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Gaseous emissions in municipal wastes composting: effect of the bulking agent

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Abstract

In this study, the emissions of Volatile Organic Compounds (VOC), CH_4, N_2O and NH_3 during composting non-source selected MSW, source selected Organic Fraction of Municipal Solid Wastes (OFMSW) with wood chips as bulking agent (OF_wood) and source selected OFMSW with polyethylene (PE) tube as bulking agent (OF_tube) and the effect of bulking agent on these emissions have been systematically studied. Emission factors are provided (in kg compound Mg^{-1} dry matter): OF_tube (CH_4: 0.0185±0.004; N_2O: 0.0211±0.005; NH_3: 0.612±0.269; VOC: 0.688±0.082) and MSW (CH_4: 0.0549±0.0171; N_2O: 0.032±0.015; NH_3: 1.00±0.20; VOC: 1.05±0.18) present lower values than OF_wood (CH_4: 1.27±0.09; N_2O: 0.021±0.006; NH_3: 4.34±2.79; VOC: 0.989±0.249). A detailed composition of VOC is also presented. Terpenes were the main emitted VOC family in all the wastes studied. Higher emissions of alpha and beta pinene were found during OF_wood composting processes.

Keywords: Composting; Gaseous emissions; VOC; Terpenes, Bulking Agent.

1. Introduction

It is well known that recycling reduces the amount of waste going to disposal (landfilling), the consumption of natural resources and also improves energy efficiency. Therefore, recycling plays an essential role towards sustainable consumption and production (SCP). Accompanying SCP, the recycling sector has increased business with a current turnover of €24 billion employing about 500,000 people in Europe, distributed in more than 60,000 companies. The EU represents the densest area in waste and recycling industries, accounting for around 50% of world share (European Environment Agency, 2010). At the same time, sustainable management of resources and waste minimization and valorization has been the common objective of plans, directives and regulations in recent decades, including Municipal Solid Waste (MSW). According to this, in recent years, there has been a proliferation, either in Spain or Europe, of new solid waste treatment plants mainly as a result of Directive 1999/31/EC on the implementation of the limitation of landfill as final destination for organic wastes. Biological treatment plants, which allow waste valorization, are recommended as the main destination for this type of wastes (Commission of the European Community, 2008).

Generation of biodegradable organic residues is increasing worldwide and strategies for its environmentally sound use are being developed and optimized. Integrated waste management is considered the key point for a successful MSW treatment. Waste separation, that increases the quality of by-products (i.e. compost, digestate and biogas) and recyclables, is a critical component of this system. Integrated waste management also enables better financing of waste management activities and minimizes the energy and labor inputs to any downstream processes (Murray, 1999). European Directive 2008/98/EC points to the recovery of mixed municipal waste

collected from private households. In order to comply with the objectives of this Directive, and to move towards an European recycling society with a high level of resource efficiency, Member States shall take the necessary measures to achieve by 2020 a minimum overall recycling percentage of a 50% by weight of paper, metal, plastic and glass from households and possibly from other origins (as far as these waste streams are similar to waste from households) (European Parliament, 2008). As a consequence of the implementation of all these Directives, by 2013, 19% of total household wastes are source selected in Spain, being the organic fraction a percentage of 20%.

As mentioned before, biological treatment plants based on anaerobic digestion and/or composting processes are being widely constructed. Focusing on the composting process, the presence of non-organic wastes (impurities) could decrease the compost quality, affect composting gaseous emissions or increase the investment costs and the energy demand due to the equipment dedicated to the separation of impurities. Bulking agents are used to provide air space in composting materials, regulate the water content or the C/N ratio (Iqbal et al. 2009). These studies show how important is the bulking agent in the composting process evolution. Gaseous emissions during the composting process are often related with the porosity of the material being composted, which depends on the type and amount of bulking agent used. Some authors have related the emissions of some volatile organic compounds (VOC) to wood wastes used as bulking agent (Komilis et al. 2004). Recent studies (Yang et al. 2013, Shao et al. 2014) have investigated the effect of several bulking agents on gaseous emissions in composting processes of organic wastes. Yang et al. (2013) have studied emissions of CH_4, N_2O and NH_3, while Shao et al. (2014) presented an in depth study on odor emissions, mainly VOC. Both studies pay attention to the composting process evolution and the quality of

the final product. However, all the experiments have been done with a degradable bulking agent: cornstalks, rice straw, sawdust, etc. Therefore, the contribution of wood chips, the bulking agent mostly used nowadays in composting facilities, to VOC emissions is not described. The presence of plastics, glass and other non-organic wastes could replace the bulking agent (wood chips) function when mixed MSW are composted.

The objective of this work is to study the emissions of VOC, CH_4, N_2O and NH_3 during the composting process of MSW and the effect of the bulking agent in these emissions. With this purpose, three wastes have been composted: non source selected MSW (high level of impurities), source selected OFMSW (low level of impurities) with wood chips as bulking agent and source selected OFMSW with polyethylene (PE) tube as bulking agent since this non-biodegradable material will not contribute to the emissions of the studied compounds. This study can provide the baseline to distinguish between the emissions from the waste itself and the bulking agent, an aspect that it is not clear in composting scientific literature.

2. Materials and Methods

2.1 Waste composted

The wastes used in the experiments were different types of municipal solid wastes. Specifically, 100 kg of non-source selected MSW from a waste treatment plant located in Zaragoza (Spain) were composted as received at the plant (MSW). In the case of source selected OFMSW two cases were studied: i) OF_wood, 100 kg of material that were already mixed with wood chips in the plant (ratio 1:1, v:v) and ii) OF_tube, 100 kg of material that were used as received at the plant. In this case, the OFMSW was manually mixed with PE tube pieces of 25 mm diameter and 4 to 15 cm long (ratio 1:1,

v:v). Both OFMSW were obtained from a composting plant in Manresa (Barcelona, Spain). All the composting experiments with the three wastes considered (MSW, OF_wood and OF_tube) were carried out with aliquots of 25 kg per reactor and performed in duplicate.

Air-filled porosity was determined using an air pycnometer according to previous studies (specific details about the methodology can be found in Ruggieri et al., 2009). The results of air-filled porosity for OF_wood and OF_tube, mixed in the laboratory, initial MSW (not mixed, the waste collected was composted as collected from the plant) and final samples for the six trials can be found in Table 1. A homogeneous sample from each waste and each mixture (waste plus bulking agent) was stored at -18 ºC to be used for waste characterization.

The main characteristics of the initial wastes and the final products obtained from each experiment are presented in Table 1. Dry and organic matter, conductivity and pH have been determined in triplicate following the standard procedures for composting samples (US Department of Agriculture and US Composting Council, 2001).

2.2 Composting pilot plant

The results presented in this study were obtained in a pilot scale composting plant using two near-to-adiabatic non-commercial cylindrical reactors with an operating volume of 50 L each and forced aeration. A schematic diagram of the pilot reactors and a detailed description can be found elsewhere (Puyuelo et al., 2010).

Gas samples were collected in 1-L Tedlar® bags for VOC N_2O, CH_4 and NH_3 determination. Also a 250-mL glass gas collector was used for samples taken for VOC

137 composition determination. In all cases, one sample per day and per reactor was
138 withdrawn.

139 The data acquisition system is a PLC Data Acquisition. It consists of a
140 microcontroller that interprets the potential changes of the sensors connected to its
141 inputs in numerical values. It also realizes the reverse function: converting numerical
142 values into voltage, thereby allowing performing an automatic control. Temperature
143 (PT100 sensor, Desin Instruments, Barcelona, Spain), exhaust gas oxygen concentration
144 (Alphasense, A2O2, UK) and inlet airflow (Bronkhorst Hitec, The Netherlands) were
145 monitored during the experimental trials. According to the values of oxygen
146 concentration, airflow and temperature, the PLC acts on the flow meter, allowing
147 airflow from 0.2 to 10 liters per minute. The controller performs roughly 25 readings
148 per second, sending to the reader a temporal data every second and a real data each
149 minute. The communication is done by a serial port interface. Data are visualized
150 through the connection of the PLC data acquisition system to an internal Ethernet
151 network.

152 The control strategy used in the experiments has been presented in Puyuelo et al.
153 (2010). The main objective of this strategy is to obtain an automatic airflow regulation
154 that maximizes the biological activity in the reactor measured as OUR (Oxygen Uptake
155 Rate). OUR control permits the optimization of energy consumption during the process
156 while achieving a high degree of stability in the final product. Briefly, the controller
157 works in cycles of 1 hour. The designed OUR control loop compares the variations in
158 the OUR measurements reached among the successive cycles according to the airflow
159 applied. After completing a cycle, the oxygen level is revised to avoid percentages
160 below 5 % of oxygen concentration in air (v/v). If the level is below this limit, airflow
161 will be increased by 50 %. If an adequate oxygen level has been measured, the next step

will be the control loop based on the OUR measurement and the applied flow comparison between two consecutive cycles. For both parameters, three situations are possible, i.e., the system determines if the current value is lower than, higher than or equal to the previous value. Different absolute thresholds were established to define the superior and inferior limits in which the variation of OUR and airflow can be considered negligible. The limit to detect OUR variation was defined as 0.5 % of the maximum OUR achieved in previous experiments in the reactor (approximately 15 g O_2 h^{-1}). The range considered for the airflow measurements was 0.05 L min^{-1}. Considering the airflow measurements, the controller checks the OUR variation. Next, the controller determines if the OUR variation obtained is linked to an increase, decrease or a constant airflow.

2.3. Stability degree

On the basis of the methodology proposed by Adani et al. (2006) to assess the degree of biological stability, the dynamic respiration index (DRI) was measured using a respirometer (Ponsá et al., 2010). Briefly, the determination consists of placing 150 g of sample in a 500-mL Erlenmeyer flask and incubating the sample in a water bath at 37 ºC. A constant airflow was supplied through the sample, and the oxygen content in the outgoing gases was measured. From this assay, DRI was determined as the maximum average value of respiration activity measured during 24 hours, expressed in mg O_2 g^{-1} OM h^{-1}. A detailed description of this dynamic respirometer can be found at Ponsá et al. (2010). All the samples were analyzed in triplicate.

185 *2.4. Determination of gaseous emissions*

186 VOC, CH_4 and N_2O analysis was performed by means of gas chromatography
187 (Agilent Technologies 6890N Network GC system, Madrid, Spain) as explained in
188 Colón et al. (2012). All samples were analyzed in triplicate for each compound. The
189 deviation found per each triplicate was lower than 5% for all the compounds except for
190 VOC that was less than 10%.

191 Ammonia concentration was measured in situ at the gas outlet of the composting
192 reactor by means of an ammonia sensor (Industrial Scientific sensor iTX-T82, Oakdale,
193 PA, USA) with a measurement range of 0 to 1200 ppmv. The sensor was placed inside a
194 hermetic recipient with inlet and outlet holes that allowed gas circulation. The
195 measurement was taken when the value was stabilized during a period of constant flow.
196 Ammonia was measured just before the water trap installed to protect the rest of
197 measurement devices from moisture avoiding the effect of ammonia solubilization in
198 the condensate water from the composting process exhaust gases.

199

200 *2.5. GC-MS detection*

201 A sample from each process was taken daily in a 250 mL glass gas collector.
202 VOC characterization was performed using air samples analyzed by SPME (Solid Phase
203 Micro Extraction)/GC-MS, as previously reported by other authors (Orzi et al., 2010).

204 A manual SPME device with divinylbenzene
205 (DVB)/Carboxen/polydimethylsiloxane (PDMS) 50–30 μm fiber from Supelco
206 (Bellefonte, PA, USA) was used. The compounds were adsorbed from the air samples
207 by exposing the fiber (preconditioned for 1 h at 270 °C, as suggested by the supplier) to
208 the sample in the glass gas collector for 30 min at room temperature. A solution of
209 deuterated *p*-xylene in methanol was used as internal standard (IS).

VOC characterization was performed using a Gas Chromatograph (Agilent 5975C) coupled with a 7890 Series GC/MSD. Volatile compounds were separated using a capillary column for VOC (Agilent Technologies DB-624) measuring 60 m x 0.25 mm with a film thickness of 1.40 μm. Carrier gas was helium at a flow rate of 0.8 mL min^{-1}. VOC were desorbed by exposing the fiber in the GC injection port for 3 min at 250 °C. A 0.75-mm internal diameter glass liner was used, and the injection port was in splitless mode. The temperature program was isothermal for 2 min at 50 °C, raised to 170 °C at a rate of 3 °C min^{-1} and, finally, to 230 ºC at a rate of 8 °C min^{-1}. The transfer line to the mass spectrometer was maintained at 235 °C. The mass spectra were obtained by electron ionization at 70 eV, a multiplier voltage of 1379 V and collecting data over the mass range of 33–300.

Deuterated *p*-xylene was used to determine the fiber and GC-MS response factors for 15 typical compounds emitted in composting processes according to the literature (Scaglia et al., 2011; Suffet et al., 2009). These 15 compounds were diluted in methanol at the same concentration as deuterated *p*-xylene. This solution (10 μL) was injected into the glass gas collector with 10 μL of deuterated *p*-xylene in methanol solution. The fiber was exposed for 30 minutes to the resulting solution and injected into the GC-MS using the same method as described above. The area obtained for each compound was compared to deuterated *p*-xylene to determine each response factor. The aim of determining these response factors is to increase the reliability of the quantitative analysis.

Compounds were identified by comparing their mass spectra with the mass spectra contained in the NIST (USA) 98 library. A semi-quantitative analysis for all the identified compounds was performed by direct comparison with the internal standard. Quantitative analysis was performed for *m*-xylene, *n*-decane, alpha-pinene, beta-pinene,

limonene, toluene, dimethyl disulfide, hexanal, styrene, cyclohexanone, nonanal, decanal, eucalyptol, pyridine and 2-pentanone. These compounds have been the most common VOC found in previous experiments (Maulini-Duran et al., 2013), representing different VOC families.

3. Results and Discussion

3.1. Process evolution

As mentioned before, air filled porosity was determined for initial and final materials of each process. OFMSW was mixed with wood chips (OF_wood) and PE tube (OF_tube), respectively, until adjusting AFP to adequate values. MSW presented adequate AFP without addition of bulking agent due to the presence of impurities. Initial and final AFP values for the three materials are summarized in Table 1. These values are within the range recommended for an adequate development of the composting process (Ruggieri et al., 2009).

The evolution of the composting process of the three wastes studied was followed through OUR, temperature, airflow and oxygen concentration. Similar OUR, oxygen, temperature and airflow profiles were observed in the duplicates for the same waste. Figure 1 shows the profiles obtained for all these parameters for one replicate of each experiment: OFMSW with wood chips as bulking agent (replicate OF_wood-I, Figure 1a), OFMSW with PE tube as bulking agent (replicate OF_tube-I, Figure 1b) and MSW (replicate MSW-I, Figure 1c).

The six trials reached thermophilic conditions during the first day of process, according to the biodegradability of the material. The maximum temperature reached during OF_wood composting (Figure 1a) was of 68 ºC in both trials. The reactors needed approximately 17 days to return to mesophilic conditions. The thermophilic

peak matched with the highest OUR value (21 g O_2 h^{-1}) and therefore the highest airflow provided (7.5 L min^{-1}).

During OF_tube composting (Figure 1b) the maximum temperature achieved was 56 ºC, lower than that of OF_wood. In this case the inert bulking agent used was an empty tube that allowed air passing through the bulking material, thus increasing the air filled porosity. Indeed, air filled porosity in OF_tube trials was more than 10% higher than the other wastes composted during the experiments. This higher porosity enhances heat dissipation, reaching lower temperatures and cooling faster than the other trials, reaching mesophilic conditions around the 9^{th} day of process. Maximum OUR and airflow values were 9 g O_2 h^{-1} and 4.8 L min^{-1}, respectively.

The maximum temperature achieved during the composting process of MSW was 68ºC (as was in OF_wood composting). The airflow supplied in both MSW trials was lower than in the other experiments (2.2 L min^{-1}), matching again the highest airflow and the highest OUR value (10 g O_2 h^{-1}) with the beginning of the thermophilic phase.

According to the temperature profile and DRI values of the final material obtained for replicates of each waste composted (Table 1), the composting process evolution was satisfactory, and the final product was stabilized (Adani et al. ,2006).

3.2 Gaseous emissions

The daily evolution of VOC, CH_4, N_2O and NH_3 emissions for each waste is shown in Figure 2. Error bars indicate the differences between the two replicates. In Table 2, the emission factors for VOC, CH_4, N_2O and NH_3 are also summarized for each trial in terms of kg of compound emitted per Mg of treated waste.

285 *CH_4 emissions*

286 Figure 2a presents the evolution of methane emissions during the composting
287 process of the three waste mixtures. As can be seen in Figure 2a, there is a very
288 significant difference between CH_4 emissions from OF_wood and from the other two
289 wastes. Methane emissions are related to the presence of anaerobic zones, maybe due to
290 excessive moisture and insufficient porosity or an inappropriate aeration system strategy
291 (Amlinger et al., 2008). Carbon is used as an electron acceptor when other more
292 energetically favorable electron acceptors, including oxygen, nitrogen, iron, manganese
293 and sulphur, have been exhausted (Brown et al., 2008). Moisture and porosity (Table 1)
294 were in the optimal ranges in all the experiments. In addition, as observed in Figure 1a
295 the oxygen content was always over 17% after the first day of process. However the
296 presence of a high content of rapidly biodegradable organic matter could lead to oxygen
297 depletion, creating anaerobic areas in the solid matrix. The main methane emission
298 during OF_wood composting process can be observed from day 6 to day 21 (Figure 2a),
299 when the microbial activity is decreasing. He et al. (2000) reported that composting
300 wastes with a high easily biodegradable matter content such as food wastes, could lead
301 to the formation of anaerobic zones due to compaction effects. Material compaction was
302 detected at the end of the experiments as the composting reactors were neither opened
303 nor the material turned for the whole process. However, it cannot be ascertained
304 whether the compaction occurred at the initial or final stages of the process. On the
305 other hand, there is a small difference between initial and final porosity. Ruggieri et al.
306 (2008) stated that changes in air-filled porosity from initial to final samples in the
307 composting process are not representative of what has been occurring in the reactor
308 during the process. These authors detected the lowest air-filled porosity values after 48
309 hours of composting process. In OF_wood composting experiments a 6L reduction

between initial and final volume of the waste in the reactor was observed thus indicating compaction even if air-filled porosity values do not show it. Volume reduction for OF_tube and MSW were 3.4 and 2 L, respectively. Values in Table 2 confirm that CH_4 emission factor for the OF-wood processes was higher than the emission of the other processes.

In fact, lower methane emission during MSW and OF_tube composting processes (maximum values achieved in days two and five of process and corresponding to 0.004 kg of CH_4 Mg of dry waste $^{-1}$ for both wastes), may be explained by the lower compaction effect due to a lower content in biodegradable organic matter. Also the shorter thermophilic phase observed comparing MSW and OF_tube with OF_wood could be the explanation of these different emissions. Jiang et al. (2011) related higher methane emission with long thermophilic phases.

N_2O emissions

N_2O emissions evolution is presented in Figure 2b. The main N_2O emissions released during the six composting processes carried out were found during the first week. There is some controversy in the literature about N_2O emissions. El Kader et al. (2007), composting farm manure, and Yang et al. (2013), composting kitchen waste, reported the highest N_2O emissions during the first week of composting process. However, Fukumoto et al. (2003) related the inhibition of N_2O emissions with thermophilic temperatures, which occur usually during the first week of the process. Regarding the different wastes composted in this study, there are no significant differences between the emissions factors obtained for N_2O emissions, as can be observed in Table 2. Since the type of biodegradable organic matter is the same in the three wastes maybe the type of bulking agent has no effect in N_2O emissions.

335

336 *NH_3 emissions*

337 Figure 2c reports ammonia emissions for the different wastes treated. Although also
338 in the case of ammonia, OF_wood is the waste presenting the highest emissions during
339 the whole composting process, there is an important deviation in the highest emission
340 point. However, even the lowest value for OF_wood reported in Table 2 (2.4 kg NH_3
341 Mg^{-1} dry matter) doubles the highest value presented for the other two wastes
342 (corresponding to MSW-I, 1 kg NH_3 Mg^{-1} dry matter). Pagans et al. (2006) reported that
343 NH_3 emissions were strongly related with the thermophilic phase of composting. The
344 trend observed in Figures 1 and 2c during all the trials agrees with this proposal.

345

346 *VOC emission*

347 In Figure 2d, total daily VOC emissions produced during the three experiments
348 are shown. As described by Komilis et al. (2004) the main emission of VOC was
349 detected during the first days in all the experiments, in the mesophilic to thermophilic
350 transition. Scaglia et al. (2011) reported that VOC, odor emissions and biological
351 activity were strongly related. In any composting process high temperatures are caused
352 by high biological activity. Even when enough aeration is provided to the reactor, these
353 factors cause some anoxic zones in the matrix that contribute to VOC emissions
354 (Maulini-Duran et al. 2013). During the OF_wood and MSW composting processes
355 more VOC have been emitted than during the OF_tube composting process. This could
356 be related again with the sustained thermophilic phase observed in OF_wood and MSW
357 processes in comparison with OF_tube. Also, a higher DRI reduction was achieved in
358 these wastes, reflecting a higher biological activity. Observing Figure 1, DRI reduction
359 is in agreement with the comparison of OUR profiles, where OF_wood and MSW

present higher values than OF_tube. Initial OF_wood has a higher DRI than the other treated wastes, which means a high content of biodegradable organic matter that could lead to the occurrence of anaerobic zones and the achievement of higher temperatures during the process.

Gaseous emissions and process evolution

Traditionally, the composting process can be divided into three stages, depending on the temperature evolution. The first period begins at day 0 of the experiment until the thermophilic temperature is reached (45ºC). The second stage coincides with the thermophilic period (>45ºC) and the third period corresponds to the return to mesophilic temperatures (<45ºC) (Haug, 1993).

No CH_4 was emitted during the first period of OF_wood composting process, 86 % in the second period and 14 % in the third period. In OF_tube, CH_4 was also emitted mainly during the second period (74 %), 7% in the first period and 19% third period. These differences could be caused by the fast OUR increase in OF_wood composting process and, therefore, a high airflow at the beginning of this process. The percentage distribution in MSW composting process is very similar than that of OF_tube: 17%, 73% and 10% (1^{st}, 2^{nd} and 3^{rd} period, respectively).

N_2O emissions during the first period of OF_wood composting were 2 %, 92% during the second period and 7 % during the third period. In OF_tube composting N_2O emissions are 8 % in the first period, 83 % during the second period and 9 % during the third period. N_2O emissions detected in MSW composting process were: 14% (1^{st} period), 84% (2^{nd} period) and 2% (3^{rd} period). N_2O emissions for OFMSW and MSW were lower than raw sludge emissions in the same conditions (Maulini-Duran et al., 2013). For all the processes, the emission is higher during the thermophilic stage in the

three cases. However, N_2O concentration values were close to the detection limit of the analysis, thus involving higher errors between replicates (Figure 2b). This fact makes difficult to discard the inhibition of N_2O production at thermophilic temperatures.

Similar trends are also detected in NH_3 emissions during all the composting processes carried out. Only 3 % of the NH_3 emissions in OF_wood composting process occurred during the first period, 93 % was emitted during the second period and 4 % during the third one. In MSW emission percentages distribution was 1% (1^{st} period), 92% (2n period) and 7% (3^{rd} period) while in OF_tube composting, 78% of NH_3 was emitted during the second period and 28% during the third one; no NH_3 was emitted during the first period.

Also VOC emission detected during the composting processes studied follows a similar distribution during the three established periods for the three wastes. For OF_wood and MSW, the percentages are exactly the same: 9% in the first period, 90% during the second period and 1% in the third period. During OF_tube composting process, 15% of VOC were emitted during the first period, 82% during the second one and 3 % during the third period.

Analyzing these data, it is clear that gaseous emissions are strongly related with OUR values and temperature rise and, consequently, with the biological activity of the process. In a previous work, where raw and anaerobically digested sludge were composted, the relationship between composting periods and compounds emissions distribution was not so clear (Maulini-Duran et al., 2013). However, values of OUR, airflow and temperatures were clearly lower, especially in the case of anaerobically digested sludge where no thermophilic temperatures were reached.

The trends in VOC, CH_4, N_2O and NH_3 emissions and the emission factors reported in Table 2, could be of interest for plant designers and operators, particularly,

410 to the design of gaseous emissions equipment and to its operation. It is worthwhile to
411 mention that the deviation found between duplicates is in the low range (three values
412 out of twelve higher than 40%) when compared to similar studies of composting
413 emissions of wastes of high heterogeneity (Colón et al., 2012; Maulini-Duran et al.,
414 2013; Maulini-Duran et al., 2014).

415 On the other hand, although N_2O emission factor is the lowest among the
416 analyzed contaminants, the greenhouse effect of this compound has to be taken into
417 account. The global warming potential of N_2O is 298 kg CO_2 eq., higher than the
418 methane potential (34 kg CO_2 eq) (IPCC, 2013).

419 The use of a synthetic bulking agent points to a reduction in CH_4, NH_3 and VOC
420 emissions and to a lower compaction. However, from our results wood chips have some
421 advantages in front of PE bulking agent, such as moisture adjustment, higher
422 temperatures, better organic matter stabilization and the fact that another organic waste
423 is being valorized (pruning waste, shredded pallets…)

424

425 *3.3. VOC characterization by SPME/GC-MS*

426 A large number of emitted VOC was identified during the six composting
427 processes. These compounds have been classified into the following chemical families:
428 alcohols, esters, furans, ketones, aliphatic hydrocarbons, aromatic hydrocarbons,
429 aldehydes, halogenated compounds, nitrogen-containing compounds, sulphur-
430 containing compounds and terpenes. The total percentages of each VOC family emitted
431 are summarized in Table 3 for each composting process. A quantitative analysis has
432 also been carried out with some specific and typical VOC emitted during a composting
433 process (Scaglia et al., 2011). In particular, fifteen typical VOC have been identified,

434 but only 10 of these compounds have been found in the composting processes studied.
435 These 10 compounds and their amounts are summarized in Table 4.
436 As can be seen in Table 3, aldehydes emission was almost zero during all the
437 composting processes studied. Also halogenated compounds have been only found
438 during one of the MSW composting processes, in a very low percentage (Table 3).
439 Avoiding source selecting before composting, batteries and remains of some toxic
440 products were found in the initial waste. That could be the reason for finding
441 halogenated compounds in gaseous emissions only during MSW composting process.
442 Furans and esters were present in gaseous emissions from almost all the
443 composting trials with similar percentages, all of them around 1% (Table 3). These
444 compounds were emitted at low concentrations during the whole composting processes.
445 At the end of the process these percentages rise slightly due to the decrease in the
446 emission of the other VOC found. No relationship seem to exist between furans and
447 esters emissions and process evolution suggesting that these compounds were not
448 generated during the composting process but their emission could be a consequence of
449 stripping. Some of the esters found are phthalate acid esters that have been used for over
450 50 years in the manufacture of resins and plastics such as PVC (Clarke and Smith,
451 2011). This fact could explain why esters emission was higher in MSW composting
452 processes.
453 Nitride molecules have been also emitted with similar percentages in all the
454 trials (Table 3). This family is mainly represented by pyridine, related to putrid odor
455 (Suffet et al., 2009). Pyridine emissions have been quantified and reflected in Table 4.
456 The quantity of pyridine emitted is similar in OF_wood and MSW trials, but lower in
457 OF_tube.

458 Percentages of sulphide molecules emitted during MSW and OF_wood
459 processes are higher than in OF_tube composting process. The same trend is observed
460 in Table 4, with the main sulphide molecule emitted: dimethyl disulphide. This
461 compound is the most emitted VOC during MSW and OF_wood composting processes.
462 Dimethyl disulphide is a strong odorant and its concentration should be kept bellow
463 odor threshold values to avoid complaints against waste treatment installations.
464 Dimethyl disulphide was detected in all the samples analyzed during the different
465 experiments, always over the odor threshold, 0.007 mg m^{-3} (Environmental Protection
466 Agency, 2010).
467 Percentages of aliphatic and aromatic hydrocarbons are clearly higher in MSW
468 composting process than in OF_wood and OF_tube. The quantitative analysis confirms
469 this trend with toluene, xylene and decane, present in MSW composting emissions but
470 not detected during source selected OFMSW composting trials. Styrene, another
471 aromatic hydrocarbon, has been detected during all the processes with similar
472 quantities. Styrene emission may be related to the organic fraction itself while the origin
473 of toluene, xylene and decane is more related with impurities. Aromatic hydrocarbons
474 are described as indicators of hazardous compounds and odor nuisance sources
475 (Palmiotto et al., 2014).
476 Ketones emission could be a consequence of alcohols oxidation, also in other
477 studies percentages of ketones and alcohols are related (Maulini-Duran et al., 2013).
478 Alcohols percentage is higher in OF_tube and OF_wood than in MSW composting. The
479 same trend is observed for ketones. 2-pentanone and various cycloketones are common
480 in air contaminants. 2-pentanone has been quantified, similar emission factor have been
481 found in all the experiments carried out.

Summarizing, predominant VOC families (percentages in emissions over 5%) and individual compounds for OF_wood were terpenes, alcohols, ketones and sulphide molecules, with dimethyl disulphide as the main emitted compound. In the case of OF_tube, terpenes and alcohols dominate in VOC emissions being limonene and dimethyl disulphide the individual compounds with higher concentration. Finally in MSW composting, terpenes, aromatic hydrocarbons and aliphatic hydrocarbons presented the higher percentages while dimethyl disulphide and limonene presented the highest concentration.

One of the aims of this study was to ascertain the main origin of terpenes in the composting emissions. Terpenes are always the VOC family presenting the highest percentage in composting emissions not only in the case of OFMSW and MSW but also in other wastes such as sludge (Maulini-Duran et al. 2013). Staley et al. (2006) described terpenes as the main compounds responsible for odorous pollution at composting facilities. Eitzer (1995) noted that terpenes were the characteristic intermediates produced from the aerobic degradation of organic matter during composting.

Also in the experiments presented in this work, terpenes were the most emitted family of VOC in all the trials carried out. The difference observed in terpenes emission percentages between OF_wood-I and OF_wood II trials (Table 3) is due to the different amount of alcohols emitted in the two processes. Accordingly, the same percentage effect is observed during MSW processes. In the case of MSW-I more hydrocarbons (aliphatic and aromatic) were emitted than in MSW-II. Unexpectedly, the highest percentage of terpenes is emitted during OF_tube composting process, with very low variation between duplicates. Regarding Table 4, the quantitative analysis of limonene is highly homogenous between the different composted wastes, being slightly higher in

MSW composting processes. However, alpha-pinene emission is clearly higher in OF_wood trials than during OFMSW composting processes without wood chips as bulking agent. The same trend is observed for beta-pinene emission, but with lower differences between the different wastes. Alpha-pinene comparison is even clearer if only OF_tube and OF_wood are considered (total absence of wood materials in MSW cannot be assured). From the comparison of OF_tube and OF_wood it can be stated that the same waste with different bulking agent emits similar quantities of all the other compounds quantified, but not alpha-pinene, which emission is 100-fold higher during OF_wood processes than in OF_tube ones. Büyüksönmez and Evans (2007) composted wood chips and pruning wastes, concluding that terpenes are the single most important type of VOC emitted. Specifically, alpha-pinene was the most prevalent compound representing either the largest or the major portion of the total emissions.

4. Conclusions

VOC, CH_4, N_2O and NH_3 emissions during MSW and OFMSW composting at pilot scale were mainly produced in coinciding with maximum temperature and biological activity.

VOC, CH_4 and NH_3 emission factors in OFMSW composting with wood chips as bulking agent were higher than in OFMSW composting with PE tube (synthetic bulking agent). Terpenes were the main VOC family found in all cases, regardless the presence of wood in the reactor. Alpha and beta pinene emission was higher during composting with wood chips. However, wood chips present some composting advantages in front of PE such as moisture adjustment and waste stabilization.

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Figure Legends

Figure 1. Evolution of temperature, airflow, OUR and oxygen content during composting: (a) OF_wood, (b) OF_tube and (c) MSW. Due to the similarity of profiles, only one graph is shown for each waste representing the six trials carried out. Legend in Fig 1a is the same for Fig 1b and 1c.

Figure 2. Daily emission factors (kg of compound Mg^{-1} treated waste) evolution for (a) CH_4, (b) N_2O, (c) NH_3 and (d) VOC, for the six trials carried out. Values presented are an average of the two duplicated reactors for each waste with the corresponding deviation. Legend in Fig 2a is the same for Fig 2b, 2c and 2d.

Table 1. Characterization of the initial waste mixtures and materials obtained at the end of the process.

Material	Dry Matter (%, wb*)	Organic Matter (%, db*)	DRI* (mg O_2 g^{-1} OM h^{-1})	pH	Conductivity (µs/cm)	Air filled porosity (%)
OF-wood	40 ± 5	78 ± 1	2.9 ± 0.2	7.05	2034	70
OF-wood-I (final product)	37 ± 0.3	72 ± 2	0.5 ± 0.1	8.72	2789	67
OF-wood-II (final product)	37 ± 2.4	73 ± 3	1.1 ± 0.0	8.78	3198	66
OF-tube	38 ± 2	82 ± 0	1.9 ± 0.0	5.80	1877	80
OF-tube-I (final product)	38 ± 2	73 ± 6	1.2 ± 0.2	8.74	2930	85
OF-tube-II (final product)	39 ± 1	65 ± 4	1.0 ± 0.01	8.69	2540	84
MSW	41 ± 2	68 ± 2	1.9 ± 0.1	6.72	3750	69
MSW-I (final product)	41 ± 5	32 ± 5	0.8 ± 0.1	8.78	2370	69
MSW-II (final product)	43 ± 1	45 ± 1	0.9 ± 0.1	8.56	3560	69

Table 2. Emission Factors for VOC, CH_4, N_2O and NH_3 (kg of compound emitted Mg^{-1} of dry matter). For each waste, values for each replication are presented jointly with the average of the two duplicated reactors with the corresponding deviation.

Trials	CH_4	N_2O	NH_3	VOC
OF_wood-I	1.34	0.0250	6.32	1.16
OF_wood-II	1.21	0.0169	2.37	0.813
OF_wood_mean	1.27 ± 0.09	0.0210 ± 0.006	4.34 ± 2.79	0.989 ± 0.249
OF_tube_I	0.0155	0.0173	0.422	0.630
OF_tube_II	0.0214	0.0250	0.802	0.745
OF_tube_mean	0.0185 ± 0.004	0.0211 ± 0.005	0.612 ± 0.269	0.688 ± 0.082
MSW-I	0.0428	0.0429	1.15	1.19
MSW-II	0.0670	0.0221	0.860	0.924
MSW_mean	0.0549 ± 0.017	0.0325 ± 0.015	1.00 ± 0.20	1.05 ± 0.18

Table 3. Percentages of different VOC families emitted during the six processes studied.

Trial	Terpenes	Furans	Esters	Alcohols	Ketones	Nitride molecules	Sulphide molecules	Aliphatic hydrocarbons	Aromatic hydrocarbons	Aldehydes	Halogenated compounds
OF_wood-I	58.6	1.0	0.0	15.5	9.3	1.8	7.4	3.1	3.3	0.0	0.0
OF_wood-II	72.3	1.4	0.0	5.2	7.1	0.8	7.4	2.5	3.2	0.0	0.0
OF_tube_I	81.6	0.0	0.9	8.7	3.2	0.7	2.0	1.0	1.8	0.1	0.0
OF_tube_II	81.5	0.1	0.9	6.9	3.3	0.8	3.2	1.7	1.5	0.1	0.0
MSW-I	47.5	1.3	0.8	2.1	1.2	0.6	4.8	16.0	25.1	0.0	0.5
MSW-II	61.0	1.4	1.6	6.0	2.9	0.5	6.6	6.6	13.3	0.0	0.0

Table 4. Total emission of quantified VOC (kg of compound emitted Mg^{-1} of dry matter).

Trial	Styrene	2-pentanone	alpha-pinene	beta-pinene	limonene	dimethyl disulfide	Pyridine	Toluene	Xylene	Decane
OF_wood-I	0.0000646	0.00191	0.01636	0.0116	0.0914	0.0734	0.000882	n.d.	n.d.	n.d.
OF_wood-II	0.00140	0.00144	0.03636	0.00647	0.0760	0.118	0.00206	n.d.	n.d.	n.d.
OF_tube_I	0.00171	0.0134	0.00053	0.000882	0.113	0.0121	0.000290	n.d.	n.d.	n.d.
OF_tube_II	0.00122	0.00333	0.00038	0.00143	0.0593	0.0138	0.0000582	n.d.	n.d.	n.d.
MSW-I	0.00205	0.00649	0.00514	n.d.	0.175	0.327	0.00249	0.0176	0.00340	0.0151
MSW-II	0.00154	0.00548	0.00700	0.00415	0.124	0.285	0.00108	0.00451	0.00255	0.00783

Figure 1

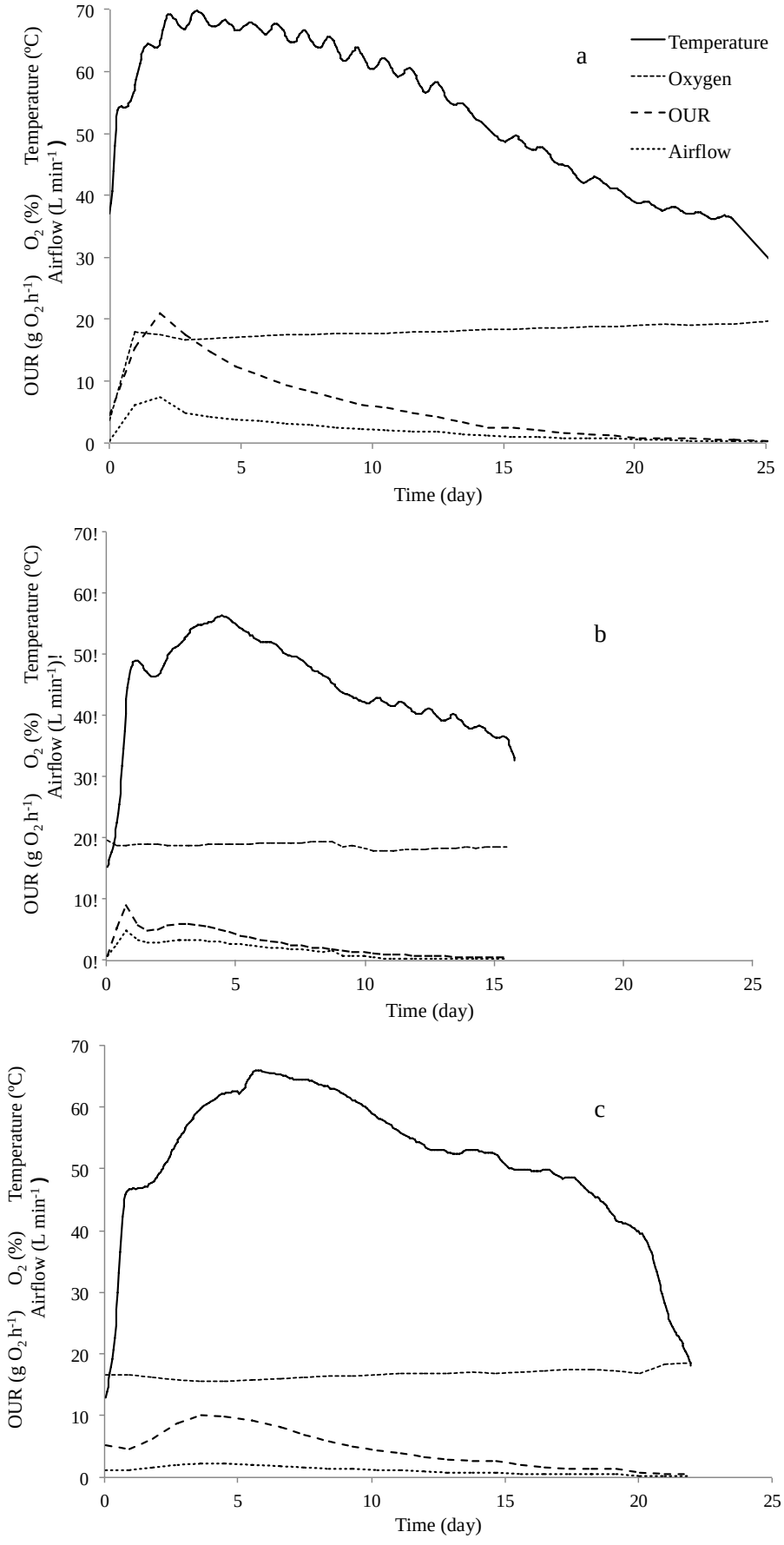
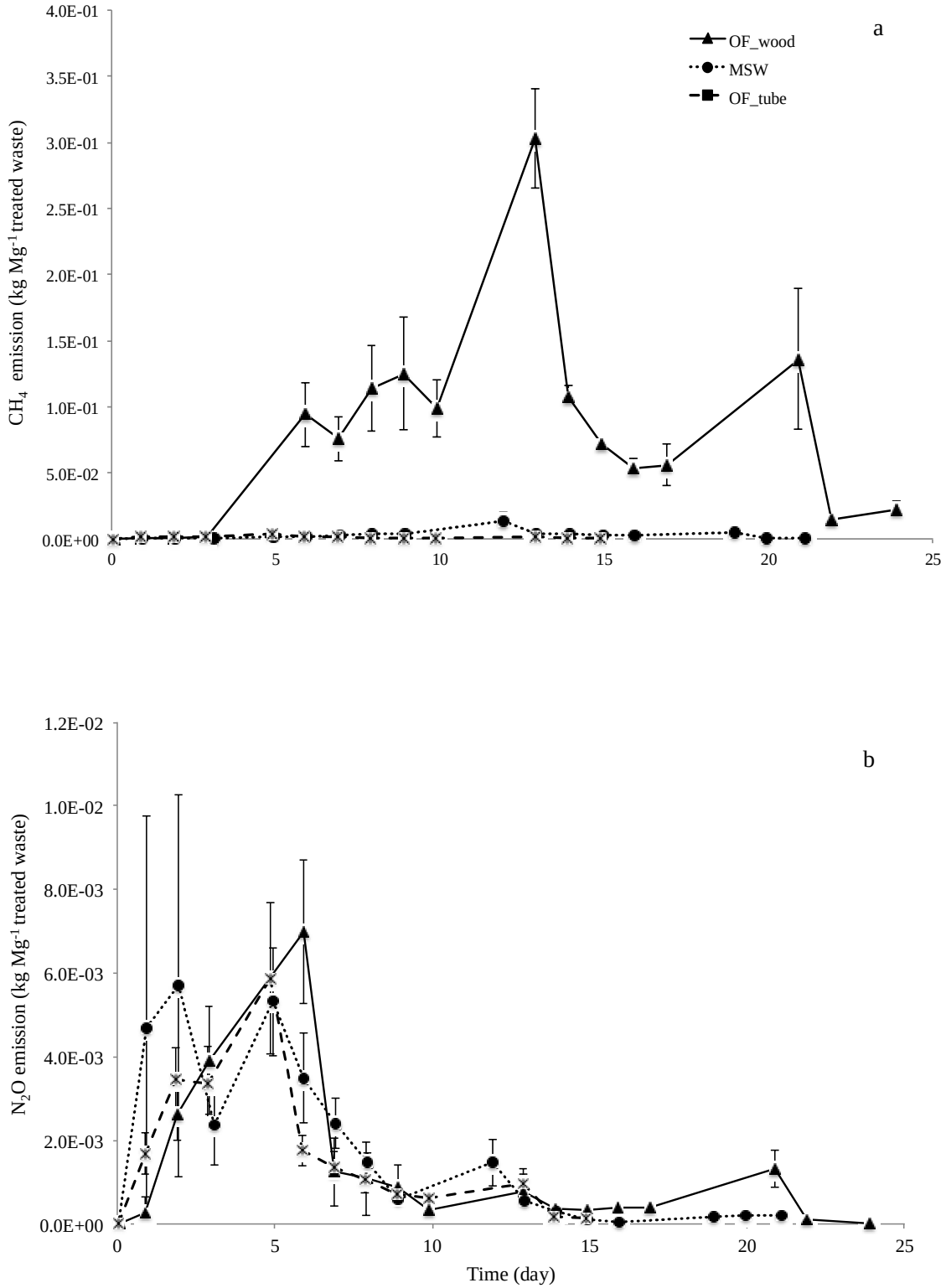
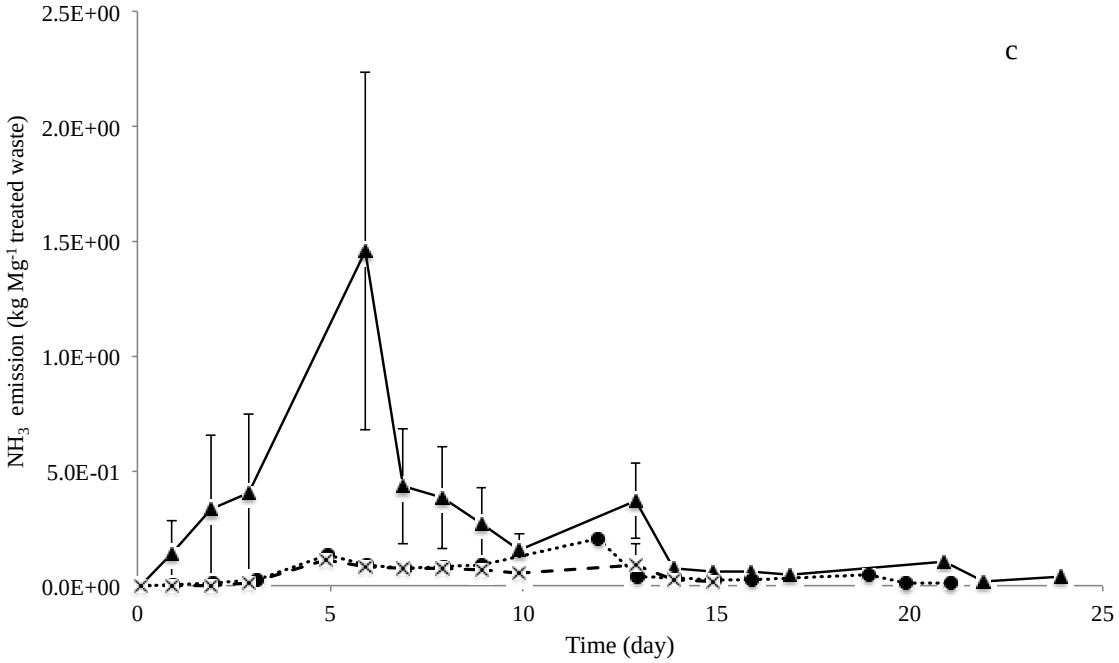
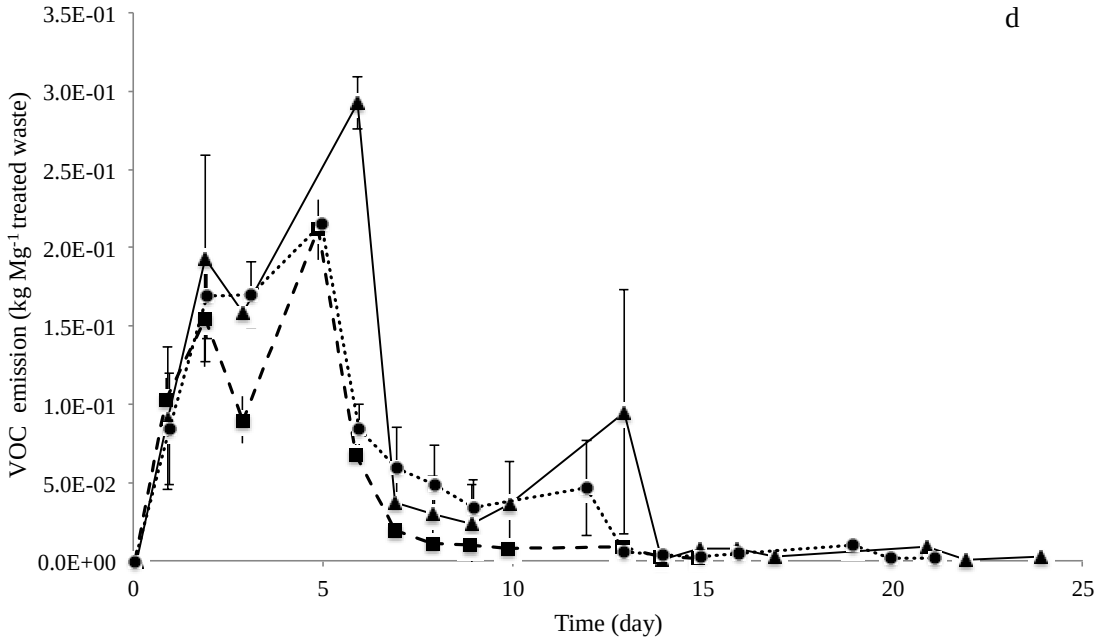

a
Temperature
Oxygen
OUR
Airflow
OUR (g O2 h-1) O2 (%) Airflow (L min-1) Temperature (ºC)
Time (day)
b
OUR (g O2 h-1) O2 (%) Airflow (L min-1)! Temperature (ºC)
Time (day)
c
OUR (g O2 h-1) O2 (%) Airflow (L min-1) Temperature (ºC)
Time (day)

Figure 2


a
OF_wood
MSW
OF_tube
CH4 emission (kg Mg-1 treated waste)
4.0E-01
3.5E-01
3.0E-01
2.5E-01
2.0E-01
1.5E-01
1.0E-01
5.0E-02
0.0E+00
0
5
10
15
20
25
b
N2O emission (kg Mg-1 treated waste)
1.2E-02
1.0E-02
8.0E-03
6.0E-03
4.0E-03
2.0E-03
0.0E+00
Time (day)


c
2.5E+00
2.0E+00
1.5E+00
1.0E+00
5.0E-01
0.0E+00
NH3 emission (kg Mg-1 treated waste)
0
5
10
15
20
25
Time (day)


d
3.5E-01
3.0E-01
2.5E-01
2.0E-01
1.5E-01
1.0E-01
5.0E-02
0.0E+00
VOC emission (kg Mg-1 treated waste)
0
5
10
15
20
25
Time (day)