

Inventory and Treatment of Compost Maturation emissions in a Municipal Solid Waste Treatment Facility

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Abstract

Emissions of volatile organic compounds (VOCs) from the compost maturation building in a municipal solid waste treatment facility were inventoried by solid phase microextraction and gas chromatography-mass spectrometry. A large diversity of chemical classes and compounds were found. The highest concentrations were found for n-butanol, methyl ethyl ketone and limonene (ppm_v level). Also, a range of compounds exceeded their odor threshold evidencing that treatment was needed. Performance of a chemical scrubber followed by two parallel biofilters packed with an advanced packing material and treating an average airflow of 99300 m³ h⁻¹ was assessed in the treatment of the VOCs inventoried. Performance of the odor abatement system was evaluated in terms of removal efficiency by comparing inlet and outlet abundances. Outlet concentrations of selected VOCs permitted to identify critical odorants emitted to the atmosphere. In particular, limonene was found as the most critical VOC in the present study. Only six compounds from the odorant group were removed with efficiencies

27 higher than 90%. Low removal efficiencies were found for most of the compounds
28 present in the emission showing a significant relation with their chemical properties
29 (functionality and solubility) and operational parameters (temperature, pH and inlet
30 concentration). Interestingly, benzaldehyde and benzyl alcohol were found to be
31 produced in the treatment system.

32

33 **Keywords:** Volatile Organic Compounds, SPME/GC-MS, emissions inventory,
34 chemical scrubber plus biofilter, treatment efficiency

35

36 **Abbreviations**

37 SPME/GC-MS: solid phase microextraction / gas chromatography-mass spectrometry

38 MSW: municipal solid waste

39 MSWTF: municipal solid waste treatment facility

40 VOC: volatile organic compound

41

42 **1. Introduction**

43 The rapid increase in volume and types of solid and hazardous wastes as a result of
44 continuous economic growth, urbanization and industrialization, is becoming a
45 burgeoning problem for national and local governments to ensure effective and
46 sustainable management of wastes (United Nations Environment Programme, 2009). It
47 was estimated that in 2006 the total amount of municipal solid waste (MSW) generated
48 globally reached 2.02 billion tones, a 7% annual increase since 2003. It was further
49 estimated that between 2007 and 2011, the global generation of municipal wastes would
50 rise by 37.3%, equivalent to roughly 8% increase per year. The EU estimates that its 25
51 member states produce 700 million tons of agricultural wastes annually (Global Waste

52 Management Market Assessment, 2007). In this scenario, municipal solid waste
53 treatment facilities (MSWTF), whose main goal is to reduce the biodegradable organic
54 matter content and stabilize wastes by means of chemical and biological processes
55 (solid waste stream can contain a range of 35–50% of organic materials), have received
56 special attention from European authorities (Ponsa et al., 2008).

57

58 During processing of solid wastes, generation of gases with complex mixtures of
59 compounds creates odor problems in a huge number of sources. The importance of
60 managing odorous emissions at these facilities has become more significant in recent
61 years, mainly due to the increasing number of complaints and reported failures in the
62 performance of odor abatement systems (Gostelow et al., 2001; Lebrero et al., 2011).
63 Gaseous emissions in MSWTF are typically generated by decomposition of nitrogen-
64 based compounds, sulfur-based compounds and a wide range of compounds dominated
65 by volatile organic compounds (VOCs) (Eitzer, 1995). However, most references in
66 literature target the analysis of the composting process and its emissions
67 characterization, while VOC emissions inventories are lacking from compost
68 maturation areas, and particularly from MSWTF. The majority of the studies devoted to
69 composting facilities include the emissions of the process as a whole, mainly if the
70 process takes place in enclosed facilities where gaseous emissions treatment is not often
71 performed separately.

72

73 Adsorption and chemical scrubbing have been traditionally used as cost-effective,
74 simple and safe methods for controlling odors either as primary treatment and/or as
75 polishing stage in odor abatement. However, other techniques such as biofilters,
76 biotrickling filters or bioscrubbers have spread as efficient treatment processes for odor

77 removal, and more recently employed specifically in MSWTFs (last 10-20 years). In
78 general, low removal efficiencies are commonly reported for VOCs, which is related to
79 the complexity of the VOCs mixture emitted and the variability throughout the
80 composting process (Pagans et al., 2007). Moreover, in the case of emissions from
81 MSWTF, high gas flows must be treated which entail bioreactors with large bed
82 volumes. To avoid extreme designs, biofilters often are designed and operated at short
83 gas contact times, which affects mainly VOCs abatement due to the low solubility of
84 these compounds and the corresponding mass transfer limitation.

85

86 The complex nature of MSWTF odors provides many challenges with regards to
87 monitoring and control of these emissions, particularly in the design and operation of
88 odor abatement processes. To this aim as well as to manage emissions to an acceptable
89 level to limit receptor impact, deeper knowledge on real emissions composition and
90 removal efficiencies of odor abatement processes are required because, even at trace
91 level concentrations, most VOCs are malodorous and have very low odor thresholds
92 (Leonardos et al., 1969). The objectivity, repeatability and accuracy of the identification
93 and quantification of chemical compounds presented in the emission are warranted to
94 properly manage the facility as well as to design and operate treatment systems. A large
95 number of instrumental techniques are used with this purpose, including gas
96 chromatography; colorimetric reaction-based assays; catalytic, infrared and
97 electrochemical sensors; differential optical absorption spectroscopy; and fluorescence
98 spectrometry (Dewulf and Van Langenhove, 1999; Muñoz et al., 2010).

99

100 However, a limited number of full-scale studies have assessed the removal performance
101 of complex mixtures of VOCs. Often, the monitoring approach to evaluate the

102 performance is based on total carbon removal using total-VOC analyzers equipped with
103 photoionization detectors (Lafita et al., 2011; Martínez-Soria et al., 2009), which is an
104 alternative unable to assess the fate of individual compounds present in the gases to be
105 treated. Among the instrumental techniques presented above, gas chromatography is
106 viewed as the most precise and powerful analytical tool for the quantification and
107 identification of VOCs and volatile sulfur compounds (Dewulf and Van Langenhove,
108 2002). To increase the accurate quantification of compounds, solid phase
109 microextraction (SPME) is used as a pre-concentration technique based on the
110 adsorption of volatile compounds using microfibers coated with polymeric
111 organosilicon compounds (Ábalos et al., 2002; Larroque et al., 2006).

112

113 The aim of this study was to provide a VOCs emissions inventory and to analyze the
114 performance of two full-scale biofilters packed with an advanced packing material and a
115 chemical scrubber for the treatment of gaseous emissions from a compost maturation
116 building at a MSWTF in the Barcelona Metropolitan area. Removal efficiencies and
117 odorant concentrations were determined by SPME/GC-MS for a range of VOCs present
118 in the inlet and outlet of the abatement system to identify critical compounds emitted to
119 the atmosphere.

120

121 **2. Materials and methods**

122 *2.1. Full-scale biofilters and chemical scrubber characteristics*

123 The MSWTF under study is located in the metropolitan area of Barcelona (Spain). The
124 yearly nominal treatment capacity of the facility is around 240000 tons of solid residues
125 while approximately 38000 tons of compost are produced per year. Compost is
126 produced in two different, completely independent lines. Line 1 process organic MSW

127 separate collected while line 2 processes unsorted MSW. In both lines mechanical
128 pretreatments are performed to separate non-proper materials such as metals, glasses or
129 plastics. After pretreatment, a combined process consisting in anaerobic digestion
130 followed by digestate composting is performed in Line 1. Line 1 compost is not
131 matured and produced as high-quality compost useful for gardening and agricultural
132 uses. In line 2, pretreatment is followed by direct composting of waste in composting
133 tunnels. Later, a maturation stage allows further compost refining to produce compost
134 categorized as stabilized organic waste not adequate for gardening and agricultural uses.
135 In terms of gas treatment, the composting stage of both Line 1 and 2 takes place in the
136 same building in independent tunnels. Then, composting emissions of line 1 and 2 are
137 mixed and treated in a set of 4 scrubbers followed by four biofilters. Instead, maturation
138 off-gases are independently treated in the treatment units under study. Waste gases
139 collected from the maturation area are blown through an acid chemical scrubber and
140 two identical biofilters running in parallel (Figure 1).

141

142 Fig. 1: Schematic of the maturation building, emissions treatment system and sampling
143 locations at the MSWTF

144

145 The acid chemical treatment consists of a 12.6 m^3 acid chemical scrubber that treats a
146 measured average airflow of $99300 \text{ m}^3 \text{ h}^{-1}$ corresponding to an average gas contact time
147 of around 0.5 s. At such low gas contact time, only ammonia removal takes place in this
148 reactor due to the low solubility of VOCs (Baquerizo et al., 2009). Airflow was
149 measured by means of an S-type Pitot tube (Kymo Instruments, France). The
150 biofiltration system is composed by two identical, covered biofilters with 30 m in length
151 and 17 m in width. The inlet gas flow is equally divided in two streams in an air plenum

152 and directed to both biofilters. Biofilters are packed with a layer of Leca[®]
153 (bloated particles of burnt clay) for proper air distribution plus 1 m of a hybrid packing
154 material which consisted of spherical clay pallets covered by a thin layer of compost.
155 Such packing material has been designed elsewhere as an advanced packing material
156 (Almarcha et al., 2013) compared to classical packing materials often consisting in
157 organic materials such as wood chips. Further details about packing materials
158 characteristics can be found elsewhere (Andreasen and Poulsen, 2013; Dorado et al.,
159 2010; Hernández et al., 2010). Thus, a treatment volume of 610 m³ and a gas contact
160 time of 44 s per biofilter were warranted. A set of sprinklers are used in each biofilter to
161 humidify the packing material. Water is sprinkled for 10 min over the top of the packing
162 material twice per day. The average humidity in the surface of the packing material was
163 52 and 55% in each biofilter. Excess water is collected at the bottom. The average pH of
164 the biofilters leachate along the study was 5 and 5.8. A desktop pH-meter was used for
165 leachate pH analysis (Crison Instruments, Spain).

166

167 ***2.2 Sample Collection and measurement***

168 Gas samples from sampling points (Figure 1) were collected in 3 L Tedlar bags (SKC
169 Inc, USA) and analyzed by SPME/GC-MS the same day they were collected. A portable
170 SKC 224-PMCTX8 Air Sampler Pump was used to collect samples from both sampling
171 points due to negative or low positive pressure in the pipes. Samples were transferred
172 into 0.125 L Supelco gas sampling bulbs with Teflon and stopcock valves. According to
173 Davoli et al. (2003), deuterated p-xylene was used as internal standard (IS) by injecting
174 in each bulb a total of 5 µL of a dilution of 2 µL of pure deuterated p-xylene (99.9%
175 atom deuterated p-xylene, Sigma Aldrich) in 100 mL of pure methanol. The final
176 concentration of the IS in each sample injected was 145.9 ppb_v.

177

178 Samples were analyzed by SPME/GC-MS according to Scaglia et al. (2011) using
179 granulated activated carbon fibers supported in fiber holders for manual injection
180 (Supelco, Bellefonte, USA). The fiber used was a bi-polar fiber, with a 50/30 μm
181 coating of Divinylbenzene / Carboxen / Polydimethylsiloxane (DVB/
182 CarboxenTM/PDMS) StableFlexTM from Supelco Analytical (Bellefonte, PA, USA).
183 Although specific tests for any particular fiber under the actual analytical conditions are
184 warranted, some general rules apply. CarboxenTM/PDMS coated fibers are often the best
185 alternative for VOCs with MW<90, appropriate for C2-C8 organic acids, C1-C8
186 alcohols, C2-C8 aldehydes, C4-C12 ethers, C3-C9 ketones and for sulfur gases
187 (Wercinski, 1999).

188

189 SPME fibers were preconditioned for 1 to 3 hours at 250°C. Pre-concentration was
190 performed by letting the SPME fiber holders injected in the gas bulbs for 30 min.
191 Sample analysis was performed using an Agilent 7820 GC with a DB-624 capillary
192 column (60 m length, 250 μm internal diameter and film thickness of 1.4 μm) coupled
193 to a 5975C series MS. The carrier gas was helium at a flow rate of 1 mL min⁻¹. Samples
194 were manually injected through the GC inlet injection port for 3 min at 250°C and the
195 injection was in splitless mode. The program temperature was at 50°C for 2 min and
196 rose to 170°C at a rate of 3°C min⁻¹ and continued to increase to 230°C at 8°C min⁻¹.
197 Each sample was run for 52 minutes. Compounds were tentatively identified by
198 comparing their mass spectra with the NIST (USA) 98 library. The mass spectrometer
199 was operated in full scan, in the m/z range of 41–200. Peak abundance area was
200 determined by an Agilent Technologies analytical software system.

201

202 The actual concentration in samples was calculated for representative analytes for each
203 chemical class of VOCs. Calibration was performed by analyzing a set of standards of
204 such representative analytes injected together with known amounts of the IS previously
205 calibrated. Abundance ratios corresponded to the abundance response factors (IRF_{sc})
206 latter used to recalculate the actual concentration of the compound (C_{sc}) based on
207 concentration of IS added to the sample (C_{is}), and the actual response of both the IS (A_{is})
208 and the selected compound (A_{sc}) (equation 1). Typical SPME/GC-MS detection limits
209 are in the range of $\mu\text{g m}^{-3}$ (Larroque et al., 2006), which corresponds to around 0.1-0.2
210 ppb_v at room temperature and atmospheric pressure for the typical molecular weights of
211 odorant VOCs. According to Prenafeta-Boldú et al. (2012), all compounds identified
212 were analyzed in terms of removal efficiency (RE) of the treatment system by
213 comparing their peak abundance area (A_{sc}) in samples taken from the inlet and outlet
214 sampling ports depicted in Figure 1 (equation 1).

215

$$216 \quad C_{sc} = C_{is} \cdot A_{sc} \cdot IRF_{sc} / A_{is} \quad (\text{Equation 1})$$

217

218 **2.3 Monitoring plan**

219 Between October 2011 and March 2012, VOCs emissions from the maturation building
220 were characterized together with the VOCs emissions from the chimney located after
221 the biofiltration system. Monitoring of the system was divided into Autumn period
222 (between September 30th and November 25th, 2011) and Winter period (between
223 February 10th and March 25th, 2012). Airflow and VOCs composition of such gases
224 were measured in both periods as described in previous sections. A portable PT100
225 (Oakton Instruments, USA) was used for temperature measurements. Systematically,
226 higher temperatures were found along Autumn period, with an average inlet airflow

227 temperature of $29.4 \pm 4.8^\circ\text{C}$, compared to Winter period, with an average inlet airflow
228 temperature of $21.2 \pm 3.1^\circ\text{C}$. Climate conditions in the Barcelona area at the time of the
229 study were responsible for such differences. Both periods were compared to have a
230 rough estimate of the influence of the temperature in the emission inventory as well as
231 on the performance of the emission treatment system.

232

233 **3. Results and Discussion**

234 ***3.1 Characterization of compost maturation emissions***

235 Emissions monitoring was carried out for a total of 26 days distributed between Autumn
236 and Winter periods by sampling the inlet and outlet gas flows of the treatment system.

237 Emissions inventory of the compost maturation building were found to be highly
238 diverse in composition. Amongst all samples, more than 500 compounds were identified
239 by SPME/GC-MS. However, a large list of them only appeared in a reduced number of
240 times or in reduced relative abundances. Also reliability of some compounds identified
241 was below 98% of matching against the NIST library. Others have not been reported to
242 produce odors. Then, the emissions inventory in terms of odorant compounds was
243 performed and compounds classified based on their occurrence in samples as well as on
244 their predominance in representative classes of VOCs. Only those compounds that were
245 found in more than 25% of the 26 inlet samples were considered as representative in
246 terms of emission inventory in the present study, which corresponded to a total of 63
247 compounds.

248

249 Odorants were classified based on odor thresholds reported in the literature (Table 1),
250 mostly from Nagata (2003) who provides an extensive list of odorants and their odor
251 detection threshold measured by the triangle odor bag method. Odorant substances were

252 grouped by common odorant classes. Most esters, aldehydes and amines have the
253 lowest odor detection thresholds as groups, even if some aromatics such as 2-
254 pentylfuran, some ketones such as methyl isoamyl ketone or some organic sulfides have
255 been reported to be detected by olfactometry in very low concentrations (Nagata, 2003).
256 It is worth mentioning that strong odorants such as most organic acids were only
257 detected in less than 3 or 4 samples. As an example, isovaleric acid, which has an odor
258 threshold of 0.078 ppb_v (Nagata, 2003) was only detected in four inlet samples. Also,
259 mercaptans, which are reported to provide the lowest odor detection thresholds (Nagata,
260 2003) as class, were analyzed in the present study but not detected in more than 25% of
261 the inlet samples analyzed. In any case, the SPME fiber used in the present study may
262 have played a role in the poor detection of some compounds such as alkanes, low MW
263 fatty acids and some mercaptans. . Table 1 also shows inlet and outlet concentrations for
264 those compounds that were calibrated. A total of 26 compounds considered as
265 representative of the different VOCs classes were quantified based on their response
266 factors to the IS.

267

268 Table 1: Odorant emission inventory and treatment efficiency of the compost
269 maturation building for compounds detected in more than 25% of the inlet samples
270 analyzed. Maximum and minimum concentrations shown between brackets. All
271 removal efficiencies were calculated based on peak abundances of inlet and outlet
272 samples.

273

274 A large variety of chemical classes and compounds were found in the emissions of the
275 compost maturation building. All aromatic and aliphatic HC, ketones, terpenes and S
276 compounds found in the compost maturation off-gases (Table 1) were identified

277 previously as common compounds in composting emissions and from MSW landfills
278 (Davoli et al., 2003; Eitzer, 1995). However, only eucalyptol, ethyl butanoate, ethyl
279 acetate, and hexanal were also found in such emissions, while a large variety and
280 concentrations of alcohols, aldehydes and esters were found at the monitored MSWTF
281 in the present study. Since the origin and type of waste treated in the facility determines
282 the nature of VOCs released (Chiriac et al., 2007), composition of process off-gases is
283 highly specific. Interestingly, Gallego et al. (2012) monitored the indoor air from
284 several locations of a MSWTF in the metropolitan area of Barcelona and found a range
285 of alkanes, aromatic hydrocarbons, alcohols, aldehydes, esters and terpenes as in the
286 present case. In addition, it is worth mentioning that results herein may be slightly
287 conditioned by the SPME fiber used. The DVB/ CarboxenTM/PDMS coated fibers used
288 in the present study are generic fibers, designed to extract compounds of a wide
289 molecular weight (MW) range. As an example, DVB/ CarboxenTM/PDMS coated fibers
290 produce average responses between low and high MW alkanes, even if best fibers for
291 low MW alkanes (C2-C16) extraction are those coated with Carboxen-PDMS
292 (Pawliszyn, 2012).

293

294 Also, process conditions such as the composting aeration rate, waste moisture or the
295 stage of the composting process influence VOC emissions (Delgado-Rodriguez et al.,
296 2012). In any case, the highest concentration peaks are produced during the composting
297 process while significantly reduced emissions must be produced during the maturation
298 stage since compost is much more stabilized at this stage. Unfortunately, no emissions
299 inventory of the compost maturation stage is found in the literature to the authors
300 knowledge. Process conditions not only influence off-gases composition but also
301 concentrations found. In the present case, a wide range of inlet concentrations were

302 found. Interestingly, concentrations were in the range of tenths to a hundred of ppb_v,
303 which are typical VOCs concentration ranges found in composting emissions (Eitzier,
304 1995). However, concentrations of 1-butanol, methyl ethyl ketone and limonene were
305 mostly found in the ppm_v level, which were unexpected concentrations since they rather
306 correspond to typical composting concentrations than to maturation concentrations. In
307 fact, average 1-butanol, methyl ethyl ketone and limonene concentrations were much
308 higher than typical concentrations reported in the ppb_v range (Davoli et al., 2003; Eitzer,
309 1995; Komilis et al., 2004; Liu et al., 2009), which was probably related to the
310 composting and maturation conditions as well as to the type of waste treated. Also,
311 results suggest an incomplete composting of the MSW that still undergoes along the
312 maturation stage.

313

314 Average inlet concentrations of a wide variety of compounds such as ethyl butanoate, 1-
315 hexanol, 1-butanol, propanol isovaleraldehyde, trimethylamine, methyl ethyl ketone,
316 dimethyl disulfide, β -pinene and limonene exceeded their odor threshold concentration
317 prior to the treatment system. The list is enlarged if maximum peak concentrations are
318 considered. Thus, treatment of compost maturation waste gases is warranted to
319 minimize the impact of the industrial facility in its surroundings.

320

321 ***3.2 Maturation emissions treatment***

322 All compounds in Table 1 were analyzed in terms of their RE in the scrubbing plus
323 biofiltration system. While t-Student tests showed no statistically significant differences
324 between inlet concentrations of Autumn and Winter periods for all compounds, except
325 for limonene, higher RE were statistically found for Autumn period compared to Winter
326 period (Table 1) for most of the compounds that showed RE below 100%. As an

327 example of the trends found for most compounds, Figure 2 shows inlet concentrations
328 and removal efficiencies found for methyl ethyl ketone, limonene and m-ethyltoluene.
329

330 Such nil influence of the measured temperature in the gas composition between Autumn
331 and Winter periods is explained by the lack of forced air through the maturation piles,
332 amongst other factors. Then, emissions from maturation piles depend on the pile
333 temperature rather than on ambient temperature of the building, which is a function of
334 the air temperature and the air renovation rate. Instead, temperature in biofilters, as well
335 as biological activity, is largely influenced by the temperature of the gas treated since
336 air is forced to pass through the packed bed of the biofilter (Devinny et al., 1999). In
337 consequence, the lower temperature of the off-gases treated along Winter period which,
338 concomitantly, meant a reduced biological activity in the biofiltration system lead to
339 reduced RE along Winter period.

340
341 Since ambient temperature changes in the range found in the present study do not have a
342 significant impact in the maturation process and, concomitantly, in the average
343 concentration of the compounds emitted, the emissions inventory described herein could
344 be representative of the year-round operation of the plant if only ambient temperature
345 influence is considered. In addition, such temperature dependency must be considered
346 when assessing biofilters performance in full-scale facilities, an obvious fact often
347 forgotten by consulting and external advisors.

348
349 Figure 2. Inlet concentration (○) and removal efficiency (●) of selected VOCs: a)
350 Methyl ethyl ketone; b) limonene; c) m-ethyltoluene

351

352 Although other authors (Lebrero et al., 2013; Prenafeta et al., 2012) did not find any
353 correlation between RE and VOCs emitted from composting and wastewater treatment
354 plants, interestingly, most of the compounds listed in Table 1 were correlated with
355 partition coefficients reported by Sander (1999). An acceptable correlation was found in
356 the present study (Figure 3). However, some compounds such as acetone, benzaldehyde
357 and benzylalcohol with medium to high solubility in water (dimensionless solubility
358 partition coefficients of $1.7 \cdot 10^{-3}$, $1.7 \cdot 10^{-3}$ and $4.5 \cdot 10^{-6}$, respectively) failed to fit in the
359 RE-solubility trend shown in Figure 3, which was linked to the performance of the
360 biological reactors. In particular, benzaldehyde showed negative REs indicating that the
361 treatment system, and mostly the biological reactors, was producing benzaldehyde that
362 was not further mineralized. Benzaldehyde has been described as intermediate in
363 metabolic pathways during the oxidation of BTEX (benzene, toluene, ethylbenzene, and
364 xylene) as a product of benzylalcohol oxidation (Duetz et al., 1994). Also,
365 benzylalcohol has been reported to be produced in side chain reactions and accumulated
366 in batch tests from toluene degradation by *Pseudomonas putida F1* (Bordel et al., 2006).
367 In any case, such intermediates have been reported as highly toxic substances
368 (sometimes even more toxic than parent compounds) that may inhibit the biological
369 oxidation to a complete mineralized carbon (Yu et al., 2001). In addition, it is
370 hypothesized that fungi were also partly colonizing both biofilters because of the acidic
371 pH values measured in the leachate. Maestre et al. (2007) showed that the breakthrough
372 of the buffering capacity of biofilters was due to the production of acidic by-products
373 such as benzoic acid, which arise from toluene degradation.

374

375 Figure 3: Correspondence between Henry coefficient (VOCs solubility) and removal
376 efficiency

377

378 Performance of the treatment system was assessed by classifying all VOCs that were
379 not completely removed in four categories (Table 2) according to the efficiency of their
380 treatment. A fifth category corresponded to all these compounds whose RE was 100%
381 (Table 1). Around 50% of the compounds were removed with REs below 50%. In
382 addition to benzaldehyde, acetone and decane were the compounds that showed lower
383 average REs with no significant differences between Autumn and Winter periods.
384 Overall, relatively low REs were found, which were partly related to the low inlet
385 concentrations found for several compounds which may hinder pollutants mass transfer
386 due to the low concentration gradient between the liquid and gas phases. It is worth
387 mentioning that Almarcha et al. (2013) claim that biofilters with advanced packing
388 materials at MSWTF as those evaluated in the present study overperform classical
389 biofilters by providing higher efficiencies in terms of VOCs removal. However, results
390 found herein indicate that RE of individual VOCs are in the range of REs found in
391 classical biofilters (Iranpour et al., 2005) for most of the compounds found at the
392 MSWTF. Also, the performance of a biofilter is influenced by several important factors
393 such as pH, moisture content, nutrients availability, temperature and microbiology of
394 the biofilter medium. Amongst them, pH is probably the one that more strongly affects
395 biofilters performance. Previous studies have reported that the optimum pH for organic
396 compounds degradation by bacteria is close to the neutrality (Mudliar et al., 2010).
397 Then, the reduced pH in the biofilters negatively affected the performance of the
398 system.

399

400 Target compounds for further treatment improvement and impact of potential
401 malodorants emitted by the facility were identified by comparing outlet concentrations

402 and REs with the odor threshold of each compound (Table 2). Two aldehydes
403 (isovaleraldehyde and nonanal), two terpenes (β -pinene and limonene), an ester (ethyl
404 butanoate) and an organosulfur compound (dimethyl disulfide) were found to exceed
405 the odor threshold at the outlet of the scrubbing plus biofiltration system and,
406 consequently, identified as critical compounds in the emissions of the MSWTF. Out of
407 the compounds quantified, limonene was found as the most critical compound at the
408 MSWTF under study since the average concentration found after the treatment system
409 exceeded by a factor of around 35 its odor threshold. However, it is important to
410 underline that, apart from the impact of individual compounds on odor emissions, the
411 sum or synergy of different compounds can also contribute to odor detection and should
412 be considered and confirmed by odor measurement campaigns. In addition, a dispersion
413 analysis is warranted to confirm potential impacts in the vicinity of the facility.

414

415 Table 2. Classification of compounds per average removal efficiencies and
416 identification of critical VOCs

417

418 In terms of non-odorant compounds, around 28% of the compounds routinely found in
419 all inlet samples above the 25% cutoff limit corresponded to inorganic, non-odorant
420 compounds. Luo and van Oostrom (1997) also found that about 85% of the compounds
421 detected during the characterization of the performance of biofilters to remove odors
422 from animal rendering plants corresponded to non-odorant substances. Amongst the
423 compounds found in the present study, some interesting results were found in terms of
424 removal or production of selected compounds in the treatment system. Silanes and
425 siloxanes were found in almost all samples, which were related to the presence of
426 glasses, bottles, cosmetics etc in the raw waste (Schweigkofler and Niessner, 1999).

427 Interestingly, CO₂ peak abundance, determined also by CG-MS, was higher in most
428 outlet samples compared to that of inlet samples. Negative RE of -114 and -34% for
429 Autumn and Winter Periods were found, respectively. The lower CO₂ production in
430 Period B correlated well with the lower temperature measured along this period. Since
431 biological VOCs mineralization leads to CO₂ production, such differences in the RE of
432 Autumn and Winter periods were related to the different biological activity in the
433 biofilters. .

434

435 **Conclusions**

436 Chemical speciation monitoring (via SPME/GC-MS) made possible the identification of
437 the most common compounds produced at a compost maturation building in a MSWTF.
438 Concentrations of compounds in the emissions inventory identified during two sampling
439 campaigns performed during autumn 2011 and winter 2012 showed no influence of
440 ambient temperature on building emissions composition. Instead, REs were superior
441 during warmer climate conditions. Building emissions concentrations varied in a wide
442 range. Several compounds appeared in concentrations at ppm_v level exceeding the odor
443 threshold concentration prior to the treatment: n-butanol, methyl ethyl ketone and
444 limonene. REs were below 50% for half of the compounds, showing an acceptable
445 correlation with their partition coefficients except for those compounds identified as
446 intermediates of the biological oxidation of aromatic hydrocarbons. Production of
447 benzaldehyde was observed in the treatment system. Also, 23% of the analyzed
448 compounds exceeded their odor threshold at the outlet of treatment, being limonene the
449 most critical (35 times higher). Only six odorant compounds were removed with
450 efficiencies higher than 90%. Results derived from the SPME/GC-MS analysis allowed
451 determining the fate of each compound individually and, ultimately, evidenced the

452 impact of parameters that affected the performance more significantly: chemical
453 functionality, solubility, inlet concentration, pH and temperature. Mainly, the low pH
454 negatively affected the performance of the biofilters since organic compounds
455 degradation by heterotrophic bacteria occurs at near neutral pH. In addition, the lower
456 temperature of the off-gases treated along Winter period lead to a reduced biological
457 activity in the biofiltration system. Finally, the low solubilities and low inlet
458 concentrations of VOCs hindered their removal in the biofilters due to mass transfer
459 limitation.

460

461 **Acknowledgements**

462 The Department of Chemical Engineering at UAB (Universitat Autònoma de
463 Barcelona) is a unit of Biochemical Engineering of the Xarxa de Referència en
464 Biotecnologia de Catalunya (XRB), Generalitat de Catalunya. We deeply acknowledge
465 Jéssica Jiménez for her help and field support at the MSWTF. Shafik Husni is a
466 fellowship sponsored by the Malaysian Government under program Skim Latihan
467 Akademik Bumiputra (SLAB) with grant code KPT830105025267.

468

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