

Comparing Static Headspace and Dynamic Flux Hood Measurements of Biosolids Odour Emissions

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Malodorous emissions from biosolids limit opportunities for their reuse. Potential emissions may be measured from the headspace of samples or dynamic emissions swept from surface of samples using hood methods. The static headspace method is widely used to represent potential emissions from heaped anaerobic piles of biosolids, whilst dynamic flux hoods measure potential ambient emissions from the surface of biosolids piles taking into account some dilution. Methods were compared using replicates of different biosolid samples to highlight differences between the potential odour measurements. The resultant odorants emitted from the samples as they were aged were analysed using TD-GC-SCD/NCD. Whilst the different methods showed similar behavior of emissions as they were aged, the odorant concentrations varied dramatically between methods. A greater variety of volatile sulfur compounds (VSCs) were observed using the headspace method, perhaps due to the higher concentrations typical of the headspace method exceeding the analytical equipment's limit of detection. VSC emissions using the static headspace method were seen to decrease after the initial days of storage until they were undetectable. The ongoing VSCs emitted from aged biosolids, using the dynamic flux hood method, is likely due to the interplay between anaerobic and aerobic conditions. The differences between the two methodologies identified the need to understand the suitability of measurement methods.

1. Introduction

Environmental odours can be measured in-situ emissions, or from samples of the source itself. The measurement of ambient in-situ emissions from specific materials can be difficult to relate wholly to the one source and/or may be at low concentrations below the detection limits of analytical equipment. Measurements taken from samples of the source of the odours can allow easier transport, whilst a variety of methods can be used to determine sample potential emissions rather than those actually on site (Lebrero *et al.*, 2011). Malodorous emissions from biosolids are a concern for both the wastewater treatment plant (WWTP) operators as well as the community surrounding the WWTP and land application sites (Gostelow *et al.*, 2001). Emissions from anaerobically stabilised biosolids have been well characterised in recent years and the dominant odorant species causing nuisance emissions were sulfur containing compounds (Adams, 2004).

A variety of methods have been used to generate emissions from biosolids samples, the most common of which is the static headspace method. The static headspace method, developed by Glindemann *et al.* (2006) was chosen based on its small equipment requirements and reproducibility. The basis for its application is the simulation of conditions in the middle of anaerobic heaped biosolids storage piles. Well-supported ageing trends have been established for centrifugally dewatered anaerobically digested biosolids, typical profiles show a peak in emissions occurring in the initial days of storage, being much reduced from day 7 onwards (Higgins *et al.*, 2006). The timing of the peaks is used to recommend appropriate times for outloading such heaped piles of biosolids (Adams, 2004). The U.S. Environmental Protection Agency (EPA) endorsed dynamic flux hood method is commonly used in environmental odour sampling. Hoods are commonly used to simulate emissions produced by ventilation in storage rooms (Wang *et al.*, 2011), rather than wind tunnels which simulate the higher velocities achieved by wind (Prata Jr *et al.*, 2014). The basis of this method is the

production of emissions from a nitrogen sweep applied to the biosolids surface simulating the effect of air movement stripping emissions from the biosolids pile surface. Emissions produced using the dynamic flux hood method can predict the levels of emissions expected in the ambient conditions of the biosolids storage sheds, or when applied to land. Both methods measure the potential for odour emissions from biosolids, however they vary in their approach as well as in equipment used.

An adapted static headspace method and the dynamic flux hood method were both used to evaluate potential emissions from biosolids samples generated using different dewatering centrifuge set-points. Dewatering has been identified as a key process affecting biosolids emission profiles (Higgins *et al.*, 2008). Therefore the methods can be evaluated on a range of samples with expected different emission profiles. Comparison of the results generated using these methods gives operators a greater understanding of solids management options as well as the drawbacks or suitability of the different measurement methods.

2. Material and Method

2.1 Sampling

Biosolids grab samples (~10L) were taken from a tertiary WWTP directly after dewatering. Eight biosolids samples were taken and each sample corresponded to different sets of dewatering centrifuge parameters. Corresponding samples were analysed for total solids (wt%), volatile solids (% of total solids) and pH using standard methods.

2.2 Emission measurements

For dynamic flux hood (DFH) analysis a US EPA endorsed dynamic flux hood was applied to the surface of biosolid samples. Nitrogen gas was used to sweep the surface and the resulting emissions were sampled using the lung method into Nalophan bags (3L) in duplicate. Emissions samples were taken on the day of sample delivery, as well as days 3, 7, and 14 with the samples stored in large plastic containers in ambient conditions between measurements.

The adapted static headspace (SH) method had 1L of air added to 100g samples of biosolids stored in double walled Nalophan bags. Analysis was carried out the day after the bags were made, as well as days 3, 7 and 14. Samples were stored at room temperature between measurements.

Nalophan bags for both methods were attached directly to an Air Server CIA Advantage sampler and 50mL of the emissions transferred to a UNITY thermal desorption unit (both from Markes International, UK). Gas chromatography coupled with a sulfur chemiluminescence detector and a nitrogen chemiluminescence detector in parallel (TD-GC-SCD/NCD) was used for the analysis of volatile organic sulfur compounds (VOSCs) and ammonia. Settings for analytical system are described in Le *et al.*, (2013). The average detection threshold for the VOSCs in the SCD was 8ppb and 235ppb for ammonia in the NCD.

Hydrogen sulfide (H₂S) measurements were taken directly from the Nalophan bags prior to other analysis. H₂S from the SH samples was measured initially, however measurements >50ppm were returned. These high concentrations were above the detection limit and safe working concentrations of the Jerome 631 gold film hydrogen sulfide analyser (Arizona Instruments), so measurements were ceased for this method.

2.3 Quantification and data analysis

Resulting chromatograms were compared to standard curves for a set of 11 standard sulfur compounds and ammonia solutions for peak quantification. The potential odour impacts of the emissions were evaluated by converting the concentrations to odour activity values (OAV) (Sivret *et al.*, 2016). The concentration of odorants are normalised against each other using their detection thresholds (DT) using Eq(1). Detection thresholds used in this study were from Nagata *et al.*, (2003).

$$OAV = \frac{\text{Concentration (ppm)}}{DT \text{ (ppm)}} \quad (1)$$

3. Results and discussion

The emissions for the dynamic flux hood and static headspace methods are shown in Figure 1. A range of VOSCs were detected using both methods, however higher proportions of methyl mercaptan (MT) compared to the other compounds were noted in the SH method. Its greater presence in the headspace samples is likely due to both its volatility and its instability in aerobic conditions being converted to dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS) by oxidation dimerisation (Lomans *et al.*, 2002). The higher concentrations observed with the SH method are expected as there is no dilution of the emissions, compared to the DFH method with the nitrogen sweep flows. Higher concentrations could be an advantage when high sensitivity analytical equipment isn't available. Propyl mercaptan (n-PT) was identified in the SH method likely associated

with the increased concentrations, allowing levels to be detected with analytical equipment. Only 2% of variation in the VOSC results ($R^2=0.98$), and 11% for the Ammonia results ($R^2=0.89$), between the duplicates for the DFH method are attributed to errors. Showing the analytical measurements (TD-GC-MS) used to evaluate the two methods give reproducible results.

Dimethyl sulfide (DMS) was detected in the emissions from both methods; it's commonly detected alongside MT as its formed using a similar pathway (Lomans *et al.*, 2002). The degradation of VOSCs as biosolids are aged is associated with their microbial cycling, with peak emissions occurring due to the imbalance between the VOSC producers and degraders (Higgins *et al.*, 2006). The differences between the baseline VOSC emissions for both methods are likely associated with the aerobic conditions of the biosolids storage for DFH method and the anoxic conditions of the SH method and interactions with the methanogen populations. Methanogens are known degraders of VOSCs and favour anaerobic conditions (Chen *et al.*, 2005).

The Day 0 emissions from Samples 1 and 5 were higher than others when ageing in the DFH, however this effect wasn't evident in the Day 1 results for the SH method. Samples 2, 3 and 4 had higher levels of VOSCs on day 3 compared to the initial day 0, perhaps signified by lower VOSC producer activity in the initial days, influenced by those particular combinations of dewatering parameters. This effect was not evident in the SH method, likely due to the anaerobic incubation and longer incubation period, being sampled on day 1 rather than day 0, perhaps resulting in a shorter time for methanogen population to re-establish.

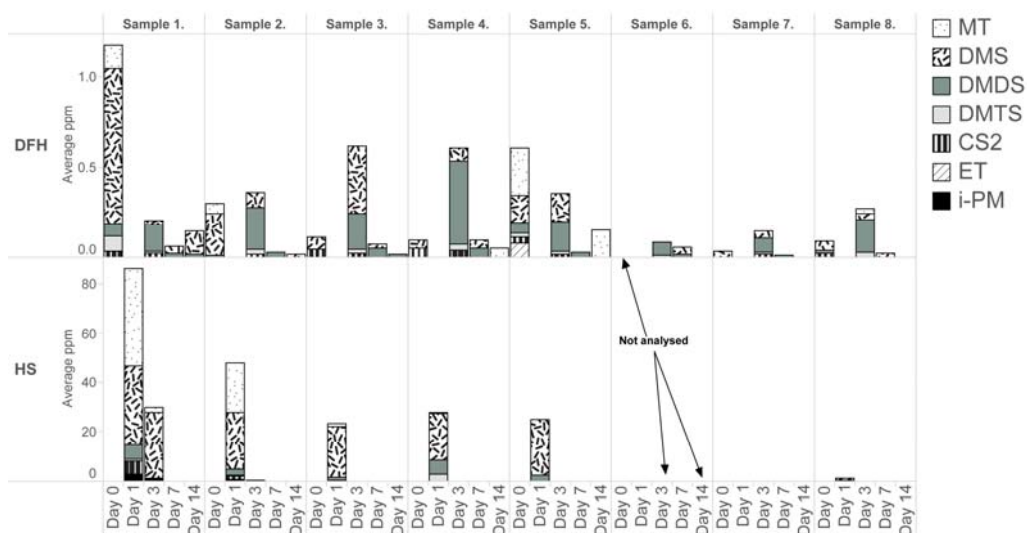


Figure 1: Average concentrations of VOSCs emitted from DFH and SH methods as the eight samples are aged.

Samples 6-8 had lower VOSC emissions than the other samples for both analysis methods, whilst ammonia emissions appeared greater (Figure 2). The chemical and physical properties of the biosolids were not significantly different from the other samples as shown in Table 1, despite the use of different dewatering parameter. The low concentrations were most predominant for the SH method with only low levels (<5 ppm) of sulfur compounds being detected on the initial day of sampling. The lower levels are perhaps associated with less inhibition of the methanogens using the dewatering parameters for those samples. The lower SH emissions of VOSCs are most likely influenced by methanogen activity and the overall microbial activity, signified by the ammonia emissions, isn't apparently affected. Emissions from the DFH method were reduced compared to the other samples; some levels of VOSCs were still detected, reinforcing the role of methanogens, as they would be partially inhibited in the cake surface due to exposure to ambient conditions.

High concentrations of ammonia were measured for the DFH method as shown in Figure 2. Ammonia concentrations were higher than the total volatile sulfur compounds (VSCs) and levels appeared to decrease as the biosolids were aged. Ammonia is a degradation product of organic matter, such as amino acids which have a high nitrogen level. Therefore, its greater levels of emissions are likely associated with the ongoing degradation of organic matter in the dewatered biosolids. Ammonia is considered volatile and easily stripped from the biosolids. However, even though it's easily produced and emitted from biosolids its odour detection threshold are orders of magnitude higher than that of VSCs (Nagata *et al.*, 2003) so it isn't assigned as a dominant odorant in terms of receptor impact. Ammonia emissions from the SH method were of a similar

concentration to the VSCs, however levels increased as the biosolids were aged unlike with the DFH trends. This increase over time is likely associated with the ongoing build up of ammonia in the headspace associated with organic degradation. This shows that the headspace is a cumulative result of the emissions from the biosolids over storage time, rather than an instantaneous snap-shot of emissions from the biosolids as shown by the DFH method.

Table 1: Chemical properties for the received fresh biosolid samples.

	TS (wt%)	VS (%)	pH
Sample 1.	21.83	79.18	-na-
Sample 2.	19.67	78.5	7.2
Sample 3.	20.91	74.3	7.39
Sample 4.	22.15	73.6	7.21
Sample 5.	18.82	71.28	7.13
Sample 6.	19.87	75.21	7.17
Sample 7.	21.48	70.37	6.98
Sample 8.	20.13	77.64	7.13

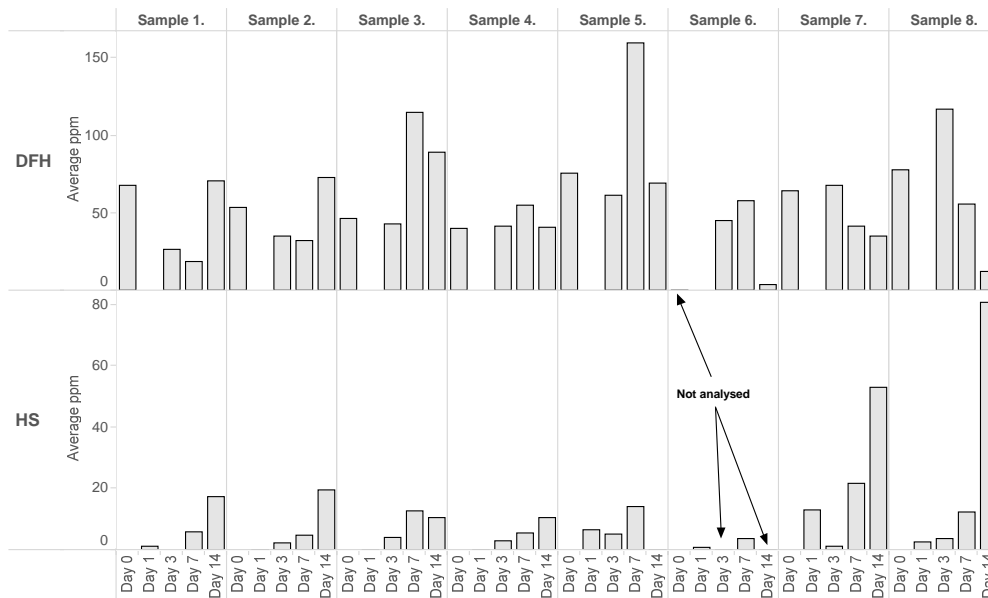


Figure 2: Ammonia emissions from DFH and SH methods as the eight samples are aged.

The SH method used in this study was adapted from that prescribed by Glindeman *et al.*, (2006). The availability of a thermal sealer for the sampling bags and the sampling mantle of the TD-GC-SCD/NCD removed the requirement for syringe sampling of the headspace of individual storage bottles which can introduce errors. However, the reduction in headspace volume over the sampling time may affect the emission levels. This is not considered significant as the concentrations of VSCs decreased with storage time and volume reduction, rather than increasing if the rate of emission were constant and the reduction in volume significant. It's unknown if the increase in NH_3 concentrations in the SH method is associated with organic degradation and NH_3 generation, or the reduction in headspace and a constant emission rate.

The H_2S emissions from the DFH samples shown in Figure 3, mostly decreased as the samples were stored. Whilst H_2S appeared at concentrations higher than the cumulative VSCs for the DFH samples, as results were not measured for the SH method, it isn't investigated further in this study. Whilst H_2S was once commonly used as a surrogate for odour emissions (Gostelow *et al.*, 2001), VSCs due to their lower odour detection thresholds and offensive characters are increasingly becoming the focus of odour emission studies.

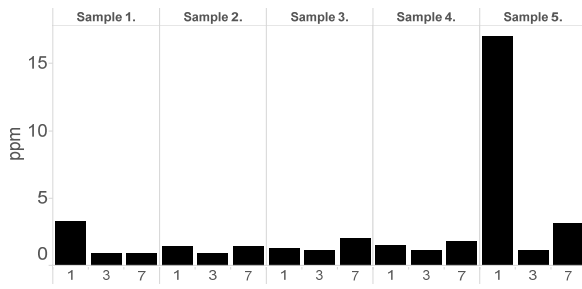


Figure 3: Hydrogen sulfide results from the DFH initial samples with storage days.

The OAVs results in Figures 4 and 5. show that MT is the dominant odorant, excluding H₂S, contributing to nuisance emissions for both sampling methods. Samples 1 and 5 had the highest OAVs for the Day 0 emissions using DFH, Sample 1 was the highest for Day 1 of SH, while the Sample 5 SH sample only produced low amounts of MT leading to a very small OAV. The proportion of n-PT is of interest in the SH results as it wasn't detected in the DFH method, however due to its low odour detection threshold may contribute to the overall odour character. As higher levels of MT, as well as n-PT, are detected using the SH method this method may overestimate the potential odour impact. The OAV of DFH is thought more relevant to represent the potential odour impact of in-situ emission due to the interplay between anaerobic and aerobic sludge conditions which have been described in a field study by Rosenfeld *et al.*, 2001. The results show that there is a need to understand the suitability of each method when interpreting emission results. Ultimately both methods represent the odour potential from biosolids, however, from different situations.

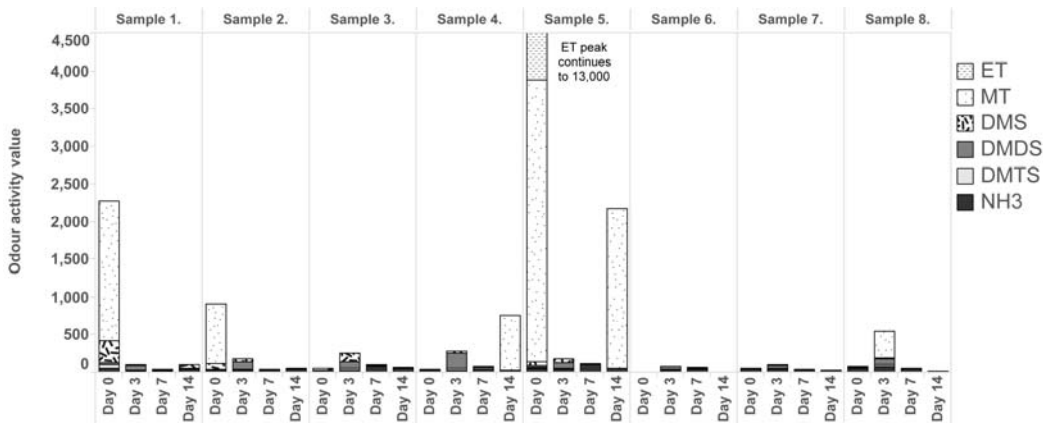


Figure 4: Dynamic flux hood odour activity results.

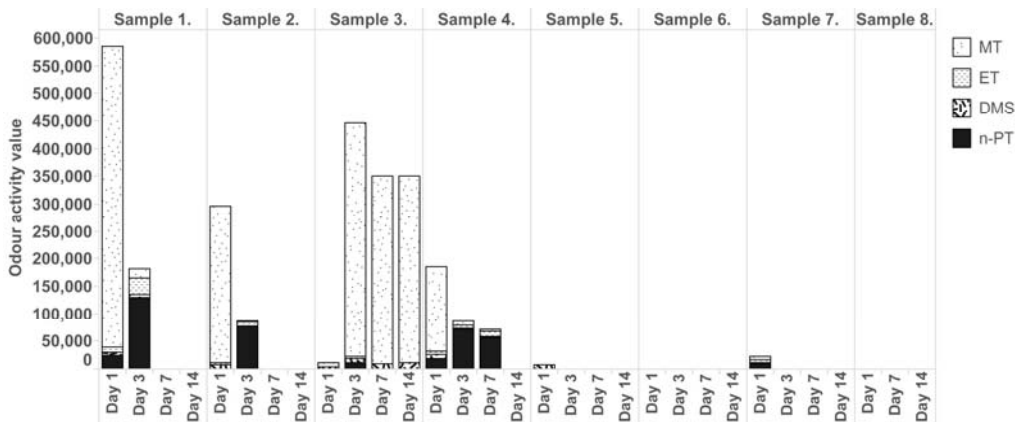


Figure 5: Static headspace odour activity results.

4. Conclusions

The comparison of headspace and dynamic fluxhood sampling of ageing biosolids showed differences in emissions, which could be attributed to the microbial activity in the samples. The higher concentrations and larger range of sulfur based compounds detected using the headspace method has the advantage of identifying odorous compounds at low concentrations. However, the method is based on simulating the anaerobic conditions in biosolids heaped piles, rather than the interplay of anaerobic and aerobic regions on the surface of the sample that the dynamic fluxhood method measures. The differences between the two methodologies identified the need to understand the suitability of sampling methods used to measure potential odorous emissions.

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Reference

- Adams G.M., 2004, Identifying and Controlling Municipal Wastewater Odor Phase II: Impacts of Inplant Parameters on Biosolids Odor Quality, IWA Publishing.
- Chen Y.C., Higgins M.J., Maas N.A., Murthy S.N., Toffey W., Foster D., 2005, Roles of methanogens on volatile organic sulfur compound production in anaerobically digested wastewater biosolids. *Water Science & Technology*, 52, 67-72.
- Glindeman D., Murthy S.N., Higgins M.J., Chen Y.C., Novak J. T., 2006, Biosolids incubation method for odorous gas measurement from dewatered sludge cakes. *J. Residuals Sci. Technol*, 3, 153-160.
- Gostelow P., Parsons S., Stuetz R.M., 2001, Odour measurements for sewage treatment works. *Water Research*, 35, 579-597.
- Higgins M.J., Adams G., Chen Y.C., Erdal Z., Forbes R.H., Glindeman D., Hargreaves J.R., McEwan D., Murthy S.N., Novak J.T., Witherspoon J, 2008, Role of protein, amino acids, and enzyme activity on odor production from anaerobically digested and dewatered biosolids. *Water Environ Res*, 80, 127-35.
- Higgins M.J., Chen Y.C., Yarosz D.P., Murthy S.N., Maas N.A., Glindeman, D., Novak J. T., 2006, Cycling of volatile organic sulfur compounds in anaerobically digested biosolids and its implications for odors. *Water Environ Res*, 78, 243-52.
- Le, H., Sivret, E., Parcsi, G. and Stuetz, R. 2013, Stability of Volatile Sulfur Compounds (VSCs) in sampling bags—impact of temperature. *Water Science & Technology* 68(8), 1880-1887.
- Lebrero R., Bouchy L., Stuetz R., Munoz R., 2011, Odor assessment and management in wastewater treatment plants: a review. *Critical Reviews in Environmental Science and Technology*, 41, 915-950.
- Lomans B. P., Van Der Drift C., Pol A., Op Den Camp H. J. M., 2002, Microbial cycling of volatile organic sulfur compounds. *Cellular and Molecular Life Sciences*, 59, 575-88.
- Nagata Y., 2003, Measurement of odor threshold by triangle odor bag method. *Odor measurement review*, 118-127.
- Prata Jr, A., Santos, J., Timchenko, V. and Stuetz, R.M. (2014) Use of computational fluid dynamics in the analysis of a portable wind tunnel for sampling of odorous emissions at liquid surfaces. *Chem. Eng. Trans* 40, 14.
- Rosenfeld P., Henry C., Dills R., Harrison R., 2001, Comparison of Odor Emissions from Three Different Biosolids Applied to Forest Soil. *Water, Air, and Soil Pollution*, 127, 173-191.
- Sivret E., Wang, B., Parcsi, G., Stuetz, R.M., 2016, Prioritisation of odorants emitted from sewers using odour activity values. *Water Research*, 88, 308-321.
- Wang T., Sattayatewa C., Venkatesan D., Noll K.E., Pagilla K.R., Moschandreas D.J., 2011, Comparison of two dynamic measurement methods of odor and odorant emission rates from freshly dewatered biosolids. *Journal of Environmental Monitoring*, 13, 1746-1752.