

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

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- Correlation of chemical composition and odor concentration for emissions from pig 1
- slaughterhouse sludge composting and storage 2
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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; OCINT, 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.

Abstract

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 to 1.65 x 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.

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

OAV_{MAX} consisting of the highest OAV value associated with an individual compound
within the sample.
2. Materials and methods
2.1. Experimental conditions
The composting experiments were performed in 300 L reactors consisting of insulated
stainless cylinders, 800 mm in height and 700 mm in diameter. Immediately after loading
the reactors, a low aeration rate of 1.3 L.h ⁻¹ .kg ⁻¹ of wet sludge was applied during 5 days.
Thereafter, the aeration rate was increased to 9.3 L.h ⁻¹ .kg ⁻¹ wet sludge and maintained
constant till the end of the experiment. A rotameter (FL-821-V, OMEGA Engineering Inc.,
Stamford, USA) regulated the in-coming airflow while a volumetric gas meter measured
the flow (Gallus 2000, Actaris, Liberty Lake, USA). The reactor were equipped to
continuously monitor the compost temperature and its total mass using respectively two
Pt100 probes and weigh sensors. Concentrations in O ₂ and CO ₂ were continuously
measured in both the in-coming and out-going airflows using respectively a paramagnetic
analyzer (MAGNOS 206, ABB, Zurich, Switzerland) and an IR spectrometric analyzer
(URAS 26, ABB, Zurich, Switzerland). Every 10 days, the compost was turned. The
composting treatment was stopped after 36 days.
The composting experiments were carried out using PSS mixed with bulking agent. The
sludge was collected from the primary wastewater treatment process of a pig
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 kg.kg ⁻¹ . For a BA/PSS of 0.73 kg.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 L.h ⁻¹ was
145	applied to the cell, for a value of 1.72 to 3.95 L.h ⁻¹ .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 kg.kg ⁻¹ and under an aeration rate of
151	6.05 L.h ⁻¹ .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.

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,

dimethyl sulfide and hydrogen sulfide was lost respectively in Tedlar and Nalophan bags, 179 after 4 to 8 hours of storage [25-26-27]. Even though the recovery of odorants in sampling 180 bags is an important issue and can lead to odor concentration underestimation, Van 181 Harreveld [28] showed that odor is stable in Nalophan bags for a period of 4 to 12 hours. 182 Since sample bags were analyzed within 4 to 6 hours and because of similar treatment, 183 chemical composition and odor concentration from the same sampling bag could be 184 compared and considered to represent the emission sampled. 185 Since gaseous emissions from the raw compost required a large dilution level before 186 olfactometry, namely 131,000 folds, samples had to be pre-diluted, using three methods 187 providing a range of 12.6 to 500. The first method consisted in directly connecting to the 188 189 olfactometer, a double orifice probe mixing the gas sample with dry clean air, where the size of the respective orifices provided a dilution ratio of 100. The dilution rate of the probe 190 was controlled using a Gilibrator 2 calibration system (Gilian, Clearwater, USA). The 191 second method consisted in precisely measuring 250 mL of gas sample using a glass 192 sampling bulb with a PTFE stopcock (Supelco, Bellefonte, USA). Using the olfactometer, 193 the 250 ml volume was then injected into a Nalophan bag containing 5, 30 or 35L of dry 194 clean air for a dilution rate of respectively of 21, 121 or 141. Thus, the accuracy of the 195 dilution was determined by that of the olfactometer airflow controls. The third dilution 196 method consisted in withdrawing a diluted sample from a Nalophan bag using a gas tight 197 syringe (Supelco) and then injecting into a new Nalophan bag filled with a known volume 198 of clean air. The pre-diluted rate was applied to the odor concentration level measured by 199 200 olfactometry. According to Wardencki [29], the collection and storage of gas samples in a glass bulb leads to a significant loss of hydrogen sulfide and methanethiol. However, in this 201

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

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

2.3. Olfactory measurements

224	The dynamic dilution offactometer 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 OU.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 ±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 ₂ SO ₄ , 1N), and;
263	the second to trap in series, hydrogen sulfide (H ₂ S) 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 ₂ S 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, NH ₄ ⁺ /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 ₃ BO ₃ , 40 g.L ⁻¹) and then back-titration with sulfuric acid (H ₂ SO 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 $0.286~\text{mg.m}^{-3}$. The reaction of H_2S with PbNO $_3$ and of RSH with $HgCl_2$
276	produced a PbS and Hg(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 HgCl2 were calculated as methanethiol leading to
279	Hg(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 ₂ S and
288	RSH traps.

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 mL 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	$\mu g.m^{-3}$, 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 N_2 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

detection thresholds (ODT) as per a recent database [36]. When several odor detection
thresholds were available for a single compound, only the most recent value was used. In
general, recent odor detection threshold values were lower than the old ones, leading to
higher odor activity values. However, the order of magnitude for many individual
compounds could be considerably different [6-11]. According to Parker et al [6], the
central tendency of the odor detection threshold values was well descript by geometric
means compared to harmonic means (which were lower) and arithmetic means (which were
higher and influenced by the larger individual values). Thus when several recent odor
detection threshold values were available, a geometric mean was used in order to obtain a
central tendency of the odor activity value.
As highlighted for some compounds in Table 2, the GC-MS detection level (method
detection limit or MDL) was higher than the odor detection threshold, leading for some
samples, to the under-estimation of the odor activity value. In Table 2, the ratio
$(MDL_{MAX})/ODT$ indicates the level of underestimation for these compounds, where
MDL_{MAX} is the highest method detection limits observed during samples according the gas
volume passed throughout Carbotraps. Nevertheless, only trimethylamine (TMA) showed
an important odor activity value underestimation, with an $MDL_{MIN}\!/ODT$ and

MDL_{MAX}/ODT ranging between 217 and 11333, respectively. Sulfurs, aldehyde and alcohol

compounds showed a maximal OAV underestimation of around 10, or even less. For such

compounds, the method detection limits showed low underestimation of odor activity value

Table 2

determination.

Gaseous compounds identified from emissions collected during the composting and the 358 storage of pig slaughterhouse sludge 359 A last and important bias for odor activity value determination can result from the use 360 of sorbent tubes and the subsequent thermal desorption in TD-GC/MS. Indeed, mercaptans 361 and especially methanethiol can be oxidized to form di- and tri-sulfides [59] which were 362 largely quantified during chromatogram processing. This reinforces the assumption that 363 mercaptan were mainly methanethiol. Consequently, the odor activity value from 364 methanethiol could double when adding the odor activity value from organo-sulfides, thus 365 leading to odor activity values overestimation. However, the source of the organo-sulfide 366 was uncertain, whether from composting or from mercaptan oxidization, or from a 367 368 combination of both. For every compound, its odor activity value (OAV) was calculated from the ratio of its 369 chemical concentration to its odor detection threshold. All the chemical concentrations and 370 OAV are provided in Supplementary Materials 3 and 4, respectively. The odor activity 371 values of methenamine, 1,3 pentadiene and 3-pentanone-2-methyl were not calculated 372 because of their unknown odor detection threshold. 373 Two correlations were calculated to link gas sample odor concentration (OC) to its 374 375 chemical composition: OAV_{MAX}, assuming that odor concentration is equal to the OAV of the most odorous compound, and; OAV_{SUM}, assuming that odor concentration is equal to 376 the sum of all compound OAV. The values of OC, and OAV_{MAX} and OAV_{MAX 2} (the first 377 and second highest odor activity value per sample) and OAV_{SUM} are given in 378

379

Supplementary Material 4.

380 The relevance of the two types of correlation was evaluated based on the percentage by which OAV_{MAX} and OAV_{SUM} fell within the 95% interval of confidence for the 381 corresponding measured odor concentration (OC), as computed for every sample (EN 382 13725 [12]): 383 OC / $(10^{2.0} * \text{Sr} / \sqrt{n}) < \text{OC} < \text{OC} * (10^{2.0} * \text{Sr} / \sqrt{n})$ 384 with, n is the number of bags analyzed, from 1 to 3, and Sr is the standard deviation 385 calculated from the repeatability, namely 0.1721. The mean value of $(10^{2.0} * \text{Sr} / \sqrt{n})$ was 386 found to be 1.65, whereby OC / 1.65 < OC < OC x 1.65. 387 Consequently, each odor concentration (OC) measure is linked to: two boundaries of 388 the confidence interval as above-mentioned, the highest odor activity value (OAV_{MAX}) 389 (resulting from a single compound) and the sum of the odor activity values from all 390 391 compounds in the gas sample (OAV_{SUM}). The correlation extent between OC and either OAV_{MAX} or OAV_{SUM} was estimated 392 through a simple linear regression using a log transformation to limit distribution variance 393 between the variables (OAV_{SUM}, OAV_{MAX} and OC). This log transformation better 394 illustrated data patterns and allowed for the use of a simple correlation type $Log(OAV_{MAX})$ 395 or $Log(OAV_{SUM}) = 1 Log(OC)$ to link the variables. The logarithmic expression of the 396 odor concentration should not be considered as an indirect indicator of the odor intensity, 397 and extension of odor concentration. Moreover, using a "log-log correlation" graphically 398 399 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 the basis of the Relative Deviation, computed for the mixtures showing an OAV_{MAX} or 401

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	RD= $(OAV_{MAX} \text{ or } OAV_{SUM}\text{-}OC_{INT})*100/OC_{INT}$ (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.

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

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Olfactometry consists initially in diluting a gas sample until its odor cannot be perceived by all panellists, and then, increasing its concentration, with lower dilutions, until all trained human panelists are able to detect the odor. Theoretically in the absence of synergistic effects, the olfactory stimulus should come from the most odorant compound namely the one requiring the highest dilution rate to be odorless. In this context, Zahn et al. [60] showed that the synergistic effects were minor for swine odors. Thus, odor concentration should correlate to the odor activity value of the most odorant compound namely OAV_{MAX}. Considering the 66 gas samples analyzed, OAV_{MAX} displayed only three compounds responsible for the odors, namely mercaptans (presumed to be methanethiol), trimethylamine and hydrogen sulfide, respectively at 64, 21 and 15% of the gaseous mixtures studied. Similarly by multivariate analyses, Hansen et al. [18] identified hydrogen sulfide, methanethiol, trimethylamine, and 4-methylphenol as the main odorous compounds emitted from growing-finishing hogs facilities. Finally, these three compounds were presumed to be mostly responsible for odor concentration (OC) because of their very high odor activity values (OAV) in all 66 samples. Fig. 1 gives Log (OAV_{MAX}) values as function of Log (OC). The dotted lines represent the 95 % confidence interval for Log (OC), namely Log (OC / 1.65) < Log (OC) < Log (OC * 1.65). The values for Log (OAV_{MAX}) fell outside this interval mostly for mixtures within methanethiol, estimated as the most odorous compound and especially at low and high concentrations, namely when OAV_{MAX} was under 8 x 10^3 and over 6 x 10^4 . This

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 Log (OAV $_{MAX}$)= 0.98Log (OC). Furthermore, the coefficient of determination
453	$(R^2=0.90)$ denoted a strong linear association between Log (OAV_{MAX}) and Log (OC) ,
454	suggesting that Log (OAV $_{MAX}$) could be a good predictor of Log (OC).
455	
456	Fig. 1
457	Predicted Log (OAV $_{MAX}$) as function of measured Log (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 olfatometry. Hollow points stand outside
460	the confidence interval of OC.
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462	Fig. 2 gives Log (OAV $_{SUM}$) values as function of Log(OC). As for Log(OAV $_{MAX}$),
463	$Log(OAV_{SUM})$ fell outside the $Log(OC)$ 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 x 10^3 and over 6 x 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 Log (OAV $_{SUM}$) = 1*Log(OC), namely Log(OAV $_{SUM}$) = 1.02 Log (OC), with a
468	coefficient of determination R^2 =0.87. In conclusion, Log (OAV _{SUM}) can also be an
469	acceptable predictor of Log (OC).

170	Fig. 2
171	Predicted Log (OAV $_{SUM}$) as function of measured Log (OC); OAV $_{SUM}$ was obtained by
172	summing the OAV of every odorous compound found in the gas sample; Odor
173	concentration (OC) was measured by olfatometry. Hollow points are out of the confidence
174	limits of the OC measure.
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176	However to determine odor concentration, on basis of Fig. 1 and 2, OAV_{MAX} showed a
177	higher coefficient of determination than $\textsc{OAV}_{\textsc{SUM}}.$ Although $\textsc{OAV}_{\textsc{MAX}}$ and $\textsc{OAV}_{\textsc{SUM}}$ are
178	functions which are far apart, their linear regression shows a numerically similarity (Log
179	(OAV_{SUM}) =1.04Log (OAV_{MAX}) and R^2 =0.98; data not show). Consequently, for most of
180	the samples analyzed, the odor activity value (OAV) was mainly displayed by a single
181	compound. In other words, a limited percentage of the odor activity charge is displayed by
182	secondary compounds. Therefore, a quantitative study of $\textsc{OAV}_{\textsc{MAX}}$ and $\textsc{OAV}_{\textsc{SUM}}$
183	correlation with the odor concentration must be investigated.
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185	3.3. Quantitative evaluation of odor activity
186	Table 3 gives the numbers of samples where only OAV_{MAX} , only OAV_{SUM} and when
187	both values fell outside the 95% confidence interval of the odor concentration
188	measurement. The mean of the absolute Relative Deviation value is also presented.
189	

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	$\mathrm{OAV}_{\mathrm{MAX}}$, namely at 68% versus 103% for $\mathrm{OAV}_{\mathrm{SUM}}$. 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

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 $_{\mbox{\scriptsize MAX}}.$ Moreover, 50% of the OAV $_{\mbox{\scriptsize MAX}}$ 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 3×10^3 OU.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.

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Limited research work correlates the highest odor activity values for a gas sample to its odor concentration. However, several studies correlated the odor intensity with respect of the VDI 3881 [61], ASTM E544-10 [62]) measured at supra-threshold with the theoretical intensity derived from compound concentration forming synthetic mixtures. Kim and Park [9] showed that odor intensity could be determined by a single predominant compound rather than by the sum or average of all individuals. Kim [63] and Zhao et al. [64] also found that the odor intensity from compound mixtures with similar chemical properties could be mostly characterized by averaging the odor intensity potential of all the contributors. The relevance of the "highest odor activity value compound model" must be cautiously considered as further investigation is necessary. The literature has generally favoured the correlation between odor concentration (OC) and the sum of the odor activity values for a gas sample (OAV_{SUM}) even if the numerical addition of odor activity value, representing the theoretical dilution factor, does not correspond to the method used in olfactometry. Kim and Park [9] found a strong correlation (Pearson coefficient of 0.866) between OAV_{SUM} and OC, without presenting sufficient data to appreciate the closeness between OAV_{MAX} and OAV_{SUM}. Parker et al. [6] correlated OC to OAV_{SUM}, to find a 2 to 3 fold underestimation of OC. However, the range of measured odor concentrations was quite low, namely from 3 x 10¹ to 8 x 10³ OU.m⁻³. In this range, OAV_{SUM} can be easily underestimated, especially for compounds with a very low odor detection threshold. In this study, supplementary materials 4 lists all cases with compounds detected below their detection limits. Moreover, supplementary materials 4 presents the maximum odor activity value underestimation, defined as the ratio of the method detection

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

clearly identified.

3.4. Emissions profiles of odor concentration and the main odorous compounds Fig. 4a, 4b and 4c compares Log (OAV) and Log (OC) for the leading odorous compounds of the gas sample collected during the composting processes applied. As previously mentioned, the similarity between a sample's odor concentratin (OC) and its highest odor activity value (OAV $_{MAX}$) or the sum of its odor activity values (OAV $_{SUM}$) required a cautious interpretation because of the "log-log correlation". Nevertheless, the Log (OAV $_{MAX}$) profile emissions (hollow points) better described Log (OC) variations. For the first 4.6 days, OAV $_{MAX}$ was much lower than OC and methanethiol was the most odorant compound. Thereafter, OAV $_{MAX}$ followed, as expected, the same trend as OC and was relatively close, confirming that OAV $_{MAX}$ is a good predictor of OC. Then, hydrogen

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

sulfide was found as the most odorous compound except for the samples on day 15 with a

peak of trimethylamine, whatever the process conditions. The odor emissions decreased

significantly after 15 to 20 days at which time no leading odorous compound could be

the easily biodegradable fraction of organic matter, responsible for the highest O₂ demand, 579 seemed to produce conditions for the emission of the most odorous compounds. 580 The distribution of the odor activity value within a sample also indicates the 581 perspectives for odor abatement, with the removal of the most odorous compounds not 582 necessarily generating a strong odor decrease. The extent of the odor decrease will depend 583 584 of the next highest odor activity value perceptible during odor concentration measurement. Consequently odor treatment must target in decreasing order, the compounds showing the 585 highest odor activity value. Thus, the number of compounds to be targeted for odor 586 abatement can vary greatly. 587 588 Fig. 3 589 Composting emissions profiles of odor concentration (OC) and odor activity value (OAV) 590 for the leading odorous compounds, namely methanethiol (CH₃SH), trimethylamine (TMA) 591 and hydrogen sulfodoride (H₂S). Full points indicate that the highest odor activity value is 592 produced by TMA, H₂S or CH₃SH. 593 594 The Fig. 5a, 5b, 5c and 5d give the log (OAV) profiles of the leading odorous 595

always produced the highest odor activity value from gas samples likely because of the low redox potential created by the storage conditions. Slight discrepancies were found between

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PSS mixed with BA, as high concentrations of mercaptan were produced (Fig. 5a and 5b).

odor concentration and the highest odor activity value when storing fresh PSS and fresh

compounds and the log (OC) measured during the various storage processes. Methanethiol

In contrast, the 15 and 30 days composts were responsible for lower mercaptan

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

Fig. 4

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.

4. Conclusion

The objective of this research was to correlate the chemical characterization of odor emissions with their odor concentration as measured by olfactometry. The emissions analysed in this project were obtained from the composting and storage of pig slaughterhouse sludge. Two correlations were investigated to relate odor concentration (OC) with the chemical composition of the gas sample. The first, based on principles of olfactometric analysis, assumed that the highest odor activity value of the gas sample (OAV $_{MAX}$) corresponded to OC, whereas the second used the sum of the odor activity 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 OU.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	
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648	and their cooperation during the odor measurements.
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Table 1

Mixtures compositions and experimental conditions

	Storage experiments					Composting experiments			
Material composition	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		
Experimental conditions									
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

Sludge CAS Quantification Calibration ODT MDL _{MAX} ODT B			,			
Compounds	number		coefficient	(mg.m ⁻³)	/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]; Smeet et al. [43]
Methenamine	100-97-0	140	1000+	N-D	-	- 1
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		301	0.0087	9	ADEME [45]
Methanethiol	74-93-1	_	_	0.00031	_	Nagata [37], Greenman et al. [44]
Hydrogen sulfide	7783-06-4	<u>-</u>	_	0.00053		Nagata [37]; Ueno et al. [46]. McGinley and McGinley [47]
Alcohols						
1-Butanol	71-36-3	56	1240	0.45	T.	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]
Ehtyl hexanol	104-76-7	57	1000+	0.8	_	Nagy et al. [50]
Ethyl alcohol	64-17-5	31	1000†	0.8	-	Nagata [37]
			1000†			
Isopropyl alcohol	67-63-0	45		65	-	Nagata [37]
Methanol	67-56-1	31	2600	43	-	Nagata [37]
Aromatic hydrocarbons	100.05.0	0.4	2120	0.025		N
Phenol	108-95-2	94	2130	0.035	2	Nagata [37]; Don [51]; Hoshika [52]
Styrene	100-42-5		1095	0.149	-	Nagata [37]
Toluene	108-88-3	91	3611	0.38	-	Cometto-Muniz and Abraham [53]
Aliphatic hydrocarbons	504 60 0		1.40.7	N. D.		
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						b 3
Butanal *	123-72-8	43	1000+	0.0016	25	Nagata [37]; Cometto-Muniz and Abraham [58]
N.D. no data found: ODT: o						

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

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

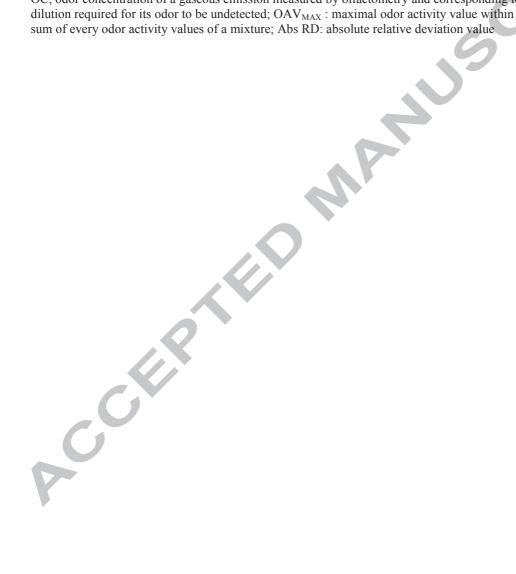
^{*} Compounds with an ODT lower than the GC-MS method detection limit.

^{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	Mean Abs RD (%)			
	mixture	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



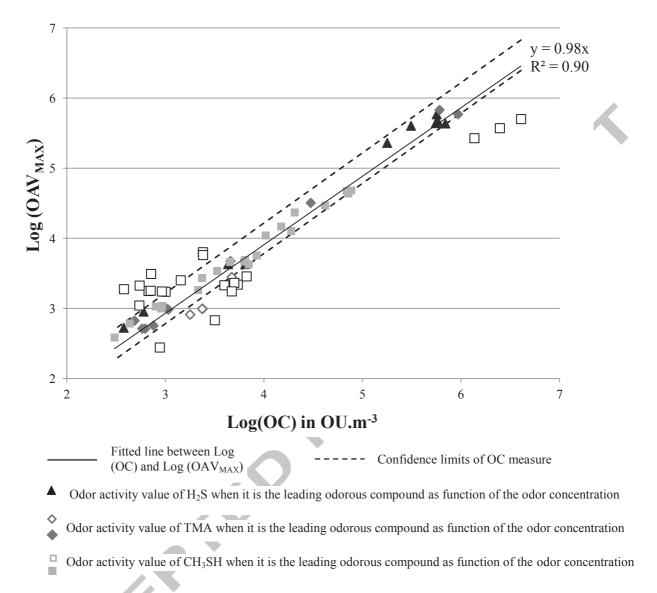
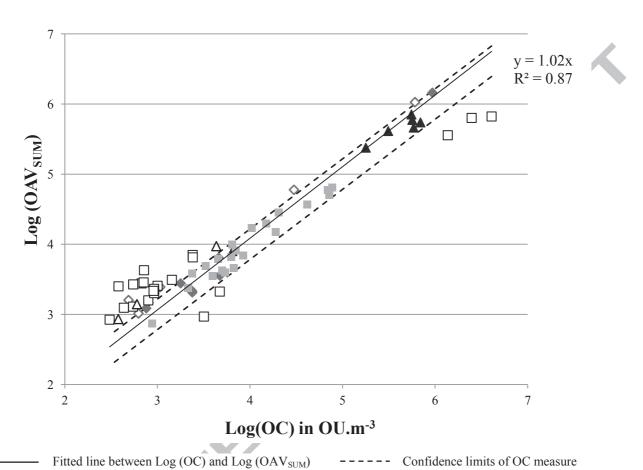


Fig.1 Predicted Log (OAV_{MAX}) as function of measured Log (OC) (OAV_{MAX} is the odor activity value (OAV) of the most odorous compound, namely the compound with the highest concentration/odor detection threshold value; the odor concentration (OC) was measured by olfatometry. Hollow points stand outside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

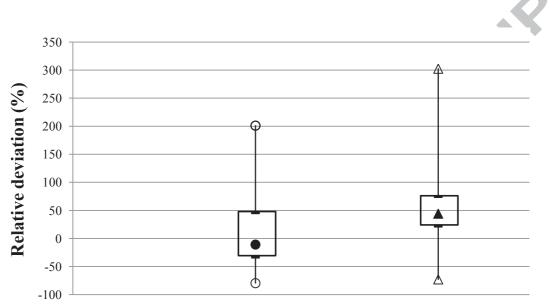


Sum of the odor activity value of a sample when H₂S is the leading odorous compound as function of the odor concentration

Sum of the odor activity value of a sample when TMA is the leading odorous compound as function of the odor concentration

Sum of the odor activity value of a sample when CH₃SH is the leading odorous compound as function 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.

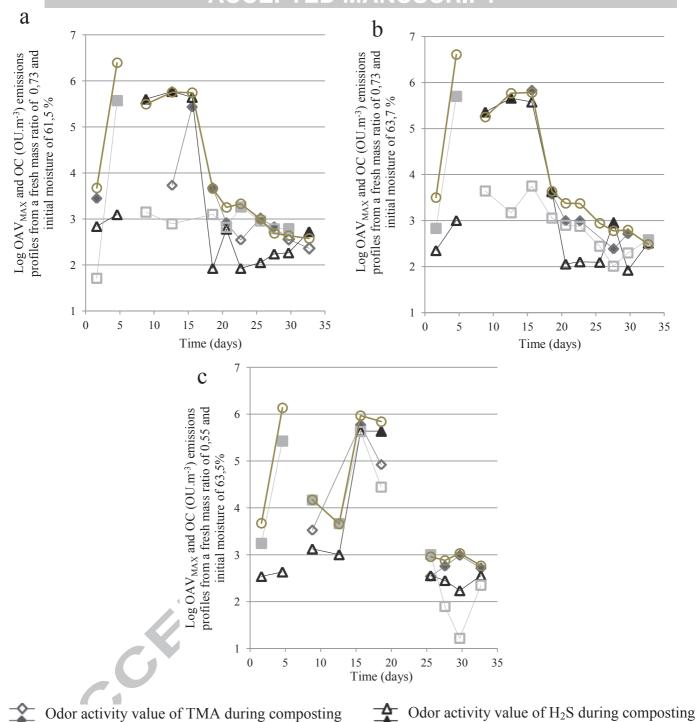


Fig. \square Composting emissions profiles of odor concentration (OC) and odor activity value (OAV) for the leading odorous compounds, namely methanethiol (CH₃SH), trimethylamine (TMA) and hydrogen sulfide (H₂S). Full points indicate that the highest odor activity value is produced by TMA, H₂S or CH₃SH.

-O- Olfactory odor concentration (OC)

Odor activity value of CH₃SH during composting

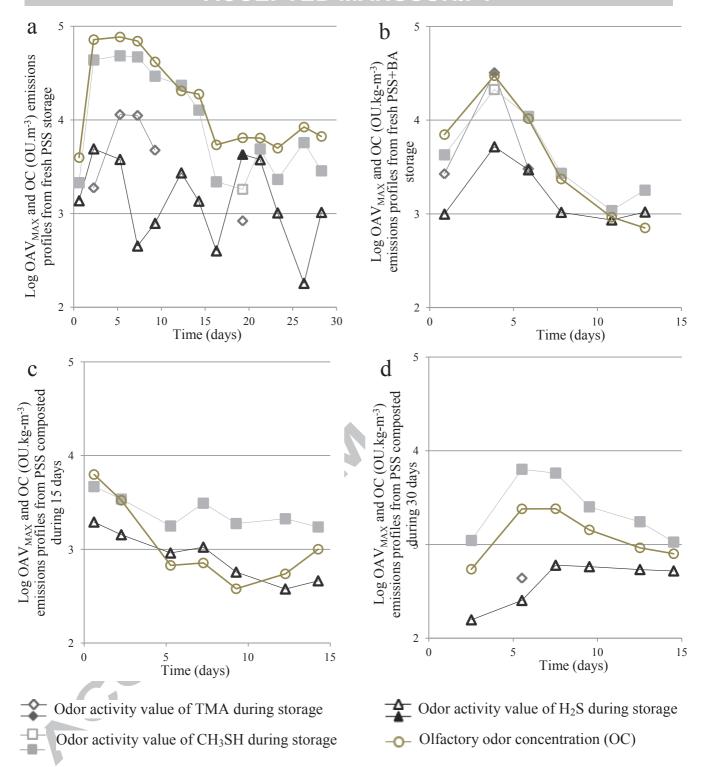


Fig. \square Emissions profiles of odor concentration (OC) and odor activity values (OAV) for the leading odorous compounds, namely methanethiol (CH₃SH), trimethylamine (TMA) and hydrogen sulfide (H₂S), emitted during the storage of fresh pig slaughterhouse sludge (PSS),

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.



□ig□lig□□□

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

 $\mathrm{OAV}_{\text{SUM}}$ assumed that OC was equal to the sum of all OAV for sample

