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# Relationships between emitted volatile organic compounds and their concentration in the pile during municipal solid waste composting



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#### ABSTRACT

Composting operations taking place at municipal solid waste (MSW) treatment plants represent a source of volatile organic compounds (VOC) to the atmosphere. Understanding the variables governing the release of VOC at these facilities is crucial to assess potential health risks for site workers and local residents. In this work the changes in the VOC composition of a composting pile were monitored and compared to the VOC emmitted from the same pile in order to understand the impact of composting operations on the release of VOC. More than one hundred VOC were indentified in the solid phase of the composting piles, which were dominated by terpenes (about 50% of the total amount of VOC) and in a lower quantity alcohols, volatile fatty acids and aromatic compounds. There was a reduction in the total concentration of VOC in the pile during composting, from 45 to 35 mg/kg, but the compostion and distribution of VOC families remained stable in the pile even in the mature compost. However, there was no correlation between the emitted VOC and their concentration in the composting pile. The VOC emission pattern was affected by the biological activity in the pile (measured by temperature, CO<sub>2</sub> evolution and the presence of  $CH_4$  emissions). The highest VOC emissions were detected at early stages of the process, alongside with the generation of CH<sub>4</sub> in the pile, and then decreased sharply in the mature compost as a consequence of biodegradation and volatilisation. These results pointed to the importance of composting operation rather than the composition of the raw materials on the release of VOC in composting plants. © 2018 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Routine operations taking place at organic waste treatment plants are the source of potential chemical and biological hazards to site workers and local residents (Vilavert et al., 2012). The emission of volatile organic compounds (VOC) represents one the main health and environmental concerns from a public point of view due to the nuisance caused by odour and toxicity of some of these compounds. VOC are defined as any compound of C (with the exception of C oxides, carbonates and hydrogen carbonates) having an initial boiling point less than or equal to 250 °C measured at a standard pressure of 101.3 kPa (EC, 2004). These compounds, under normal atmospheric conditions of temperature and pressure, can evaporate and become a potential risk to human health (Domingo and Nadal, 2009). VOC can also represent a risk to the environment, associated to the reduction of stratospheric ozone and to the photochemical formation of ozone at terrestrial level (Atkinson, 2000).

\* Corresponding author. *E-mail address:* monedero@cebas.csic.es (M.A. Sánchez-Monedero). Composting represents a widely accepted technology for the biological treatment and stabilisation of organic wastes. VOC can be produced and released at different stages of the composting process, from the handling of raw materials and mainly during the microbial transformations underwent by the organic matter (OM) during the process (Miller, 1993). In fact, hundreds of different VOC species have been identified in the air released from composting plants (Domingo and Nadal, 2009). The most common chemical families identified in the VOC are volatile organic acids, aromatic and aliphatic compounds, S and N compounds, alcohols, ketones, aldehydes and terpenes (Miller, 1993; Schiavon et al., 2017). Considering the large number and variety of VOC emitted from municipal solid waste plants and the exposure risk for plant operators, it is necessary to identify the main sources and factors controlling their release to the atmosphere.

The largest VOC emissions are generally found at the waste reception area and tipping floor, where wastes are discharged, and during the initial phase of composting, where the OM undergoes the most intense biodegradation (Eitzer, 1995). Key parameters affecting the VOC generation are aeration, temperature, moisture and type of substrates (Miller, 1993; Pagans et al.,



2006; Delgado-Rodríguez et al., 2011). Consequently, the control of these operational parameters during the process can lead to a reduction of the VOC emission to the atmosphere. A deficient aeration and an excess of moisture can originate temporary anaerobic spots in the pile producing malodorous substances such as volatile organic acids and S-containing compounds. Delgado-Rodríguez et al. (2011) found that VOC emissions can be reduced in aerobic piles by ensuring high C/N ratios (above 50) and medium moisture contents (around 55%). In addition, Maulini-Duran et al. (2013) observed that the aeration strategy also affected the composition of VOC emissions. These authors suggested the use of an aeration controller, based on the biological activity of the pile, to produce a stable VOC emission profile. Temperature is also an important factor affecting the emission of VOC from the piles (Maulini-Duran et al., 2014). High temperatures in a composting pile, typically above 60 °C, favour VOC volatilisation by increasing their vapour pressure. On the other hand, temperature also governs the  $O_2$  availability in the pile (Scaglia et al., 2011) and consequently the activity of aerobic microorganisms responsible of OM degradation (including the degradation of VOC).

Despite the importance of the above mentioned operational parameters on the release of VOC from composting plants, the type of raw material treated in composting plants is also expected to play an important factor governing the VOC emission pattern (Kim et al., 1995). Pagans et al. (2006) reported higher VOC emissions in laboratory-scale reactors treating raw and anaerobic digested sludge compared to the organic fraction of MSW or animal by-products. Most of the published literature on this topic has been devoted to the identification and quantification of VOC emissions from different waste treatment facilities but there is limited information on the relationship between these emissions and the VOC present in the pile (Pierucci et al., 2005), and how the changes in the composition of the organic wastes being treated during the process would affect the release of VOC to the atmosphere.

The aim of this study was to evaluate the relationship between the concentration and diversity of VOC present in the solid phase of the composting pile and the levels of VOC released to the atmosphere. The identification of the main variables affecting the release of VOC would assist in the selection of the operational conditions to minimise odour and related health risks in MSW composting plants.

#### 2. Materials and methods

#### 2.1. Description of the composting plant and sampling locations

The MSW composting plant evaluated in this study is part of a mechanical biological treatment plant located in South Spain processing about 40.000 tonnes of mixed household wastes per year. The materials entering the plant are subjected to a pretreatment by manual sorting and a rotating trommel screen for the removal of bulking items and the recovery of recyclable materials from the mixed waste stream. The remaining organic fraction undergoes a composting process which consists in a bioxidative phase (3–5 days) in static piles with forced aeration in closed biocells, and a composting phase (3–4 weeks) in trapezoidal windrows (30 m length  $\times$  2 m height), turned once a week with a turning machine

in a roofed composting pad. This composting mixture is screened to less than 20 mm and stored in static piles, about 3–4 m height, in the open to allow maturation before commercialization (or for its use as landfill daily cover).

From all the operational activities taking place in the plant, only those located in the open were selected as potential sources of VOC to the atmosphere: The open composting pad and the pile of mature compost located outdoors. MSW pretreatment and the first bioxidation step of the composting process were not considered as potential VOC sources since they took place in enclosed buildings and the exhaust air from these areas was blown directly through the biofilter.

#### 2.2. VOC sampling and analysis in the gas and solid phases

To assess the amount of VOC generated in the composting plant, a solid sample was taken from a composting pile at different stages of the process (after 1, 2 and 3 weeks) and from the mature compost pile stocked outdoors (approximately 8 weeks of maturation). Gas samples were also taken from the surface of the pile at the same stages to evaluate the amount of VOC emitted to the air.

Solid samples (around 5 kg fresh weight) were taken from each pile by mixing six sub-samples taken along the whole profile of the pile (from the top to the bottom of the mixture). Three replicates, separated by 5 m, were taken along the whole length of each pile. The samples were kept refrigerated and analysed within 24 h for VOC and OM concentrations. The characteristics of the composting mixtures at different stages are presented in Table 1.

A static closed chamber technique was used to measure the emission of VOC from the surface of the composting piles (Sommer et al., 2004). Gas samples were taken from three high-density polyethylene chambers (Volume:  $0.036 \text{ m}^3$ ; area:  $0.07 \text{ m}^2$ ) placed at different locations along the whole length of the pile: the chambers were placed on the top of the piles, separated by approximately 5 m, and pushed 5 cm into the pile. Gas samples were taken within the headspace after 5 min of accumulation using a 60 mL disposable syringe, transferred to a Tedlar<sup>®</sup> gas sampling bag and analysed within 12 h to minimise the degradation of VOC in the sampling bags (Trabue et al., 2006).

The analysis of VOC was performed by means of head-space solid phase extraction (HS-SPME), by adapting the methodology described by Higashikawa et al. (2013). Aliquots of 1 g (solid samples) or 20 mL (gas samples) were introduced in 20 mL glass vials and supplemented with 2  $\mu$ l of internal standard solution (0.5 mg/l hexadeuterobenzene) and sealed with PTFE-faced septa and aluminium crimp-caps (Agilent Technologies). Equilibration was achieved by preconditioning the vial for 20 min at 40 °C. The SPME fiber used for the extraction was DVD/CAR/PDMS, 50/30  $\mu$ m (divinylbenzene/carboxen/polydimethylsiloxane; Supelco, Bellefonte, PA) and conditioned for 1 h at 270 °C in the injector port before the first use. For adsorption of volatiles the fiber was exposed to the headspace of sample vials during 20 min at 40 °C. For thermal desorption the needle was inserted into the splitless injection port (250 °C) of the GC-MS system for 5 min.

The identification and quantification of the VOCs were performed in an Agilent 7890A gas chromatograph equipped with an Agilent 5975C series inert MSD with triple axis detector. The vola-

Table 1

General characteristics of the municipal solid waste (MSW) composting piles (Data shown as mean ± standard deviation, n = 3).

	Week 1	Week 2	Week 3	Week 8 - mature
Composting time (weeks)	1	2	3	8
Temperature (°C)	59.2 ± 1.8	72.1 ± 0.8	71.8 ± 3.7	34.1 ± 1.4
Moisture (%)	49.6 ± 5.4	36.4 ± 15.3	40.6 ± 8.3	27.1 ± 7.6
Organic matter (%)	52.2 ± 6.3	47.6 ± 4.3	41.6 ± 9.5	53.7 ± 1.9

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