Laboratory Scale Investigations of Potential Odour Reduction Measures in Biosolids Phase I

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Executive Summary

Odour production in biosolids is a complex process influenced by several factors including, but not limited to process variables within anaerobic digestion and dewatering processes, as well as the relationships between odours and concentration of odorants. Many compounds have been associated with odours from biosolids facilities. Some of the most relevant include volatile organic sulphur compounds (VOSCs) such as: methanethiol (MT), dimethyl sulphide (DMS), dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS), as well as inorganic sulphur compounds such as hydrogen sulphide (H_2S) (Higgins *et al*., 2008). Nitrogenous compounds such as trimethylamine (TMA), ammonia, and volatile fatty acids (VFA) can also be potential sources of odour (Higgins *et al*., 2008). Odorous volatile aromatic compounds (OVACs) such as toluene, ethylbenzene, styrene, *p*-cresol, indole and skatole have also been identified in headspace samples from stored biosolids (Chen *et al*., 2006). Due to differences in biosolids characteristics, treatment processes and operating conditions associated with different wastewater treatment plants (WWTPs), the chosen odour reduction strategies need to be based on the site-specific conditions at each WWTP. In most cases, "trial-and-error" laboratory or pilot-scale approaches are required to find the most suitable odour reduction strategy.

This study investigated the potential sources of odours from biosolids produced from a Western Australian Wastewater Treatment Plant (Woodman Point) and examined potential odour reduction strategies on a laboratory scale. The odour reduction methods that were trialled were chemical addition and reduction of centrifuge speed. The chemical addition trials were conducted by adding alum, polyaluminium chloride or ferric chloride to digested sludge that had been sampled prior to the dewatering stage. Trials of chemical addition (alum) to plant dewatered cake were also undertaken. The impact of reducing the centrifuge speed on biosolids odour was also investigated using a laboratory scale centrifuge that had been calibrated to operate such that the shear forces on the sample would be representative, as closely as possible, to those on the plant. To assess the effectiveness of the odour reduction measures trialled in this study, headspace solid-phase microextraction coupled with gas chromatography-mass spectrometry (HS SPME-GC-MS) methods for the analysis of volatile sulphur compounds (e.g. DMS, DMDS, DMTS) and other volatile organic compounds (toluene, ethylbenzene, styrene, *p*-cresol, indole, skatole and geosmin) were developed.

Based on the results obtained from this preliminary (Phase I) study, the following conclusions were made:

- The main odorous compounds identified in fresh (less than a week old) biosolids samples from Woodman Point WWTP included DMS, DMDS, DMTS and traces of geosmin. Indole and skatole were identified in older biosolid samples that were stored at room temperature for a few months and exhibited a strong faecal/nauseating odour. Other compounds, which were tentatively identified based on their mass spectra and/or library matches, but not confirmed with authentic analytical standards, included various long chain aliphatic hydrocarbons, terpenes, alkyl benzenes and other aromatic compounds. It should be noted that the analytical methods were aimed at detection of known odour compounds and non-target analytes would not necessarily be detected.
- A 20% reduction in centrifuge speed resulted in an approximately 30% reduction in the peak TVOSC concentration, however the solids content of the resulting cake was also reduced, which is undesirable from the point of view of WWTP operations.
- Aluminium sulphate addition (at a dose of 4% aluminium on dry weight basis) to digested sludge prior to dewatering offered the best odour reduction strategy amongst the options that were investigated, resulting in approximately 40% reduction in peak TVOSC concentration, relative to a control sample.

- In future studies, it would be beneficial to correlate the odour compounds identified using chemical analysis (HS SPME-GC-MS) with dilution olfactometry measurements or other quantitative odour measurements.

While studies conducted in this project utilised sludge and biosolids samples from just one WWTP (Woodman Point), future studies will expand the scope to include biosolids and sludge sourced from other WWTPs. This will provide information on odorous compounds in biosolids produced at other Western Australian WWTPs and whether the trialled odour reduction strategies are applicable to more than one type of wastewater treatment system.

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Acronyms and Abbreviations

DEDS	Diethyl Disulphide
DMDS	Dimethyl Disulphide
DMS	Dimethyl Sulphide
DMTS	Dimethyl Trisulphide
DS	Dry solids
DVB-CAR-PDMS	Divinylbenzne-carboxen-polydimethylsiloxane
EMS	Ethyl methyl sulphide
ET	Ethanethiol
HS	Headspace
GC-MS	Gas Chromatography-Mass Spectrometry
H_2S	Hydrogen Sulphide
MEDS	Methyl Ethyl Disulphide
MT	Methanethiol (also known as methyl mercaptan)
OVACs	Odorous Volatile Aromatic Compounds
SIM	Selective Ion Monitoring
SPME	Solid-Phase Microextraction
PDMS-DVB	Polydimethylsiloxane-divinylbenzene
tDS	tonne of dry solids
TMA	Trimethylamine
TVOSCs	Total Volatile Organic Sulphur Compounds
VFA	Volatile Fatty Acids
VOSCs	Volatile Organic Sulphur Compounds
WCWA	Water Corporation of Western Australia
WERF	Water Environment Research Foundation
WWTP	Wastewater Treatment Plant

1.0 Introduction

Beneficial reuse of biosolids using land application is a viable and important practice for the wastewater industry as well as for the agricultural community. Land application offers a low-cost disposal option for biosolids and a low-cost nutrient source/soil amendment for a variety of applications including agricultural and mine site reclamation projects. However, one of the main limitations that may restrict land application programs is nuisance odours associated with biosolids.

Odour production in biosolids is influenced by many complex factors. These include: (1) reactions of proteins, amino acids and enzyme activity; (2) relationships between odours and concentrations of odorants; (3) impact of process variables upstream of the anaerobic digestion stage; (4) process variables within the anaerobic digestion stage and various enhancements to the anaerobic digestion process; (5) the impact of the biosolids dewatering and conveyance processes; (6) polymer addition; (7) chemical addition and (8) storage of biosolids cake (Adams, *et al.*, 2008). Many compounds have been associated with odours from biosolids facilities, with some of the most relevant including volatile organic sulphur compounds (VOSCs) such as methanethiol (MT), dimethyl sulphide (DMS), dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS), as well as inorganic sulphur compounds such as hydrogen sulphide (H_2S) (Higgins *et al*., 2008). Nitrogenous compounds such as trimethylamine (TMA), ammonia, and volatile fatty acids (VFA) are also potential sources of odour (Higgins *et al*., 2008). Odorous volatile aromatic compounds (OVACs) such as toluene, ethylbenzene, styrene, *p*-cresol, indole and skatole have also been identified in headspace samples from stored biosolids (Chen *et al*., 2006). The Water Environment Research Foundation (WERF) conducted a multi-phase collaborative study to better understand odour formation in biosolids as well as to develop management practices to minimise these odours (Adams *et al*., 2003a; Adams *et al*., 2003b, 2008). These studies were based on an in-depth sampling and analysis of biosolids and headspace samples from several different wastewater treatment plants (WWTPs) across North America. One of the outcomes of this study was the development of the *Biosolids Odour Reduction Roadmap* (Figure 1) as a decision tool, enabling users to obtain guidance on biosolids issues that were potentially present at their WWTP (Adams *et al*., 2008). A key recommendation from this study noted that no single odour reduction strategy suited all wastewater treatment facilities. Consideration must be given to the site-specific conditions that make up the sludge and biosolids characteristics such as, sewerage inflow, treatment processes used and operational aspects (e.g. sludge handling times, sludge temperature etc). In most cases, “trial-and-error” laboratory or pilot-scale approaches are required to find the most suitable odour reduction strategy.

We applied this ‘trial-and-error” approach to determine the most suitable odour reduction strategy for biosolids produced at Woodman Point WWTP. The key driver for choosing Woodman Point was that the produced sludge and biosolids were perceived to be more odorous compared to similar materials produced at other treatment plants. Additionally, during the course of the project Woodman Point was less likely to have interruptions in the sludge handling / production process. The plant was also easy to access and sample, and it has the most current technology for processing sludge. It is an activated sludge plant which uses sequencing batch reactors (SBR) and egg-shaped digesters to process the sludge. The advantage of using SBR over the conventional aeration tank systems is that the biological treatment and clarification are completed in a single step, thereby reducing costs and space (Water Corporation, 2012). The egg-shaped digesters are operated in the mesophilic range (35 – 37 °C) and offer several advantages over the conventional cylindrical anaerobic digesters, namely better mixing and heating.

1.1 Project Aims

The aims of this study were to: (1) investigate the chemical compounds responsible for the odour in biosolids from our test site; (2) investigate the use of metal coagulants (aluminium sulphate, polyaluminium chloride and ferric chloride) as means of odour reduction and (3) investigate

whether reducing centrifuge speed is effective in reducing odour in biosolids cake from our test site. At this preliminary stage of the study all experimentation was limited to laboratory scale work.

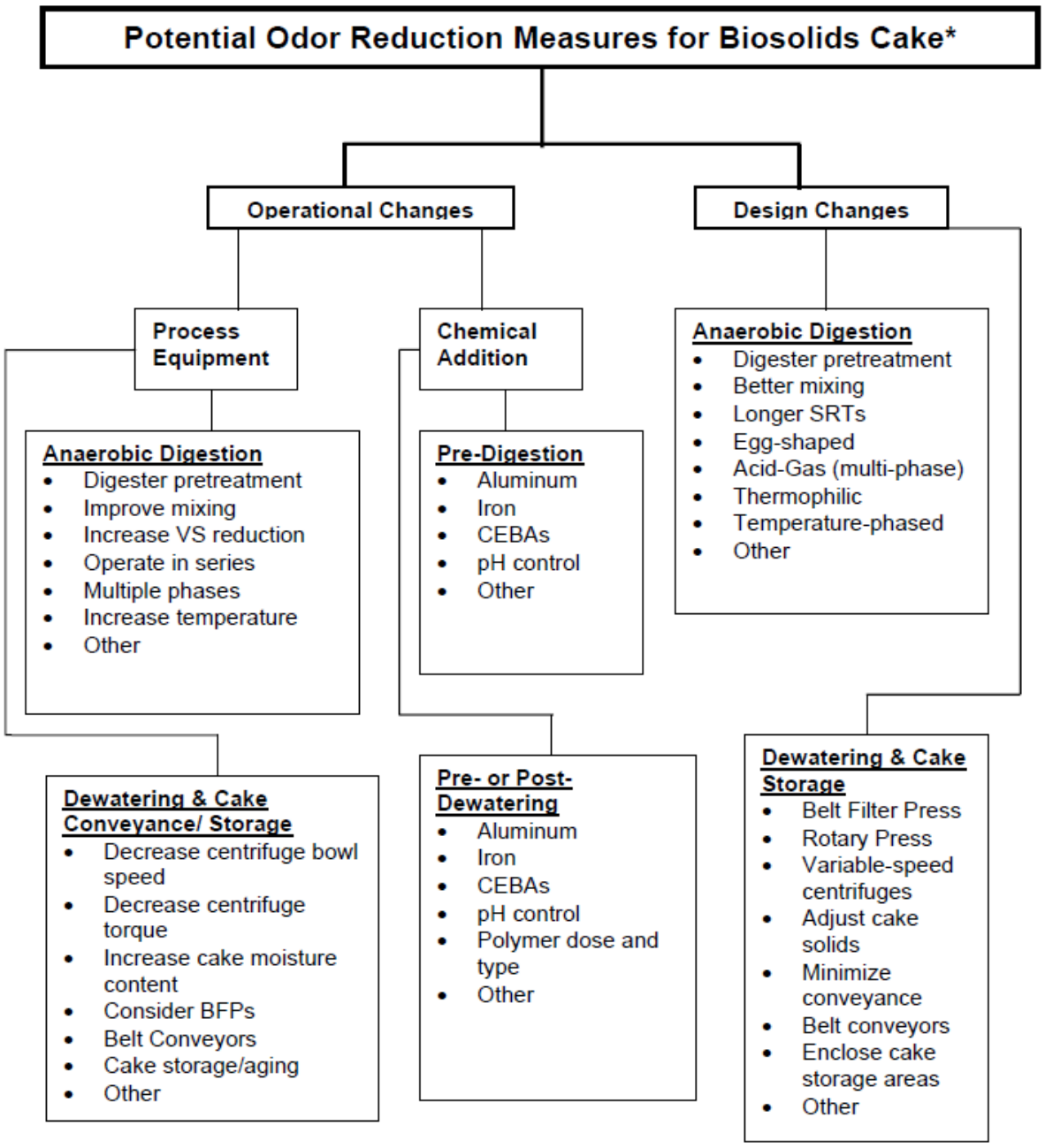

Figure 1: A Summary Chart of Potential Odour Reduction Measures. * **Note:** None of these options should be considered independently of the others. Odour reductions in one area may impact processes and odours in other areas. Therefore, a consolidated and customised approach is required for each WWTP (adapted from Adams, *et al*., 2008).

2.0 Methods and Materials

2.1 General

Anaerobically digested sludge (DS 3.7%, SRT 19 days) and plant dewatered biosolids cake (DS 16.9%) samples were obtained from Woodman Point Wastewater Treatment Plant. Polymer used for dewatering was a powder polymer FO4800SSH from SNF (supplied by Water Corporation) with a molecular weight of approximately 8 million and a charge density of 80%. Aluminium sulphate and polyaluminium chloride, used in the chemical addition trials were sourced from water treatment plant operations at Water Corporation of Western Australia (WCWA). Aluminium sulphate was used as a 56% w/v solution. Polyaluminium chloride (PAC23 from Orica) was used a 23% w/v solution in aluminium oxide. Ferric chloride was used as a 36% w/v solution, prepared in-house from analytical grade ferric chloride (Sigma-Aldrich). Analytical standards for: sodium thiomethoxide, ethanethiol, DMS, DMDS, DMTS, ethyl methyl sulphide (EMS), diethyl disulphide (DEDS), toluene, ethylbenzene, styrene, *p*-cresol, indole, skatole and geosmin were purchased from Sigma-Aldrich at purity ≥ 99%. Deuterated dimethyl disulphide (DMDS-d_6) was purchased from Sigma-Aldrich at 98 atom % D. Deuterated ethylbenzene (ethylbenzene-d_{10}) was purchased from Cambridge Isotope Laboratories Inc at 98 atom % D. Methanol was HPLC grade from Fischer Scientific. Anhydrous granular sodium sulphate was purchased from Ajax Finechem and was baked at 400 °C for a minimum of 4 hours prior to use. Two SPME fibres were used: 50/30 µm divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS) and 65 µm polydimethylsiloxane-divinylbenzene (PDMS-DVB).

2.2 Laboratory scale dewatering

600 g – 800 g of anaerobically digested sludge in a 1 L glass beaker was stirred at 200 rpm for 30 seconds using a jar tester. A polymer solution (0.3% w/v; polymer dose based on the average amount used at Woodman Point of ~ 16kg polymer/tDS centrifuge feed sludge dry solids) was added and the resulting mixture was stirred at 200 rpm for another 30 seconds and then stirred at 50 rpm for 90 seconds. The mixing regime was based on the mixing regime reported by Higgins (2010). The sludge mixture was then dewatered using a laboratory centrifuge (Heraeus Multifuge 3S with a maximum rotational radius of 18.2 cm) at 3850 rpm for 20 minutes. The combined wet cake was then pressed between 2 medium-density fibreboards (MDF) (300 mm x 300 mm; 7mm thick) encased in polyethylene wrap and lined with sheets of Whatman No 1 filter paper to absorb the excess water. Pressure was applied by placing weights totalling approximately 8 kg on top of the MDF boards. To simulate the high shear experienced in the plant centrifuge, the sample cake was processed through a manual food mincer (Avanti food mincer #8) which pushed the cake through a "scroll-conveyor", followed by extrusion through several openings, each 8 mm in diameter. The lab dewatered biosolids cake had a similar texture and odour to the plant dewatered sample. The solids content of the lab dewatered cake was comparable to that of the plant dewatered cake.

2.3 Chemical addition to digested sludge prior to dewatering

Individual samples of digested sludge (approximately 800 g each) in 1 L glass beakers were treated with aluminium sulphate (alum), polyaluminium chloride and ferric chloride at doses of 2% and 4% of metal on a dry weight basis. The samples were mixed using a jar tester. The mixing regime used is shown in Figure 2. A control sample, with no chemical addition was also prepared. The samples were dewatered using the dewatering procedure described above. Details of the exact quantities of sludge, polymer solution and chemical are given in Appendix 1.

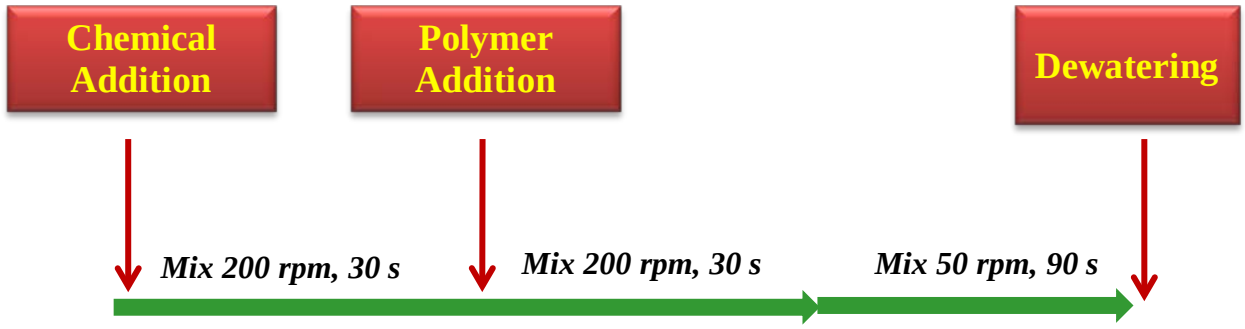

Figure 2. Mixing regime used in the chemical addition trials (adapted from Higgins, 2010).

The bulk of the resulting biosolids cake samples (approximately 200 g) were incubated at room temperature in 1 L Schott bottles. In parallel, smaller samples (50 – 80 mg) of the resulting biosolids cake were also incubated in several Teflon-lined screw cap vials (20 mL). All samples were wrapped in aluminium foil to protect from light. Both sets of samples were monitored for evolution of sulphur compounds (DMS, EMS, DMDS, DEDS and DMTS) by HS SPME-GC-MS every other day for 20 days. The samples were also analysed for the production of OVACs (toluene, ethylbenzene, styrene, *p*-cresol, indole, and skatole) by HS SPME-GC-MS weekly for 37 days.

2.4 Chemical addition to plant dewatered cake

Samples of the plant dewatered biosolids (approximately 85 g) in 400 mL glass beakers were treated with aluminium sulphate hydrate (Sigma-Aldrich) at doses of 2% and 4% of metal on a dry weight basis and mixed manually with a stainless steel spatula for approximately 2 minutes. A control sample (no chemical addition) was treated in the same way. Details of the exact quantities of cake and chemical are shown in Appendix 2. The bulk of the samples were incubated at room temperature in 250 mL Schott bottles. In parallel, smaller samples (50 – 80 mg) of the resulting biosolids cake were also incubated in several Teflon-lined screw cap vials (20 mL). All samples were wrapped in aluminium foil to protect from light. Both sets of samples were monitored for evolution of sulphur compounds by HS SPME-GC-MS every other day for 14 days. The samples were also analysed for the production of OVACs by HS SPME-GC-MS weekly for 16 days.

2.5 Centrifuge speed trials

Samples of digested sludge (approximately 600 g) were dewatered at 3850 rpm (control), 3460 rpm (10% reduction in speed, relative to control) and 3080 rpm (20% reduction in speed, relative to control) using the dewatering procedure described above. Details of the exact quantities of sludge, and polymer solution are shown in Appendix 3. The bulk of the resulting biosolids cake samples (approximately 190 g) were incubated at room temperature in 500 mL Schott bottles. In parallel, smaller samples (50 – 80 mg) of the resulting biosolids cake were also incubated in several Teflon-lined screw cap vials (20 mL). All samples were wrapped in aluminium foil to protect from light. Both sets of samples were monitored for evolution of sulphur compounds by HS SPME-GC-MS every other day for 20 days. The samples were also analysed for the production of OVACs by HS SPME-GC-MS weekly for 23 days.

2.6 HS SPME-GC-MS procedure for the analysis of sulphur compounds

Sulphur compounds (DMS, EMS, DMDS, DEDS and DMTS) were analysed by headspace SPME using a 50/30 µm DVB-CAR-PDMS fibre, followed by GC–MS analysis. SPME was performed using a Gerstel MPS2 Autosampler interfaced with a Hewlett Packard 6890N GC and a Hewlett Packard 5973 Network Mass Selective Detector. For the bulk biosolids samples, a 50 – 80 mg sub-sample was placed into a Teflon-lined screw cap vial (20 mL) and 10 mL of a 500 ng/L DMDS-d_6 internal standard solution in MilliQ water was added, followed by 3 g of anhydrous sodium

sulphate. For the smaller samples that were incubated in the Teflon-lined screw cap vials (20 mL), 100 µL of a 50 µg/L DMDS-d_6 internal standard solution in methanol was injected through the Teflon septum of the vial lid (no water added). The SPME fibre was introduced into the headspace of each of the vials and extraction was carried out for 10 minutes at 40 °C. The fibre was then desorbed at 230 °C for 4 minutes in the injector port of the GC, while the analytes were simultaneously cryofocused on the GC column at 0 °C. GC separation of the sulphur compounds was carried out using helium as the carrier gas at 1.0 mL/min, and a 30 m x 0.25 mm x 1 µm ZB-5MS (Phenomenex®) capillary column. The mass spectrometer (MS) operated in selected ion monitoring (SIM) mode and for each sulphur compound, the most abundant ion was used for quantitation and 1 – 2 characteristic *m/z* ions were selected for MS confirmation. Details of the GC temperature program and the *m/*z ions monitored are given in Appendix 4. Samples were analysed against standards of the pure compounds with deuterated DMDS (DMDS-d_6) as an internal standard. Standard and internal standard solutions were prepared in methanol.

2.7 HS SPME-GC-MS procedure for the analysis of OVACs

The OVACs (toluene, ethylbenzene, styrene, *p*-cresol, indole and skatole) were analysed using a similar procedure to that described above for the sulphur compounds except that a 65 µm DVB/PDMS fibre was used, and extraction was carried out for 30 minutes at 60 °C. The fibre was desorbed at 250 °C for 5 minutes in the injector port of the GC and the analytes were not cryofocused. Details of the GC temperature program and the *m/*z ions monitored are given in Appendix 4. Samples were analysed against standards of pure compounds using deuterated ethylbenzene (ethylbenzene-d_{10}) as an internal standard. Standard and internal standard solutions were prepared in methanol.

3.0 Results and Discussion

3.1 Validation and optimisation of the HS SPME-GC-MS methods for the analysis of sulphur compounds and OVACs

GC-MS conditions for the analysis of sulphur compounds and OVACs were optimised, in order to achieve maximum sensitivity, good baseline separation of analytes and Gaussian peak shapes. In order to optimise the sensitivity of the method and to minimise interferences from other compounds, the mass spectrometer was operated in SIM mode. In this mode the mass spectrometer is tuned to only detect the target analytes and to disregard interfering compounds.

HS SPME parameters (fibre type, extraction temperature and time, and desorption conditions) were optimised to give the best analyte responses, while minimising analyte degradation and carry-over. These parameters were optimised using Teflon-lined screw cap vials (20 mL) containing aqueous solutions of the analytes (5 µg/L). For the sulphur compounds the best analyte responses were obtained with the 50/30 µm DVB-CAR-PDMS fibre, while the 65 µm PDMS-DVB fibre gave the best responses for the OVACs and geosmin. Details of the optimised conditions for each method are described in Sections 2.6 and 2.7.

Analysis of blank samples was carried out to ensure the absence of interfering substances and analytical contaminants. A blank sample contained all of the reagents used in the analysis except for the sample, i.e. MilliQ water, internal standard and sodium sulphate. Analysis of the blank samples confirmed the absence of interfering compounds.

The linearity of the responses obtained from the analysis of the sulphur compounds and OVACs, and sensitivity and precision of the two methods were evaluated. The results are summarised in Appendix 5. Linear calibration curves with high correlation coefficients were achieved for all

analytes. The method limits of detection and quantification (MLODs and MLOQs) for all analytes were all below their odour threshold concentrations (Table 1).

Table 1. Odour threshold concentrations for the analytes of interest.

Compound	Odour detection threshold in water (µg/L)
Dimethyl sulphide	0.3[a]
Dimethyl disulphide	12[b]
Dimethyl trisulphide	0.01[b]
Toluene	24[c]
Ethylbenzene	2.4[c]
Styrene	730[d]
p-cresol	55[e]
Indole	300[f]
Skatole	1.2[f]
Geosmin	0.01[g]

[a] Buttery *et al*. (1990)
[b] Buttery *et al*. (1976)
[c] Alexander *et al*.(1982)
[d] Baker (1963)
[e] Buttery *et al*. (1988)
[f] Yan *et al*. (2011)
[g] Suffet *et al*. (1999)

3.2 Thermal degradation of analytes

Certain sulphur compounds can be susceptible to thermal degradation under certain GC conditions. For example, dimethylpolysulphides (e.g. DMDS, DMTS) are susceptible to disproportionation and thermal degradation, with thermally induced disproportionation resulting in the formation of lower dimethylpolysulphide homologues and elemental sulphur (Kristiana *et al*., 2010). In order to confirm that thermal degradation of analytes had not occurred using our method conditions, aqueous solutions of individual compounds (10 µg/L) were analysed with the MS operating in full scan mode. The resulting chromatograms were examined for any degradation products by extracting the relevant mass ions corresponding to possible degradation products. To investigate whether there were any interactions between compounds, aqueous solutions containing different combinations of two compounds (each at 10 µg/L) were also analysed and the resulting chromatograms analysed for evidence of compound interactions and the presence of by-products resulting from interaction between compounds (i.e. "scrambled" compounds). For majority of the sulphur compounds there was no evidence of degradation products or "scrambled" compounds. However, methanethiol was oxidised to DMDS (major peak) and DMTS (minor peak). Ethanethiol (ET) was oxidised to DEDS (major) with only a very minor peak visible for ET. A mixture of MT and ET showed major peaks for DEDS and the "scrambled" compound methyl ethyl disulphide (MEDS) as well as smaller peaks for DMDS and DMTS. Since MT and ET were oxidised to DMDS and DMTS; and DEDS, respectively, and also reacted with each other, they were excluded from the mixed standard solution. Based on these observations, it was assumed that any MT present in the biosolids would be transformed to DMDS and DMTS. Similarly, any ET present in the biosolids would be converted to DEDS.

3.3 Odorous compounds identified in biosolids samples from Woodman Point WWTP

Analysis of a relatively fresh biosolids sample (less than a week old) using the HS SPME-GC-MS method for the analysis of sulphur compounds showed the presence of DMS, DMDS and DMTS. No EMS or DEDS were observed in biosolids samples, suggesting that neither of these ethylated sulphur compounds (EMS, DEDS) were major contributors to the odours. A typical chromatogram of a biosolids sample is shown in Figure 3.

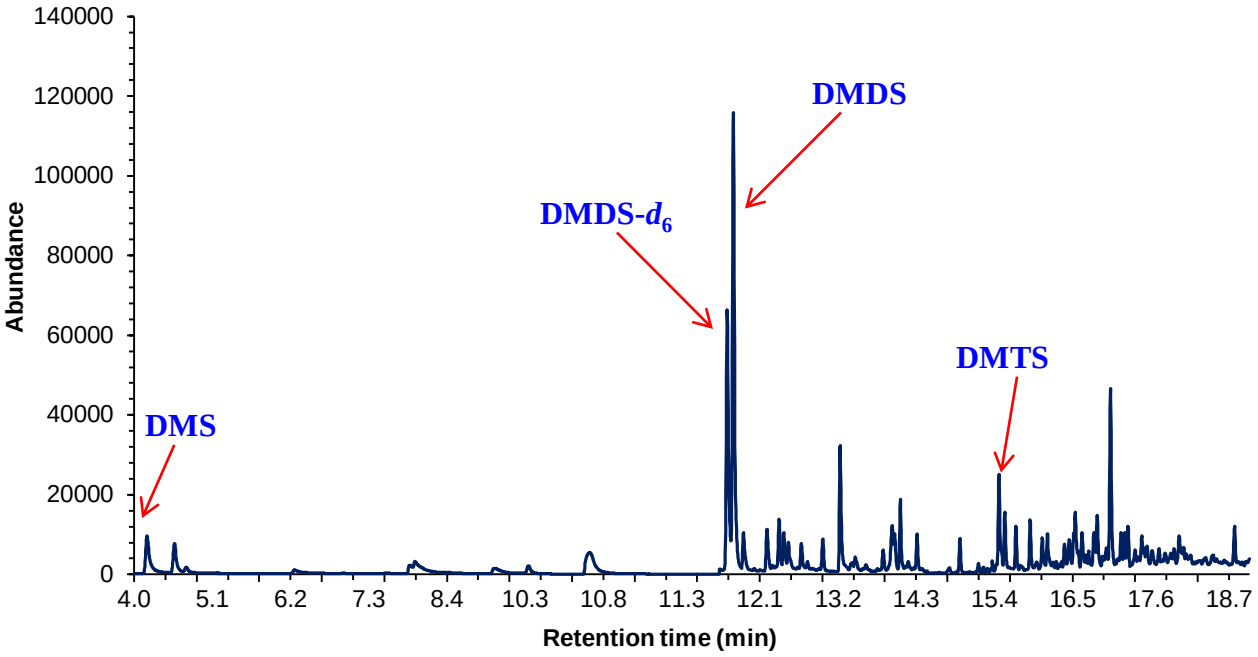

Figure 3. Typical chromatogram of a biosolids sample, showing peaks for DMS, DMDS and DMTS. Sample analysed using the HS SPME-GC-MS method for analysis of sulphur compounds in selected-ion monitoring mode using a ZB-5MS capillary column with DMDS-d_6 as the internal standard.

Analysis of an older biosolids sample which had been stored at room temperature for a few months, using our HS SPME-GC-MS method for OVACs, showed strong peaks for indole and skatole (Figure 4). These samples exhibited a strong faecal/nauseating odour.

Using our method for the analysis of OVACs, the presence of geosmin was also detected in fresher biosolids samples, which still contained some sulphur compounds but exhibited a more earthy/musty odour. Other types of compounds which were tentatively identified based on their mass spectra and/or library matches, but not confirmed with authentic analytical standards, included various long chain aliphatic hydrocarbons, terpenes, alkyl benzenes and other aromatic compounds. It is likely that some of these compounds may have also contributed to the earthy musty odour.

3.4 Analysis of samples from the odour reduction trials.

Odours from biosolids samples obtained during odour reduction trials were assessed in terms of the concentration of the total volatile organic sulphur compounds (TVOSC), measured as the sum of the DMS, DMDS and DMTS concentrations present in the biosolids samples and compared with a control sample. Odour reduction (or increase) was considered to be the reduction (or increase) in the TVOSC concentration relative to the control sample.

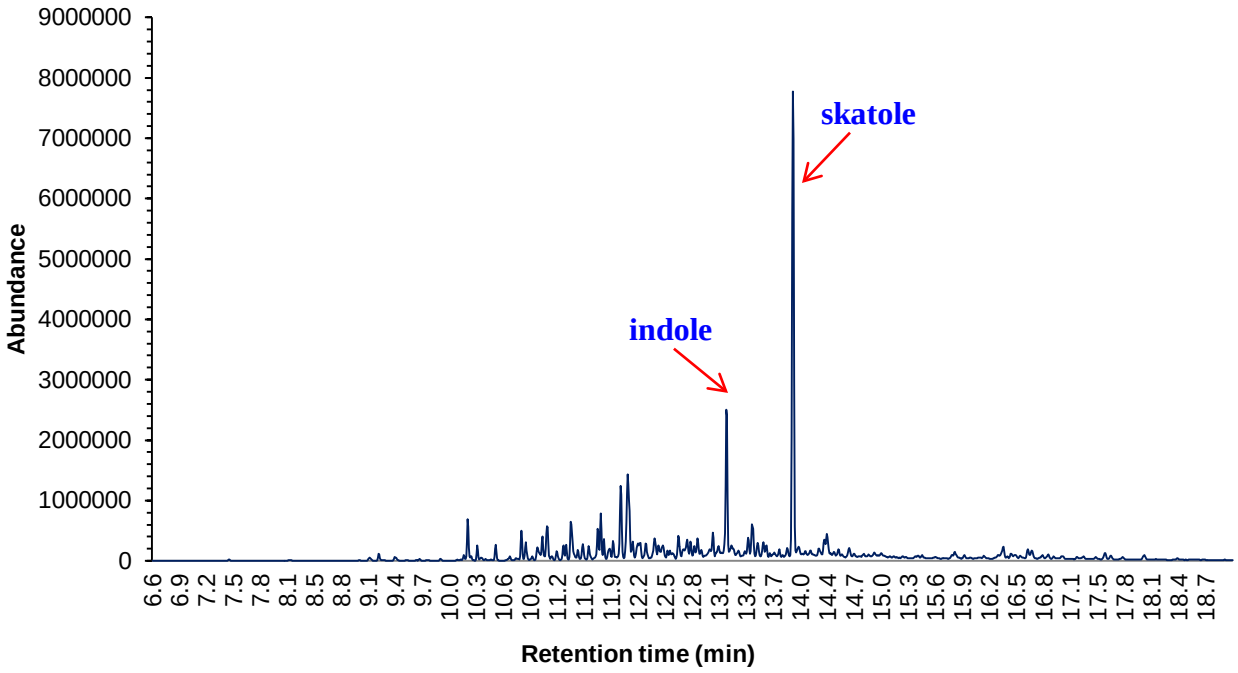

Figure 4. Typical chromatogram of a stored biosolids sample showing the presence of indole and skatole. Sample analysed using the HS SPME-GC-MS method for analysis of OVACs in selected-ion monitoring mode using a ZB-5MS capillary column.

Previously reported methods for the analysis of odorous compounds in biosolids have been conducted in the gas phase. For example, Glindemann *et al*. (2006) used a static headspace method for the analysis of odorous gases from dewatered sludge cakes. This method utilised gas tight bottles for incubating biosolids and involved manual sampling and injection of the headspace gases into the GC using a gas tight syringe (Glindemann *et al*., 2006). This method enables comparison of the odour of samples from different wastewater plants and process locations. The method also mimics the ageing of large biosolids storage piles, in both the odour generation and consumption cycles and has been used in several biosolids odour projects (e.g. Glindemann *et al*., 2006; Higgins *et al*., 2004; Adams *et al*., 2003b). However, manual injections of the headspace gases into the GC inlet are time consuming and laborious, and limited to analysis of only a few samples. Turkmen, *et al.* (2004) have reported the use of SPME coupled with GC-MS for the analysis of DMS, DMDS, methyl merceptan, H_2S, CS_2, trimethylamine and dimethylamine in anaerobically digested wastewater sludge. However, this method required the use of a complicated set-up for SPME calibration and sampling of the gaseous odorants. Visan and Parker (2004) have used SPME-GC-MS for the analysis of TMA, DMS, DMDS and methyl mercaptan in stored biosolids. This method used permeation devices and complicated apparatus for sampling of gaseous standards of the odorants and involved manual injection of the SPME fibre into the GC injector (Vissan and Parker, 2004).

The limited resources allocated to this project did not allow for comprehensive sampling and analysis of gaseous samples and we therefore focussed only on analysis of the odorous compounds in the headspace of wet biosolids. Thus the bulk biosolids samples, incubated in 1 L Schott bottles, were analysed as "aqueous" samples as described in Section 2.6. This method did not require any complex sampling equipment, was reproducible and the analysis was fully automated, allowing for a higher throughput of samples. In an effort to simulate analysis of the odorous compounds in the gas phase, the smaller samples incubated in the Teflon-lined screw cap vials were analysed as non-aqueous samples (Section 2.6). Good repeatability and reproducibility were obtained for the "aqueous" method (Appendix 5) but since the matrix effects had not been fully investigated, the method can only be considered as semi-quantitative at this point. For these samples the TVOSC

concentration was measured as the sum of the DMS, DMDS and DMTS concentrations present in the biosolids sample and is expressed in nanograms per gram (ng/g) of moist biosolids sample used.

Only a qualitative analysis was possible for the non-aqueous samples incubated in the Teflon-lined screw cap vials as the reproducibility of the internal standard responses in these samples was poor, possibly due to difficulties in obtaining representative samples when using small samples. Therefore, the odour reductions/increases reported in this study are based on analyses of the aqueous samples.

3.5 Chemical addition to digested sludge prior to dewatering

A 37% reduction of peak TVOSC concentration was observed for an alum dose of 2% (based on aluminium), while a 4% alum dose resulted in a 40% reduction of peak TVOSC concentration, relative to the control sample (Figure 5). The odour reductions observed in our laboratory trials were lower than the odour reductions observed by the WERF research team. In their laboratory trials, Adams *et al*. (2008) reported that a dose of 0.5% alum (based on aluminium) added to digested sludge prior to dewatering resulted in approximately 80% reduction of peak TVOSC concentration, while a 2% alum dose gave approximately 90% reduction in peak TVOSC concentration. The reasons for the observed differences in the odour reductions obtained in our laboratory trials and those reported by Adams *et al*. could be due to a number of different factors, namely the sludge properties, type of polymer used, chemical contact time, mixing, shear and interactions between the metal and polymer.

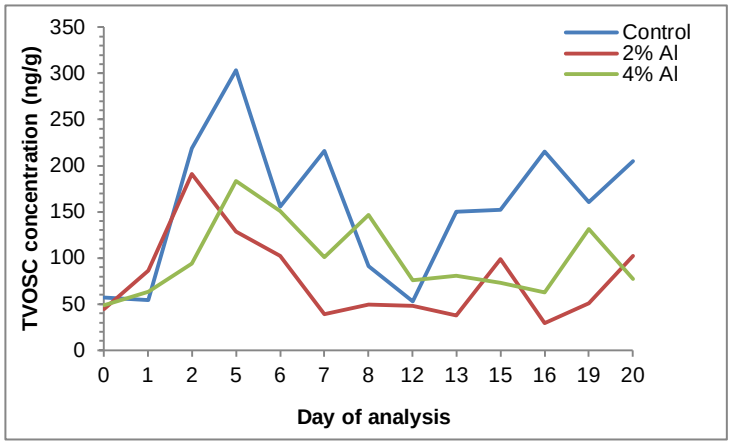

Figure 5. Effect of aluminium sulphate addition to digested sludge on TVOSC concentrations for biosolids samples analysed as aqueous sub-samples taken from the bulk biosolids sample.

A dose of 2% polyaluminium chloride (based on aluminium) resulted in an 11% increase in the peak TVOSC concentration in the resulting cake, while a 4% dose gave a 40% reduction in the peak TVOSC concentration of the biosolids cake, relative to the control (Figure 6). Addition of iron at the 2% dose resulted in only a slight decrease (23%) in peak TVOSC concentration, while addition of iron at the 4% dose resulted in a 50% increase in peak TVOSC concentration, relative to control (Figure 7). The observed increase in TVOSC concentration obtained with the 4% iron dose in our trials is somewhat consistent with earlier findings of the WERF study. Results from Phase III of the WERF study showed that, in general, an increase in iron concentration in the sludge or biosolids resulted in higher TVOSC concentrations in the dewatered biosolids headspace, especially if iron was added prior to or during digestion (Adams, *et al.*, 2008). It was also found that, addition of ferric chloride to anaerobically digested sludge before dewatering did not reduce TVOSC emissions from cake until the iron dose was at least 8% on a dry mass-mass basis (Adams, *et al.*, 2008). Results from recent laboratory studies, using batch anaerobic digestion, have shown that iron addition to the digester feed reduced TVOSC concentrations in the resulting biosolids cake by 50 to

over 95% for most of the sludges (Novak *et al.*, 2010). Direct addition of iron (4% dose) to biosolids cake also significantly reduced the TVOSC concentrations (Higgins, 2010). The contradictory results obtained from various studies using iron are most likely due to the sludge properties, location of iron addition and polymer-iron interactions (Higgins, 2010).

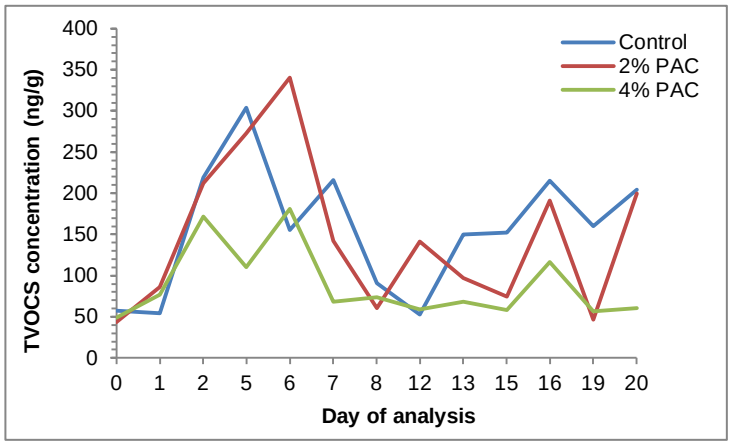

Figure 6. Effect of polyaluminium chloride addition to digested sludge on TVOSC concentrations for biosolids samples analysed as aqueous sub-samples taken from the bulk biosolids sample.

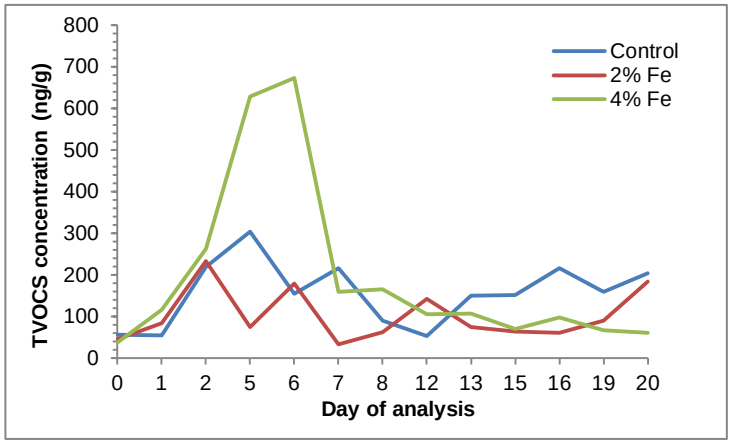

Figure 7. Effect of ferric chloride addition to digested sludge on TVOSC concentrations for biosolids samples analysed as aqueous sub-samples taken from the bulk biosolids sample.

Comparison of TVOSC profiles in Figures 5 – 7 showed that in all three cases the TVOSC concentrations peaked within the first week of incubation and then decreased, which was consistent with previously reported research (e.g. Higgins *et al.*, 2003; Adams *et al.*, 2008).

Although quantitative analysis of the non-aqueous samples was not possible, the TVOSC profiles obtained from the analysis of these samples were plotted (Figures 8 – 10) for comparison with the aqueous samples. For the non-aqueous samples, the amount of TVOSC was measured as the total peak area of the DMS, DMDS and DMTS peak areas corrected for the weight of the biosolids sample. A major difference between the TVOSC profiles obtained from the analysis of the aqueous samples and the TVOSC profiles obtained from the analysis of the non-aqueous samples was the point at which the TVOSC levels peaked. In the non-aqueous samples peak TVOSC amounts were observed at Day 1 of incubation for most samples, while for the aqueous samples peak TVOSC concentrations were observed between Day 2 and Day 6 of the incubation period. The reasons for this difference could be due to the way in which the samples were incubated. The samples analysed

in the aqueous phase were incubated as bulk samples (approximately 200 g in 1L Schott bottles), while the non-aqueous samples were incubated as smaller samples (50 – 80 mg in 20 mL vials). Thus the amount of biosolids cake in the bulk samples was approximately 2500 times greater than the amount of biosolids cake in the smaller samples. This would change the conditions within the biosolids cake, e.g. oxygenation and possibly moisture distribution as well as the rate of diffusion of odorous compounds out of the biosolids mass.

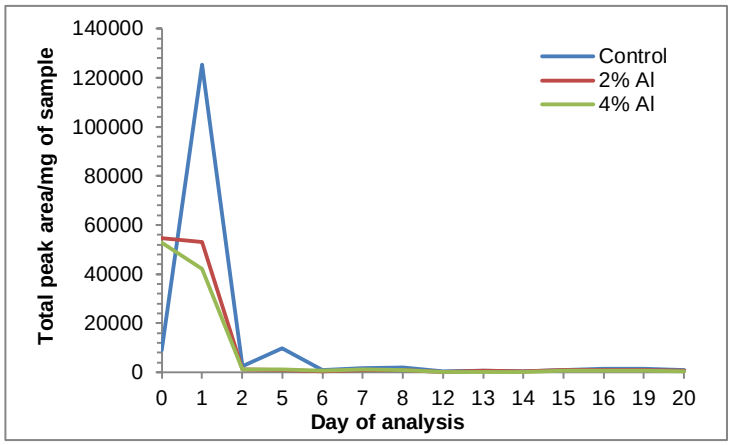

Figure 8. Effect of aluminium sulphate addition to digested sludge on the amount of TVOSC (measured as the total peak area of the DMS, DMDS and DMTS peak areas) for non-aqueous biosolids samples incubated in the Teflon-lined screw cap vials.

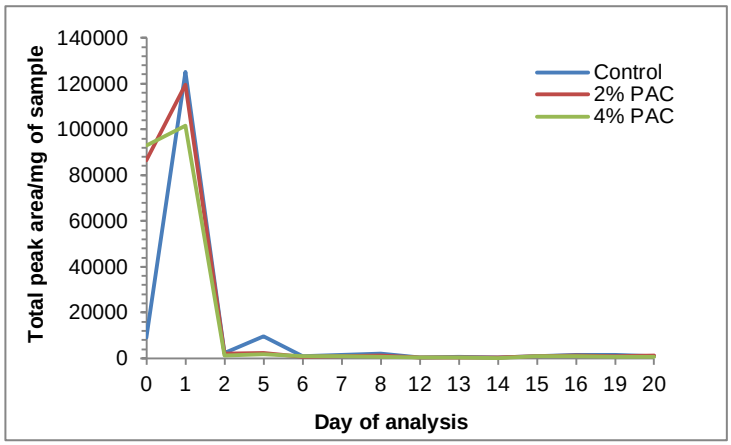

Figure 9. Effect of polyaluminium chloride addition to digested sludge on the amount of TVOSC (measured as the total peak area of the DMS, DMDS and DMTS peak areas) for non-aqueous biosolids samples incubated in the Teflon-lined screw cap vials.

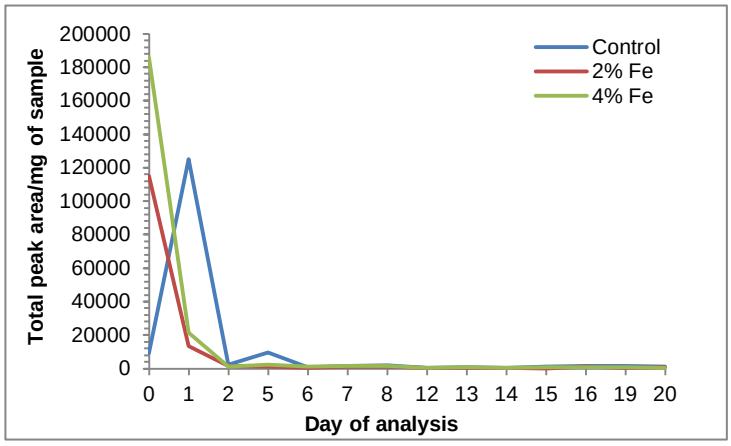

Figure 10. Effect of ferric chloride addition to digested sludge on the amount of TVOSC (measured as the total peak area of the DMS, DMDS and DMTS peak areas) for non-aqueous biosolids samples incubated in the Teflon-lined screw cap vials.

3.6 Chemical addition to plant dewatered cake

Higgins, (2010) reported that adding metal salts directly to the cake gave a better TVOSC reduction compared to adding the salts during the conditioning and dewatering step. However, addition to the cake also resulted in a greater reduction in the pH of the cake to levels probably below those desirable for land application. In our laboratory trials a 2% dose of aluminium sulphate (based on aluminium) resulted in a 24% increase in peak TVOSC concentration, while addition of 4% aluminium sulphate resulted in approximately 70% decrease in peak TVOSC concentration, relative to the control sample (Figure 11). However, the pH of the cake treated with 4% aluminium sulphate was also significantly reduced (pH 4.2) to levels that may not be suitable for land application. These results are consistent with the results reported by Higgins (2010).

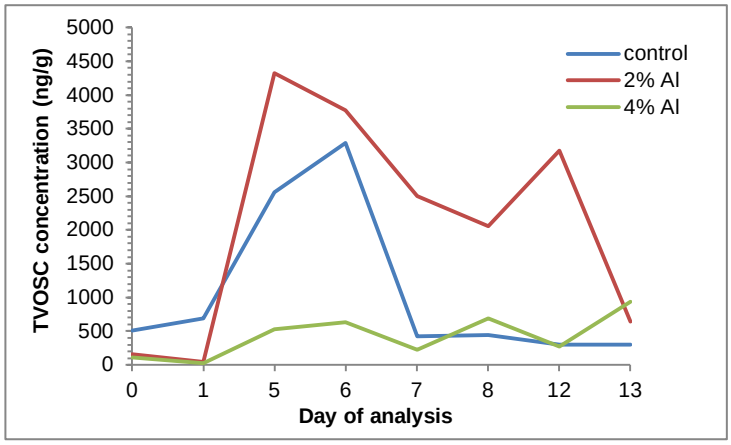

Figure 11. Effect of aluminium sulphate addition to plant dewatered biosolids cake on TVOSC concentrations for biosolids samples analysed as aqueous sub-samples taken from the bulk biosolids sample.

3.7 Centrifuge speed trials

Based on a series of dewatering trials, Adams *et al*. (2008) reported that odour emissions from cakes dewatered by high solids centrifuges were higher than cakes dewatered by other means (e.g. low-solids centrifuges or belt presses). This was mainly attributed to the high shear imparted on biosolids during centrifuge dewatering, as a result of higher bowl speeds and/or torque conditions. The shear created by centrifugation may increase the amount of bioavailable protein for odour

production. Thus reducing the centrifuge bowl speed and/or torque can reduce the amount of shear imparted on biosolids, thereby reducing the odour of the dewatered cake (Adams *et al.*, 2008). In a full-scale test, a 10% reduction in centrifuge bowl speed on one high-solids centrifuge resulted in 20% reduction of TVOSC emissions from dewatered cake with no observed reduction in cake solids concentration (Adams *et al.*, 2008).

The effect of centrifuge speed on odour reduction in biosolids cake was also examined in this study. The digested sludge was dewatered at 3850 rpm (control), 3460 rpm (10% reduction in speed, relative to control) and 3080 rpm (20% reduction in speed, relative to control). In our laboratory trials, a 20% reduction in centrifuge speed (3080 rpm) resulted in an approximate 30% decrease in peak TVOSC concentration, relative to the control (Figure 12). However, the solids content of the resulting cake was also significantly reduced (Table 2) which would not be desirable from the point of view of WWTP operations.

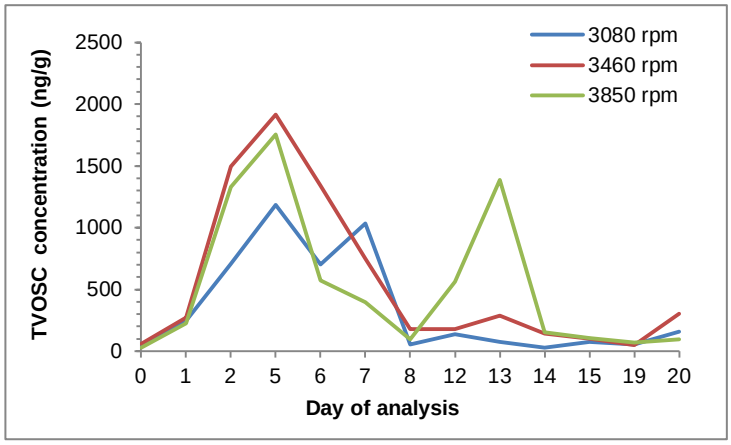

Figure 12. Effect of centrifuge speed on the concentration of TVOSC in dewatered biosolids cake for biosolids samples analysed as aqueous sub-samples taken from the bulk biosolids sample.

Table 2. Dry solids content of biosolids samples dewatered at different centrifuge speeds.

Centrifuge speed	Dry solids content of resulting cake
3850 rpm	15%*
3460 rpm	11%
3080 rpm	10%

*This value is within 2% of the dry solids content of the plant dewatered cake (16.9%) derived from the same digested sludge.

3.8 Analysis of OVACs in biosolids samples from the odour reduction trials

Studies have shown that one of the major causes of odours during the first 1-2 weeks of biosolids storage is due to the production of VOSCs *via* the microbial degradation of sulphur-containing amino acids (Higgins, *et al.*, 2003, 2006; Chen, *et al.*, 2006). However, results from human odour panels have shown that stored biosolids were still odorous even after the VOSCs were below the detection limit when analysed by gas chromatography with a flame ionisation detector (GC-FID) (Chen, *et al.*, 2006). Therefore, some other odorous compounds with low odour detection thresholds are responsible for the malodour after the VOSCs have abated (Chen, *et al.*, 2006). The odour in stored biosolids has been attributed to odorous volatile aromatic compounds (OVACs) such as, toluene, ethylbenzene, styrene, *p*-cresol, indole and skatole (Chen, *et al.*, 2004, 2006). In some cases, the OVACs were present even after 45 days of storage. The gas production profiles indicated

that these compounds decreased as the VOSCs increased, and started to accumulate only after the VOSCs have depleted (Chen, *et al.*, 2004, 2006). It has been proposed that due to substrate competition, microorganisms may preferentially degrade sulphur containing amino acids over aromatic amino acids and that the VOSCs may have an inhibitory effect on the production of OVACs (Chen, *et al*., 2004, 2006).

In this study, the laboratory dewatered biosolids cakes from the odour reduction trials and the plant dewatered cake samples were also monitored for the formation of OVACs to: (1) determine if formation of the OVACs could be detected as the concentrations of the sulphur compounds decreased and (2) in the case of the chemically treated cake samples, to investigate if chemical addition had any effect on their reduction. No significant concentrations of OVACs were observed in any of the cake samples analysed during the monitoring period. In most cases the compounds were either at or below limits of quantification for the method. This is most likely because the monitoring period was not long enough for significant amounts of OVACs to form. The longest monitoring period over the course of the trials was 37 days, while the biosolids sample that showed significant peaks for indole and skatole (Figure 4) had been stored for a few months. It has been reported that indole and skatole begin to form at approximately 40 days, peak at approximately 100 days and begin to disappear at about 125 – 135 days of incubation (Novak, 2012).

4.0 Conclusions and future work

This study identified some of the major odorous compounds in biosolids samples obtained from a Western Australian WWTP and investigated chemical addition and reduction of centrifuge speed as potential odour reduction strategies.

The main odorous compounds identified in fresh biosolids samples from Woodman Point WWTP included DMS, DMDS, DMTS and traces of geosmin. Indole and skatole were identified in old biosolids samples exhibiting a faecal/nauseating odour. Other compounds which were tentatively identified based on their mass spectra or library matches, but not confirmed, included various long chain aliphatic hydrocarbons, terpenes, alkyl benzenes and other aromatic compounds.

Aluminium sulphate addition (4% as aluminium) to digested sludge prior to dewatering offered the best odour reduction strategy amongst the options that were investigated, resulting in approximately 40% reduction in peak TVOSC concentration, relative to a control sample.

Although some odour reduction (up to 30%) was observed at lower centrifuge speeds, the solids content of the resulting cakes was also reduced, which would not be desirable from the point of view of WWTP operations.

The analytical method used for the analysis of the sulphur compounds needs to be refined to enable a more reliable quantitative assessment of the biosolids odour. In most cases, the results obtained from the HS SPME-GC-MS analyses were in general agreement with qualitative observations by a single trained odour assessor. In future studies, it would be beneficial to include dilution olfactometry measurements to obtain a more rigorous assessment of the overall odour generated from biosolids cake and to correlate/compare the results with measurements obtained using HS SPME-GC-MS. In addition, it would be useful to determine the nature of odour compounds in aged biosolids, in which the very objectionable and most organoleptically potent compounds such as VOSCs and organic nitrogen compounds have been depleted. It would also be advantageous to determine whether these odours are considered objectionable or not, and at what concentrations do the odours become acceptable.

While studies conducted in this project utilised sludge and biosolids samples from just one WWTP, future studies will expand the scope to include biosolids and sludge sourced from other WWTPs. This would provide information on odorous compounds in biosolids produced at other WWTPs and determine whether the trialled odour reduction strategies are applicable to more than one type of wastewater treatment system.

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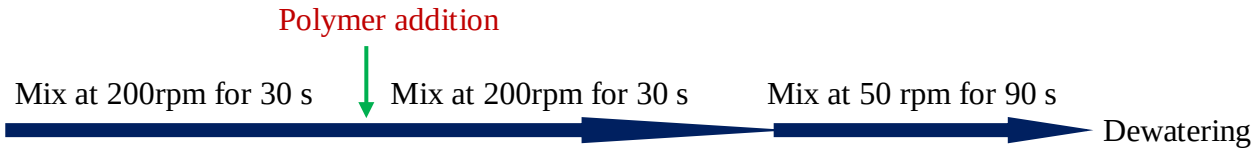
APPENDIX 1

Chemical addition to digested sludge prior to dewatering – supporting information

Date	22 February 2012
Sample	**Control**
Weight of beaker	256.1 g
Weight of beaker + digested sludge	1056 g
Weight of digested sludge	799.1 g
Dry Solids (DS) content of digested sludge as determined by CWQRC (%w/w)	3.7%
Amount of dry sludge in the digested sludge sample *= (DS/100) x Weight of sludge*	29.57 g
Volume of polymer solution (0.3%w/v) added Average polymer usage is 16kg per ton of dry sludge 16000 g of polymer per 1000 kg of dry sludge X g of polymer per ? kg of dry sludge X = (?/1000) x 16000 = ? g of polymer 0.3 g in 100 mL ? g in X mL X = (?/0.3) x 100 = volume of polymer solution required (mL)	158 mL
Amount of biosolid cake obtained after dewatering and processing	244 g

Mixing regime for control sample



Date	22 February 2012
Sample	**2% Al (added as aluminium sulphate)**
Weight of beaker	335.5 g
Weight of beaker + digested sludge	1215.2 g
Weight of digested sludge	879.7 g
Dry Solids (DS) content of digested sludge as determined by CWQRC (%w/w)	3.7%
Amount of dry sludge in the digested sludge sample *= (DS/100) x Weight of sludge*	32.55 g
Volume of polymer solution (0.3%w/v) required Average polymer usage is 16kg per ton of dry sludge 16000 g of polymer per 1000 kg of dry sludge X g of polymer per ? kg of dry sludge X = (?/1000) x 16000 = ? g of polymer 0.3 g in 100 mL ? g in X mL X = (?/0.3) x 100 = volume of polymer solution required (mL)	174 mL
Concentration of aluminium sulphate solution (mol/L) (concentration based on 56% w/v aluminium sulphate)	1.64 mol/L
Amount of aluminium required *= amount of dry sludge in sample x 0.02*	0.65 g
Moles of Al *= (amount of dry sludge in sample x 0.02)/27*	0.024 moles
Moles of $Al_2(SO_4)_3$ *= moles of Al / 2*	0.012 moles
Volume of $Al_2(SO_4)_3$ solution required (mL) *=(moles of aluminium sulphate / conc of $Al_2(SO_4)_3$ solution) x 1000*	7.4 mL
Amount of biosolid cake obtained after dewatering and processing	204 g

Date	22 February 2012
Sample	**4% Al (added as aluminium sulphate)**
Weight of beaker	254.0 g
Weight of beaker + digested sludge	996.3 g
Weight of digested sludge	742.3 g
Dry Solids (DS) content of digested sludge as determined by CWQRC (%w/w)	3.7%
Amount of dry sludge in the digested sludge sample *= (DS/100) x Weight of sludge*	27.46 g
Volume of polymer solution (0.3%w/v) required Average polymer usage is 16kg per ton of dry sludge 16000 g of polymer per 1000 kg of dry sludge X g of polymer per ? kg of dry sludge X = (?/1000) x 16000 = ? g of polymer 0.3 g in 100 mL ? g in X mL X = (?/0.3) x 100 = volume of polymer solution required (mL)	146 mL
Concentration of aluminium sulphate solution (mol/L) (concentration based on 56% w/v aluminium sulphate)	1.64 mol/L
Amount of aluminium required *= amount of dry sludge in sample x 0.04*	1.098 g
Moles of Al *= (amount of dry sludge in sample x 0.04)/27*	0.041 moles
Moles of $Al_2(SO_4)_3$ *= moles of Al / 2*	0.020 moles
Volume of $Al_2(SO_4)_3$ solution required (mL) *=(moles of aluminium sulphate / conc of $Al_2(SO_4)_3$ solution) x 1000*	12.4 mL
Amount of biosolid cake obtained after dewatering and processing	198 g

Date	22 February 2012
Sample	**2% Al (added as polyaluminium chloride (PAC))**
Weight of beaker	247.9 g
Weight of beaker + digested sludge	1017.5 g
Weight of digested sludge	769.6 g
Dry Solids (DS) content of digested sludge as determined by CWQRC (%w/w)	3.7%
Amount of dry sludge in the digested sludge sample *= (DS/100) x Weight of sludge*	28.5 g
Volume of polymer solution (0.3%w/v) required Average polymer usage is 16kg per ton of dry sludge 16000 g of polymer per 1000 kg of dry sludge X g of polymer per ? kg of dry sludge X = (?/1000) x 16000 = ? g of polymer 0.3 g in 100 mL ? g in X mL X = (?/0.3) x 100 = volume of polymer solution required (mL)	152 mL
PAC (23% w/v as Al_2O_3) – Concentration of Al_2O_3 in solution (mol/L) *=(23/102)/0.1*	2.25 mol/L
Amount of aluminium required *= amount of dry sludge in sample x 0.02*	0.57 g
Moles of Al *= (amount of dry sludge in sample x 0.02)/27*	0.021 moles
Moles of Al_2O_3 *= moles of Al / 2*	0.010 moles
Volume of Al_2O_3 solution required (mL) *=(moles of aluminium oxide / 2.25) x 1000*	4.7 mL
Amount of biosolid cake obtained after dewatering and processing	227 g

Date	22 February 2012
Sample	**4% Al (added as polyaluminium chloride (PAC))**
Weight of beaker	255.2 g
Weight of beaker + digested sludge	1070.1 g
Weight of digested sludge	814.9 g
Dry Solids (DS) content of digested sludge as determined by CWQRC (%w/w)	3.7%
Amount of dry sludge in the digested sludge sample *= (DS/100) x Weight of sludge*	30.15 g
Volume of polymer solution (0.3%w/v) required Average polymer usage is 16kg per ton of dry sludge 16000 g of polymer per 1000 kg of dry sludge X g of polymer per ? kg of dry sludge X = (?/1000) x 16000 = ? g of polymer 0.3 g in 100 mL ? g in X mL X = (?/0.3) x 100 = volume of polymer solution required (mL)	161 mL
PAC (23% w/v as Al_2O_3) – Concentration of Al_2O_3 in solution (mol/L) *=(23/102)/0.1*	2.25 mol/L
Amount of aluminium required *= amount of dry sludge in sample x 0.04*	1.21 g
Moles of Al *= (amount of dry sludge in sample x 0.04)/27*	0.045 moles
Moles of Al_2O_3 *= moles of Al / 2*	0.022 moles
Volume of Al_2O_3 solution required (mL) *=(moles of aluminium oxide / 2.25) x 1000*	10 mL
Amount of biosolid cake obtained after dewatering and processing	224 g

Date	22 February 2012
Sample	**2% Fe (added as $FeCl_3$)**
Weight of beaker	256.9 g
Weight of beaker + digested sludge	1057.3 g
Weight of digested sludge	800.4 g
Dry Solids (DS) content of digested sludge as determined by CWQRC (%w/w)	3.7%
Amount of dry sludge in the digested sludge sample *= (DS/100) x Weight of sludge*	29.61 g
Volume of polymer solution (0.3%w/v) required Average polymer usage is 16kg per ton of dry sludge 16000 g of polymer per 1000 kg of dry sludge X g of polymer per ? kg of dry sludge X = (?/1000) x 16000 = ? g of polymer 0.3 g in 100 mL ? g in X mL X = (?/0.3) x 100 = volume of polymer solution required (mL)	158 mL
Concentration of $FeCl_3$ solution (mol/L) **(concentration based on a 36% w/v solution)**	2.22 mol/L
Amount of iron required *= amount of dry sludge in sample x 0.02*	0.59 g
Moles of Fe *= (amount of dry sludge in sample x 0.02)/56*	0.011 moles
Volume of $FeCl_3$ solution required (mL) *=(moles of iron required / conc of $FeCl_3$ solution) x 1000*	4.8 mL
Amount of biosolid cake obtained after dewatering and processing	205 g

Date	22 February 2012
Sample	**4% Fe (added as $FeCl_3$)**
Weight of beaker	250.9 g
Weight of beaker + digested sludge	1075.8 g
Weight of digested sludge	824.9 g
Dry Solids (DS) content of digested sludge as determined by CWQRC (%w/w)	3.7%
Amount of dry sludge in the digested sludge sample *= (DS/100) x Weight of sludge*	30.52 g
Volume of polymer solution (0.3%w/v) required Average polymer usage is 16kg per ton of dry sludge 16000 g of polymer per 1000 kg of dry sludge X g of polymer per ? kg of dry sludge X = (?/1000) x 16000 = ? g of polymer 0.3 g in 100 mL ? g in X mL X = (?/0.3) x 100 = volume of polymer solution required (mL)	163 mL
Concentration of $FeCl_3$ solution (mol/L) **(concentration based on a 36% w/v solution)**	2.22 mol/L
Amount of iron required *= amount of dry sludge in sample x 0.04*	1.22 g
Moles of Fe *= (amount of dry sludge in sample x 0.04)/56*	0.022 moles
Volume of $FeCl_3$ solution required (mL) *=(moles of iron required / conc of $FeCl_3$ solution) x 1000*	10 mL
Amount of biosolid cake obtained after dewatering and processing	212 g

APPENDIX 2

Chemical addition to plant dewatered cake – supporting information

Date	14 March 2012
Sample	**Control**
Weight of beaker	129.002 g
Weight of beaker + biosolid	213.549 g
Weight of biosolid	84.547 g
Dry Solids (DS) content of biosolid as provided by Water Corp (%w/w)	16.9%
Amount of dry solid in biosolid sample *= (DS/100) x Weight of biosolid*	14.29 g

Date	14 March 2012
Sample	**2% Al (added as aluminium sulphate)**
Weight of beaker	149.267 g
Weight of beaker + biosolid	235.033 g
Weight of biosolid	85.766 g
Dry Solids (DS) content of biosolid as provided by Water Corp (%w/w)	16.9%
Amount of dry solid in biosolid sample *= (DS/100) x Weight of biosolid*	14.49 g
Amount of aluminium required *= amount of dry solids in biosolid sample x 0.02*	0.29 g
Moles of Al *= (amount of dry solids in biosolid sample x 0.02)/27*	0.011 moles
Moles of $Al_2(SO_4)_3$ *= moles of Al / 2*	0.0054 moles
Amount of $Al_2(SO_4)_3.xH_2O$ required (x = 18; MW = 666 mol/g)	3.57 g

Date	14 March 2012
Sample	**4% Al (added as aluminium sulphate)**
Weight of beaker	154.872 g
Weight of beaker + biosolid	239.246 g
Weight of biosolid	84.374 g
Dry Solids (DS) content of biosolid as provided by Water Corp (%w/w)	16.9%
Amount of dry solid in biosolid sample *= (DS/100) x Weight of biosolid*	14.26 g
Amount of aluminium required *= amount of dry solids in biosolid sample x 0.04*	0.57 g
Moles of Al *= (amount of dry solids in biosolid sample x 0.04)/27*	0.021 moles
Moles of $Al_2(SO_4)_3$ *= moles of Al / 2*	0.0106 moles
Amount of $Al_2(SO_4)_3.xH_2O$ required (x = 18; MW = 666 mol/g)	7.03 g

APPENDIX 3

Centrifuge speed trials – supporting information

Date	7 March 2012
Sample	**Batch 1**
Weight of beaker	334.7 g
Weight of beaker + digested sludge	975.3 g
Weight of digested sludge	640.6 g
Dry Solids (DS) content of digested sludge as provided by Water Corp (%w/w)	3.8%
Amount of dry sludge in the digested sludge sample *= (DS/100) x Weight of sludge*	24.34 g
Volume of polymer solution (0.3%w/v) added Average polymer usage is 16kg per ton of dry sludge 16000 g of polymer per 1000 kg of dry sludge X g of polymer per ? kg of dry sludge X = (?/1000) x 16000 = ? g of polymer 0.3 g in 100 mL ? g in X mL X = (?/0.3) x 100 = volume of polymer solution required (mL)	130 mL

Date	7 March 2012
Sample	**Batch 2**
Weight of beaker	247.8 g
Weight of beaker + digested sludge	842.9 g
Weight of digested sludge	595.1 g
Dry Solids (DS) content of digested sludge as provided by Water Corp (%w/w)	3.8%
Amount of dry sludge in the digested sludge sample *= (DS/100) x Weight of sludge*	22.61 g
Volume of polymer solution (0.3%w/v) added Average polymer usage is 16kg per ton of dry sludge 16000 g of polymer per 1000 kg of dry sludge X g of polymer per ? kg of dry sludge X = (?/1000) x 16000 = ? g of polymer 0.3 g in 100 mL ? g in X mL X = (?/0.3) x 100 = volume of polymer solution required (mL)	121 mL

Batches 1 and 2 were combined and divided equally among 24 centrifuge tubes (50 mL each). One set of 8 tubes was dewatered at 3850 rpm (control speed); a second set of 8 tubes was dewatered at 3460 rpm (10% reduction in speed relative to the control speed) and a third set of 8 tubes was dewatered at 3080 rpm (20% reduction in speed relative to the control speed). The amounts of dewatered and processed biosolid cake obtained for each centrifuge speed are shown in Table 3.

Table 3. Amount of dewatered and processed biosolid cake obtained for each centrifuge speed.

Centrifuge speed	Amount of processed biosolid cake obtained
3850 rpm	202.6g
3460 rpm	198.7 g
3080 rpm	183.2 g

APPENDIX 4

GC temperature programs and the *m/z* ions monitored for HS SPME-GC-MS methods for the analysis of sulphur compounds and OVACs

GC and MS conditions for the HS SPME-GC-MS method for the analysis of sulphur compounds

GC Conditions

Initial temp: 0 °C (On)
Initial time: 2.00 min
Ramps:

#	Rate (°C/min)	Final temp (°C)	Final time (min)
1	5.00	35	0.00
2	15.00	315	10
3	0.0 (off)		

CRYO (CO2)
Cryo: On
Cryo fault: Off
Cryo timeout: 120.00 min (Off)
Quick cryo cool: Off
Ambient temp: 25 °C

Post temp: 0 °C

Post time: 0.00 min

Run time: 37.67 min

FRONT INLET (SPLIT/SPLITLESS)
Mode: Splitless
Initial temp: 230 °C (On)
Pressure: 4.94 psi (On)
Purge flow: 100.0 mL/min
Purge time: 1.00 min
Total flow: 103.9 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 8.00 min
Gas type: Helium

COLUMN
Capillary Column
Model Number: Zebron 7HG-G010-22 ZB-5MS
Max temperature: 330 °C
Nominal length: 30.0 m
Nominal diameter: 250.00 µm
Nominal film thickness: 1.00 µm
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 4.94 psi
Average velocity: 35 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

MS conditions

MS PARAMETERS
Acquisition mode: SIM
Solvent Delay: 2.50 min
EM Absolute: False

EM Offset: 306
Resulting EM Voltage: 2564.7

Table 4. Characteristic mass ions of sulphur compounds selected for MS analysis (ions in italics were used for quantification).

Compound	**Characteristic *m/z* ions**
dimethyl sulphide (DMS)	*m/z* 47 and *62*
ethyl methyl sulphide (EMS)	*m/z 61* and 76
dimethyl disulphide (DMDS)	*m/z* 79 and *94*
dimethyl disulphide-d_6 (DMDS-d_6)	*m/z* 82 and *100*
diethyl disulphide (DEDS)	*m/z* 66, 94 and *122*
dimethyl trisulphide (DMTS)	*m/z* 79 and *126*

GC and MS conditions for the HS SPME-GC-MS method for the analysis of OVACs

GC Conditions
Initial temp: 40 °C (On)
Initial time: 5.00 min
Ramps:

#	Rate (°C/min)	Final temp (°C)	Final time (min)
1	20.00	200	0.00
2	10.00	280	0.00
3	20.00	300	10.00
4	0.0 (off)		

CRYO (CO2)
Cryo: Off
Cryo fault: Off
Cryo timeout: 120.00 min (Off)
Quick cryo cool: Off
Ambient temp: 25 °C

Post temp: 0 °C

Post time: 0.00 min

Run time: 32.00 min

FRONT INLET (SPLIT/SPLITLESS)
Mode: Splitless
Initial temp: 250 °C (On)
Pressure: 7.33 psi (On)
Purge flow: 100.0 mL/min
Purge time: 1.00 min
Total flow: 103.9 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 8.00 min
Gas type: Helium

COLUMN
Capillary Column
Model Number: Zebron 7HG-G010-22 ZB-5MS
Max temperature: 330 °C

Nominal length: 30.0 m
Nominal diameter: 250.00 µm
Nominal film thickness: 1.00 µm
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 7.33 psi
Average velocity: 36 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

MS conditions

MS PARAMETERS
Acquisition mode: SIM
Solvent Delay: 6.50 min
EM Absolute: False
EM Offset: 306
Resulting EM Voltage: 2282.4

Table 5. Characteristic mass ions of OVACs and geosmin selected for MS analysis (ions in italics were used for quantification).

Compound	**Characteristic *m/z* ions**
toluene	*m/z* 65, *91* and 92
ethylbenzene	*m/z* 91 and *106*
ethylbenzene-d_{10}	*m/z* 98 and *116*
styrene	*m/z 104* and 105
p-cresol	*m/z 107* and 108
indole	*m/z* 63, 90 and *117*
skatole	*m/z* 65, 103, *130* and 131
geosmin	*m/z 112*, 125 and 182

APPENDIX 5

Method validation data for HS SPME-GC-MS methods for the analysis of sulphur compounds and OVACs

Method validation parameters for the HS SPME-GC-MS method for the analysis of sulphur compounds

Table 6. Sensitivity, linearity and precision of the method for the analysis of sulphur compounds by HS SPME-GCMS.

	DMS	EMS	DMDS	DEDS	DMTS
MLOD (ng/L)	10	0.5	1	0.2	0.6
MLOQ (ng/L)	22	1	2	0.4	2
Repeatability (%RSD)	8%	9%	1%	4%	9%
Reproducibility (%RSD)	10%	10%	3%	5%	5%
Typical r^2 values	0.984 – 0.993	0.982 – 0.998	0.998 – 0.999	0.981 – 0.984	0.968 – 0.983

The method limits of detection and quantification (MLODs and MLOQs) were calculated from six blank MilliQ analyses, via the mean concentration plus 3 times the standard deviation for the MLOD, and 10 times for the MLOQ.

Repeatability and reproducibility were assessed using a mixed standard solution (500 ng/L) by analysis of 4 samples in a day and a total of 4 samples over 4 different days, respectively, with calculations of the associated % RSD.

The linearity of the responses obtained from the analysis of the sulphur compounds was evaluated by constructing calibration curves for each analyte over the concentration range of interest. A calibration curve for each analyte was obtained by plotting the ratios of the peak areas of the analyte and the internal standard *vs* the concentration of the analyte. Linear calibration curves with high correlation coefficients (Table 6) were achieved for all sulphur compounds analysed.

Method validation parameters for the HS SPME-GC-MS method for the analysis of OVACs and geosmin

Table 7. Sensitivity, linearity and precision of the method for the analysis of OVACs and gesomin by HS SPME-GC-MS.

	toluene	ethylbenzene	styrene	*p*-cresol	indole	skatole	geosmin
MLOD (ng/L)	530	60	10	5	10	9	4
MLOQ (ng/L)	1000	120	20	10	20	12	5
Repeatability (%RSD)	5%	2%	1%	7%	7%	6%	6%
Reproducibility (%RSD)	6%	4%	5%	13%	12%	7%	15%
Typical r^2 values	0.964 – 0.994	0.990 – 0.997	0.996 – 0.998	0.894 – 0.996	0.948 – 0.988	0.947 – 0.986	0.964 – 0.987

The MLODs and MLOQs were calculated from the analyses of six MilliQ blanks containing 50 ng/L of ethylbenzene-d_{10} internal standard, via the mean concentration plus 3 times the standard deviation for the MLOD, and 10 times for the MLOQ.

Repeatability and reproducibility were assessed using a mixed standard solution (500 ng/L) by analysis of 4 samples in a day and a total of 4 samples on two different days, respectively, with calculations of the associated % RSD.

The linearity of the responses obtained from the analysis of the OVACs and geosmin was evaluated by constructing calibration curves for each analyte over the concentration range of interest. A calibration curve for each analyte was obtained by plotting the ratios of the peak areas of the analyte and the internal standard *vs* the concentration of the analyte. Linear calibration curves with high correlation coefficients (Table 7) were achieved for all the compounds analysed.

APPENDIX 6

Communication of project outcomes

PUBLICATIONS

Refereed papers

- Gruchlik, Y., Heitz, A., Joll, C., Fouché L., Penney, N. and Charrois, J. (2012). Laboratory scale investigations of potential odour reduction strategies in biosolids. *Water*, **39**(7), 58-64.

Conference papers

- Gruchlik, Y., Heitz, A., Joll, C., Fouché L. and Penney, N. (2012). Laboratory scale investigations of potential odour reduction strategies in biosolids. *AWA Biosolids and Source Management National Conference*, Gold Coast, Queensland, Australia, 18 – 20 June 2012.

Submitted conference abstracts

- Gruchlik, Y., Heitz, A., Joll, C., Fouché L., Penney, N. and Charrois, J. (2012). Reduction of odour in biosolids: Laboratory trials to determine the efficacy of treatments. Submitted to OzWater 2013.
- Gruchlik, Y., Heitz, A., Joll, C., Fouché L., Penney, N. and Charrois, J. (2012). Odour reduction strategies for biosolids produced from a Western Australian Wastewater Treatment Plant: Results from Phase I Laboratory Trials. Submitted to the 5th IWA Odours and Air Emissions Conference to be held in March 2013 – abstract has been accepted for an oral presentation.

PRESENTATIONS

Platform presentations

- Laboratory scale investigations of potential odour reduction strategies in biosolids. *AWA Biosolids and Source Management National Conference*, Gold Coast, Queensland, Australia, 18 – 20 June 2012.

Workshops

- Odour Reduction in Biosolids, Australian and New Zealand Biosolids Partnership Road Show, Water Corporation, Perth, WA, 20 October 2010.
- Odour Reduction in Biosolids, Water Corporation's R&D Project Forum, Water Corporation, 23 November 2010.

REPORTS

- Monthly progress reports to the Water Corporation of Western Australia (22 reports).

APPENDIX 7

Copy of the AWA Water Journal paper

Gruchlik, Y., Heitz, A., Joll, C., Fouché L., Penney, N. and Charrois, J. (2012). Laboratory scale investigations of potential odour reduction strategies in biosolids. *Water*, **39**(7), 58-64.

refereed paper

LABORATORY SCALE INVESTIGATIONS OF POTENTIAL ODOUR REDUCTION STRATEGIES IN BIOSOLIDS

Results from Phase 1 trials of chemical addition and centrifuge speed methods at Woodman Point WWTP

Y Gruchlik, A Heitz, C Joll, H Driessen, L Fouche, N Penney, J Charrois

Abstract

This study investigated sources of odours from biosolids produced from a Western Australian wastewater treatment plant and examined potential odour reduction strategies on a laboratory scale. Odour reduction methods that were trialled included chemical additions and reduction of centrifuge speed. Chemical addition trials were conducted by adding alum, polyaluminium chloride or ferric chloride to digested sludge that had been sampled prior to the dewatering stage. Trials of chemical addition (alum) to plant dewatered cake were also undertaken. The impact of reducing centrifuge speed on biosolids odour was also investigated using a laboratory scale centrifuge calibrated to operate such that the shear forces on the sample would, as closely as possible, represent those on the plant.

To identify the odorous compounds present in biosolids and to assess the effectiveness of the odour reduction measures, headspace solid-phase microextraction coupled with gas chromatography-mass spectrometry (HS SPME-GC-MS) methods were developed. Target odour compounds included volatile sulphur compounds (e.g. DMS, DMDS, DMTS) and other volatile organic compounds (toluene, ethylbenzene, styrene, *p*-cresol, indole, skatole and geosmin).

In our laboratory trials, aluminium sulphate added to digested sludge prior to dewatering offered the best odour reduction strategy among the options that were investigated, resulting in approximately 40% reduction in peak concentration of the total volatile organic sulphur compounds (TVOSC), relative to a control sample.

Keywords: Odour, biosolids, sludge, volatile sulphur compounds, odour reduction, odorants.

Introduction

Beneficial reuse of biosolids using land application is a viable and important practice for the water industry and the agricultural community. Land application offers a low-cost disposal option for biosolids and a low-cost nutrient source/soil amendment for a variety of applications including agricultural and mine site reclamation projects. However, one of the main limitations that may restrict land application programs is nuisance odours associated with biosolids.

Odour production in biosolids is influenced by many complex factors. These include: (1) reactions of proteins, amino acids and enzyme activity; (2) relationships between odours and concentrations of odorants; (3) impact of process variables upstream of the anaerobic digestion stage; (4) process variables within the anaerobic digestion stage and various enhancements to the anaerobic digestion process; (5) impact of the biosolids dewatering and conveyance processes; (6) polymer addition; (7) chemical addition; and (8) storage of biosolids cake (Adams *et al.*, 2008).

Many compounds have been associated with odours from biosolids facilities. Some of the most relevant include volatile organic sulphur compounds (VOSCs) such as: methanethiol (MT), dimethyl sulphide (DMS), dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS), as well as inorganic sulphur compounds such as hydrogen sulphide (H_2S) (Higgins *et al*., 2008). Nitrogenous compounds such as trimethylamine (TMA), ammonia and volatile fatty acids (VFA) are also potential sources of odour (Higgins *et al*., 2008). Odorous volatile aromatic compounds (OVACs) such as toluene, ethylbenzene, styrene, *p*-cresol, indole and skatole have also been identified in headspace samples from stored biosolids (Chen *et al*., 2006).

The Water Environment Research Foundation (WERF) conducted a multi-phase collaborative study investigating several factors that influence odour formation in biosolids (Adams *et al*., 2003a; Adams *et al*., 2003b, 2008). This study was based on an in-depth sampling and analysis of biosolids and headspace samples from several different wastewater treatment plant (WWTP) facilities across North America and involved laboratory scale experiments as well as field trials. A key recommendation from this study noted that no single odour reduction strategy suited all wastewater treatment facilities. Consideration must be given to the site-specific conditions that make up the sludge and biosolids characteristics, such as sewerage inflow, treatment processes used and operational aspects (e.g. sludge handling times, sludge temperature etc). In most cases, "trial-and-error" laboratory or pilot-scale approaches are required to find the most suitable odour reduction strategy.

In order to assess the effectiveness of any potential biosolids odour reduction strategy, appropriate sampling and analytical techniques are required to accurately measure the odorous compounds present in the biosolids cake. In the WERF studies, Glindemann *et al*. (2006) used a static headspace method for the analysis of odorous gases from dewatered sludge cakes in the laboratory. In this method the static headspace gases were analysed for volatile sulphur compounds (MT, DMS, DMDS and carbon disulphide) and TMA by cryo-trapping-GC-MS. This method utilised gas-tight bottles for incubating biosolids and involved manual sampling and injection

of the headspace gases into the GC inlet using a gas-tight syringe (Glindemann *et al*., 2006). Although this method has been reported to be representative of the biosolids storage pile interior, easy to use and highly reproducible (Glindemann *et al.*, 2006), manual injections of the headspace gases into the GC inlet are time consuming and laborious, and limited to analysis of only a few samples.

Solid-phase microextraction (SPME) has been used in the analysis of trace levels of volatile organic sulphur compounds as well as other volatile organic compounds (VOCs) in various matrices, such as aqueous (e.g. Kristiana *et al*., 2010), headspace (e.g. Kim *et al*., 2002) and ambient air (e.g. Haberhauer-Troyer *et al*., 1999). This technique is rapid, relatively inexpensive, easily automated and solvent-free. It also allows for minimal sample handling, which is highly desirable in the analysis of volatile compounds.

In this procedure, the analytes of interest are adsorbed onto a thin polymer film or porous carbonaceous materials that are bonded to a fused silica fibre (SUPELCO, Bulletin 923, 1998; Visan and Parker, 2004). Ideally, equilibrium is reached between the odour matrix and fibre, but for accuracy and precision, consistent sampling time, temperature and fibre immersion depth are more important than equilibrium (SUPELCO, Bulletin 923, 1998; Visan and Parker, 2004).

SPME is compatible with analyte separation/detection by GC-MS or HPLC and gives linear results for wide concentrations of analytes. When SPME is coupled with GC-MS, the analytes adsorbed onto the fibre are released by way of thermal desorption in the vapourising injector port of the GC and are transferred onto the GC column (Pawliszyn, 1997). By controlling the polarity and thickness of the coating on the fibre, maintaining consistent sampling time, and adjusting several other extraction parameters, highly consistent and quantifiable results can be obtained from low concentrations of analytes (SUPELCO, Bulletin 923, 1998).

SPME coupled with GC-MS has been used for the analysis of odorous compounds in several biosolids projects. For example, Turkmen *et al.* (2004) have reported the use of SPME-GC-MS for the analysis of DMS, DMDS, methyl merceptan, H_2S, CS_2, trimethylamine and dimethylamine in anaerobically digested wastewater sludge. However, this method required the use of a complicated set-up for SPME calibration and sampling of the gaseous odorants. Visan and Parker (2004) used SPME-GC-MS for the analysis of TMA, DMS, DMDS and methyl mercaptan in stored biosolids. This method used permeation devices and complicated apparatus for sampling of gaseous standards of the odorants and involved manual injection of the SPME fibre into the GC injector (Vissan and Parker, 2004).

In this study we have used SPME-GC-MS for the analysis of odorous compounds in the headspace of wet biosolids. In this method the biosolids samples were analysed as "aqueous" samples. This method does not require any complex sampling equipment, is reproducible and the analysis is fully automated, allowing for a higher throughput of samples.

Figure 1. An aerial view of Woodman Point WWTP, Perth, Western Australia.

Project Aims

The aims of this study were to: (1) determine the most suitable odour reduction strategy for biosolids produced at our test site and (2) develop analytical methods to identify the chemical compounds responsible for the odour in biosolids from our test site and to assess the effectiveness of the trialled odour reduction measures. In this paper we present the results from Phase I laboratory scale trials of chemical addition and centrifuge speed trials as means of odour reduction. The methodology used to conduct these trials and to identify the odorous compounds is also described.

The Test Site

Woodman Point WWTP (Figure 1) in the Perth metropolitan area was chosen as the test site for this study. The key driver for choosing Woodman Point was that the produced sludge and biosolids were perceived to be more odorous compared to similar materials produced at other treatment plants. Additionally, during the course of the project Woodman Point was less likely to have interruptions in the sludge handling/production process. The plant was also easy to access and sample, and it has the most current technology for processing sludge. The plant typically handles between 120–140 million litres of wastewater per day (120–140ML/d) with 99% of the wastewater being derived from households (Water Corporation, 2012). It is an activated sludge plant that uses sequencing batch reactors (SBR) and egg-shaped digesters (Figure 2) to process the sludge.

The advantage of using SBR over the conventional aeration tank systems is that the biological treatment and clarification are completed in a single step, thereby reducing costs and space (Water Corporation, 2012). The egg-shaped digesters are operated in the mesophilic range (35–37°C) and offer several advantages over the conventional cylindrical anaerobic digesters, namely better mixing and heating. The digester feed is a 1:1 mixture of primary sludge and waste-activated sludge with a typical dry solids (DS) content of 4–6% and the average solids retention time (SRT) is > 20 days. The digested sludge (dry solids content of 2–4%) is then dewatered using high solids centrifuges. The resulting dewatered biosolids cake has a dry solids content of approximately 17–19% (Water Corporation, 2012).

Materials and Methods

Chemicals and materials

Anaerobically digested sludge (DS 3.7%, SRT 19 days) and plant-dewatered biosolids cake (DS 16.9%) samples were obtained from Woodman Point WWTP. Polymer used for dewatering was a powder polymer FO4800SSH from SNF (supplied by Water Corporation) with a molecular weight of approximately 8 million and a charge density of 80%. Aluminium sulphate and polyaluminium chloride, used in the chemical addition trials, were sourced from water treatment

Figure 2. Egg-shaped digesters at Woodman Point WWTP. At 38 metres high, they are the largest of their type in the Southern Hemisphere.

plant operations at Water Corporation of Western Australia (WCWA). Aluminium sulphate was used as a 56% w/v solution. Polyaluminium chloride (PAC23 from Orica) was used as a 23% w/v solution in aluminium oxide. Ferric chloride was used as a 36% w/v solution, prepared in-house from analytical grade ferric chloride (Sigma-Aldrich).

Analytical standards for: sodium thiomethoxide, ethanethiol, DMS, DMDS, DMTS, ethyl methyl sulphide (EMS), diethyl disulphide (DEDS), toluene, ethylbenzene, styrene, *p*-cresol, indole, skatole and geosmin were purchased from Sigma-Aldrich at purity ≥ 99%. Deuterated dimethyl disulphide (DMDS-d_6) was purchased from Sigma-Aldrich. Deuterated ethylbenzene (ethylbenzene-d_{10}) was purchased from Cambridge Isotope Laboratories Inc. Methanol was HPLC grade from Fischer Scientific. Anhydrous granular sodium sulphate was purchased from Ajax Finechem and was baked at 400°C for a minimum of four hours prior to use. Two SPME fibres were used: 50/30 µm divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS) and 65 µm polydimethylsiloxane-divinylbenzene (PDMS-DVB).

Laboratory scale dewatering

For our laboratory-scale dewatering procedure, 600–800g of digested sludge in a 1L glass beaker was stirred at 200rpm for 30 seconds using a jar tester. A polymer solution (0.3% w/v; polymer dose was based on the average amount used at Woodman Point WWTP) was added and the resulting mixture was stirred at 200rpm for another 30 seconds and then stirred at 50rpm for 90 seconds. This mixing regime was based on the mixing regime reported by Higgins (2010).

The sludge mixture was then dewatered using a laboratory centrifuge (Heraeus Multifuge 3S with a maximum rotational radius of 18.2cm) at 3850rpm for 20 minutes. The combined wet cake was then pressed between two medium-density fibreboards (MDF) (300mm x 300mm; 7mm thick) encased in polyethylene wrap and lined with sheets of Whatman No 1 filter paper to absorb the excess water. Pressure was applied by placing weights totalling approximately 8kg on top of the MDF boards.

To simulate the high shear experienced in the plant centrifuge, the sample cake was processed through a manual food mincer (Avanti food mincer #8) which pushed the cake through a "scroll-conveyor", followed by extrusion through several openings, each 8mm in diameter. The lab-dewatered biosolids cake had a similar texture and odour to the plant dewatered sample. The solids content of the lab-dewatered cake was comparable to that of the plant dewatered cake.

Chemical addition to digested sludge prior to dewatering

Individual samples, of anaerobically digested sludge (approximately 800g each) in 1L glass beakers, were treated with aluminium sulphate (alum), polyaluminium chloride and ferric chloride at doses of 2% and 4% of metal on a dry weight basis. The samples were mixed using a jar tester. The mixing regime used was based on that reported by Higgins (2010) and is shown in Figure 3. A control sample, with no chemical addition, was also prepared. The samples were dewatered using the dewatering procedure described above.

The resulting biosolids cake samples (approximately 200g) were incubated at room temperature in 1L Schott bottles. The samples were wrapped in aluminium foil to protect from light and were monitored for evolution of sulphur compounds (DMS, EMS, DMDS, DEDS and DMTS) by HS SPME-GC-MS every other day for 20 days. The samples were also analysed for the production of OVACs (toluene, ethylbenzene, styrene, *p*-cresol, indole, and skatole) by HS SPME-GC-MS weekly for 37 days.

Chemical addition to plant-dewatered cake

Samples of the plant dewatered biosolids (approximately 85g) in 400mL glass beakers were treated with aluminium sulphate hydrate at doses of 2% and 4% of metal on dry weight basis and mixed manually with a stainless steel spatula for approximately two minutes. A control sample (no chemical addition) was prepared in the same way. The cake samples were incubated at room temperature in 250mL Schott bottles. Samples were wrapped in aluminium foil to protect from light and were monitored for evolution of sulphur compounds by HS SPME-GC-MS every other day for 14 days. The samples were also analysed for the production of OVACs by HS SPME-GC-MS weekly for 16 days.

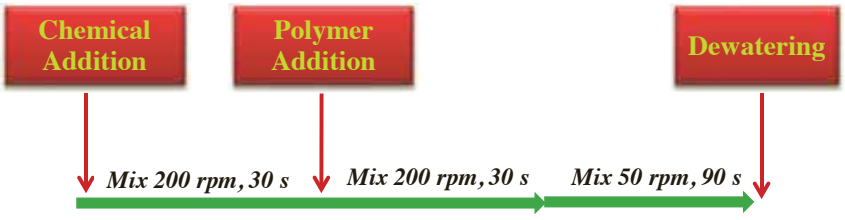


Figure 3. Mixing regime used in trials of chemical addition to digested sludge.

Centrifuge speed trials

Samples of digested sludge (approximately 600g) were dewatered at 3850rpm (control speed), 3460rpm (10% reduction in speed, relative to control) and 3080rpm (20% reduction in speed, relative to control) using the dewatering procedure described above. The resulting biosolids cake samples (approximately 190g) were incubated at room temperature in 500mL Schott bottles. Samples were wrapped in aluminium foil and monitored for evolution of sulphur compounds by HS SPME-GC-MS every other day for 20 days. The samples were also analysed for the production of OVACs by HS SPME-GC-MS weekly for 23 days.

HS SPME-GC-MS procedure for the analysis of sulphur compounds

Sulphur compounds (DMS, EMS, DMDS, DEDS and DMTS) were analysed by headspace SPME using a 50/30 µm DVB-CAR-PDMS fibre, followed by GC–MS analysis. SPME was performed using a Gerstel MPS2 Autosampler interfaced with a Hewlett Packard 6890N GC and a Hewlett Packard 5973 Network Mass Selective Detector. A 50–80mg sample of biosolids cake was placed into a Teflon-lined screw cap vial (20mL) and 10mL of a 500ng/L DMDS-d6 internal standard solution in MilliQ water was added, followed by 3g of anhydrous sodium sulphate. The SPME fibre was introduced into the headspace of the vials and extraction was carried out for 10 minutes at 40°C. The fibre was then desorbed at 230°C for four minutes in the injector port of the GC, while the analytes were simultaneously cryofocused on the GC column at 0°C. GC separation of the sulphur compounds was carried out using helium as the carrier gas at 1.0mL/min, and a 30m x 0.25mm x 1 µm ZB-5MS (Phenomenex®) capillary column. The mass spectrometer (MS) operated in selected ion monitoring (SIM) mode and for each sulphur compound, the most abundant ion was used for quantitation and 1–2 characteristic m/z ions were selected for MS confirmation. Samples were analysed against standards of the pure compounds with deuterated DMDS (DMDS-d6) as an internal standard.

HS SPME-GC-MS procedure for the analysis of OVACs and geosmin

The OVACs (toluene, ethylbenzene, styrene, *p*-cresol, indole and skatole) and geosmin were analysed using a similar procedure to that described above for the sulphur compounds except that a 65 µm PDMS-DVB fibre was used, and extraction was carried out for 30 minutes at 60°C. The fibre was desorbed at 250°C for five minutes in the injector port of the GC and the analytes were not cryofocused. The MS operated in SIM mode and for each compound, the most abundant ion was used for quantitation and 1–2 characteristic m/z ions were selected for MS confirmation. Samples were analysed against standards of pure compounds using deuterated ethylbenzene (ethylbenzene-d_{10}) as an internal standard.

Results and Discussion

Validation and optimisation of the HS SPME-GC-MS methods for the analysis of sulphur compounds and OVACs

GC-MS conditions for the analysis of sulphur compounds and OVACs were optimised, in order to achieve maximum sensitivity, good baseline separation of analytes and Gaussian peak shapes. In order to optimise the sensitivity of the method and to minimise interferences from other compounds, the mass spectrometer was operated in SIM mode.

HS SPME parameters (fibre type, extraction temperature and time, and desorption conditions) were optimised to give the best analyte responses, while minimising analyte degradation and carry-over. These parameters were optimised using Teflon-lined screw cap vials (20mL) containing aqueous solutions of the analytes (5 µg/L). For the sulphur compounds the best analyte responses were obtained with the 50/30 µm DVB-CAR-PDMS fibre, while the 65 µm PDMS-DVB fibre gave the best responses for the OVACs and geosmin. Details of the optimised conditions for each method are described in the Methods section above.

The linearity of the responses obtained from the analysis of the sulphur compounds and OVACs, and sensitivity and precision of the two methods were evaluated. Linear calibration curves with high correlation coefficients were achieved for all analytes. The method limits of detection and quantification (MLODs and MLOQs) were calculated from six blank MilliQ analyses, via the mean concentration plus three times the standard deviation for the MLOD, and 10 times for the MLOQ. The MLODs and MLOQs for all analytes were all below their odour threshold concentrations (Table 1). Good repeatability (1%–9% RSD) and reproducibility (3%–10% RSD) were obtained for the HS SPME-GC-MS method for the analysis of sulphur compounds. The HS SPME-GC-MS method for the analysis of OVACs and geosmin also showed good repeatability (1%–7% RSD) and reproducibility (4%–15% RSD). However, since the matrix effects had not been fully investigated, the methods can only be considered as semi-quantitative at this point.

Thermal degradation of analytes

Certain sulphur compounds can be susceptible to thermal degradation under certain GC conditions. For example, dimethylpolysulphides (e.g. DMDS, DMTS) are susceptible to disproportionation and thermal degradation, with thermally induced disproportionation resulting in the formation of lower dimethylpolysulphide homologues and elemental sulphur (Kristiana *et al*., 2010).

In order to confirm that thermal degradation of analytes had not occurred using our method conditions, aqueous solutions of individual compounds (10 µg/L) were analysed with the MS operating in full scan mode (50–300 m/z). The resulting chromatograms were examined for degradation products by extracting the relevant mass ions corresponding to possible degradation products. To investigate whether there were any interactions between compounds, aqueous solutions containing different combinations of two compounds (each at 10 µg/L) were also analysed and the resulting chromatograms analysed for evidence of compound interactions and the presence of by-products resulting from interaction between compounds (i.e. "scrambled" compounds).

Table 1. Odour threshold concentrations for the analytes of interest.

Compound	Odour detection threshold in water (µg/L)
Dimethyl sulphide	0.3[a]
Dimethyl disulphide	12[b]
Dimethyl trisulphide	0.01[b]
Toluene	24[c]
Ethylbenzene	2.4[c]
Styrene	730[d]
p-cresol	55[e]
Indole	300[f]
Skatole	1.2[f]
Geosmin	0.01[g]

[a] Buttery *et al.* (1990)
[b] Buttery *et al.* (1976)
[c] Alexander *et al.* (1982)
[d] Baker (1963)
[e] Buttery *et al.* (1988)
[f] Yan *et al.* (2011)
[g] Suffet *et al.* (1999)

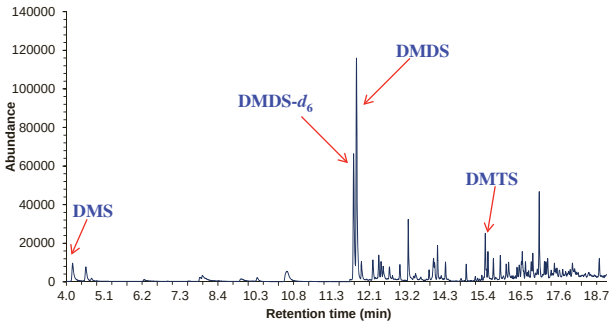


Figure 4. Typical chromatogram of a biosolids sample, showing peaks for DMS, DMDS and DMTS. Sample analysed using the HS SPME-GC-MS method for analysis of sulphur compounds in selected-ion monitoring mode using a ZB-5MS capillary column.

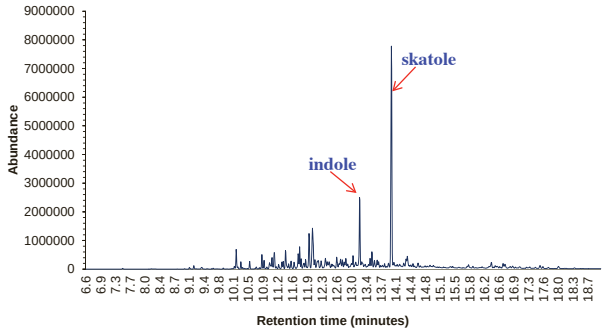


Figure 5. Typical chromatogram of a stored biosolids sample showing the presence of indole and skatole. Sample analysed using the HS SPME-GC-MS method for analysis of OVACs in selected-ion monitoring mode using a ZB-5MS capillary column.

For the majority of the sulphur compounds there was no evidence of degradation products or "scrambled" compounds. However, methanethiol was oxidised to DMDS (major peak) and DMTS (minor peak). Ethanethiol (ET) was oxidised to DEDS (major) with only a very minor peak visible for ET. A mixture of MT and ET showed major peaks for DEDS and the "scrambled" compound methyl ethyl disulphide (MEDS) as well as smaller peaks for DMDS and DMTS. Since MT and ET were oxidised to DMDS and DMTS, and DEDS, respectively, and also reacted with each other, they were excluded from the mixed standard solution. Based on these results, it was assumed that any MT present in the biosolids would be transformed to DMDS and DMTS. Similarly, any ET present in the biosolids would be converted to DEDS.

Odorous compounds identified in biosolids samples from Woodman Point WWTP

Analysis of a relatively fresh biosolids sample (less than a week old) using the HS SPME-GC-MS method for the analysis of sulphur compounds showed the presence of DMS, DMDS and DMTS. No EMS or DEDS were observed in biosolids samples. A typical chromatogram of compounds detected in a biosolids sample is shown in Figure 4.

A biosolids sample, which had been stored at room temperature for a few months, exhibited a very strong faecal/nauseating odour, probably caused by indole and skatole, which showed strong peaks in chromatograms obtained using HS SPME-GC-MS (Figure 5). These compounds were not detected in the fresh biosolids samples. This finding is consistent with WERF reports that one of the major sources of odours during the first 1–2 weeks of biosolids storage is due to the production of VOSCs by microbial degradation of sulphur-containing amino acids (Higgins, *et al.*, 2003, 2006; Chen *et al*., 2006), while the OVACs start to accumulate only after VOSCs have been depleted (Chen *et al.*, 2004; 2006).

Using our method for the analysis of OVACs, the presence of geosmin was also detected in fresher biosolids samples, which still contained some sulphur compounds but exhibited a more earthy/musty odour. Other types of compounds which were tentatively identified based on their mass spectra and/or library matches, but not confirmed with authentic analytical standards, included various long chain aliphatic hydrocarbons, terpenes, alkyl benzenes and other aromatic compounds, and some of these may well have contributed to the earthy musty odour.

Analysis of biosolids samples from the odour reduction trials

In this preliminary study, we have focussed only on analysing odorous compounds in the headspace of wet biosolids. Thus,

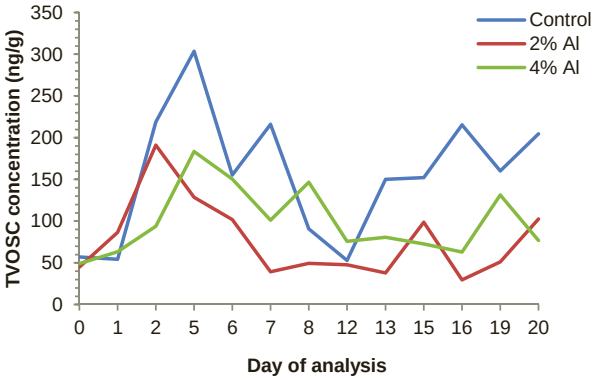


Figure 6. Effect of aluminium sulphate addition to digested sludge on TVOSC production.

the biosolids samples were analysed as "aqueous" samples as described in the Methods Section. Although the method is not fully quantitative at this point, it is reproducible, simple, relatively quick and fully automated. Odours of the biosolids samples from the subsequent odour reduction trials were assessed in terms of the concentration of total volatile organic sulphur compounds (TVOSC), measured as the sum of the DMS, DMDS and DMTS concentrations present in the biosolids sample, and expressed as nanogram per gram of moist biosolids sample used (ng/g). Thus, the odour reduction (or increase) was considered to be the reduction (or increase) in the TVOSC concentration relative to a control sample.

Chemical addition to digested sludge prior to dewatering

A 37% reduction of peak TVOSC concentration was observed for an alum dose of 2% (based on aluminium), while a 4% alum dose resulted in a 40% reduction of peak TVOSC concentration, relative to the control sample (Figure 6). The odour reductions observed in our laboratory trials were lower than the odour reductions observed by the WERF research team. In their laboratory trials, Adams *et al*. (2008) reported that a dose of 0.5% alum (based on aluminium) added to digested sludge prior to dewatering resulted in approximately 80% reduction of peak TVOSC concentration, while a 2% alum dose gave approximately 90% reduction in peak TVOSC concentration. The reasons for the observed differences in the odour reductions obtained in our laboratory trials and those reported by Adams *et al*. could be due to a number of different factors, namely the sludge properties, type of polymer used, chemical contact time, mixing, shear and interactions between the metal and polymer.

A dose of 2% polyaluminium chloride (based on aluminium) resulted in an 11% increase in the peak TVOSC concentration

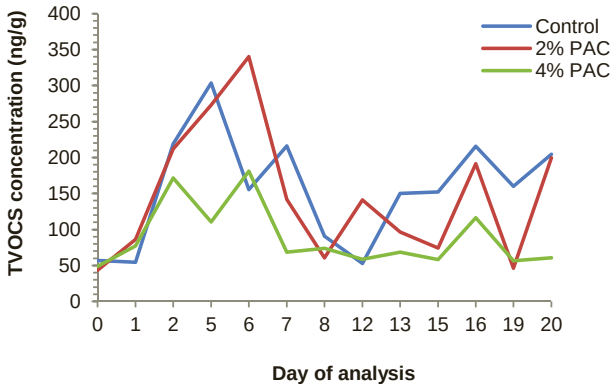


Figure 7. Effect of polyaluminium chloride addition to digested sludge on TVOSC production.

in the resulting cake, while a 4% dose gave a 40% reduction in the peak TVOSC concentration of the biosolids cake, relative to the control (Figure 7). Addition of iron at the 2% dose resulted in only a slight decrease (23%) in peak TVOSC concentration, while addition of iron at the 4% dose resulted in a 50% increase in peak TVOSC concentration, relative to control (Figure 8). The observed increase in TVOSC concentration obtained with the 4% iron dose in our trials is somewhat consistent with earlier findings of the WERF study.

Results from the Phase III WERF study showed that, in general, an increase in iron concentration in the sludge or biosolids resulted in higher TVOSC concentrations in the dewatered biosolids headspace, especially if iron was added prior to or during digestion (Adams, *et al.*, 2008). It was also found that addition of ferric chloride to anaerobically digested sludge before dewatering did not reduce TVOSC emissions from cake until the iron dose was at least 8% on a dry mass-mass basis (Adams, *et al.*, 2008).

Results from recent laboratory studies, using batch anaerobic digestion, have shown that iron addition to the digester feed reduced TVOSC concentrations in the resulting biosolids cake by 50 to over 95% for most of the sludges (Novak *et al*., 2010). Direct addition of iron (4% dose) to biosolids cake also significantly reduced the TVOSC concentrations (Higgins, 2010). The contradictory results obtained from various studies using iron are most likely due to the sludge properties, location of iron addition and polymer-iron interactions (Higgins, 2010).

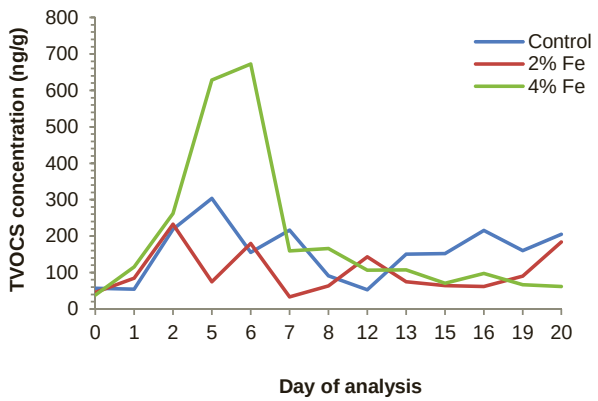


Figure 8. Effect of ferric chloride addition to digested sludge on TVOSC production.

Comparison of TVOSC profiles in Figures 6 to 8 showed that in all three cases the TVOSC concentrations peaked within the first week of incubation and then decreased, which was consistent with previously reported research (e.g. Higgins *et al*., 2003; Adams *et al*., 2008).

Chemical addition to plant-dewatered cake

Higgins (2010) reported that adding metal salts directly to the cake gave a better TVOSC reduction compared to adding the salts during the conditioning and dewatering step. However, addition to the cake also resulted in a greater reduction in the pH of the cake to levels probably below those desirable for land application. In our laboratory trials, a 2% dose of aluminium sulphate (based on aluminium) resulted in a 24% increase in peak TVOSC concentration, while addition of 4% aluminium sulphate resulted in approximately 70% decrease in peak TVOSC concentration, relative to the control sample. However, the pH of the cake treated with 4% aluminium sulphate was also significantly reduced (pH 4.2) to levels that may not be suitable for land application. These results are consistent with the results reported by Higgins (2010).

Centrifuge speed trials

Reducing the centrifuge bowl speed and/or torque can reduce the amount of shear imparted on biosolids, thereby reducing the odour of the dewatered cake (Adams *et al*., 2008). In a full-scale test, a 10% reduction in centrifuge bowl speed on one high-solids centrifuge resulted in 20% reduction of TVOSC emissions from dewatered cake with no observed reduction in cake solids concentration (Adams *et al*., 2008).

In our laboratory trials, a 20% reduction in centrifuge speed (3080rpm) resulted in an approximate 30% decrease in peak TVOSC concentration, relative to the control. However, the solids content of the resulting cake was also significantly reduced which would not be desirable from the point of view of WWTP operations.

Analysis of OVACs in biosolids samples from the odour reduction trials

No significant concentrations of OVACs were detected in biosolids samples derived from chemically treated digested sludge. In most cases compounds were either at or below limits of quantification for the method. However, traces of geosmin were detected in all biosolids samples.

Conclusions and Future Work

This study identified some of the major odorous compounds in biosolids samples obtained from a Western Australian WWTP and investigated chemical addition and reduction of centrifuge speed as potential odour reduction strategies. In this study all experimentation was limited to laboratory scale work.

Aluminium sulphate addition (4% based on aluminium) to digested sludge prior to dewatering offered the best odour reduction strategy among the options that were investigated, resulting in approximately 40% reduction in peak TVOSC concentration, relative to a control sample. Reduction of centrifuge speed would not be a viable option for our test WWTP as it resulted in a reduction in the solids content of the resulting biosolids cake.

In most cases, results obtained from the HS SPME-GC-MS analyses were in general agreement with qualitative observations by a single trained odour assessor. In future studies, it would be beneficial to include dilution olfactometry measurements to obtain a more rigorous assessment of the overall odour generated from biosolids cake and to correlate/compare the results with measurements obtained using HS SPME-GC-MS. In addition, it would be useful to determine the nature of odour compounds in aged biosolids in which the very

objectionable and most organoleptically potent compounds such as VOSCs and organic nitrogen compounds have been depleted. It would also be advantageous to determine whether these odours are considered objectionable or not, and at what concentrations do the odours become acceptable.

While studies conducted in this project utilised sludge and biosolids samples from just one WWTP, future studies will expand the scope to include biosolids and sludge sourced from other WWTPs. This would provide information on odorous compounds in biosolids produced at other WWTPs and determine whether the trialled odour reduction strategies are applicable to more than one type of wastewater treatment system.

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