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**A systematic study of the gaseous emissions from biosolids composting: raw sludge  
versus anaerobically digested sludge**

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**Abstract**

Volatile organic compound (VOC) and ammonia, that contribute to odor pollution, and methane and nitrous oxide, with an important greenhouse effect, are compounds present in gaseous emission from waste treatment installations, including composting plants. In this work, gaseous emissions from the composting of raw (RS) and anaerobically digested sludge (ADS) have been investigated and compared at pilot scale aiming to provide emission factors and to identify the different VOC families present. CH<sub>4</sub> and N<sub>2</sub>O emissions were higher in ADS composting (0.73 and 0.55 kg Mg<sup>-1</sup> sludge, respectively) than in RS composting (0.01 kg Mg<sup>-1</sup> sludge for both CH<sub>4</sub> and N<sub>2</sub>O). NH<sub>3</sub> and VOCs emitted were higher during the RS composting process (19.37 and 0.21 kg Mg<sup>-1</sup> sludge, respectively) than in ADS composting (0.16 and 0.04 kg Mg<sup>-1</sup> sludge). Significant differences were found in the VOC compositions emitted in ADS and RS composting, being more diverse in RS than ADS composting.

**Keywords:** Composting; Gaseous emissions; Greenhouse gases; Sludge; VOC.

## 1. Introduction

During the mechanical, biological and chemical treatment of wastewater, large amounts of sludge are generated. Sludge is rich in organic matter, nitrogen, phosphorus, calcium, magnesium, sulfur and other microelements, which makes wastewater sludge a useful raw material to be composted. In addition to these elements, sludge can also contain toxic compounds (heavy metals, pesticides) and pathogenic organisms (bacteria, eggs of parasites) (Kosobucki et al., 2000).

Composting is a suitable treatment for sewage sludge from municipal wastewater treatment plants (Pagans et al., 2006a; Gea et al., 2007). Due to its high moisture content, sludge cannot be composted alone; sludge needs to be mixed with a dry material that acts as a bulking agent, absorbing the excess moisture and providing the composting mass with an appropriate degree of porosity for aeration (Sánchez-Monedero et al., 2001; Tremier et al., 2005). Sludge characteristics depend on the origin of the water treated, as well as on the treatment followed (especially if the sludge is raw or anaerobically digested).

Sustainable management of resources, waste minimization and valorization of waste have been the common objectives of plans, directives and regulations in recent decades. In recent years, there has been a proliferation, either in Spain or Europe, of new waste treatment plants as a result of the Directive 1999/31/EC on the limitation of

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VOC: Volatile Organic Compound; RS: Raw Sludge; ADS: Anaerobically Digested Sludge; OUR: Oxygen Uptake Rate; DRI: Dynamic Respiration Index; GC-MS: Gas Chromatography-Mass Spectrometry; GHG: Greenhouse Gas; SPME: Solid Phase MicroExtraction; DVB: Divinylbenzene; PDMS: Polydimethylsiloxane; IS: Internal Standard; DOM: Dissolved Organic Matter

landfill as final destination for organic wastes, especially biological treatment plants (Commission of the European Community, 2008). However, the social rejection that this type of facility provokes from citizens is well-known. In many cases, the problem regarding organic waste treatment is caused by the inconvenience of the unpleasant odors released during the biological treatment.

These odors are associated mainly with the emissions of volatile organic compounds (VOCs) (e.g., terpenes, alcohols, ketones, sulfur-containing compounds and amines) and ammonia (Goldstein et al., 2002; Komilis et al., 2004). However, the discomfort caused by these emissions is often magnified by a lack of reliable data from the existing plants, which could provide objectivity and scientific rigor to this topic. In addition to VOCs, other compounds emitted during the composting process are CH<sub>4</sub> and N<sub>2</sub>O, which are considered greenhouse gases (GHGs). Although composting or anaerobic digestion are generally considered environmentally beneficial, they can increase or decrease their benefits depending on the associated emissions (Colón et al., 2012).

Eitzer (1995) and Staley et al. (2006) have performed studies that are particularly relevant for the characterization of emissions from organic waste biological treatments. Eitzer (1995) exhaustively determined the volatile organic compounds present in the emissions from municipal waste composting plants and their relationship to the process. Staley et al. (2006) studied the emission of VOCs from aerobic and anaerobic processes. This study emphasized the contribution to the overall emissions of the stripping phenomena caused by the forced aeration in the aerobic processes. Terpenes and ketones were determined as the most abundant compounds. On the pilot scale, Pagans et al. (2006b) determined the influence of the type of waste in the total emission of VOCs, comparing certain urban and industrial wastes. Komilis et al. (2004)

determined the main VOCs emitted in yard waste composting (mainly terpenes, alkylbenzenes, ketones and alkanes), food waste (sulfides, acids and alcohols), and the process stage where the emissions were higher (thermophilic stage). Goldstein (2002) suggested terpenes, alcohols, aldehydes, volatile fatty acids, ammonia, and various sulfur-containing compounds as being mainly responsible for the odor in composting plants.

$\text{NH}_3$  emissions are related directly to the content of ammonium, urea and other organic nitrogen in the biomass.  $\text{NH}_3$  emissions depend on temperature, aeration and the pH value of the composting material (Hellebrand and Kalk, 2001).

$\text{N}_2\text{O}$  is emitted during biological nitrogen removal through nitrification and subsequent denitrification (He et al., 2001, Sánchez-Monedero et al., 2001)). In both processes, nitrous oxide is formed, but a detailed understanding of the factors that produce nitrous oxide emissions is currently missing. Because nitrous oxide has a greenhouse gas potential approximately 300 times greater than that of carbon dioxide (IPCC, 2007), nitrous oxide can contribute strongly to the carbon footprint of the composting plant.

$\text{CH}_4$  is formed as a byproduct of microbial respiration in severely anaerobic environments when carbon is the only electron acceptor available. Carbon is used as an electron acceptor when other more energetically favorable electron acceptors, including oxygen, nitrogen, iron, manganese and sulfur, have been exhausted (Brown et al., 2008).

The objective of this work was to study and update the current knowledge of the VOC,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{NH}_3$  emissions during the composting process for sludge produced in wastewater treatment plants. To determine these emissions, the two primary types of sludge currently produced in these plants, anaerobically digested sludge and raw sludge,

have been composted on the pilot scale with continuous aeration based on an oxygen uptake rate (OUR) maximization control. Emission factors (amount of compound emitted per amount of waste treated) are provided for the studied compounds. Emission factors permit the comparison among treatment processes with different inputs and scales. Special attention has been directed to VOC emissions, identifying and quantifying the main compounds emitted.

## **2. Materials and Methods**

### *2.1 Waste composted*

The wastes used in these experiments were raw sludge (RS) from a wastewater treatment plant located in Manresa (Barcelona, Spain) and anaerobically digested sludge (ADS) from a wastewater treatment plant located in Sabadell (Barcelona, Spain). Both plants serve a large population (more than 100,000 inhabitants) and include nitrification-denitrification and anaerobic digestion of sludge. In both cases, sludge samples were taken from the wastewater treatment plant after the dewatering step (centrifugation). Sludge was mixed in the laboratory with wood chips as a bulking agent with a volumetric ratio of 1:3. Air-filled porosity was determined using an air pycnometer according to previous studies (specific details about the methodology can be found in Ruggieri et al., 2009). The results for air-filled porosity were 41.8 % and 47.8 % in RS and ADS experiments, respectively. These values are within the range recommended for an adequate development of the composting process of sludge (Ruggieri et al., 2009). Experiments were performed on the pilot scale (50 L reactors) and in duplicate. After collection and mixing, a homogeneous sample from both sludge samples and each mixture was stored at -18 °C to be used for waste characterization.

The main characterization parameters of the initial sludge collected, the composted mixture and the final products obtained from each experiment are presented in Table 1.

## *2.2 Composting pilot plant*

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

Gas samples were collected in 1-L Tedlar® bags for VOCs, N<sub>2</sub>O, CH<sub>4</sub> and NH<sub>3</sub> determination. Also a 250-mL glass gas collector was used for samples taken for VOC composition determination.

The data acquisition and control system consisted of an acquisition chassis (cDAQ-9172, National Instruments, USA) connected to a PC and using LabView 8.6 software (National Instruments, USA). Temperature (PT100 sensor, Desin Instruments, Barcelona, Spain), exhaust gas oxygen concentration (Xgard, Crown, UK) and inlet airflow were monitored during the experimental trials. The temperature probe and oxygen sensor were connected to the data acquisition chassis. The input and output electrical signals of the flow meter were connected directly to the PC through an RS-232 serial port. All data were recorded and presented in a graph or in the program interface from the OUR control.

This control strategy has been presented in Puyuelo et al. (2010). The main objective of this controller is to obtain an automatic airflow regulation to maximize the biological activity in the reactor measured as OUR. OUR control permits the optimization of energy consumption during the process while achieving a high degree

of stability in the final product. Briefly, the controller works in cycles of 1 hour. The designed OUR control loop compares the variations in the OUR measurements reached among the successive cycles according to the airflow applied. After completing a cycle, the oxygen level is revised to avoid percentages below 5 % (v/v). If the level is below this limit, airflow will be increased by 50 %. If an adequate oxygen level has been measured, the next step will be the control loop based on the OUR measurement and the applied flow comparison between two consecutive cycles. For both parameters, three situations are possible, i.e., the system determines if the current value is lower than, higher than or equal to the previous value. Different absolute thresholds were established to define the superior and inferior limits in which the variation of OUR and airflow can be considered negligible. The limit to detect OUR variation was defined as 0.5 % of the maximum OUR achieved in previous experiments in the reactor (approximately  $15 \text{ g O}_2 \text{ h}^{-1}$ ). The range considered for the airflow measurements was  $0.05 \text{ L min}^{-1}$ . Considering the airflow measurements, the controller checks the OUR variation. Next, the controller determines if the OUR variation obtained is linked to an increase, decrease or a constant airflow. From this algorithm, the system regulates the necessary inlet airflow to optimize the OUR achieved during the whole process and ensures the prevalence of full aerobic conditions.

### *2.3. Stability degree*

On the basis of the methodology proposed by Adani et al. (2006) to assess the degree of biological stability, the dynamic respiration index (DRI) was measured using a respirometer (Ponsá et al., 2010). Briefly, the determination consists of placing 150 g of sample in a 500-mL Erlenmeyer flask and incubating the sample in a water bath at 37 °C. A constant airflow was supplied through the sample, and the oxygen content in the

outgoing gases was measured. From this assay, DRI was determined as the maximum average value of respiration activity measured during 24 hours, expressed in  $\text{mg O}_2 \text{ g}^{-1} \text{ OM h}^{-1}$ .

#### *2.4. Determination of gaseous emissions*

VOC,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  analysis was performed by means of gas chromatography (Agilent Technologies 6890N Network GC system, Madrid, Spain) as explained in Colón et al. (2012).

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

#### *2.5. GC-MS detection*

A sample from each process was taken daily in a 250 mL glass gas collector. VOC characterization was performed using air samples analyzed by SPME (Solid Phase Micro Extraction)/GC-MS as previously reported in different publications (Davoli et al., 2003; d'Imporzano et al., 2008; Orzi et al., 2010).

A manual SPME device with divinylbenzene (DVB)/Carboxen/polydimethylsiloxane (PDMS) 50–30  $\mu\text{m}$  fiber from Supelco (Bellefonte, PA, USA) was used. The compounds were adsorbed from the air samples

by exposing the fiber (preconditioned for 1 h at 270 °C, as suggested by the supplier) to the sample in the glass gas collector for 30 min at room temperature. A solution of deuterated *p*-xylene in methanol was used as internal standard (IS).

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

Deuterated *p*-xylene has been used to determine the fiber and GC-MS response factors for 15 typical compounds emitted in composting processes according to the literature (Rosenfeld and Suffet, 2004; Scaglia et al., 2011; Suffet et al., 2009). These 15 compounds have been diluted in methanol at the same concentration as deuterated *p*-xylene. This solution (10  $\mu\text{L}$ ) has been injected into the glass gas collector with 10  $\mu\text{L}$  of deuterated *p*-xylene in methanol solution. The fiber had been exposed for 30 minutes to the resulting solution and injected into the GC-MS using the same method as described above. The area obtained for each compound has been compared to deuterated *p*-xylene to determine each response factor. The aim of determining these response factors is to gain the ability to make a more confident quantitative analysis.

Compounds were identified by comparing their mass spectra with the mass spectra contained in the NIST (USA) 98 library. A semi-quantitative analysis for all the identified compounds was performed by direct comparison with the internal standard. Quantitative analysis was performed for *m*-xylene, *n*-decane, alpha-pinene, beta-pinene, limonene, toluene, dimethyl disulfide, hexanal, styrene, cyclohexanone, nonanal, decanal, eucalyptol, pyridine and 2-pentanone.

### **3. Results and Discussion**

#### *3.1. Process evolution*

For each waste composted, temperature, airflow, oxygen concentration and OUR profiles were determined. Figure 1 shows profiles of all these parameters for one RS composting process (replicate RS-I, Figure 1a) and for one ADS composting process (Replicate ADS-II, Figure 1b), representing the four trials carried out.

During the composting of raw sludge, the process reached thermophilic conditions before the first day of processing with maximum values of approximately 55 °C in both replicates. After three days, the system returned to mesophilic conditions. The thermophilic peak matched with the lowest oxygen value and the highest OUR value and therefore the highest airflow. According to the temperature profile and DRI values of the final material, in both replicates after 12 days of processing (Table 1), the composting process evolution was correct, and the final product was stabilized.

Regarding the composting of anaerobically digested sludge, the anaerobically digested sludge did not achieve thermophilic conditions, reaching maximum temperatures of approximately 40 °C. Previous studies reported that maximum temperatures and time maintained in ADS composting are lower than the same parameters for raw sludge. Maximum temperatures reached are related to the initial DRI

value of the sludge:bulking agent mixture (Gea et al., 2007). About the stability degree, as observed in Table 1, the DRI of the initial mixture was highly similar to the DRI of both final products, ADS-I and ADS-II, possibly explaining why the maximum temperature values were notably low, as the DRI mixture values in ADS were already stable values. This sludge was biologically treated by anaerobic digestion in the original wastewater treatment plant before the laboratory-scale composting process, indicating an important stabilization of the organic matter and removing the potential for a full composting process. A high proportion of bulking agent (1:3 v:v) was necessary to adjust the moisture content, contributing to a lower biological activity for the mixture. The entire process evolution is shown in Figure 1b. After 12 days, the systems returned to room temperature in both ADS replicates.

### *3.2 Gaseous emissions*

The daily evolution of VOC, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> emissions for each experiment is shown in Figure 2. In Table 2, the total emissions of VOC, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> are also summarized for each trial in terms of kg of compound emitted per Mg of sludge treated.

#### *CH<sub>4</sub> emissions*

During the composting process, the main mechanism favoring CH<sub>4</sub> emissions is related to the presence of anaerobic zones. The occurrence of low oxygen zones could be due to excessive moisture and insufficient porosity or an inappropriate aeration system strategy (Amlinger et al., 2008; Puyuelo et al., 2010). In this case, moisture (Table 1) and porosity (41.8 % for RS and 47.8 % for ADS) were within the optimal ranges (Ruggieri et al., 2009). Although the aeration system (OUR controller) supplied

sufficient airflow, the presence of a high content of rapidly biodegradable organic matter could lead to oxygen depletion, thus creating anaerobic areas in the solid matrix. This has also been observed in wastes with a high rapidly biodegradable matter content such as food wastes due to compaction effects (He et al., 2000). In the RS composting process, methane is released during the two first days (Figure 2b) at the same time that the process reaches the thermophilic stage (Figure 1a). The highest emissions were detected during the high-rate stage, as has recently been described by Ahn et al. (2011) during dairy manure composting.

Figure 2b shows that the level of methane emitted by the ADS composting process is 60 times higher than methane emitted in RS experiments. In ADS experiments, methane is emitted during the eight first days of processing, possibly as a consequence of the stripping of CH<sub>4</sub> produced in the previous anaerobic digestion process. The sludge comes from an anaerobic digestion process and contains a high quantity of anaerobic bacteria, which can be reactivated under low oxygen concentrations to produce methane.

### *N<sub>2</sub>O emissions*

Temperature, nitrogen content and aeration rate are parameters related to N<sub>2</sub>O emissions (Hellebrand and Kalk, 2001). Several authors have shown that the highest N<sub>2</sub>O emissions are detected during the initial step of the composting process (He et al., 2001), but there is no information, to the best of our knowledge, concerning the entire emissions from several types of sludge. Figure 2c shows a clear difference observed in the behavior of N<sub>2</sub>O emissions during RS and ADS composting. Emissions of RS were produced in the first days of the composting process. In ADS composting, the maximum emissions were detected on the 8<sup>th</sup> process day. Nevertheless, Fukumoto et al. (2003)

suggested that temperature inhibits mechanisms for N<sub>2</sub>O generation, and in the case of RS, maximum N<sub>2</sub>O emissions coincided with the maximum temperature. During the first days of ADS composting, low levels of N<sub>2</sub>O were emitted, but from the eighth day, high N<sub>2</sub>O concentrations were detected in accordance with the moment that ammonia emission decreases, as also suggested by Fukumoto et al. (2003). Other authors have observed that thermophilic temperatures do not favor nitrification process and N<sub>2</sub>O from denitrification is also observed in the maturation stage (He et al., 2000). More research is necessary to explore the mechanisms and dynamics of nitrification and denitrification in composting (Sánchez-Monedero et al., 2001).

#### *NH<sub>3</sub> emissions*

NH<sub>3</sub> emissions are dependent on C/N ratio, temperature, pH and airflow (Hellebrand and Kalk, 2001). In a comprehensive study about NH<sub>3</sub> emission from several highly biodegradable organic wastes, Pagans et al. (2006a) demonstrated an exponential trend of NH<sub>3</sub> emissions during the thermophilic phase of composting followed by a steady linear emission at the end of the process. This proposed mechanism was observed for all the wastes studied including raw and digested sludge. These results are in agreement with those observed in the present study (Fig 2d). In particular, RS ammonia emission profiles obtained in this study followed a similar trend in the temperature curve, i.e., the highest NH<sub>3</sub> emission appeared with the thermophilic temperatures (Figure 2d). Ammonia emissions are reported to be highest during the first several days. During ADS composting, two stages of high emissions were detected (the second and third days, and the fifth and seventh), reaching values below the values detected in RS composting. In this case, initial emissions could be due to stripping of

ammonia produced during the previous anaerobic digestion process, while the second peak could be more closely related to biological activity during the composting process.

It is important to highlight that considering the entire  $\text{NH}_3$  emissions (Table 2), RS composting produced 100-fold more emissions than the ADS process.

Regarding the final total nitrogen content, the ADS final content is higher than the RS final content (Table 1). However, He et al. (2001) did not observe a significant statistical correlation between  $\text{N}_2\text{O}$  concentration in the exhaust gas and  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and total N content in the solid waste.

#### *VOC emission*

In Figure 2a, total daily VOC emissions produced during the 12 days of experiments are shown. For RS-I and RS-II, the main generation of VOCs was detected during the first days of the experiment in the mesophilic to thermophilic transition, as described by Komilis et al. (2004). Other authors have observed similar trends and a good correlation with biological activity and VOC and odor emissions have been reported (Scaglia et al., 2011). In ADS-II, no thermophilic peak coincided with a VOC peak; the lowest total VOC emissions were measured (Table 2). In ADS-I (Figure 2a), a VOC emission peak was observed from days 4 to 7, which produced an increase in total emissions, explaining the differences shown between ADS-I and ADS-II in Table 2. Shen et al. (2012) reported VOC emissions of  $0.47 \text{ g C kg DM}^{-1}$  when composting raw sludge at industrial scale in aerated piles, observing a difference within VOCs emitted and produced ( $1.09 \text{ g C kg DM}^{-1}$ ). Values obtained in the present work are higher in both RS trials (0.97 and 0.65 for RS-I and RS-II, respectively) similar in RS-I to those reported by Shen et al. (2012) as VOCs produced. The differences in scale

(pilot vs industrial) and aeration strategy could be responsible of the differences observed among values (Pagans et al., 2006a; Colón et al., 2012).

Smet et al. (1999) reported that VOCs are emitted mainly in the first stages of the process, even in the reception of waste. VOC emissions have also been related to the presence of anoxic conditions (d'Imporzano et al., 2008). According to this study, VOCs are the products of the anoxic biodegradation that occurs in the biofilm particle when oxygen becomes a limiting factor for the aerobic oxidation of the microbial available substrate, i.e., the dissolved organic matter (DOM) (d'Imporzano et al., 2008; Hamelers, 2004). The oxygen concentration in the particle biofilm depends on the oxygen concentration in the free air space, the oxygen uptake rate to degrade the substrate and the temperature. Even if the reactor receives sufficient airflow during the entire process, VOCs will also be emitted. When a high DOM concentration exists, there is also a high OUR, which means a fast consumption of oxygen; consequently, the presence of oxygen can be limited (Hamelers, 2004). The achievement of thermophilic conditions contributes to the increase in these emissions. As Komilis et al. (2004) described, VOC emissions are related more to process heating than to biological decomposition. Figure 2a shows that the emissions are higher for the raw sludge in both replicates.

This result confirms that VOC emissions in RS composting are higher compared with ADS composting because RS composting has a higher DRI, which means a high content of biodegradable organic matter that could lead to the occurrence of anaerobic zones and achievement of higher temperatures during the process.

### *Gaseous emissions and process evolution*

The composting process can be divided into three stages, depending on the temperature evolution. The first period begins at day 0 of the experiment until the thermophilic temperature is reached (0 - 1 days for RS). The second stage coincides with the thermophilic period (1 - 3 days for RS), and the third period corresponds to the return to mesophilic temperatures (3 - 12 days for RS). For ADS, the process does not reach thermophilic temperatures, but the three stages can also be related to the temperature reached. The periods for ADS are 0 - 3 days, 3 - 8 days and 8 -12 days.

CH<sub>4</sub> emissions (10 %) in RS composting occurred during the first period of the composting process, 49 % in the second period and 41 % in the third period. In ADS, CH<sub>4</sub> was emitted mainly during the second period (52 %), but CH<sub>4</sub> emission was notably high during the first period (35 %) and lower during the third period (13 %).

N<sub>2</sub>O emissions during the first period of RS composting were 56 %, 40 % during the second period and 4 % during the third period, clearly related to process temperature. In ADS, composting the trend is reversed: the N<sub>2</sub>O emissions are only 1 % in the first period, 54 % during the second period and 45 % during the third period. In this case, N<sub>2</sub>O and temperature relationship is not clear enough although N<sub>2</sub>O emissions are not detected during temperature rising.

Only 5 % of the NH<sub>3</sub> emissions in RS composting occurred during the first period, 35 % was emitted during the second period and 60 % during the third one. For ADS composting, the trend was again reversed: 48 % of the ammonia was emitted during the first period and 52 % during the second period. No emission of ammonia was detected during the third period of the ADS composting process. This fact can be related to ammonia emission due to stripping of the amount of this compound contained in ADS sludge rather than to process biological degradation.

For RS, 11 % of the total VOCs were emitted during the first period, 48 % were emitted during the second period and the 41 % over the last period. For ADS, 45 % of the total VOCs were emitted during the first period, 43 % during the second period, and 12 % of the VOCs were emitted during the third period.

### *3.3. VOCs characterization by SPME/GC-MS*

VOC emissions and composition were characterized by SPME/GC-MS. The main objective was the identification of a large number of compounds emitted during the composting process. To simplify the discussion, VOCs have been classified as belonging to the following chemical families: alcohols, esters, furans, ketones, aliphatic hydrocarbons, aromatic hydrocarbons, nitrogen-containing compounds, sulfur-containing compounds and terpenes.

According to Eitzer (1995), most volatile organic compounds in aerobic composting plants are emitted at the early stages of processing, i.e., at the tipping floors, at the shredder and at the initial active composting region. This result agrees with our study in the sense that the number of compounds detected during the process decreased from the thermophilic phase to the end of the composting process (see supplementary information, Figure S1).

Certain of the observed VOC families (alcohols, ketones, aliphatic hydrocarbons, nitrogen-containing compounds, and sulfur-containing compounds) were extensively degraded during the biological process while other VOC families did not show any measurable reduction as a consequence of the composting process because they are xenobiotic compounds, such as certain aromatic hydrocarbons or halogenated compounds, or other carcinogenic products, such as furans (Scaglia et al., 2011). In our study, halogenated compounds were not found during the entire process. However,

furans or aromatic hydrocarbons were emitted at low concentrations all during the process, most likely as a consequence of stripping.

The total percentages of each VOC family emitted are summarized in Table 3. VOC percentages detected for each sludge type (RS and ADS) are highly different although, in almost all cases, terpenes are the VOC family most emitted (except in ADS-I experiment). Terpenes have been described as the main compounds responsible for odorous pollution at composting treatment installations (Staley et al., 2006). Low pH values achieved and maintained for prolonged periods have been related to odors in food waste composting (Sundberg et al., 2013). This is not the case in sludge composting where pH is maintained around neutral conditions. RS terpene percentages are almost twice the percentages found in ADS composting, possibly because ADS underwent a previous anaerobic digestion process, where organic matter was extensively degraded.

A quantitative analysis has also been carried out with some specific and typical VOCs emitted during a composting process. Fifteen typical compounds have been identified, but only 10 of these compounds have been found in these composting processes. These 10 compounds and their amounts are summarized in Table 4 with the remaining five compounds not found. Table 4 shows that the three terpenes that were quantified are alpha- and beta-pinene and limonene. The amounts of these three terpenes emitted are notably similar for each trial and sludge type, with alpha-pinene the main terpene being detected in RS-I. Limonene was emitted in amounts similar to alpha- and beta-pinene, much higher in RS than in ADS. Limonene is related to the fruity or citrusy sensorial experience (Suffet et al., 2009). Büyüksönmez and Evans (2007) reported that terpenes are more closely related to the material used as a bulking agent than to the main waste composted and the biological process. Pagans et al.

(2006b) concluded that the bulking agent ratio (wood chips:sludge) affects VOC emissions during the composting process and their elimination by biofiltration. High ratios of bulking agent, as is the case in sludge composting, could therefore lead to high emissions of terpenes (Pagans et al., 2006b). According to other authors (Eitzer, 1995), terpenes could also be produced as an intermediate in the aerobic metabolism. The maximum concentrations measured for alpha- and beta-pinene and limonene during the composting process were  $49 \text{ mg m}^{-3}$  (RS-II),  $10 \text{ mg m}^{-3}$  (RS-I) and  $4.2 \text{ mg m}^{-3}$  (RS-II). These concentrations are above the odor threshold reported by Tsai et al. (2008) (Table 4). During several hot spots in the process, the usual human nose would therefore smell these compounds. In the entire ADS composting process, no amount of terpene emissions passed the odor threshold (Table 4).

The less abundant families were furans and esters. Esters are present only during the RS composting process but at a very low percentage (0.02 % maximum, Table 3). In the ADS composting process, esters have not been found. Furans, mainly represented by 2-pentylfuran, have been reported to be toxic and may be carcinogenic, but they are naturally based compounds that could be found in fruit (Scaglia et al., 2011). This type of molecule is related to grassy, woody and smoky odors (Suffet et al., 2009).

Regarding alcohols, Scaglia et al. (2011) reported that these compounds are emitted mainly during the first biostabilization stage when oxygen could be a limiting factor, due to the high level of microbial activity. This information agrees with the RS process, where alcohols were emitted mainly during the first half of the process and practically disappear in the last days. In the ADS composting process, the semiquantitative analysis (Table 3) indicates that the percentage of alcohols was higher than in the RS composting process (13 – 24 % vs. 7 – 11 %), most likely due to a lower total emission in the ADS process, where very few VOCs have been detected.

Acetone and various cycloketones mainly represent the ketone family. These compounds could be produced by oxidation of alcohols, which could explain why ketones have not been found in the ADS composting process where the presence of alcohols was also very low. Cyclohexanone and 2-pentanone have been quantified but have been found only in the RS composting process at low concentrations, being found at higher concentrations in RS-II (Table 4). These compounds are associated with wastewater, municipal solid waste, and composting processes. Cyclohexanone and 2-pentanone are common air and water contaminants (Rosenfeld and Suffet, 2004).

Nitrogen-containing compounds are represented by pyridine, a product related to a putrid odor (Suffet et al., 2009), and acetamide, which can be derived from acetic acid. Pyridine has been quantified and has appeared only in RS composting with higher emissions in RS-II (Table 4). The analysis indicated that a high percentage of VOCs emitted in ADS composting corresponded to nitrogen-containing compounds (15 to 24 %), while for RS, this family only accounted for 0.08 %. As it occurred with alcohols, a high percentage in the analysis is indicative of the proportion of the compound in the emissions.

Dimethyl sulfide and dimethyl trisulfide have been detected as the main sulfur-containing compounds. These emissions are related to sensorial experiences, such as rotten eggs, rotten vegetables or garlic (Suffet et al., 2009). The semiquantitative analysis indicates that this family represents approximately 8 % of the total VOC emissions in the RS composting process and 5 – 11 % in the ADS process. Dimethyl disulfide has been quantified (Table 4) in all of the trials. This compound is formed when sulfur is used as an electron acceptor (Amlinger et al., 2008) and is a very common sulfur emission from biological decomposition processes in general. The presence of these compounds can be indicative of the presence of CH<sub>4</sub> (Amlinger et al.,

2008). This observation pertains to the ADS, but not the RS, where the peak emission of dimethyl disulfide occurs when methane emissions have already ceased.

Dimethyl disulfide emissions are higher in RS composting than in ADS composting (0.08, 0.1 and 0.0002, 0.001 kg of dimethyl disulfide emitted  $\text{Mg}^{-1}$  of sludge treated, respectively). For both cases, dimethyl disulfide is the single volatile organic compound that is most emitted. This high level of dimethyl disulfide emissions could be due to the reduction of sulfur to hydrogen sulfide during the anaerobic digestion process. The maximum concentration of dimethyl disulfide detected during the composting process was  $0.052 \text{ mg m}^{-3}$  in RS-II, much higher than the reported odor threshold ( $0.0088 \text{ mg m}^{-3}$ ). All of the samples analyzed by GC-MS from all of the experiments carried out were above the odor threshold value.

The aliphatic hydrocarbon family is represented by various large alkanes, such as bicyclo[3.1.1]heptane, 6,6-dimethyl- or 2,2,4,4,6,8,8-heptamethylnonane. The percentage detected over the entire profile of VOC emissions is very low for the RS composting process (0.1 - 0.4 %). In the ADS composting process, aliphatic hydrocarbons represent a significant percentage (8 – 13 %) of the total VOC emissions, possibly because of the overall low VOC emissions.

Aromatic hydrocarbons have been found in all the experiments. Toluene and different derivatives of methylbenzene are the main aromatic hydrocarbons found. The sensorial experience related to these compounds is similar to that of dark viscid substances obtained by the destructive distillation of organic matter such as coal, wood, or peat (Suffet et al., 2009). In all experiments, semiquantitative analysis indicates that the aromatic hydrocarbon percentage is below 6.5 % (Table 3), these compounds are emitted during the entire process. The aromatic hydrocarbons that have been quantified are *m*-/*p*-xylene, styrene and toluene. Styrene and *m*-/*p*-xylene have been found only in

the RS composting process, but toluene has been found in both cases, higher in ADS composting (Table 4). Toluene is usually found at high concentrations in terms of mg per dry kg of initial substrate during any composting process (Komilis et al., 2004). Styrene, *m-/p-* xylene and toluene maximum concentrations are below the odor threshold reported by Tsai et al. (2008).

Regardless the family of VOC considered it is clear that the emission of VOCs in sludge composting presents an inherent variability, being more noticeable when the overall emissions are lower as in the case of ADS. For this reason, it is strongly recommended to perform replications in these studies as well as to work in a process scale that allows improving the precision of the exhaust gas emissions measurement.

#### **4. Conclusions**

Emission factors have been calculated for VOC, CH<sub>4</sub>, NH<sub>3</sub> and N<sub>2</sub>O during RS and ADS composting under OUR aeration control. VOC families in emissions have been identified and quantification of main compounds performed. CH<sub>4</sub> and N<sub>2</sub>O emission factors were higher in ADS than in RS composting while reverse tendency has been observed for NH<sub>3</sub> and VOC, mainly responsible of odor pollution. Terpenes are the VOC family dominating emissions during the entire process.

This study provides relevant information for exhaust gas treatment equipment and highlights the importance of conducting replications to obtain reliable data on composting emissions.

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## References

1. Adani, F., Ubbiali, P., Genevini, P., 2006. The determination of biological stability of composts using the Dynamic Respiration Index: the results of experience after two years, *Waste Manage.* 26, 41-48.
2. Ahn, H.K., Mulbry, W., White, J.W., Kondrad, S.L., 2011. Pile mixing increases greenhouse gas emissions during composting of dairy manure. *Bioresource Technol.* 102, 2904-2909.
3. Amlinger, F., Peyr, S., Cuhls., 2008. Greenhouse gas emissions from composting and mechanical biological treatment. *Waste Manage. Res.* 26, 47-60.
4. Brown, S., Kruger, C., Subler, S., 2008. Greenhouse Gas Balance for Composting Operations. *J. Environ. Qual.* 37, 1396–1410.
5. Büyüksönmez, F., Evans, J., 2007. Biogenic Emissions from green waste and comparison to the emissions resulting from composting part II: Volatile Organic Compounds (VOCs). *Compost Sci. Util.* 15, 191-199.
6. Colón, J., Cadena, E., Pognani, M., Barrena, R., Sánchez, A., Font, X., Artola, A., 2012. Determination of the energy and environmental burdens associated with the biological treatment of source-separated Municipal Solid Wastes. *Energy Environ. Sci.* 5, 5731-5741.
7. Commission of the European Community, 2008. Green Paper on the management of bio-waste in the European Union, <http://eur->

lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2008:0811:FIN:EN:PDF

(Accessed April 2013)

8. Davoli, E., Gangai, M.L., Morselli, L., Tonelli, D., 2003. Characterisation of odorants emissions from landfills by SPME and GC-MS. *Chemosphere* 51, 357-368.
9. D'Imporzano, G., Crivelli, F., Adani, F., 2008. Biological compost stability influences odor molecules production measured by electronic nose during food-waste high-rate composting. *Sci. Total Environ.* 402, 278-286.
10. Eitzer, B.D., 1995. Emissions of volatile organic chemicals from municipal solid waste composting facilities. *Environ. Sci. Technol.* 29, 896-902.
11. Fukumoto, Y., Osada, T., Hanajima, D., Haga, K., 2003. Patterns and quantities of NH<sub>3</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions during swine manure composting without forced aeration-effect of compost pile scale. *Bioresource Technol.* 89, 109–114.
12. Gea, T., Barrena, R., Artola, A., Sánchez, A., 2007. Optimal bulking agent particle size and usage for heat retention and disinfection in domestic wastewater sludge composting. *Waste Manage.* 27, 1108-1116.
13. Goldstein, N., 2002. Getting to Know the Odor Compounds, *Biocycle* 43, 42-44.
14. Hamelers, H.V.M., 2004. Modeling composting kinetics: a review of approaches. *Rev. Environ. Sci. Biotechnol.* 3, 331-342.
15. He, Y., Ianmori, Y., Motoyuki, M., Kong, H., Iwami, N., Sun, T., 2000. Measurements of N<sub>2</sub>O and CH<sub>4</sub> from the aerated composting of food waste. *Sci. Total Environ.* 254, 65-74.
16. Hellebrand, H. J., Kalk, W-D., 2001. Emission of methane, nitrous oxide, and ammonia from dung windrows. *Nutr. Cycl. Agroecosys.* 60, 83–87.

17. IPCC, 2007. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M. and Miller, H.L. (eds), IPCC, Cambridge, United Kingdom and New York, NY, USA.
18. Komilis, D.P., Ham, R.K., Park, J.K., 2004. Emission of volatile organic compounds during composting of municipal solid wastes, *Water Res.* 38, 1707-1714.
19. Kosobucki, P., Chmarzyński, A., Buszewski, B., 2000. Sewage sludge composting. *Pol. J. Environ. Stud.* 9, 243-248.
20. Orzi, V., Cadena, E., D'Imporzano, G., Artola, A., Davoli, E., Crivelli, M., Adani, F., 2010. Potential odor emission measurement in organic fraction of municipal solid waste during anaerobic digestion: Relationship with process and biological stability parameters, *Bioresource Technol.* 101, 7330-7337.
21. Pagans, E., Barrena, R., Font, X., Sánchez, A., 2006a. Ammonia emissions from the composting of different organic wastes. Dependence on process temperature, *Chemosphere*, 62, 1534-1542.
22. Pagans, E., Font, X., Sánchez, A., 2006b. Emission of volatile organic compounds from composting of different solid wastes: Abatement by biofiltration, *J. Haz. Mat.* 131, 179-186.
23. Ponsá, S., Gea, T., Sánchez, A., 2010. Different indices to express biodegradability in organic solid wastes, *J. Environ. Qual.* 39, 706-712.
24. Puyuelo, B., Gea, T., Sánchez, A., 2010. A new control strategy for composting process based on the oxygen uptake rate, *Chem. Eng. J.* 165, 161-169.

25. Rosenfeld, P. E., Suffet I.H., 2004 Understanding odorants associated with compost, biomass facilities and the land application of biosolids. *Water Sci. Technol.* 49 (9), 193-199.
26. Ruggieri, L., Gea, T., Artola, A., Sánchez, A., 2009. Air filled porosity measurements by air pycnometry in the composting process: A review and correlation analysis, *Bioresource Technol.* 100, 2655-2666.
27. Sánchez Monedero, M.A., Roig, A., Paredes, C., Bernal, M.P., 2001. Nitrogen transformation during organic waste composting by the Rutgers system and its effects on pH, EC and maturity of the composting mixtures. *Bioresource Technol.* 78, 301–308.
28. Scaglia, B., Orzi, V., Artola, A., Font, X., Davoli, E., Sánchez, A., Adani, F., 2011. Odours and volatile organic compounds emitted from municipal solid waste at different stage of decomposition and relationship with biological stability, *Bioresource Technol.* 102, 4638–4645.
29. Shen, Y., Chen, T.B., Gao, D., Zheng, G., Liu, H., Yang, Q., 2012. Online monitoring of volatile organic compound production and emission during sewage sludge composting. *Bioresource Technol.* 123, 463-470.
30. Smet, E., Van Langenhove, H., De Bo, I., 1999. The emission of volatile compounds during the aerobic and the combined anaerobic/aerobic composting of biowaste. *Atmos. Environ.* 33, 1295-1303.
31. Staley, B.F., Xu, F., Cowie, S.J., Barlaz, M.A., Hater, G.R., 2006. Release of trace organic compounds during the decomposition of municipal solid waste components, *Environ. Sci. Technol.* 40, 5984-5991.

32. Suffet, I.H., Decottignies, V., Senante, E., Bruchet, A., 2009. Sensory assessment and characterization of odor nuisance emissions during the composting of wastewater biosolids. *Water Environ. Res.* 81 (7), 670-679.
33. Sundberg, C., Yu, D., Franke-Whittle, I., Kauppi, S., Smårs, S., Insam, H., Romantschuck, Jönsson, H., 2013. Effects of pH and microbial composition on odour in food waste composting. *Waste Manage.* 33, 204-211.
34. Tremier, A., de Guardia, A., Massiani, C., Paul, E., Martel, J.L., 2005. A respirometric method for characterising the organic composition and biodegradation kinetics and the temperature influence on the biodegradation kinetics, for a mixture of sludge and bulking agent to be cocomposted. *Bioresource Technol.* 96, 169–180.
35. Tsai, C.J., Chen, M.L., Ye, A.D., Chou, M.S., Shen, S.H., Mao, I.F., 2008. The relationship of odor concentration and the critical components emitted from food waste composting plants. *Atmos. Environ.* 42, 8246-8251.

## Figure Legends

**Figure 1.** Evolution of temperature, airflow, OUR profile and oxygen percentage. Due to the similarity of temperature, flow, oxygen and OUR profiles, only one graph is shown for the RS composting process (a) and another for the ADS composting process (b), representing the four trials carried out. Legend in Fig 1a is the same for Fig 1b.

**Figure 2.** Daily emission factors (kg of compound  $\text{Mg}^{-1}$  treated sludge) evolution of VOCs (a),  $\text{CH}_4$  (b),  $\text{N}_2\text{O}$  (c) and  $\text{NH}_3$  (d) for RS-I, RS-II, ADS-I and ADS-II. In the case of Figures 2b, 2c and 2d, the left axis corresponds to ADS composting emissions and the right axis corresponds to RS composting emissions.

**Table 1.** Characterization of the initial RS and ADS, the mixture with bulking agent and final products obtained after 12 days of experiment (RS-I and RS-II: duplicates for raw sludge composting; ADS-I and ADS-II: duplicates for anaerobically digested sludge composting)

Material	Dry Matter (%, wb*)	Organic Matter (%, db*)	DRI* (mg O <sub>2</sub> g <sup>-1</sup> OM h <sup>-1</sup> )	Total Organic Carbon (% db)	Total Nitrogen Kjeldahl (% db)	pH	Conductivity (µs/cm)
Raw sludge	21.1 ± 0.2	80.2 ± 0.1	5.2 ± 0.9	72 ± 9	3.2 ± 0.2	7.02	1299
Mixture RS- bulking agent	45 ± 6	95.7 ± 0.9	1.6 ± 0.3	74 ± 4	2.4 ± 0.4	7.02	968
RS-I (Final product)	37 ± 1	94 ± 2	1.07 ± 0.02	72 ± 4	2.98 ± 0.02	8.78	1065
RS-II (Final product)	32 ± 2	94 ± 2	0.50 ± 0.06	72 ± 8	2.9 ± 0.1	8.99	1322
Anaerobically digested sludge	17.1 ± 0.1	70.3 ± 0.5	1.2 ± 0.1	69 ± 6	7 ± 1	7.94	1153
Mixture ADS- bulking agent	42 ± 1	85 ± 3	0.56 ± 0.04	70 ± 6	5.5 ± 0.3	7.95	943
ADS-I (Final product)	28.8 ± 0.7	85 ± 1	0.43 ± 0.07	63 ± 9	2.2 ± 0.4	8.24	1067
ADS-II (Final product)	30.2 ± 0.8	85 ± 1	0.55 ± 0.03	65 ± 3	2.95 ± 0.04	8.19	1084

\*OM: Organic Matter; wb: wet basis; db: dry basis; DRI: Dynamic Respirometric Index.

**Table 2.** Emission factors of VOCs, CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> (kg of compound emitted Mg<sup>-1</sup> of sludge treated). (RS-I and RS-II: duplicates, raw sludge composting; ADS-I and ADS-II: duplicates, anaerobically digested sludge composting)

<b>Trial</b>	<b>VOCs</b>	<b>CH<sub>4</sub></b>	<b>N<sub>2</sub>O</b>	<b>NH<sub>3</sub></b>
RS-I	2.1E-01	1.4E-02	6.4E-03	8.71E-01
RS-II	1.4E-01	1.2E-02	2.7E-03	2.8E-01
ADS-I	4.3E-02	7.3E-01	5.6E-01	4.8E-03
ADS-II	2.3E-02	8.3E-01	4.9E-01	3.5E-03

**Table 3.** Percentages of different VOC families emitted during the four processes studied (RS-I and RS-II: duplicates, raw sludge composting; ADS-I and ADS-II: duplicates, anaerobically digested sludge composting)

<b>Trial</b>	<b>Terpenes</b>	<b>Furans</b>	<b>Esters</b>	<b>Alcohols</b>	<b>Ketones</b>	<b>Nitrogen-containing Compounds</b>	<b>Sulfur-containing Compounds</b>	<b>Aliphatic hydrocarbons</b>	<b>Aromatic hydrocarbons</b>
RS-I	72.0	0.11	0.00	8.90	4.16	0.06	11.1	0.37	3.27
RS-II	64.3	0.07	0.01	15.1	5.14	0.03	11.4	0.13	3.78
ADS-I	24.9	0.17	0.00	4.42	0.17	37.6	16.4	8.35	7.95
ADS-II	33.4	11.3	0.00	22.9	0.00	6.50	6.95	13.2	5.79

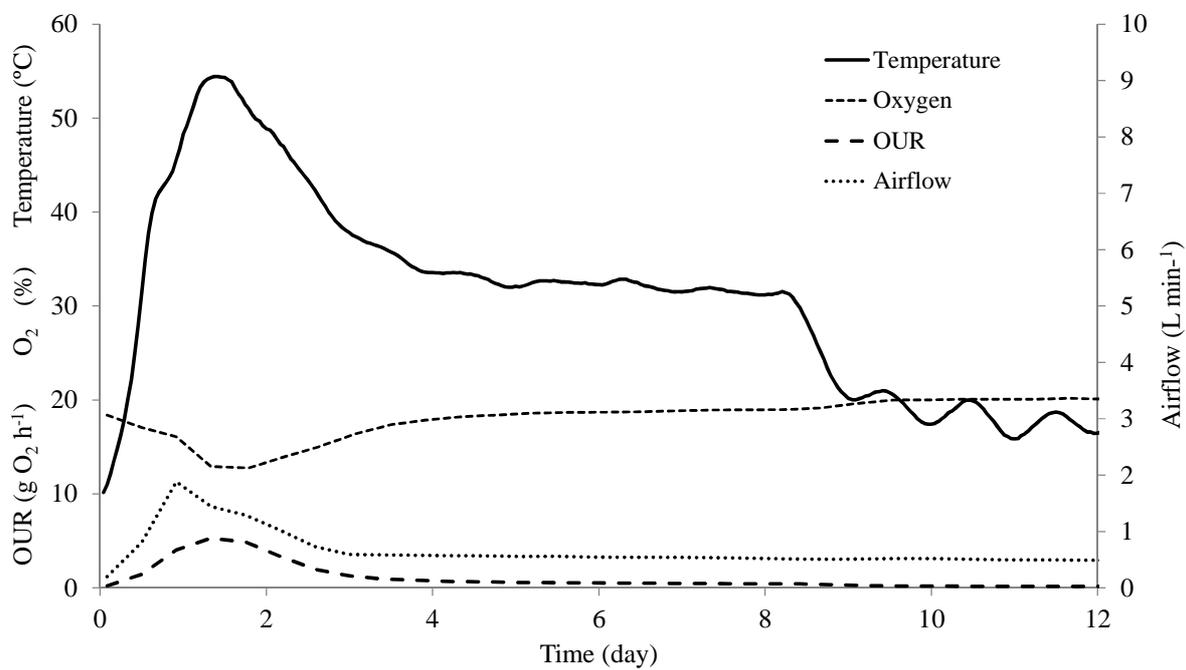
**Table 4.** Total emission of quantified VOCs (kg of compound emitted Mg<sup>-1</sup> of sludge treated (RS-I and RS-II: duplicates, raw sludge composting; ADS-I and ADS-II: duplicates, anaerobically digested sludge composting))

kg of Compound Mg <sup>-1</sup> of sludge treated	alpha-Pinene	beta-Pinene	Limonene	Cyclohexanone	2-Pentanone	Pyridine	Dimethyl disulfide	<i>m-/p-</i> Xylene	Toluene	Styrene
RS-I	6.4E-03	4.4E-03	7.2E-04	1.8E-04	0.0E+00	5.9E-05	1.0E-01	1.5E-04	7.1E-06	3.7E-05
RS-II	1.4E-02	1.4E-03	1.2E-03	3.6E-04	8.4E-04	2.5E-04	1.5E-01	3.8E-05	0.0E+00	5.9E-05
ADS-I	4.3E-05	3.8E-05	1.3E-05	0.0E +00	0.0E+00	0.0E+00	1.9E-03	0.0E+00	2.8E-05	0.0E+00
ADS-II	1.2E-05	0.0E+00	6.3E-06	0.0E+00	0.0E+00	0.0E+00	2.9E-04	0.0E+00	3.9E-05	0.0E+00
Maximum concentration emitted (mg m <sup>-3</sup> )	4.9E+01 (RS-II)	1.0E+01 (RS-I)	4.2E+00 (RS-II)	1.4E+00 (RS-II)	5.4E+00 (RS-II)	1.2E+00 (RS-II)	5.2E+02 (RS-II)	5.4E-01 (RS-I)	3.1E-01 (RS-I)	2.9E-01 (RS-II)
Odor threshold (mg m <sup>-3</sup> )*	3.9E+00	3.9E+00	2.5E+00	-	-	-	8.8E-03	2.2E+00	5.9E+00	6.2E-01

\* Tsai et al. 2008

**Figure 1**

a)



b)

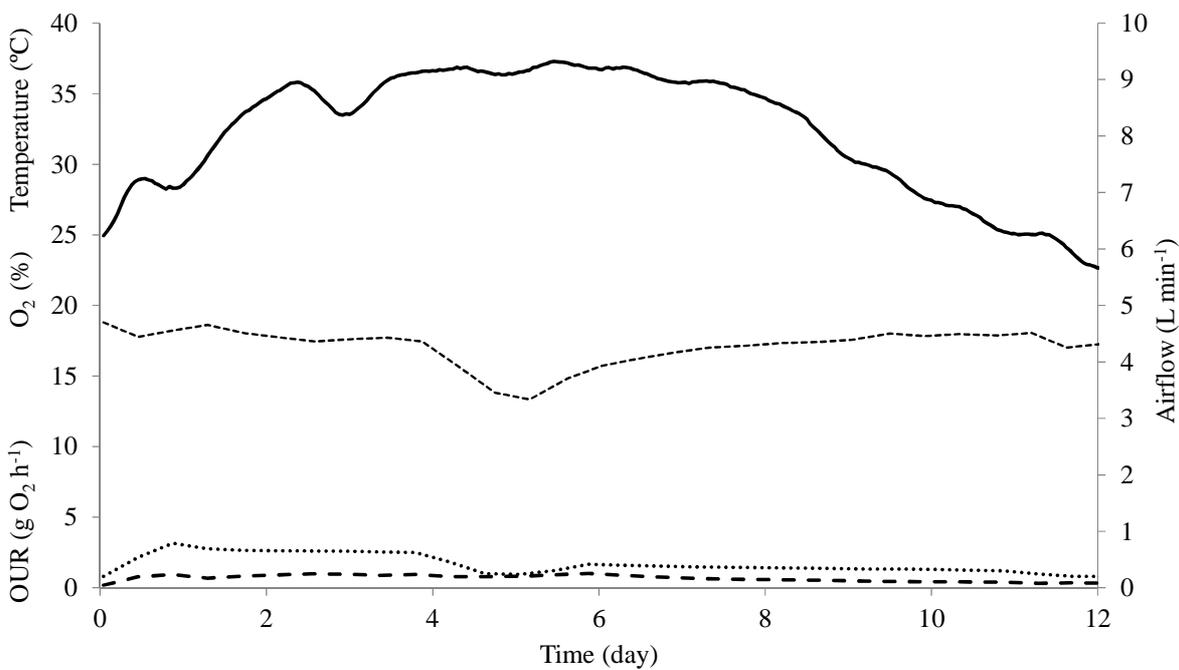
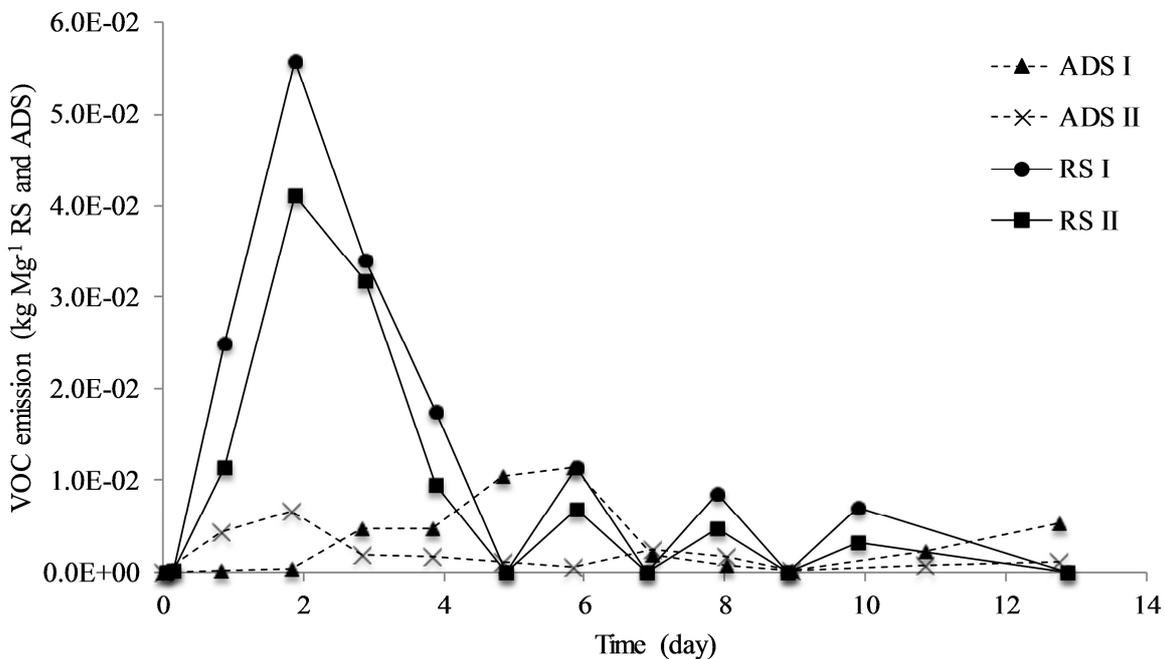
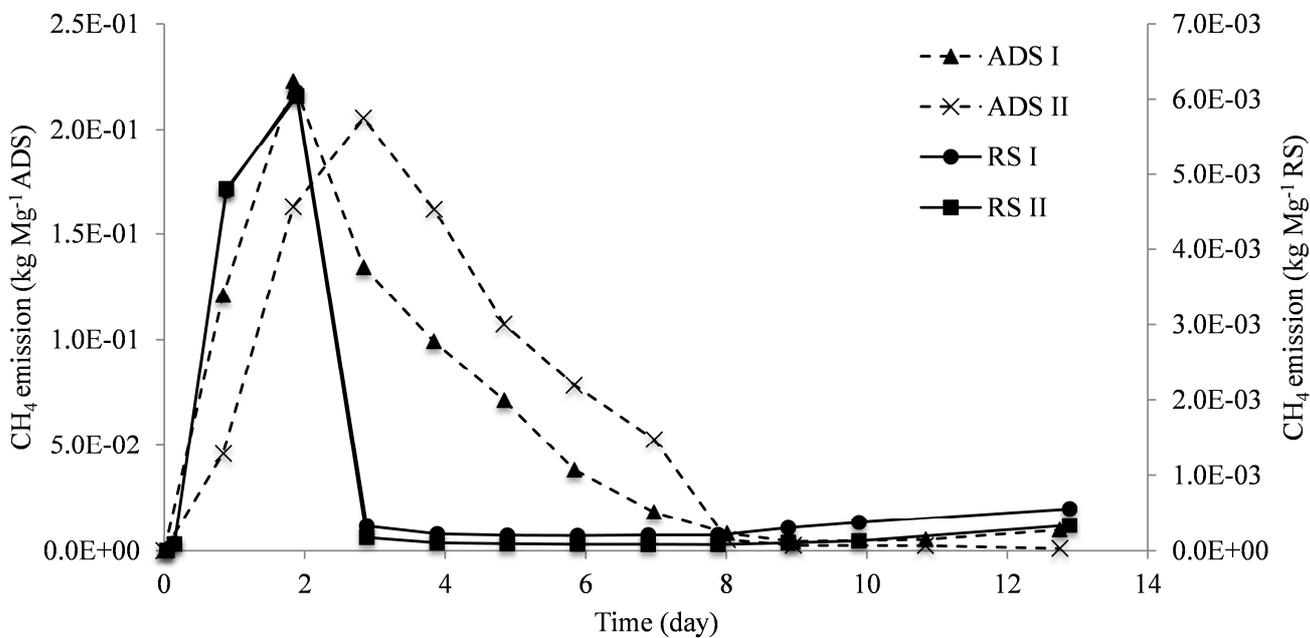


Figure 2

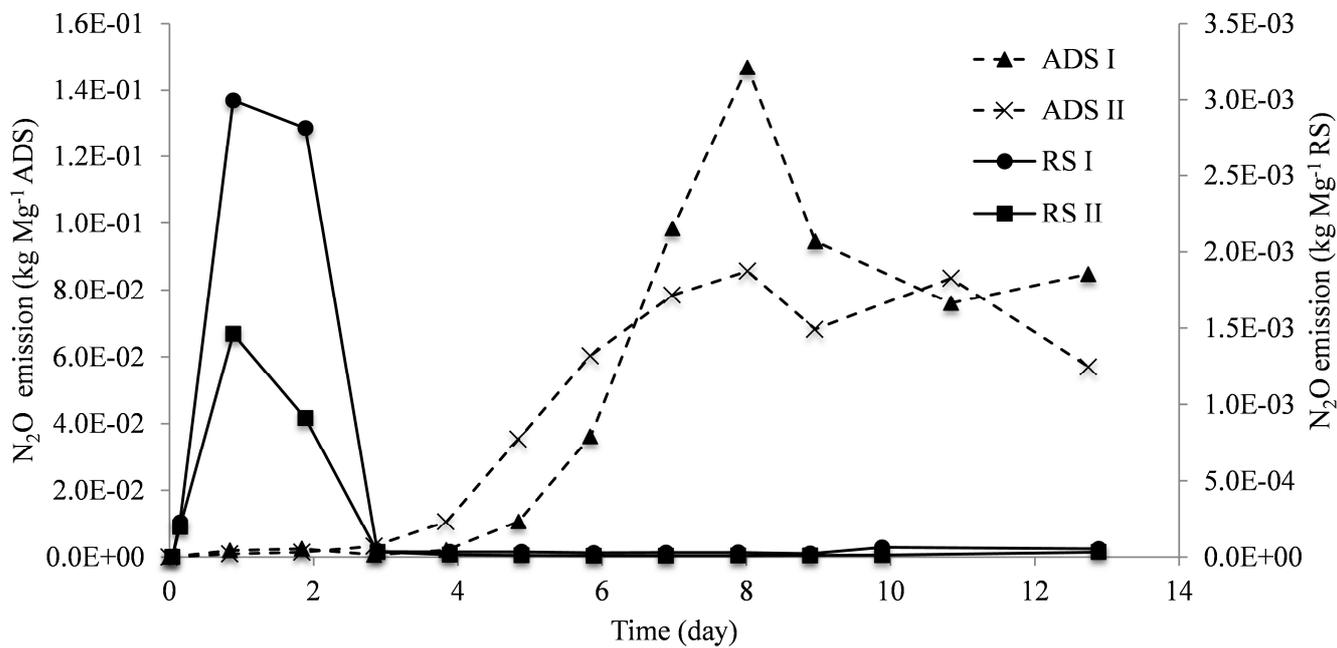
a)



b)



c)



d)

