Characterisation of volatile organic compounds (VOCs) released by the composting of different waste matrices

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Abstract

The complaints arising from the problem of odorants released by composting plants may impede the construction of new composting facilities, preclude the proper activity of existing facilities or even lead to their closure, with negative implications for waste management and local economy. Improving the knowledge on VOC emissions from composting processes is of particular importance since different VOCs imply different odour impacts. To this purpose, three different organic matrices were studied in this work: dewatered sewage sludge (M1), digested organic fraction of municipal solid waste (M2) and untreated food waste (M3). The three matrices were aerobically biodegraded in a bench-scale bioreactor simulating composting conditions. A homemade device sampled the process air from each treatment at defined time intervals. The samples were analysed for VOC detection. The information on the concentrations of the detected VOCs was combined with the VOC-specific odour thresholds to estimate the relative weight of each biodegraded matrix in terms of odour impact. When the odour formation was at its maximum, the waste gas from the composting of M3 showed a total odour concentration about 60 and 15,000 times higher than those resulting from the composting of M1 and M2, respectively. Ethyl isovalerate showed the highest contribution to the total odour concentration (> 99%). Terpenes (α-pinene, β-pinene, p-cymene and limonene) were abundantly present in M2 and M3, while sulphides (dimethyl sulphide and dimethyl disulphide) were the dominant components of M1.

Main finding

The composting of untreated food waste may generate a total odour concentration that is 60 and 15,000 times higher than those expected from the composting of dewatered sludge and digested food waste, respectively.

Keywords: mechanical-biological treatments, composting, odour, sewage sludge, food waste

1. Introduction

Mechanical-biological treatments (MBTs) of municipal solid waste (MSW) have been increasingly adopted in many industrialised countries as an efficient way for reducing the amount of waste sent to landfill, for improving the heating value of the waste sent to incineration, and for upgrading the organic fraction of MSW (OFMSW) by producing compost to be re-used in agriculture.

Aerobic MBTs (*i.e.*, composting, bio-stabilisation and bio-drying) use ambient air drawn from outside to biologically oxidise the organic component of waste. The process air, once it passes through the waste piles, is capable of stripping particles and volatile substances that are present in the waste, together with intermediate products formed during the biodegradation process. Thus, the air becomes enriched in substances like ammonia (NH_3), volatile organic compounds (VOCs), hydrogen sulphide (H_2S) and, to a minor extent, heavy metals, polychlorinated biphenyls and polychlorinated dibenzo-*p*-dioxins that may be present as traces in the waste (Austrian Federal Environment Agency, 1998; Schiavon et al., 2016a).

Besides carbon dioxide, which is the main product of biological oxidation, VOCs represent one of the dominant groups of chemicals generated in MBTs (Gutiérrez et al., 2015). VOCs are precursors of tropospheric ozone and, therefore, they indirectly contribute to global warming. Several VOCs have adverse effects on human health, and long-term exposure to some of them can increase the risk of developing cancer over a lifetime (Kume et al., 2008). Finally, due to their volatility and their low odour threshold, some VOCs can be easily perceived by the sense of smell and may cause odour nuisance (Sarkar et al., 2003). VOCs are generated by incomplete aerobic biodegradation and in local anaerobic regions in the waste piles promoting anaerobic biodegradation (Canovai et al., 2004; Domingo and Nadal, 2009; Diaz et al., 2011). Anaerobic conditions were reported as a favourable factor towards the formation of sulphides, while incomplete aerobic biodegradation is responsible for the formation of other VOCs, such as esters, ketones, alcohols and volatile fatty acids (Pagans et al., 2006). The creation of local anaerobic regions is favoured in waste piles characterised by low porosity (Shao et al., 2014). Following their formation, VOCs are released from MBT plants into the atmosphere, mainly through air leaks from the compartments of the plant. An additional contribution may derive from incomplete removal from the waste-gas treatment line. Indeed, although outlet concentrations generally do not exceed tens of ppm (Dorado et al., 2014), the effluent flow rate of a medium-size MBT plant is typically in the order of 10^4 Nm^3 h^{-1} (Schiavon et al., 2016b) and the resulting emission of

VOCs may account for 10^2-10^3 g h^{-1}. Therefore, non-negligible contributions of VOCs to the environment are expected from MBTs (Ragazzi et al., 2014).

Odour nuisance is tightly linked with the waste sector (Canovai et al., 2004). The public concern and the complaints arising from the problem of odours may impede the construction of new MBT facilities, may preclude the proper activity of an existing MBT plant and may even lead to its closure (Beloff et al., 2000).

The literature on the health effects of odour emissions from waste treatments is scarce (Giusti, 2009) and results are controversial (Aatamila et al. 2011). However, increased reporting of symptoms such as headache, respiratory problems, excessive tiredness, and nausea, are associated with exposure to odorants (Aatamila et al. 2011). Though odours may be classified as "harmless" (*i.e.*, not toxic or hazardous) according to public health authorities, they may still have adverse effects on individuals and communities (Beloff et al., 2000). These effects include discomfort (such as reduced enjoyment of property), psychological impacts, property devaluation (Isakson and Ecker, 2008), tourism and employment decline.

In this sense, the reduction of odour emissions from composting plants would imply many advantages. Firstly, the location of plants depends on two main issues at least: the odour acceptability in the neighbourhood (Cariou et al., 2016a) and the operating costs, which have to be minimised (Diaz et al., 2011). Odour abatement would allow the plant location to be chosen mainly (if not entirely) on cost reduction, and plants could be located nearby densely populated areas in order to minimise transport and collection costs. Secondly, a major reduction of odour emissions would also reduce public concern and complaints from people living nearby composting plants, since adverse effects on individuals and communities (*e.g.*, discomfort, property devaluation and tourism decline) would be limited to a smaller area. Thirdly, symptoms associated with exposure to odour emissions would be reduced, with a corresponding reduction in public and private health spending. Finally, properly designed removal technologies would allow existing plants to reduce their social cost impact (Beloff et al., 2000). In particular, despite an investment in abatement equipment may be required, the risk of lawsuits from neighbours or citizen groups and the risk of fines and penalties from regulatory agencies would be reduced.

Although it is not easy to assess societal costs associated with odour emission (Beloff et al. 2000), overall, the cost for enhanced odour abatement systems would be probably lower than the cost incurred for shutting down and relocating a plant (with transportation cost increasing with the distance from the original location).

A first step towards the understanding of the implications of odorant VOCs released by composting processes and towards the development of improved abatement technologies requires a deeper analysis of VOC emissions. Indeed, little is known about which VOCs are released by composting plants as a function of the kind of input waste. Improving the knowledge on VOC emissions associated with composting processes is of particular importance since different VOCs imply different odour impacts. VOC speciation depends on the substrate that is composted and on the conditions under which the composting process is carried out (Turan et al., 2007; Phan et al., 2012). Thus, the problem of odorant VOC emissions from composting plants lacks a systematic characterisation of the released VOCs. Studies carried out during the last decade report the results of odorant characterisations of OFMSW (Sironi et al., 2006; Tsai et al., 2008; Zhang et al., 2013; Maulini-Duran et al., 2014) or zootechnical waste (Webb et al., 2014; Jo et al., 2015; Dunlop et al., 2016; Szulejko et al., 2016). The different conditions under which the various studies were carried out complicate the inter-comparison of the obtained results.

In the light of this scarcity and inhomogeneity of information, this paper aims at filling this gap in the scientific literature in a unified and repeatable approach. For the first time, this study analyses in detail the possible formation of odorant VOCs from the aerobic biodegradation of different waste matrices under the same process conditions, through a specific bench-scale experimentation set up for this purpose. Three matrices of organic origin are characterised and aerobically biodegraded in a bench-scale bioreactor. Samples of the process air, collected at the outlet of the bioreactor using a homemade automatic sampler, were analysed for VOC detection, speciation and quantification. The information on the concentrations of the detected VOCs was combined with the VOC-specific odour thresholds available from the literature, with the aim of estimating the odour concentrations associated with the VOCs released by the aerobic biodegradation of each waste matrix. Finally, the relative contribution of each matrix was estimated in terms of VOC-related odour emissions during the aerobic biodegradation process. Indeed, this study does not claim to provide the VOC and odour concentrations expected in the emission of real-scale composting plants but intends to estimate the expected relative weight of each matrix in terms of odour contribution. The choice to carry out each test under the same operating conditions allows for the inter-comparison of the relative VOC-related odour contributions.

2. Materials and methods

2.1 Waste matrices

Three waste matrices were chosen to characterise the emissions deriving from the aerobic degradation of waste biomass. The first matrix (M1) is composed of dewatered sewage sludge from a wastewater treatment plant (WWTP) mixed with green waste (80% and 20% m/m, respectively); the second matrix (M2) contains digested OFMSW and green waste (80% and 20% m/m, respectively); the third matrix (M3) contains untreated food waste and green waste (70% and 30% m/m, respectively). All mixing ratios are on a wet basis, in order to reproduce the mixing procedure that normally occurs in waste treatment plants. Dewatered sewage sludge was taken at the end of the sludge treatment line of a local municipal WWTP, after sludge conditioning and mechanical dewatering. Digested OFMSW was taken immediately downstream of the digester of an MBT plant performing anaerobic digestion and post-composting. Untreated food waste was taken from the accumulation chamber of the sorted food waste arriving at a local composting plant. Here, an efficient selective collection system is implemented, and a 67% selective collection rate is achieved (Rada et al., 2014). The green waste was added to the main organic matrices as a structuring material to ensure adequate porosity to the entire waste samples and, consequently, to allow for a uniform aeration of the samples. In MBT facilities, the fraction of green waste that is mixed with the primary waste is normally in the range 20–30%, depending on the porosity of the waste mixture. The higher fraction of green waste in M3 (30%) is compatible with composting plants using untreated food waste as the primary input waste and is explained with the higher compactness of untreated food waste compared with dewatered sewage sludge and digested OFMSW.

After being mixed with green waste, each matrix was stored in a refrigerator at the temperature of -30 °C. A small sample (1 kg) of each matrix was analysed for water content, total solids and total volatile solids, according to the Italian national standard CNR IRSA 2 Q 64 Vol 2 (CNR, 1984). Total solids were determined after drying at 105 °C, water content was calculated as the complementary fraction of total solids, total volatile solids were calculated by the difference between total solids and total residual solids, the latter being determined after incineration at 550 °C.
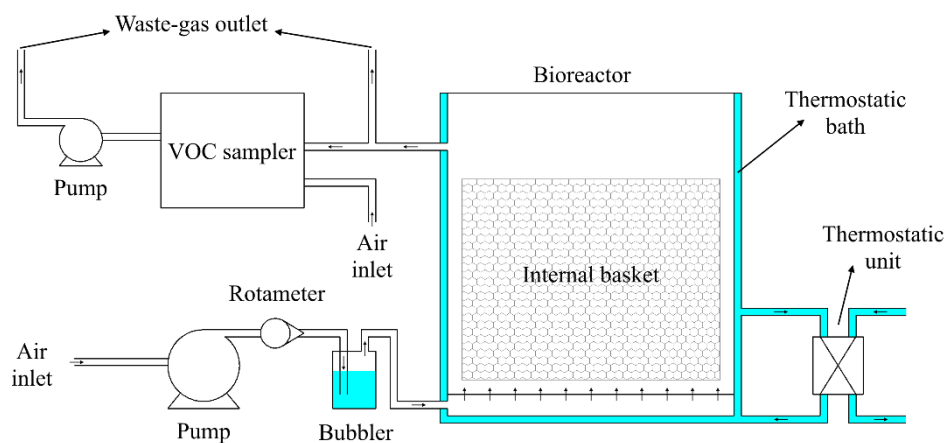
Figure 1: Scheme of the aerobic bioreactor and auxiliary components.

2.2 Aerobic bioreactor

The aerobic bioreactor consists of a cylindrical double-walled airtight reaction chamber, the gas feed line and the waste-gas line (Figure 1). The reaction chamber contains a cylindrical stainless-steel basket (internal diameter of 260 mm and height of 180 mm), which serves as the support for each waste matrix. The base of the basket has several holes with a diameter of 2 mm to let the air pass through the waste sample and allow establishing aerobic biodegradation conditions. A free volume is available for turbulence generation and air mixing between the bottom of the reaction chamber and the base of the basket. The process air enters the reaction chamber from the lower part and exits from the top. The process air consists of ambient air drawn by a Full Teflon® membrane pump (N 820 FT.18, KNF GmbH, Germany) controlled by a rotameter and a manometer to regulate the flow rate. The latter was set at 2 L min^{-1} for the whole duration of the experiments. Before entering the reaction chamber, the process air passes through a bubbler containing distilled water to humidify the air. The reaction chamber is kept at the temperature of 30 °C by a thermostatic bath controlled by a thermostatic unit (GTR 190/2000, Isco Inc., USA) to ensure optimum temperature conditions for biodegradation. A temperature sensor (TFK 325, WTW GmbH, Germany), inserted in a specific casing at the bottom of the reaction chamber, monitors the temperature of the thermostatic bath. After entering the reaction chamber, the process air passes through the waste sample. Part of the waste-gas flow exiting the reaction chamber is periodically sent to the VOC sampler while the main flow goes to an exhaust system.

2.3 VOC sampling

VOC sampling was carried out through an automatic sampler that was intentionally built for on-field sampling at mechanical-biological treatment facilities. A diaphragm vacuum pump (N 840.3 FT.18, NKF GmbH, Germany) aspirates a fraction of the exhaust into an automatic gas sampler.

The latter consists of eight charcoal tubes (Large Tubes 400mg/200mg, Aquaria Srl, Italy), whose inlet and exit are controlled by 3-way ball valves (B-42XS6MM, Swagelok, USA) driven by servo motors (D 7550 BB MG, DYMOND, USA), which in turns are controlled by a multifunction I/O device (NI USB6009, National Instruments, USA). The latter also acts on a mass-flow controller (500 sccm full-scale 1179A, MKS Instruments Inc., USA) that sets the flux of the gas to be sampled (500 sccm for 30 minutes). To avoid gas condensation, the whole sampling unit is heated at a constant temperature of 42 °C by a controlling circuit. VOCs contained in the sampled flow are adsorbed on the charcoal. To take into account the adsorption/desorption efficiency of the charcoal, the extraction efficiency of the activated carbon was measured. To this purpose, a synthetic air flow (80% N_2 and 20% O_2) was mixed with a known VOC concentration. The efficiency was then calculated as the ratio between the experimental concentration and the nominal concentration.

Eight measurements were carried out over six days. Every measurement required two carbon tubes, one to sample ambient air and the other to sample the exhaust gas. For each matrix, blank samples and exhaust samples were taken at the following time intervals after the start-up of the aerobic biodegradation process: 8 h, 16 h, 24 h, 48 h, 72 h, 96 h and 120 h.

2.4 VOC analysis

VOCs were analysed by chromatographic techniques. Gas chromatography was performed by using a gas-chromatograph (GC) with a flame ionisation detector (FID) (Trace GC Ultra, Thermo Finningan). A DB5 column was used for this purpose (length: 60 m; diameter: 0.25 mm; film width: 0.25 μm). The temperature program was set as follows: 40°C, 7 min; 110°C, 5°C min^{-1}; 220 °C, 10 °C min^{-1} ; 300 °C, 20 °C min^{-1}; 300 °C, 9 min. The carrier gas was helium, with a flow of 2.5 ml min^{-1}; the injector was heated at 240 °C and a split of 1/50 was chosen. The sample was obtained desorbing the compounds contained in the activated carbon in 1 ml of carbon disulphide (CS_2) for 30 minutes, and the injected volume was 1 μl. An internal

standard (naphthalene) was added before injection. The FID response was calibrated by using external standards (analytical grade pure compounds).

2.5. VOC-related odour potential estimation

Ambient-air odour concentrations are assessed through dynamic olfactometry. In Europe, the European Standard EN 13725:2003 regulates odour analysis, which is carried out by a panel of examiners with an olfactometer; the number of dilutions necessary to reach the odour threshold (OT) corresponds to the number of odour units (OU) (European Committee for Standardisation, 2003). Conventionally, the OT is the lowest odour concentration perceived by 50% of the population. The concentration corresponding to the OT is conventionally equal to 1 OU/m^3.

Since one of the aims of this paper is to quantify the relative ratio of the VOC-related odour contribution of each waste matrix being composted, independently of the dispersion of the waste gas in the atmosphere, the conventional approach, based on dynamic olfactometry, can be replaced by a simplified method, based on the concept of odour activity value (OAV). This method consists of three steps:

- the quantification of the concentrations of the VOCs detected in the samples taken from the emissions of each composting process;

- the calculation of the odour concentration associated to each detected VOC, by dividing its concentration by its odour threshold (OT);

- the estimation of the total odour concentration in each sample, by summing up the odour levels of the detected VOCs.

The OAV methodology was recently adopted in a study to assess the contribution of each odorant in a swine facility (Jo et al., 2015). OTs for several compounds are available in the literature. For instance, Cometto-Muñiz et al. (1998) estimated the OTs, eye irritation thresholds, nasal pungency and nasal localisation of six terpenes. In another study, which lasted 12 years, Nagata (2003) estimated the OTs of 223 compounds, including several VOCs. This simplified approach unavoidably relies on two strong hypotheses:

- the relationship between VOC concentration and odour concentration is assumed to be linear;

- the estimated total odour concentration is the result of additive contributions from single VOCs.

Linearity is verified for relatively high levels (> 1 ppm), while, for some compounds, odour concentration seems to increase logarithmically with VOC concentration in low concentration ranges (< 1 ppm) (Tsai et al., 2008). Thus, the hypothesis of linearity may overestimate the total odour concentration associated with VOC emissions. The second hypothesis neglects synergic or neutralisation effects in a mixture of VOCs. Synergy and neutralisation are complex phenomena not fully understood yet. In this study, addition is assumed as a reasonable compromise between the two.

3. Results and discussion

3.1 VOC emissions

The results of the analyses on the three waste matrices showed that M1, M2 and M3 are characterised by a 30%, 47% and 17% content of total solids, respectively. Matrix M3 is characterised by the lowest content of volatile solids (7%) and by the highest water content (83%). Matrices M1 and M2 are marked by comparable contents of total volatile solids, which are equal to 19% and 21%, respectively.

The analysis of the mass spectra revealed the major presence of terpenes (especially α-pinene, β-pinene, p-cymene and limonene), organosulphur compounds (dimethyl sulphide and dimethyl disulphide) and esters (ethyl isovaleric acids). Other compounds (dimethyl trisulphide, ethyl isobutyrate, myrcene and sabinene) were present in trace and not quantified. Two dominant VOCs were clearly detected in the samples taken from the composting of matrix M1: dimethyl sulphide and dimethyl disulphide. Sulphides are normal constituents of the gaseous emissions from WWTPs and their formation is favoured under reduced redox conditions and, thus, in anaerobic regions promoting fermentation of organic sulphur-based compounds (Smet and Van Langenhove, 1998; Devai and Delaune, 2002). Sulphide formation has recently been associated with biodegradation of sulphur-containing amino acids (Higgins et al., 2006). The maximum total VOC concentration (intended as the sum of the concentrations of the two dominant VOCs) is achieved 16 h after the beginning of the composting process (Figure 2a). At such conditions, dimethyl disulphide represents more than 97% of the species present in the effluent (Figure 3a). Subsequently, its concentration decreases with time and becomes almost constant after 48 h, until the end of the test. The relatively high generation of
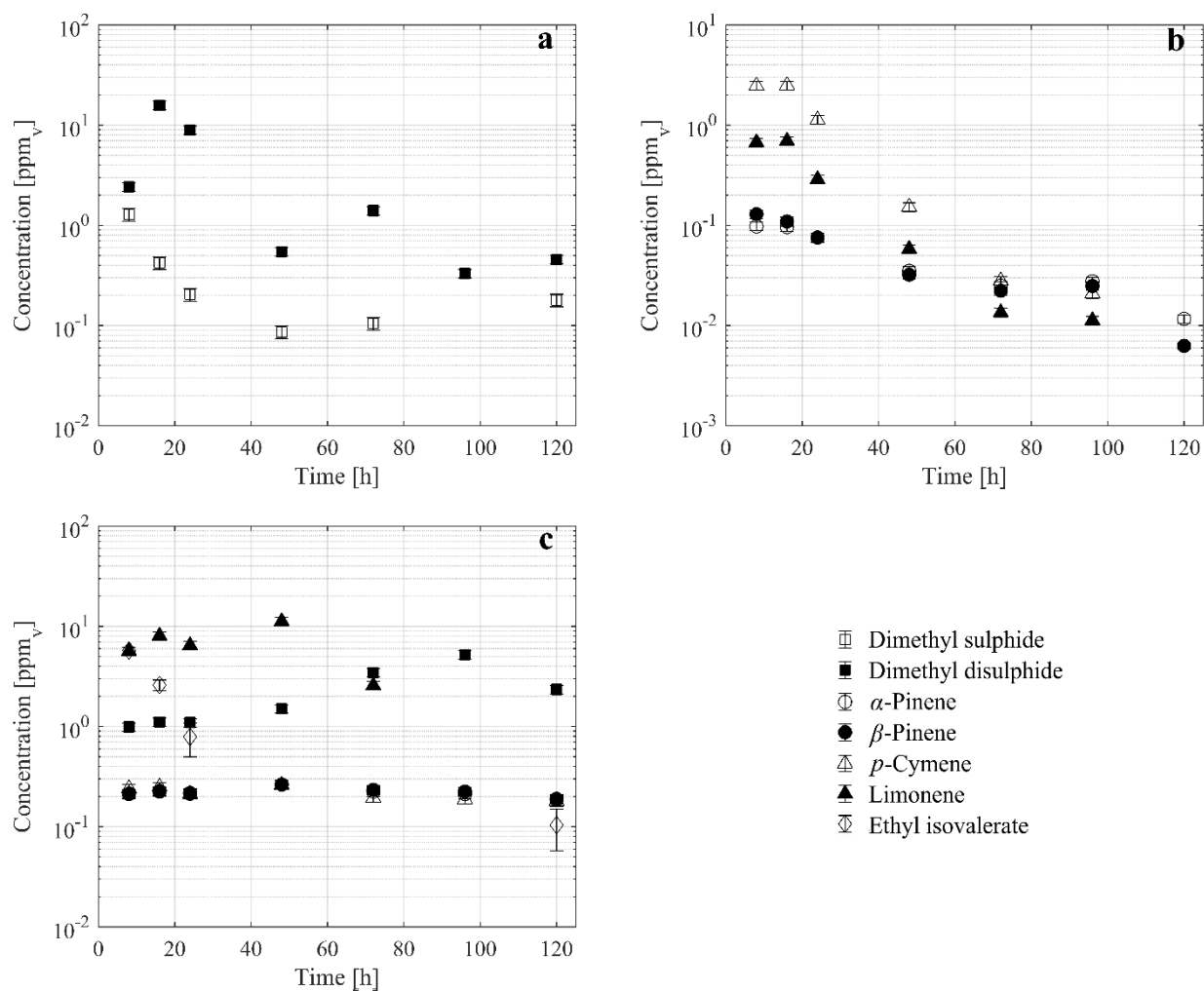
Figure 2: Trend of the concentrations of the VOCs detected in matrices *a)* M1, *b)* M2 and *c)* M3.

VOCs occurring in the initial stage of composting is typical of batch processes and was recently documented by Bhattacharya et al. (2016).

In the emissions from the composting of M2, the dominant detected VOCs are terpenes, which may originate from fruit and vegetable waste, and as intermediate products of aerobic degradation of organic matter (Moreno et al., 2014). The maximal total VOC concentration is achieved 16 h after the beginning of the test (Figure 2b). Under such conditions, the most abundant VOC is *p*-cymene (accounting for about 73%), followed by limonene (21%) (Figure 3b). Minor contributions derived from *β*-pinene and *α*-pinene, whose concentrations did not exceed 0.1 ppm_v in these tests. The concentrations of all these species decreased in the course of the experiment.
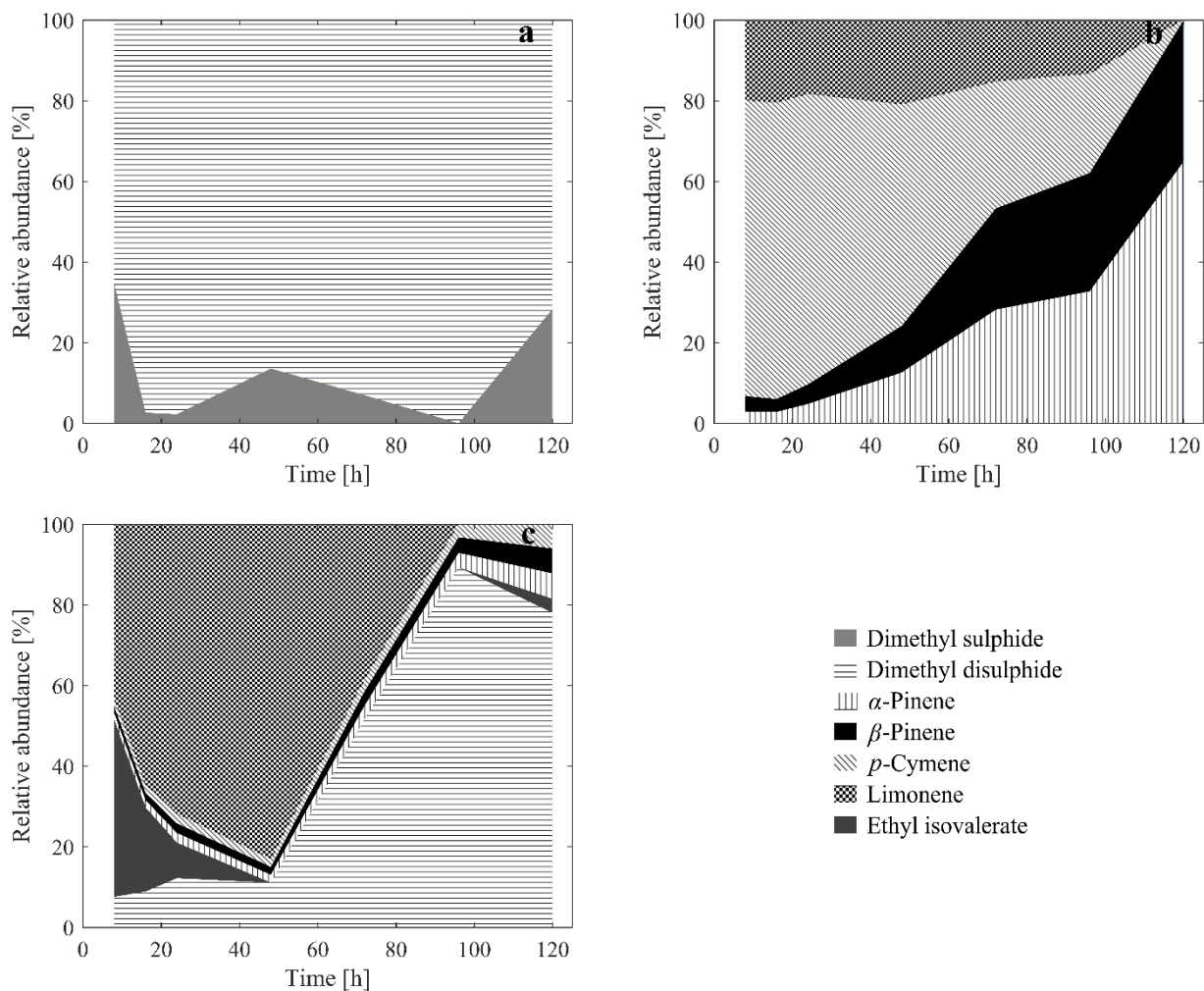
Figure 3: Relative abundances of the VOCs detected in matrices *a)* M1, *b)* M2 and *c)* M3.

The following VOCs were detected in the emissions from the aerobic biodegradation of M3: limonene, dimethyl disulphide, *α*-pinene, *β*-pinene, *p*-cymene and ethyl isovalerate. The maximal total VOC concentration in the emissions from the aerobic biodegradation of M3 is achieved 48 h from the beginning of the test (Figure 2c). Under such conditions, limonene is the most abundant compound (accounting for about 83% of the total VOC concentration), followed by dimethyl disulphide (about 11%) and by *α*-pinene, *β*-pinene and *p*-cymene, with equal contributions (2% each) (Figure 3c). This time interval corresponds to the maximum concentrations of the four terpenes. Ethyl isovalerate was detected only during the first 24 h, reaching its maximum after 8 h. The presence of this compound was recently documented in the indoor air of a waste treatment facility (Gallego et al., 2014). The concentration of dimethyl disulphide continued increasing till reaching its maximum 96 h after the beginning of the test. The persistence of sulphides up to several days after the start of the composting process was observed in a previous study (Shao et al., 2014).

Despite its lower content of volatile solids, M3 generated the highest concentration of VOCs in comparison to the other two waste matrices. This can be attributed to the lower biological stability of food waste, due to the higher presence of water-soluble and, thus, readily available organic compounds with respect to digested OFMSW and dewatered sludge (Dimambro et al., 2015). The excellent correlation between VOC emissions and respirometric index observed by Scaglia et al. (2011) supports this hypothesis.

In agreement with the results of a previous work (Pagans et al., 2006), the maximum VOC concentrations were observed in the first part of the three tests, specifically during the first 48 h. It is worth reminding that VOC concentrations were measured with the only aim of estimating the relative weight in terms of the odorant load associated with each matrix undergoing aerobic biodegradation. A direct comparison with the concentrations in the waste gas of real-scale plants may lead to misleading results: first of all, this study investigates the release of odorant VOCs in the starting phase of the composting process, while the waste gas from a composting plant is the result of the aspiration of the air from different compartments; in addition, waste may be flipped over with modalities that differ from one facility to another. In this sense, small-scale studies like this are the only option to ensure that every waste matrix is subject to the same conditions. This requirement is necessary to produce comparable results among different matrices being composted and to allow this approach to be replicable.

3.2 Odour potentials of the VOC emissions

Although the VOCs generated by the three waste matrices are not harmful to human health, they are characterised by relatively low OTs. Therefore, if high VOC concentrations are achieved, the emissions from the composting of the three matrices under investigation may cause potential odour impact. The OTs of the dominant VOCs range from 0.013 ppb$_v$ for ethyl isovalerate to 1,200 ppb$_v$ for *p*-cymene (Table 1). Ethyl isovalerate is characterised by an OT that is lower than the OTs of the other VOCs by two to five orders of magnitude.

Table 1: OTs of the dominant VOCs detected in the three analysed waste matrices.

VOC	Matrix	OT [ppb$_v$]
Dimethyl sulphide	M1, M3	3.0[a]
Dimethyl disulphide	M1	2.2[a]
α-Pinene	M2, M3	18[a]
β-Pinene	M2, M3	33[a]
p-Cymene	M2, M3	1200[b]
Limonene	M2, M3	38[a]
Ethyl isovalerate	M3	0.013[a]

[a] Nagata (2003)
[b] Cometto-Muñiz et al. (1998)

The OT of a specific compound shows broad variability in the literature (van Gemert, 2011), due to the different techniques adopted by the authors over the years for OT determination (Cariou et al., 2016b). In the present study, single OT values were adopted from a single reference study (Nagata, 2003) to ensure that the OTs of the here considered VOCs were determined with the same method. The only exception concerns *p*-cymene, whose OT was not determined by Nagata (2003); for this reason, the value proposed by Cometto-Muñiz et al. (1998) was chosen. In addition to the uncertainties related to the sampling and analytical techniques for compound quantification, the uncertainties of OT measurements certainly affect the estimation of odour concentrations based on the OAV approach, and such constraint must be considered when interpreting the obtained results.

This considered, dimethyl disulphide turns out to be the highest contributor to the odour concentration in the emissions from matrix M1 (Figure 4a), accounting for about 98% when the total odour concentration reaches its maximum, *i.e.*, 8 h after the beginning of the tests. Limonene is the highest contributor to the odour concentration calculated in the emissions from M2 (Figure 4b). Its contribution accounts for about 61% when the maximum total odour concentration is achieved, *i.e.*, 16 h after the beginning of the tests. Under these conditions, *α*-pinene, *β*-pinene and *p*-cymene contributes to 19%, 13% and 7% of the total odour concentration, respectively. The dominant contribution of limonene persists till 24 h after the beginning of the tests. After this time, *α*-pinene becomes the dominant VOC, although the concentrations of all species continuously decrease during the trial (Figure 2b). The maximal odour concentration from the composting of matrix M3 is achieved 8 h after the beginning of the tests and does not correspond to the maximal total VOC concentration, which is observed after 48 h (Figure 2c). The reason is that ethyl isovalerate, which is the VOC characterised by the lower OT, reaches its maximum concentration after 8 h from the beginning of the composting process. Under these conditions, ethyl isovalerate gives the highest contribution to the estimated
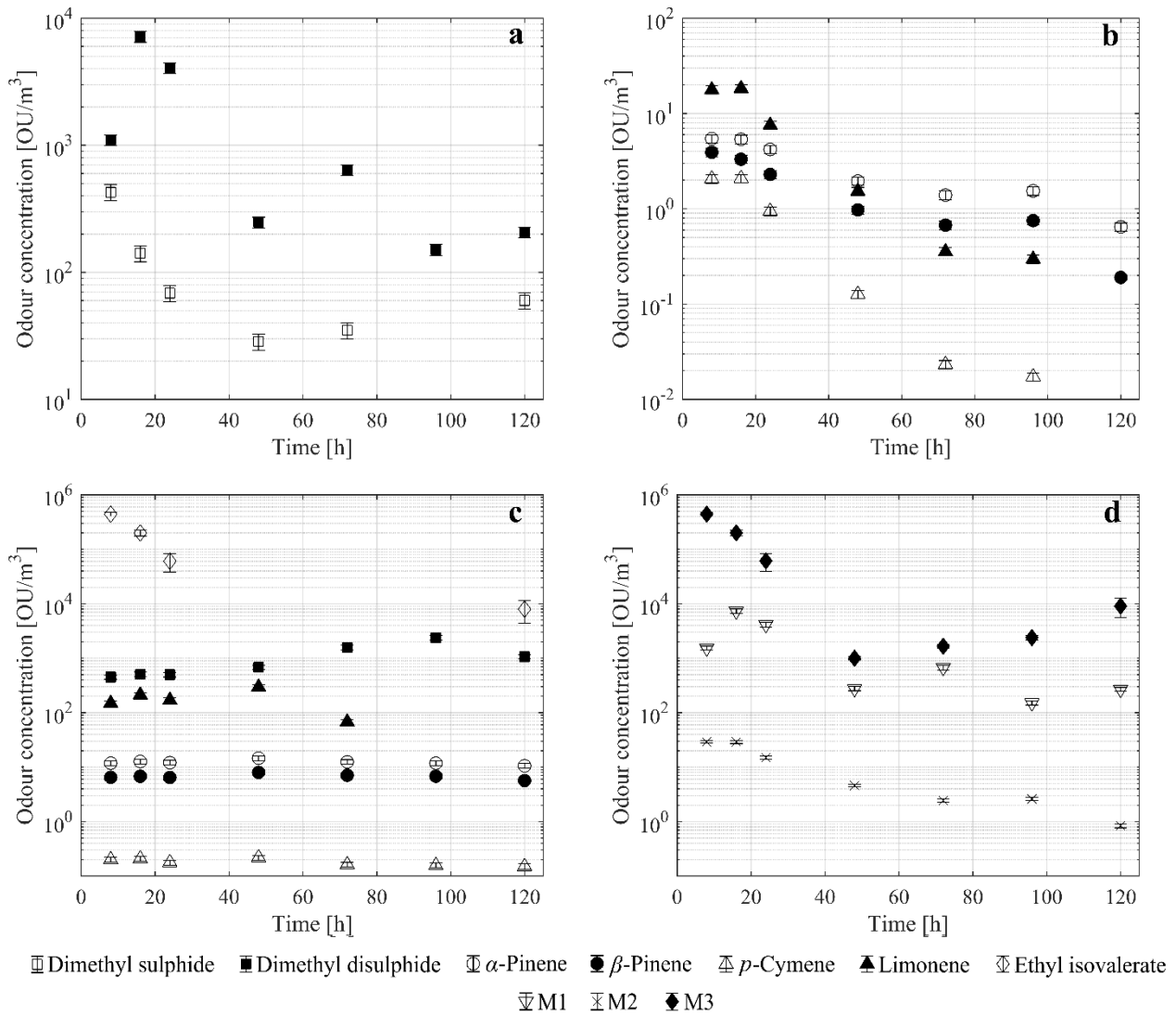
Figure 4: Trend of the odour concentrations of the VOCs detected in matrices *a)* M1, *b)* M2 and *c)* M3, and *d)* trend of the estimated total odour concentrations of the three matrices.

total odour concentration in the emissions from M3, accounting for more than 99%, and continues giving the dominant odour contribution among the other VOCs until 24 h after the beginning of the test. Dimethyl disulphide is the second highest contributor to the total odour concentration of M3 and is the most persistent odorant VOC detected. Sulphides are ascribed as the dominant contributors to total odour concentration from waste treatments (Defoer et al., 2002; Zhao et al., 2015). The third highest contributor is limonene, followed by α-pinene, β-pinene and *p*-cymene.

Concerning total odour concentrations (Figure 4d), M3 shows the highest odour potential compared with M1 and M2: the estimated maximum total odour concentration of M3 is 440,800 OU/m³, while the estimated

maximum odour concentrations of M1 and M2 are 7,290 OU/m^3 and 29 OU/m^3, respectively. The latter is considerably lower than the previous two, especially if compared with untreated food and green waste (M3). Due to the same reasons explained in section 3.1 concerning VOC concentrations, the odour concentrations estimated in this study should not be taken as those expectable in the waste gas of real composting plants, but allow estimating the relative weight of one matrix on the others in terms of odour release. In this framework, the total odour concentration in the waste gas from M3 is about 60 and 15,000 times higher than the maximum total odour concentrations estimated for M1 and M2, respectively (Figure 4d). This is because M3 (food and green waste) is the less stabilised waste matrix under investigation. As mentioned in section 2.1, M1 (dewatered sewage sludge) and M2 (digested OFMSW) underwent prior treatments that are functional to their respective processes of origin, and that partially stabilise the waste matrices under study.

In addition to the well-known advantages of an anaerobic digestion stage in terms of exploitation of the released biogas for heat and electric energy production, the results concerning M2 and M3 indicate that a pre-treatment of OFMSW with anaerobic digestion before composting can be considered as an efficient strategy to significantly reduce the odour potential of food waste.

4. Conclusions

The aerobic biodegradation of different waste matrices entails the emission of different odorant VOCs. Due to the presence of odorants with very different OTs, the expected total VOC-related odour concentration in the waste gas may differ by several orders of magnitude depending on the type of waste being composted. Non-stabilised waste (*e.g.*, untreated food waste) contributes to the highest estimated VOC-related odour concentration in the waste gas, leading to the formation of terpenes, sulphides and compounds with very low OT, such as ethyl isovalerate. Nevertheless, if the aim is to estimate the total potential odour impact expected from waste composting, other odorants whose OTs are lower than their concentrations in the effluents should be considered and quantified in the emissions. For instance, NH_3 and H_2S are commonly found in the emissions from composting. However, their analysis falls out of the aim of this work, which focuses on VOCs. To estimate the total expected odour impact, the analytical methodology should be modified to include NH_3 and H_2S as target compounds. However, the here adopted approach to estimate odour

concentrations suffers from limitations related to the uncertainties in the determination of OT values in the literature. This point must be considered when interpreting the estimates of odour concentrations based on the OAV approach. To improve the reliability of this approach, the techniques adopted for OT determination require refinement, standardisation and a larger number of measurements on single odorants. In addition, improving the accuracy of the sampling and analytical methods would further reduce the uncertainties of the OAV approach.

This in-depth study, aimed at characterising the odorant VOCs emitted from different waste matrices and their relative odour contribution, represents the first step towards the identification of composting processes that may imply significant adverse impacts, in terms of odour nuisance, in the vicinity of MBT facilities. In addition to providing a VOC characterization for various waste matrices and broadening the existing literature on this topic, this study presents a replicable methodology to characterise the relative weight, in terms of VOC-related odorant load, associated with the waste matrices being composted. Such characterisation allows predicting the potential criticalities of specific composting plants and, if necessary, allows adopting proper measures to reduce their odour emissions. For instance, in the case of raw food waste (M3), the use of buffer removal technologies, such as activated carbon adsorption or scrubbers, is suggested to limit the high odour impact expected during transient phases, like the start-up phase of biofilters or maintenance periods. The release of odorants could also be significantly reduced by applying structural changes to the traditional composting process: as previously mentioned, by comparing the results concerning M2 and M3, an anaerobic digestion step, inserted upstream of the composting phase, may reduce the impact of odorant VOCs by approximately four orders of magnitude with respect to direct composting of food waste. Similar improvements are expected with reference to other important odorants, such as NH_3 and H_2S.

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