

Identification of odorant characters using GC-MS/O in biosolids emissions from aerobic and anaerobic stabilisation

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ABSTRACT

Malodorous emissions from biosolids limit potential re-use opportunities. Emissions from anaerobically stabilised biosolids have been widely studied. In contrast, emissions from aerobically stabilised biosolids have not been well documented. Individual odorants in complex emissions can be detected using sensorial analysis methods, such as gas chromatography mass spectroscopy coupled with an odour detection port (GC-MS/O) where assessors sniff the GC effluent to identify odorants present. In this study, GC-MS/O was used to study and compare emissions from biosolids produced from aerobically and anaerobically stabilised biosolids from different wastewater treatment plants (WWTPs). The WWTPs varied in size, catchments and dewatering technology. Three GC-MS/O assessors were used for the sensorial analysis. The identified odorants varied significantly between the two sites using aerobic stabilisation, in number of odour characters detected, as well as their intensity. Different odour characters were noted from biosolids generated at the aerobic digestion sites compared to characters from biosolids generated at the anaerobic digestion site. Biosolids from the aerobic digestion sites had medicinal, acrid or putrid type odours not noted from the anaerobic site. However, descriptors of biosolids emissions were commonly noted as: rotten vegetables, seaweed, garbage, garlic, or bad-breath. Many of the descriptors were associated with the presence of sulfur-type compounds. The importance of assessor variability was also highlighted in the paper where certain characters were not detected or were described differently by assessors.

Key words | aerobic digestion, anaerobic digestion, biosolids, odours, odour detection port (ODP), sensorial analysis

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INTRODUCTION

Biosolids produced in Australia are predominantly applied directly to land. Emissions from these products can cause nuisance odours in communities surrounding the wastewater treatment plants (WWTPs), transportation routes and application sites. Typically, large urban WWTPs use anaerobic stabilisation, while smaller rural/regionally based WWTPs may use aerobic stabilisation to meet regulatory land application criteria (Nowak 2006). The retention time in the anaerobic digester as well as dewatering and conveying technology used in biosolids processing has been identified to affect resultant emissions from anaerobically stabilised biosolids (Erdal *et al.* 2008). A well operated aerobic stabilisation process should result in a well stabilised and odourless product (Ganczarczyk *et al.* 1980;

Tchobanoglous *et al.* 2003). Yet, in many WWTPs, the odour properties of aerobically digested biosolids may not be well understood and depend on digester retention time, temperature, as well as the presence of anoxic zones in biological nutrient recovery systems (Koers & Mavinic 1977; Tonkovic 1999). To date, the authors have not found a comprehensive analysis of odours or odorants from aerobically stabilised biosolids.

Community complaints due to malodours can be difficult to interpret due to the subjectivity in odour perception (Gostelow *et al.* 2001). Odour quality refers to how the odour is described and remains a rather subjective property of olfactory perception (Yeshurun & Sobel 2009). Odour descriptions being attributed to brands or products is

common as humans associate odours with their personal history (Dietrich *et al.* 2014). While each person is thought to have their own unique olfactory detection capability (Secundo *et al.* 2015).

A range of formalised methods for the measurements of olfactory properties of emissions have been developed in order to improve the reproducibility and reliability of odour measurements. An example of which is GC-MS/O, where initially the emission mixture is run through the gas chromatography (GC) column which separates compounds according to size and charge. Following this, assessors sniff the GC effluent in parallel with mass spectroscopy analysis allowing the identification of individual odorants in an odour mixture (Brattoli *et al.* 2013). The method is sensitive and relevant for the identification of odorants as it uses human receptors directly, rather than identifying compounds and then linking with reported olfactory properties from the literature. The method also overcomes potential shortcomings of the analytical identification of odorants with extremely low odour thresholds, such as geosmin, which cannot typically be accurately measured by GC-MS in screening analyses. Therefore, GC-MS/O is a useful first step in identifying odorants present in an emission, before using compound specific characterisation for quantification. In this study, GC-MS/O was used to identify differences in odorant characters from biosolids collected at two WWTPs using aerobic and one WWTP using anaerobic stabilisation of biosolids.

METHODOLOGY

Biosolids sampling and WWTP description

The two WWTPs using aerobic stabilisation of biosolids, Aerobic-1 and Aerobic-2 were located in a regional area north of Sydney, Australia. They treated municipal wastewater from 35,000 and 115,000 population equivalents (PE), respectively. The WWTP stabilising biosolids using anaerobic digestion, Anaerobic-1, was based in Sydney, Australia and treated wastewater from 210,000 PE. Anaerobic-1 digested both primary and waste activated sludge (WAS), while the aerobic sites only digested WAS. Process flow diagrams for the biosolids processing at the three WWTPs are shown in Figure S1 (available with the online version of this paper). Aerobic-1 used belt filter presses for biosolids dewatering resulting in a solids content of 12–15 wt%. Aerobic-2 and Anaerobic-1 used centrifugal dewatering and achieved solids contents of 15–18 wt% and 19–22 wt%,

respectively. Samples of freshly dewatered biosolids (10 L) from Aerobic-1 and Aerobic-2 were transported overnight in sealed plastic buckets at ambient temperatures to the laboratory for analysis. Samples of dewatered biosolids (10 L) from Anaerobic-1 were transported and delivered on the same day of sampling. Five samples were taken from the both Aerobic-1 over a period of two weeks and Aerobic-2 over a period of four weeks. Twenty-one samples were collected at Anaerobic-1 over a period of eight weeks.

Emission generation

Emissions from the biosolids cakes were generated using a flux hood based on the US-EPA design, operated in compliance with AS/NZ 4323.4:2009 (Standards Australia/Standards New Zealand 2009). Flux hood sampling was carried out at ambient conditions (20–25 °C). The flux hood was operated with a 5 L/min flow of nitrogen, and after purging for 30 min emissions were adsorbed onto Tenax TA sorbent tubes for 10 min using a sampling flowrate of 100 mL/min controlled by vacuum sampling pump (Air-Chek2000, SKM Inc.). Sorbent tubes were collected using a sampling mantle allowing parallel collection of quadruplicate samples. The flow through each sorbent tube was controlled by individual calibrated flow control valves.

Emission analysis

Sorbent tubes were analysed using a gas chromatograph (GC) equipped with a mass spectrometer (MS) detector (Agilent 6890N GC, 5973NS MS, Agilent Technologies, USA) and an olfactory detection port (ODP) (Gerstel GmbH & Co., Germany). The GC column used was DB-VRX (30 m × 0.25 mm × 1.4 µm). Sorbent tubes were loaded with an Ultra automatic sampler and thermally desorbed using a Unity thermal desorber (TD) (both from Markes International, UK). The volatile and semi-volatile compounds in emission samples were concentrated onto a general purpose cold trap (Markes International, UK) prior to injection to the GC. Operating conditions used in the TD-GC-MS system are detailed in Wang *et al.* (2012). The eluent from the GC was split between the MS operating in scan mode and the ODP using a split ratio of 2:3 (MS:ODP).

The ODP system incorporated a humidifier in the make-up gas to reduce olfactory fatigue in assessors. All odour stimulus chromatograms were recorded using the Gerstel ODP Recorder software (Gerstel GmbH & Co., Germany). Assessors recorded odour intensity, on a scale of 1–4 (weak to strong) as well as descriptions of the odours sniffed

through the ODP. Assessors each analysed one of the sorbent tubes taken for each sample.

The same three assessors, identified as ODP1, ODP2 and ODP3, were used in the ODP analysis of biosolids from all sites. ODP assessors were evaluated based on their olfactory threshold for n-butanol, which is a standard technique for establishing olfactory sensitivity used for panellist selection for olfactometry analysis (EN: 13725). The n-butanol sensitivities of the assessors were 21, 25 and 41 ppb for ODP1, 2 and 3, respectively. All assessors were trained. The number of biosolid samples analysed by each ODP assessor is shown in Table 1.

Data analysis

The ODP events were matched to peaks on the MS chromatogram based on retention time in the GC. Odour descriptors made by the assessors were edited, by removing plurals, capitals, simplifying phrases, expanding acronyms of chemical names and correcting spelling mistakes, in order to collate the frequency with which certain terms were used to describe odours.

Odour events detected by the assessors were grouped according to the retention time at which they were perceived, as well as common odour characters. Odour events were assigned to a primary odour category taken from odour wheels (Suffet & Rosenfeld 2007), following discussions with the ODP assessors. In addition, extra categories were added as in acrid to describe the burning, acrid and astringent odours, also umami/savoury to describe the baking, cheese, yeast odours detected by ODP 1 and 2.

Many of the descriptors identified seemed to be discrete, with a descriptor only being detected once at many retention times with a low intensity of 1. One method to explore the data is using a rating system such as the modified frequency (MF%) method, shown in Equation (1) (Brattoli *et al.* 2013). This method was used to identify common or high intensity odour events from the biosolids produced at the different sites and by the different ODP assessors. In addition, using MF% allows comparison of the odour events between the WWTPs by comparing frequency

rather than total number of odour events detected.

$$MF\% = \sqrt{(F\% \times I\%)} \quad (1)$$

where F is the frequency (number of times detected out of total runs). I is the intensity (intensity divided by the highest possible intensity).

RESULTS AND DISCUSSION

Odour characters

As time is limited in ODP analysis, assessors can find odour characters difficult to describe, especially if they are of low intensity, or close to the odour detection threshold of the odorant. The ranges of odour descriptors identified at the sites by each of the assessors are shown as word maps in Figure 1. Odour events which could not be described were noted as '?' (Figure 1). The description of odours is usually more difficult than their detection; this is why the detection threshold is typically 2–4 orders of magnitude lower than the recognition thresholds (Dietrich *et al.* 2014). Odour descriptions are difficult as they require language and memory processing time; typically, it is easier to identify than describe odours (Yeshurun & Sobel 2009).

ODP 2 typically detected more odour events than the other assessors; however, the language varied greatly for odour events with the lowest intensities. ODP 3 was consistent in the detection of certain compounds and in the language used (Figure 1), detecting a small number of odour events which were assigned a higher intensity. The range of assessor descriptors used in observations at different sites is valuable in describing all odorants likely to be detected by the community affected by nuisance emissions.

Descriptors relating to sulfur compounds, such as sulfur, rotten cabbage, garlic, seaweed or directly attributed to sulfur compounds such as dimethyl trisulfide were common for all sites and assessors (Figure 1). Other characteristics such as 'musty' were typical of biosolids from the anaerobic site with the geosmin character being identified specifically.

Odour event groupings

The density function of the number of odour events identified by the ODP assessors for the biosolids taken from the three different WWTPs are shown in Figure 2. The odour events were grouped according to both retention time and odour character (Figure S2, available with the online version

Table 1 | Number of emission samples from each biosolids source analysed by each assessor

Site	Number of biosolids cakes analysed (ODP1, ODP2, ODP3)
Aerobic-1	5 (4,3,4)
Aerobic-2	5 (5,5,0)
Anaerobic-1	21 (20, 19, 21)

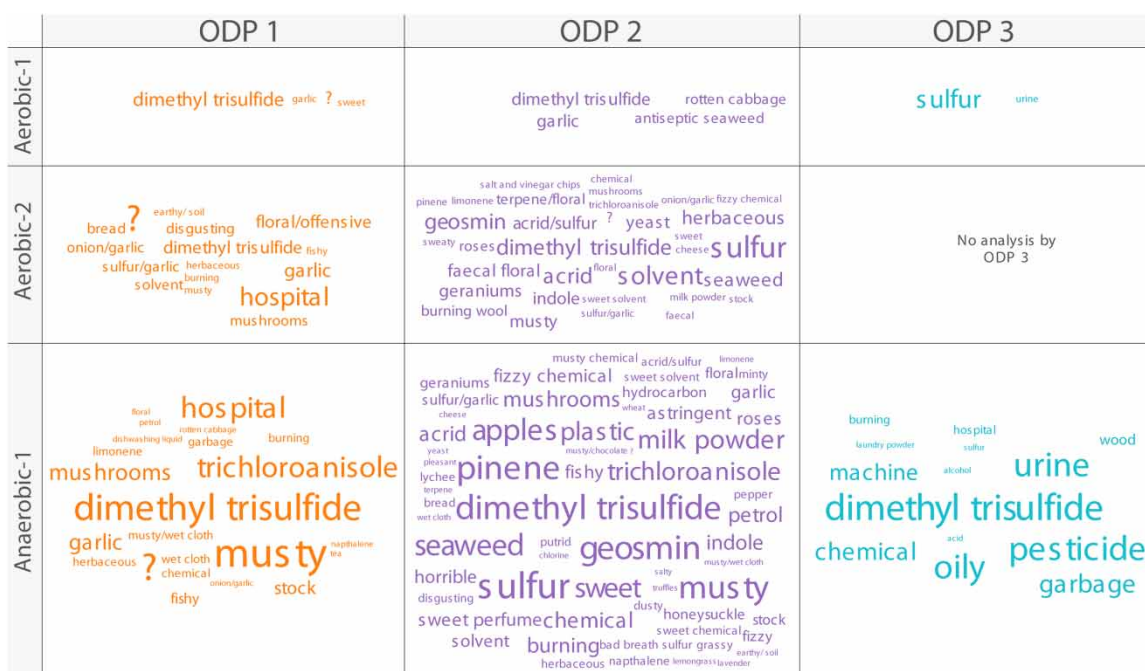


Figure 1 | Word map showing types of descriptors assigned to odorants identified throughout the GC-MS/O chromatogram by each assessor for each site. The size of the text indicates a higher frequency of use by the assessors.

of this paper). The descriptors, retention times and primary odour groupings of the odour events identified by the assessors are shown in Table S1 (available online).

The dominant primary odour category for all assessors and sites was sulfide/cabbage/garlic, identified using MF% (Figure 3). Such odour categories, due to the unpleasant hedonic tone, are likely to be associated with community nuisance impacts.

The names of likely odorants for odour events are shown in Table S1. However, this paper is not focused on the chemical characterisation of odorants, instead focusing on the use of GC-MS/O as a sensorial tool for describing the odorants present. The odorants were identified based on the MS profile (for dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide and pinene) and/or operator descriptions (geosmin). Further research is needed to identify the odorants responsible for the unknown odour events.

In some cases, descriptors varied between samples, assessors or from that reported in the literature. While this variation is indicative of human variability, another complication is that the concentration of the odorants also influences the perceived odorant characters. Thiols may be perceived as pleasant fruity odours at low concentration yet at high concentration are particularly putrid, such as *p*-menth-1-ene-8-thiol which has a grapefruit odour at low concentrations (Chastrette 1998).

Variation in odour perception between WWTP sites

The intensity and frequency of odour events detected in emissions from Aerobic-2 biosolids appeared to be somewhat greater than those from Anaerobic-1 biosolids, as demonstrated by MF% in Figure 3. This contrasted with the minimal number of odour events, detected from Aerobic-1, which appeared to be composed of only sulfur-type odours (Figure 3). The overall number of different odour events detected in emissions from Anaerobic-1 and Aerobic-2 biosolids were comparable (Figure 3), however, different odour types were detected between the sites. Solvent/hydrocarbon and medicinal primary odour characters were frequently detected in Aerobic-2 emissions, however, their intensities were low. The different compounds/odour events detected perhaps resulted due to different degradation by-products produced during aerobic compared to anaerobic stabilisation. Additionally, samples from the aerobic sites were stored overnight before analysis, unlike the samples from Anaerobic-1 which were analysed on the same day of sampling. Interestingly, odour emissions from the biosolids produced at Aerobic-1 were still low, despite the additional day storage. This may be attributable to the use of belt filter presses for dewatering at Aerobic-1, compared to the use of centrifugal dewatering used at the other sites. High shear dewatering using centrifuges has

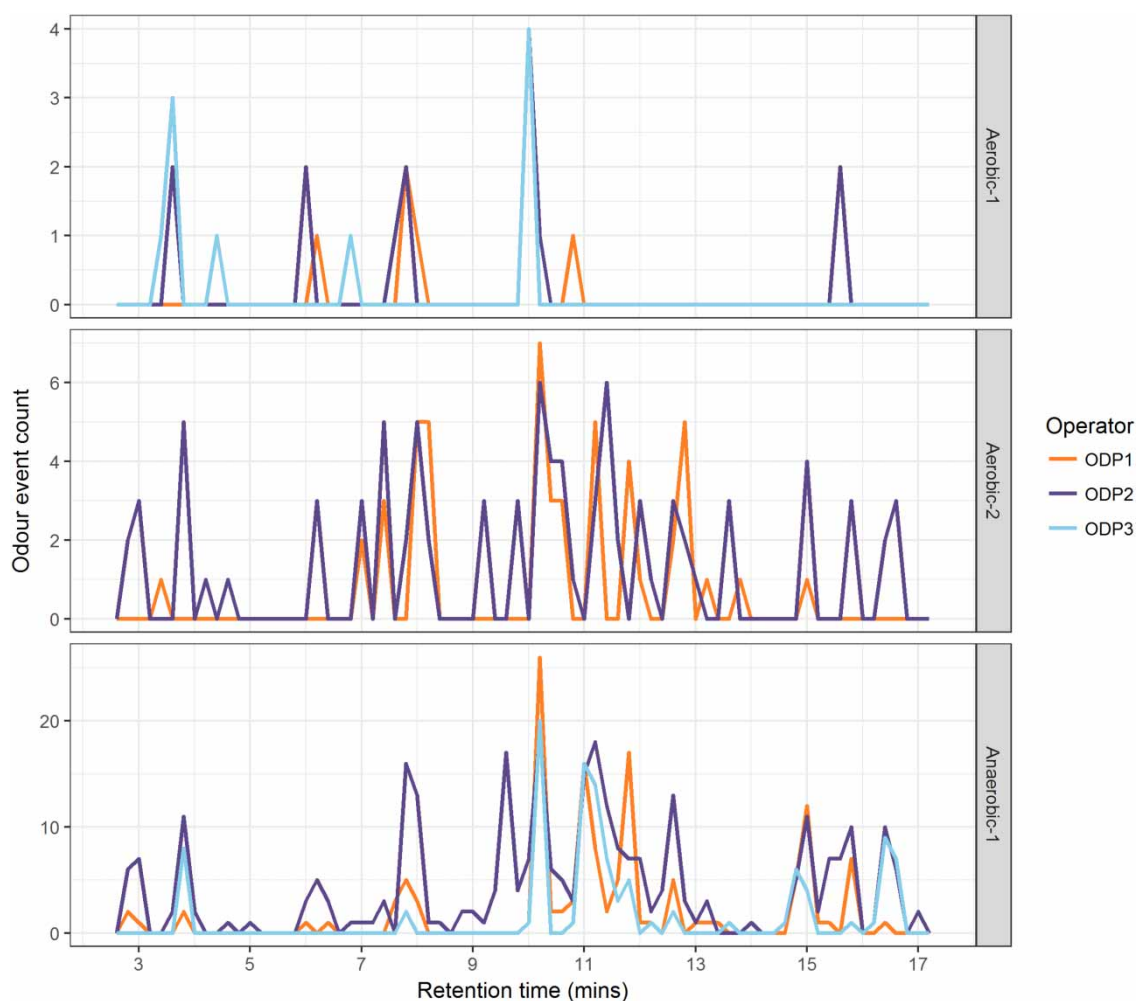


Figure 2 | Counts of odour events identified by ODP assessors for each site. Bins of 0.1 min were used to group the retention times. (Note that ODP3 did not analyse the samples from Aerobic-2.)

been shown to produce greater emissions in anaerobically stabilised dewatered sludge, due to the freeing of previously bound proteins which when microbially degraded produces sulfur-based compounds (Novak *et al.* 2006). The mass transfer rates of certain odourants, particularly hydrophobic compounds, are affected by the water content of the sludge or soils (Wong & Wania 2011). Therefore, the lower odour emissions from Aerobic-1 samples may also be related to its lower solids content. The effect of storage on the emission profile of the biosolids were not investigated in this study, however, the higher moisture content may increase the septicity during storage.

Aerobic-1 and -2 had comparable aerobic digester sludge ages (17–23 and 20 days, respectively). While digester temperatures were not reported as the sites were geographically close, climate variations were not thought to be significant. Elucidating if the variations in emissions from

the different aerobically stabilised biosolids were due to the dewatering method or upstream factors such as digestion performance (age, temperature), biological nutrient recovery or sewer catchment influences is an important area for further study. In addition, a more comprehensive analysis of biosolids composition, microbial activity and the effect of ageing should be included in future studies of odour generation from aerobically stabilised biosolids.

The GC-MS/O study of emissions from the stabilised biosolids showed that a range of odourants are present and possess a range of odour qualities. The value of GC-MS/O lies in its ability to identify significant odourants from complex emissions. In addition, GC-MS/O can highlight the implicit variability in human perception of odours (Barczak *et al.* 2018). Shortcomings with the use of sorbent tubes and GC-MS in the retention and analysis of small or unstable compounds such as hydrogen sulfide or

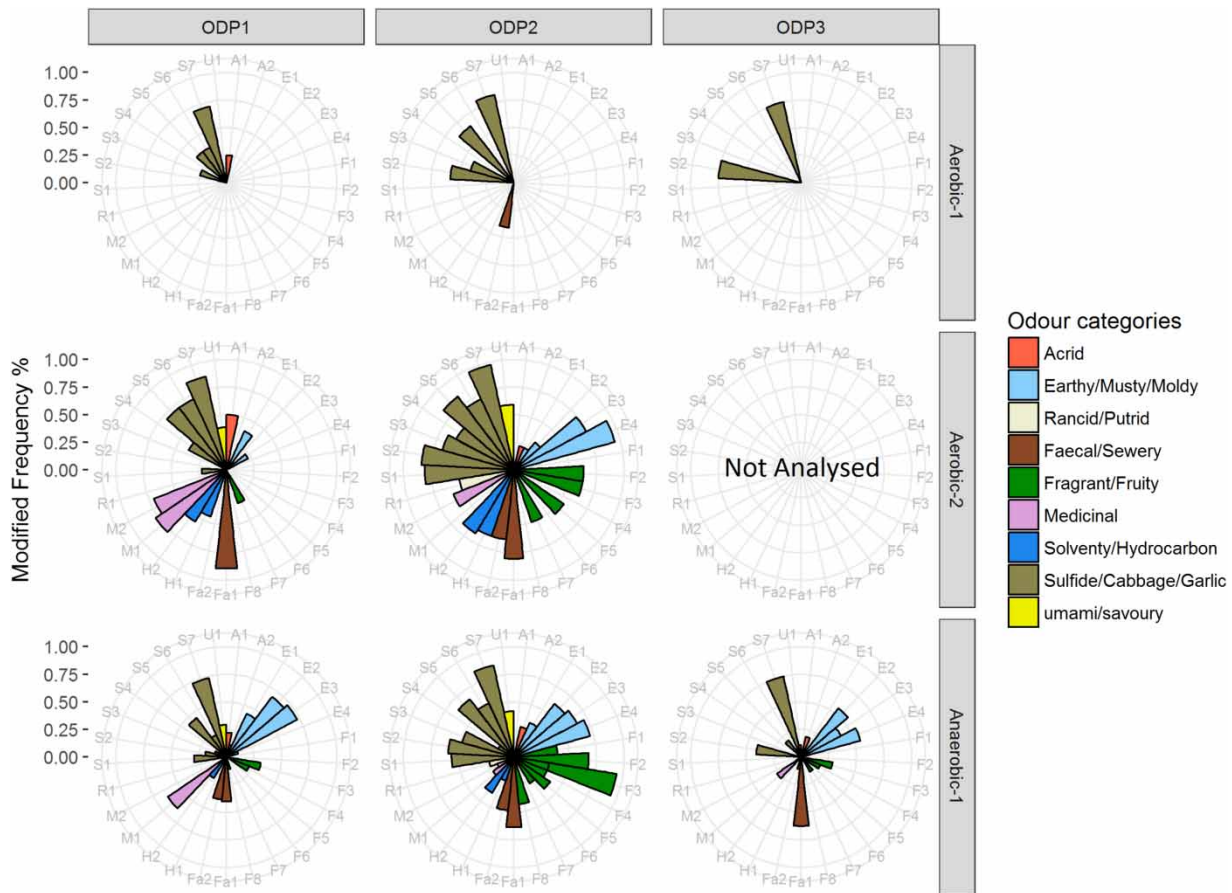


Figure 3 | Modified frequency (MF%) of ODP events detected by different assessors for the Aerobic-1, Aerobic-2 and Anaerobic-1 sites. Likely odour categories are indicated by colours, odour events are reported in Table S1 (available with the online version of this paper).

mercaptans (Sivret *et al.* 2010), may be overcome using targeted chemical analysis or olfactory analysis of the bulk emission. For the latter, methods such as the odor profile method have been effectively implemented to identify types of odour characters in emissions from waste management facilities, compost sites, wastewater plants, as well as drinking water (Burlingame 1999; Decottignies *et al.* 2009; Suffet *et al.* 2009; Curren *et al.* 2016). The combination of both olfactory and analytical methods to identify odorants responsible for high intensity odour characters should be the focus of future emission studies.

CONCLUSION

The characterisation of types of odours emitted from aerobically stabilised biosolids has previously not been well documented. In this study, two different aerobically stabilised biosolids cakes were analysed using GC-MS/O and

detected odours compared to those from anaerobically stabilised biosolids. The perceived odour characters from the two aerobically stabilised sites varied significantly, with fewer odour events detected from the Aerobic-1 site. Different dewatering processes and total solids may influence emissions from aerobically stabilised biosolids, however, further studies are needed to elucidate the effect of wastewater treatment plant performance on biosolids emissions. Odours from the anaerobically stabilised biosolids were somewhat comparable to emissions from Aerobic-2 plant, with a range of odour events being detected. Odour characters typical of sulfur-type compounds were frequently detected in all biosolids emissions by all assessors, supporting their importance in nuisance emissions. The variability of human assessors' perceptions of other odours highlights the need for methods such as GC-MS/O which combine sensorial and analytical measurements. Future studies should focus on the identification of odorants responsible for high intensity odour characters

as well as their relationship with upstream biosolids processing.

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