

1 **Degradation of biogas in a simulated landfill cover soil at laboratory**
2 **scale: Compositional changes of main components and volatile organic**
3 **compounds**

4 Antonio Randazzo^{a,b,*}, Francesca Zorzi^a, Stefania Venturi^{a,b}, Gabriele Bicocchi^a, Gregorio
5 Viti^a, Fabio Tatàno^c, Franco Tassi^{a,b}

6
7 *^aDepartment of Earth Sciences, University of Florence, Via G. La Pira 4, 50121 Firenze,*
8 *Italy*

9 *^bIGG - Institute of Geosciences and Earth Resources, CNR - National Research Council of*
10 *Italy, Via G. La Pira 4, 50121 Firenze, Italy*

11 *^cDiSPeA - Department of Pure and Applied Sciences, Section ChEM - Chemistry,*
12 *Environment, and Materials, University of Urbino “Carlo Bo”, Campus Scientifico “E.*
13 *Mattei”, 61029 Urbino, Italy*

14
15 * Corresponding author. Department of Earth Sciences, University of Florence, Via G.
16 La Pira 4, 50121, Firenze, Italy. E-mail: antonio.randazzo@unifi.it (A. Randazzo).

17
18 Submitted to Waste Management

19
20
21 **Keywords:** *Anaerobic digestion, Biogas, Degradation, Landfill gas, Landfill cover soil,*
22 *VOCs*

23 **Abstract**

24 A laboratory experiment lasting 28 days was run to simulate a typical landfill system and
25 to investigate the compositional changes affecting the main components (CH₄, CO₂, and
26 H₂) and nonmethane volatile organic compounds from biogas generated by anaerobic
27 digestion of food waste and passing through a soil column. Gas samples were periodically
28 collected from both the digester headspace and the soil column at increasing distances
29 from the biogas source. CH₄ and H₂ were efficiently degraded along the soil column. The
30 isotopic values of $\delta^{13}\text{C}$ measured in CH₄ and CO₂ from the soil column were relatively
31 enriched in ¹³C compared to the biogas. Aromatics and alkanes were the most abundant
32 groups in the biogas samples. Among these compounds, alkylated benzenes and long-
33 chain C₃₊ alkanes were significantly degraded within the soil column, whereas benzene
34 and short-chain alkanes were recalcitrant. Terpene and O-substituted compounds were
35 relatively stable under oxidising conditions. Cyclic, alkene, S-substituted, and halogenated
36 compounds, which exhibited minor amounts in the digester headspace, were virtually
37 absent in the soil column. These results pointed out how many recalcitrant potentially
38 toxic and polluting compounds tend to be relatively enriched along the soil column,
39 claiming action to minimise diffuse landfill gas (LFG) emissions. The proposed
40 experimental approach represents a reliable tool for investigating the attenuation capacities
41 of landfill cover soils for LFG components and developing optimised covers by adopting
42 proper soil treatments and operating conditions to improve their degradation efficiencies.

43 **1. Introduction**

44 Landfilling represents the most common option for municipal waste (MW) management
45 on a global scale, also in the expected temporal projection by 2050 (Chen et al., 2020a).
46 However, the costs of measures needed to mitigate the potential environmental impacts

47 from landfilling may be relevant (Nahman, 2011; Rabl et al., 2008). In fact, two potential
48 contaminating outputs, i.e., leachate and landfill gas (LFG), are generated during the
49 lifetime of a landfill by the degradation of deposited heterogeneous waste categories
50 (Allen et al., 1997). Among these waste categories, the organic fraction of MW (OFMW),
51 which primarily consists of food waste (FW) (Panigrahi and Dubey, 2019), poses major
52 concerns for landfill management since its moisture content and biodegradability may
53 contribute significantly to LFG and leachate generation (Alibardi and Cossu, 2015;
54 Campuzano and González-Martínez, 2016).

55 LFG consists mainly of CO₂ and CH₄ (Tassi et al., 2009), followed by other relevant
56 components such as N₂, O₂, and H₂ (Muñoz et al., 2015), and it includes small fractions (<
57 1% by vol) of nonmethane volatile organic compounds (hereafter, VOCs) (Duan et al.,
58 2021). CH₄ in LFG accounts for greenhouse gas emissions (Capaccioni et al., 2011).
59 Several VOCs are recognised as potential pollutants contributing to (i) negative
60 tropospheric impacts, (ii) the greenhouse effect, (iii) photochemical smog, and (iv)
61 groundwater contamination (Martí et al., 2014; Nair et al., 2019; Ravina et al., 2020).
62 Some of the VOCs have also demonstrated carcinogenic effects or a strong odorous
63 impact (Cogliano et al., 2011; Gallego et al., 2012).

64 Placement of soil-based covers on landfill surfaces represents the most economical and
65 reliable method for reducing diffuse LFG emissions into the atmosphere (Majdinasab and
66 Yuan, 2017). Landfill cover soils (i) host active populations of methanotrophic bacteria
67 (Cébron et al., 2007; Kjeldsen and Scheutz, 2018) and (ii) sustain the growth and
68 development of different bacterial communities that metabolise selected VOCs (Alvarez-
69 Cohen and McCarty, 1991; Alvarez-Cohen and Speitel, 2001). Degradation processes and
70 related microbial activities leading to LFG attenuation in landfill cover soils are generally
71 explored through (i) in situ measurements or (ii) laboratory experiments. The former

72 approach is based on chemical analyses of interstitial gas samples collected at different
73 depths along vertical profiles within full-scale landfill cover soils whose physicochemical
74 and biological parameters are expected to vary in both horizontal and vertical directions
75 (Tassi et al., 2009; Randazzo et al., 2020; Scheutz et al., 2008). Instead, laboratory
76 experiments are carried out by investigating the degradation rates of selected gases
77 contained in artificial simplified gas mixtures by using soil incubations and simulated soil
78 columns under optimal conditions (e.g., Scheutz and Kjeldsen, 2003, 2004, 2005).

79 The use of gas mixtures in laboratory experiments that have physicochemical
80 characteristics close to the characteristics of typical LFG is necessary to improve the
81 comprehension of biochemical mechanisms for degrading of LFG components in landfill
82 cover soil.

83 This study concerns a laboratory experiment designed and optimised to reliably simulate a
84 landfill system consisting of a digester filled with degrading FW and connected to a soil
85 column in which the generated biogas is degraded under oxidising conditions. Gas
86 samples from the digester headspace and the soil column were periodically collected and
87 analysed to monitor the temporal evolution of the composition of biogas released by the
88 digester and to investigate the fates of the biogas components (CH_4 , CO_2 , H_2 , VOCs, and
89 isotopic signatures in $^{13}\text{C-CO}_2$ and $^{13}\text{C-CH}_4$) within the soil column. The aims of this
90 study were (i) to evaluate the relative efficiencies of biodegradation processes occurring
91 within a cover soil for the different LFG components and (ii) to provide an indication of
92 the effective mitigation of the diffuse LFG emissions into the atmosphere.

93 **2. Biodegradation processes of LFG in soils**

94 Gaseous components in soils undergo several biodegradation processes triggered by soil
95 enzymes (Bilen and Turan, 2021). Under aerobic conditions, CH_4 is effectively oxidised

96 by methanotrophic bacteria. This reaction is catalysed by the nonspecific CH₄
97 monooxygenase (MMO) enzyme, which is also found to react with aromatic and aliphatic
98 compounds, including those containing halogen atoms (Alvarez-Cohen and McCarty,
99 1991; Alvarez-Cohen and Speitel, 2001; Hanson and Hanson, 1996). Accordingly, many
100 aromatics are removed efficiently from landfill cover soils hosting methanotrophic
101 communities (Merouani et al., 2022; Qin et al., 2020a, 2020b). Unspecific MMO
102 enzymes, as well as aromatic-specific monooxygenase or dioxygenase genes, catalyse the
103 breaking of the C–H chemical bonds in the aromatic ring through a complex series of
104 reactions, such as epoxidation, hydrolysis, dehydrogenation, and hydroxylation (Su et al.,
105 2014), which form highly toxic pyrocatechol and phenol byproducts (Lee et al., 2011;
106 Nunes-Halldorson et al., 2004).

107 Various microorganisms can metabolise alkanes under aerobic conditions. In particular,
108 degradation of C₂-C₁₇ alkanes is carried out by different microbial enzymes depending on
109 the molecular chain length (Wang and Shao, 2013). Specifically, C₂-C₄ alkanes are
110 degraded by microorganisms having enzymes such as MMO, while degradation of C₅-C₁₇
111 alkanes involves enzymes containing soluble cytochrome P450s and integral-membrane
112 non-heme iron monooxygenase (AlkB). Aerobic degradation pathways for *n*-alkanes may
113 proceed through terminal and subterminal chain oxidation (Rojo, 2009). Terminal chain
114 oxidation starts with hydroxylation of the final methyl group to produce a primary alcohol
115 that is converted to an aldehyde and finally to a fatty acid. Subterminal chain oxidation
116 proceeds through hydroxylation of a secondary carbon atom and generates a secondary
117 alcohol that is converted to the corresponding ketone and then to an ester. The ester is then
118 hydrolysed to produce an alcohol and a fatty acid. Accordingly, the contents of alkanes
119 and O-substituted compounds in interstitial gases from landfill cover soils are expected to
120 show an inverse correlation (Randazzo et al., 2020; Tassi et al., 2009).

121 The fates of cyclics and alkenes in landfill cover soils are expected to be similar to the
122 fates of alkanes (Randazzo et al., 2020), with both organic groups catabolised by MMO
123 and alkane hydroxylases (Abbasian et al., 2015; Van Beilen and Funhoff, 2007).

124 Laboratory experiments have demonstrated that numerous chloro-, chlorofluoro-, and
125 hydrochlorofluoro-carbon compounds can be cometabolised by methanotrophic bacteria
126 under physicochemical conditions similar to the conditions expected for landfill cover
127 soils (Jechorek et al., 2003; Koh et al., 1993; Schuetz et al., 2003). Under aerobic
128 conditions, chlorocarbons are degraded at a lower rate as the Cl/C ratios increase, and
129 fully chlorinated aliphatics, as well as F-containing compounds, are poorly degraded
130 (Scheutz et al., 2004).

131 Biochemical processes degrading S-substituted VOCs exhibiting significant
132 concentrations in LFG, such as dimethylsulfide (DMS), dimethyldisulfide (DMDS), and
133 methanethiol (MT) (Duan et al., 2021), have been investigated extensively over the past
134 decades (e.g., De Bok et al., 2006; Phae and Shoda, 1991; Xia et al., 2014), since these
135 compounds contribute significantly to the odourous impact (Liu et al., 2018; Piccardo et
136 al., 2022). Different microbial communities, especially methanotrophs and sulfur-
137 oxidising bacteria (Lee et al., 2012, 2017, 2018), remove sulfur-reduced compounds in
138 landfill cover soils (Pecorini et al., 2020). Biochemical reactions involving different
139 enzymes can affect DMS, DMDS, MT, and dimethylsulfoxide (DMSO), mostly producing
140 formaldehyde which, in turn, is assimilated into the biomass or converted to CO₂ and H₂S
141 (Schäfer et al., 2010).

142 Little is known about the fate of terpenes in landfill cover soils, although some basic
143 studies have shown that these compounds can be significantly biodegraded under aerobic
144 conditions (Misra and Pavlostathis, 1997; Misra et al., 1996).

145 **3. Materials and methods**

146 *3.1. Materials*

147 The FW was collected from the household and food service sectors and sorted into the
148 following components: fruit, vegetable, pasta/rice, bread/bakery, meat/fish, dairy, and
149 other (i.e., food not falling into the previous components). The relative amounts (Table 1)
150 were combined to approximate an indicative FW composition for the Italian situation (De
151 Laurentiis et al., 2018; Zhang et al., 2013). The FW sample was macerated with an electric
152 blender to decrease the substrate size and enhance biodegradation (Carchesio et al., 2014;
153 Zhang et al., 2014) and stored for 1 day at room temperature (25 °C) in 1 L bottles with no
154 headspace.

155 The inoculum (INO), which was collected from a municipal wastewater treatment plant
156 located in Central Italy, consisted of anaerobic sludge derived from the anaerobic
157 digestion (AD) stage.

158 The natural soil was collected from a periurban forest at an altitude of 250 m above sea
159 level (a.s.l.) after removal of the surface layer (approximately 20 cm thick). The resulting
160 grain size distribution was determined by following the recommendations of the American
161 Society for Testing and Materials (ASTM 1998, 2007). The soil granulometric classes
162 consisted of (% by wt): 11.5% gravel, 62.2% sand, 22.4% silt, and 3.9% clay.
163 Consequently, the soil was identified as silty sand according to the Unified Soil
164 Classification System. In the laboratory, the soil was manually milled and sieved with a 2-
165 mm mesh.

166 *3.2. Experimental setup*

167 The experimental apparatus used to simulate a landfill system was constructed following
168 the indications from previous studies (Kightley et al., 1995; Scheutz and Kjeldsen, 2005).

169 The apparatus consisted of (1) a 20-L tank (hereafter: digester) coupled with (2) a dark

170 polypropylene (PP) cylinder (height = 105 cm, inner diameter = 7 cm) (hereafter: soil
171 column) (Fig. 1). The adopted volume of the digester was within the wide range of 0.1 to
172 120 L derivable in the literature for reactor volumes used to perform anaerobic
173 biodegradability batch assays (Raposo et al., 2011a). The digester was filled with a FW-
174 INO mixture (1:1 on a volatile solid basis; Carchesio et al., 2014), and a small (< 1 L)
175 headspace was left. INO addition was functional to provide the necessary microorganisms
176 for allowing AD to proceed (Angelidaki and Sanders, 2004). No control digester with INO
177 as a blank was set because the experimental procedure did not require quantification of
178 CH₄ production specifically attributable to the FW substrate (Angelidaki and Sanders,
179 2004; Carchesio et al., 2014). The soil column was packed from the bottom with (i) gravel
180 (15-cm thick) and (ii) the considered wet soil (90-cm thick). The bottom of the cylinder
181 was tapped with a dark PP plate equipped with an inlet port connected to the digester
182 through a silicone tube (inner diameter = 3 mm). At the top of the digester, the silicone
183 tube connector was equipped with a three-way stopcock for biogas sampling. The top of
184 the soil column remained uncapped to allow free escape of the biogas and the interaction
185 with the above air environment, as expected at full-scale in a landfill. The gravel layer,
186 consisting of calcareous stones (diameter = 0.5 cm), was placed to homogenise biogas
187 fluxes. The soil column was equipped with six sampling ports, placed along the vertical
188 axis (spaced 15 cm except the upper one at 7.5 cm), where 5.5 cm long polyamide tubes
189 (inner diameter = 4 mm) were inserted up to the middle of the inner cylinder diameter and
190 connected to three-way stopcocks on the outside. The experiment was performed outdoors
191 (i.e., under a roof in the internal courtyard of the Department of Earth Sciences at the
192 University of Florence) during the summer season (27 ± 6 °C) and lasted 28 days. This
193 duration time was close to the mean of 32 days resulting from an international
194 interlaboratory study on anaerobic biodegradability tests for organic substrates (Raposo et

195 al., 2011b). Additionally, this duration time was consistent with the 30-day period for
196 anaerobic biodegradability tests first recommended by Owen et al. (1979) to ensure, in
197 most cases, complete decomposition of biodegradable substrates. To prevent temperature
198 variations, the digester was placed within a polystyrene box.

199 Once filled with the FW-INO mixture, the digester was closed and placed for 1 day at 25
200 °C. Following this initial time (hereafter, day 0), the digester was connected to the soil
201 column after flushing the biogas through the connection tube to avoid air contamination.
202 Periodically, the digester was gently shaken to homogenise the mixture.

203 *3.3. Gas sampling and analysis*

204 Gas samples from the digester and the six ports along the soil column were collected twice
205 a week using a 60-mL Luer lock syringe (Beroject III[®]) and transferred into 12-mL glass
206 vials (Labco Exetainer[®], Manhattan, KS, USA) equipped with a pierceable rubber caps.
207 The glass vials were prefilled with deionised water and acidified with ultrapure HCl to
208 avoid CO₂ dissolution, which was displaced by the biogas entering the vials through a
209 needle inserted into the cap. With this procedure, air contamination in the soil column was
210 minimised by pulling out small gas volumes (~ 20 mL).

211 The main gaseous components (CO₂, CH₄, N₂, H₂, O₂, and Ar) were analysed using a
212 Shimadzu 15A gas chromatograph (GC) with a thermal conductivity detector (TCD)
213 (Shimadzu, Columbia, MD, USA). CH₄ at concentrations < 0.05% by vol and light
214 hydrocarbons (C₂-C₃) were analysed using a Shimadzu 14A GC with a flame ionisation
215 detector (FID) (Shimadzu, Columbia, MD, USA). The analytical errors for both GC-TCD
216 and GC-FID were < 5%.

217 Carbon isotopic signatures (¹³C/¹²C) in CO₂ (δ¹³C-CO₂) and CH₄ (δ¹³C-CH₄), expressed as
218 ‰ vs. V-PDB, were analysed by cavity ring-down spectroscopy (CRDS) using a Picarro

219 G2201-i analyser (Picarro, Santa Clara, CA, USA). The analytical error for CRDS was <
220 1.15‰ vs. V-PDB.

221 C₄₊ VOCs were analysed according to the solid-phase microextraction (SPME) method
222 (Arthur and Pawliszyn, 1990) using a Thermo Trace Ultra GC combined with a Thermo
223 DSQ quadrupole mass spectrometer (MS) (ThermoFisher Scientific, Waltham, MA,
224 USA). The SPME fibre, consisting of a divinylbenzene and carboxen -
225 polydimethylsiloxane assembly (Supelco; Bellefonte, PA, USA), was exposed to the
226 samples (stored into the vials) for 15 min. C₄₊ VOCs absorbed by the fibre were desorbed
227 into the headspace of the GC and passed to the quadrupole MS. GC/MS operating settings
228 are described in detail in Tassi et al. (2009). C₄₊ VOCs were identified from the retention
229 times of the chromatographic peaks and by comparing the mass spectra with the mass
230 spectra database of the National Institute of Standards and Technology library (NIST,
231 2005). Quantitative analyses were performed with an external standard calibration
232 procedure based on calibration curves created by analysing standard mixtures containing
233 different organic functional groups, as described by Tassi et al. (2012). The limit of
234 quantification and the relative standard deviation (RSD) were determined by linear
235 extrapolation from the lowest standard used for the calibration curve adopting the area of a
236 peak with a signal/noise ratio of 5, and from five replicate analyses of the standard
237 mixtures, respectively. The RSD values were < 5%.

238 **4. Results**

239 The concentrations of CO₂, CH₄, H₂, N₂, Ar, and O₂, the values of ¹³C/¹²C ratios in CO₂
240 and CH₄, and the compositions of VOCs in the gas samples collected from the digester
241 and the soil column are reported in Table S1 (Supplementary material).

242 *4.1. Composition of main gaseous components and values of $\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CH}_4$*

243 Carbon dioxide, CH₄, and H₂ in the biogas from the headspace of the digester ranged from
244 34.3 to 64.1%, from 1.72 to 24.1%, and from 0.01 to 15.3% by vol, respectively (Table
245 S1, Supplementary material). N₂, O₂, and Ar ranged from 17.0 to 58.7%, from 0.02 to
246 4.50%, and from 0.21 to 0.72% by vol, respectively (Table S1, Supplementary material).
247 The $\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CH}_4$ values ranged from -22.6 to 4.1‰ and from -48.8 to -25.1‰
248 vs. V-PDB, respectively (Table S1, Supplementary material).

249 Gases from the soil column showed relatively low CH₄, CO₂, and H₂ concentrations
250 (ranging from 0.005 to 0.93%, from 0.73 to 2.6%, and from 0.001 to 0.29% by vol,
251 respectively) and high N₂, Ar, and O₂ contents (ranging from 79.3 to 95.4%, from 0.97 to
252 1.19%, and from 0.41 to 18.9% by vol, respectively) (Table S1, Supplementary material).
253 In particular, the CH₄, CO₂, and H₂ concentrations decreased as the O₂ contents increased
254 towards the top of the soil column. In contrast, N₂ and Ar concentrations as well as $\delta^{13}\text{C-}$
255 CO₂ and $\delta^{13}\text{C-CH}_4$ values (ranging from -13.1 to 12.2‰ and from -55.5 to 17.1‰ vs. V-
256 PDB, respectively: Table S1, Supplementary material) fluctuated with no identifiable
257 vertical trends.

258 *4.2. Composition of VOCs*

259 Up to 50 VOCs were measured in the biogas samples from the headspace of the digester,
260 and the sums on the different sampling days ranged from 7,230 to 130,840 ppbv (Table
261 S1, Supplementary material). VOCs were dominated by aromatics (mainly toluene) and
262 alkanes (mostly ethane), which represented up to 58 and 45% of the total VOC
263 concentration (ΣVOCs), respectively (Fig. 2). Terpenes ranged from 0.03 to 4.6% ΣVOCs
264 (Fig. 2), whereas cyclic and O-substituted species were up to 0.48 and 0.20% ΣVOCs ,
265 respectively. Alkene, halogenated, and S-substituted compounds were < 0.03% ΣVOCs .

266 Overall, the interstitial gas samples collected along the soil column showed total amounts
267 of VOCs (from 12 to 1,664 ppbv: Table S1, Supplementary material) significantly lower
268 than the FW biogases and strongly decreasing upwards. VOCs detected in the soil column
269 consisted of alkanes, aromatics, terpenes, and O-substituted compounds in proportions that
270 varied over time and along the vertical profile, ranging from 29 to 86%, from 2.6 to 51%,
271 from 3.7 to 46%, and from 3.7 to 29% Σ VOCs, respectively (Fig. 2). Alkenes and cyclics
272 (< 0.43% Σ VOCs) occurred sporadically, while halogenated and S-substituted compounds
273 were not detected.

274 **5. Discussion**

275 *5.1. Main gaseous components and carbon isotopic signature ($\delta^{13}\text{C-CH}_4$ and $\delta^{13}\text{C-CO}_2$)*

276 *5.1.1. Temporal evolutions in the digester headspace*

277 The AD process of the FW substrate proceeded during the whole experiment, as shown by
278 the relatively high concentrations of the main AD-related components (AD_c , i.e., CO_2 ,
279 CH_4 , and H_2 : Angelidaki and Batstone, 2010) compared to those of the air-related
280 components (air_c , i.e., N_2 , O_2 , and Ar) in the biogas samples collected from the headspace
281 of the digester (Fig. 3a). As expected, the lowest AD_c/air_c ratio was measured at the
282 beginning of the experiment (Fig. 3a) due to the initial air contained in the digester
283 headspace. In the following days, the AD_c/air_c ratio increased abruptly until day 6, then it
284 remained almost constant until day 17, dropped drastically on day 20 and increased again
285 until the end of the experiment (Fig. 3a). The negative peak that occurred on day 20 (Fig.
286 3a) suggested a strong decrease in biogas production that favoured air entering the
287 digester. The increase in the AD_c/air_c ratio in the last week (Fig. 3a) may have indicated a
288 slight renewal of the AD process. The increase seen for the N_2/O_2 ratio up to day 17 (Fig.

289 3b) was consistent with the overall decrease in the air_c in the first part of the experiment
290 (Fig. 3a). This trend was likely dictated by (i) effective rinsing of the digester headspace
291 by the relatively high biogas outflow and (ii) relative consumption of O_2 by microbial
292 consortia in the earliest steps (i.e., hydrolysis and acidogenesis) of the AD process (Chen
293 et al., 2020b; Nguyen and Khanal, 2018). In the last week of the experiment, the N_2/O_2
294 ratio decreased (Fig. 3b), possibly indicating that air contamination, occurred on day 20,
295 continued in the following days, notwithstanding the biogas production showing a slight
296 renewal (Fig. 3a).

297 The evolution of the biogas composition in the digester headspace depended on the
298 balance between the biogas moving upwards and the air descending from the soil column.
299 The former was driven mostly by convection due to the slight overpressure caused by the
300 ongoing AD process; the latter was due mainly to diffusion caused by the strong
301 concentration gradient of the air components. Accordingly, the reduction in biogas
302 production that occurred after the first two weeks of the experiment caused a decrease in
303 biogas convection, which allowed air diffusion into the digester headspace. In agreement
304 with the trends seen for the AD_c/air_c and N_2/O_2 ratios (Fig. 3a, 3b), the CH_4/CO_2 ratio in
305 the digester headspace showed an increasing trend until day 17, followed by a decreasing
306 trend (Fig. 3c), with the methanogenesis process hindered by increasing O_2 (Botheju and
307 Bakke, 2011). This temporal pattern was consistent with the composition of biogas
308 produced by the AD process in previous experiments (Brown et al., 2012; Chen et al.,
309 2020c). The CH_4/CO_2 ratios measured in this experiment (ranging from 0.05 to 0.5; Fig.
310 3c) were lower than the CH_4/CO_2 ratios generally expected for organic substrates (0.5-3.9;
311 Poulsen and Adelard, 2016; Poulsen et al., 2017). This may have been related to different
312 aspects, such as chemical composition of the FW as well as operating conditions,
313 including temperature and the substrate to inoculum ratio (Capson-Tojo et al., 2016;

314 Gunaseelan, 2004; Negri et al., 2020). The low carbon to nitrogen ratio and high
315 biodegradability generally seen with FW (Bong et al., 2018; Zhao et al., 2021) may inhibit
316 methanogenic activity, leading to (i) excessive release of free ammonia that may damage
317 bacterial cell membranes (Zhao et al., 2021) and (ii) quick accumulation of volatile fatty
318 acids (VFAs) that may decrease the pH and limit the development of methanogens (Kawai
319 et al., 2014; Ye et al., 2018; Yuan et al., 2019). However, the relatively high H₂/CH₄ ratios
320 recorded in the digester headspace from day 3 to day 17 (Fig. 3d) suggested that the low
321 CH₄/CO₂ ratios were probably related to dominating AD steps such as acidogenesis and
322 acetogenesis (Greses et al., 2021). Indeed, these steps produce relatively high amounts of
323 CO₂ and H₂ (D' Silva et al., 2021). However, these two compounds promote CH₄
324 production since they are consumed by hydrogenotrophic methanogens (Guo et al., 2010;
325 Zhang et al., 2020) or autotrophic acetogens that provide the acetate substrate for
326 acetoclastic methanogenesis (Valdez-Vazquez and Poggi-Varaldo, 2009).

327 The methanogenesis pathways occurring during the AD process may be conveniently
328 reconstructed by investigating the stable carbon isotopic signature in CO₂ and CH₄
329 (Conrad, 2005). In particular, acetate dismutation was the main pathway generating CO₂
330 and CH₄ in the first two weeks, as the corresponding $\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CH}_4$ values were
331 consistent with those generally expected for acetoclastic methanogenesis (from -30 to -0
332 ‰ vs. V-PDB and from -30 to -15 ‰ vs. V-PDB, respectively: Polag et al., 2015;
333 Randazzo et al., 2020) (Fig. 3e). In contrast, hydrogenotrophic methanogenesis, which is
334 generally characterised by isotopically heavier C-CO₂ and lighter C-CH₄ (up to 20 ‰ vs.
335 V-PDB and from -60 to -40 ‰ vs. V-PDB, respectively: Polag et al., 2015; Randazzo et
336 al., 2020), may have been the major process generating CO₂ and CH₄ in the last days of
337 the experiment (Fig. 3e). This change suggested that, after day 13 (Fig. 3e), acetate was
338 largely consumed, and CO₂ started to degrade. However, the CH₄/CO₂ ratio decrease seen

339 from day 17 (Fig. 3c) indicated the possible occurrence of other concomitant processes
340 (leading to net CO₂ production) that may involve oxidation of CH₄, as suggested by the
341 concurrent, progressive decrease in the N₂/O₂ ratio (Fig. 3b).

342 5.1.2. Features along the soil column

343 The temporal evolutions of the AD_c/air_c ratios in the interstitial gas samples collected at
344 the selected depths along the soil column were consistent with the temporal evolution of
345 biogas production, which showed a peak on day 17 (Fig. 4a), i.e., just before biogas
346 production decreased. Therefore, in the first 17 days, the flow of biogas from the digester
347 counteracted air permeation from the top of the soil column. After day 17, when biogas
348 production in the digester decreased, interstitial soil pores were rapidly enriched in the air_c
349 (Fig. 4a). According to these considerations, the experiment consisted of two phases: (i)
350 high biogas production from the beginning to day 17 of the experiment (hereafter, the HB
351 period) and (ii) low biogas production, after day 17 to the conclusive day (hereafter, the
352 LB period).

353 In both periods, interstitial soil gas samples were largely dominated by air, as indicated by
354 the low AD_c/air_c ratios that even decreased upwards (i.e., at increasing distances from the
355 digester) (Fig. 4a). This was accompanied by a general decrease in the (CH₄+H₂)/CO₂
356 ratios towards the top of the soil column (Fig. 4b). This evidence indicated that advective
357 transport (Scheutz et al., 2009) of biogas along the aerobic soil column was associated
358 with microbial degradation of CH₄ and H₂ within the soil by different microbial consortia
359 (Hanson and Hanson, 1996; Schuler and Conrad, 1990), while CO₂ was less reactive,
360 representing the byproduct of CH₄ oxidation (Pratt et al., 2013). The occurrence of
361 oxidation processes was also supported by the N₂/O₂ ratios, which were higher than that of
362 air, especially in the deepest part (> 45 cm depth) of the soil column (Fig. 4c). During the

363 HB period, the $(\text{CH}_4+\text{H}_2)/\text{CO}_2$ ratio showed a relatively low decrease towards the top of
364 the soil column with respect to the following LB period (Fig. 4b), indicating that when
365 biogas production in the digester was relatively high, its convection through the soil
366 column was more efficient, counteracting the aerobic degradation of the reduced gas
367 species (He et al., 2008; Randazzo et al., 2020).

368 Notably, no clear trend was observed for the H_2/CH_4 ratio along both (HB and LB)
369 vertical profiles (Fig. 4d), indicating that the degradation processes likely affected these
370 gaseous components to comparable extents. The distinct H_2/CH_4 ratios in the HB and LB
371 profiles properly reflected the H_2/CH_4 ratios of the biogas source in the pertaining
372 temporal periods (Fig. 4d).

373 The $\delta^{13}\text{C}-\text{CO}_2$ and $\delta^{13}\text{C}-\text{CH}_4$ values were generally higher than those revealed in the
374 biogas from the digester (Fig. 4e, 4f); this was expected, since microorganisms prefer to
375 metabolise ^{12}C , resulting in the enrichment of both $^{13}\text{C}-\text{CO}_2$ and $^{13}\text{C}-\text{CH}_4$ in the residual
376 gases (Randazzo et al., 2020). The lower $^{13}\text{C}-\text{CO}_2$ enrichment in the HB profile with
377 respect to LB may have been due to the heavier CO_2 provided by biogas in the last period
378 (Fig. 4e). Similarly, the higher values of $\delta^{13}\text{C}-\text{CH}_4$ in the HB profile were related to the
379 heavier CH_4 released by the AD process in the first 17 days (Fig. 4f).

380 5.2. VOCs

381 5.2.1. Generation by AD of FW

382 In the biogas samples from the digester headspace, the temporal evolution of the total
383 concentration of VOCs (Fig. 5a) was consistent with biogas production; it increased in the
384 HB period and decreased in the following LB period.

385 In particular, aromatics, which dominated the overall VOC chemical composition in all
386 the biogas samples (Fig. 5a), showed the highest relative amounts in the HB period and

387 declined from day 17 (Fig. 5a) when benzene started to enrich on alkylated benzenes
388 (Σ alkylbenzenes) (Fig. 5b). Presumably, O_2 entering from day 17 into the headspace of the
389 digester (Fig. 3b) promoted degradation of the aromatic compounds by preferentially
390 oxidising the alkylated compounds. Indeed, alkylated benzenes such as toluene,
391 ethylbenzene, and xylene are recognised to be more degradable than benzene because their
392 substituent groups are easily attacked by microorganisms (El-Naas et al., 2014). The
393 presence of relatively high contents of aromatics in the FW biogas samples (Fig. 5a) was
394 not surprising, considering that several compounds of this group have been detected in
395 cheese, beef, fish, eggs, fruits, and dairy and bakery products (Fleming-Jones and Smith,
396 2003; Qian and Reineccius, 2002). Moreover, vegetables, fruits, and cereals contain high
397 levels of lignin (Tao et al., 2020), a natural aromatic polymer whose degradation may
398 release a wide variety of aromatic compounds (Kamimura et al., 2019). Finally, the
399 presence of aromatic compounds in foods may potentially be associated with
400 environmental pollution or contamination by food processing procedures. In fact, aromatic
401 compounds may: (i) be absorbed by fruits and vegetables, including apples, blackberries,
402 cucumbers, spinaches, cabbages, lettuces, and scallions, from contaminated soil, air, and
403 water (Chang et al., 2013; Dela Cruz et al., 2014); (ii) originate from peculiar food
404 treatments such as smoking and heating, including grilling and roasting (Plaza-Bolaños et
405 al., 2010); and (iii) derive from flavouring additives (Frank et al., 2019; Paulino et al.,
406 2021).

407 The contents of alkanes, which were relatively high in all FW biogas samples, decreased
408 during the HB period and increased until the end of the experiment (Fig. 5a). In particular,
409 the alkanes were characterised by high values for the ratio of (ethane+propane) to longer-
410 chain C_{3+} alkanes (Σ ALK C_{3+}) (Fig. 5c), which highlighted a substantial release of lighter
411 molecules. Furthermore, the sharp rise of this ratio during the LB period (Fig. 5c), when

412 O₂ contents increased in the digester headspace (Fig. 3b), suggested that oxidation
413 processes occurring in the headspace mostly affected longer-chain alkanes. The
414 occurrence of alkanes in the biogas samples could be linked to the presence of vegetables
415 in the degrading FW substrate (Table 1); in fact, alkanes are frequently contained in
416 vegetables as components of the cuticle waxes of plant tissues (Srbinovska et al., 2020).
417 Moreover, alkanes, in association with alkenes, may be produced by the irradiation
418 treatments commonly employed for preserving and sterilising food (Hwang et al., 2001).
419 Terpenes were the third most abundant organic group in the biogas samples (Fig. 5a),
420 except at the beginning of the experiment (< 0.03% Σ VOCs). Their relative amounts
421 increased until a peak on day 20 (Fig. 5a), when air entered the digester headspace (Fig.
422 3a), and then remained almost constant, demonstrating that they were recalcitrant to
423 oxidation. These compounds are naturally emitted and synthesised by plants and
424 determine the aromas and flavours of fruits and vegetables (Siegmund, 2015). In addition,
425 as flavour and fragrance agents, terpenes are commonly employed in the food industry
426 (Tetali, 2019), which explains their relatively high abundances in the biogas samples (Fig.
427 5a). The relatively high amounts of limonene (Table S1, Supplementary material), which
428 typically provides the flavour of citrus fruits (Battista et al., 2020; Ravichandran et al.,
429 2018), may be dictated by the presence of orange and mandarin orange peels in the
430 considered FW substrate.

431 The relative contents of cyclic compounds increased during the first 6 days, fluctuated
432 until day 13, and then slowly decreased until the end of the experiment (Fig. 5a). This
433 evolution indicated that either these compounds were released mainly during the
434 decomposition of the fresh FW or they underwent degradation during the LB period when
435 environmental conditions were more oxidising. In contrast, the relative amounts of
436 alkenes, after a rapid decrease in the first 3 days, peaked on day 20 with a further decrease

437 until the end of the experiment, confirming the instability of these compounds under
438 relatively high oxidising conditions (Abbasian et al., 2015). The presence of cyclic and
439 alkene compounds in all biogas samples (Fig. 5a) may have been due to degradation of
440 vegetables and fruits, as they are constituents of the wax coatings of plant tissues
441 (Randazzo et al., 2022). Cyclics and alkenes are also found in many essential oils
442 synthesised in leaves, flowers, and fruits of plants (Mugao et al., 2020; Vergis et al.,
443 2015).

444 The contents of O-substituted compounds (i.e., esters, ketones, aldehydes, and alcohols)
445 increased during the first 6 days and then fluctuated until the end of the experiment (Fig.
446 5a). O-substituted compounds are typical food flavouring components (Panakkal et al.,
447 2021) and have been detected during initial anaerobic decomposition of easily
448 biodegradable wastes (Liu et al., 2020) and in composting facilities (Mustafa et al., 2017).
449 The relatively low concentrations detected for O-substituted compounds in the biogas
450 samples (Fig. 5a) may be related to both (i) low content in the investigated FW substrate
451 and (ii) consumption during AD since they are recognised as intermediate metabolites in
452 the process (Duan et al., 2014; Wieczorek et al., 2011; Wikandari et al., 2015).

453 Halogenated compounds were detected from day 3, and their relatively low concentrations
454 showed a decreasing trend along the AD time (Fig. 5a). Low amounts of these compounds
455 in the FW biogas were expected, as they have been commonly detected at low levels in
456 various foods, including meats, cheeses, oils, and dairy and baked products (Fleming-
457 Jones and Smith, 2003). These compounds may enter the food chain by (i) accumulation
458 in vegetal and animal tissues from polluted air, water, and soil and (ii) contamination from
459 packaging and processing practices (Thakali and MacRae, 2021).

460 Finally, S-substituted compounds are typically emitted by degradation of fermented foods
461 rich in sulfur-containing organic compounds (Zheng et al., 2020). Among the numerous

462 compounds pertaining to this group, only DMS and DMSO were detected at relatively low
463 concentrations in the FW biogas and presented a peak (as a sum) on day 13 (Fig. 5a). The
464 absence of DMSO in the first 6 days of the experiment (Table S1, Supplementary
465 material) was followed by a decrease in the calculable DMS/DMSO ratio from day 10
466 until day 27 (Fig. 5d), when only DMSO was detected. This indicated that DMSO may
467 have been derived from DMS oxidation, a process common in nature (Hopkins et al.,
468 2016; Lee et al., 1999), that particularly occurred when enough O₂ was available in the
469 digester headspace (Table S1, Supplementary material).

470 5.2.2. Features along the soil column

471 VOCs measured at relatively low amounts in biogas samples from the digester headspace
472 were only sporadically detected (alkenes and cyclics) or virtually absent (S-substituted and
473 halogenated compounds) in gas samples from the soil column, mostly due to air dilution.
474 Notably, the composition of the measured VOCs in gas samples from the soil column was
475 rather different than the composition of the measured VOCs in biogas samples collected
476 from the digester headspace, being generally dominated by alkanes, terpenes, and O-
477 substituted compounds, while aromatics showed lower amounts (Fig. 2). This
478 compositional evolution indicated that VOCs generated by the AD of FW were affected
479 not only by air dilution during migration through the soil column but also by degradation
480 processes to different extents, depending on the stabilities of the various VOCs under
481 increasing oxidising conditions (when approaching the top of the soil column).

482 Among alkanes, the increasing trends of (ethane+propane)/ \sum ALK C₃₊ values towards the
483 top of the soil column in both the HB and LB periods suggested a certain hierarchy for
484 aerobic biodegradation; longer chains were more readily degraded (Fig. 6a), as observed
485 for biogas samples from the digester headspace, whereas recalcitrant compounds (i.e.,

ethane and propane) were progressively enriched as the O₂ content increased (Fig. 5c). According to the degradation processes expected for alkanes under strongly oxidising conditions, which generate oxygenated compounds as intermediate or final products (Singh et al., 2012), the values of the $\sum\text{OXY}/\sum\text{ALKA}$ ($\sum\text{O}$ -substituted compounds/ \sum alkanes) ratio for gases from the HB and LB column profiles (Fig. 6b) were significantly higher than the $\sum\text{OXY}/\sum\text{ALKA}$ ratios from the digester headspace (equal to 0.005 ± 0.001 and 0.005 ± 0.0004 , respectively), where oxidation of the alkanes was controlled by the limited O₂ availability. Coherently, the increasing rate of $\sum\text{OXY}/\sum\text{ALKA}$ values was higher in the upper 15 (for LB) and 30 (for HB) cm of the soil column (Fig. 6b), where the exposition of alkanes migrating from the digester to adverse (oxidising) conditions was longer than when they passed through the lower column levels. Gases collected from the soil column during the LB period showed lower and less variable $\sum\text{OXY}/\sum\text{ALKA}$ ratios than those collected during the HB period (Fig. 6b). This was likely related to the decrease in biogas production in the digester and the relative enrichment of recalcitrant short-chain alkanes in the LB period (Fig. 5c), which hindered secondary production of the O-substituted compounds.

The degradation of aromatics, which explained the abovementioned distinction between the composition of VOCs from the soil column with respect to the composition of VOCs from the digester headspace, was supported by the increasing trends seen for benzene/ \sum alkylbenzenes ratios while moving upwards along the soil column in both the HB and LB periods (Fig. 6c). This confirmed that alkylated benzenes were easily degraded compared to benzene, as observed for the biogas samples from the digester headspace under the relatively high oxidising conditions of the LB period (Fig. 5b). As a result, the potentially toxic benzene was passively enriched upwards along the soil column.

511 The relatively high abundance of recalcitrant short-chain alkanes (Fig. 6a) and the rapid
512 degradation of alkylated aromatics (Fig. 6c), which were dominant among the aromatic
513 group in biogases from the digester (Fig. 5b), explained the increasing trend seen for the
514 $\sum\text{ALKA}/\sum\text{ARO}$ ($\sum\text{alkanes}/\sum\text{aromatics}$) ratio upwards along the soil column (Fig. 6d),
515 although alkanes are generally known to be more affected by biodegradation than
516 aromatics due to the high stability of the aromatic ring (Fathepure, 2014).

517 The concentrations of odorous terpenes ($\sum\text{TER}$) showed an opposite trend during the HB
518 period with respect to those of alkanes and aromatics, as displayed by the increase in the
519 values of the $\sum\text{TER}/\sum(\text{ALKA}+\text{ARO})$ ratio upwards along the soil column (Fig. 6e); this
520 suggested that they were the most recalcitrant among the detected VOCs. Actually, during
521 the LB period, the biogas from the digester headspace was particularly enriched in
522 recalcitrant alkane and aromatic compounds (Fig. 5b, 5c) and the values of
523 $\sum\text{TER}/\sum(\text{ALKA}+\text{ARO})$ were almost constant (Fig. 6e), indicating a similar fate for
524 terpenes, ethane, propane, and benzene. The increasing trend seen for the
525 $\sum\text{TER}/\sum(\text{ALKA}+\text{ARO})$ ratio towards the top of the soil column during the HB period
526 (Fig. 6e) may have been exacerbated by α -pinene intake from the air, as indicated by its
527 relative enrichment among terpenes in the gas samples from the upper layers of the soil
528 column, especially during the first days of the experiment when the soil gas was not
529 completely rinsed by the biogas inflow (Table S1, Supplementary material). In fact, α -
530 pinene is a persistent compound and frequently occurs at significant levels in both indoor
531 and outdoor air (Villanueva et al., 2018; Waidyanatha et al., 2022).

532 **6. Conclusions**

533 Biogas was generated by the AD of the selected waste category (FW) in the digester and
534 passed through the soil column, which indicated that the developed experimental setup

535 reliably simulated a typical landfill system. The results of this experiment showed that the
536 physicochemical and biological processes occurring within the simulated landfill cover
537 soil effectively degraded the biogas permeating from the underneath digester, indicating
538 the capacity of cover soils to mitigate a wide range of gaseous compounds expected in the
539 LFG. The biodegradation processes were highly selective for specific main gaseous
540 components and VOCs. In fact, gases permeating towards the top of the soil column were
541 strongly depleted in CH₄, H₂, alkylated benzenes, and long-chain alkanes, whereas they
542 were relatively enriched in CO₂ and selected organic volatiles, such as short-chain alkanes,
543 benzene, O-substituted compounds, and terpenes. These recalcitrant gaseous species are
544 toxic and odoriferous and may cause severe environmental impacts if high amounts are
545 released into the atmosphere. Therefore, actions aimed at minimising the impacts of LFG
546 diffuse emissions from landfill sites should focus mainly on recalcitrant components, since
547 the others are expected to be efficiently degraded by cover soils.

548 The experimental setup used in this study provided useful information on the fates of
549 biogas components permeating a soil column, and the findings could be used to increase
550 and optimise the attenuation capacities of landfill cover soils. On this basis,
551 complementary works should be focused on further experiments by: (i) implementing
552 parallel lines of the setup and varying the operating conditions (e.g., soil moisture,
553 thickness, compaction, and leachate application); (ii) digesting different organic waste
554 categories, i.e., those commonly disposed of at landfills, as degrading substrates; (iii)
555 treating soils with organic amendments, such as compost or digested sludge, to improve
556 LFG degradation efficiency.

557 **Acknowledgements**

558 This study was financially supported by the Laboratory of Fluid and Rock Geochemistry
559 of the Department of Earth Sciences at the University of Florence and, secondarily, by the
560 Research Unit in Sanitary-Environmental Engineering at the University of Urbino “Carlo
561 Bo”. The authors thank Mr. M. Di Domenico at the Hera in Rimini (Emilia-Romagna
562 Region, Italy) for providing the inoculum (anaerobic sludge sample). Dr.-Eng. A. Folino,
563 previously at the University of Urbino “Carlo Bo”, is mentioned for the support in
564 organising the inoculum collection. The authors are also grateful to T. Burrese, F.
565 Giannetti, L. Chelucci, and M. Rumachella for their assistance in collecting the food waste
566 substrate.

567 **References**

- 568 Abbasian, F., Lockington, R., Mallavarapu, M., Naidu, R., 2015. A comprehensive review
569 of aliphatic hydrocarbon biodegradation by bacteria. *Appl. Biochem. Biotechnol.*
570 176, 670–699. <https://doi.org/10.1007/s12010-015-1603-5>
- 571 Alibardi, L., Cossu, R., 2015. Composition variability of the organic fraction of municipal
572 solid waste and effects on hydrogen and methane production potentials. *Waste*
573 *Manag.* 36, 147–155. <https://doi.org/10.1016/j.wasman.2014.11.019>
- 574 Allen, M.R., Braithwaite, A., Hills, C.C., 1997. Trace organic compounds in landfill gas at
575 seven U.K. waste disposal sites. *Environ. Sci. Technol.* 31, 1054–1061.
576 <https://doi.org/10.1021/es9605634>
- 577 Alvarez-Cohen, L., McCarty, P.L., 1991. Effects of toxicity, aeration, and reductant
578 supply on trichloroethylene transformation by a mixed methanotrophic culture. *Appl.*
579 *Environ. Microbiol.* 57, 228–235. <https://doi.org/10.1128/aem.57.1.228-235.1991>
- 580 Alvarez-Cohen, L., Speitel, G.E., 2001. Kinetics of aerobic cometabolism of chlorinated

581 solvents. *Biodegradation* 12, 105–126. <https://doi.org/10.1023/A:1012075322466>

582 Angelidaki, I., Batstone, D.J., 2010. Anaerobic digestion: Process, in: Christensen, T. H.
583 (Eds.), *Solid Waste Technology & Management*, vol. 2, John Wiley & Sons Ltd.,
584 Chichester, UK, pp. 583–600.

585 Angelidaki, I., Sanders, W., 2004. Assessment of the anaerobic biodegradability of
586 macropollutants. *Rev. Environ. Sci. Bio/Technol.* 3, 117–129.
587 <https://doi.org/10.1007/s11157-004-2502-3>

588 Arthur, C.L., Pawliszyn, J., 1990. Solid phase microextraction with thermal desorption
589 using fused silica optical fibers. *Anal. Chem.* 62, 2145-2148.
590 <https://doi.org/10.1021/ac00218a019>

591 ASTM (American Society for Testing and Materials), 1998. Standard Practice for Wet
592 Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil
593 Constants. D2217-85, ASTM International, West Conshohocken, PA, USA.

594 ASTM, 2007. Standard Test Method for Particle-Size Analysis of Soils. D422-63, ASTM
595 International, West Conshohocken, PA, USA. [http://dx.doi.org/10.1520/D0422-](http://dx.doi.org/10.1520/D0422-63R07)
596 [63R07](http://dx.doi.org/10.1520/D0422-63R07)

597 Battista, F., Remelli, G., Zanzoni, S., Bolzonella, D., 2020. Valorization of residual orange
598 peels: Limonene recovery, volatile fatty acids, and biogas production. *ACS Sustain.*
599 *Chem. Eng.* 8, 6834–6843. <https://doi.org/10.1021/acssuschemeng.0c01735>

600 Bilen, S., Turan, V., 2022. Enzymatic analyses in soils, in: Amaresan, N., Patel, P., Amin,
601 D. (Eds.), *Practical Handbook on Agricultural Microbiology*. Springer Protocols
602 Handbooks. Humana, New York, NY, pp. 377-385. [https://doi.org/10.1007/978-1-](https://doi.org/10.1007/978-1-0716-1724-3_50)
603 [0716-1724-3_50](https://doi.org/10.1007/978-1-0716-1724-3_50)

604 Bong, C.P.C., Lim, L.Y., Lee, C.T., Klemeš, J.J., Ho, C.S., Ho, W.S., 2018. The
605 characterisation and treatment of food waste for improvement of biogas production
606 during anaerobic digestion – A review. *J. Clean. Prod.* 172, 1545–1558.
607 <https://doi.org/10.1016/j.jclepro.2017.10.199>

608 Botheju, D., Bakke, R., 2011. Oxygen effects in anaerobic digestion – a review. *Open*
609 *Waste Manag. J.* 4, 1–19. <https://doi.org/10.2174/1876400201104010001>

610 Brown, D., Shi, J., Li, Y., 2012. Comparison of solid-state to liquid anaerobic digestion of
611 lignocellulosic feedstocks for biogas production. *Bioresour. Technol.* 124, 379–386.
612 <https://doi.org/10.1016/j.biortech.2012.08.051>

613 Campuzano, R., González-Martínez, S., 2016. Characteristics of the organic fraction of
614 municipal solid waste and methane production: A review. *Waste Manag.* 54, 3–12.
615 <https://doi.org/10.1016/j.wasman.2016.05.016>

616 Capaccioni, B., Caramiello, C., Tatàno, F., Viscione, A., 2011. Effects of a temporary
617 HDPE cover on landfill gas emissions: Multiyear evaluation with the static chamber
618 approach at an Italian landfill. *Waste Manag.* 31, 956–965.
619 <https://doi.org/10.1016/j.wasman.2010.10.004>

620 Capson-Tojo, G., Rouez, M., Crest, M., Steyer, J.P., Delgenès, J.P., Escudié, R., 2016.
621 Food waste valorization via anaerobic processes: A review. *Rev. Environ. Sci.*
622 *Biotechnol.* 15, 499–547. <https://doi.org/10.1007/s11157-016-9405-y>

623 Carchesio, M., Tatàno, F., Lancellotti, I., Taurino, R., Colombo, E., Barbieri, L., 2014.
624 Comparison of biomethane production and digestate characterization for selected
625 agricultural substrates in Italy. *Environ. Technol.* 35 (17), 2212–2226.
626 <https://doi.org/10.1080/09593330.2014.898701>

627 Cébron, A., Bodrossy, L., Chen, Y., Singer, A.C., Thompson, I.P., Prosser, J.I., Murrell,
628 J.C., 2007. Identity of active methanotrophs in landfill cover soil as revealed by
629 DNA-stable isotope probing. *FEMS Microbiol. Ecol.* 62, 12–23.
630 <https://doi.org/10.1111/j.1574-6941.2007.00368.x>

631 Chang, M.L., Wang, M.J., Kuo, D.T.F., Shih, Y.H., 2013. Sorption of selected aromatic
632 compounds by vegetables. *Ecol. Eng.* 61, 74–81.
633 <https://doi.org/10.1016/j.ecoleng.2013.09.059>

634 Chen, D.M.C., Bodirsky, B.L., Krueger, T., Mishra, A., Popp, A., 2020a. The world's
635 growing municipal solid waste: Trends and impacts. *Environ. Res. Lett.* 15.
636 <https://doi.org/10.1088/1748-9326/ab8659>

637 Chen, Q., Wu, W., Qi, D., Ding, Y., Zhao, Z., 2020b. Review on microaeration-based
638 anaerobic digestion: State of the art, challenges, and perspectives. *Sci. Total Environ.*
639 710, 136388. <https://doi.org/10.1016/j.scitotenv.2019.136388>

640 Chen, D., Zuo, X., Li, J., Wang, X., Liu, J., 2020c. Carbon migration and metagenomic
641 characteristics during anaerobic digestion of rice straw. *Biotechnol. Biofuels* 13, 1–
642 13. <https://doi.org/10.1186/s13068-020-01770-4>

643 Cogliano, V.J., Baan, R., Straif, K., Grosse, Y., Lauby-Secretan, B., El Ghissassi, F.,
644 Bouvard, V., Benbrahim-Tallaa, L., Guha, N., Freeman, C., Galichet, L., Wild, C.P.,
645 2011. Preventable exposures associated with human cancers. *J. Natl. Cancer Inst.*
646 103, 1827–1839. <https://doi.org/10.1093/jnci/djr483>

647 Conrad, R., 2005. Quantification of methanogenic pathways using stable carbon isotopic
648 signatures: A review and a proposal. *Org. Geochem.* 36, 739–752.
649 <https://doi.org/10.1016/j.orggeochem.2004.09.006>

650 D' Silva, T.C., Isha, A., Chandra, R., Vijay, V.K., Subbarao, P.M. V., Kumar, R.,
651 Chaudhary, V.P., Singh, H., Khan, A.A., Tyagi, V.K., Kovács, K.L., 2021.
652 Enhancing methane production in anaerobic digestion through hydrogen assisted
653 pathways – A state-of-the-art review. *Renew. Sustain. Energy Rev.* 151.
654 <https://doi.org/10.1016/j.rser.2021.111536>

655 De Bok, F.A.M., Van Leerdam, R.C., Lomans, B.P., Smidt, H., Lens, P.N.L., Janssen,
656 A.J.H., Stams, A.J.M., 2006. Degradation of methanethiol by methylotrophic
657 methanogenic archaea in a lab-scale upflow anaerobic sludge blanket reactor. *Appl.*
658 *Environ. Microbiol.* 72, 7540–7547. <https://doi.org/10.1128/AEM.01133-06>

659 Dela Cruz, M., Christensen, J.H., Thomsen, J.D., Müller, R., 2014. Can ornamental potted
660 plants remove volatile organic compounds from indoor air? — A review. *Environ.*
661 *Sci. Pollut. Res.* 21, 13909–13928. <https://doi.org/10.1007/s11356-014-3240-x>

662 De Laurentiis, V., Corrado, S., Sala, S., 2018. Quantifying household waste of fresh fruit
663 and vegetables in the EU. *Waste Manag.* 77, 238–251.
664 <https://doi.org/10.1016/j.wasman.2018.04.001>

665 Duan, Z., Lu, W., Li, D., Wang, H., 2014. Temporal variation of trace compound emission
666 on the working surface of a landfill in Beijing, China. *Atmos. Environ.* 88, 230–238.
667 <https://doi.org/10.1016/j.atmosenv.2014.01.051>

668 Duan, Z., Scheutz, C., Kjeldsen, P., 2021. Trace gas emissions from municipal solid waste
669 landfills: A review. *Waste Manag.* 119, 39–62.
670 <https://doi.org/10.1016/j.wasman.2020.09.015>

671 El-Naas, M.H., Acio, J.A., El Telib, A.E., 2014. Aerobic biodegradation of BTEX:
672 Progresses and prospects. *J. Environ. Chem. Eng.* 2, 1104–1122.
673 <https://doi.org/10.1016/j.jece.2014.04.009>

674 Fathepure, B.Z., 2014. Recent studies in microbial degradation of petroleum hydrocarbons
675 in hypersaline environments. *Front. Microbiol.* 5, 1–16.
676 <https://doi.org/10.3389/fmicb.2014.00173>

677 Fleming-Jones, M.E., Smith, R.E., 2003. Volatile organic compounds in foods: A five
678 year study. *J. Agric. Food Chem.* 51, 8120–8127. <https://doi.org/10.1021/jf0303159>

679 Frank, S., Hofmann, T., Schieberle, P., 2019. Quantitation of benzene in flavourings and
680 liquid foods containing added cherry-type flavour by a careful work-up procedure
681 followed by a stable isotope dilution assay. *Eur. Food Res. Technol.* 245, 1605–1610.
682 <https://doi.org/10.1007/s00217-019-03267-3>

683 Gallego, E., Roca, F.J., Perales, J.F., Sánchez, G., Esplugas, P., 2012. Characterization
684 and determination of the odorous charge in the indoor air of a waste treatment facility
685 through the evaluation of volatile organic compounds (VOCs) using TD-GC/MS.
686 *Waste Manag.* 32, 2469–2481. <https://doi.org/10.1016/j.wasman.2012.07.010>

687 Greses, S., Tomás-Pejó, E., González-Fernández, C., 2021. Short-chain fatty acids and
688 hydrogen production in one single anaerobic fermentation stage using carbohydrate-
689 rich food waste. *J. Clean. Prod.* 284, 124727.
690 <https://doi.org/10.1016/j.jclepro.2020.124727>

691 Gunaseelan, V.N., 2004. Biochemical methane potential of fruits and vegetable solid
692 waste feedstocks. *Biomass and Bioenergy* 26, 389–399.
693 <https://doi.org/10.1016/j.biombioe.2003.08.006>

694 Guo, X.M., Trably, E., Latrille, E., Carrre, H., Steyer, J.P., 2010. Hydrogen production
695 from agricultural waste by dark fermentation: A review. *Int. J. Hydrogen Energy* 35,
696 10660–10673. <https://doi.org/10.1016/j.ijhydene.2010.03.008>

697 Hanson, R.S., Hanson, T.E., 1996. Methanotrophic bacteria. *Microbiol. Rev.* 60, 439–471.

698 <https://doi.org/10.1128/membr.60.2.439-471.1996>

699 He, R., Ruan, A., Jiang, C., Shen, D-S., Shen, 2008. Responses of oxidation rate and
700 microbial communities to methane in simulated landfill cover soil microcosms.
701 *Bioresour. Technol.* 99, 7192–7199. <https://doi.org/10.1016/j.biortech.2007.12.066>

702 Hopkins, F.E., Bell, T.G., Yang, M., Suggett, D.J., Steinke, M., 2016. Air exposure of
703 coral is a significant source of dimethylsulfide (DMS) to the atmosphere. *Sci. Rep.* 6,
704 1–11. <https://doi.org/10.1038/srep36031>

705 Hwang, K.T., Hong, J.S., Yang, J.S., Sohn, H.S., Weller, C.L., 2001. Detection of alkanes
706 and alkenes for identifying irradiated cereals. *JAOCS, J. Am. Oil Chem. Soc.* 78,
707 1145–1149. <https://doi.org/10.1007/s11746-001-0403-z>

708 Jechorek, M., Wendlandt, K.D., Beck, M., 2003. Cometabolic degradation of chlorinated
709 aromatic compounds. *J. Biotechnol.* 102, 93–98. [https://doi.org/10.1016/S0168-](https://doi.org/10.1016/S0168-1656(03)00005-1)
710 [1656\(03\)00005-1](https://doi.org/10.1016/S0168-1656(03)00005-1)

711 Kamimura, N., Sakamoto, S., Mitsuda, N., Masai, E., Kajita, S., 2019. Advances in
712 microbial lignin degradation and its applications. *Curr. Opin. Biotechnol.* 56, 179–
713 186. <https://doi.org/10.1016/j.copbio.2018.11.011>

714 Kawai, M., Nagao, N., Tajima, N., Niwa, C., Matsuyama, T., Toda, T., 2014. The effect of
715 the labile organic fraction in food waste and the substrate/inoculum ratio on AD for a
716 reliable methane yield. *Bioresour. Technol.* 157, 174–180.
717 <https://doi.org/10.1016/j.biortech.2014.01.018>

718 Kightley, D., Nedwell, D.B., Cooper, M., 1995. Capacity for methane oxidation in landfill
719 cover soils measured in laboratory-scale soil microcosms. *Appl. Environ. Microbiol.*
720 61, 592–601. <https://doi.org/10.1128/aem.61.2.592-601.1995>

721 Kjeldsen, P., Scheutz, C., 2018. Chapter 9.5 - Landfill gas management by methane
722 oxidation, solid waste landfilling, in: Cossu, R., Stegmann, R. (Eds.), Solid Waste
723 Landfilling, Elsevier, pp. 477–497. [https://doi.org/10.1016/b978-0-12-407721-](https://doi.org/10.1016/b978-0-12-407721-8.00024-3)
724 [8.00024-3](https://doi.org/10.1016/b978-0-12-407721-8.00024-3)

725 Koh, S.C., Bowman, J.P., Sayler, G.S., 1993. Soluble methane monooxygenase production
726 and trichloroethylene degradation by a type I methanotroph, *Methylomonas*
727 *methanica* 68-1. *Appl. Environ. Microbiol.* 59, 960–967.
728 <https://doi.org/10.1128/aem.59.4.960-967.1993>

729 Lee, P.A., De Mora, S.J., Levasseur, M., 1999. A review of dimethylsulfoxide in aquatic
730 environments. *Atmos. - Ocean* 37, 439–456.
731 <https://doi.org/10.1080/07055900.1999.9649635>

732 Lee, E.H., Park, H., Cho, K.S., 2011. Effect of substrate interaction on oxidation of
733 methane and benzene in enriched microbial consortia from landfill cover soil. *J.*
734 *Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng.* 46, 997–1007.
735 <https://doi.org/10.1080/10934529.2011.586266>

736 Lee, J.H., Kim, T.G., Cho, K.S., 2012. Isolation and characterization of a facultative
737 methanotroph degrading malodor-causing volatile sulfur compounds. *J. Hazard.*
738 *Mater.* 235–236, 224–229. <https://doi.org/10.1016/j.jhazmat.2012.07.047>

739 Lee, E.H., Moon, K.E., Cho, K.S., 2017. Long-term performance and bacterial community
740 dynamics in biocovers for mitigating methane and malodorous gases. *J. Biotechnol.*
741 242, 1–10. <https://doi.org/10.1016/j.jbiotec.2016.12.007>

742 Lee, Y.Y., Jung, H., Ryu, H.W., Oh, K.C., Jeon, J.M., Cho, K.S., 2018. Seasonal
743 characteristics of odor and methane mitigation and the bacterial community dynamics

744 in an on-site biocover at a sanitary landfill. *Waste Manag.* 71, 277–286.
745 <https://doi.org/10.1016/j.wasman.2017.10.037>

746 Liu, Y., Lu, W., Wang, H., Huang, Q., Gao, X., 2018. Odor impact assessment of trace
747 sulfur compounds from working faces of landfills in Beijing, China. *J. Environ.*
748 *Manage.* 220, 136–141. <https://doi.org/10.1016/j.jenvman.2018.04.122>

749 Liu, Y., Yang, H., Lu, W., 2020. VOCs released from municipal solid waste at the initial
750 decomposition stage: Emission characteristics and an odor impact assessment. *J.*
751 *Environ. Sci.* 98, 143–150. <https://doi.org/10.1016/j.jes.2020.05.009>

752 Majdinasab, A., Yuan, Q., 2017. Performance of the biotic systems for reducing methane
753 emissions from landfill sites: A review. *Ecol. Eng.* 104, 116–130.
754 <https://doi.org/10.1016/j.ecoleng.2017.04.015>

755 Martí, V., Jubany, I., Pérez, C., Rubio, X., De Pablo, J., Giménez, J., 2014. Human health
756 risk assessment of a landfill based on volatile organic compounds emission,
757 immission and soil gas concentration measurements. *Appl. Geochemistry* 49, 218–
758 224. <https://doi.org/10.1016/j.apgeochem.2014.06.018>

759 Merouani, E.F.O., Khabiri, B., Ferdowsi, M., Benyoussef, E.H., Malhautier, L., Buelna,
760 G., Jones, J.P., Heitz, M., 2022. Biofiltration of methane in presence of ethylbenzene
761 or xylene. *Atmos. Pollut. Res.* 13, 101271. <https://doi.org/10.1016/j.apr.2021.101271>

762 Misra, G., Pavlostathis, S.G., 1997. Biodegradation kinetics of monoterpenes in liquid and
763 soil-slurry systems. *Appl. Microbiol. Biotechnol.* 47, 572–577.
764 <https://doi.org/10.1007/s002530050975>

765 Misra, G., Pavlostathis, S.G., Perdue, E.M., Araujo, R., 1996. Aerobic biodegradation of
766 selected monoterpenes. *Appl. Microbiol. Biotechnol.* 45, 831–838.

767 <https://doi.org/10.1007/s002530050770>

768 Mugao, L.G., Gichimu, B.M., Muturi, P.W., Mukono, S.T., 2020. Characterization of the
769 volatile components of essential oils of selected plants in Kenya. *Biochem. Res. Int.*
770 2020. <https://doi.org/10.1155/2020/8861798>

771 Muñoz, R., Meier, L., Diaz, I., Jeison, D., 2015. A review on the state-of-the-art of
772 physical/chemical and biological technologies for biogas upgrading. *Rev. Environ.*
773 *Sci. Biotechnol.* 14, 727–759. <https://doi.org/10.1007/s11157-015-9379-1>

774 Mustafa, M.F., Liu, Y., Duan, Z., Guo, H., Xu, S., Wang, H., Lu, W., 2017. Volatile
775 compounds emission and health risk assessment during composting of organic
776 fraction of municipal solid waste. *J. Hazard. Mater.* 327, 35–43.
777 <https://doi.org/10.1016/j.jhazmat.2016.11.046>

778 Nahman, A., 2011. Pricing landfill externalities: Emissions and disamenity costs in Cape
779 Town, South Africa. *Waste Manag.* 31, 2046–2056.
780 <https://doi.org/10.1016/j.wasman.2011.05.015>

781 Nair, A.T., Senthilnathan, J., Nagendra, S.M.S., 2019. Emerging perspectives on VOC
782 emissions from landfill sites: Impact on tropospheric chemistry and local air quality.
783 *Process Saf. Environ. Prot.* 121, 143–154. <https://doi.org/10.1016/j.psep.2018.10.026>

784 Negri, C., Ricci, M., Zilio, M., D'Imporzano, G., Qiao, W., Dong, R., Adani, F., 2020.
785 Anaerobic digestion of food waste for bio-energy production in China and Southeast
786 Asia: A review. *Renew. Sustain. Energy Rev.* 133.
787 <https://doi.org/10.1016/j.rser.2020.110138>

788 Nguyen, D., Khanal, S.K., 2018. A little breath of fresh air into an anaerobic system: How
789 microaeration facilitates anaerobic digestion process. *Biotechnol. Adv.* 36, 1971–

790 1983. <https://doi.org/10.1016/j.biotechadv.2018.08.007>

791 NIST (National Institute of Standards and Technology), 2005. Mass Spectral Library
792 (NIST/EPA/NIH), Gaithersburg, USA.

793 Nunes-Halldorson, V.D.S., Steiner, R.L., Smith, G.B., 2004. Residual toxicity after
794 biodegradation: Interactions among benzene, toluene, and chloroform. *Ecotoxicol.*
795 *Environ. Saf.* 57, 162–167. [https://doi.org/10.1016/S0147-6513\(03\)00032-0](https://doi.org/10.1016/S0147-6513(03)00032-0)

796 Owen, W.F., Stuckey, D.C., Healy, J.B., Young, L.Y., McCarty, P.L., 1979. Bioassay for
797 monitoring biochemical methane potential and anaerobic toxicity. *Water Res.* 13,
798 485–492. [https://doi.org/10.1016/0043-1354\(79\)90043-5](https://doi.org/10.1016/0043-1354(79)90043-5)

799 Panakkal, E.J., Kitiborwornkul, N., Sriariyanun, M., Ratanapoompinyo, J., Yasurin, P.,
800 Asavasanti, S., Rodiahwati, W., Tantayotai, P., 2021. Production of food flavouring
801 agents by enzymatic reaction and microbial fermentation. *Appl. Sci. Eng. Prog.* 14,
802 297–312. <https://doi.org/10.14416/j.asep.2021.04.006>

803 Panigrahi, S., Dubey, B.K., 2019. A critical review on operating parameters and strategies
804 to improve the biogas yield from AD of organic fraction of municipal solid waste.
805 *Renew. Energy* 143, 779–797. <https://doi.org/10.1016/j.renene.2019.05.040>

806 Paulino, B.N., Sales, A., Felipe, L., Pastore, G.M., Molina, G., Bicas, J.L., 2021. Recent
807 advances in the microbial and enzymatic production of aroma compounds. *Curr.*
808 *Opin. Food Sci.* 37, 98–106. <https://doi.org/10.1016/j.cofs.2020.09.010>

809 Pecorini, I., Rossi, E., Iannelli, R., 2020. Mitigation of methane, NMVOCs and odor
810 emissions in active and passive biofiltration systems at municipal solid waste
811 landfills. *Sustain.* 12, 3203. <https://doi.org/10.3390/SU12083203>

812 Phae, C.G., Shoda, M., 1991. A new fungus which degrades hydrogen sulfide,

813 methanethiol, dimethyl sulfide and dimethyl disulfide. *Biotechnol. Lett.* 13, 375–380.
814 <https://doi.org/10.1007/BF01027686>

815 Piccardo, M.T., Geretto, M., Pulliero, A., Izzotti, A., 2022. Odor emissions: A public
816 health concern for health risk perception. *Environ. Res.* 204, 112121.
817 <https://doi.org/10.1016/j.envres.2021.112121>

818 Plaza-Bolaños, P., Frenich, A.G., Vidal, J.L.M., 2010. Polycyclic aromatic hydrocarbons
819 in food and beverages. *Analytical methods and trends. J. Chromatogr. A* 1217, 6303–
820 6326. <https://doi.org/10.1016/j.chroma.2010.07.079>

821 Polag, D., May, T., Müller, L., König, H., Jacobi, F., Laukenmann, S., Keppler, F., 2015.
822 Online monitoring of stable carbon isotopes of methane in anaerobic digestion as a
823 new tool for early warning of process instability. *Bioresour. Technol.* 197, 161–170.
824 <https://doi.org/10.1016/j.biortech.2015.08.058>

825 Poulsen, T.G., Adelard, L., 2016. Improving biogas quality and methane yield via co-
826 digestion of agricultural and urban biomass wastes. *Waste Manag.* 54, 118–125.
827 <https://doi.org/10.1016/j.wasman.2016.05.020>

828 Poulsen, T.G., Adelard, L., Wells, M., 2017. Improvement in CH₄/CO₂ ratio and CH₄
829 yield as related to biomass mix composition during anaerobic co-digestion. *Waste*
830 *Manag.* 61, 179–187. <https://doi.org/10.1016/j.wasman.2016.11.009>

831 Pratt, C., Walcroft, A.S., Deslippe, J., Tate, K.R., 2013. CH₄/CO₂ ratios indicate highly
832 efficient methane oxidation by a pumice landfill cover-soil. *Waste Manag.* 33, 412–
833 419. <https://doi.org/10.1016/j.wasman.2012.10.020>

834 Qian, M., Reineccius, G., 2002. Identification of aroma compounds in Parmigiano-
835 Reggiano cheese by gas chromatography/olfactometry. *J. Dairy Sci.* 85, 1362–1369.

836 [https://doi.org/10.3168/jds.S0022-0302\(02\)74202-1](https://doi.org/10.3168/jds.S0022-0302(02)74202-1)

837 Qin, L., Huang, X., Xue, Q., Liu, L., Wan, Y., 2020a. In-situ biodegradation of harmful
838 pollutants in landfill by sludge modified biochar used as biocover. *Environ. Pollut.*
839 258. <https://doi.org/10.1016/j.envpol.2019.113710>

840 Qin, L., Xu, Z., Liu, L., Lu, H., Wan, Y., Xue, Q., 2020b. In-situ biodegradation of
841 volatile organic compounds in landfill by sewage sludge modified waste-char. *Waste*
842 *Manag.* 105, 317–327. <https://doi.org/10.1016/j.wasman.2020.02.022>

843 Rabl, A., Spadaro, J. V., Zoughaib, A., 2008. Environmental impacts and costs of solid
844 waste: A comparison of landfill and incineration. *Waste Manag. Res.* 26, 147–162.
845 <https://doi.org/10.1177/0734242X07080755>

846 Randazzo, A., Asensio-Ramos, M., Melián, G. V., Venturi, S., Padrón, E., Hernández,
847 P.A., Pérez, N.M., Tassi, F., 2020. Volatile organic compounds (VOCs) in solid
848 waste landfill cover soil: Chemical and isotopic composition vs. degradation
849 processes. *Sci. Total Environ.* 726, 138326.
850 <https://doi.org/10.1016/j.scitotenv.2020.138326>

851 Randazzo, A., Folino, A., Tassi, F., Tatàno, F., de Rosa, S., Gambioli, A., 2022. Volatile
852 organic compounds from green waste anaerobic degradation at lab-scale: Evolution
853 and comparison with landfill gas. *Detritus*, 19, 63–74. [https://doi.org/10.31025/2611-](https://doi.org/10.31025/2611-4135/2022.15188)
854 [4135/2022.15188](https://doi.org/10.31025/2611-4135/2022.15188)

855 Raposo, F., De La Rubia, M.A., Fernández-Cegrí, V., Borja, R., 2011a. Anaerobic
856 digestion of solid organic substrates in batch mode: An overview relating to methane
857 yields and experimental procedures. *Renew. Sustain. Energy Rev.* 16, 861–877.
858 <https://doi.org/10.1016/j.rser.2011.09.008>

859 Raposo, F., Fernández-Cegrí, V., De la Rubia, M.A., Borja, R., Béline, F., Cavinato, C.,
860 Demirer, G., Fernández, B., Fernández -Polanco, M., Frigon, J.C., Ganesh, R.,
861 Kaparaju, P., Koubova, J., Méndez, R., Menin, G., Peene, A., Scherer, P., Torrijos,
862 M., Uellendahl, H., Wierinckm, I., de Wilde, W., 2011b. Biochemical methane
863 potential (BMP) of solid organic substrates: Evaluation of anaerobic biodegradability
864 using data from an international interlaboratory study. *J. Chem. Technol. Biotechnol.*
865 86, 1088–1098. <https://doi.org/10.1002/jctb.2622>

866 Ravichandran, C., Badgujar, P.C., Gundev, P., Upadhyay, A., 2018. Review of
867 toxicological assessment of d-limonene, a food and cosmetics additive. *Food Chem.*
868 *Toxicol.* 120, 668–680. <https://doi.org/10.1016/j.fct.2018.07.052>

869 Ravina, M., Facelli, A., Zanetti, M., 2020. Halocarbon emissions from hazardous waste
870 landfills: Analysis of sources and risks. *Atmosphere* 11, 375.
871 <https://doi.org/10.3390/ATMOS11040375>

872 Rojo, F., 2009. Degradation of alkanes by bacteria. *Environ. Microbiol.* 11, 2477–2490.
873 <https://doi.org/10.1111/j.1462-2920.2009.01948.x>

874 Schäfer, H., Myronova, N., Boden, R., 2010. Microbial degradation of dimethylsulphide
875 and related C₁-sulphur compounds: Organisms and pathways controlling fluxes of
876 sulphur in the biosphere. *J. Exp. Bot.* 61, 315–334. <https://doi.org/10.1093/jxb/erp355>

877 Scheutz, C., Kjeldsen, P., 2003. Capacity for biodegradation of CFCs and HCFCs in a
878 methane oxidative counter-gradient laboratory system simulating landfill soil covers.
879 *Environ. Sci. Technol.* 37, 5143–5149. <https://doi.org/10.1021/es026464>

880 Scheutz, C., Kjeldsen, P., 2004. Environmental factors influencing attenuation of methane
881 and hydrochlorofluorocarbons in landfill cover soils. *J. Environ. Qual.* 33, 72–79.

882 <https://doi.org/10.2134/jeq2004.7200>

883 Scheutz, C., Kjeldsen, P., 2005. Biodegradation of trace gases in simulated landfill soil. J.
884 Air Waste Manag. Assoc. 55, 878–885.

885 <https://doi.org/10.1080/10473289.2005.10464693>

886 Schuetz, C., Bogner, J., Chanton, J., Blake, D., Morcet, M., Kjeldsen, P., 2003.
887 Comparative oxidation and net emissions of methane and selected non-methane
888 organic compounds in landfill cover soils. Environ. Sci. Technol. 37, 5150–5158.

889 <https://doi.org/10.1021/es034016b>

890 Scheutz C., Mosbæk H., Kjeldsen P., 2004. Attenuation of methane and volatile organic
891 compounds in landfill soil covers. J. Environ. Qual., 33, 61-
892 71. <https://doi.org/10.2134/jeq2004.6100>

893 Scheutz, C., Bogner, J., Chanton, J.P., Blake, D., Morcet, M., Aran, C., Kjeldsen, P., 2008.
894 Atmospheric emissions and attenuation of non-methane organic compounds in cover
895 soils at a French landfill. Waste Manag. 28, 1892–1908.

896 <https://doi.org/10.1016/j.wasman.2007.09.010>

897 Scheutz, C., Kjeldsen, P., Bogner, J.E., De Visscher, A., Gebert, J., Hilger, H.A., Huber-
898 Humer, M., Spokas, K., 2009. Microbial methane oxidation processes and
899 technologies for mitigation of landfill gas emissions. Waste Manag. Res. 27, 409–
900 455. <https://doi.org/10.1177/0734242X09339325>

901 Schuler, S., Conrad, R., 1990. Soils contain two different activities for oxidation of
902 hydrogen. FEMS Microbiol. Ecol. 73, 77–83. [https://doi.org/10.1111/j.1574-
903 6968.1990.tb03927.x](https://doi.org/10.1111/j.1574-6968.1990.tb03927.x)

904 Siegmund, B., 2015. Biogenesis of aroma compounds: Flavour formation in fruits and

905 vegetables, in: Parker, J.K., Elmore, J.S., Methven, L. (Eds.), Flavour Development,
906 Analysis and Perception in Food and Beverages, Woodhead Publishing, 2015,
907 pp. 127-149. <https://doi.org/10.1016/b978-1-78242-103-0.00007-2>

908 Singh, S.N., Kumari, B., Mishra, S., 2012. Microbial degradation of alkanes, in: Singh, S.
909 (Eds.), Microbial Degradation of Xenobiotics. Environmental Science and
910 Engineering, Springer, Berlin, Heidelberg, pp. 439-469. https://doi.org/10.1007/978-3-642-23789-8_17

912 Srbinovska, A., Conchione, C., Ursol, L.M., Lucci, P., Moret, S., 2020. Occurrence of n-
913 alkanes in vegetable oils and their analytical determination. Foods 9, 1546.
914 <https://doi.org/10.3390/foods9111546>

915 Su, Y., Xia, F.F., Tian, B.H., Li, W., He, R., 2014. Microbial community and function of
916 enrichment cultures with methane and toluene. Appl. Microbiol. Biotechnol. 98,
917 3121–3131. <https://doi.org/10.1007/s00253-013-5297-8>

918 Tao, J., Li, S., Ye, F., Zhou, Y., Lei, L., Zhao, G., 2020. Lignin—An underutilized,
919 renewable and valuable material for food industry. Crit. Rev. Food Sci. Nutr. 60,
920 2011–2033. <https://doi.org/10.1080/10408398.2019.1625025>

921 Tassi, F., Montegrossi, G., Vaselli, O., Liccioli, C., Moretti, S., Nisi, B., 2009.
922 Degradation of C₂-C₁₅ volatile organic compounds in a landfill cover soil. Sci. Total
923 Environ. 407, 4513–4525. <https://doi.org/10.1016/j.scitotenv.2009.04.022>

924 Tassi, F., Capechiacci, F., Cabassi, J., Calabrese, S., Vaselli, O., Rouwet, D., Pecoraino,
925 G., Chiodini, G., 2012. Geogenic and atmospheric sources for volatile organic
926 compounds in fumarolic emissions from Mt. Etna and Vulcano Island (Sicily, Italy).
927 J. Geophys. Res. Atmos. 117. <https://doi.org/10.1029/2012JD017642>

928 Tetali, S.D., 2019. Terpenes and isoprenoids: A wealth of compounds for global use.

929 Planta 249, 1–8. <https://doi.org/10.1007/s00425-018-3056-x>

930 Thakali, A., MacRae, J.D., 2021. A review of chemical and microbial contamination in
931 food: What are the threats to a circular food system? *Environ. Res.* 194, 110635.
932 <https://doi.org/10.1016/j.envres.2020.110635>

933 Valdez-Vazquez, I., Poggi-Varaldo, H.M., 2009. Hydrogen production by fermentative
934 consortia. *Renew. Sustain. Energy Rev.* 13, 1000–1013.
935 <https://doi.org/10.1016/j.rser.2008.03.003>

936 Van Beilen, J.B., Funhoff, E.G., 2007. Alkane hydroxylases involved in microbial alkane
937 degradation. *Appl. Microbiol. Biotechnol.* 74, 13–21. [https://doi.org/10.1007/s00253-](https://doi.org/10.1007/s00253-006-0748-0)
938 [006-0748-0](https://doi.org/10.1007/s00253-006-0748-0)

939 Vergis, J., Gokulakrishnan, P., Agarwal, R.K., Kumar, A., 2015. Essential oils as natural
940 food antimicrobial agents: A Review. *Crit. Rev. Food Sci. Nutr.* 55, 1320–1323.
941 <https://doi.org/10.1080/10408398.2012.692127>

942 Villanueva, F., Tapia, A., Lara, S., Amo-Salas, M., 2018. Indoor and outdoor air
943 concentrations of volatile organic compounds and NO₂ in schools of urban, industrial
944 and rural areas in Central-Southern Spain. *Sci. Total Environ.* 622–623, 222–235.
945 <https://doi.org/10.1016/j.scitotenv.2017.11.274>

946 Waidyanatha, S., Black, S.R., Witt, K.L., Fennell, T.R., Swartz, C., Recio, L., Watson,
947 S.L., Patel, P., Fernando, R.A., Rider, C.V., 2022. The common indoor air pollutant
948 α -pinene is metabolised to a genotoxic metabolite α -pinene oxide. *Xenobiotica* 52,
949 301-311. <https://doi.org/10.1080/00498254.2022.2070047>

950 Wang, W., Shao, Z., 2013. Enzymes and genes involved in aerobic alkane degradation.
951 *Front. Microbiol.* 4, 1–7. <https://doi.org/10.3389/fmicb.2013.00116>

952 Wieczorek, A.S., Drake, H.L., Kolb, S., 2011. Organic acids and ethanol inhibit the

953 oxidation of methane by mire methanotrophs. *FEMS Microbiol. Ecol.* 77, 28–39.
954 <https://doi.org/10.1111/j.1574-6941.2011.01080.x>

955 Wikandari, R., Sari, N.K., A'yun, Q., Millati, R., Cahyanto, M.N., Niklasson, C.,
956 Taherzadeh, M.J., 2015. Effects of lactone, ketone, and phenolic compounds on
957 methane production and metabolic intermediates during anaerobic digestion. *Appl.*
958 *Biochem. Biotechnol.* 175, 1651–1663. <https://doi.org/10.1007/s12010-014-1371-7>

959 Xia, F.F., Su, Y., Wei, X.M., He, Y.H., Wu, Z.C., Ghulam, A., He, R., 2014. Diversity
960 and activity of sulphur-oxidizing bacteria and sulphate-reducing bacteria in landfill
961 cover soils. *Lett. Appl. Microbiol.* 59, 26–34. <https://doi.org/10.1111/lam.12240>

962 Ye, M., Liu, J., Ma, C., Li, Y.Y., Zou, L., Qian, G., Xu, Z.P., 2018. Improving the stability
963 and efficiency of anaerobic digestion of food waste using additives: A critical review.
964 *J. Clean. Prod.* 192, 316–326. <https://doi.org/10.1016/j.jclepro.2018.04.244>

965 Yuan, Y., Hu, X., Chen, H., Zhou, Y., Zhou, Yefeng, Wang, D., 2019. Advances in
966 enhanced volatile fatty acid production from anaerobic fermentation of waste
967 activated sludge. *Sci. Total Environ.* 694, 133741.
968 <https://doi.org/10.1016/j.scitotenv.2019.133741>

969 Zhang, Y., Arnold, R., Paavola, T., Vaz, F., Neiva Correia, C., Cavinato, C., Kusch,
970 S., Heaven, S., 2013. Compositional analysis of food waste entering the source
971 segregation stream in four european regions and implications for valorisation via
972 anaerobic digestion, in: Cossu, R., He, P., Kjeldsen, P., Matsufuji, Y., Reinhart, D.,
973 Stegmann, R. (Eds.), *Proceedings of Sardinia 2013, Fourteenth International Waste*
974 *Management and Landfill Symposium*, CISA Publisher, Padova, Italy.

975 Zhang, C., Su, H., Baeyens, J., Tan, T., 2014. Reviewing the anaerobic digestion of food
976 waste for biogas production. *Renew. Sustain. Energy Rev.* 38, 383–392.

977 <https://doi.org/10.1016/j.rser.2014.05.038>

978 Zhang, L., Kuroki, A., Tong, Y.W., 2020. A mini-review on in situ biogas upgrading
979 technologies via enhanced hydrogenotrophic methanogenesis to improve the quality
980 of biogas from anaerobic digesters. *Front. Energy Res.* 8, 1–7.
981 <https://doi.org/10.3389/fenrg.2020.00069>

982 Zhao, D., Yan, B., Liu, C., Yao, B., Luo, L., Yang, Y., Liu, L., Wu, F., Zhou, Y., 2021.
983 Mitigation of acidogenic product inhibition and elevated mass transfer by biochar
984 during anaerobic digestion of food waste. *Bioresour. Technol.* 338, 125531.
985 <https://doi.org/10.1016/j.biortech.2021.125531>

986 Zheng, G., Liu, J., Shao, Z., Chen, T., 2020. Emission characteristics and health risk
987 assessment of VOCs from a food waste anaerobic digestion plant: A case study of
988 Suzhou, China. *Environ. Pollut.* 257, 113546.
989 <https://doi.org/10.1016/j.envpol.2019.113546>

990

991

992

993

994

995

996

997