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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.

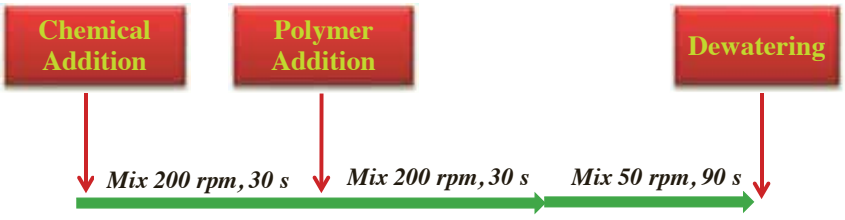

Figure 3. Mixing regime used in trials of chemical addition to digested sludge.

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)

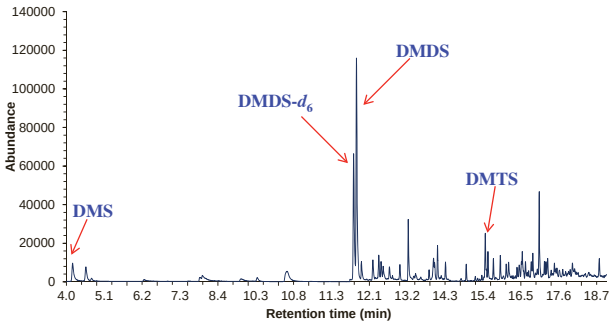

Figure 4. Typical chromatogram of a biosolids sample, showing peaks for DMS, DMDS and DMTS. Sample analysed using the HS SPME-GC-MS method for analysis of sulphur compounds in selected-ion monitoring mode using a ZB-5MS capillary column.

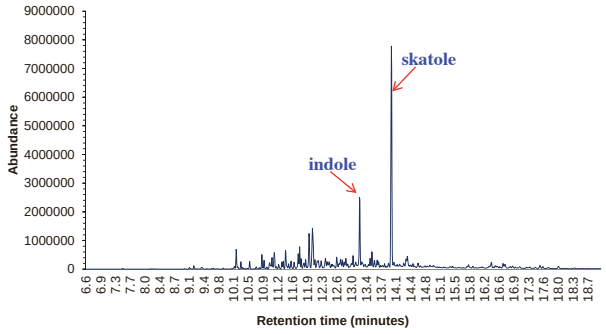

Figure 5. Typical chromatogram of a stored biosolids sample showing the presence of indole and skatole. Sample analysed using the HS SPME-GC-MS method for analysis of OVACs in selected-ion monitoring mode using a ZB-5MS capillary column.

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,

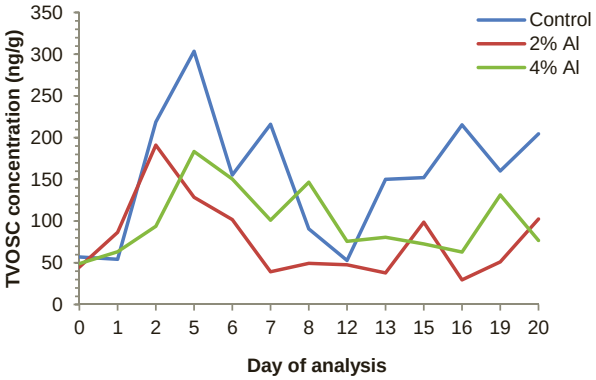

Figure 6. Effect of aluminium sulphate addition to digested sludge on TVOSC production.

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

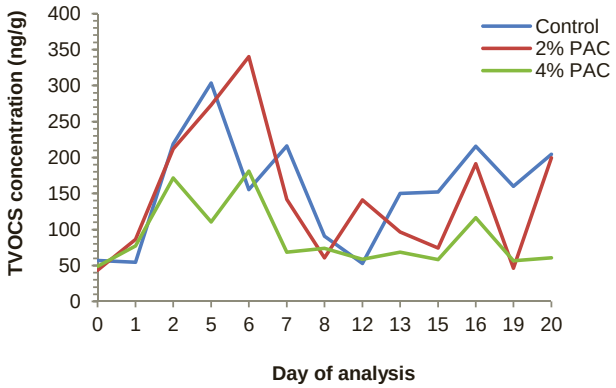

Figure 7. Effect of polyaluminium chloride addition to digested sludge on TVOSC production.

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).

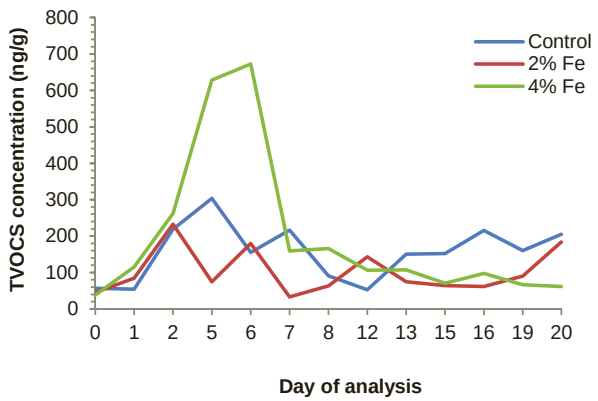

Figure 8. Effect of ferric chloride addition to digested sludge on TVOSC production.

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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The Authors

Dr Yolanta Gruchlik (email: Y.Gruchlik@curtin.edu.au) is a Research Fellow with the Curtin Water Quality Research Centre (CWQRC) at Curtin University, Perth, Western Australia. She is currently leading a project investigating potential odour reduction strategies in biosolids and has also been involved in several projects related to drinking water quality.

Associate Professor Anna Heitz is a Senior Process Specialist with Arenko Pty Ltd and a former CWQRC Director. **Associate Professor Cynthia Joll** is the Deputy Director of the CWQRC and an academic staff member of Curtin University's Chemistry Department. **Associate Professor Jeffrey Charrois** is the current CWQRC Director. **Hanna Driessen** is a PhD student and **Lise Fouche** is researcher at the CWQRC. **Nancy Penney** is a Biosolids Strategist at the Water Corporation and Chair of the Australian and New Zealand Biosolids Partnership (ANZBP).

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