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► To cite this version:

Vincent Blazy, Amaury De-Guardia, Jean Claude Benoist, Mylène Daumoin, Fabrice Guiziou, et al.. Correlation of chemical composition and odor concentration for emissions from pig slaughterhouse sludge composting and storage. Chemical Engineering Journal, Elsevier, 2015, 276, pp.398-409. 10.1016/j.cej.2015.04.031 . hal-01146565

HAL Id: hal-01146565

<https://hal-univ-rennes1.archives-ouvertes.fr/hal-01146565>

Submitted on 4 Nov 2015

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1 **Correlation of chemical composition and odor concentration for emissions from pig**
2 **slaughterhouse sludge composting and storage**

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Abbreviations :

BA, bulking agent ; CH₃SH, methanethiol ; GC-MS, gas chromatograph coupled with a mass spectrometer ; H₂S, hydrogen sulfide; MDL, sampling and GC-MS method detection limit; NH₃, ammonia ; OAV, odor activity value of a gaseous odorous compound defined as the ratio of its concentration to its odor detection threshold; OC, odor concentration of a gas volume measured by olfactometry and corresponding to the number of dilution required in order its odor is not detected anymore ; OC_{INT}, bound of the confidence interval of the odor concentration measure, OAV_{MAX}, odor activity value of the compound exhibiting the highest concentration to ODT ratio in a gaseous mixture; OAV_{MAX2}: odor activity value of the compound exhibiting the second highest concentration to ODT ratio in a gaseous mixture; OAV_{SUM}, summation of the odor activity values of every odorous compound contained in a gaseous mixture ; ODT, odor detection threshold ; PSS, pig slaughterhouse sludge ; RSH, mercaptan ; TMA, trimethylamine ; RD, Relative Deviation ; VOC, volatile organic compound.

18 **Abstract**

19

20 The objective of this study was to correlate the chemical composition and the odor
21 concentration of emissions produced during storage and composting of pig slaughterhouse
22 sludge (PSS). Seven experimental conditions were monitored using composting reactors
23 with forced aeration and cells designed to simulate storage. Sixty six gas samples were
24 collected and characterized by both GC-MS and olfactometry. Two types of correlation
25 were investigated between the chemical composition and the odor concentration (OC) of
26 every gas sample. The odor activity value for a given emitted compound (OAV) was
27 computed as the ratio of its chemical concentration to its odor detection threshold (ODT).
28 The correlation OAV_{MAX} considered that the OC of a gas sample was equal to its highest
29 OAV whereas the correlation OAV_{SUM} considered that the odor of the gas sample was
30 equal to the sum of the OAV of every compound contained in the gas sample. As per
31 Standard EN 13725, both OAV_{MAX} and OAV_{SUM} were compared using a confidence level
32 for OC defined as $[OC/1.65 \text{ to } 1.65 \times OC]$. Whereas OAV_{MAX} values were within the
33 confidence level of OC for 62% of the 66 gas samples, OAV_{SUM} values were within this
34 confidence level for only 53%. Validating OAV_{MAX} as a satisfying correlation between
35 chemical composition and OC, only three compounds among the 66 identified namely
36 trimethylamine, hydrogen sulfide and methanethiol, accounted for the prediction of OC
37 measured during composting and storage of PSS.

38

39

40

41 **Highlights**

42 PSS composting and storage gas samples were determined by chemical and olfactory
43 analyses

44 For gas samples, correlations between the chemical composition and its OC was
45 investigated

46 OAV_{MAX} assumed that OC was equal to the sample's highest OAV value

47 OAV_{SUM} assumed that OC was equal to the sum of all OAV for sample

48 The 3 most odorant compound offered a good prediction of the olfactory results.

49 *Keywords: gaseous emission, odor, chemical composition, composting, storage, pig*
50 *slaughter house sludge*

51

52 **1. Introduction**

53

54 Odor emissions from composting plants are a common source of annoyance. Odorous
55 nuisance can have significant impact on environmental health [1] and the quality of life.

56 Negative neighbourhood reactions to composting odors may lead to temporary or definite
57 closure and a lack of acceptance of new facilities [2]. Good management of composting

58 operations can help minimize odor impacts, although odor generation cannot be avoided

59 [3]. Odor management should take into account operational conditions such as composting

60 facility aeration process, levels of confinement, emission sources identification, collecting

61 and treatment of gaseous emissions [4]. Such difficulties in controlling compost facility

62 odor nuisance demonstrate the lack of efficiency of present and often expensive solution

63 technologies.

64 Cost-effective strategies for solving odor problems require the identification of the
65 major contributing odorants compounds as found in the gaseous mixture released [5]. This
66 requires the correlation of the emission's chemical composition and its odor concentration.
67 Targeting the most responsible compounds, such correlation can provide criteria for the
68 development of: i) odor prevention and abatement strategies; ii) odor characterization
69 using analysis of specific indicator compounds, and; iii) specific sensors for online odor
70 monitoring.

71 The first main step towards linking the chemical composition of a sample and its odor
72 concentration is to define how to integrate the odorous potential of an individual compound
73 in a complex odor mixture. Indeed, each compound contributes to a different extent to
74 overall odor concentration [6]. Based on the odor detection threshold (ODT-the minimal
75 concentration of a single compound which is perceived by 50% of the population), the odor
76 activity value (OAV) has been widely used [6-11]. It was defined as the ratio of the
77 chemical concentration to the odor detection threshold of a single targeted compound
78 within a sample. The odor activity value is a dimensionless value also interpreted as the
79 theoretical dilution factor required to reach the odor detection threshold of the compound.
80 Thus, the first step in achieving this correlation consists in linking the odor activity value of
81 individual compound (or their theoretical dilutions factors) to the dilution factor required by
82 olfactometry to reach the threshold dilution for the complex emission. This dilution factor
83 is equivalent to its odor concentration, or OC, as defined by EN 13 725 [12]. A first
84 mathematical function used to correlate the odor activity value (OAV) and the odor
85 concentration (OC) consisted in numerically adding the OAV of all individual compound
86 identified in the emission (OAV_{SUM}). The value OAV_{SUM} was used by Gallego et al. [11] to

87 predict the concentration of composting odors in the absence of olfactometry. For odorous
88 emissions produced by food and industrial wastes, Kim and Park [9] found a strong
89 correlation between OC and OAV_{SUM} . In contrast, for odor emissions from cattle shelters,
90 Parker et al. [6] found a poor correlation ($R^2 = 0.16$ to 0.52) between OC and OAV_{SUM} .

91 Taking into account potential synergic effects between a large numbers of compounds,
92 multivariate analyses coupled with regression methods were widely investigated. These
93 complex methods were directly used by: Noble et al. [13] for mushroom composting;
94 Hanajima et al. [14] for swine manure; Mao et al. [15] and Tsai et al. [2] for food waste,
95 and; Defoer et al. [16] for green waste. Multivariate analyses were also used to correlate
96 odor to odorant compounds for swine facilities [17-18] or the headspace above stored slurry
97 [19-20]. These investigations produced no clear correlation allowing for the prediction of
98 composting or livestock odor. Indeed, each model led to a specific relationship [16] and
99 moreover, showed no cause-and-effect relationship [5] between the odor concentration and
100 the chemical composition of the gaseous samples. These drawbacks indicated the
101 complexity of the human sensory perception and the limits of these methods.

102 The objective of this study was to find a simpler and generic model to correlate the
103 chemical composition and the odor concentration of emissions produced during composting
104 under forced aeration and during storage. Pig slaughterhouse sludge (PSS) was the waste
105 studied in this experiment. Seven laboratory experiments were monitored to simulate
106 composting and storage of PSS. Sixty six gas samples were collected and characterized by
107 both GC-MS and olfactometry. Two types of correlation were investigated to link the
108 chemical composition and the odor concentration (OC) of every gas sample: the first was
109 the sum of the odor activity values (OAV_{SUM}), defined earlier, and; the second was

110 OAV_{MAX} consisting of the highest OAV value associated with an individual compound
111 within the sample.

112

113 2. Materials and methods

114

115 2.1. Experimental conditions

116

117 The composting experiments were performed in 300 L reactors consisting of insulated
118 stainless cylinders, 800 mm in height and 700 mm in diameter. Immediately after loading
119 the reactors, a low aeration rate of 1.3 L.h⁻¹.kg⁻¹ of wet sludge was applied during 5 days.
120 Thereafter, the aeration rate was increased to 9.3 L.h⁻¹.kg⁻¹ wet sludge and maintained
121 constant till the end of the experiment. A rotameter (FL-821-V, OMEGA Engineering Inc.,
122 Stamford, USA) regulated the in-coming airflow while a volumetric gas meter measured
123 the flow (Gallus 2000, Actaris, Liberty Lake, USA). The reactor were equipped to
124 continuously monitor the compost temperature and its total mass using respectively two
125 Pt100 probes and weigh sensors. Concentrations in O₂ and CO₂ were continuously
126 measured in both the in-coming and out-going airflows using respectively a paramagnetic
127 analyzer (MAGNOS 206, ABB, Zurich, Switzerland) and an IR spectrometric analyzer
128 (URAS 26, ABB, Zurich, Switzerland). Every 10 days, the compost was turned. The
129 composting treatment was stopped after 36 days.

130 The composting experiments were carried out using PSS mixed with bulking agent. The
131 sludge was collected from the primary wastewater treatment process of a pig
132 slaughterhouse. The primary pig slaughterhouse sludge had collected at the plant, following

133 its sieving using 6 mm and 1 mm sieves, its coagulation and flotation, and its
134 centrifugation. At the laboratory, the sludge was stored in bags at -18°C . The content of
135 each bag was dumped into opened bins to be thawed at 4°C , one week before being used.

136 The bulking agent (BA) consisted of oak and ekki wood chips with a particle size
137 ranging from 0 to 40 mm. The characteristics of the feedstock (pig slaughterhouse sludge
138 plus wood chips) are provided in the supplementary materials 1. The wet mass BA/PSS
139 ratios applied were respectively 0.55 and $0.73 \text{ kg}\cdot\text{kg}^{-1}$. For a BA/PSS of $0.73 \text{ kg}\cdot\text{kg}^{-1}$, the
140 two moisture contents tested were 61.2 % to 63.7 %.

141 The storage cells were 28 L airtight stainless steel cylindrical vessels, with a height of
142 900 mm height and a diameter of 200 mm. The cover of the storage vessel was equipped
143 with an air inlet and outlet to sample the volume over the stored material. Each vessel was
144 filled with 720 mm of PSS with and without BA. A constant aeration rate of $40 \text{ L}\cdot\text{h}^{-1}$ was
145 applied to the cell, for a value of 1.72 to $3.95 \text{ L}\cdot\text{h}^{-1}\cdot\text{kg}^{-1}$ of wet material. The gas samples
146 were collected by connecting bags to the storage vessel ventilation exhaust port. The
147 vessels were emptied after 14 to 30 days of storage.

148 The storage vessels were filled with fresh PSS, fresh PSS mixed with BA, and PSS
149 composted for 15 and 30 days. The PSS composts were obtained from the composting
150 experiments carried out with a BA/PSS ratio of $0.83 \text{ kg}\cdot\text{kg}^{-1}$ and under an aeration rate of
151 $6.05 \text{ L}\cdot\text{h}^{-1}\cdot\text{kg}^{-1}$ of wet sludge. For the storage experiments with PSS composts, the larger
152 wood chip particles were removed from the PSS + BA composted mixture using a rotary
153 sieve with 10 mm openings.

154

155

156 **Table 1**

157 Mixtures compositions and experimental conditions

158

159 2.2. Gas sampling, pre-dilution and preparation before odor measurement

160 The samples were collected manually using single-use Nalophan bags (EN 13 725
161 [12]), with a volume of 35 to 70 L, depending on the expected odor concentration.

162 Nalophan bags were directly connected to the reactor exhaust or to the storage vessel
163 sampling port. It took from 30 to 60 minutes to fill the Nalophan bags depending on their
164 volume and the treatment aeration rate. A glass bottle condenser was placed between the
165 reactor exhaust and the bag used for sampling, to remove condensate, during the initial
166 period of composting when hot moist gases were released. Gaseous emissions were
167 sampled every two days from the start, still the end of each experiment. For each sampling
168 session, two to three Nalophan bags were filled to duplicate or triplicate the measurement
169 results. The analysis of several samples at any given time enhanced the accuracy of the
170 odor concentration measurements.

171 To limit deterioration, chemical composition and odor concentrations measurements
172 were conducted within 4 to 6 hours of collection. When possible, both analyses were
173 carried out in less than few hours. The removal of water before sampling and the use of
174 sampling bags could lead to odorant losses [8, 21], and consequently odor emission
175 underestimation. It has been demonstrated that sample odor decreased when stored over 24
176 hours. Indeed, the recovery of odorants stored in sampling Tedlar bags [22-23-24], or
177 Tedlar versus Nalophan [25-26-27] was analyzed after 4 to 24hours, to show that most
178 odorants can be lost after 24 hours [12]. Less than 5 and 10% of the odor of methanethiol,

179 dimethyl sulfide and hydrogen sulfide was lost respectively in Tedlar and Nalophan bags,
180 after 4 to 8 hours of storage [25-26-27]. Even though the recovery of odorants in sampling
181 bags is an important issue and can lead to odor concentration underestimation, Van
182 Harreveld [28] showed that odor is stable in Nalophan bags for a period of 4 to 12 hours.
183 Since sample bags were analyzed within 4 to 6 hours and because of similar treatment,
184 chemical composition and odor concentration from the same sampling bag could be
185 compared and considered to represent the emission sampled.

186 Since gaseous emissions from the raw compost required a large dilution level before
187 olfactometry, namely 131,000 folds, samples had to be pre-diluted, using three methods
188 providing a range of 12.6 to 500. The first method consisted in directly connecting to the
189 olfactometer, a double orifice probe mixing the gas sample with dry clean air, where the
190 size of the respective orifices provided a dilution ratio of 100. The dilution rate of the probe
191 was controlled using a Gilibrator 2 calibration system (Gilian, Clearwater, USA). The
192 second method consisted in precisely measuring 250 mL of gas sample using a glass
193 sampling bulb with a PTFE stopcock (Supelco, Bellefonte, USA). Using the olfactometer,
194 the 250 ml volume was then injected into a Nalophan bag containing 5, 30 or 35L of dry
195 clean air for a dilution rate of respectively of 21, 121 or 141. Thus, the accuracy of the
196 dilution was determined by that of the olfactometer airflow controls. The third dilution
197 method consisted in withdrawing a diluted sample from a Nalophan bag using a gas tight
198 syringe (Supelco) and then injecting into a new Nalophan bag filled with a known volume
199 of clean air. The pre-diluted rate was applied to the odor concentration level measured by
200 olfactometry. According to Wardencki [29], the collection and storage of gas samples in a
201 glass bulb leads to a significant loss of hydrogen sulfide and methanethiol. However, in this

202 study, glass bulbs or glass syringes were sparsely used even to stored samples for less than
203 few minutes before being mixed with dry and odorless gas in Nalophan bags. Moreover, as
204 described below for the composting experiments, a glass condenser preceded the hydrogen
205 sulfide and mercaptan traps. Because a similar treatment was used for all samples,
206 hydrogen sulfide and mercaptan odor concentration could be compared.

207 When possible, a pure and a pre-diluted bag were analyzed to verify the dilution
208 accuracy and adjust the dilution coefficient for olfactometric characterization. This
209 coefficient was computed by dividing the carbon mass from each compound of the two
210 bags. Pre-dilution factor ranged from 3 % to 39 % with a mean value of 19.5 %, and the use
211 of a correction factor improved the accuracy of the pre-dilution procedure. However, the
212 relative OC deviation measured between two pre-diluted bags from the same sample ranged
213 from 0 to 20.8% with a mean value of 10.3% against 9.8% for the bags analyzed without
214 pre-dilution. This low difference showed that even though the accuracy of the pre-dilution
215 methods had to be corrected, their repeatability was quite satisfactory (data not shown). In
216 decreasing order, the accuracy of the dilution methods are: gas tight syringe; glass sampling
217 bulb, and; dilution probes. Since many samplings required a dilution factor of over 100, the
218 glass sampling bulb was mostly used. The tight syringe was used only once for each
219 composting reactors, just before the composting airflow adjustment because of the low
220 aeration rate resulting in highly concentrated samples required a dilutions factor of 200 to
221 500.

222

223 2.3. Olfactory measurements

224 The dynamic dilution olfactometer ONOSE-8 (Consumaj, Canada) was used to
225 determine the odor concentrations (OC) of the studied samples. The Onose-8 olfactometer
226 was designed to respect the EN 13725 [12] standards. The apparatus was calibrated using
227 the Gilibrator 2 calibration system (Gilian, Clearwater, USA) which handles a wide range
228 of flow rates.

229 The olfactory method consisted in firstly applying a dilution rate to the gas sample high
230 enough not to be detected by the 6 panellists. Then, the dilution rate was reduced until odor
231 was detected. The mass flow controllers of the ONOSE-8 provide a dilution scale ranging
232 from 16 to 131 000. Triple force-choice was the principle used where all trained panelists
233 have to identify among three ports that contaminated. The panelist group consisted of 19
234 persons, each being selected based on their sensitivity to the n-butanol reference gas as
235 described in the EN 13725 [12] standards. At least 6 odor panelists were selected for each
236 olfactometric session. Each bag, even from identical sampling, was presented three times to
237 the panel. The first presentation used a dilution step factor of 4, to rapidly introduce the
238 panelists to the odor stimuli. The result of this presentation was systematically removed and
239 not considered. Then, two additional series of ascending concentration ratios with a step
240 factor of 2 were presented to prevent olfactory adaptation or a loss of sensitivity. The
241 geometric mean of the panel detection thresholds from these two series was used to
242 compute the odor concentration of the sub-sample contained in the bag. The final odor
243 concentration of the gas sample, expressed in $\text{OU}\cdot\text{m}^{-3}$, was the geometric mean of the odor
244 concentrations of the 2 to 3 bags analyzed. All the odor concentrations of each sample
245 analyzed are shown in the supplementary material 2. According to Hansen et al., [30-31],
246 olfactometer dilution systems can alter the odorous charge of a compound. Reduced sulfure

247 compounds, such as hydrogen sulfide, methanethiol and dimethyl sulfide, can be affected
248 differently when flowing through the olfactometer system, as they can suffer an average
249 loss of 55-60%, 27-35% and 9.3-21%, respectively. Furthermore, the recovery of other
250 odorants, such as carboxylic acids, trimethylamine and 3-methylphenol, were also
251 significantly affected by the pulse duration leading to unstable signals within the 60-second
252 pulse. Although such losses were not investigated in this study, the Onose-8 olfactometer
253 offers accurate mass flow controllers with a limited error margin of $\pm 0.2\%$ (0% to 20% of
254 the total range) and $\pm 1\%$ (20% to 100% of the total range). Moreover, panelists were
255 invited to detect the odorous stimulus after the mass flow controllers showed a stable
256 signal. This precaution favors odorant recovery.

257

258 2.4. Chemical characterization of gases

259

260 2.4.1. Quantification of NH_3 , H_2S and mercaptans emissions

261 Using airflow taps on the gas exhaust lines after the glass condenser, two gas lines
262 were placed in parallel: the first to trap ammonia (NH_3) in sulfuric acid (H_2SO_4 , 1N), and;
263 the second to trap in series, hydrogen sulfide (H_2S) in a formic/formate acid buffer solution
264 0.1N with 10 mg.L^{-1} lead nitrate (PbNO_3), and then mercaptans (RSH) in acid (0.1 N) with
265 10 mg.L^{-1} mercuric dichloride (HgCl_2). The aeration rate through each line, namely for the
266 NH_3 and H_2S traps, followed in series by the RSH trap, was fixed by a flow meter (FL-821-
267 V, OMEGA Engineering Inc., USA) at 80 L.h^{-1} and measured using a volumetric gas meter
268 (Gallus 2000, USA).

269 For the NH_3 traps, $\text{NH}_4^+/\text{NH}_3$ content was quantified by steam distillation (method
270 modified from NFT 90-015-1 [32], Gerhardt Vapodest 50, Germany) into boric acid
271 (H_3BO_3 , 40 g.L^{-1}) and then back-titration with sulfuric acid (H_2SO_4 , 0.2 N). Duplicate
272 results were validated by a coefficient of variation below 5%. The titration detection limit
273 was 0.014 mgN.mL^{-1} of trap. Considering the mean trap volume of 200mL at a density of
274 1023 g.m^{-3} during a sampling period of 24h, the method detection limits for ammonia in the
275 exhaust gas was 0.286 mg.m^{-3} . The reaction of H_2S with PbNO_3 and of RSH with HgCl_2
276 produced a PbS and $\text{Hg}(\text{SR})_2$ precipitate recovered by filtration through glass fibre filters
277 (Satorius, France). The precipitates were dried at 55°C and weighed. In this study, all
278 mercaptans emissions trapped in HgCl_2 were calculated as methanethiol leading to
279 $\text{Hg}(\text{SCH}_3)_2$ precipitate. This potentially led to under-estimating the odor contribution of
280 mercaptans since the odor detection threshold of methanethiol is higher than that of other
281 mercaptans such as ethanethiol, propanethiol, and 1- butanethiol. The concentrations of the
282 compounds analysed by chemical traps was computed as the mean values of their emissions
283 between two odor sampling sessions.

284 For the composting experiments, the traps were changed every 24h for the first 15 days
285 and then every time the gas was sampled for odor measurement. For the storage
286 experiments, the traps were also changed every time the gas was sampled for odor
287 measurement, namely every two days. Saturation was never observed for the NH_3 , H_2S and
288 RSH traps.

289

290 2.4.2. VOCs identification and quantification

291 The chemical gas samples characterization included the identification and the
292 quantification of VOCs. Thus, the gas samples collected in Nalophan bags were
293 concentrated by passing through Carbotraps (Carbotrap 349, PerkinElmer, USA) using a
294 vacuum pump (Giliar, USA) equipped with a constant low flow module set at $50 \text{ mL}\cdot\text{min}^{-1}$.
295 Considering that VOCs concentrations were unknown, several Carbotraps were prepared
296 for each sample by passing different volumes, namely 500, 1000, 1500, 3000 mL.
297 Accordingly, such volumes were associated with detection limits of 80, 40, 26 and 13
298 $\mu\text{g}\cdot\text{m}^{-3}$, respectively. The Carbotraps were stored at 4°C for less than one week before
299 being desorbed and analyzed by GC-MS [33].

300 The desorption was carried out by a Thermal Desorption unit (TurboMatrix 550,
301 Perkin Elmer) coupled with a Clarus 500 GC-MS detector (Perkin Elmer). Then, these were
302 separated through the capillary column (CP-WAX 58, 25m x 0.15mm; Film 0.25 Varian,
303 USA). Analytical conditions of thermal desorption and column separation, were provided
304 by Blazy et al. [34]. Chromatogram processing depended on the detection mode used by
305 mass spectrometry for detecting separated compounds. Indeed, 2 simultaneous acquiring
306 modes were used. A full scan (FS) acquisition (20-300 amu) allowed for the identification
307 of compounds with 2 sets of criteria: (1) GC retention times and mass spectra matched with
308 the calibrated compounds, and; (2) the mass spectra obtained from a reference library
309 (National Institute of Standards and Technology, NIST, Gaithersburg, USA). A quantitative
310 assessment of VOCs was performed by a single ion resolution (SIR) acquisition which
311 quantified specific masses of compounds (m/z , major characteristic ion in the spectra) as

312 area counts under peaks for separated VOCs. A calibration was performed to convert the
313 measured area into a compound mass.

314 The calibration procedure consisted in injecting into an N₂ filled Tedlar bags, a known
315 volume of the compound of high purity (Acros Organics, Alfa Aesar or Sigma Aldrich) at a
316 concentrations of 13 to 5000 µg.m⁻³. According to the method described previously, each
317 bagged compound was trapped onto a Carbotrap and thereafter analyzed by GC-MS. The
318 fact that the Tedlar bags could not recovery the total amount of injected compound lead to
319 an underestimation of the GC-MS quantification. Finally, the calibration curves were
320 obtained by plotting the GC integrated areas versus the concentration of the bagged
321 compound. A linear regression curve was obtained with the calibration data, except with
322 light amines at low concentrations because of their poor detection by GC-MS, as expected.
323 This process also demonstrated that the thermal desorption allowed to recover a very high
324 percentage of the trapped VOCs.

325 The GC-MS was not calibrated for all identified compound. Non calibrated compounds
326 were quantified by assuming a response factor equal to 1000, which represents the average
327 value obtained with all of the calibrations.

328

329 **3. Results and discussion**

330

331 **3.1. Determination and evaluation of odor activity**

332 The GC-MS analysis of the 66 samples yielded 39 compounds presented in the Table 2
333 along with: their CAS (Chemical Abstracts Service) number; the ion used for their
334 quantification; whether or not they associated with a calibration procedure and; their odor

335 detection thresholds (ODT) as per a recent database [36]. When several odor detection
336 thresholds were available for a single compound, only the most recent value was used. In
337 general, recent odor detection threshold values were lower than the old ones, leading to
338 higher odor activity values. However, the order of magnitude for many individual
339 compounds could be considerably different [6-11]. According to Parker et al [6], the
340 central tendency of the odor detection threshold values was well described by geometric
341 means compared to harmonic means (which were lower) and arithmetic means (which were
342 higher and influenced by the larger individual values). Thus when several recent odor
343 detection threshold values were available, a geometric mean was used in order to obtain a
344 central tendency of the odor activity value.

345 As highlighted for some compounds in Table 2, the GC-MS detection level (method
346 detection limit or MDL) was higher than the odor detection threshold, leading for some
347 samples, to the under-estimation of the odor activity value. In Table 2, the ratio
348 $(MDL_{MAX})/ODT$ indicates the level of underestimation for these compounds, where
349 MDL_{MAX} is the highest method detection limits observed during samples according the gas
350 volume passed throughout Carbotraps. Nevertheless, only trimethylamine (TMA) showed
351 an important odor activity value underestimation, with an MDL_{MIN}/ODT and
352 MDL_{MAX}/ODT ranging between 217 and 11333, respectively. Sulfurs, aldehyde and alcohol
353 compounds showed a maximal OAV underestimation of around 10, or even less. For such
354 compounds, the method detection limits showed low underestimation of odor activity value
355 determination.

356

357 **Table 2**

358 Gaseous compounds identified from emissions collected during the composting and the
359 storage of pig slaughterhouse sludge

360 A last and important bias for odor activity value determination can result from the use
361 of sorbent tubes and the subsequent thermal desorption in TD-GC/MS. Indeed, mercaptans
362 and especially methanethiol can be oxidized to form di- and tri-sulfides [59] which were
363 largely quantified during chromatogram processing. This reinforces the assumption that
364 mercaptan were mainly methanethiol. Consequently, the odor activity value from
365 methanethiol could double when adding the odor activity value from organo-sulfides, thus
366 leading to odor activity values overestimation. However, the source of the organo-sulfide
367 was uncertain, whether from composting or from mercaptan oxidization, or from a
368 combination of both.

369 For every compound, its odor activity value (OAV) was calculated from the ratio of its
370 chemical concentration to its odor detection threshold. All the chemical concentrations and
371 OAV are provided in Supplementary Materials 3 and 4, respectively. The odor activity
372 values of methenamine, 1,3 pentadiene and 3-pentanone-2-methyl were not calculated
373 because of their unknown odor detection threshold.

374 Two correlations were calculated to link gas sample odor concentration (OC) to its
375 chemical composition: OAV_{MAX} , assuming that odor concentration is equal to the OAV of
376 the most odorous compound, and; OAV_{SUM} , assuming that odor concentration is equal to
377 the sum of all compound OAV. The values of OC, and OAV_{MAX} and $OAV_{MAX 2}$ (the first
378 and second highest odor activity value per sample) and OAV_{SUM} are given in
379 Supplementary Material 4.

380 The relevance of the two types of correlation was evaluated based on the percentage by
 381 which OAV_{MAX} and OAV_{SUM} fell within the 95% interval of confidence for the
 382 corresponding measured odor concentration (OC), as computed for every sample (EN
 383 13725 [12]):

$$384 \quad OC / (10^{2.0} * Sr / \sqrt{n}) < OC < OC * (10^{2.0} * Sr / \sqrt{n})$$

385 with, n is the number of bags analyzed, from 1 to 3, and Sr is the standard deviation
 386 calculated from the repeatability, namely 0.1721. The mean value of $(10^{2.0} * Sr / \sqrt{n})$ was
 387 found to be 1.65, whereby $OC / 1.65 < OC < OC * 1.65$.

388 Consequently, each odor concentration (OC) measure is linked to: two boundaries of
 389 the confidence interval as above-mentioned, the highest odor activity value (OAV_{MAX})
 390 (resulting from a single compound) and the sum of the odor activity values from all
 391 compounds in the gas sample (OAV_{SUM}).

392 The correlation extent between OC and either OAV_{MAX} or OAV_{SUM} was estimated
 393 through a simple linear regression using a log transformation to limit distribution variance
 394 between the variables (OAV_{SUM} , OAV_{MAX} and OC). This log transformation better
 395 illustrated data patterns and allowed for the use of a simple correlation type $\text{Log}(OAV_{MAX})$
 396 or $\text{Log}(OAV_{SUM}) = 1 \text{Log}(OC)$ to link the variables. The logarithmic expression of the
 397 odor concentration should not be considered as an indirect indicator of the odor intensity,
 398 and extension of odor concentration. Moreover, using a “log-log correlation” graphically
 399 favors a closeness between OC and OAV_{MAX} or OAV_{SUM} , especially for high values of OC.

400 Therefore, the relevance of OAV_{SUM} and OAV_{MAX} predictions were also estimated on
 401 the basis of the Relative Deviation, computed for the mixtures showing an OAV_{MAX} or

402 OAV_{SUM} prediction outside the confidence interval of odor concentrations. Values for
403 Relative Deviations (RDs) were computed with the closest odor concentration interval
404 bounds (OC_{INT}) according to the Eq.1:

$$405 \quad RD = (|OAV_{MAX} \text{ or } OAV_{SUM} - OC_{INT}|) * 100 / OC_{INT} \quad (1)$$

406 with OC_{INT} being the closest interval bounds of OAV_{MAX} or OAV_{SUM}, in OU.m⁻³, and
407 where OAV_{MAX} and OAV_{SUM} are dimensionless. Values for Relative Deviation (RD) are
408 found in Supplementary Material 5 and expressed in %. A box plot figure was drawn to
409 study the distributional characteristics of the RD of OAV_{MAX} and OAV_{SUM} predictions with
410 OC_{INT}.

411 Only the sum of the odor activity values (OAV_{SUM}) determination was
412 affected by underestimation resulting from method detection limit. Therefore, the influence
413 of the method detection limits on OAV_{SUM} computations was investigated. The maximum
414 underestimated odor activity value is computed (supplementary material 4), defined as the
415 ratio between the method detection limits by the odor detection threshold of the
416 compounds, and added in the OAV_{SUM} computation. The method detection limits was
417 observed to produce 0 to 55% deviation on the sum of the odor activity values
418 (supplementary material 4). Trimethylamine has a very low odor detection threshold mainly
419 involved in the determination of OAV_{SUM}. However, the mean Relative Deviation between
420 the computed OAV_{SUM} (with or without taking in account the method detection limit) was
421 of 5.6%, indicating a limited influence of method detection limits on OAV_{SUM}
422 determination.

423

424 3.2. Qualitative evaluation of the highest odor activity value and the sum of the odor
425 activity value from a gas sample

426 Olfactometry consists initially in diluting a gas sample until its odor cannot be
427 perceived by all panellists, and then, increasing its concentration, with lower dilutions, until
428 all trained human panelists are able to detect the odor. Theoretically in the absence of
429 synergistic effects, the olfactory stimulus should come from the most odorant compound
430 namely the one requiring the highest dilution rate to be odorless. In this context, Zahn et al.
431 [60] showed that the synergistic effects were minor for swine odors. Thus, odor
432 concentration should correlate to the odor activity value of the most odorant compound
433 namely OAV_{MAX} . Considering the 66 gas samples analyzed, OAV_{MAX} displayed only three
434 compounds responsible for the odors, namely mercaptans (presumed to be methanethiol),
435 trimethylamine and hydrogen sulfide, respectively at 64, 21 and 15% of the gaseous
436 mixtures studied. Similarly by multivariate analyses, Hansen et al. [18] identified hydrogen
437 sulfide, methanethiol, trimethylamine, and 4-methylphenol as the main odorous compounds
438 emitted from growing-finishing hogs facilities. Finally, these three compounds were
439 presumed to be mostly responsible for odor concentration (OC) because of their very high
440 odor activity values (OAV) in all 66 samples.

441 Fig. 1 gives $\text{Log}(OAV_{MAX})$ values as function of $\text{Log}(OC)$. The dotted lines represent
442 the 95 % confidence interval for $\text{Log}(OC)$, namely $\text{Log}(OC / 1.65) < \text{Log}(OC) < \text{Log}$
443 $(OC * 1.65)$. The values for $\text{Log}(OAV_{MAX})$ fell outside this interval mostly for mixtures
444 within methanethiol, estimated as the most odorous compound and especially at low and
445 high concentrations, namely when OAV_{MAX} was under 8×10^3 and over 6×10^4 . This
446 resulted either from the low relevance of the OAV_{MAX} correlation for the low

447 concentration, from the insufficient accuracy of the chemical characterization method
448 (hydrogen sulfide and mercaptans samples correspond to that collected during almost 24h
449 while samples for odor concentration and GC/MS quantification were collected during less
450 than one hour), or from the assumption that mercaptans were mostly methanethiol.
451 Nevertheless, the slope of the fitted line lies is very close to that of the confidence intervals
452 with $\text{Log}(\text{OAV}_{\text{MAX}}) = 0.98\text{Log}(\text{OC})$. Furthermore, the coefficient of determination
453 ($R^2=0.90$) denoted a strong linear association between $\text{Log}(\text{OAV}_{\text{MAX}})$ and $\text{Log}(\text{OC})$,
454 suggesting that $\text{Log}(\text{OAV}_{\text{MAX}})$ could be a good predictor of $\text{Log}(\text{OC})$.

455

456 **Fig. 1**

457 Predicted $\text{Log}(\text{OAV}_{\text{MAX}})$ as function of measured $\text{Log}(\text{OC})$; OAV_{MAX} is the odor activity
458 value (OAV) of the most odorous compound, namely the compound with the highest
459 concentration/ODT value; OC was measured by olfactometry. Hollow points stand outside
460 the confidence interval of OC.

461

462 Fig. 2 gives $\text{Log}(\text{OAV}_{\text{SUM}})$ values as function of $\text{Log}(\text{OC})$. As for $\text{Log}(\text{OAV}_{\text{MAX}})$,
463 $\text{Log}(\text{OAV}_{\text{SUM}})$ fell outside the $\text{Log}(\text{OC})$ confidence interval mostly for mixtures where
464 methanethiol was the most odorous compound and especially when at low and high
465 concentrations, namely when OAV_{MAX} was under 8×10^3 and over 6×10^4 . As for Log
466 (OAV_{MAX}), the slope of the fitted line was very close to that of the confidence interval,
467 where $\text{Log}(\text{OAV}_{\text{SUM}}) = 1 \cdot \text{Log}(\text{OC})$, namely $\text{Log}(\text{OAV}_{\text{SUM}}) = 1.02 \text{Log}(\text{OC})$, with a
468 coefficient of determination $R^2=0.87$. In conclusion, $\text{Log}(\text{OAV}_{\text{SUM}})$ can also be an
469 acceptable predictor of $\text{Log}(\text{OC})$.

470 **Fig. 2**

471 Predicted Log (OAV_{SUM}) as function of measured Log (OC); OAV_{SUM} was obtained by
472 summing the OAV of every odorous compound found in the gas sample; Odor
473 concentration (OC) was measured by olfactometry. Hollow points are out of the confidence
474 limits of the OC measure.

475

476 However to determine odor concentration, on basis of Fig. 1 and 2, OAV_{MAX} showed a
477 higher coefficient of determination than OAV_{SUM} . Although OAV_{MAX} and OAV_{SUM} are
478 functions which are far apart, their linear regression shows a numerical similarity (Log
479 (OAV_{SUM})=1.04Log (OAV_{MAX}) and $R^2=0.98$; data not show). Consequently, for most of
480 the samples analyzed, the odor activity value (OAV) was mainly displayed by a single
481 compound. In other words, a limited percentage of the odor activity charge is displayed by
482 secondary compounds. Therefore, a quantitative study of OAV_{MAX} and OAV_{SUM}
483 correlation with the odor concentration must be investigated.

484

485 3.3. Quantitative evaluation of odor activity

486 Table 3 gives the numbers of samples where only OAV_{MAX} , only OAV_{SUM} and when
487 both values fell outside the 95% confidence interval of the odor concentration
488 measurement. The mean of the absolute Relative Deviation value is also presented.

489

490 **Table 3**

491 Comparison of the absolute Relative Deviation of OAV_{MAX} and OAV_{SUM} with respect to
492 the 95% confidence interval for odor concentration measurement

493

494 The highest odor activity value in a gas sample (OAV_{MAX}) was within the confidence
495 interval of odor concentration (OC) for 62% gas samples (Fig. 1) whereas the sum of the
496 odor activity values of a gas sample (OAV_{SUM}) for 52% (Fig. 2). For all the OAV_{MAX} and
497 the OAV_{SUM} outside the confidence interval, the mean Relative Deviations (RDs) were of
498 53 and 73%, respectively. As result, the mean absolute RD value indicated that OAV_{MAX}
499 was, on the average, closer to the corresponding odor concentration interval than OAV_{SUM} .
500 Similarly, when the mixtures showed that both, OAV_{MAX} and OAV_{SUM} , were outside the
501 confident interval of the odor concentration, the Relative Deviation remained lower for
502 OAV_{MAX} , namely at 68% versus 103% for OAV_{SUM} . Finally, the Fig. 3 shows the
503 distributional characteristics of the Relative Deviation when the highest odor activity value
504 (OAV_{MAX}) and the sum of the odor activity values (OAV_{SUM}) from a gas sample were
505 outside the confident interval of the odor concentration measurement.

506

507 **Fig. 3**

508 Box plot of the Relative Deviation between the closest odor concentration interval
509 boundaries (OC_{INT}) and the maximal odor activity value within a sample outside the odor
510 concentration confident interval, and; between OC_{INT} and the sum of every odor activity
511 values of a sample outside the odor concentration confident interval

512

513 The range of Relative Deviation (RD) between the sum of the odor activity values from
514 a gas sample (OAV_{SUM}) and the closest odor concentration interval boundaries (OC_{INT}) was
515 larger than the range of RD between the highest odor activity value from a gas sample
516 (OAV_{MAX}) and OC_{INT} (Fig. 3). The OAV_{SUM} varied from -73 to 300% against
517 -80 to 200% for OAV_{MAX} . Moreover, 50% of the OAV_{MAX} data set was displayed in a
518 relative deviation interval of -33 to 45%, whereas, for OAV_{SUM} , this interval ranged from
519 22 to 74%. Since the Relative Deviation for OAV_{MAX} was closer to OC_{INT} than that
520 computed for OAV_{SUM} , OAV_{MAX} better predicted the odor concentration (OC) with
521 OAV_{SUM} overestimating OC.

522 The Relative Deviation between OC and OAV_{MAX} or OAV_{SUM} was very high
523 especially when OC was low, namely under $3 \times 10^3 \text{ OU}\cdot\text{m}^{-3}$. Even if the statistical analysis
524 of too few samples with such a low odor concentration was not possible, the following
525 were investigated with no resulting conclusion: the influence on odors of some mitigating
526 effects such as NH_3 concentration [2]; the number of sample compounds with a
527 concentration exceeding the odor detection threshold; the distribution of the odor activity
528 value among compounds within the sample, such as OAV_{MAX}/OAV_{MAX2} and as provided in
529 the supplementary material 5), and; the closeness of the odor activity values among
530 compounds (results not shown). Also, the relative deviation was influenced by: the method
531 used for mercaptans analysis; the exclusion of compounds without known odor detection
532 threshold; too high or too low a value for the geometric mean of odor detection threshold;
533 the assumption that odor is linearly correlated to concentration, and; the negligible synergy
534 assumed among odorous compounds.

535 Limited research work correlates the highest odor activity values for a gas sample to its
536 odor concentration. However, several studies correlated the odor intensity with respect of
537 the VDI 3881 [61], ASTM E544-10 [62]) measured at supra-threshold with the theoretical
538 intensity derived from compound concentration forming synthetic mixtures. Kim and Park
539 [9] showed that odor intensity could be determined by a single predominant compound
540 rather than by the sum or average of all individuals. Kim [63] and Zhao et al. [64] also
541 found that the odor intensity from compound mixtures with similar chemical properties
542 could be mostly characterized by averaging the odor intensity potential of all the
543 contributors. The relevance of the “highest odor activity value compound model” must be
544 cautiously considered as further investigation is necessary.

545 The literature has generally favoured the correlation between odor concentration (OC)
546 and the sum of the odor activity values for a gas sample (OAV_{SUM}) even if the numerical
547 addition of odor activity value, representing the theoretical dilution factor, does not
548 correspond to the method used in olfactometry. Kim and Park [9] found a strong correlation
549 (Pearson coefficient of 0.866) between OAV_{SUM} and OC, without presenting sufficient data
550 to appreciate the closeness between OAV_{MAX} and OAV_{SUM} . Parker et al. [6] correlated OC
551 to OAV_{SUM} , to find a 2 to 3 fold underestimation of OC. However, the range of measured
552 odor concentrations was quite low, namely from 3×10^1 to 8×10^3 OU.m⁻³. In this range,
553 OAV_{SUM} can be easily underestimated, especially for compounds with a very low odor
554 detection threshold. In this study, supplementary materials 4 lists all cases with compounds
555 detected below their detection limits. Moreover, supplementary materials 4 presents the
556 maximum odor activity value underestimation, defined as the ratio of the method detection

557 limits by the odor detection threshold of the considered compound for each compounds and
558 the sum of the odor activity value of a gas sample.

559

560 3.4. Emissions profiles of odor concentration and the main odorous compounds

561 Fig. 4a, 4b and 4c compares Log (OAV) and Log (OC) for the leading odorous
562 compounds of the gas sample collected during the composting processes applied. As
563 previously mentioned, the similarity between a sample's odor concentration (OC) and its
564 highest odor activity value (OAV_{MAX}) or the sum of its odor activity values (OAV_{SUM})
565 required a cautious interpretation because of the "log-log correlation". Nevertheless, the
566 Log (OAV_{MAX}) profile emissions (hollow points) better described Log (OC) variations. For
567 the first 4.6 days, OAV_{MAX} was much lower than OC and methanethiol was the most
568 odorant compound. Thereafter, OAV_{MAX} followed, as expected, the same trend as OC and
569 was relatively close, confirming that OAV_{MAX} is a good predictor of OC. Then, hydrogen
570 sulfide was found as the most odorous compound except for the samples on day 15 with a
571 peak of trimethylamine, whatever the process conditions. The odor emissions decreased
572 significantly after 15 to 20 days at which time no leading odorous compound could be
573 clearly identified.

574 Accordingly, mercaptans were emitted when the need for O_2 was highest and when the
575 redox potential was the lowest whereas hydrogen sulfide was emitted at a slightly lower
576 redox potential. Finally, the second and the third material turning operation, on days 22 and
577 29, influenced neither OAV_{MAX} nor OC (Fig. 4a, 4b and 4c) emissions while an increase in
578 O_2 consumption and temperature indicated that biodegradation was still in progress. Thus,

579 the easily biodegradable fraction of organic matter, responsible for the highest O₂ demand,
580 seemed to produce conditions for the emission of the most odorous compounds.

581 The distribution of the odor activity value within a sample also indicates the
582 perspectives for odor abatement, with the removal of the most odorous compounds not
583 necessarily generating a strong odor decrease. The extent of the odor decrease will depend
584 of the next highest odor activity value perceptible during odor concentration measurement.
585 Consequently odor treatment must target in decreasing order, the compounds showing the
586 highest odor activity value. Thus, the number of compounds to be targeted for odor
587 abatement can vary greatly.

588

589 **Fig. 3**

590 Composting emissions profiles of odor concentration (OC) and odor activity value (OAV)
591 for the leading odorous compounds, namely methanethiol (CH₃SH), trimethylamine (TMA)
592 and hydrogen sulfide (H₂S). Full points indicate that the highest odor activity value is
593 produced by TMA, H₂S or CH₃SH.

594

595 The Fig. 5a, 5b, 5c and 5d give the log (OAV) profiles of the leading odorous
596 compounds and the log (OC) measured during the various storage processes. Methanethiol
597 always produced the highest odor activity value from gas samples likely because of the low
598 redox potential created by the storage conditions. Slight discrepancies were found between
599 odor concentration and the highest odor activity value when storing fresh PSS and fresh
600 PSS mixed with BA, as high concentrations of mercaptan were produced (Fig. 5a and 5b).
601 In contrast, the 15 and 30 days composts were responsible for lower mercaptan

602 concentrations and, even with similar trends, a larger discrepancy between odor
603 concentration and the highest odor activity values. A more accurate identification of the
604 mercaptans would likely improve this correlation.

605

606 **Fig. 4**

607 Emissions profiles of odor concentration (OC) and odor activity values (OAV) for the
608 leading odorous compounds, namely methanethiol (CH₃SH), trimethylamine (TMA) and
609 hydrogen sulfide (H₂S), emitted during the storage of fresh pig slaughterhouse sludge
610 (PSS), fresh pig slaughterhouse sludge mixed with bulking agent (PSS+BA) and composted
611 pig slaughterhouse sludge after 15 and 30 days of treatment. Full points indicate that the
612 highest odor activity value is produced by TMA, or H₂S or CH₃SH.

613

614 **4. Conclusion**

615

616 The objective of this research was to correlate the chemical characterization of odor
617 emissions with their odor concentration as measured by olfactometry. The emissions
618 analysed in this project were obtained from the composting and storage of pig
619 slaughterhouse sludge. Two correlations were investigated to relate odor concentration
620 (OC) with the chemical composition of the gas sample. The first, based on principles of
621 olfactometric analysis, assumed that the highest odor activity value of the gas sample
622 (OAV_{MAX}) corresponded to OC, whereas the second used the sum of the odor activity
623 values for each compound in the sample.

624 The value of the highest OAV quantitatively gave a better prediction of the odor
625 activity value, as compared to that of the sum of OAVs. However, OAV_{MAX} and OAV_{SUM}
626 were two close mathematical functions, as both showed a good linear regression with the
627 odor concentration, indicating that both could predict the odor concentration. A qualitative
628 comparison of OAV_{MAX} and OAV_{SUM} indicated that OAV_{MAX} was a more relevant
629 predictor than OAV_{SUM} which tended to overestimate the odor concentration.

630 Three main odorous compounds were found to produce OAV_{MAX} in the 66 samples
631 analyzed: trimethylamine, hydrogen sulfide and mercaptans. Accordingly, the odor
632 determination by dilution-to-threshold method was mostly characterized by the compound
633 with the highest odor activity value (OAV_{MAX}). Nevertheless, OAV_{MAX} did not always fall
634 within the 95% confidence interval established for the odor concentration, because:
635 mercaptans were mostly represented by methanethiol; the quantification method for
636 hydrogen sulfide and mercaptans was not sufficiently accurate; no synergy was presumed
637 between compounds forming the gas samples, and; odor threshold determination was drawn
638 on geometric means to describe the central tendency of the threshold value. Regardless of
639 the mathematical function used for correlation, odor activity values were a poor predictor
640 for low odor concentrations, namely under $1000 \text{ OU}\cdot\text{m}^{-3}$, likely because very low odor
641 detection threshold are often below the GC-MS detection limits leading to an
642 underestimation of the odor activity value.

643

644 **Acknowledgements**

645 The authors wish to acknowledge La Région Bretagne and l'Université Européenne de
646 Bretagne for their financial contributions and that of the Natural Science and Engineering

647 Research Council of Canada. We would also like to thank the panelists for their investment
648 and their cooperation during the odor measurements.

649

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Table 1

Mixtures compositions and experimental conditions

Material composition	Storage experiments				Composting experiments		
	Fresh PSS	Fresh PSS+BA	PSS compost at 15 days	PSS compost at 30 days	Fresh PSS		
PSS or compost fresh mass (kg)	24.44	11.57	10.75	11.07	59.76	58.52	58.75
Bulking agent fresh mass (kg)	-	9.63	-	-	43.75	42.84	32.25
Water added (kg)	-	-	-	-	-	6.83	-
Fresh mass ratio (BA/PSS)	-	0.83	-	-	0.73	0.73	0.55
Mixture moisture (%)	76.3	51.9	46.1	35.6	61.2	63.7	63.6
<i>Experimental conditions</i>							
Mean aeration rate (L.h ⁻¹)	42.2	38.4	42.5	41.7	553	554	556
number of turning material	-	-	-	-	3	3	3
end of the experimentation (days)	29.6	13.9	15.7	15.9	35.5	35.5	35.5

PSS: pig slaughterhouse sludge; BA: bulking agent

Table 2

Gaseous compounds identified from emissions collected during the composting and the storage of pig slaughterhouse sludge

Compounds	CAS number	Quantification ion (m/z)	Calibration coefficient	ODT (mg.m ⁻³)	MDL _{MAX} /ODT	ODT References
Ketones						
2 Butanone	78-93-3	43	680	22.7	-	Nagata [37]
2 Butanone-3- methyl	563-80-4	72	645	1.8	-	Nagata [37]
2 Butanone 3,3 dimethyl	75-97-8	43	1000†	0.176	-	Nagata [37]
2 Hexanone	591-78-6	58	1000†	0.098	-	Nagata [37]
2-Pentanone	107-87-9	86	680	0.098	-	Nagata [37]
2-Pentanone-3-methyl	565-61-7	43	977	0.098	-	Nagata [37]
3 Pentanone 2methyl	565-69-5	43	1000†	N-D	-	-
Acetone	67-64-1	58	500	101	-	Nagata [37], Dalton et al. [38]
Acetophenone*	98-86-2	105	71	0.0175	4.6	Korneev [39]; Savenhed et al. [40]; Imasheva [41]; Tkach [42]
N-compounds						
Ammonia	7664-41-7	-	-	1.45	-	Nagata [37] ; Smeets et al. [43]
Methenamine	100-97-0	140	1000†	N-D	-	-
Trimethylamine*	75-50-3	58	775	0.00006	1333	Nagata [37]; Greenman et al. [44]
S-compounds						
Dimethyl disulfide*	624-92-0	94	1068	0.0085	9	Nagata [37]
Dimethyl sulfide*	75-18-3	62	915	0.0076	11	Nagata [37]
Dimethyl trisulfide*	3658-80-8	126	301	0.0087	9	ADEME [45]
Methanethiol	74-93-1	-	-	0.00031	-	Nagata [37], Greenman et al. [44]
Hydrogen sulfide	7783-06-4	-	-	0.00053	-	Nagata [37]; Ueno et al. [46]. McGinley and McGinley [47]
Alcohols						
1-Butanol	71-36-3	56	1240	0.45	-	Ueno et al. [46] ; Cain et al. [48]
1-Butanol- 3- methyl	123-51-3	56	1000†	0.01	8	Nagata [37]
1-Pentanol	71-41-0	31	1400	0.256	-	Nagata [37] ; Yang et al. [49]
1-Propanol	71-23-8	56	1000†	0.24	-	Nagata [37]
1-Propanol-2-methyl	78-83-1	43	1000†	0.033	2	Nagata [37]
2-Butanol	78-92-2	45	1000†	0.66	-	Nagata [37]
Ethyl hexanol	104-76-7	57	1000†	0.8	-	Nagy et al. [50]
Ethyl alcohol	64-17-5	31	1000†	0.99	-	Nagata [37]
Isopropyl alcohol	67-63-0	45	1000†	65	-	Nagata [37]
Methanol	67-56-1	31	2600	43	-	Nagata [37]
Aromatic hydrocarbons						
Phenol	108-95-2	94	2130	0.035	2	Nagata [37]; Don [51]; Hoshika [52]
Styrene	100-42-5	104	1095	0.149	-	Nagata [37]
Toluene	108-88-3	91	3611	0.38	-	Cometto-Muniz and Abraham [53]
Aliphatic hydrocarbons						
1-3-Pentadiene	504-60-9	67	1405	N-D	-	-
Terpenes						
Alpha-pinene	80-56-8	91	975	0.1	-	Nagata [37]
Camphor	76-22-2	95	1000†	0.49	-	Gundlach and Kenway [54]
Limonene	138-86-3	68	2	0.134	-	Nagata [37]
S and N compounds						
Thiocyanic acid methyl ester	556-64-9	73	416	0.75	-	Katz and Talbert [55]
Acids						
Acid acetic	64-19-7	60	460	0.016	5	Nagata [37], Wise et al. [56], Miyazawa et al. [57]
Propanoic acid	79-09-4	60	1000†	0.017	2	Nagata [37]
Hexanoic acid*	142-62-1	60	1000†	0.0048	17	Cometto-Muniz and Abraham [58]
Aldehyde						
Butanal *	123-72-8	43	1000†	0.0016	25	Nagata [37]; Cometto-Muniz and Abraham [58]

N-D: no data found; ODT: odor detection threshold as referenced from the odor detection threshold database [36];

MDL_{MAX}/ODT indicates how many times the highest GC-MS method detection limit (MDL_{MAX}) exceeded the odor detection threshold (ODT) for a compound;

* Compounds with an ODT lower than the GC-MS method detection limit.

1000†: the coefficient used when the compound was not calibrated.

Table 3

Comparison of the absolute relative deviation of OAV_{MAX} and OAV_{SUM} with respect to the 95% confidence interval for odor concentration measurement

	Number of mixture	Mean Abs RD (%)	
		OAV_{MAX}	OAV_{SUM}
OAV_{MAX} and OAV_{SUM} are outside the confident limits of OC measure	16 (24%)	68	103
OAV_{MAX} is outside the confident limits of OC measure	25 (38%)	53	-
OAV_{SUM} is outside the confident limits of OC measure	31 (47%)	-	73

OC, odor concentration of a gaseous emission measured by olfactometry and corresponding to the number of dilution required for its odor to be undetected; OAV_{MAX} : maximal odor activity value within a mixture; OAV_{SUM} : sum of every odor activity values of a mixture; Abs RD: absolute relative deviation value

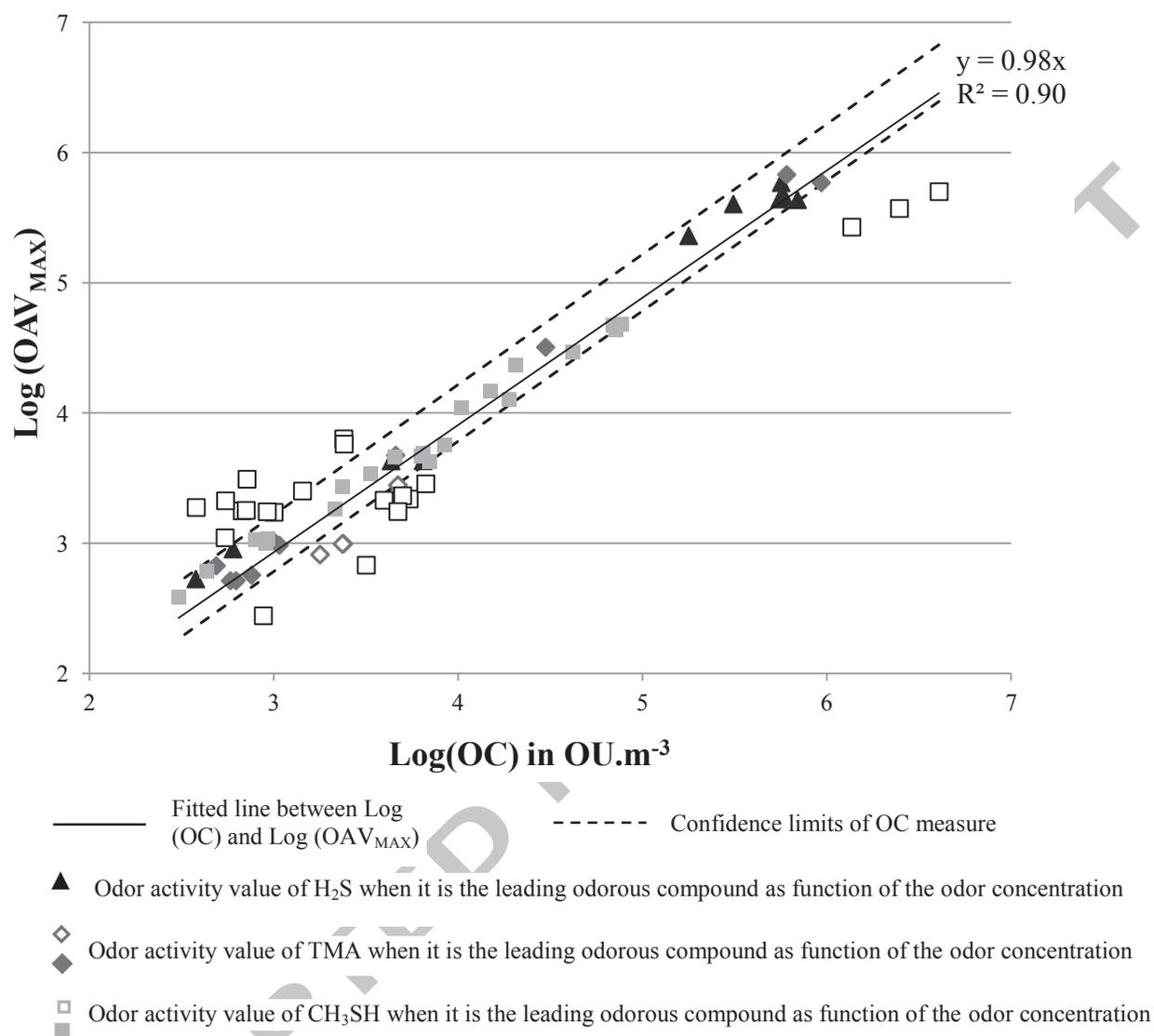


Fig.1 Predicted Log (OAV_{MAX}) as function of measured Log (OC) (OAV_{MAX} is the odor activity value (OAV) of the most odorous compound, namely the compound with the highest concentration/odor detection threshold value; the odor concentration (OC) was measured by olfactometry. Hollow points stand outside the confidence interval of the odor concentration).

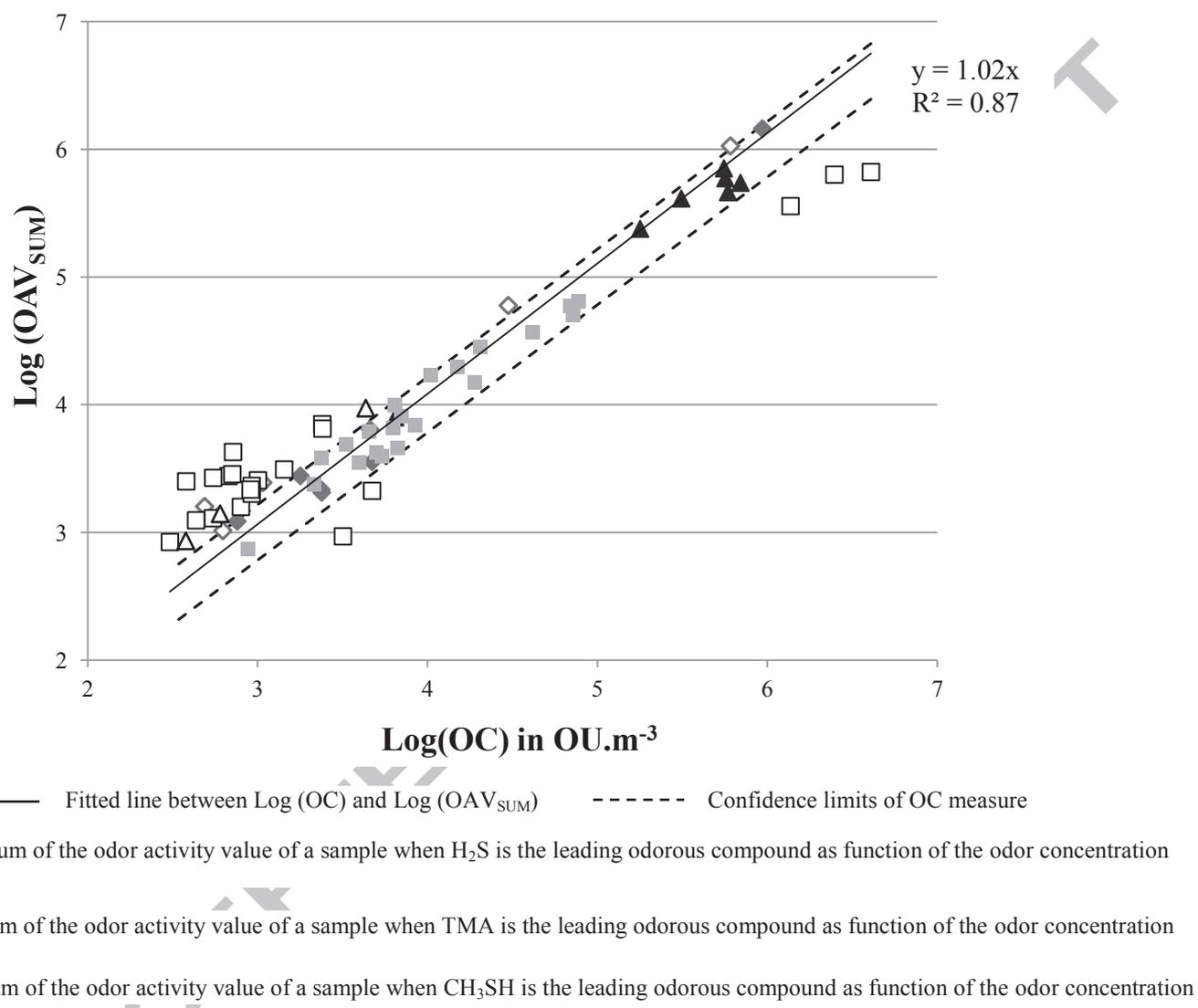
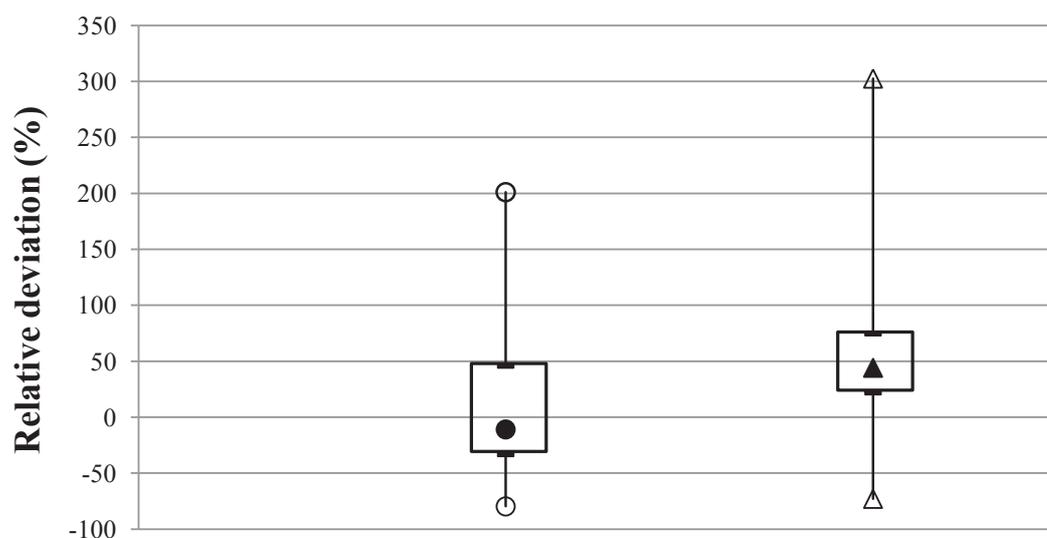


Fig.2. Predicted Log (OAV_{SUM}) as function of measured OC (OAV_{SUM} was obtained by summing the OAV of every odorous compound found in the gas sample; the odor concentration (OC) was measured by olfatometry. Hollow points are out of the confidence limits of the OC measure).



- Box plot of the Relative Deviation between the closest odor concentration interval boundaries and the maximal odor activity value within a sample outside the odor concentration confident interval
- ▲ Box plot of the Relative Deviation between the closest odor concentration interval boundaries and the sum of every odor activity values of a sample outside the odour concentration confident interval

Fig.3. Box plot of the Relative Deviation between the closest odor concentration interval boundaries (OC_{INT}) and the maximal odor activity value within a sample outside the odor concentration confident interval, and; between OC_{INT} and the sum of every odor activity values of a sample outside the odor concentration confident interval.

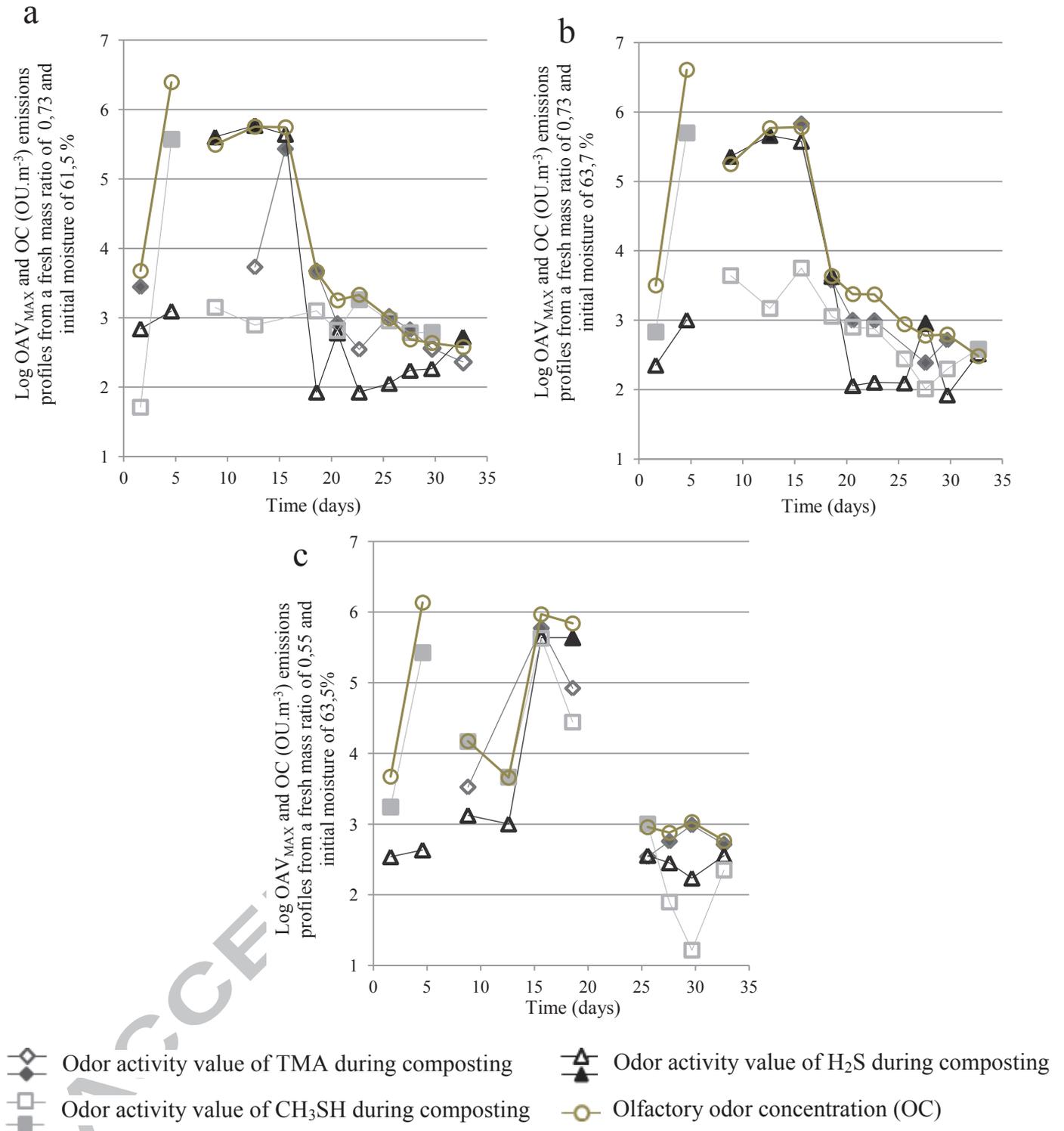


Fig. 1. Composting emissions profiles of odor concentration (OC) and odor activity value (OAV) for the leading odorous compounds, namely methanethiol (CH₃SH), trimethylamine (TMA) and hydrogen sulfide (H₂S). Full points indicate that the highest odor activity value is produced by TMA, H₂S or CH₃SH.

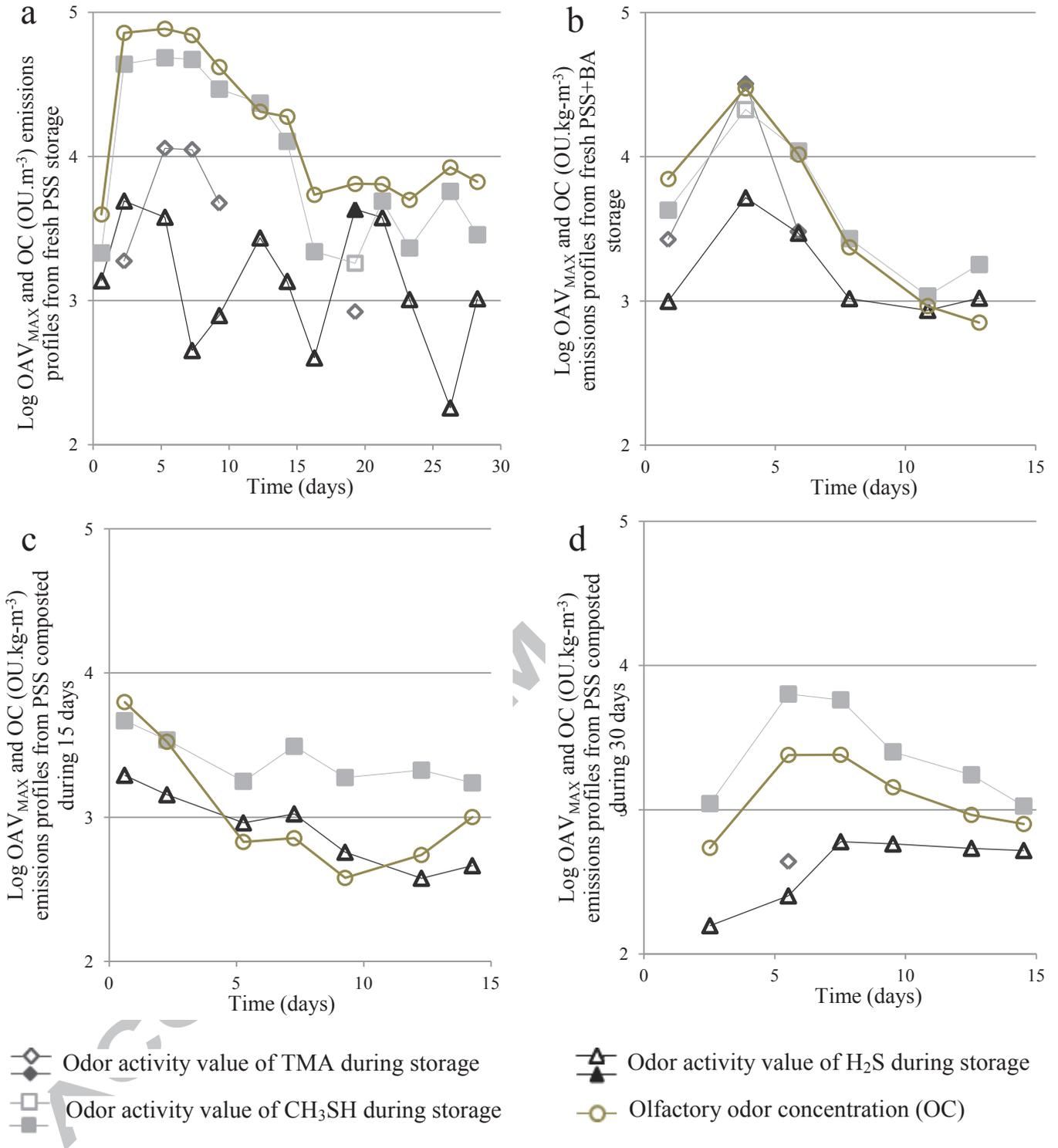


Fig. 1. Emissions profiles of odor concentration (OC) and odor activity values (OAV) for the leading odorous compounds, namely methanethiol (CH₃SH), trimethylamine (TMA) and hydrogen sulfide (H₂S), emitted during the storage of fresh pig slaughterhouse sludge (PSS),

fresh pig slaughterhouse sludge mixed with bulking agent (PSS+BA) and composted pig slaughterhouse sludge after 15 and 30 days of treatment. Full points indicate that the highest odor activity value is produced by TMA, or H₂S or CH₃SH.

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PSS composting and storage gas samples were determined by chemical and olfactory analyses

For gas samples, correlations between the chemical composition and its OC was investigated

OAV_{MAX} assumed that OC was equal to the sample's highest OAV value

OAV_{SUM} assumed that OC was equal to the sum of all OAV for sample

The 3 most odorant compound offered a good prediction of the olfactory results.