CHEMICAL ENGINEERING TRANSACTIONS
VOL. 68, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Selena Sironi, Laura Capelli

ISBN 978-88-95608-65-5; **ISSN** 2283-9216
DOI: 10.3303/CET1868030

Evaluation of the Odorous Compounds Emitted in a Full-Scale Sewage Sludge Composting Plant and Its Relationship with the Biological Stability

Daniel González[a], Joan Colón[c], Antoni Sánchez[a], David Gabriel[b,*]

[a]Composting Research Group (GICOM) Dept. of Chemical, Biological and Environmental Engineering, Universitat Autònoma de Barcelona, 08193-Bellaterra (Barcelona), Spain.
[b]Group of biological treatment of liquid and gaseous effluents (GENOCOV) Dept. of Chemical, Biological and Environmental Engineering, Universitat Autònoma de Barcelona, 08193-Bellaterra (Barcelona), Spain.
[c]BETA Technology Centre: "U Science Tech", University of Vic-Central University of Catalonia, 08500-Vic (Barcelona), Spain.
david.gabriel@uab.cat

Volatile organic compounds (VOCs) and ammonia are some of the compounds present in gaseous emissions from waste treatment installations that contribute to odour pollution. In the present work, a characterisation of the VOCs emitted during the biological treatment of raw sludge (RS) by composting in dynamic windrows followed by a curing phase in a full-scale sewage sludge composting plant was conducted, aiming to provide a specific inventory of the odorous compounds emitted. In addition, the biological stability evolution during the whole process was monitored in order to ensure the proper stabilisation of the material. Waste stability and odorous compound analysis considered both a first phase where a mixture of RS and vegetal fraction (RS – VF) was actively composted in continuous dynamic windrows and a second standard curing phase in trapezoidal turned piles, where material reached maturation. The dynamic windrows were operated at 4 days of composting time, each one of 86 Mg approximately. From an initial biological activity –defined by the Dynamic Respiration Index (DRI)– of the RS – VF mixture of 2.2 ± 0.3 g $O_2 \cdot kg^{-1}$ $OM \cdot h^{-1}$, the reduction achieved at the end of the first composting phase was about a 48 %, and finally at the end of the curing phase was about a 79 %, ensuring the biological stabilisation of the material. Different VOC families were identified and up to 20 specific compounds were also quantified in the gaseous emissions generated throughout the entire process. Terpenes such as α-pinene or limonene were found during the whole process, sulphur compounds such as dimethyl sulphide (DMS) or dimethyl disulphide (DMDS) where emitted during the first stages of the composting process and decreased as the material was stabilised while carboxylic acids such as butanoic acid were normally found at higher concentrations in the middle of the composting process.

1. Introduction

Sewage sludge composting is regarded as an environmental friendly technology to decompose organic matter into a stable end product, which can be safely used as fertiliser or soil conditioner. However, as other kind of biological treatment strategies, it causes unavoidable environmental and social issues such as gaseous emissions, which are responsible for odour nuisance among other related problems. Such emissions are typically generated during the organic matter, nitrogen and sulphur-based compounds degradation and are mainly constituted by ammonia and different families of volatile organic compounds (VOCs) (Maulini-Duran et al., 2013), which can be easily perceived by the sense of smell and may cause odour nuisance due to their volatility and their low odour threshold (Sarkar et al., 2003). Some of the VOCs that appear in the gaseous emissions generated in composting processes are terpenes, alcohols, ketones, organosulphur compounds or nitrogenated compounds (Komilis et al., 2004). Moreover, it is known that VOCs emissions are related to process temperature, aeration, pH of the composting material as well as with biological waste reactivity (D'Imporzano et al., 2008), which raises the need of a reliable process performance.

Please cite this article as: González D., Colon J., Sánchez A., Gabriel D., 2018, Evaluation of the odorous compounds emitted in a full-scale sewage sludge composting plant and its relationship with the biological stability., Chemical Engineering Transactions, 68, 175-180
DOI: 10.3303/CET1868030

Among the different approaches for assessing the odour pollution resulting from a specific treatment process, chemical analysis of the odorous gaseous emissions has been proven to be helpful to identify the potential odorant compounds and to track down their sources of formation, apart from being a cost-effective strategy to correlate chemical composition with odour concentration (Cariou et al., 2016).

Different works have been carried out in laboratory- or pilotscale in order to identify and quantify the VOCs emitted during the composting process of sewage sludge (Maulini-Durant et al., 2013; Schiavon et al., 2017), but few full-scale dedicated literature is available. The aim of this study, which is part of a larger odour assessment project, was to identify, quantify and report an inventory of the main VOCs present in the gaseous emissions generated in a full-scale sewage sludge composting plant, along with a biological stabilisation monitoring during the treatment process in order to ensure its proper performance.

2. Materials and methods

2.1 Composting plant

The composting plant studied is a full-scale sewage sludge composting plant located in Majorca (Spain) that treats about 8,000 Mg per year of dehydrated raw sludge (RS) from primary and secondary settlers of different wastewater treatment plants, all together with around 5,000 Mg per year of vegetal fraction (VF) provided by the pruning of parks and gardens, which is used as bulking agent in a 1:3 v/v ratio to get the initial RS – VF mixture. Yearly, the plant produces an average of 4,000 Mg of compost. Table 1 shows the physicochemical characteristics of the two main RS treated at the plant during the last year (RS1 and RS2, provided by two different wastewater treatment plants), the bulking agent and the initial mixture prepared in the plant (RS – VF). US Composting Council analytical methodology (US Composting Council, 1997) was followed to obtain moisture, organic matter content, pH and electrical conductivity

Table 1: Physicochemical properties of the two main raw sludge treated at the plant (RS1, RS2), the bulking agent (VF) and the RS – VF mixture (Means ± std deviation).

Physicochemical properties	RS1	RS2	VF	RS – VF
Moisture (%)	86.8 ± 0.0	86.1 ± 0.0	15.5 ± 0.4	58.3 ± 0.5
Organic matter (%, dry matter basis)	79.1 ± 0.2	84.4 ± 0.5	85.3 ± 2.1	79.1 ± 1.2
Total Nitrogen (%, dry matter basis)	6.7 ± 0.1	7.8 ± 0.3	–	–
pH	6.57	6.79	8.41	7.16
Electrical conductivity ($mS \cdot cm^{-1}$)	2.41	2.38	0.95	2.91
Dynamic Respiration Index ($g\ O_2 \cdot kg^{-1}\ OM \cdot h^{-1}$)	8.1 ± 1.2	8.6 ± 0.0	–	2.2 ± 0.3

The composting process consists of two different phases, an initial stage of controlled degradation of the organic matter carried out in four dynamic windrows of approximately 30 m long and 3 m wide, followed by a curing phase in trapezoidal turned piles of about 85 Mg. The first stage has a windrow residence time (WRT) of 4 days, which is generally lower than the typical WRT for this kind of process (Rosenfeld et al., 2004), and it is turned over three times per day with an automatic mixer, whereas the curing phase normally lasts 31 days and it is turned once every 15 days. The atypical first stage WRT is a consequence of the undersized capacity of the plant, which was firstly designed to treat less RS than what is currently being composted.

2.2 Sampling

2.2.1. Solid samples

For the present study, seven different and representative samples were obtained (RS1, RS2, two different RS – VF initial mixture samples, a sample of the outlet material from the dynamic windrow and two samples of the curing phase material at 15 and 31 days, respectively) and analysed in triplicates in order to determine moisture, organic matter content and biological stability of the material throughout the process. Because of the heterogeneity of the processed material, these representative samples from different stages of the process were obtained by means of the quartering method (Cosenza et al., 2018). Finally, all samples obtained were frozen to -20 ºC and stored until the moment of analysis, which causes no changes in their biodegradability properties, as previously reported by Pognani et al. (2012).

2.2.2. Gaseous samples

Among the variety of sampling methodologies extended to obtain representative VOC samples, during this work direct sampling with adsorption tubes was used (Markes International, Inc., Gold River, CA, USA). Essentially, this methodology is based in the sampling method proposed by Wang et al. (2012). Particularly in this study case, and because of the variety of VOCs aimed to be detected, adsorption tubes packed with two different hydrophobic adsorbents were used to maximise the retention of the target VOCs, being Tenax® TA (Markes International, Inc., Gold River, CA, USA) used to trap heavier polar and apolar compounds such as aromatics (approximately analyte volatility range: n-C_7 to n-C_{30}) and Carbograph™ 1TD (Markes International, Inc., Gold River, CA, USA) used to trap lighter compounds such as ketones, alcohols or aldehydes (approximately analyte volatility range: n-C_5 to n-C_{14}).

A total of 17 gaseous samples were obtained from different points and moments of the biological treatment. Five of them were taken at different consecutive points along the same dynamic windrow (P0, P1, P2, P3, P4) during the first controlled composting step, each of them representing the VOC emission of the waste mixture with a specific age inside the dynamic windrow (P0 for the initial mixture, P1: 0.8 days, P2: 1.6 days, P3: 2.4 days, and P4; 3.2 days, from the inlet to the outlet of the dynamic windrow). The other 12 samples were taken from the surface of the curing pile and were distributed during three consecutive sampling days (4 sampling points per day), coinciding with the day before, the moment of and the day after the turning of the material.

2.3 Analysis

2.3.1. Biological stability

Based on the methodology proposed by different authors to assess the degree of biological stability of an organic sample (Adani et al., 2006), the Dynamic Respiration Index (DRI) was measured using a dynamic respirometer (Ponsá et al., 2010). The determination consists of placing 120-150 g of sample in a 500 mL Erlenmeyer flask and incubating it in a water bath at 37 ºC. A constant airflow is supplied through the sample, and the oxygen content in the outgoing gases is measured by means of an oxygen sensor. From this assay, DRI was determined as the maximum average value of respiration activity measured during the 24 hours of maximum activity according to Eq (1).

$$DRI_{\mathrm{t}} = \frac{\left(O_{2,\mathrm{i}} - O_{2,\mathrm{o}}\right) \cdot F \cdot 31.98}{22.4 \cdot 10^3 \cdot DM} \tag{1}$$

Where DRI_t is the Dynamic Respiration Index for a given time t (g O_2·kg^{-1} OM·h^{-1}); $O_{2,i}$-$O_{2,o}$ is the difference in oxygen content between airflow in and out of the reactor at that given time (molar fraction); F is the volumetric airflow measured under normal conditions (1 atm and 273.15 K) (mL·h^{-1}); 31.98 is the oxygen molecular weight (g·mol^{-1}); 22.4·10^{-3} is the volume occupied by one mole of ideal gas under normal conditions (mL); OM is the organic matter content of the mixture loaded in the respirometer (kg).

2.3.2. TD-GC/MS

A standard solution with 35 different compounds, considered as representative of VOCs emissions from composting processes, was prepared in methanol. Then, seven dilutions were prepared for calibration. 1.5 μL of a liquid standard dilution were loaded onto a sorbent tube via a calibration solution loading rig (Markes International, Inc., Gold River, CA, USA) and flushed with pure He (100 mL·min^{-1}) during 3 min to fully evaporate the VOCs and be retained by the sorbent bed. Then the tube was immediately analysed and the process repeated for each liquid standard dilution.

Thermal desorption of the samples trapped into the adsorption tubes was conducted with a UNITY-2 thermal desorber (Markes International, Inc., Gold River, CA, USA). The sorbent tubes were heated at 290 ºC for 8 min while high purity He was passed through them at a flow rate of 50 mL·min^{-1}, in order to desorb the VOCs and focus them onto a cold trap at -10 ºC. Then, the cold trap was heated to 305 ºC at a 40 ºC·s^{-1} rate for 5 min to desorb the VOCs trapped and to inject them into the chromatographic column. A 1:10 split ratio was used during all the process to prevent column overloading.

The gas flowed to the chromatographic column through a transfer line heated at 250 ºC to prevent condensation. VOC analysis was performed using a GC-MSD (Agilent 7820A GC, Agilent 5975 MSD, Agilent Technologies, Inc., Santa Clara, CA, USA). The chromatographic column used was a DB-624 capillary column (60 m x 0.25 mm x 1.4 μm, Agilent Technologies, Inc.). The head pressure of the column was 45 kPa in order to have a gas flow rate of 1 mL·min^{-1} into the column using He as the carrier gas. The temperature program for the GC was an initial isothermal stage at 50 ºC during 2 min, then a first temperature step to 170 ºC at a 3 ºC·min^{-1} and followed by a last rise up to 280 ºC at a 8 ºC·min^{-1} rate. Finally, the mass spectrometer acquired data in scan mode with m/z interval ranging from 35 to 355 amu and the compounds where identified by matching the mass spectra with a mass spectrum library (Wiley275 library) available in the GC-MS system.

3. Results

3.1 Biological stabilization evolution

Figure 1 shows the evolution of the biological stability of the material throughout the treatment process, expressed by the DRI.

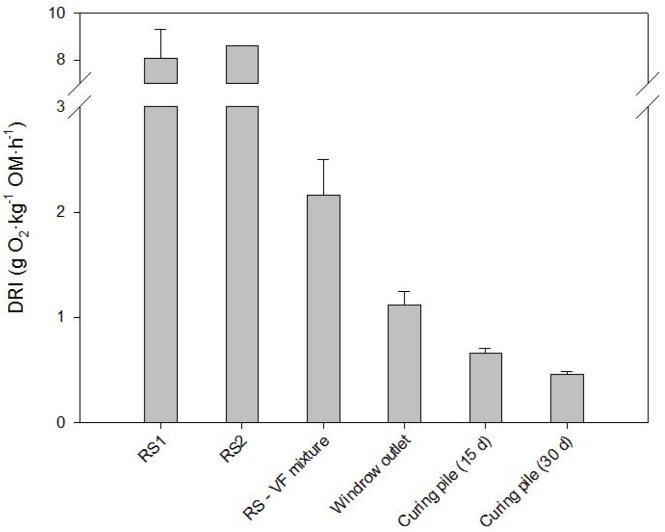

Figure 1: Evolution of the biological stability of the material during its processing, expressed by DRI values.

The first two bars represent the two main sludge treated at the plant along the year (RS1 and RS2), which correspond to typical non-digested sludge DRI values found elsewhere (Barrena et al., 2011). The initial RS – VF presents a lower DRI value, about 2.2 ± 0.3 g O_2·kg^{-1} OM·h^{-1} –74 % reduction when compared with RS– because of the mixture of the RS with the bulking agent, which is supposed to have a minimum biological activity. Once the material has passed through the first step of controlled composting in the dynamic windrows, its biological activity decreases a 48 % down to 1.1 ± 0.1 g O_2·kg^{-1} OM·h^{-1}. As proposed by the European Commission in the Working Document – Biological Treatment of Biowaste, 2nd Draft (CIC, 2017), an organic solid waste is biologically stable when it DRI value does not exceed 1.0 g O_2·kg^{-1} OM·h^{-1}, so in this case a curing step may be necessary to finally stabilise the material. It was observed that applying a curing phase of 31 days, the end material DRI value was decreased down to 0.5 ± 0.0 g O_2·kg^{-1} OM·h^{-1} and a biologically stable material was obtained.

3.2 VOCs characterization

Figure 2 shows the distribution of the different kind of VOC families that were found in each of the gaseous samples obtained from a dynamic windrow and from the curing pile during the monitoring period.

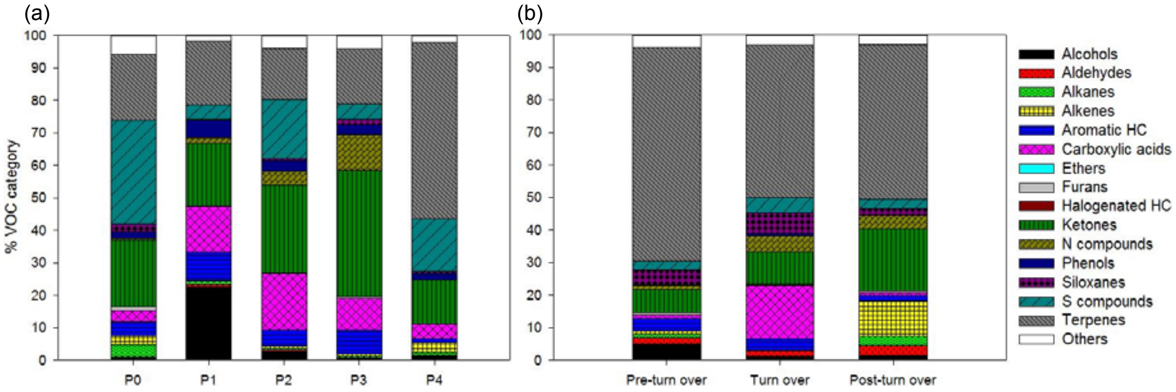

Figure 2: Distribution of the different VOC families found in each sample, expressed in % of abundance respect the whole sample, in (a) a dynamic windrow and (b) the curing pile for the three different days of monitoring.

It can be observed from Figure 2a that the main VOCs found during the controlled composting phase are terpenes –with α-pinene as predominant–, ketones –mainly 2-butanone and 3-pentanone–, carboxylic acids –mainly acetic and butanoic acids– and sulphur compounds –with dimethyl sulphide (DMS) and dimethyl disulphide (DMDS) as predominant–. Organosulphur compounds were mainly formed and emitted during the first stage of the controlled composting and are typically found in gaseous emissions generated by related sewage sludge processing (Schiavon et al., 2017). Their abundance was highly reduced in the curing pile samples once the material is being stabilised. Terpenes emission seemed to increase in the composting stage and were found in the gaseous emissions generated by the curing pile in more than 50 % abundance as the material became biologically stable. The emission of terpens such as α-pinene or limonene are normally related to the vegetal fraction and particularly to the high RS – VF v/v ratio (1:3) used to treat the mixture. On the other hand, organic acids were also formed and emitted in the first stages of the decomposition process and decreased towards the curing step (Figures 2a and 2b). Finally, ketones were found during the dynamic windrow process nearly at the same percentage of abundance in each sample (20-30 %) as well as in the curing phase samples, with a 10-20 % abundance, with no clear correlation with biological stability of the material.

Among all the gaseous samples collected during the study, up to 20 different VOCs were quantified at ppb$_v$ level by the TD-GC/MS technique. Results are presented in Table 2 with the corresponding odour detection threshold (ODT).

Table 2: Quantified VOCs in the gaseous samples obtained from the dynamic windrow monitoring, with its odour detection threshold (ODT), expressed in ppb$_v$ ("Below": compound concentration below the lower detection limit; "-": not detected compound).

Family	Compound	ODT (ppb$_v$)	P0	P1	P2	P3	P4
Alcohols	1-butanol	38^a	–	188.8	*Below*	–	–
Aldehydes	Benzaldehyde	350^b	–	2.9	*Below*	–	–
	Isovaleraldehyde	0.1^a	–	37.1	–	–	–
	Octanal	0.01^a	–	6.2	–	–	–
Alkanes	Heptane	670^a	2.0	5.4	1.8	*Below*	–
	Indole	0.3^a	0.6	4.9	–	–	–
	Skatole	0.006^a	0.3	1.5	–	–	–
Aromatic HC	Toluene	330^a	*Below*	4.0	–	–	–
	Benzene	2700^a	*Below*	–	–	–	–
	Styrene	35^a	–	0.6	–	–	–
Carboxylic acids	Butanoic acid	0.19^a	9.9	146.0	49.4	46.3	–
Ketones	2-butanone	440^a	159.4	519.1	251.4	388.8	–
	2-pentanone	28^a	6.1	29.9	6.6	5.0	–
Nitrogenated compounds	Pyridine	63^a	–	7.1	–	–	23.0
Phenols	Phenol	5.6^a	13.6	152.4	33.4	40.5	–
Sulphur compounds	DMS	3^a	547.9	28.9	17.8	65.5	–
	DMDS	2.2^a	132.9	151.2	395.2	113.4	81.5
Terpenes	α-pinene	18^a	33.2	91.5	39.3	63.2	43.7
	β-pinene	33^a	2.7	6.7	0.4	–	2.0
	Limonene	38^a	1.4	13.3	0.2	*Below*	–
	p-cymene	1200^c	0.1	9.3	*Below*	*Below*	–
	Eucalyptol	12^b	–	77.9	*Below*	–	–

^{a} Nagata (2003)
^{b} Leffingwell (2017)
^{c} Cometto-Muñiz et al. (1998)

More than half of the compounds quantified in the dynamic windrow exceeded their ODT, and some were found to be smell-relevant compounds as well as responsible for the typical odour of this kind of sewage sludge treatment. As observed in Figure 2, sulphur compounds had their higher contribution to odorant emissions in the first stages of the controlled composting process, showing a maximum concentration of 547.9 ppb$_v$ of DMS at the inlet material and a maximum concentration of 395.2 ppb$_v$ of DMDS nearly at the middle of the dynamic windrow. Similarly, maximum concentrations of organic acids –146.0 ppb$_v$ of butanoic acid– or ketones –519.1 ppb$_v$ of 2-butanone– were found in the first stages of the process, though the latter group did not exceed ODT. Also, ketones smell is not described as annoying. On the other hand, despite its high abundance and concentration detected (up to 91.5 ppb$_v$ of α-pinene), terpenes are not typically described as odour nuisance compounds.

4. Conclusions

The objective of this work was to present a reliable inventory of the VOCs present in the gaseous emissions generated throughout the biological treatment of sewage sludge in a full-scale composting plant at different stages of the stabilisation process along with a monitoring of the biological stabilisation performance.

The first results showed that the composting process had a convenient performance in terms of biological stabilisation, expressed as DRI, when a first controlled composting phase was followed by a curing phase. When focusing on VOCs emission, it was observed the variety of compounds that appear in the different stages of the composting process, with VOC families such as organosulphur compounds, carboxylic acids, ketones or terpenes as predominant ones. Among other operational and process parameters, it can be stated that biological stability presents a strong influence in the kind and amount of the different VOCs emitted during the composting process.

References

Adani, F., Ubbiali, P., Genevini, P., 2006, The determination of biological stability of composts using the dynamic respiration index: The results of experience after two years, Waste Management, 26, 41-48.

Barrena, R., Gea, T., Ponsá, S., Ruggieri, L., Artola, A., Font, X., Sánchez, A., 2011, Categorizing raw material biodegradability via respiration activity measurement: A review, Compost Science & Utilization, 19(2), 105-113.

Cariou, S., Chaignaud, M., Montreer, P., Fages, M., Fanlo, J.L., 2016, Odour concentration prediction by gas chromatography and mass spectrometry (GC-MS): Importance of VOCs quantification and odour threshold accuracy, Chemical Engineering Transactions, 54, 67-72.

CIC, 2017, Consorzio Italiano Compostatori, Working document of biological treatment of biowaste, 2nd draft (European Commission), <compost.it/www/pubblicazioni_on_line/biod.pdf> accessed on September 2017.

Cometto-Muñiz, J.E., Cain, W.S., Abraham, M.H., Kumarsingh, R., 1998, Sensory properties of selected terpenes: thresholds for odor, nasal pungency, nasal localization, and eye irritation. Annals of the New York Academy of Sciences, 855, 648-651.

Cosenza, A., Di Bella, G., Torregrossa, M., Viviani, G., 2018, Biological stability of organic fraction of municipal solid wastes during composting processes, Environmental Engineering Science, 32 (1).

D'Imporzano, G., Crivelli, F., Adani, F., 2008, Biological compost stability influences odor molecules production measured by electronic nose during food-waste high-rate composting, Science of the Total Environment, 402, 278-284.

Komilis, D.P., Ham, R.K., Park, J.K., 2004, Emission of volatile organic compounds during composting of municipal solid wastes, Water Research, 38, 1707-1714.

Leffingwell & Associates 2018, <leffingwell.com/odorthre.htm> accessed on January 2018.

Maulini-Duran, C., Artola, A., Font, X., Sánchez, A., 2013, A systematic study of the gaseous emissions from biosolids composting: Raw sludge versus anaerobically digested sludge, Bioresource Technology, 147, 43-51.

Nagata, Y., 2003, Odor measurement review, Measurement of odor threshold by triangle odor bag, Ministery of Environmental Government of Japan, 122-123.

Ponsá, S., Gea, T., Sánchez, A., 2010, Different indices to express biodegradability in organic solid wastes, Journal of Environmental Quality, 39, 706-712.

Pognani, M., Barrena, R., Font, X., Sánchez, A., 2012, Effect of freezing on the conservation of the biological activity of organic solid wastes, Bioresource Technology, 104, 832-836.

Rosenfeld, P., Grey, M., Sellew, P., 2004, Measurement of biosolids compost odor emissions from a windrow, static pile and biofilters, Water Environment Research, 76(4), 310-315.

Sarkar, U., Longhurst, P.J., Hobbs, S.E., 2003, Community modelling: A tool for correlating estimates of exposures with perception of odour from municipal solid waste (MSW) landfills, Journal of Environmental Management, 68, 133-140.

Schiavon, M., Martini, L.M., Corrà, C., Scapinello, M., Coller, G., Tosi, P., Ragazzi, M., 2017, Characterisation of volatile organic compounds (VOCs) released by the composting of different waste matrices, Environmental Pollution, 231, 845-853.

US Composting Council, 1997, Test methods for the examination of composting and compost (TMECC), The US Composting Council, Bethesda, Maryland, USA.

Wang, B., Sivret, E.C., Parcsi, G., Wang, X., Stuetz, R.M., 2012, Characterising volatile organic compounds from sewer emissions by thermal desorption coupled with gas-chromatography-mass spectrometry, Chemical Engineering Transactions, 30, 73-78.