

LABORATORY SCALE INVESTIGATIONS OF POTENTIAL ODOUR REDUCTION STRATEGIES IN BIOSOLIDS – PHASE II

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Yolanta Gruchlik¹, Anna Heitz², Lise Fouché¹, Hannah Thurlow³, Nancy Penney³ and Jeff Charrois¹

¹Curtin Water Quality Research Centre (CWQRC), Department of Chemistry, Curtin University, GPO Box U1987, Perth, Western Australia, 6845.

²Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, Western Australia, 6845.

³Water Corporation of Western Australia, Project Building A, 27 Lemnos Street, Shenton Park, Western Australia, 6008.

2nd Summary Report

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Executive Summary

This report is the second summary report for Phase II of this project, produced for the Water Corporation of Western Australia (WCWA) and the Australian and New Zealand Biosolids Partnership (ANZBP). In the reporting period from January 2013 – July 2013 experiments of alum addition at doses of 0% (control), 2% and 4% of aluminium (Al) on a dry weight basis, to liquid biosolids from WWTPs 1 and 2, and processed sludge from WWTPs 3 and 4 were conducted on a laboratory scale. In each case the alum was added prior to dewatering. The lab dewatered cakes obtained from these experiments were analysed for the evolution of volatile sulphur compounds (dimethyl sulphide (DMS), dimethyl disulphide (DMDS), and dimethyl trisulphide (DMTS)) by head space solid-phase microextraction coupled with gas chromatography mass spectroscopy (HS SPME-GC-MS). The cakes were also analysed by dynamic olfactometry to obtain a measure of the overall odour. Based on the HS SPME-GC-MS and olfactometry results obtained from the lab generated cakes from WWTPs 1, 2, 3 and 4 the following conclusions were made:

- Alum addition was effective in reducing odours in biosolids from wastewater treatment plants that use mesophilic anaerobic digestion to process wastewater sludge (WWTPs 1 and 2). For WWTP 1, addition of 4% Al to liquid biosolids prior to dewatering resulted in a 50% reduction in the overall odour concentration (Figure 4e and Table 3) in the lab dewatered cake, relative to the control sample. For WWTP 2, addition of 4% Al to liquid biosolids prior to dewatering resulted in approximately 58% reduction in the overall odour concentration (Figure 4f and Table 3) in the lab dewatered cake, relative to the control.
- Alum addition did not reduce odours in biosolids from wastewater treatment plants which use oxidation ditch processes (WWTPs 3 and 4). Although HS SPME-GC-MS results suggested an 81% reduction in the peak TVOSC concentration for lab dewatered cakes from WWTP 3 and a 50% reduction in the peak TVOSC concentration for cakes from WWTP 4 at the 4% Al dose (Figures 4c and 4d, and Table 3), the olfactometry results showed significant increases in the overall odour concentrations for lab dewatered cakes from both WWTPs at the 2% and 4% Al doses (Figures 4g and 4h, and Table 3).
- No linear correlations were observed between the TVOSC concentrations (HS SPME-GC-MS) and the overall odour concentrations (olfactometry) in these experiments. The lack of correlation between the HS SPME-GC-MS results and the olfactometry results may, in part, be due to the different methods in which the samples were prepared and analysed (Figures 2 and 3) as well as the presence of other odour compounds which were not analysed quantitatively by the HS SPME-GC-MS method but would have contributed to the overall odour concentrations determined by olfactometry.
- Biosolids from WWTPs 3 and 4 contained much higher TVOSC concentrations and were significantly more odorous than biosolids from WWTPs 1 and 2.

Although alum addition to liquid biosolids from WWTPs 1 and 2 was effective in reducing odours in the resulting lab dewatered cakes, alternative odour reduction measures need to be investigated for processed sludge from WWTPs 3 and 4 which use oxidation ditch processes. Potential odour reduction options that will be investigated in the next stage of this project include: addition of potassium permanganate and/or calcium nitrate to processed sludge (WWTP 4) prior to dewatering. For comparison, addition of potassium permanganate and calcium nitrate to liquid biosolids (WWTP 1) will also be included in this study. To reduce the discrepancies between the HS SPME-GC-MS results and the olfactometry results, modifications to the HS SPME-GC-MS sample preparation and analytical method will be investigated to ensure that samples are analysed in a comparable manner using the two different approaches.

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Acronyms and Abbreviations

ANZBP	Australian and New Zealand Biosolids Partnership
DAFT	Dissolve air floatation thickener
DMDS	Dimethyl disulphide
DMS	Dimethyl sulphide
DMTS	Dimethyl trisulphide
DS	Dry solids
EAS	Excess activated sludge
ESD	Egg-shaped digester
HS	Headspace
GC-MS	Gas chromatography-mass spectrometry
MLE	Modified Ludzack-Ettinger process
OD	Oxidation ditch
OVACs	Odorous volatile aromatic compounds
RST	Rotary screw thickener
SBR	Sequencing batch reactor
SPME	Solid-phase microextraction
SRT	Sludge retention time
TOU	The Odour Unit
TVOSCs	Total volatile organic sulphur compounds
WCWA	Water Corporation of Western Australia
WWTP	Wastewater treatment plant

1.0 Introduction

This report is the second summary report for Phase II of this project investigating odour reduction in biosolids, produced for the Water Corporation of Western Australia (WCWA) and the Australian and New Zealand Biosolids Partnership (ANZBP). In this reporting period (January 2013 – July 2013) we investigated the addition of aluminium sulphate (alum) to treated wastewater sludge from different wastewater treatment plants (WWTPs) in Western Australia. Aluminium sulphate addition to liquid biosolids prior to dewatering was found to be the most promising odour reduction measure among the different odour reduction options investigated in the Phase I study (Gruchlik, *et al.*, 2012a and 2012b). The aim of the current Phase II study was to determine if this odour reduction strategy is applicable to wastewater sludge and biosolids produced from a wider variety of treatment processes. Four WWTPs were chosen for study in this Phase: two used mesophilic anaerobic digestion (WWTPs 1 and 2) and two used oxidation ditch processes (WWTPs 3 and 4). All four WWTPs used centrifuge dewatering. A more detailed summary of the processes at each of the WWTPs chosen for this study is shown in Table 1.

Table 1. Summary of processes at wastewater treatment plants selected for this study (adapted from Agarwalla, 2012).

Process	WWTP 1	WWTP 2	WWTP 3	WWTP 4
Screening	step screen	step screen	step screen	band screen
Grit removal	yes	yes	yes	yes
Primary settling	yes	yes	none	none
Primary sludge thickening	RST	none	none	none
Secondary treatment	SBR	MLE	OD	OD
EAS Thickening	DAFT	DAFT	DAFT	DAFT
Sludge digestion	anaerobic digestion (ESD)	Conventional anaerobic digestion	none	none
Sludge dewatering	centrifuge	centrifuge	centrifuge	centrifuge
Sludge conditioning	none	none	none	none
SRT aeration tanks (days)	16 – 22	10 – 12	20 – 25	20 – 25
SRT digester (days)	20 +	20	N/A	N/A

RST = rotary screw thickener. SBR = sequencing batch reactor. MLE = modified Ludzak-Ettinger process. OD = oxidation ditch. EAS = excess activated sludge. DAFT = dissolved air floatation thickener. ESD = egg-shaped digesters. SRT = sludge retention time. N/A = not applicable.

Aluminium sulphate addition experiments, at doses of 0% (control), 2% and 4% of aluminium (Al) on a dry weight basis, to liquid biosolids from WWTPs 1 and 2 and processed sludge from WWTPs 3 and 4 were conducted on a laboratory scale. In all cases the alum was added prior to dewatering. The cakes obtained from these experiments were analysed for the evolution of volatile sulphur compounds: dimethyl sulphide (DMS), dimethyl disulphide (DMDS), and dimethyl trisulphide

(DMTS) by headspace solid-phase microextraction coupled with gas chromatography mass spectroscopy (HS SPME-GC-MS). The cakes were also analysed by dynamic olfactometry to obtain a measure of the overall odour and to determine if there were any correlations between the HS SPME-GC-MS results and the olfactometry measurements. Results obtained from these experiments are presented and discussed in this report. The methodologies used to conduct the alum addition experiments, HS SPME-GC-MS analyses of the dewatered cakes, and the olfactometry measurements are also summarised.

2.0 Methodology

2.1 Sample description

Samples of liquid biosolids (post digestion, pre dewatering) were obtained from WWTPs 1 and 2, while samples of processed sludge (post oxidation ditch, pre dewatering) were obtained from WWTPs 3 and 4. The samples were packed in coolers and transported to the laboratory for use in bench-scale trials of aluminium sulphate addition. Aluminium sulphate (56 % w/v aqueous solution) was supplied by the Water Corporation. Details of the processed sludge/liquid biosolids properties (after treatment, pre dewatering) and the type of polymer used during dewatering are shown in Table 2. The percentage dry solids (% DS) was determined by drying a known amount of processed sludge/liquid biosolids to constant weight in an oven at 120 °C. Percentage dry solids was calculated according to Equation 1.

$$\text{Eqn 1: } \% \text{ DS} = (\text{weight of dry residue} \div \text{weight of wet sludge or liquid biosolids}) \times 100$$

Table 2. Select processed-sludge/liquid biosolids parameters and polymer characteristics used during dewatering.

Treatment plant	Sampling date	% DS	Sludge retention time (SRT) (days)	Type of polymer used during dewatering *	Form in which polymer was dosed
WWTP 1	5/4/2013	3.6	21	Powder polymer FO4800SSH (SNF Pty Ltd)	0.3% w/v aqueous solution
WWTP 2	26/4/2013	1.4	27	Emulsion polymer EMA8845MBL (SNF Pty Ltd)	0.6% v/v aqueous solution
WWTP 3	11/4/2013	3.4	22	Emulsion polymer Core Shell 71301 (Nalco Pty Ltd)	0.3% v/v aqueous solution
WWTP 4	2/5/2013	3.4	22	Emulsion polymer EMA8845MBL (SNF Pty Ltd)	0.5% v/v aqueous solution

*Polymer was supplied by the Water Corporation and polymer dose was based on the average amount used at each WWTP and adjusted accordingly to lab scale experiments.

2.2 Aluminium sulphate (alum) addition to liquid biosolids and processed sludge prior to dewatering

The experiments involving alum addition were conducted in accordance with previously described methods (Gruchlik *et al.*, 2012a; 2012b), except that in this study the alum addition experiments were conducted in duplicate. Figure 1 below shows the order of chemical addition, the mixing regime and the dewatering conditions used to treat liquid biosolids from WWTPs 1 and 2 and processed sludge from WWTPs 3 and 4.

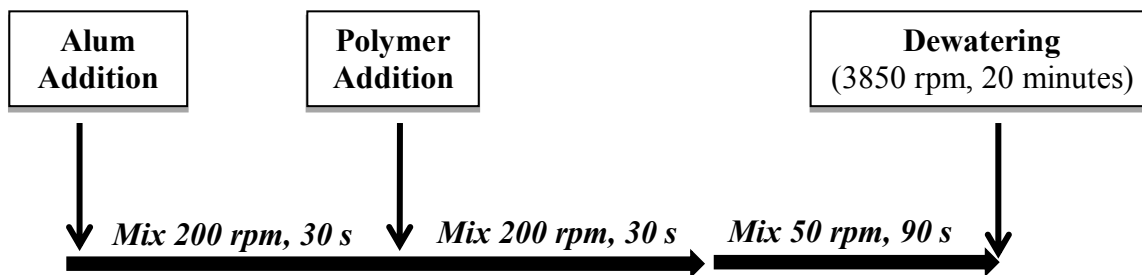


Figure 1. Mixing regime used for alum addition to liquid biosolids and processed sludge.

Approximately 25 – 30 g of the dewatered cake sample from each duplicate was incubated at room temperature in 100 mL Schott bottles. Samples were wrapped in aluminium foil to protect them from light. Subsamples of these samples were taken periodically and were monitored for evolution of volatile sulphur compounds (DMS, DMDS, and DMTS) by HS SPME-GC-MS on day 0 (day of the experiment), and then day 1, 2, 3, 4, 7, 8, 9, 11, 15, 18 and 21 of incubation.

Remaining cake samples, from each duplicate, were combined into a single sample and placed into a 500 mL Schott bottle such that the cake occupied approximately 40% of the bottle volume (i.e. approximately 150 – 200 g of cake). Samples were wrapped in aluminium foil and stored at room temperature. These samples were collected by The Odour Unit on day 1 and were analysed by dynamic olfactometry on day 1, 2, 3, 4, 7, 8, 9, 11, 15, 18 and 21 of incubation.

2.3 Summary of HS SPME-GC-MS analyses

HS SPME-GC-MS analyses of the lab dewatered cakes were conducted by CWQRC using previously described methods (Gruchlik *et al.*, 2012a; 2012b). Figure 2 summarises how the samples were prepared and then analysed by HS SPME-GC-MS for the volatile sulphur compounds: DMS, DMDS and DMTS.

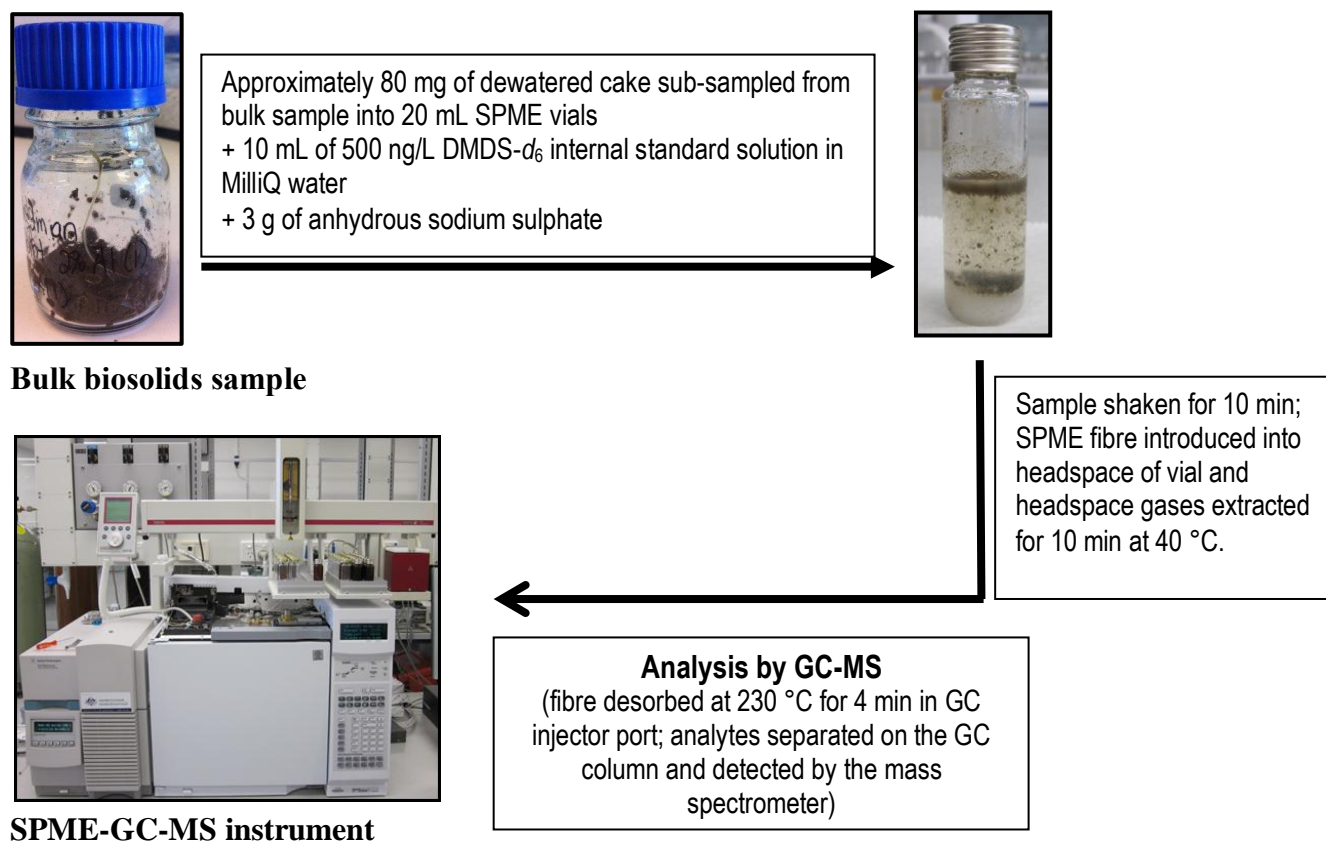


Figure 2. Summary of biosolids analysis by HS SPME-GC-MS.

The HS SPME-GC-MS results were used to assess odours from cake samples obtained from the alum addition trials 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 dewatered cake samples, and compared with a control sample. TVOSC concentration was expressed as microgram per gram of moist cake sample used ($\mu\text{g/g}$). Reduction (or increase) in the TVOSC concentration was considered to be the reduction (or increase) in the peak TVOSC concentration relative to the control sample.

2.4 Summary of the olfactometry analyses

Dynamic olfactometry analyses were conducted by The Odour Unit (TOU) in accordance with the Australian Standard 'Determination of Odour Concentration by Dynamic Olfactometry AS/NZS4323.3:2001'. Dynamic olfactometry involves the repeated presentation of both a diluted odour sample and an odour-free air stream to a panel of qualified assessors through two adjacent ports on the olfactometer. TOU routinely uses four to six trained assessors or panellists, with four qualified panellists being the minimum allowed under the Australian Standard. The method for odour concentration analysis involves the odorous gas sample initially being diluted to the point where it cannot be detected by any member of the panel. Each panellist steps up to the olfactometer in turn, takes a sniff from each port, then chooses which port contains the odour and enters their response. After each round of the testing process the concentration of the odorous gas is systematically increased (doubled) and re-presented to the panellists. A round is completed when all panellists have correctly detected the presence of the odour with certainty. The odour is presented to the panel for three rounds and results taken from the latter two rounds, as stated in the Australian Standard AS/NZS 4323.3:2001 (Standards Australia, 2001).

The olfactometer used for the analysis of our samples was Odormat Series V02. The precision and accuracy of this instrument were compliant with the Australian Standard AS/NZS4323.3:2001. The lower detection limit (LDL) for the olfactometer was determined to be 16 ou (four times the lowest dilution setting). The measurements were performed in an air- and odour-conditioned room. The room temperature was maintained at 25 °C or less, with temperature fluctuations of less than ± 3 °C. The measurements were performed using standards for which the traceability to the national standard has been demonstrated. Four panellists were used for the analysis of our samples. The panellists were individually selected by TOU to comply with fixed criteria and were monitored over time to keep within the limits of the Australian Standard. The results from the panellists were traceable to primary standards of *n*-butanol in nitrogen.



Figure 3. Lab dewatered cake samples in 500 mL Schott bottles with modified lids for analysis by dynamic olfactometry.

The Odour character was also assessed, however, AS4323.3:2001 and NATA (National Association of Testing Authorities) accreditations do not cover the performance of this service.

The sample preparation method was developed by the CWQRC and The Odour Unit: dewatered cake sample (~200 g) was placed in a 500 mL Schott bottle, such that the cake occupied approximately 40% of the bottle volume. The Schott bottle lid was modified with an inlet and outlet port (Figure 3). Dry nitrogen (25L) was then passed into the inlet and collected in an odour sample bag attached to the outlet. The odour concentration in odour units (ou) of the collected sample was then determined by dynamic olfactometry. The overall odour reduction (or increase) was considered to be the reduction (or increase) in the peak odour concentration relative to the control sample.

3.0 Results and discussion

In order to assess an odour nuisance, odour formation, emission, dispersion and perception need to be considered. However, there is no single measure that is suitable for this purpose (Gostelow and Parsons, 2000). Analytical measurements characterise odours in terms of their chemical composition (i.e. odorants), but they say little about the perceived effect of the odour. Sensory measurements use the human nose and characterise odours in terms of their perceived effect but do not provide information on their chemical composition (Gostelow and Parsons, 2000). In this study a combination of analytical (HS SPME-GC-MS) and sensory (dynamic olfactometry) measurements was used to assess odours from lab dewatered cakes from different WWTPs.

3.1 Comparison between the HS SPME-GC-MS and olfactometry results

Figure 4 shows a comparison of the TVOSC concentration profiles (a – d) obtained from the HS SPME-GC-MS analyses of lab dewatered cakes from WWTPs 1, 2, 3 and 4 (treated with alum prior to dewatering) with the corresponding odour profiles obtained from olfactometry measurements (e – h). Peak odour concentrations (ou) and peak TVOSC concentrations ($\mu\text{g/g}$) are listed in Table 3, along with the odour character observed at peak odour concentration. The days at which odour concentrations and TVOSC concentrations peaked, as well as % odour and % TVOSC reductions (or increases) are also shown.

Comparison of peak odour concentrations for lab dewatered cakes from WWTPs 1, 2, 3 and 4 showed that cakes from WWTPs 3 and 4 were much more odorous than biosolids from WWTPs 1 and 2 (Figure 4 e – h, and Table 3). WWTPs 3 and 4 use oxidation ditch processes to treat sludge, while WWTPs 1 and 2 use mesophilic anaerobic digestion. Lab generated cakes from WWTPs 3 and 4 also contained significantly higher TVOSC concentrations than cakes from WWTPs 1 and 2 (Figure 4 a – d and Table 3). This is consistent with earlier observations by a CWQRC odour panel and previous HS SPME-GC-MS results for plant dewatered biosolids obtained from the same WWTPs (Gruchlik, *et al.*, 2013).

Addition of 4% Al to liquid biosolids from WWTP 1 prior to dewatering resulted in a 30% reduction in the peak TVOSC concentration (Figure 4a and Table 3) and a 50% reduction in the peak odour concentration (Figure 4e and Table 3) in the lab dewatered cake, relative to the control sample. For liquid biosolids from WWTP 2, addition of 4% Al prior to dewatering resulted in approximately 47% reduction in the peak TVOSC concentration (Figure 4b and Table 3) and a 58% reduction in the peak odour concentration (Figure 4f and Table 3) in the lab dewatered cake, relative to the control. Although HS SPME-GC-MS results suggested an 81% reduction in the peak TVOSC concentration for lab dewatered cake from WWTP 3 at the 4% Al dose (Figure 4c and Table 3), the olfactometry results showed a significant increase in the odour concentration for both Al doses (Figure 4g and Table 3). Similarly, HS SPME-GC-MS results for WWTP 4 suggested a 50% reduction in the peak TVOSC concentration at the 4% Al dose (Figure 4d and Table 3), however the olfactometry results showed significant increases in the odour concentrations, particularly at the 2% Al dose (Figure 4h and Table 3).

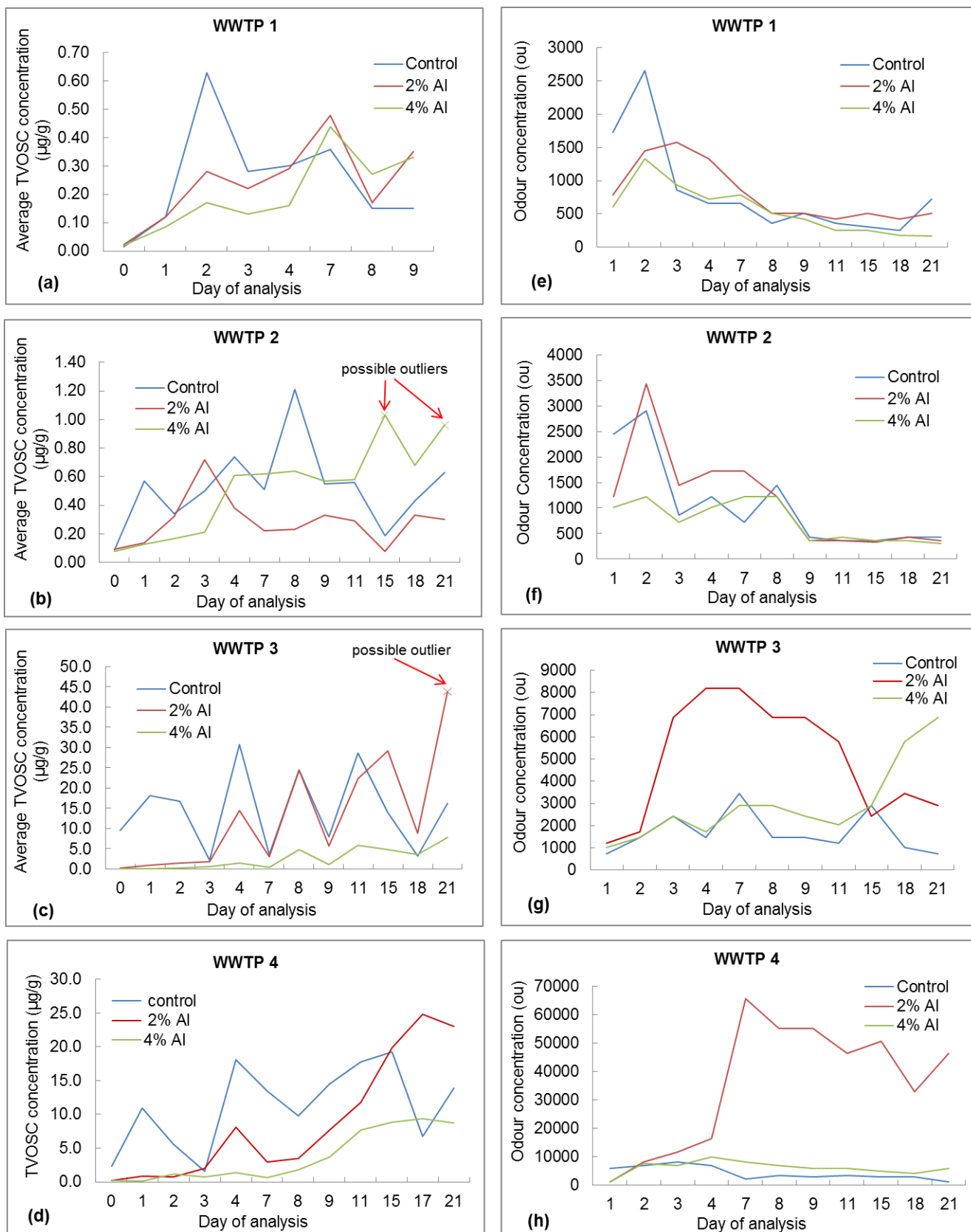


Figure 4. Comparison of TVOSC concentration profiles (a – d) obtained from HS SPME-GC-MS analyses; with odour profiles (e – h) determined by dynamic olfactometry for lab dewatered cakes from WWTPs 1, 2, 3 and 4. Each sample was treated with alum prior to dewatering.

Table 3. Peak odour concentrations[#], odour characteristics[#] and peak TVOSC concentrations^{*} for lab dewatered cakes from WWTPs 1, 2, 3 and 4, as well as % odour and % TVOSC reductions.

Sample	Peak Odour Concentration [#] (ou) [in 25L of nitrogen]	% Odour reduction or increase [§] relative to control	Day at which odour concentration peaked	Odour character at peak odour concentration	Peak TVOSC concentration [*] (µg/g)	% TVOSC reduction or increase [§] relative to control	Day at which TVOSC concentration peaked
WWTP 1 Control	2,660	-	2	Shellfish/rubbery/cabbage	0.6	-	2
WWTP 1 2% Al	1,580	40%	3	Shellfish/rubbery	0.5	24%	7
WWTP 1 4% Al	1,330	50%	2	Shellfish/light vinegar	0.4	30%	7
WWTP 2 Control	2,900	-	2	Shellfish/cabbage	1.2	-	8
WWTP 2 2% Al	3,440	-16%	2	Shellfish/cabbage	0.7	40%	3
WWTP 2 4% Al	1,220	58%	2	Shellfish/stale laundry/earthy	0.6	47%	8
WWTP 3 Control	3,440	-	7	Sewage/faecal/gassy	31	-	7
WWTP 3 2% Al	8,190	-58%	7	Sewage/faecal/gassy/shellfish	29	5%	15
WWTP 3 4% Al	6,890	-50%	21	Sewage/spring onions	5.9	81%	11
WWTP 4 Control	8,190	-	3	Sewage	19	-	15
WWTP 4 2% Al	65,600	-88%	7	Sewage/H ₂ S	25	-22%	17
WWTP 4 4% Al	9,740	-16%	4	Faecal/gut/foul	9.4	51%	17

[#]Odour concentrations were determined by The Odour Unit using dynamic olfactometry. The odour character was determined by The Odour Unit's odour panel. ^{*}Concentrations of total volatile organic sulphur compounds (TVOSC) were determined by CWQRC using HS SPME-GC-MS, and are based on the sum of the DMS, DMDS and DMTS concentrations. [§]Odour increase is denoted by a negative value.

Table 4. Summary of some of the odorous compounds associated with biosolids (adapted from Rosenfeld and Suffet, 2004; Chen *et al.*, 2006).

Compound	Odour character	Air odour threshold (ppmv)
<i>Sulphur Compounds</i>		
Hydrogen sulphide	Rotten eggs	0.0005
Carbon disulphide	Disagree, sweet	0.0077
Dimethyl sulphide	Rotten cabbage	0.001
Dimethyl disulphide	Rotten cabbage	0.000026
Dimethyl trisulphide	Rotten cabbage	0.0012
Methyl mercaptan	Rotten cabbage	0.00002
Allyl mercaptan	Garlic coffee	0.0001
Propyl mercaptan	Unpleasant	0.0001
Amyl mercaptan	Putrid	0.00002
<i>Volatile Fatty Acids</i>		
Acetic acid	Vinegar	1.019
Propionic acid	Rancid, pungent	0.028
Isobutyric and butyric	Rancid	0.0003
Isovaleric acid	Unpleasant	0.0006
Valeric acid	Unpleasant	0.0006
<i>Odorous Volatile Aromatic Compounds (OVASCs)</i>		
Indole	Faecal nauseating	0.13-1.5 ppb
Skatole	Faecal nauseating	0.065-0.15 ppb
p-cresol	Medicine	0.011-5.4 ppb

The observed differences and lack of correlations between the TVOSCs concentrations (HS SPME-GC-MS results) and the odour concentrations (olfactometry results) may have been due to the differences in sample handling and sample preparation prior to assessment of the odorous components. Dynamic olfactometry is dynamic as the name suggests, which means that the headspace is constantly renewed. In the SPME method the headspace is static and the extent of volatilisation of each compound depends on the partition of the analyte between liquid and headspace under static conditions, which may well be quite different from dynamic conditions. For the HS SPME-GC-MS analyses, a small sub-sample was removed from the bulk biosolids sample and analysed in an aqueous solution in a static manner (vs dynamic in olfactometry) (Figure 2). Analysis by this method is likely to result in maximum release of the odour compounds into the headspace; in fact the analytical method was initially designed in this way to ensure maximum recovery of analytes. However, in the dynamic olfactometry method the sample was treated in quite a different manner: in olfactometry analyses the cake remained undisturbed and the headspace gases were sampled in a dynamic manner prior to analysis (Figure 3) at ambient temperature. In addition, sub-sampling from a bulk sample, as was done for the HS SPME-GC-MS method, could have resulted in inconsistencies due to the heterogeneous nature of the biosolids material (it is unlikely that each subsample was representative of the bulk biosolids sample).

Other factors that could have contributed to the discrepancies between the HS SPME-GC-MS results and the olfactometry measurements may have been the presence of other compounds which were not quantitated by our HS SPME-GC-MS method. For example, carbon disulphide and hydrogen sulphide have very low odour threshold concentrations (Table 4) and could therefore have contributed to the overall odour concentrations determined by olfactometry, even if present in low concentrations. Other (non-sulphur) compounds, such as indole, skatole, *p*-cresol and some volatile

fatty acids, were not quantitatively analysed by the HS SPME-GC-MS method for sulphur compounds. However these compounds would have contributed significantly to the overall odour concentrations due to their low odour threshold concentrations (Table 4). This is particularly evident in cake samples from WWTPs 3 and 4. Cakes from these two WWTPs consistently showed significant peaks for indole and skatole in addition to the sulphur compounds DMS, DMDS and DMTS. These samples were also described as having a sewage/faecal/foul odour (Table 3). A qualitative GC scan of a cake sample from WWTP 4 treated with 2% Al showed the presence of significant peaks for indole, skatole and *p*-cresol as well as minor peaks for isovaleric and butyric acids in addition to the volatile sulphur compounds DMS, DMDS and DMTS. Indole, skatole and *p*-cresol were not detected in cakes from WWTPs 1 and 2 during the course of the monitoring period.

Another potentially significant limitation in linking analytical and olfactometry measurements is the effect of mixtures (Gostelow and Parsons, 2000). Odours released from biosolids are comprised of very complex mixtures of compounds and these can have both additive and antagonistic effects (Lehtinen and Veijanen, 2011). For example, studies on mixtures of two to twelve odorants suggested that odorants are additive, i.e. a mixture of odorants will have a stronger odour than any of the component odorants alone (Gostelow and Parsons, 2000; Patterson, *et al.*, 1993; Laska and Hudson, 1991).

4.0 Conclusions and future work

In this part of the study we have investigated whether alum addition to wastewater sludge from different treatment processes would be effective in reducing odour in the resulting dewatered cake. Based on the HS SPME-GC-MS and olfactometry results obtained from lab generated cakes from the 4 WWTPs used in this study the following conclusions were made:

- Alum addition was effective in reducing odour in biosolids from WWTPs 1 and 2, which use anaerobic digestion to process sludge. A 50% reduction in the overall odour concentration, relative to control, was observed for lab dewatered biosolids from WWTP 1 at the 4% Al dose, while a 58% reduction in the overall odour concentration was observed for lab dewatered biosolids from WWTP 2 at the 4% Al dose, relative to a control sample.
- Alum addition did not reduce odour in biosolids from WWTP 3 and 4, which use oxidation ditch processes. Although HS SPME-GC-MS results suggested an 81% reduction in the peak TVOSC concentration for lab dewatered cakes from WWTP 3 and a 50% reduction in the peak TVOSC concentration for lab dewatered cakes from WWTP 4 at the 4% Al dose, the olfactometry results showed significant increases in the overall odour concentrations for cakes from both WWTPs at both Al doses. This may have been because not all of the potential odour-causing compounds were captured in the chemical analyses.
- No simple linear correlations were observed between the TVOSC concentrations (chemical analyses by HS SPME-GC-MS) and the odour concentrations (olfactometry). This lack of correlation between the results may, in part, have been due to the different methods in which the samples were analysed as well as the presence of other odour compounds which were not quantitated by the HS SPME-GC-MS method but contributed to the overall odour concentrations determined by olfactometry. The full identification and quantification of **all** the odorants present in a sample may not always be possible in a single analytical method due to the different physico-chemical properties of the odorants present.
- Biosolids from WWTPs 3 and 4 (oxidation ditch processes) were significantly more odorous than biosolids from WWTPs 1 and 2 (mesophilic anaerobic digestion).

Although alum addition to liquid biosolids from WWTPs 1 and 2 was shown to be promising as an odour reduction option for anaerobically digested biosolids, alternative odour reduction measures need to be investigated for processed sludge from WWTPs 3 and 4 which use oxidation ditch processes.

Possible options for further investigation include: addition of potassium permanganate and/or calcium nitrate to processed sludge prior to dewatering. Permanganate (MnO_4^- , Mn(VII)) has been widely used by water utilities for treatment of taste and odour complaints (Hu, *et al.*, 2010). Mn(VII) is a strong oxidant that reacts selectively with organic compounds that contain electron-rich moieties such as phenolic, olefin, amino, thiol, ether, aldehyde and ketone groups (Hu, *et al.*, 2010). Potassium permanganate has been added to liquid biosolids before dewatering and has been reported to improve dewaterability (Shammas and Wang, 2007; US EPA, 2000). Chemical dosing with nitrate salts such as potassium or calcium nitrate has been used to minimise the sulphide-associated odours in sewer systems (de Sena, *et al.*, 2013; He, *et al.*, 2009). The presence of nitrate promotes the growth of nitrate-reducing bacteria that, in large numbers, will compete for available carbon sources, thereby reducing or stopping the growth of sulphate-reducing bacteria, which in turn should prevent the production of reduced sulphur compounds (de Sena, *et al.*, 2013).

The effect of oxidant addition on sludge odours and the relationship between the oxidation-reduction potential (ORP) and sludge odours was also studied by Arispe (2005). ORP is a key parameter for the release of certain odorous compounds from wastewater and biosolids (Arispe, 2005). ORP measurements give an indication of the anaerobic nature of the material. The more negative the ORP value, the more reducing the conditions in the system, increasing the production of reduced sulphur compounds (Arispe, 2005). Thus it may be possible to control the on-site odour release of sludge handling processes by increasing the ORP with the addition of an oxidant. Arispe (2005) investigated the effect of the addition of potassium ferrate (K_2FeO_4), sodium hypochlorite (NaOCl), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and potassium permanganate (K_2MnO_4) on sludge odours. Of the four oxidants tested, calcium nitrate was the best oxidant at reducing both methyl mercaptan and dimethyl sulphide. For reduction of dimethyl sulphide alone potassium permanganate gave the best results (Arispe 2005).

In the next part of this study, addition of potassium permanganate and calcium nitrate to processed sludge from WWTP 4 will be explored. As a comparison addition of potassium permanganate and calcium nitrate to digested sludge from WWTP 1 will also be investigated. Further improvements to the HS SPME-GC-MS analytical method will be investigated to enable identification and quantification of other odorants (e.g. indole and skatole) in a single method. In addition, options will be investigated for ensuring that both the olfactometry and chemical analyses use similar methods for sample preparation and sample handling.

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