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González Alé, Daniel; Colón Jordà, Joan; Sanchez, Antoni; [et al.]. «A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant». *Journal of hazardous materials*, Vol. 373 (July 2019), p. 733-740. 8 pàg. DOI 10.1016/j.jhazmat.2019.03.131

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Accepted Manuscript

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PII: S0304-3894(19)30413-3
DOI: <https://doi.org/10.1016/j.jhazmat.2019.03.131>
Reference: HAZMAT 20512

To appear in: *Journal of Hazardous Materials*

Received date: 16 December 2018
Revised date: 22 March 2019
Accepted date: 30 March 2019

Please cite this article as: González D, Colón J, Sánchez A, Gabriel D, A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant, *Journal of Hazardous Materials* (2019), <https://doi.org/10.1016/j.jhazmat.2019.03.131>

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A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant

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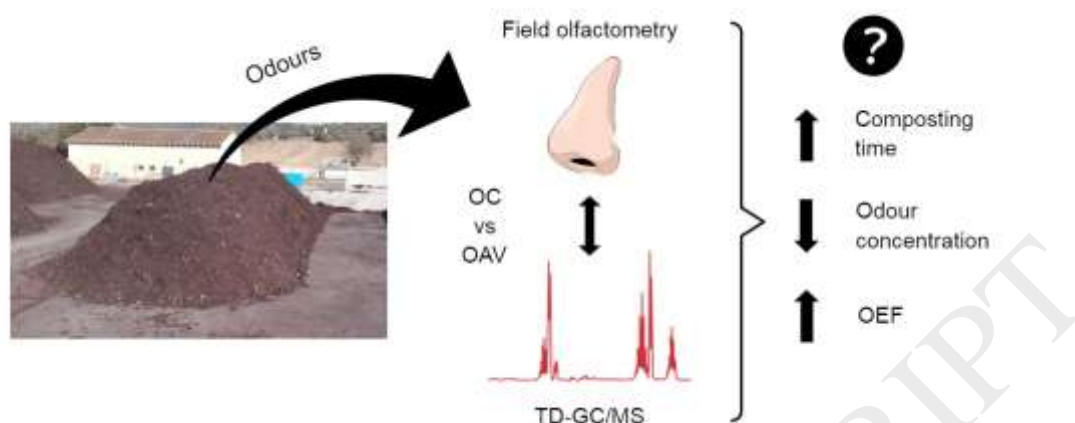
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Graphical abstract



Highlights

- Odours and volatile organic compounds emissions depend on the composting time.
- Global odour emission factors of $4.42\text{E}+06$ and $5.97\text{E}+06$ $\text{ou}\cdot\text{Mg}^{-1}$ RS-VF were obtained.
- Isovaleraldehyde, butyric acid, DMS, DMDS and α -pinene were the major odorants.
- Odour activity value is not a good predictor for odour concentration.

Abstract

Sewage sludge management is known to cause odour impact over the environment. However, an information gap exists about odour emissions quantification from different treatment strategies. In the present work, odorous emissions generated in a full-scale sewage sludge composting plant were characterized, aiming at providing specific odour emission factors (OEF) and to determine their variability depending on the composting

time. Additionally, characterization of VOCs emitted during the process was conducted through TD-GC/MS analyses. Odour emission and VOCs characterization considered both (1) a first stage where a raw sludge and vegetal fraction mixture were actively composted in dynamic windrows and (2) a second curing stage in static piles. After increasing the composting time, a reduction of 40% of the maximum odour concentration referred to the dynamic windrow stage was estimated, whereas a reduction of 89% of the maximum odour concentration was achieved after turning of curing piles. However, global OEF increased from $4.42\text{E}+06$ to $5.97\text{E}+06$ $\text{ou}\cdot\text{Mg}^{-1}$ $\text{RS} - \text{VF}$ when the composting time increased. Finally, different VOCs such as isovaleraldehyde, indole, skatole, butyric acid, dimethyl sulphide and dimethyl disulphide were identified as main potential odour contributors. Results obtained are a valuable resource for plant management to choose an appropriate sewage sludge composting strategy to mitigate odour emissions.

Keywords: Full-scale composting plant, sewage sludge, gaseous emissions, VOC, odour emission rate, odour emission factor.

1. Introduction

European countries produce more than 3.5 million Mg of sewage sludge (SS) during the treatment of urban wastewater [1], which must be treated to minimize its negative environmental impacts. Nowadays, different technologies and strategies are being applied to handle and manage SS produced in European countries such as land application, composting or anaerobic digestion. The last two have become the main biological treatment processes used in Europe [2]. Composting is considered an environmental friendly technology that reduces sludge volume and transport costs, it decomposes organic matter (OM) into a stable end product and removes malodorous compounds as well as pathogens and weeds.

The principal purpose of SS composting is to obtain a biological stable product. However, composting generates unavoidable environmental and social concerns. Especially, gaseous emissions are responsible for odour nuisance and atmospheric pollution. Different compounds can be found in gaseous emissions from composting, which are related to the decomposition of OM, nitrogen- and sulphur-based compounds. Specifically, ammonia, hydrogen sulphide and a wide range of volatile organic compounds (VOCs) are the main compounds found in gaseous emissions from SS composting facilities responsible of odour pollution [3,4].

Odour emissions can be characterised using high performance analytical techniques for the identification and quantification of odorants, such as gas chromatography coupled to mass spectrometry (GC/MS). However, chemical analysis of complex odour mixtures, especially those coming from organic wastes, is difficult to be related to the sensation perceived by a human receptor. In this sense, sensorial techniques such as dynamic olfactometry or field olfactometry are frequently used for odour impact assessment purposes. These techniques are capable of quantifying odours in terms of intensity and/or

concentration [5]. A useful tool for odour assessment and its prediction in full-scale plants are odour emission factors (OEFs) [6,7], which are analogue to those defined by the US Environmental Protection Agency [8] for other pollutants or chemical compounds. Briefly, in the estimation of OEFs for industrial facilities, the odour concentration (OC, $\text{ou}\cdot\text{m}^{-3}$) is related to the emitted air flow ($\text{m}^3\cdot\text{s}^{-1}$) and normalised with respect to one or more reference parameters such as the mass of waste treated, the emitting surface or time units among others.

Another cost-effective strategy to obtain complementary odour information about gaseous emissions is the use of individual odour activity values (OAV), which can help in the identification of the major odour contributors in a complex gas mixture. Based on the odour detection threshold (ODT), the OAV has been widely used [9–11]. OAV is defined as the ratio of the chemical concentration to the ODT of a single compound in a given sample. Despite the fact that synergistic and antagonistic effects are produced among odorants in complex gas mixtures, some authors have tried to correlate the sum of individual OAV (OAV_{SUM}) with OC [12]. However, it is important to mention that this approach has several limitations when correlating chemical concentration with OC. Limitations originate in the difficulty of quantifying each specific compound present in gaseous emissions as well as in the uncertainty of the synergistic or antagonistic effects among different compounds present in a complex odour mixture [13,14]. Besides, if a specific compound with no previously determined ODT contributes to odour, it can result in an underestimation of the odorous nuisance [9]. Finally, the nature of the waste to be treated plays an important role on the correlation obtained between the key odour components and the OC of a complex mixture. Consequently, results with high dispersion and a wide variety of correlations have been reported in different studies with different wastes [15–17].

In a previous work [18], a full-scale SS composting plant was evaluated to verify the proper biological stabilization of the material and to determine the emission factors of ammonia and total VOCs. It was observed that by increasing the composting time, a better waste stabilization was achieved and that the ammonia emission factor was reduced a 32%. This finding is important since it permits to correlate the stabilization of organic waste (systematically studied by Dynamic Respiration Index) with the reduction of gaseous emissions. However, a lack of scientific information about the specific odour emissions from full-scale SS composting processes exists. In addition, estimation of the potential odour impact derived from these facilities is often not determined. With the previous results, it was hypothesized that by increasing the composting process time, odour emission impact should decrease due to the better stabilization achieved. However, this stabilization must be properly measured if some consistent conclusion must be obtained. Consequently, the aim of the present work was to study the odorous emissions generated during the SS composting process to provide specific OEFs and to determine their variability depending on the composting time as indicators in the further selection and development of odour control strategies. In addition, a systematic characterization of the VOCs emitted during the biological process was conducted through TD-GC/MS analyses to identify the different species of VOCs and their potential odour contribution. Finally, a correlation between the OAV_{SUM} and the measured OC is presented to support that the OAV_{SUM} cannot be a single measure to predict OC of complex odour mixtures. To the author's knowledge, this is the first scientific work where odour emissions from a full-scale SS composting plant are thoroughly studied. In this sense, it is important to highlight that composting studies at lab or pilot-scale present several problems as active composting and maturation stages are very difficult to separate. In this paper, both stages have been systematically studied in terms of VOCs and odour emissions and presenting

the related OEFs and a characterization of the VOCs emitted during the composting process.

2. Materials and methods

2.1. Composting plant

The study was conducted between August and September of 2017 in a full-scale SS composting plant located in Majorca (Spain), coinciding with the worst scenario in terms of odour emission due to the high ambient temperatures (average temperature of 26.6 °C). This plant treats approximately 8000 Mg·year⁻¹ of raw sludge (RS) from primary and secondary settlers of different wastewater treatment plants (WWTP), altogether with 5000 Mg·year⁻¹ of vegetal fraction (VF) from the pruning of parks and gardens, used as bulking agent. Both materials are used to form a mixture of RS and VF (RS – VF) in a 1:3 v/v ratio (1:1.2 w/w ratio, wet basis). As end product, the plant produces an average amount of about 4000 Mg·year⁻¹ of compost. Table 1 shows the physical-chemical characteristics of the main RS treated at the plant, which is a mixture of primary and secondary settlers sludge mainly provided by two different WWTP, the bulking agent used (VF) and the initial mixture prepared in the plant (RS – VF).

The typical operation of the composting process in the plant, namely 4-days windrow residence time (WRT), consists of two different stages. First, an initial decomposition stage of controlled degradation of the OM carried out in four dynamic windrows, with 4 days of WRT, turning the material 3 times per day with an automatic mixer and a treatment capacity of 12.4 Mg RS – VF·d⁻¹. Afterwards, a curing stage of the treated material is made in trapezoidal static piles of about 75 Mg RS – VF during 31 days. Curing piles were turned once in the middle of the curing process. During the study, a second treatment strategy was tested, namely 14-days WRT. The WRT of the material in

two of the dynamic windrows was increased from 4 to 14 days (a typical WRT for the first decomposition stage of SS composting) by decreasing the automatic turning of the material to 1 time every 3 days. Consequently, the treatment capacity was reduced down to 3.6 Mg RS – VF·d⁻¹. The curing total mass was maintained (75 Mg RS – VF) but the curing phase time was reduced to 16 days because the material left the windrow stage fully stabilised. Both situations were compared to confirm the effect of the composting time on the OM degradation and the biological stability achieved [18], and particularly to quantify and compare odour and individual VOCs emissions of each treatment strategy once each process reached steady-state conditions.

2.2. Material characterization

Eight different solid samples representing different points of the entire treatment process were analysed in triplicates to determine moisture, OM content and the biological stability of the material, the latter in terms of Dynamic Respiration Index (DRI), as explained in [18]. In order to determine the biological stability of each sample, DRI was measured using a dynamic respirometer [19], which is based on the methodology proposed in previous works to assess the degree of biological stability of organic materials [20].

2.3. Odour emissions

2.3.1. Odour sampling and analysis

Both stages of the composting process (dynamic windrow stage and curing stage) were aerated by natural convection created during thermophilic conditions because of the temperature gradient between the material and ambient air. Thus, emission sources corresponded to passive emission sources. As mentioned by different authors [21,22], determination of odour flow from passive area sources requires knowledge of the carrier

gas flow rate introduced in the sampling device as well as the corresponding OC of the emission. Odour samples were obtained using a flux chamber (FC) provided by Scentroid (IDES Canada Inc., Whitchurch-Stouffville, ON, Canada). The FC sampling methodology, which is a USEPA recommended methodology [23], has been widely reported and discussed [24–26], and it is preferred because it provides more consistent, less variable odour results [27].

During sampling campaigns, a semi-spherical stainless steel FC (0.443 m of base diameter, 0.154 m² of base area and 0.045 m³ of volume) equipped with stainless steel fittings and TeflonTM sampling lines was used to obtain gaseous samples. Pure nitrogen was introduced inside the FC at a flow rate of 4 L·min⁻¹ during 30 minutes, which is equivalent to 3 FC residence times, to reach constant concentrations inside the chamber before sampling [24]. A Nalophan[®] bag was placed inside a hermetic sampling drum where, by means of a vacuum pump, the gaseous sample was directed from the FC into the bag to avoid cross-contamination [5]. Figure 1 shows a schematic of the sampling train used to obtain the gaseous samples.

To evaluate the odour emission of both biological treatment strategies (4-d WRT and 14-d WRT), 46 gaseous samples were obtained for OC analysis. For each treatment strategy, 23 different samples were obtained. Five gaseous samples were taken at different points along the first stage of the composting process in both dynamic windrows, representing a specific age of the material inside the windrows (P0 for the initial RS – VF mixture; P1: 0.8 and 2.8 days for the 4-d WRT and 14-d WRT dynamic windrows respectively; P2: 1.6 and 5.6 days respectively; P3: 2.4 and 8.4 days respectively; P4: 3.2 and 11.2 days respectively). Additionally, 18 different samples were taken from the surface of each curing pile during three consecutive days –six samples per day–,

coincident with the day before, at the moment of and the day after the turning of the curing pile (Figure 1S of Supplementary Information).

The OC analysis of each sample was conducted by means of a Scentroid SM-100 portable field olfactometer (IDES Canada Inc.) [28]. Immediately after sampling, all odorous samples were analysed two times by the same panellist in a separated, closed and well-ventilated room, which was maintained at 22°C, leaving 10 minutes between analyses.

2.3.2. Calculation of the OER

To evaluate the Odour Emission Rate (OER) of an open-air process, first the calculation of the Specific Odour Emission Rate (SOER) is required (Eq. 1) [5].

$$SOER = \frac{OC \cdot F_{N_2}}{A_{FC}} \quad \text{Eq. (1)}$$

where SOER is the specific odour emission rate ($\text{ou} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$); OC is the odour concentration ($\text{ou} \cdot \text{m}^{-3}$); F_{N_2} is the nitrogen flow rate introduced into the FC ($\text{m}^3 \cdot \text{s}^{-1}$); A_{FC} is the surface covered by the FC (m^2).

For each process stage of each treatment strategy, an average SOER was calculated with all the individual SOER obtained from each sampling point. Then, the OER for each process stage was calculated by multiplying the average SOER by the total emitting surface—the dynamic windrow surface or the curing pile surface, respectively—according to Eq. 2 [5].

$$OER = SOER \cdot A_S \quad \text{Eq. (2)}$$

where OER is the odour emission rate ($\text{ou} \cdot \text{s}^{-1}$); SOER is the average specific odour emission rate ($\text{ou} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$); A_S is the total area of the emitting surface (m^2).

2.3.3. Estimation of the OEF

OEFs are developed with the objective of obtaining a simple method for estimating the overall OER of an industrial site based on a specific activity index, which should represent the process evaluated [6,29]. Due to the reported proportionality between plant capacity and odour emissions, OEFs were related to the plant capacity ($\text{Mg RS} - \text{VF} \cdot \text{d}^{-1}$) of each treatment strategy [7,30] and therefore expressed as $\text{ou} \cdot \text{Mg}^{-1} \text{RS} - \text{VF}$, according to Eq. 3. OEFs were evaluated separately for each stage of both treatment strategies by dividing the OER of each stage by the related plant capacity.

$$OEF = \frac{OER}{I} \quad \text{Eq. (3)}$$

where OEF is the odour emission factor ($\text{ou} \cdot \text{Mg}^{-1} \text{RS} - \text{VF}$); OER is the odour emission rate ($\text{ou} \cdot \text{d}^{-1}$); I is the plant capacity as specific activity index ($\text{Mg RS} - \text{VF} \cdot \text{d}^{-1}$).

2.4. VOCs characterisation

2.4.1. VOCs sampling

34 gaseous samples –17 samples for each treatment strategy– were obtained from different sampling points and moments of the biological treatment in order to characterise the VOCs emitted by the entire treatment process. The same sampling strategy as for the odour sampling was used in the dynamic windrows (section 2.3.1). Then, for each treatment strategy, a total of 12 samples were taken from the surface of each curing pile during three consecutive days –four samples per day–, coincident with the day before, at the moment of and the day after the turning of the curing pile (Figure 1S, Supplementary Information).

Direct sampling was performed by means of adsorption tubes (Markes International, Inc., Gold River, CA, USA) coupled to a PCXR4 sampling pump (SKC Inc., Eighty Four,

PA, USA) to obtain 1.8 L samples, similarly to the methodology explained in [31]. Adsorption tubes packed with two different hydrophobic adsorbents (Tenax® TA and Carbograph™ 1TD, Markes International) were used to maximise the retention of target VOCs. Once the sample was obtained, thermal desorption (TD) tubes were sealed with Swagelock end caps fitted with PTFE ferrules and stored at 4°C until the moment of analysis. Samples were analysed 6 days after sampling due to location issues but before the maximum recommended time (7 days) to preserve the stability of VOCs in the sorbent tubes [32].

2.4.2. TD-GC/MS detection

A liquid VOCs custom mix solution was prepared with 35 standard compounds in methanol (Sigma-Aldrich Química SL, Madrid, Spain), considered as representative of VOCs emissions from composting processes. Then, seven dilutions were prepared for calibration. TD was performed with a UNITY-2 thermal desorber (Markes International, Inc.). Sorbent tubes were heated at 290°C for 8 minutes while flowing high purity He at a flow rate of 50 mL·min⁻¹ to desorb the VOCs onto a cold trap at -10°C. Then, the cold trap was heated up to 305°C at a 40°C·s⁻¹ rate for 5 minutes to desorb the VOCs trapped and to inject them into the chromatographic column. A 1:10 split ratio was used during all the process to prevent column overloading. The gas was then directed to the chromatographic column through a transfer line heated at 250°C to prevent condensation. Similarly to previous studies [3,33,34], VOCs analysis was performed using an Agilent 7820 Gas Chromatograph (GC) coupled to an Agilent 5975 Mass Spectrometer (MS) (Agilent Technologies, Inc., Santa Clara, CA, USA). The chromatographic column used for the analysis was a DB-624 capillary column (60 m x 0.25 mm x 1.4 µm, Agilent Technologies, Inc.), with a He gas flow rate of 1 mL·min⁻¹ as the carrier gas. The temperature program for the GC was an initial isothermal stage at 50°C during 2 minutes,

then a first temperature ramp to 170°C at a 3°C·min⁻¹ rate, followed by a second ramp up to 280°C at a 8°C·min⁻¹ rate. Finally, the MS acquired data in scan mode with m/z interval ranging from 35 to 355 amu. Compounds were identified by matching the mass spectra with the Wiley275 mass spectrum library available in the GC-MS system.

2.4.3. Potential odour contributors

As indicator of the contribution to odour of a quantified compound present in a gaseous sample containing a mixture of odorant compounds, the OAV can be calculated as the ratio of the quantified compound concentration and its ODT [10,12,35,36]. Then, the higher the ratio, the more likely an odorant contributes to perceived nuisance odours. OAV is calculated using Eq. 4 [12].

$$OAV_i = \frac{C_i}{ODT_i} \quad \text{Eq. (4)}$$

where OAV_i is the odour activity value of the target compound (dimensionless); C_i is the concentration of the target compound (ppb_v); ODT_i is the odour detection threshold of the target compound (ppb_v).

3. Results

3.1. Biological stability

Table 2 shows the biological stabilization in terms of DRI values obtained during the operation of both treatment strategies. Although equivalent information was reported and discussed previously [18], it was necessary to be reported herein to relate the odour and specific VOCs emissions to the waste stability evolution.

Concisely, with the results presented in Table 2 it can be observed that by increasing the WRT of the dynamic windrows from 4 to 14 days, the composting process experiments a more optimum evolution in terms of biological stability achieved at the end

of the first degradation phase. Besides, during the maturation phase, gaseous emissions will decrease when using a WRT of 14 days due to the higher biological stability achieved, as it will be discussed below. One of the advantages of working at full-scale is the fact that both active composting and maturation stages can be studied separately in terms of VOCs characterization and odour emission and its progressively stabilization during composting [3].

3.2. Odour concentration

Odour emissions were analysed during both the dynamic windrow composting and the curing phase of the two treatment strategies. Figure 2 shows the OCs registered in each one of the samples obtained from the dynamic windrows operating at 4 and 14 days WRT, respectively. It was observed that for both strategies, OC as well as the dispersion of its measurements tended to decrease as the process went on and the material stability increased. However, there was a difference of 36% between the maximum OC for the 4-d WRT process ($5091 \text{ ou}\cdot\text{m}^{-3}$) and the 14-d WRT process ($3274 \text{ ou}\cdot\text{m}^{-3}$). Moreover, a 78.4% reduction was observed between the OC of the samples obtained from the output materials of the 4-d WRT dynamic windrow and those from the 14-d WRT dynamic windrow ($2573 \text{ ou}\cdot\text{m}^{-3}$ and $557 \text{ ou}\cdot\text{m}^{-3}$, respectively). These results are in accordance with the DRIs observed for the outlet material of the dynamic windrows of both strategies (Table 2). A lower OC was found in the gaseous emissions generated by the most biologically stable material. According to previous works [37,38], a peak of odour emission was observed during the initial time of the composting process. Then, the emission tended to decrease as the biological stability of the material increased.

Figures 3 and 4 show the odour emission maps of the curing piles of the 4-d WRT and the 14-d WRT processes, respectively, for the three sampling days. This sampling strategy was adopted in order to monitor the worst scenario in terms of odour emission

and odour impact generated by the curing piles, which should coincide with the turning of the material. Much lower OC were measured in the gaseous emissions of the 14-d WRT curing pile. Besides, it is important to notice and compare the increase of the OC measured in the 4-d WRT curing pile the day after turning the material with the OC registered in the 14-d WRT curing pile for the same day. Due to the fact that there was nearly no biological activity during the 14-d WRT curing stage, the OC emitted was near to typical ambient air OC [39]. On the contrary, the material treated by the 4-d WRT strategy was not stable at the end of the dynamic windrow stage and the biological activity continued during the curing phase, what could explain the higher OC registered during the turning of the curing pile.

3.3. OEF from odour emission data

Table 3 reports the OERs calculated for each odour source for both strategies tested. A 44.8% reduction was observed between the global OERs of the 14-d WRT with respect to that of the 4-d WRT. Specially, the most significant reduction was observed in the curing phase OERs, where the 14-d WRT OER was a 90% lower than the 4-d WRT OER. In general, as observed with the OCs measured, the OERs decreased in accordance with the biological stabilisation of the material throughout the process. Accordingly, the 14-d WRT treatment strategy showed the lower OERs. The OER provides valuable information about the instantaneous odour emission of each emission source, what can be used to assess the impact of each treatment strategy in a surrounding area in a punctual moment depending on the atmospheric conditions through dispersion modelling [40]. Results showed that the 14-d WRT treatment strategy had less odour impact over a surrounding area than the 4-d WRT treatment strategy for a specific moment and atmospheric conditions. Although just two WRTs were assessed in the study, these results

are a valuable starting point for SS composting plant managers to choose a composting strategy to mitigate impact of odour emissions.

Table 4 shows the estimated OEFs of each phase of both treatment strategies and the global OEFs related to each treatment strategy. In contrast with the OERs, the estimated OEFs of the dynamic windrow stage tended to increase by increasing the WRT from 4 to 14 days due to the different RS – VF mass treated per day between both treatment strategies. On the other hand, although a large OEF reduction was observed during the curing stage when increasing the WRT from 4 to 14 days, an increment of 35% was observed due to the WRT increase from 4 to 14 days when comparing the global OEFs estimated for both treatment strategies. These factors are a good tool to perform a general estimation of the OU emitted per Mg of RS – VF treated in the studied conditions and to characterize the odour emissions related to a treatment process. However, they will also depend on different factors such as plant capacity, the characteristics of the waste to be treated, the bulking agent used, the C/N ratio of the mixture, the ambient temperature, etc. Moreover, to the authors' knowledge, this is the first work where OEFs are estimated for a full-scale SS composting plant, information that can be used as a fair value to estimate the odour impact derived from a new facility of similar characteristics.

To put the obtained results into context, the calculated OEFs have been compared with other reported OEFs from different wastes and/or treatments. Zarra et al. [22] reported an OEF of $4.15 \cdot 10^6$ ou·Mg⁻¹ for the receiving unit of an anaerobic-aerobic integrated treatment plant of the organic fraction of municipal solid waste. Sironi et al. [7,41] studied the odorous emissions of 40 mechanical-biological treatment plants treating municipal solid wastes (MSW) and reported an average OEF of $1.01 \cdot 10^8$ ou·Mg⁻¹ for this kind of treatment facilities. Despite these OEFs are not fully comparable with OEFs obtained for the SS composting process under study, they represent a good approach because no

references describing OEFs of full-scale SS composting plants have been found in literature. These novel results can be a helpful tool for plant managers or researchers to estimate odour emissions and to predict odour impact from new composting facilities, and highlight the importance of waste stabilization profiles in such emissions.

3.4. VOC characterization

Characterization was made by comparing the VOCs families detected in each sample as well as by quantifying the concentration of 22 out of the 35 detected compounds. Figure 5 shows the distribution of the different VOC families in the 4 and the 14-d WRT strategies, respectively, while in Tables 1S and 2S of Supplementary Information all quantified VOCs are presented with their ODT.

As can be observed in Figures 5a and 5c, the main VOCs found in the dynamic windrows were terpenes –with α -pinene as predominant–, ketones –mainly 2-butanone and 3-pentanone–, sulphur compounds –dimethyl sulphide (DMS) and dimethyl disulphide (DMDS)– and carboxylic acids –mainly acetic and butyric acids–. Generally, organosulphur compounds were mainly formed and emitted during the first stage of both treatment strategies and are common compounds found in gaseous emissions generated during SS composting [42]. The emission of terpenes such as α -pinene and limonene was related to the VF used as bulking agent for the composting process and, particularly in this study, due to the high RS – VF v/v ratio used. It is also interesting to notice some differences between both treatment strategies during the first stage. Particularly, the emission of carboxylic acids due to the WRT variation was predominant in the initial part of the 14-d WRT process. In contrast, carboxylic acids continuously appeared along the gaseous emissions generated in the 4-d WRT dynamic windrow.

Figures 5b and 5d show the distribution of VOCs found in the gaseous samples obtained from the curing piles of both treatment strategies. It is important to notice that in the 4-d WRT curing pile the most abundant VOCs were ketones and terpenes, being over a 50% abundance in each monitoring event. By contrast, in the 14-d WRT curing pile a higher variability was observed with the appearance of siloxanes (which can appear in sewage sludge gases due to the decomposition of silicoorganic compounds or by slow decomposition of the chromatographic column), aldehydes and carboxylic acids just after turning the material. Again, this is the first study where specific characterisation of the VOCs emissions from a maturation stage of a full-scale SS composting process has been assessed. Nonetheless, [34] presented an inventory with the most relevant VOCs in the emissions from the maturation stage of the composting of MSW in a treatment facility. Some similarities with the present study were found such as a high variety of VOCs and the predominance of alcohols, terpenes and ketones.

More than half of the compounds quantified in some of the gaseous samples exceeded their ODT, and some were found to be smell-relevant compounds as well as responsible for the typical odour emitted during SS treatment. Table 5 shows the maximum OAVs for all the compounds with an OAV above 1, quantified in at least one gaseous sample. Isovaleraldehyde, butanoic acid, DMS, DMDS and α -pinene were present in all gaseous emissions generated during both treatment strategies except in the 14-d WRT curing pile gaseous emissions, being the maximum overall odour contributors in the gaseous emissions monitored. Moreover, some compounds such as indole, skatole or phenol were only found in the gaseous emissions generated in the first stage of both biological treatment strategies. In general, the odour contributors found in this work corresponded to compounds typically listed in similar studies [9,36,42,43].

To correlate the OAV and the OC, some authors have used the numerical addition of the OAV of all individual components quantified in the emissions (OAV_{SUM}). Blazy et al. [12] found a good linear correlation between the log transformation of the variables OAV_{SUM} and OC ($R^2 = 0.87$) during pig slaughterhouse sludge composting and storage at lab-scale. In contrast, Parker et al. and Wenjing et al. [16,44] were unable to strongly correlate the OC with the OAV in a swine farm ($0.30 < R^2 < 0.52$) or in a sanitary landfill ($R^2 = 0.39$), respectively. In the case under study, Figure 6 shows the linear correlation obtained with the gaseous samples grabbed during all the experimental period for both treatment strategies.

The relevance of the correlation was evaluated based on the percentage by which OAV_{SUM} fell within the 95% interval of confidence for the corresponding measured OC. The linear correlation obtained did not present a strong linear association ($R^2 = 0.60$). A 57% of the OAV_{SUM} estimated in this study fell within the 95% confidence interval of the OC measurement. These results showed that OAV_{SUM} is not a good predictor of OC for this kind of complex odour mixtures derived from SS composting, probably because the approach is not robust enough. Main reasons could include the type of waste under study, the existence of synergistic and masking effects between emitted compounds, the presence of some VOCs not quantified in this research or the over-underestimation of OCs.

4. Conclusions

Results obtained indicated that odours and VOCs emitted depend on the composting time. By increasing the WRT from 4 to 14 days, lower OCs were measured in both the dynamic windrow composting and the curing stages. However, due to the increase of the WRT and thereby the reduction of the material treated per time unit, the global OEF increased by 35%.

Terpenes, organosulphur compounds, ketones and carboxylic acids were found to be the most abundant VOCs present in the gaseous emissions, being isovaleraldehyde, butyric acid, DMS, DMDS and α -pinene the major odour contributors. A weak correlation was found between OAV_{SUM} and OC ($R^2 = 0.60$), which indicate that in this case OAV_{SUM} is not a good predictor of OC.

In conclusion, the study conducted in a full-scale SS composting plant presents valuable information about the relationship between composting time and odour emissions of this kind of processes that contributes to fill the knowledge gap in industrial facilities related to odour emission and odour impact.

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Legends to Figures

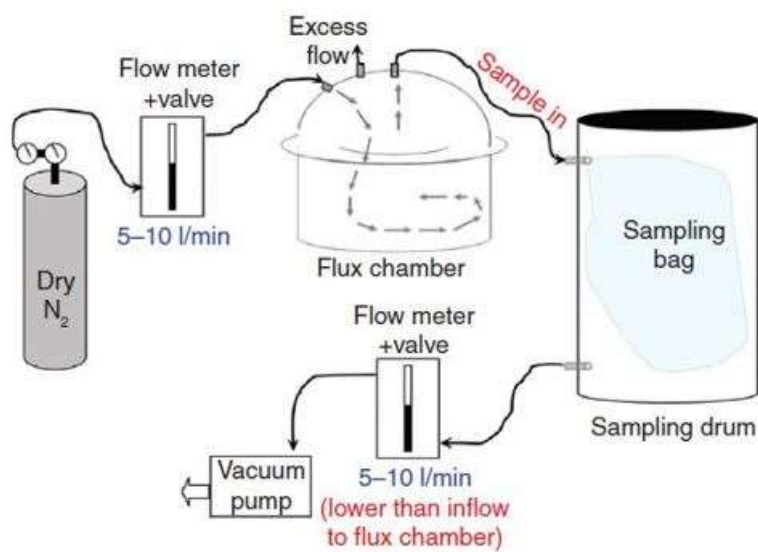


Figure 1. Odour sampling by means of the lung method from an area source using a flux chamber.

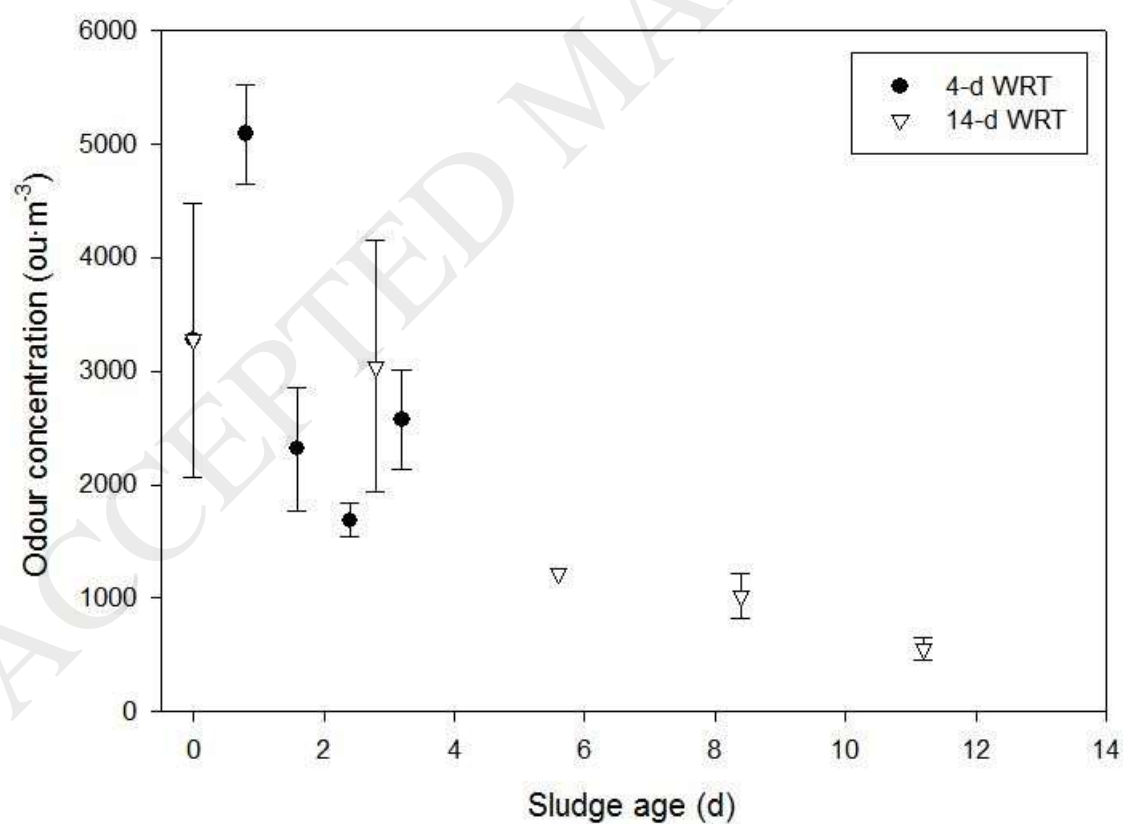


Figure 2. Odour concentration profiles obtained in the dynamic windrow composting stage, in $\text{ou}\cdot\text{m}^{-3}$ (black dots: odour concentration in the 4-d WRT dynamic windrow samples; white triangles: odour concentration in the 14-d WRT dynamic windrow samples).

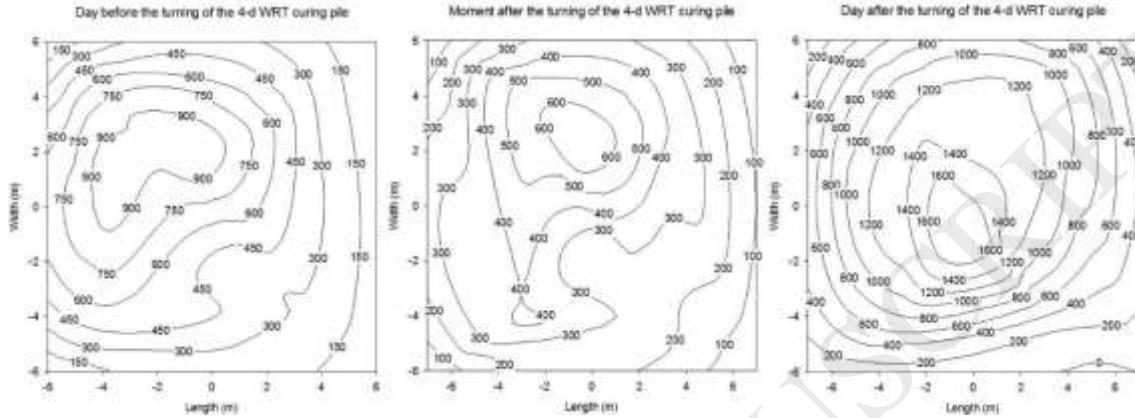


Figure 3. Odour concentration maps of the 4-d WRT curing pile for the three consecutive sampling days (iso-emission curves in $\text{ou}\cdot\text{m}^{-3}$).

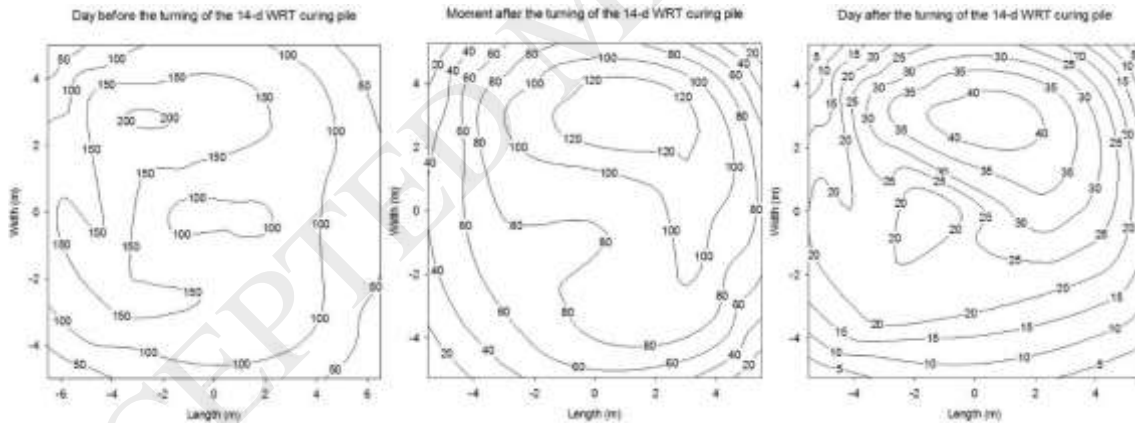


Figure 4. Odour concentration maps of the 14-d WRT curing pile for the three consecutive sampling days (iso-emission curves in $\text{ou}\cdot\text{m}^{-3}$).

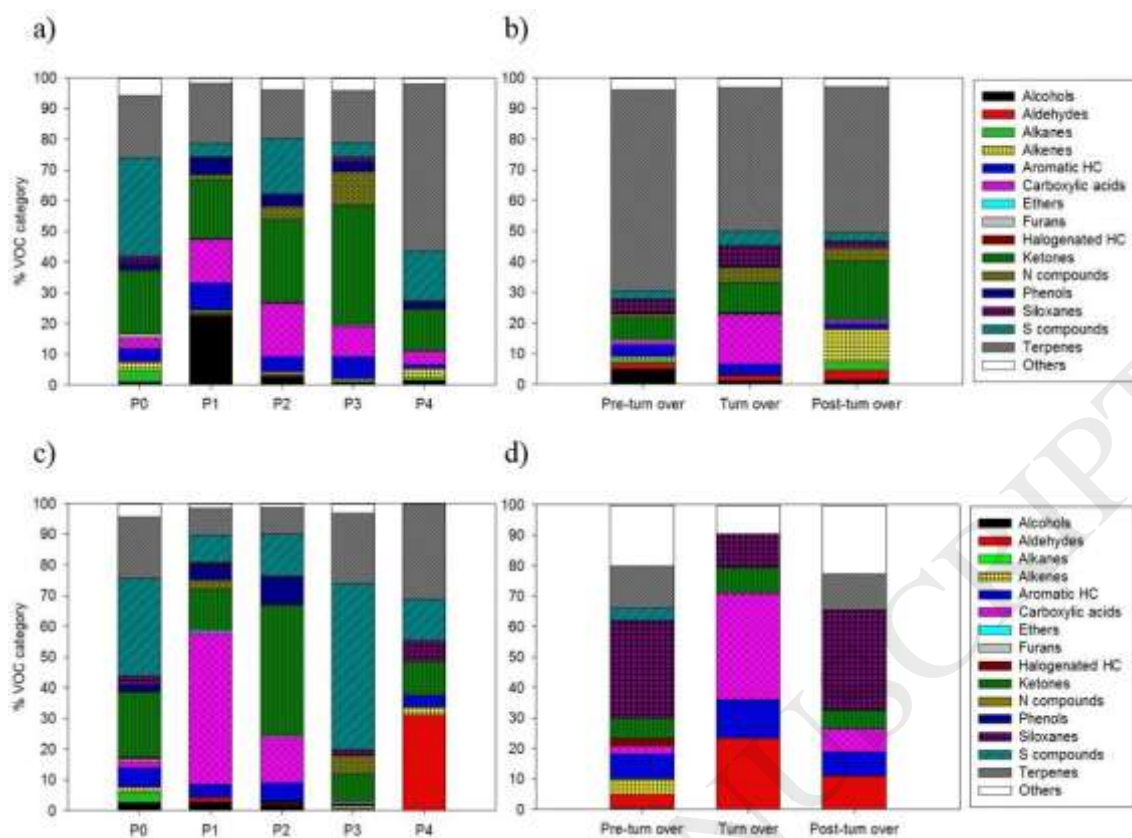


Figure 5. Distribution of the different VOC families found in each sample, expressed in % of abundance respect the whole sample, in (a) the 4-d WRT dynamic windrow, (b) the 4-d WRT curing pile, (c) the 14-d WRT dynamic windrow and (d) the 14-d WRT curing pile.

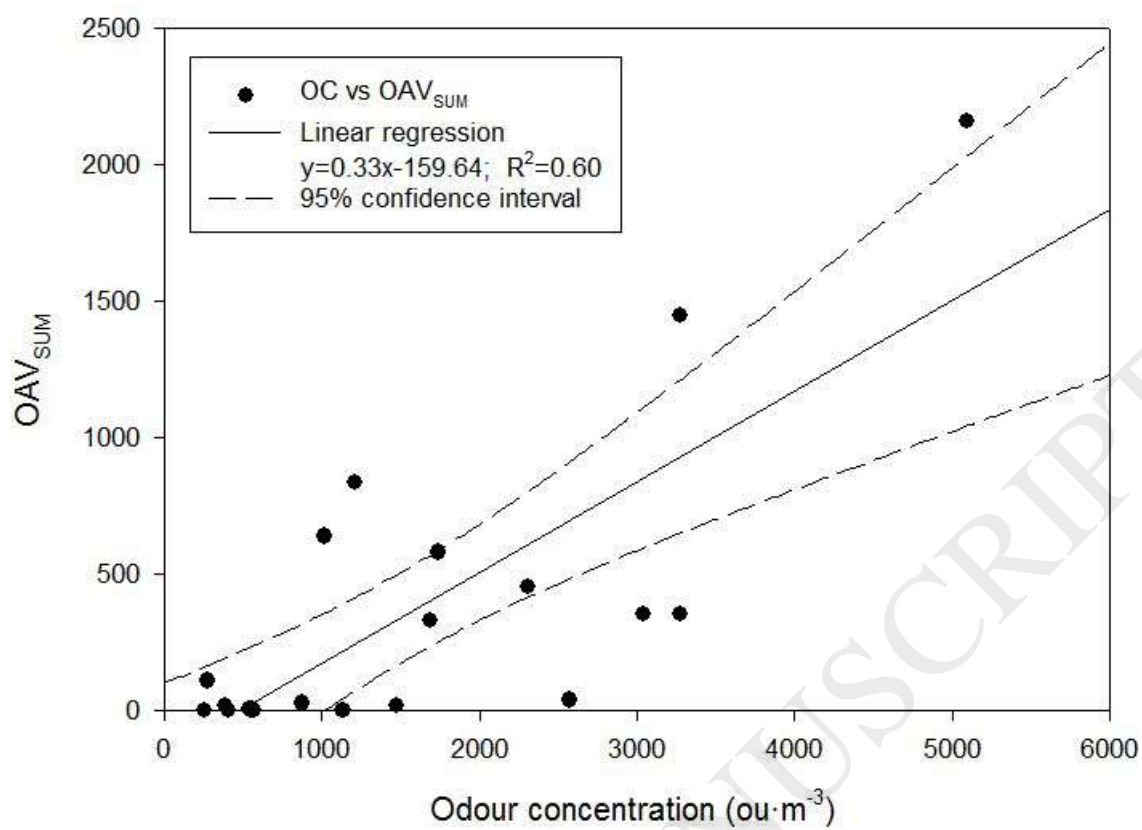


Figure 6. OAV_{SUM} vs odour concentration linear correlation for the gaseous samples obtained during the experimental period.

Tables

Table 1. Physical-chemical properties of the raw sludge (RS), the bulking agent (VF) and the RS – VF mixture.

Physicochemical properties	RS	VF	RS – VF mixture
Moisture (%)	86.5 ± 0.5	15.5 ± 0.4	60.4 ± 2.3
Organic matter (%)	81.8 ± 3.7	85.3 ± 2.1	77.3 ± 1.5
C/N ratio	6.8 ± 0.3	50	28.9 ± 0.5
pH	6.7 ± 0.2	8.4	7.2 ± 0.3
Electrical conductivity (mS/cm)	2.4 ± 0.0	1.0	2.9 ± 0.1

Table 2. Biological stability evolution of the material along both treatment processes in terms of DRI.

Dynamic Respiration Index (DRI, g O ₂ ·kg ⁻¹ OM·h ⁻¹)				
Treatment strategy	RS – VF mixture	Dynamic windrows outlet material	15 days of curing	Final material before screening
4-d WRT	2.2 ± 0.3	1.1 ± 0.1	0.7 ± 0.0	0.5 ± 0.0
14-d WRT	2.2 ± 0.3	0.6 ± 0.0	0.4 ± 0.1	< 0.1

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Table 3. Odour emission rates (OER) calculated for each treatment phase (4 dynamic windrows and curing) of both treatment strategies under study (4 and 14 days WRT).

Treatment phase	Odour Emission Rate (ou·min ⁻¹)	
	4-d WRT	14-d WRT
Dynamic windrows	2.47E+04	1.48E+04
Curing pile	2.60E+03	2.60E+02
Global	2.73E+04	1.51E+04

Table 4. Odour emission factors (OEF) estimated for each treatment phase (4 dynamic windrows and curing) of both treatment strategies under study (4 and 14 days WRT).

Treatment phase	Odour Emission Factor ($\text{ou} \cdot \text{Mg}^{-1} \text{RS} - \text{VF}$)	
	4-d WRT	14-d WRT
Dynamic windrow	2.87E+06	5.87E+06
Curing pile	1.55E+06	9.75E+04
Global	4.42E+06	5.97E+06

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Table 5. Maximum Odour Activity Value (OAV) of the major odour contributors quantified in the gaseous samples obtained from both treatment strategies monitoring.

Family	Compound	4-d WRT strategy		14-d WRT strategy	
		Dynamic windrow	Curing pile	Dynamic windrow	Curing pile
Aldehydes	Isovaleraldehyde	371.1	542.3	56.0	–
	Octanal	623.0	–	–	–
Alkanes	Indole	16.5	–	9.7	–
	Skatole	256.7	–	716.7	–
Carboxylic acids	Butanoic acid	768.6	109.3	471.6	–
Phenols	Phenol	27.2	–	28.6	–
Sulphur compounds	DMS	182.6	1.1	382.8	–
	DMDS	179.6	32.4	632.2	–
Terpenes	α -pinene	5.1	4.9	4.1	–