Combinations of perturbed
 297 values were chosen randomly, from the uniformly distributed populations of each model
 298 parameter over the $\pm 5\%$ range to equally weight extreme and mean values.

299 **Table 1.** Field observations and independently determined parameters utilised in mass balance

Parameter	Type	Source
$J_{CH_4, surface}$	Gas flux of CH ₄ at the surface	Chamber ^a
$J_{CO_2, surface}$	Gas flux of CO ₂ at the surface	Chamber ^a
$X_{CH_4, waste}$	Gas composition CH ₄ at lift base	Soil gas probe ^a
$X_{CO_2, waste}$	Gas composition CO ₂ at lift base	Soil gas probe ^a
$^{13}F_{CH_4, waste}$	Carbon isotope CH ₄ at lift base	Soil gas probe ^a
$^{13}F_{CO_2, waste}$	Carbon isotope CO ₂ at lift base	Soil gas probe ^a
$^{13}F_{CH_4, surface}$	Carbon isotope CH ₄ at surface	Chamber ^a
$^{13}F_{CO_2, surface}$	Carbon isotope CO ₂ at surface	Chamber ^a
α_{OX}	Fractionation factor: CH ₄ oxidation	Soil temperature ^b
α_{AD}	Fractionation factor: digestion	Soil gas probe ^c

300 ^a obtained by gas sampling; ^b defined by clay-temperature regression equation (Eq. 2) ^c defined
 301 by apparent fractionation factor equation (Eq. 3) for carbon based on probe 4 data

302 **Table 2.** Average values of stoichiometric parameters applied in the mass balance model

Parameter	Type	Source	Value
$\Psi_{CH_4,OX}$	Coefficient CH ₄ : CH ₄ oxidation	Reactor ^a	0.970
$\Psi_{CH_4,AD}$	Coefficient CH ₄ : digestion	Reactor ^a	0.461
F _{solid}	Carbon isotope CO ₂ produced from composting of MSW	Batch ^b	0.01084

303 ^aBased on (Rafiee et al., 2018); ^bBased on (Rafiee et al., 2017).

304 **3. RESULTS AND DISCUSSION:**

305 **3.1 Differentiation of activity types based on isotopic data**

306 Table 3 summarises the variations with time of molecular and isotopic gas compositions at the
 307 soil surface and at the deepest spear in the waste, i.e. 1.84 m and 1.57 m depth from the top of
 308 the waste layer at site 1 and site 5, respectively. Compositional data from sampling probes were
 309 corrected by the dilution factors from short-circuiting testing as described (Table S.1
 310 *Supplementary materials*). Overall, the impact of short-circuiting, ranged from 1-15%, which
 311 was accounted for in analyses. Given the packing density of the waste at the facility, settlement
 312 of the waste mass was anticipated to be minimal and as such the conditions of the soil gas probes
 313 were not expected to deteriorate in the remainder of the experimental study.

314 The predominant reactions within the control volume can be interpreted directly from the data
 315 in Table 3, where the boundary conditions at the base of the waste lift and at the surface of the
 316 landfill are examined. The compositional gas trends within the waste at both sampling sites are
 317 similar. The isotopic abundance varied between approximately -55.4‰ to -59.5‰ (¹³δC-CH₄) and
 318 -279‰ to -306‰ (²δH-CH₄), which is comparable to expected ranges for deep landfill

319 environments (Hackley et al., 1996, Chanton et al., 2005). This seems to indicate that anaerobic
320 digestion was the predominant activity within the waste zone of the control volume (Whiticar et
321 al., 1986, Whiticar, 1999). For static chamber samples obtained at the soil surface, the molecular
322 composition had relatively equal CH₄ and CO₂ volume fractions. The emitted value of $\delta^{13}\text{C-CH}_4$
323 varied by less than 15% at both sites which would imply constant fractionation associated with
324 anaerobic digestion(Chanton et al., 2007).

325 The $^{13}\delta\text{C-CO}_2$ values at both monitored sites revealed some additional information about
326 processes within the control volume. The emitted $\delta^{13}\text{C-CO}_2$ values from the soil surface evolved
327 from -1.1 ‰ to +12.0 ‰, while $\delta^{13}\text{C-CO}_2$ values from the waste layer remained within a
328 narrower range, i.e. between 15.1 and 18.2 ‰ across the two sites and over all sampling events.
329 These isotopic shifts are consistent with results reported by Baedecker and Back (1979) and
330 (Hackley et al., 1996) who found that $\delta^{13}\text{C-CO}_2$ values for young (<1 – 2 years), intermediate (2
331 – 7 years) and mature (7 – 12 years) landfill cells ranged from -5.1 ‰ to +12.4 ‰, +15‰, and
332 +16 ‰ to +12.4 ‰, respectively. It was expected that that the $\delta^{13}\text{C-CO}_2$ signature for freshly
333 landfilled organic waste would reflect values ranging from -10 ‰ to -30 ‰, which are typical of
334 terrestrial plants (O'Leary, 1981, Corbett et al., 2013). Once methanogenesis is well established,
335 constant input of isotopically heavy $^{13}\text{C-CO}_2$ causes an increase in the $\delta^{13}\text{C-CO}_2$ signature from
336 the initial values that are representative of composting alone (Hackley et al., 1996) . The increase
337 with time in $\delta^{13}\text{C-CO}_2$ values suggests that there is a diminishment in the proportion of aerobic
338 activity and an establishment of anaerobic digestion.

339 **Table 3.** Gas composition at mass balance boundaries: the soil surface and within the waste*

Campaign	Layer	Site 1					Site 5				
		CO ₂	CH ₄	$\delta^{13}\text{C-CO}_2$	$\delta^{13}\text{C-CH}_4$	$\delta^2\text{H-CH}_4$	CO ₂	CH ₄	$\delta^{13}\text{C-CO}_2$	$\delta^{13}\text{C-CH}_4$	$\delta^2\text{H-CH}_4$
		[%]	[%]	[‰]	[‰]	[‰]	[%]	[%]	[‰]	[‰]	[‰]
Jan'15	Surface	0.32	0.33	6.3	-54.5	n.d	0.37	0.41	-0.5	-49.7	n.d
	Waste	13.4	34.0	n.d	n.d	n.d	25.9	38.3	16.6	-55.4	n.d
Sept'15	Surface	0.41	0.45	0.7	-59.0	n.d	0.15	0.12	-1.1	-67.4	n.d
	Waste	33.9	50.2	15.1	-59.4	-305	34.5	50.4	18.2	-59.3	-282
May'16	Surface	0.29	0.39	4.3	-55.2	n.d	0.24	0.32	9.7	-57.0	n.d
	Waste	31.8	47.4	16.5	-59.5	-306	34.2	48.0	17.6	-59.1	-283
June'16	Surface	0.20	0.15	9.1	-54.0	n.d	0.23	0.22	12.0	-55.2	n.d
	Waste	34.5	52.9	16.8	-59.5	-305	35.2	50.3	17.0	-59.0	-279

340 *Results presented here reflect the boundary conditions utilised for the mass balance model at the bottom of the waste lift (spear 4) and at the landfill surface
341 (static chamber). The measurement of gas concentrations from the waste layer are average values of three replicates from spear 4 depth; surface measurements
342 are average values of duplicates for static chamber experiments; depth 0m = surface of landfill. For additional data relating to the spear profiles at study site refer
343 to *Supplementary materials section A.6* for O₂ gas composition and precision indicated in *Supplementary materials section A.6*, full gas composition and
344 precision presented in thesis; precision for $\delta^{13}\text{C} \pm 0.3\text{‰}$, $\delta^2\text{H} \pm 3\text{‰}$ at 1 standard deviation. The standard deviation in the relative error of CO₂, CH₄ was less than
345 10%.

346 **3.2 Evolution of surface gas fluxes**

347 The CH₄ and CO₂ flux trends at sites 1 and 5 are summarised in Table 4. All CH₄ gas fluxes,
 348 with the exception of the June'16 measurement at site 1, can be classified as high (i.e. fluxes >25
 349 g CH₄ m⁻²d⁻¹, based on the classification system proposed by Abichou et al. (2006). The CO₂
 350 fluxes are around 100 g CO₂ m⁻² d⁻¹ during the entire monitoring period. These persistently high
 351 levels of CO₂ gas flux could be indicative of aerobic behaviour within the waste mass. In
 352 particular, the CO₂ gas flux observed in Jan '15 (221 g CO₂ m⁻² d⁻¹) is characteristic of windrow
 353 composting facilities (250 – 2900 g CO₂ m⁻² d⁻¹; (Andersen, 2010)). The only other study that
 354 has monitored the evolution of gas composition from a freshly placed waste layer was performed
 355 by Bogner et al. (2011), who suggested that the CO₂ fluxes observed from soil covered fresh
 356 waste (50 - 250 g CO₂ m⁻² d⁻¹) was indicative of aerobic respiration activity occurring.

357 **Table 4.** Summary of gas fluxes at primary locations for model

Campaign	Site 1		Site 5	
	CH ₄ Flux	CO ₂ Flux	CH ₄ Flux	CO ₂ Flux
	[g CH ₄ m ⁻² d ⁻¹]	[g CO ₂ m ⁻² d ⁻¹]	[g CH ₄ m ⁻² d ⁻¹]	[g CO ₂ m ⁻² d ⁻¹]
Jan'15	n/a	n/a	90 ± 20	221 ± 49
Sept'15	47 ± 6	158 ± 11	30 ± 2	79 ± 60
May'16	54 ± 1	143 ± 39	79 ± 58	162 ± 99
June'16	12 ± 2	91 ± 44	93 ± 21	186 ± 40

358 Note: ± denotes the 95% confidence interval based on non-zero flux hypothesis test similar to
 359 Barlaz et al. (2004).

360 **3.3 Isotope fractionation factors based on heuristics from field data**

361 The fractionation factors for CH₄ oxidation and anaerobic digestion, α_{OX} and α_{AD} are listed in
 362 Table 5. Values of α_{OX} were calculated using Eq 2, which is a function of temperature only. α_{OX}
 363 for Jan '15 was significantly lower than other values, due to the much higher temperature
 364 prevailing in Jan '15 (31.0 °C). For the process of anaerobic digestion, calculation of the
 365 Whiticar (1999) apparent carbon fractionation factor (α_{AD}), expressed in Eq 3, revealed that, at
 366 site 1 and 5, the dominant methanogenesis pathway was CO₂ reduction (hydrogenotrophic),
 367 rather than acetoclastic methanogenesis as $\alpha_{AD} > 1.065$.

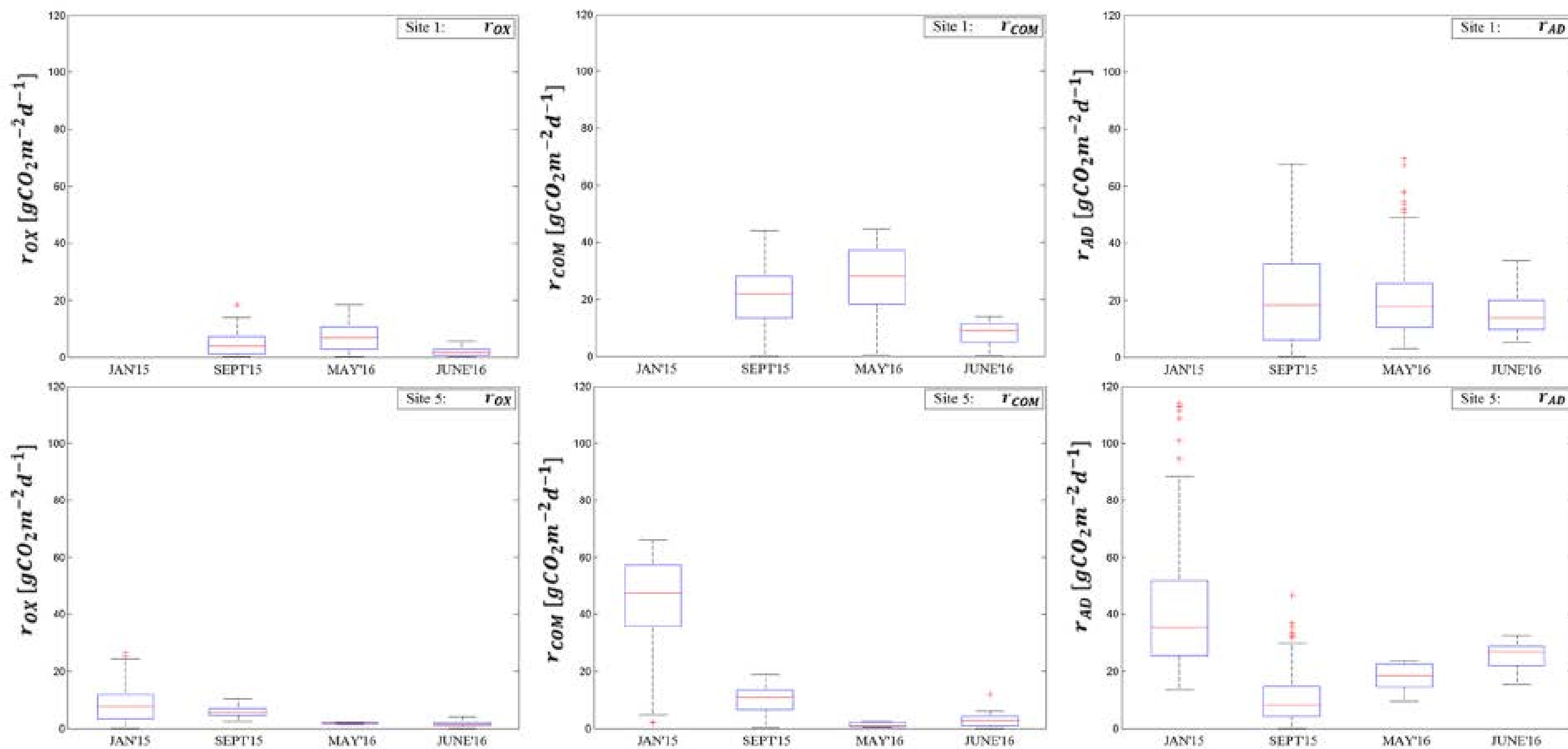
368 **Table 5.** Fractionation factors used in the mass balance model

Campaign	Site 1			Site 5		
	T [°C]	α_{OX}	α_{AD}	T [°C]	α_{OX}	α_{AD}
Jan'15	n.d.	n.d.	n.d.	31.0	1.029 ±	1.076 ±
				±0.5	0.001	0.020
Sept'15	25.7	1.031	1.078	21.5	1.033 ±	1.082 ±
	±0.5	±0.001	±0.022	±0.5	0.001	0.019
May'16	26.1	1.031	1.082	25.8	1.031 ±	1.065 ±
	±0.5	±0.001	±0.020	±0.5	0.001	0.019
June'16	23.8	1.032	1.081	23.7	1.032 ±0.001	1.081 ±
	±0.5	±0.001	±0.020	±0.5		0.020

369 Note: Temperature values presented were maximums measured at each monitoring location
 370 with a portable temperature probe. Error was propagated for calculated fractionation factors.

371 **3.4 Model application to uppermost layer of waste**

372 Figure 3 presents the distribution of solutions for r_{AD} , r_{OX} and r_{COM} for sites 1 and 5, from 4-18
373 months after waste placement. The rates are expressed in terms of CO₂ production [g CO₂ m⁻² d⁻¹].
374 Outliers (indicated by the symbol '+' in Figure 3) were defined as lying outside of $\pm 2.698\sigma$ of
375 the overall mean value for each rate, for the 500 simulations. The summary statistics for r_{OX} ,
376 r_{COM} , r_{AD} and $J_{LFG, BASE}$ are shown in Tables 6-8.



377 **Figure 3.** Distribution of r_{ox} , r_{COM} and r_{AD} predicted by the mass balance method for (a) Site 1 and (b) Site 5. No data was collected for Site 1 in January 2015. Outliers indicated by “+” defined by the $\pm 2.698\sigma$
 378 constraint.

379 The results in Figure 3, Tables 6 and 7 clearly indicate that CH₄ oxidation (r_{OX}), whose average
380 rates ranged from 1.6 to 8.6 g CO₂ m⁻² d⁻¹, was the least important of the three reactive processes.
381 r_{AD} spanned averages from 10.6 to 45.3 g CO₂ m⁻² d⁻¹ at site 5 and is less pronounced at site 1.
382 The lower level of r_{AD} behaviour in site 1 was anticipated, since site 1 is located close to the crest
383 of the landfilled slope, where it is more likely that desiccation cracks provided a pathway for O₂
384 migration into the waste mass, therefore sustain aerobic activity.

385 It is difficult to make comparisons with CH₄ oxidation efficiencies determined in landfill cover
386 systems, as this depends on the CH₄ load entering the cover, the age of the waste lift and the
387 geophysical characteristics of the cover. The r_{OX} values predicted by the mass balance technique
388 can be expressed in units of CH₄ consumption (g CH₄ m⁻²d⁻¹), by using the average
389 stoichiometric ratio $\Psi_{CH_4,OX}$. This results in a CH₄ consumption rate at site 1 and 5 spanning
390 from 0 – 4.7 g CH₄ m⁻²d⁻¹. It is encouraging that the CH₄ oxidation rates predicted by the mass
391 balance are similar to those found by Einola et al. (2009) (2.7- 4.8 g CH₄ m⁻²d⁻¹) for a bio-cover
392 with peat and sludge compost (40:60v/v%) submitted to low biogas loads of 0.7 – 2.7 g CH₄ m⁻²
393 d⁻¹.

394 The CH₄ load to the base of the control volumes were estimated from the predicted inlet gas
395 flux average ($J_{LFG, BASE}$) and the measured gas composition at the base of the waste lift (Table 3).
396 The CH₄ loads for sites 1 and 5 ranged from 31 to 98 g CH₄ m⁻²d⁻¹, which was similar in nature to
397 flux activity described in daily and intermediate covered waste in other studies Bogner et al.
398 (2011). Since the mass balance method was applied to the shallowest layer of waste on a lift, it is
399 understandable that the oxidation capacity of the system is poor (0-40%) when r_{OX} is evaluated
400 against the initial CH₄ load.

401 For both sites, the mass balance model indicated that the aerobic activity diminished towards
 402 the end of the trial, with r_{AD} becoming a more dominant process. r_{COM} had a unique trend at each
 403 location. At site 1, composting was more pronounced towards the middle of the monitoring
 404 period (between Sept'15 and May'16), and peaked with a mean of $27.1 \text{ g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ 17 months
 405 after waste placement (May'16). There was a rapid decrease in r_{COM} during the last monitoring
 406 month (June'16), with the average composting rate decreasing to $8.1 \text{ g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$.

407 **Table 6.** Summary of r_{OX} , r_{COM} and r_{AD} values calculated for Site 1

Month	Mean Rate \pm Uncertainty [$\text{g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$]						Number of valid solutions
	r_{OX}	\pm	r_{COM}	\pm	r_{AD}	\pm	
Sept'15	4.6	0.6	20.6	1.6	20.9	2.8	139
May'16	7.2	0.5	27.1	1.3	20.0	1.4	302
June'16	2.1	0.3	8.1	0.8	15.0	1.3	99

408 **Table 7.** Summary of r_{OX} , r_{COM} and r_{AD} values calculated for Site 5

Month	Mean Rate \pm Uncertainty [$\text{g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$]						Number of valid solutions
	r_{OX}	\pm	r_{COM}	\pm	r_{AD}	\pm	
Jan'15	8.6	1.0	44.5	2.4	41.9	3.5	170
Sept'15	5.9	0.3	9.8	0.7	10.6	1.4	145
May'16	1.8	0.3	1.3	0.8	18.0	5.0	5
June'16	1.6	0.4	3.1	1.2	45.3	30.3	18

409 At site 5, r_{COM} had a maximum average of $44.5 \text{ g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$, 4 months after waste placement
 410 (Jan' 15) and decreases exponentially with time, levelling off at $1.3 \text{ g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ from May' 16.

411 This is consistent with the source of O₂ being dominated by air that was entrained with the waste
 412 at placement. The residual level of r_{COM} after May '16 could be indicative of composting as the
 413 result of ongoing O₂ migration through the soil cover into the waste layer.

414 The predicted $J_{LFG, BASE}$ values are all positive (*Supplementary materials, section A.5, Figure*
 415 *S.6*), which is anticipated as the pre-existing waste lifts would likely be contributing a gas
 416 production flux of CO₂ and CH₄ from anaerobic digestion. Site 1 appears to have consistent
 417 average $J_{LFG, BASE}$ values, with site 5 observing no clear trends in behaviour. The number of
 418 solutions that were retained towards the end of the analysis declined because r_{OX} and r_{COM}
 419 became relatively small compared to r_{AD} , leading to a high proportion of solutions to the mass
 420 balances that violate the constraint of r_{AD}, r_{OX} and $r_{COM} > 0$. Furthermore, the actual reactions
 421 occurring in the waste and in the soil, are likely to vary from the assumed stoichiometry. This
 422 effect will be more pronounced for composting and anaerobic digestion where the amount of O₂
 423 consumed in composting (de Bertoldi et al., 1983) and the production ratio of CH₄/CO₂ in
 424 anaerobic digestion will be different for fats, carbohydrates and protein (Mata-Alvarez et al.,
 425 2000).

426 **Table 8.** Summary of $J_{LFG, BASE}$ average values calculated for Site 1 and 5

Month	Mean Flow ± Uncertainty [g LFG m ⁻² d ⁻¹]	
	Site 1	Site 5
Jan'15	n.d	446 ± 6
Sept'15	182 ± 4	105 ± 2
May'16	185 ± 2	269 ± 2
June'16	126 ± 2	286 ± 3

427

428 **3.5 Supporting evidence of ongoing aerobic activity at field site**

429 Despite the differences in location on the working face and waste composition, the mass
430 balance calculations presented herein revealed that aerobic activity forms a large proportion of
431 early phase activity (4-18 months) in the uppermost layer of waste at this landfill site. It is
432 particularly noteworthy that the results in Figure 3 clearly indicate that anaerobic activity can
433 occur simultaneously with aerobic reactions, such as CH₄ oxidation and composting and that
434 these processes continue to co-exist for an extended time (12-18 months). For site 5, a
435 comparable magnitude of r_{COM} and r_{AD} is present for the first 12 months to (Sept'15). The
436 average values for r_{COM} and r_{AD} for site 1 suggest that composting and anaerobic digestion are
437 ongoing at similar rates 18 months after waste placement. This ongoing level of aerobic activity
438 within the waste layer may reflect the difficulty of compacting soil covers on landfill slopes.

439 Indeed, O₂ levels were consistently observed at 2-5 v/v% at points in the soil cover and waste
440 layers from January 2015 to September 2016, at all sampling locations (Obersky et al., 2015) .
441 For the last two months of monitoring, the trends in O₂ were examined dynamically, with full
442 distribution presented in *Supplementary materials, section A.6*. Site 5 had reduced levels of O₂
443 ingress to 0.4 - 0.6 v/v% and these appeared to stabilise. In contrast, site 1 had variable levels of
444 O₂, with fluctuations from 0.53 – 1.50 v/v% across the May and June 2016 campaigns. Given
445 this supply of O₂ into the shallow waste, it is plausible that ongoing composting could occur in
446 parallel with anaerobic digestion, for a sustained period (>18 months).

447 The contribution of composting and anaerobic digestion to the degradation of the shallow waste
448 can be converted to a chemical oxygen demand (COD) basis rather than CO₂ basis (g CO₂ m⁻² d⁻¹

449 ¹⁾ as indicated in Table 9 and 10 below.

450 **Table 9.** Composting and anaerobic digestion degradation of waste for Site 1

Month	Mean Rate of O ₂ Consumption [g COD m ⁻² d ⁻¹]			Percentage of waste degraded by [%]	
	r _{OX}	r _{COM}	r _{AD}	COM	AD
Sept'15	17.8	15.0	38.6	28.0	72.0
May'16	27.9	19.7	36.9	34.8	65.2
June'16	8.1	5.9	27.7	17.6	82.4

451
452 **Table 10.** Composting and anaerobic digestion degradation of waste for Site 5

Month	Mean Rate of O ₂ Consumption [g COD m ⁻² d ⁻¹]			Percentage of waste degraded by [%]	
	r _{OX}	r _{COM}	r _{AD}	COM	AD
Jan'15	33.4	32.4	77.3	29.5	70.5
Sept'15	22.9	7.1	19.6	26.7	73.3
May'16	7.0	0.9	33.2	2.8	97.2
June'16	6.2	2.3	83.6	2.6	97.4

453
454 For example, with anaerobic digestion, the conversion is achieved by multiplying the
455 degradation rate (g CO₂ m⁻² d⁻¹) by the stoichiometric coefficient $\Psi_{CH_4,AD}$ and the COD of CH₄
456 (4.0 g COD/g CH₄). Expressing r_{COM} on a COD basis requires the stoichiometric relationship
457 between O₂ consumption and CO₂ production in the composting reaction. For the purposes of
458 these calculations, it is assumed the degradable organic waste has the composition of cellulose.
459 It is evident that in the first 12 months after waste placement composting comprises
460 approximately 30% of waste degradation and gasified COD conversion, with this value declining

461 for the last two sampling rounds. These percentages are indicative of the activity observed at the
462 time of sampling, rather than a cumulative degradation percentage.

463 The mass balance model has indicated for site 1 and 5 that r_{COM} was of a similar rate to r_{AD} on
464 the basis of CO_2 production for at least the first year after waste placement, equivalent to
465 approximately 25% of the COD depletion being attributable to composting over the same period.
466 This is contrary to the conceptualisation of early age (1-2 years) landfill behaviour formulated in
467 the IPCC model (IPCC, 2006) and landfill gas generation models like LANDGEM (Thorneloe
468 et al., 1999) where composting is either neglected or only considered as a rapid short term
469 process during the first stage of landfill degradation. This study highlights that CH_4 oxidation,
470 composting and anaerobic digestion are significant in newly developed waste lifts.

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480 article.

481 **SUPPORTING INFORMATION AVAILABLE**

482 A.1 Short circuiting testing configuration and correction factors, A.2 Sample flush
483 technique, A.3 Parameters generated by Simlab ® for use in mass balance, A.4 Oxygen
484 composition information for profile in field trial, A.5 J_{LFG, BASE} results for site 1 and 5, A.6
485 Dynamic oxygen profiles in field trial.

486 This material is available free of charge via the Internet at <http://pubs.acs.org>.

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