DOI 10.1016/j.cej.2016.11.026

Characterization of odorous compounds and odor load in indoor air of modern complex MBT facilities.

J. Colón[a], C. Alvarez[b], M. Vinot[b], F.J. Lafuente[a], S. Ponsá[a], A. Sánchez[a] and D. Gabriel[a,*]

[a] Department of Chemical, Biological and Environmental Engineering, Universitat Autònoma de Barcelona, 08193 Barcelona, Spain
[b] I+D+i Department, URBASER S.A., 28031 Madrid, Spain

* Corresponding author:

David Gabriel

Escola d'Enginyeria

Departament d'Enginyeria Química, Biològica i Ambiental

Universitat Autònoma de Barcelona

Bellaterra, 08193-Barcelona (Spain)

Email address: david.gabriel@uab.cat

Abstract

Gaseous emissions and chemical compounds responsible for odor nuisance are the most common social concerns arising from modern municipal mechanical-biological waste treatment (MBT) facilities. Regarding to this, an inventory of indoor concentrations of hydrogen sulfide and volatile organic compounds (VOCs) along with odor analyses were carried out at three different full-scale MBT facilities. 48-hour profiles of total volatile organic compounds (tVOCs) and hydrogen sulfide were performed in selected areas (reception warehouse, pretreatment, anaerobic digestion and composting areas) and a complete gases and odor characterization were performed at two selected moments of the day according to maximum and minimum tVOCs concentrations, which corresponded to day/night variations. Terpenoids, aromatic hydrocarbons and aliphatic hydrocarbons were the families of VOCs more often detected. The average percentage of contribution of these three VOCs families was 32, 21 and 24 %, respectively, while the average percentage of contribution of other VOCs families ranged from 0.2 to 5.5 %. A multiple regression method was developed as a simple tool for odor modeling and prediction, showing that 98.5% ($p<0.001$) of the variance in odor concentration could be explained by the concentrations of hydrogen sulfide and tVOCs. Results obtained suggested that optimization of indoor ventilation systems and, concomitantly, operational costs of MBT facilities was possible in certain locations where ventilation could be reduced up to 20-25 % during night hours.

Keywords: municipal solid waste, MBT facilities, hydrogen sulfide, VOC, odor.

1. Introduction

Every year, about 2 billion tons of solid waste - including hazardous waste - are produced in the EU Member States. According to the European Environment Agency, the EU member states generate 88 million tons a year of biodegradable organic waste material (food waste, garden and public parks waste) [1]. The average citizen therefore generates 150 kg/year of biodegradable organic waste. The Landfill Directive (1999/31/EC) forces the Member States to reduce by 2016 (some countries by 2020) the amount of biodegradable municipal waste disposed to landfills without treatment to 35% of 1995 levels. In this scenario, Mechanical Biological Treatment facilities (MBT), which main goal is to reduce the biodegradable organic matter content and stabilize wastes by a combination of mechanical and biological processes, have received special attention from the European authorities [2]. Directive 2008/98/EC requires that waste has to be managed without endangering human health and harming the environment; and, in particular, without risk to water, air, soil, plants or animals; without causing a nuisance through noise or odors; and without adversely affecting the countryside or places of special interest [3].

Although the main objective of MBT facilities is to reduce the environmental impact of organic solid wastes, there are unavoidable environmental and social concerns arising from MBT plants. Gaseous emissions and chemical compounds responsible for odor nuisance are the most common. Gaseous emissions in MBT facilities are typically generated by the decomposition of nitrogen- and sulfur-based compounds and a wide range of volatile organic compounds (VOCs) [4]. VOCs constitute the main group of odorants emitted from MBTs. Ketones, alkanes, alkenes, alcohols, organic acids, terpenes and organic sulfur compounds are among the VOCs commonly reported [5,6].

While odors in areas close to MBT facilities can be eliminated or at least significantly reduced by means of end-of-pipe gas treatment technologies [7–9], personnel at these facilities undergo an inevitable exposure to VOCs [10] and other toxic compounds such as ammonia and hydrogen sulfide. Although numerous VOCs have not been classified as carcinogenic agents by the International Agency for Research on Cancer (IARC), many of them have an important toxic, non-carcinogenic, potential. Among the adverse effects of VOCs, odorants impact must be also included, as can cause diverse indirect health effects such as nauseas and vomits, reactions of hypersensitivity, and even alterations in the respiratory model. Nevertheless, systemic toxic effects of VOCs are relevant. Among these, renal, hematological, neurological and hepatic alterations, as well as mucosal irritations are the most common [10]. Once in the atmosphere, VOCs participate in photochemical reactions producing photochemical oxidants.

Threshold Limit Value-Time Weighted Average (TLV-TWA, 8 h) and Threshold Limit Value-Short term exposure limit (TLV-STEL, 15 minutes) are reported for several gaseous compounds emitted during organic wastes treatment [11]. The current standard for hydrogen sulfide reported by the Association Advancing Occupational and Environmental Health (~~AGGIH~~ACGIH) is a TLV-TWA of 1 ppmv and a TLV-STEL of 5 ppmv for short-term exposures, if no other measurable exposure occurs [11]. The Spanish legislation (INSHT) establishes a criteria of 5 ppmv as TLV-TWA and a maximum allowable peak of 10 ppmv for short periods of less than 10 minutes [12]. Regarding VOCs, several authors [10,13–15] have pointed out that the current exposure level to VOCs is lower than the maximum recommended threshold. Eitzer et al. [4] reported that even the highest concentrations from compost piles remain well-below the exposure guidelines, in most cases by several orders of magnitude. The fact that these worst cases still remain below the workplace air exposure limits indicates that these compounds, while present and of concern, do not pose a major health risk to workers at these facilities.

There are a large number of publications in relation to odors, VOCs and other gaseous emissions in waste treatment plants. However, most of these studies are focused on the emission of these compounds from processing stages such as those focused on exhaust gases coming from composting [4,16–18] anaerobic digestion [19] or landfills [20,21]. However, studies on indoor air quality in MBT facilities are relatively scarce [22–25] and can have a huge impact on both economics and safety and health issues related to waste management.

Health and odor control by means of air renewal inside the working place as well as exhaust gases treatment processes are the most energy consuming operations in a MBT facility. Usually, the operational costs related to air renewal inside the working places ranges from 30 to 60 % of the total operational costs [26]. Energy consumptions ranging from 472 to 872 MJ per ton of inlet waste have been reported during the treatment of organic wastes [27]. Operational costs of such plants are often in the order of 40–150 euros per ton of inlet waste [28–30]. Due to the high operational costs of odor control, any action related to energy optimization in ventilation systems would have a major impact in the final economical balance of MBT plants.

~~Although there are many studies related to VOCs and other gaseous emissions in waste treatment facilities, most of them are focused on exhaust gases from specific processing stages such as composting tunnels, biofilters, etc.~~ The aim of this study was to provide pollutant and odor inventories (including hydrogen sulfide and VOCs) of indoor air in selected areas from three different full-scale MBT facilities. Specifically, this work is focused on determining day/night variations in the concentration of selected compounds. Moreover, optimization of indoor air renewal is proposed, thus reducing the energy consumption and operational costs without compromising workers safety and odor exposure. ~~This study sets up the baseline for the management and improvement of odor control and indoor air ventilation at MBT facilities. In any case, further research is warranted to complement the results of this study.~~

2. Material and Methods

2.1. MBT facilities studied and sampling locations

Three MBT facilities located in Catalonia (Spain) treating source-separated organic fraction of municipal solid wastes (OFMSW) and mixed municipal solid wastes (MSW) in independent lines were studied. The main characteristics of each facility are shown in Table 1.

- MBT 1: Mixed MSW and OFMSW are treated separately in two independent lines. The MSW line has a waste treatment capacity of 160,000 tons/year and the source-selected OFMSW line has a treatment capacity of 100,000 tons/year. Four typical locations were selected as sampling points at MBT 1: 1. Reception warehouse, 2. Pretreatment area, 3. Anaerobic digestion area (which includes the recirculation/mixing of digested sludge with OFMSW and the solid-liquid separation processes) and 4. Composting hall area (which includes mixing the wastes with the bulking agent process and the filling and emptying of the composting tunnels). Locations 1, 2 and 4 are common for both MSW and OFMSW treatment lines, location 4 is related only to OFMSW treatment.
- MBT 2: Mixed MSW and OFMSW are treated in this plant. MSW and OFMSW are treated separately in two independent lines. The MSW line has a waste treatment capacity of 155,000 tons/year and the source-selected OFMSW line has a waste treatment capacity of 75,000 tons/year. Two selected locations were

chosen as sampling points at MBT 2: 1. Anaerobic digestion area (which includes the recirculation/mixing of digested sludge with OFMSW and the solid-liquid separation processes) and 2. Composting hall area (which includes mixing the wastes with the bulking agent process and the filling and emptying of the composting tunnels and it is common for both MSW and OFMSW treatment lines).

- MBT 3: Only mixed MSW is treated in this plant. The MSW line has a waste treatment capacity of 150,000 tons/year. One selected location (pretreatment area) was chosen as sampling point at MBT 3.

These MBT facilities correspond to typical configurations found at any European country. Areas were selected according to their importance in the plant in terms of gaseous emissions and odor generation potential. All the sampling points were located in exhaust pipes collecting the air of the buildings before any gas treatment operation.

2.2. Sample collection and measurement

Between October 2013 and February 2014, gases and odor emissions from the above-mentioned MBT plants and locations were characterized. Firstly, a complete 48-hour total VOCs (tVOCs) and hydrogen sulfide profiles were carried out in selected areas; these areas were the reception warehouse and the pretreatment area in MBT1 and the anaerobic digestion and the composting areas in MBT2. Secondly, two punctual samples were collected at each sampling point described in section 2.1 in a single day according to maximum and minimum tVOCs concentrations measured in the tVOCs profiles. Both maximum and minimum concentrations corresponded to day and night load variations, respectively. In all cases, day samples were collected between 12.00 pm and 19.00 pm while night samples were collected between 03.00 am and 05.00 am. The average temperature during day and night conditions was 22ºC and 19ºC, respectively.

2.2.1. In-situ measurements

At each sampling location, tVOCs and H_2S as well as temperature and relative humidity were analyzed in-situ. These gases were selected because of their importance in potential odor generation compared with other gases emitted in MBT plants (e.g. N_2O, CH_4, NH_3, CO_2). tVOCs measurements were carried out using a miniRAE 3000 PID equipped with a 9.8 eV lamp (RAE systems, USA) with a COVs detection range from 0 to 1000 ppmv_{eq} isobutylene (0.1 ppmv increments). A 9.8 eV lamp was selected because the ammonia ionization energy is higher than that of the lamp photons can measure. Thus, ammonia interferences are avoided. Hydrogen sulfide was analyzed in situ using an Ibrid MX6 multigas sensor (Industrial Scientific, USA) with a hydrogen sulfide detection range from 0 to 500 ppmv (0.1 ppmv increments). No ammonia reliable measurements were obtained due to analytical limitations with the ammonia electrochemical sensor used. A portable PT100 (Oakton Instruments, USA) was used for temperature measurements while a Testo 605-H1 thermo hygrometer was used for relative humidity and dew point assessment during gas sampling.

2.2.2. GC/MS sampling and analysis

Gas samples from sampling points were also collected in 10 L Tedlar bags (SKC Inc., USA) and analyzed by SPME/GC–MS the same day they were collected. A portable SKC 224-PMCTX8 Air Sampler Pump was used to collect samples. Samples were transferred into 0.250 L Supelco gas sampling bulbs with Teflon and stopcock valves. According to Davoli et al. [31], deuterated p-xylene was used as internal standard (IS) by injecting in each bulb a total of 10 μL of a dilution of 2 μL of pure deuterated p-xylene (99.9% atom deuterated p-xylene, Sigma Aldrich) in 100 mL of pure methanol.

Samples were analyzed by SPME/GC–MS according to Scaglia et al. [14] using granulated activated carbon fibers supported in fiber holders for manual injection (Supelco, Bellefonte, USA). The fiber used was a bipolar fiber, with a 50/30 μm coating of Divinyl-benzene/Carboxen/Polydimethylsiloxane (DVB/Carboxen™/PDMS) StableFlex™ from Supelco Analytical (Bellefonte, PA, USA).

SPME fibers were preconditioned for 1–3 h at 250ºC. Pre-concentration was performed by letting the SPME fiber holders injected in the gas bulbs for 30 min. 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 μm. Carrier gas was helium at a flow rate of 0.8 mL min^{-1}. VOCs were desorbed by exposing the fiber in the GC injection port for 3 min at 250ºC. 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 50ºC, raised to 170ºC at a rate of 3ºC min^{-1} and, finally, to 230ºC at a rate of 8ºC min^{-1}. The transfer line to the mass spectrometer was maintained at 235ºC. 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.

Calibration was performed by analyzing a set of standards of representative compounds injected together with known amounts of the IS (Internal Standard) previously calibrated. Abundance ratios corresponded to the abundance response factors (IRF_{SC}) latter used to recalculate the actual concentration of the compound (C_{SC}) based on concentration of IS added to the sample (C_{IS}), and the actual response of both the IS (A_{IS}) and the selected compound (A_{SC}) (Eq. (1)):

$$C_{SC} = C_{IS} \cdot A_{SC} \cdot \frac{IRF_{SC}}{A_{IS}} \tag{1}$$

Limits of detection, determined applying a signal-to-noise ratio of 3, ranged from 0.1 to 10 ng for the different selected compounds.

2.2.3. Odor sampling and analysis

All air samples were analyzed in triplicate using 10 L bags made of disposable Nalophan™ film and Teflon™ for tubing. In order to avoid condensation inside the Nalophan™ bags, samples were pre-diluted with nitrogen (5.0 grade) using a GSP pre-dilution probe (Odournet, Germany).

The odor concentration of a gaseous sample of odorants was determined by presenting a panel of selected and screened human assessors with that sample, varying the concentration by diluting with odor-free gas. Using various dilutions factors, the dilution factor at the 50 % detection threshold can be determined. At the dilution factor, the odor concentration is 1 ou_E m^{-3} by definition, provided that a panel is selected with a group threshold equivalent to the agreed reference value of 40 ppbv of n-butanol. The odor concentration of the analyzed sample is then expressed as a multiple of the European Odor Units per cubic meter at the standard conditions for olfactometry [32]. Olfactometry analyses were performed by a certified external laboratory (Odournet S.L, Spain) according to the European standard for dynamic olfactometry (EN13725, 2003) with a TO8 instrument from the Odournet TO-series (Odournet, Germany) within 24 hours after sampling.

2.3. Statistical analysis

All statistical analyses were performed with SPSS statistical software (version 20) (SPSS, Chicago, IL). Linear multiple regression analysis was used to predict the odor units based on H_2S and tVOCs concentrations. The Durbin-Watson test was used to corroborate no first order linear autocorrelation in the multiple linear regression data. The semi-partial regression coefficient was used to express the specific portion of variance explained by a given independent variable (H_2S and tVOCs concentrations) in the multiple linear regression analysis.

3. Results and discussion

3.1. Gases and odor measurements

Figure 1 shows the tVOCs and H_2S profiles measured in four different areas. Figure 1a and 1b correspond to the reception warehouse and the pretreatment area of MBT1, respectively. Figure 1c and 1d correspond to the anaerobic digestion area and the composting area of MBT2, respectively. As seen in these figures, there is pronounced day/night variability in both tVOCs and H_2S concentrations. Concentrations during the day were considerably higher than those during the night, which is in accordance with the types of works carried out during different periods of the day. From 6.00 am to 22.00 pm, normal operations were carried out at MBT facilities (waste treatment) while cleaning and maintenance operations were performed from 22.00 pm to 06.00 am (no waste handled). To the best of our knowledge, no previous data have been reported regarding day/night variations of tVOCs and H_2S concentrations in real full-scale MBT facilities. Theses variations could have important economic implications for MBT facilities because although the overall gases concentrations decreases during the night, ventilation and their related costs are kept constant throughout the day.

Figure 2 shows the VOCs families distribution for all compounds identified qualitatively by SPME-GC/MS. Few changes were found regarding the detected compounds from one location to another and from day to night. Terpenoids, aromatic hydrocarbons and aliphatic hydrocarbons were the compounds more commonly detected. The average percent contribution of those three VOCs families was 32, 21 and 24 %, respectively, while the remaining average percentage contribution of all the other VOC families ranged from 0.2 to 5.5 %.

Table 2 shows the individual VOCs quantified at each sampling point while Table 3 shows all the detected compounds in this study. TLV-TWA and the odor threshold are also shown in Table 2, when available. Results obtained show that neither H_2S nor VOCs concentrations exceed the TLV-TWA, as it has been observed in previous studies conducted in similar facilities [4, 14, 15, 24]. On the other hand, odor thresholds were exceeded for several compounds in all sampling points, mainly hydrogen sulfide and a wide range of VOCs including ketones (2-pentanone), aldehydes (decanal), terpenoids (eucalyptol, limonene) and organosulfurs (dimethyl disulfide) (Table 2). In addition, some compounds in Table 3 that were not quantified are strong odorants and, most likely, also exceeded the odor threshold value when detected. For example some aldehydes, esters and acids compounds have low odor threshold limits; octanal and nonanal have an odor threshold limit of 0.17 and 0.53 ppbv, respectively [33]; ethyl pentanoate has an odor threshold limit of 0.11 ppbv [34]; while propanoic and butanoic acid have an odor threshold limit of 5.5 and 0.19 ppbv, respectively [34].

3.1.1. Reception Warehouse

The reception warehouse (Figure 1a), where trucks discharge OFMSW and MSW in a pit, shows a tVOCs concentration ranging from 6000 to 20000 ppbv_{eq} isobutylene and an H_2S concentration ranging from 0 to 4000 ppbv (well below the legal values reported in the Spanish legislation). As the OFMSW and MSW reception pits are not enclosed and the organic waste is present during day and night (also trucks discharge materials during day and night), gases are emitted constantly during all day; the only difference is due to the material manipulation during the day. This fact explains why although a day/night variation can be observed with a gradual concentration increase/decrease in tVOCs, this pattern is less clear than in the rest of the MBT studied areas. The gradual increase/decrease pattern shows that gases were slowly accumulated in the reception warehouse during daily hours because of the material movement from the reception warehouse to the pretreatment area. Passive emissions from the pit caused tVOCs concentrations to gradually decrease during the afternoon/night period. The punctual sampling (Table 2) in the reception warehouse shows an important decrease, between day and night measurements, in H_2S concentration (100 %). However, only a small decrease in tVOCs is observed (17 %). In relation to odor concentration a reduction of 64 % was measured, which can be related to the absence of H_2S during the night (see Eq. (2)).

3.1.2. Pretreatment area

The pretreatment area (Figure 1b) showed a maximum tVOCs concentrations ranging from 20000 to 30000 $ppbv_{eq}$ isobutylene during the afternoon (normal operational conditions) and a minimum concentration ranging from 2000 to 7000 $ppbv_{eq}$ during the night (mainly cleaning and maintenance operations are carried out). Thus, tVOCs concentration was reduced between 80 and 90%. Also, Figure 1b shows a sharp decrease in tVOCs concentrations, which means that after the end of the pretreatment operations (22.00 pm) the air renewal system was able to reduce the gaseous compounds concentration in a short period of time. The punctual sampling (Table 2) in both MBT1 and MBT3 pretreatment areas confirmed this pattern: a tVOCs reduction of 85 and 65 % was measured in MBT1 and MBT3, respectively. H_2S was neither detected in MBT1 nor in MBT3. Finally, odor measurements in both pretreatment areas showed an odor concentration reduction from 80 to 90% between day and night. Moreover, odor concentrations below 1000 ou_E m^{-3} (night concentrations) were the lowest detected in this study. The highest tVOCs concentrations were found in the pretreatment area of MBT1. This is in accordance with previous studies that found that in composting facilities the main sources of VOCs and odorous emissions were found during fresh waste handling and manipulation [23,35]. MBT3 was operating at half of its design capacity. Consequently, lower concentrations of gases were expected.

3.1.3. Anaerobic digestion area

The anaerobic digestion area of MBT2 also showed a variation pattern in tVOCs (Figure 1c) and H_2S. In MBT2, little differences were observed in tVOCs analysis during punctual sampling. On the contrary, concentrations of H_2S were much higher during the day (as reported in the 48 h profiles). It is evident from MBT2 samples that hydrogen sulfide plays an important role in the odor concentration. It has to be pointed out that in MBT2 anaerobic digestion area, exhausted air coming from centrifuges is directly sucked to a main duct (were the samples were taken), and in any case this exhaust air was released in the workspace (H_2S concentrations in indoor air were below the legal limits), this fact explains the high hydrogen sulfide and odor concentrations measured at this location,..

Regarding MBT1, the concentration of all gases analyzed was higher during the night, which can be explained because night samples were taken while the anaerobic reactor was being fed. Small increases in both hydrogen sulfide and tVOCs in the night sampling explain the large increase in the odor concentration (165%). However, since this operation was also carried out during the day, no differences between day and night were found in MBT1.

3.1.4. Composting area

Finally, the last studied location was the composing area. A novelty of this work is that the emissions analyzed corresponded to the composting hall area (mixing and filling/emptying operations) and not directly to the composting process (composting tunnels exhaust gases) in which many studies are focused on [27,18]. Similarly to the reception warehouse, the 48-hour tVOCs and H_2S profiles in MBT2 show a gradual increase/decrease pattern with tVOCs concentration ranging from 2500 to 16000 $ppbv_{eq}$ isobutylene and H_2S concentrations ranging from 500 to 3800 ppbv. Filling/emptying operations of the composting tunnels are carried out only during the day leading to higher concentrations in the composting hall. From 10 pm to 9 am, the tVOCs concentration was below 7000 $ppbv_{eq}$ and H_2S concentrations close to 500 ppbv. The punctual sampling (Table 2) in MBT2 composting area confirmed this pattern; a tVOCs reduction of 60 % was measured in MBT2 while the H_2S concentration was below the detection limit. Such reduction in gases emissions accounted for a reduction of 65 % in odor concentration. On the contrary, MBT1 showed a reduction in hydrogen sulfide and odor concentration ranging only between 25 and 30 %. The difference between MBT1 and MBT2 is explained by the different operational management in this area. While MBT2 is working as expected, overloading of MSW in MBTW1 lead to an accumulation of organic wastes waiting to be composted in the composting area and, concomitantly, to a continuous passive emission during both day and night.

3.2. Optimization of indoor ventilation systems

Results presented in this work suggest that air ventilation systems can be optimized in several locations of MBT plants. Data obtained from tVOCs profiles and isolated analyses suggested that reception warehouse together with pretreatment areas and composting areas were subjected to improvements.

As no previous data have been found on this subject, different approaches regarding to indoor ventilation optimization can be proposed. A very conservative approach based on tVOCs profiles could be as following: the ventilation will be reduced a 50 % when a decrease in tVOCs concentration achieves a value of 50 % from its average maximum (measured in a representative period of time). Under this premise, in the worst case scenario tVOCs concentration will never be higher than the actual maximum tVOCs concentrations measured, that in fact are lower than values proposed in European regulations. This approach assumes a linear relation between air renewal rate and tVOCs concentration. Table 4 shows the percentage of saved energy using this approach.

$$\%\ \mathrm{DIVR} = \frac{\mathrm{h\ d^{-1}\ with\ [tVOCs]<50\%\ of\ [tVOCs]_{max}}}{\mathrm{24h}} \times \mathrm{K} \times 100 \qquad (2)$$

where:

% DIVR: Daily indoor ventilation reduction (%)

h d^{-1} with [tVOCs] <50% of $[tVOCs]_{max}$: hours per day in which the tVOCs concentration ([tVOCs]) is equal or lower than the average maximum tVOCs concentration ($[tVOCs]_{max}$), (h).

K : ventilation reduction target in % (50% in our case).

As a theoretical exercise, operational costs savings can be estimated. Economopoulus [29] reported operational costs of 40 €/ton of MSW for an aerobic MBT plant treating 200,000 tons MSW/year. Assuming that 45% of operational costs are related with indoor ventilation systems (ventilation costs ranges from 30 to 60%), ventilation could be reduced up to 20-25 % (Table 4). Thus, an aerobic MBT plant treating 200,000 tons MSW/year could save up to 720,000 - 900,000 €/year by optimizing the indoor ventilation system. Undoubtedly, large variability will be found from one plant to another, specially regarding the efficiency of indoor ventilation systems as well as particular management operations. Therefore, specific studies must be carried out at each facility before implementing any change in those operations. Many other approaches could be done. For example, setting an upper tVOCs threshold limit and implementing an on/off control system or even more sophisticated control strategies based on the measurements of different analyzed gases/odor concentrations Moreover, indoor air optimization should take into account local regulations that require a minimum frequency of indoor air renewal. For instance, a minimum of three air renewals per hour are recommended in MBT facilities in the studied area. In any case, in view of the potential savings related to indoor ventilation optimization further research is needed on this field. A new patent [26] has recently been published setting up optimization criteria for ventilation optimization and proposing different ventilation control strategies in MBT facilities. It is also important to remark the environmental implications of energy savings in ventilation of MBT facilities, as reported in Colón et al. [27], the higher energy consumption was the main drawback of MBT compared with low-end composting technologies without gas treatment (e.g. turned windrow composting plants). From an environmental point of view, the reduction of energy costs in enclosed buildings ventilation of MBT will favor even more high-end treatment technologies compared with simpler ones.

3.3. Odor modeling

Odor measurements and odor control are of great interest for plant managers but it is difficult to implement this analysis as a routine analysis. Despite the advances in instrumental detection technology, its application cannot yet stand alone in describing the complicated nature of odorous pollution. For instance, the perception of odor strength becomes ambiguous, if multiple odorants coexist, due to the possible occurrences of synergistic escalation, neutralization, antagonistic interference, etc. [36–38]. Gases whose concentration is above detection odor thresholds generally make a significant contribution to the overall perceived concentration [39]. On the other hand, olfactometric analyses are expensive, require complicated sampling campaigns and must be conducted by a sufficient number of panelists. Therefore, it is difficult to perform routine olfactometric analysis in MBT plants. Modeling odor concentrations using simple predictor variables obtained directly from sensors commonly used in MBT facilities would improve odor control and could be used as a tool for optimization of ventilation systems in selected areas of MBT facilities. For safety reasons, plants workers usually have multigas sensors with hydrogen sulfide sensors, and most MBT plants have PID/FID detectors for routine analysis. The main objective of this section was to select a subset of variables that provides the best prediction equation for modeling odor concentrations. A linear multiple regression analysis was used based on hydrogen sulfide and tVOCs concentrations, which had a significant effect on odor concentration ($p < 0.05$). Hence, the model explaining the relationship between odor concentration and concentrations of hydrogen sulfide and tVOCs was expressed as

$$ou_E = -1721 + 3714[H_2S] + 467[tVOCs];\ R^2 = 0.985 \quad (3)$$

Where:

ou_E: European odor units (ou_E m^{-3})

[H_2S]: hydrogen sulfide concentration (ppmv)

[VOCs]: total VOCs concentration ($ppmv_{eq}$ isobutylene)

The R^2 for the correlation showed that 98.5% ($p<0.001$) of the variance in odor concentration could be explained by the concentrations of hydrogen sulfide and tVOCs, the coefficient of both predictors were significant ($p<0.001$). Predictor H_2S showed that 45 % of the variance could be uniquely explained by the hydrogen sulfide concentration, which fits well with Blanes-Vidal et al. [40] results who reported hydrogen sulfide as the main parameter explaining odor concentrations (68% of the variance) when analyzing odors from swine manure treatment facility. On the contrary, tVOCs alone only explained 6 % of the variance. Finally, in combination both predictors explained the remaining 48 % of the variance. Figure 3 indicates that the results obtained from the experimental study are in accordance to those obtained from the proposed model. It is noteworthy that according to EN ISO 17025 [41] the uncertainty of odor measurements depends on the number of replicates, using 3 replicates (as is the case of this study) the olfactometric results of a known sample of 1000 uo_E m^{-3} can range from 600 to 1600 uo_E m^{-3}, so an uncertainty of almost 50 % should be expected at low odor concentrations.

Although more data is needed in order to validate the model, VOCs detected when analyzing municipal organic wastes were fairly constant between different facilities

[4,23,42], which points out at effectively using the tVOCs concentration from different sites. However, this model could not be useful when analyzing other kind of wastes. Different VOCs distributions with different odor patterns have been found when analyzing manures or other wastes [40]. Thus, a new model parameterization should be performed.

4. Conclusions

Total VOCs and H_2S profiles during a 48-hours period have been performed for the first time in MBT facilities. Results showed a clear pattern in tVOCs concentration with day concentrations higher than night concentrations, especially in pretreatment areas.

More than sixty chemical compounds were determined qualitatively by SPME-GC/MS. Terpenoids, aromatic hydrocarbons and aliphatic hydrocarbons showed the higher concentrations. However, esters, carboxylic acids, organosulfurs and aldehydes contributed in a greater extent to odor units in all studied locations of the facilities.

Results obtained from tVOCs and H_2S profiles as well as punctual analyses suggest that optimization of indoor ventilation systems is possible in certain locations. Ventilation could be reduced up to 20-25 % in the reception warehouse, the pretreatment area and the composting area.

Finally, a multiple regression method with tVOCs and H2S as variables has been applied for odor modeling. The R^2 for the correlation showed that 98.5% ($p<0.001$) of the variance in odor concentration could be explained by the concentrations of H2S and tVOCs as variables.

Although sampling campaigns did cover neither all seasonal variations nor all areas in each MBT facility, the data provided in this work is considered representative of typical Mediterranean MBT facilities and sets up the baseline for future odor and ventilation management schemes. This study sets up the baseline for the management and improvement of odor control and indoor air ventilation at MBT facilities. In any case, further research is warranted to complement the results of this study.~~Future work will be carried out to~~ by ~~generate~~ generating more datasets to increase the robustness of the models and optimization approaches presented in this work.

5. Acknowledgments

The authors would like to thank the managers of the MBT facilities for their valued field assistance and support during the measurement period. URBASER S.A financially supported this study.

6. References

[1] European Environmental Agency, Diverting waste from landfill, (2009).

[2] S. Ponsá, T. Gea, L. Alerm, J. Cerezo, A. Sánchez, Comparison of aerobic and anaerobic stability indices through a MSW biological treatment process, Waste Manag. 28 (2008) 2735–2742.

[3] European Commission, Directive 2008/98/EC of the European Parliamnt and of the Council, 2008.

[4] B. Eitzer, Emissions of volatile organic chemicals from municipal solid waste composting facilities, Environ. Sci. Technol. 29 (1995) 896–902.

[5] E. Smet, H. Van Langenhove, I. De Bo, The emission of volatile compounds during the aerobic and the combined anaerobic/aerobic composting of biowaste, Atmos. Environ. 33 (1999) 1295–1303.

[6] B.F. Staley, F. Xu, S.J. Cowie, M. a Barlaz, G.R. Hater, Release of trace organic compounds during the decomposition of municipal solid waste components., Environ. Sci. Technol. 40 (2006) 5984–5991.

[7] D. Gabriel, J.P. Maestre, L. Martín, X. Gamisans, J. Lafuente, Characterisation and performance of coconut fibre as packing material in the removal of ammonia in gas-phase biofilters, Biosyst. Eng. 97 (2007) 481–490.

[8] A. Dorado, S. Husni, G. Pascual, C. Puigdellivol, D. Gabriel, Characterization and treatment of compost maturation waste gases in a municipal solid waste treatment facility, Waste Manage. 34 (2014) 344-351.

[9] J. Colón, J. Martínez-Blanco, X. Gabarell, J. Rieradevall, X. Font, A. Artola, A. Sánchez, Performance of an industrial biofilter from a composting plant in the removal of ammonia and VOCs after material replacement, J. Chem. Technol. Biotechnol. 84 (2009) 1111–1117.

[10] J.L. Domingo, M. Nadal, Domestic waste composting facilities: a review of human health risks., Environ. Int. 35 (2009) 382–389.

[11] ACGIH, 2012 TLVs and BEIs: Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, Cincinnati, Ohio, 2012.

[12] INSHT, Límites de Exposición Profesional para Agentes Químicos en España, 2014.

[13] M. Nadal, I. Inza, M. Schuhmacher, M.J. Figueras, J.L. Domingo, Health risks of the occupational exposure to microbiological and chemical pollutants in a municipal waste organic fraction treatment plant., Int. J. Hyg. Environ. Health. 212 (2009) 661–669.

[14] B. Scaglia, V. Orzi, a Artola, X. Font, E. Davoli, a Sanchez, F. Adani, Odours and volatile organic compounds emitted from municipal solid waste at different stage of decomposition and relationship with biological stability., Bioresour. Technol. 102 (2011) 4638–4645.

[15] E. Gallego, X. Roca, J.F. Perales, X. Guardino, Determining indoor air quality and identifying the origin of odour episodes in indoor environments, J. Environ. Sci. 21 (2009) 333–339.

[16] S. Sironi, L. Capelli, P. Céntola, R. Del Rosso, M. Il Grande, Odour emission factors for the prediction of odour emissions from plants for the mechanical and biological treatment of MSW, Atmos. Environ. 40 (2006) 7632–7643.

[17] J. Colón, E. Cadena, M. Pognani, R. Barrena, A. Sánchez, X. Font, A. Artola, Determination of the energy and environmental burdens associated with the biological treatment of source-separated municipal solid wastes, Energy Environ. Sci. 5 (2012) 5731-5741.

[18] C. Maulini-Duran, A. Artola, X. Font, A. Sánchez, Gaseous emissions in municipal wastes composting: Effect of the bulking agent, Bioresour. Technol. 172 (2014) 260–268.

[19] D. Papurello, C. Soukoulis, E. Schuhfried, L. Cappellin, F. Gasperi, S. Silvestri, M. Santarelli, F. Biasioli, Monitoring of volatile compound emissions during dry anaerobic digestion of the Organic Fraction of Municipal Solid Waste by Proton Transfer Reaction Time-of-Flight Mass Spectrometry, Bioresour. Technol. 126 (2012) 254–265.

[20] F. Lucernoni, F. Tapparo, L. Capelli, S. Sironi, Evaluation of an Odour Emission Factor (OEF) to estimate odour emissions from landfill surfaces, Atmos. Environ. 144 (2016) 87–99.

[21] Y. Liu, W. Lu, H. Guo, Z. Ming, C. Wang, S. Xu, Y. Liu, H. Wang, Aromatic compound emissions from municipal solid waste landfill: Emission factors and their impact on air pollution, Atmos. Environ. 139 (2016) 205–213.

[22] E. Gallego, F.J. Roca, J.F. Perales, G. Sánchez, Reducing the Indoor Odorous Charge in Waste Treatment Facilities, Int. J. Waste Resour. 4 (2014) 1–5.

[23] E. Gallego, F.J. Roca, J.F. Perales, G. Sánchez, P. Esplugas, Characterization and determination of the odorous charge in the indoor air of a waste treatment facility through the evaluation of volatile organic compounds (VOCs) using TD-GC/MS, Waste Manag. 32 (2012) 2469–2481.

[24] J. Lehtinen, O. Tolvanen, U. Nivukoski, A. Veijanen, K. Hänninen, Occupational

hygiene in terms of volatile organic compounds (VOCs) and bioaerosols at two solid waste management plants in Finland, Waste Manag. 33 (2013) 964–973.

[25] J.L. Domingo, M. Nadal, Domestic waste composting facilities: A review of human health risks, Environ. Int. 35 (2009) 382–389.

[26] F. Giménez, C. Jordà, G. Buguña, L. Sancho, S. Ferrer, P. Salas, M. Álvarez Requena, PATENTE DE INVENCIÓN B1 Título: Sistema de regulación de caudales de aire de ventilación en naves de instalaciones de tratamiento de residuos sólidos urbanos y procedimiento de regulación, 2016.

[27] J. Colón, E. Cadena, M. Pognani, R. Barrena, A. Sánchez, X. Font, A. Artola, Determination of the energy and environmental burdens associated with the biological treatment of source-separated Municipal Solid Wastes, Energy Environ. Sci. 5 (2012) 5731–5741.

[28] R. Lornage, E. Redon, T. Lagier, I. Hébé, J. Carré, Performance of a low cost MBT prior to landfilling: Study of the biological treatment of size reduced MSW without mechanical sorting, Waste Manag. 27 (2007) 1755–1764.

[29] A.P. Economopoulos, Technoeconomic aspects of alternative municipal solid wastes treatment methods, Waste Manag. 30 (2010) 707–715.

[30] T. Jamasb, R. Nepal, Issues and options in waste management: A social cost–benefit analysis of waste-to-energy in the UK, Resour. Conserv. Recycl. 54 (2010) 1341–1352.

[31] E. Davoli, M.L. Gangai, L. Morselli, D. Tonelli, Characterisation of odorants emissions from landfills by SPME and GC/MS, Chemosphere. 51 (2003) 357–368.

[32] F.B. Frechen, Odours and VOCs: Measurement, Regulation and Control Techniques (2009). Kassel University Press.

[33] J.E. Cometto-Muñiz, M.H. Abraham, Odor detection by humans of lineal aliphatic aldehydes and helional as gauged by dose-response functions, Chem. Senses. 35 (2010) 289–299.

[34] Y. Nagata, Measurement of Odor Threshold by Triangle Odor Bag Method, in: Odor Meas. Rev. (2003)118–127.

[35] M. Schlegelmilch, J. Streese, W. Biedermann, T. Herold, R. Stegmann, Odour control at biowaste composting facilities., Waste Manag. 25 (2005) 917–927.

[36] M.Q. Patterson, J.C. Stevens, W.S. Cain, J.E. Cometto-Muñiz, Detection thresholds for an olfactory mixture and its three constituent compounds, Chem. Senses. 18 (1993) 723–734.

[37] S.S. Schiffman, J.L. Bennett, J.H. Raymer, Quantification of odors and odorants from swine operations in North Carolina, Agric. For. Meteorol. 108 (2001) 213–240.

[38] K.H. Kim, S.Y. Park, A comparative analysis of malodor samples between direct (olfactometry) and indirect (instrumental) methods, Atmos. Environ. 42 (2008) 5061–5070.

[39] W.S. Cain, F.T. Schiet, M.J. Olsson, R.A. de Wijk, Comparison of Models of Odor Interaction, Chem. Senses. 20 (1995) 625–637.

[40] V. Blanes-Vidal, M.N. Hansen, A.P.S. Adamsen, A. Feilberg, S.O. Petersen,

B.B. Jensen, Characterization of odor released during handling of swine slurry: Part I. Relationship between odorants and perceived odor concentrations, Atmos. Environ. 43 (2009) 2997–3005.

[41] UNE-EN ISO/IEC 17025:2005. Conformity assessment. General requirements for the competence of testing and calibration laboratories

[42] R. Chiriac, J. Carre, Y. Perrodin, L. Fine, J.M. Letoffe, Characterisation of VOCs emitted by open cells receiving municipal solid waste, J. Hazard. Mater. 149 (2007) 249–263.

Odor units predicted value (ou m^{-3})

able 1. Main characteristics of the studied industrial MBT facilities

	MBT1	MBT 2	MBT 3
Waste fraction treated	MSW (160,000 t/y) OFMSW (100,000 t/y) Source-selected packaging (27,500 t/y)	MSW (160,000 t/y) OFMSW (85,000 t/y)	MSW (150,000 t/y)
Dry pretreatment	OFMSW: manual separation + trommel + magnetic separator MSW: manual separation + trommel + ballistic separator + magnetic separator + optic separator	OFMSW: trommel + ballistic separator + magnetic separator + optic separator MSW: trommel + BRS* + trommel + ballistic separator + magnetic separator + optic separator	MSW: trommel + ballistic separator + magnetic separator
Wet pretreatment	/	OFMSW: pulper + hydrocyclon	/
Decomposition phase	MSW: composting tunnels OFMSW: dry anaerobic digestion	MSW: composting tunnels OFMSW: wet anaerobic digestion	MSW: Sorain Cecchini trenches
Curing phase	MSW: comosting trench OFMSW: composting tunnels	MSW: composting tunnels OFMSW: composting tunnels	
Exhaust gas tretament	Wet scrubber + biofilter	Wet scrubber + biofilter	Wet scrubber + biofilter

*Rotating biostabilizers

Table 2. Gaseous and odor characterization of isolated analysis performed at selected sampling points. Odors thresholds taken from Nagata [34], TLV-TWA concentrations taken from NIOSH.

	Reception Warehouse		Pretreatment Area				Anaerobic digestion Area				Composting Area				Odor threshold	TLV-TWA
	MBT 1		MBT 1		MBT 3		MBT 1		MBT 2		MBT 1		MBT 2			
	day	night	day	night	day	night	day	night	day	night	day	night	day	night		
Temperature (°C)	17.9	15.6	20.5	16.6	17.3	18.6	18.6	14.2	28.3	24.6	24.7	23.1	27.1	23.4		
Humidity (%)	57.3	59.6	62.5	57.8	48.6	45.1	57.5	58.4	52.1	50.3	95.2	96.7	49.3	43.6		
H_2S (ppmv)	0.5	-	-	-	-	-	0.9	1.1	13.3	2.1	0.8	0.6	0.9	-	0.0004	10-20
tVOCs (ppmv$_{eq}$ isobutylene)	13.2	11	31.2	4.6	10.3	3.6	18.6	23.4	31.7	27.1	10.4	4.2	17.3	7		
Toluene (mg m^{-3})	0.43	0.32	0.76	0.21	0.38	0.30	-	-	2.95	2.05	0.38	0.22	0.72	0.14	3.80	192
p-Xylene (mg m^{-3})	0.21	0.09	0.76	0.16	0.51	0.13	-	0.29	1.29	0.57	0.19	0.10	0.19	-	0.70	221
o-Xylene (mg m^{-3})	0.05	0.02	0.23	0.03	0.14	0.04	-	-	-	-	0.07	0.05	-	-	0.70	221
Styrene (mg m^{-3})	-	-	-	-	-	-	-	-	0.60	0.18	-	-	0.12	-	0.01	86
2-pentanone (mg m^{-3})	-	0.004	-	-	-	-	-	-	-	-	-	-	-	0.01	0.0053	704
α-Pinene (mg m^{-3})	0.12	0.09	0.44	0.16	-	0.10	0.58	0.66	1.13	0.42	0.13	0.02	0.29	0.09	0.23	113
β-Pinene (mg m^{-3})	0.14	1.23	-	-	-	-	0.65	0.76	-	-	-	-	0.62	-	8.90	113
Limonene (mg m^{-3})	0.86	0.73	2.22	0.02	1.55	0.71	3.67	4.09	9.69	2.96	1.87	0.01	3.11	1.23	1.70	110
Eucalyptol (mg m^{-3})	0.01	-	-	-	-	-	0.07	0.05	-	0.05	-	-	0.04	-	0.0075	-
Decane (mg m^{-3})	0.34	0.08	1.12	0.40	0.60	0.14	-	1.10	-	0.53	0.47	0.17	0.60	0.19	11.30	-
Pyridine (mg m^{-3})	-	-	-	-	-	-	-	-	-	-	-	-	0.002	-	6.47	3.2
Decanal (mg m^{-3})	-	-	-	-	0.003	0.005	-	-	0.03	-	-	-	0.03	-	0.0026	-
Dimethyl disulfide (mg m^{-3})	-	-	0.07	0.04	-	-	-	-	-	-	0.27	-	0.11	0.02	0.0085	1.9
Odor units (ou$_E$/m^3)	6379 ± 584	2277 ± 395	12358 ± 817	927 ± 81	2017 ± 803	387 ± 107	7877 ± 1244	13012 ± 6865	61954 ± 17230	24678 ± 6669	6339 ± 1895	4397 ± 254	6531 ± 1581	2276 ± 396		

Table 2~~3~~. List of all VOCs detected by SPME-GCMS in all the sampling campaigns performed at the three studied MBT facilities

Terpenoids	**Aromatic Hydrocarbons**	**Aliphatic Hydrocarbons**	**Esters**	**Ketones**	**Nitrogenated compounds**	**Acids**	**Aldehydes**	**Alcohols**	**Sulfur compounds**	**Halogenated compounds**	**Furanes**
Limonene	Toluene	Heptane	Ethyl Acetate	Acetone	Triethylamine	Acetic acid	Octanal	Ethanol	Dimethyl disulfide	Trichloroethylene	Furan, 2-pentyl
α-Pinene	2-Ethyltoluene	Decane	Butyl acetate	2-Butanone	Pyridine	Propanoic acid	Nonanal	Benzyl alcohol	Dimethyl trisulfide		
β-Pinene	3-Ethyltoluene	Undecane	Ethyl pentanoate	2-Pentanone	Caprolactam	Butanoic acid	Decanal	Others			
β-Phellandrene	Ethylbenzene	Dodecane	Ethyl hexanoate	3-Pentanone	Cyanocyclohexene	Valeric acid	Benzaldehyde				
Eucalyptol	p-Xylene	Tetradecane	Ethyl heptanoate			Others					
Carene	o-Xylene	Pentadecane	Ethyl octanoate								
Linalool	Styrene	Nonadecane	Ethyl decanoate								
Terpinen-4-ol	Benzene 1,2,3-trimethyl	Eicosane									
β-Myrcene	Benzene 1,2,4-trhimethyl	Naphthalene									
Citronellene	Others	Others									
Isocitronellene											
Sabinene											
Terpinene											
Terpinolene											
Cymene											

Table 34. Indoor ventilation optimization from selected areas.

Facility	Location	Average maximum tVOCs concentration ($ppbv_{eq}$)	Average hours a day with tVOCs concentration <50 % max. tVOCs (h)	% Daily indoor ventilation reduction
MBT1	Reception warehouse	22,500	10.0	20.8
MBT1	Pretreatment area	27,500	10.8	22.5
MBT2	Composting area	15,000	13.3	27.7