ORIGINAL ARTICLE

# Effect of aeration rate and moisture content on the emissions of selected VOCs during municipal solid waste composting

M. Delgado-Rodríguez · M. Ruiz-Montoya · I. Giraldez · R. López · E. Madejón · M. J. Díaz

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Abstract The influence of the industrial control composting conditions (aeration  $0.005-0.300 L_{air} kg^{-1}$  and moisture 40-70 %) of municipal solid waste on the composition of the selected compound emitted (limonene,  $\beta$ -pinene, 2-butanone, undecane, phenol, toluene, dimethyl sulfide, dimethyl disulfide) was studied. The highest emissions of volatile organic compounds (VOCs) were observed in the early stages of the processes. At the end of the process, low concentrations of the emitted compounds were found. Aeration rate had a strong effect on emissions. High aeration rate (0.300 L<sub>air</sub> kg<sup>-1</sup> min<sup>-1</sup>) caused normally high emissions of all selected compounds whereas low aeration rates  $(0.05 L_{air} kg^{-1} min^{-1})$  could cause anaerobiosis problems and generation of organic sulphur compounds. We observed that the effect of the moisture upon the emitted concentrations varied depending on the studied compound.

Keywords Composting · VOC · Minimization · MSW

M. Delgado-Rodríguez · M. Ruiz-Montoya · M. J. Díaz (⊠) Departamento de Ingeniería Química, Agrifood Campus of International Excellence (ceiA3), Campus de "El Carmen", Universidad de Huelva, 21071 Huelva, Spain e-mail: dblanco@uhu.es

#### I. Giraldez

Departamento de Química, Agrifood Campus of International Excellence (ceiA3), Campus de "El Carmen", Universidad de Huelva, 21071 Huelva, Spain

R. López · E. Madejón

Instituto de Recursos Naturales y Agrobiología de Sevilla, IRNAS-CSIC, Avda. Reina Mercedes 10, 41012 Seville, Spain

#### Introduction

Food waste is divided from municipal solid waste (MSW) upon collection and treatment because of its high water content, which might otherwise result in a burden on landfills and incinerators. The current official policy prefers recycling, such as composting, as a method of food waste management, because quality compost is valuable for agriculture. However, the malodor problem from the food waste composting plants presents another environmental issue, especially in countries with high population density. Malodor is probably the most demanding environmental challenge for the emerging environmental policy. Volatile organic compounds (VOCs) produced during composting are partly responsible for the unpleasant odors. They can have xenobiotic origins (e.g. aromatic hydrocarbons), owing to the presence of household wastes in the composted mixtures (e.g. unsorted municipal solid waste; MSW) [1]. In this case, the VOCs volatilize primarily during the first biological composting stages [2]. In contrast, during the composting of selected organic fractions (e.g. food wastes) VOCs are mostly of a biogenic origin and are produced predominantly during the high-rate composting phase [3]. In this case, sulphides followed by acid/esters, ketones, alcohols and terpenes, are reported to be the typical VOCs produced during composting [1]. Among the VOCs emitted by composting, more than 110 odorous compounds have been identified in composting facilities and in the air around these areas [1, 4, 5].

Malodorous components generally contain nitrogen or sulfur, amines, phenolic compounds, aldehydes, thiols, ketones and alcohols [6]. Each of these components is primarily produced by microbes, i.e. formed through the activity of microorganisms that degrade the complex organic compounds present in the organic matter. Odor problems can be reduced by preventing generation of these compounds, diluting them or treating the air to reduce their offensiveness. However, before addressing techniques for reducing the atmospheric emission, we must first consider which factor has the greatest impact on VOCs generation and then through proper management, odors can be prevented and minimized. The dependence of odors or VOCs on the composting system and certain composting parameters has been studied [7–10], however, little bibliographic data has been found that speaks to the influence of composting parameters on the VOCs emitted during the composting process.

A successful composting plant design is based on the optimization of the composting parameters and VOCs emission minimization. Moisture and aeration are the two main and easily operational parameters which can be augmented to reach both optimal process efficiency and quality of the final product [11]. From this perspective, this work aims to elucidate the optimum values for aeration and moisture content in order to minimize the main compounds emitted during the MSW composting process.

# Materials and methods

#### Materials

Municipal solid waste was collected from Córdoba's (Spain) urban waste treatment plant. This plant processes the organic fraction of selectively-collected urban waste. Some relevant characteristics of MSW are shown in Table 1, followed by the experimental design that was proposed (see "Experimental design and statistical analysis"). Centralized treatment prior to composting consisted of screening (8 cm) through a bag-opener trommel, electromagnetic separation of ferrous metals and manual separation of non-ferrous materials. Varying amounts of water were also added to obtain one of three levels of moisture: 40, 55 or 70 %. Each mixture was then transferred to the composting reactor following the experimental design indicated below, half filling the reactor (40 kg per reactor) in order to permit air exchange. The experiment was carried out in duplication.

# Composting reactors

The acrylic barrels composting reactors had a capacity of 200 L (Fig. 1). To minimize the conductive heat loss along the reactor wall, they were insulated with polyurethane foam. To ensure initial conditions, water loss was compensated daily by the addition of water during active composting phase.

**Table 1** Relevant characteristics of Municipal Solid Waste (MSW,oven dry basis) used in this study (average  $\pm$  standard deviation)

	MSW <sup>a</sup>
pH (1:5 extract)	$5.95\pm0.2$
EC (1:5 extract) (dS $m^{-1}$ )	$8.29\pm0.1$
Organic matter (g kg <sup>-1</sup> )	$690.6 \pm 8.3$
N (g kg <sup><math>-1</math></sup> )	$21.29\pm1.03$
C/N	17.1
Bulk density (g $L^{-1}$ )	$290.6 \pm 33.5$
Particle size (mm)	
>25 (%)	$47.55\pm6.0$
25-10 (%)	$28.38\pm2.9$
10-5 (%)	$13.13\pm2.2$
5-2 (%)	$7.04\pm0.8$
<2 (%)	$3.90\pm0.1$
Impurities >2 mm (%)	$31.56\pm3.6$

<sup>a</sup> Determined in MSW <5 mm and free of impurities (odb)



Fig. 1 Experimental setup composting reactors used in the study

Two temperature sensors (K thermocouples, TMC6-HA) were placed at the center and the top of the composting mass. An additional temperature sensor was placed outside the reactors to obtain the environmental temperature (Protimeter-MMS-Plus). Temperatures were recorded every 12 h in each reactor by two data loggers (HOBO, U12-006). Compressed air (at different rates following the experimental design  $0.005-0.30 L_{air} kg^{-1} min^{-1}$ ) was introduced into the bottom of each reactor and was evenly distributed to the composting mixture through a perforated plate.

# Chemical analytical methods

Feedstock MSW samples were taken before the start of the experiment. Particle size distribution was determined by a sieve shaker, and impurities (glass, plastics, metals and

stones) were hand separated and weighed. Total organic matter was determined by the weight loss after dry combustion at 540 °C [12]. Nitrogen was determined by steam distillation after Kjeldahl digestion. Organic matter and nitrogen determinations were measured in the <5 mm size fraction. The analyses were carried out in triplicate.

Flow rate was measured by a bubble flow meter which is an accurate way to measure flow rates by timing the movement of soap film bubbles up glass tubes between marks of known volume.

Moisture in the compost samples was quickly determined using an Infrared Moisture Analyzer (COBOS IB110) in order to correct moisture loss in the reactors. The pH was determined in a 1:5 ratio (in weight) compost: water extracts using a pH electrode.

Compost samples and air measurements were taken according to the rate of the composting process: at 0, 2, 6, 14, 21 and 36 days from the start of the experiment.

#### Air sampling and analysis procedure

Air samples for the VOC compounds determination were collected in Tedlar bags (Supelco, Bellefonte, PA, USA) with a vacuum pump and were transported to the laboratory. Sample flow rate and volume were  $31 \text{ mL s}^{-1}$  and 1-2 L, respectively. The flow rate vacuum pump was checked occasionally using a primary standard (soap-blue meter). Air samples were preserved at 4 °C, protected from light exposure and analyzed within 24 h.

Volatile organic compounds were preconcentrated using the solid phase microextraction (SPME) method. A SPME fiber, coated with 75  $\mu$ m carboxenpolydimethylsiloxane (Supelco, Bellefonte, PA, USA), was employed to capture VOC compounds in Tedlar bags. The SPME fibre was manually inserted into the bag for 30 min. The SPME fiber coating containing volatile compounds was inserted into the GC injection port at 230 °C and remained for 3 min for desorption. After each sample injection, fibers were kept inside the SPME needle to prevent possible contamination and were conditioned with helium at 250 °C for 10 min before reuse.

The desorption of volatile compounds was performed using an Agilent 6890 gas chromatograph system, coupled to a quadrupole Agilent 5973 electron ionization (70 eV) mass spectrometric detector (Agilent Technologies, Palo Alto, CA, USA) equipped with an Agilent HP-5MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). The GC was equipped with a split/splitless injection port operating in Splitless mode. The oven temperature was programed from 40 °C (5 min) to 270 °C (20 min) by increasing the temperature at 5 °C min<sup>-1</sup>. The transfer line was heated at 280 °C. The carrier gas was helium with a constant flow of 1 mL min<sup>-1</sup> (mean velocity 36 cm/s). The mass spectrometer was operated in scan mode (35–550 amu). Identification of volatile compounds was achieved comparing the GC retention times and mass spectra with those, when available, of the pure standard compounds. All mass spectra were also compared with the data system library (NIST 98). Quantification of samples was conducted by the external standard method following the same sampling procedure as that for on-site samples.

Experimental design and statistical analysis

In order to be able to relate the dependent (VOCs) and independent variables (moisture and aeration) with the minimum possible number of experiments, a two level, full factorial design was used [13]. These levels are called "high" and "low" or "+1" and "-1", respectively. This experimental design (Table 2) enabled the construction of first-order polynomials in the independent variables and the identification of statistical significance in the variables was used. The polynomial model used of the following type:

$$Z = a_0 + \sum_{i=1}^{n} b_i X_{\text{ni}} + \sum_{i=1;j=1}^{n} d_i X_{\text{ni}} X_{nj} \quad (i < j)$$
(1)

where Z and  $X_{ni}$  denote dependent and normalized independent variables, respectively, and  $a_0$ ,  $b_i$ , and  $d_{ij}$  are unknown constants obtained from experimental data. Independent variables were normalized ( $X_n$ ) by using the following equation:

$$X_n = (X - X_{\rm med}) / [(X_{\rm max} - X_{\rm min})/2]$$
(2)

where X is the absolute value of the independent variable concerned,  $X_{\text{med}}$  is the average value of the variable and  $X_{\text{max}}$  and  $X_{\text{min}}$  are their maximum and minimum values, respectively.

To assess the relative influence of the selected independent variables (time, moisture and aeration) on each dependent variable (volatile organic compounds and temperature), the polynomial mathematical models were obtained

Table 2 Factorial design used in composting experiments

Reactor	Aeration, moisture level	Aeration $(L_{air} kg^{-1} min^{-1})$	Moisture (%)
1	-1, +1	0.050	70
2	+1, -1	0.300	40
3	+1, +1	0.300	70
4	-1, 0	0.050	55
5	+1, 0	0.300	55
6	0, -1	0.175	40
7	0, +1	0.175	70
8	0, 0	0.175	55

Levels of independent variables

df
14.5
14.5
14.5
14.5
14.5
14.5
14.5
14.5

**Table 3** Equations yielded for each dependent variable (mg  $kg^{-1} day^{-1}$  for VOCs)

Each value is the average of three samples, on a dry weight basis. Percentages with respect to organic matter content

 $r^2$ , F and df denote coefficient of determination, Fisher–Snedecor distribution and degrees of freedom respectively. The differences between the experimental values and those estimated by using the previous equations never exceeded 10–15 % of the former

t, a and m denote the normalized value of the operation time, aeration and moisture respectively, as independent variables

*LI* limonene, *BP*  $\beta$ -pinene, *2B* 2 butanone, *UN* undecane, *PH* phenol, *TO* toluene, *DDS* dimethyl-disulfide, *DS* dimethyl-sulfide as dependent variables

(Table 3) by substituting the values of the measured independent variables for each dependent variable and applying a polynomial model analysis. Each value used to obtain the equations is the average of three measurements. The independent variables used in the equations relating to both types of variables were those having a statistically significant coefficient (viz. those not exceeding a significance level of 0.05 in Student's *t* test and having a 95 % confidence interval excluding zero).

The moisture and aeration used in the factorial design were 40, 55 and 70 % for moisture, 0.05, 0.175 and 0.3  $L_{air} kg^{-1} min^{-1}$  for aeration (Table 2). The central combination for the experimental design was as follows: Aeration 0.175  $L_{air} kg^{-1} min^{-1}$  and moisture 55 %. Composting time was considered as an independent variable in the model. VOCs were considered as dependent variables.

# **Results and discussion**

# VOCs emitted in composting plants

The composting process is an aerobic, solid-state biological process consisting of a high-rate composting phase and a compost curing phase. The first phase is characterized by an intense microbial activity leading to the decomposition of the most biodegradable material, until the biological stability is reached. During this phase most of the compounds responsible for the odor are produced. The second phase is characterized by a slow degradation process and by the transformation of the more recalcitrant molecules into humic substances [14], and is also involves the emissions of lower compounds. During the biodegradation process of organic fraction of municipal waste in composting plants, many VOCs are emitted [5, 15]. These VOCs can be arranged into common chemical classes: aromatics, ketones, hydrocarbons, terpenes, alcohols and volatile fat acids [16].

Several techniques for quantifying the most important compounds responsible for compost odors are being developed [3, 17]. To identify and quantify the volatile compounds produced in the composting process, a technique coupling gas chromatography with mass spectrometry (GC-MS) is most frequently used [5, 8, 15]. With this method, several critical odorants have been found [15, 18] in MSW degradation. Most of the commons compounds emitted during the MSW composting process [3, 15-18] were measured in the present experiment, although some of these critical compounds were not detected due to the low presence of polymer components such as plastics (benzene derivates), rubber (styrene) and other liquid oils (linear hydrocarbons, naphthalene). Eight VOCs were selected because of their availability and high concentration in our conditions. Moreover, they are representative of some important classes of compounds with high odor impact [5]. The selected VOCs were: 2-butanone, toluene, limonene,  $\beta$ -pinene, undecane, phenol, dimethylsulfide and dimethyldisulfide.

# Temperature evolution

The three typical phases of composting (short initial mesophilic, thermophilic and second mesophilic) are reflected in the models from data acquired during the experiment (Fig. 2). Higher temperatures were observed under high aeration level-low moisture and low aeration level-high moisture reactors during the experiment with respect to medium aeration reactors. These reactors reached temperatures over 60 °C after 13 days of composting. It is known that the course of decomposition of organic matter is affected by the presence of an optimum free air space [11].

## Selected VOCs evolution

The presence of terpenes in MSW can be explained as products of vegetable matter biodegradation. Alkanes and aromatics were detected in unseeded mixed paper with food wastes [1]. Sulfides could be a result of anaerobic biological decomposition. These compounds were modeled



Fig. 2 Temperature evolution in composting processes

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to evaluate the relative influence of variables on the evolution of these compounds in the composting process. Terpenes were the most prevalent VOCs emitted in MSW composting facilities [4, 19]. Limonene (Fig. 3a) and  $\beta$ -pinene (Fig. 3b) were found to be at relatively high concentrations with respect to other VOCs. A progressive decrease in both compounds was observed for the different mixtures. The decrease was generally faster in the case of  $\beta$ -pinene (Fig. 3b). At the initial composting stages, high content for both compounds was observed under low moisture contents. Nevertheless, after 15 days of composting, concentration of both compounds was very low. Emissions of both compounds were more dependent on aeration than on moisture content.

Among ketones emitted during the composting, 2-butanone (Fig. 4a) could be the most important component [20] and it has been classified as one of the most significant odor-causing VOCs in composting processes [18, 19]. In general, 2-butanone decreased with time for all the mixtures and after 15 days of composting, levels of 2-butanone were almost negligible. When aeration was low, moisture content had no effect on 2-butanone emissions whereas at high aeration rate, emissions were higher at high moisture contents. Therefore, the decrease rate for this compound was greater at high than at medium–low moisture contents.

Undecane (Fig. 4b) is a degradation product found in composting process [2]. This compound increased during the termophilic phase in our study and then decreased to very low values at 30 days of composting in all the range of moistures and aeration tested. Higher values were found at high moisture and aeration rates. At low aeration rates, moisture content had no relative effect on the emissions of this compound, however at high aeration rates, moisture had great influence.



Fig. 3 Limonene (a) and  $\beta$ -pinene (b) variation as a function of time and aeration at three moisture contents



Fig. 4 2-Butanone (a) and undecane (b) variation as a function of time and aeration at three moisture contents



Fig. 5 Phenol (a) and toluene (b) variation as a function of time and aeration at three moisture contents

Phenol and toluene are often detected in relatively high concentrations in composting processes [21, 22]. The evolution of emitted phenol and toluene under the selected composting conditions is shown in Fig. 5a and b, respectively.

Toluene emissions were higher at the most active phase of the composting process. As it occurred for other compounds, emissions were higher at high aeration rates and high moisture contents. Particularly, the rate of aeration had a great influence on the emissions, because at high aeration rates, the emission values were still noticeable at the end of the experiment. However, values close to zero were found at low aeration rates. Values of phenol emissions decreased with composting time. Although emissions were lower for high moisture contents in the mixtures, the main factor regulating these emissions was aeration; higher values were found at high aeration rates. At the end of the process similar values were found for all the mixtures, depending on the aeration rates.

The evolution of emitted organic sulphur compounds (dimethyl disulfide and dimethyl sulphide) is shown in Fig. 6a, b. At the beginning of the process an increment in emitted dimethyl disulfide (Fig. 6a) was measured that could be attributed to the rise in temperature, which indicates that the microorganisms were degrading the organic matter from the waste and a decrease in oxygen could be (a)

0.0014

0.0012

0.0010

0.0008

0.0006

0.0004

0.0002

0.0000

-1.0

-0.5

Time (0 (-1) to 36 (+1) days) 0.0

dimethyldisulfide (ppm<sub>v</sub>)

Fig. 6 Dimethyldisufide (a) and dimetilsulfide (b) variation as a function of time and aeration at three moisture contents

Aeration (0.05(-1)) 0.0

1.0

1.0

0.30<sup>(+1)Lairkg</sup>

Medium moisture con

deduced. Under these conditions, higher values under medium aeration levels were found. The volatile organic sulphur compounds produced from anaerobic conditions in composting piles due to either incomplete or insufficient aeration were mainly emitted during the thermophilic stage [17, 23, 24]. After the thermophilic stage, a progressive descent was found and negligible values (negative values in the modeling) were detected at the end of composting.

In the case of the dimethyl sulfide the maximum values were detected at the beginning of the process and after that a decrease was found.

In general both compounds were more dependent on the aeration than on the moisture contents of the mixtures.

#### Conclusions

The highest emissions of VOCs were in the early stages of the MSW composting process (initial and thermophilic phases). At the end of the process, all the conditions tested lead to very low concentrations of emitted compounds.

Among the independent variables, aeration rate had a strong effect on VOCs emissions. High aeration rates  $(0.300 L_{air} kg^{-1} min^{-1})$  caused normally high emissions of all selected compounds in the early stages of the composting process whereas low aeration rates (0.05  $L_{air} kg^{-1}$ min<sup>-1</sup>) could cause anaerobiosis problems and generation of organic sulphur compounds. Therefore, ideal conditions for minimizing emissions, without anaerobiosis, could be  $0.175 L_{air} kg^{-1} min^{-1}$ .

The effect of the moisture is dependent upon the studied compound in the MSW composting process. Consequently, a medium moisture value (55 %) could be a suitable balance to control compound emissions.

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1.0 1.0

Aeration (0.05 (-1)

0.30 (+1) Lair

# References

8.0e-4

6.0e-4

4 0e-4

2.0e-4

0.0

-0.5

 $T_{im_{\Theta}}(0\ (-1)\ to\ 36\ (+1)\ days)$ 0.0

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