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# Emissions of volatile sulfur compounds (VSCs) throughout wastewater biosolids processing

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#### HIGHLIGHTS

#### G R A P H I C A L A B S T R A C T

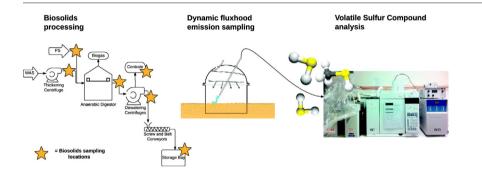
- H<sub>2</sub>S and methyl mercaptan were key odorants detected above olfactory thresholds
- Primary sludge, dewatered and stored biosolids emitted highest VSC concentrations
- Intra and inter site variability in VSC emissions were observed
- H<sub>2</sub>S emissions from the primary sludge were related to Fe dosing and organic matter
- Volatile organic sulfur compounds related to Fe/Al ratio and digester performance

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#### ABSTRACT

Volatile sulfur compounds (VSCs) are important contributors to nuisance odours from the processing of wastewater sludge and biosolids. However, emission characteristics are difficult to predict as they vary between sites and are likely to be affected by biosolids processing configuration and operation. VSC emissions from biosolids throughout 6 wastewater treatment plants (WWTPs) in Sydney, Australia were examined in this study. H<sub>2</sub>S was the VSC found at the highest concentrations throughout the WWTPs, with concentrations ranging from 7 to  $39,000 \,\mu\text{g/m}^3$ . Based on odour activity values (OAVs), H<sub>2</sub>S was typically also the most dominant odorant. However, methyl mercaptan (MeSH) was also found to be sensorially important in the biosolids storage areas given its low odour detection threshold (ODT). High concentrations of VOSCs such as MeSH in the storage areas were shown to potentially interfere with H<sub>2</sub>S measurements using the Jerome 631-X H<sub>2</sub>S sensor and these interferences should be investigated in more detail. The VSC composition of emissions varied throughout biosolids processing as well as between the different WWTPs. The primary sludge and biosolids after dewatering and during storage, were key stages producing nuisance odours as judged by the determination of OAVs. Cluster analysis was used to group sampling locations according to VSC emissions. These groups were typically the dewatered and stored biosolids, primary and thickened primary sludge, and waste activated sludge (WAS), thickened WAS, digested sludge and centrate. Effects of biosolids composition and process operation on VSC emissions were evaluated using best subset regression. Emissions from the primary sludge were dominated by H<sub>2</sub>S and appeared to be affected by the presence of organic matter, pH and Fe content. While volatile organic sulfur compounds (VOSCs) emitted from the produced biosolids were shown to be correlated with upstream factors such as Fe and Al salt dosing, anaerobic digestion and dewatering parameters.

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### 1. Introduction

Odour emissions from wastewater treatment plants (WWTPs) can cause nuisance impacts, leading to psychosomatic health effects and community opposition (Hayes et al., 2014). These odour emissions are predominantly composed of volatile sulfur compounds (VSCs) (Vincent, 2001). However, non sulfur containing odorants such as ammonia, amines, organic acids, aldehydes and ketones have also been identified throughout biosolids processing (Gostelow et al., 2001). The sensorial importance of odorants in mixtures can be compared using odour activity values (OAVs). OAVs were calculated by dividing an odorants concentration by its odour detection threshold (ODT). Therefore, an OAV > 1 is likely to be just perceptible at an emissions source. Higher OAVs are able to be detected further away from the emission source. Odour nuisance impacts on the community can occur with prolonged exposure to foul odours (Nicell, 2009). Therefore high OAV values increase the potential for nuisance impacts, especially for VSC due to their unappealing odour characters (Devai and DeLaune, 1999).

Hydrogen sulfide ( $H_2S$ ) has traditionally been used as a surrogate for odour emissions (Gostelow et al., 2001; Muezzinoglu, 2003). However, volatile organic sulfur compounds (VOSCs) such as methyl mercaptan (MeSH) and dimethyl sulfide (DMS) can also contribute to malodour due to their low odour detection thresholds (ODTs) (Devai and DeLaune, 1999). Other VOSCs that have been detected throughout WWTPs and sewers include the mercaptans, ethyl mercaptan (EtSH), 1-butyl mercaptan (1-BtSH) and propyl mercaptan (PrSH); and the sulfides, carbonyl sulfide (COS), carbon disulfide (CS<sub>2</sub>), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS), ethyl methyl sulfide (EMS) and diethyl disulfide (DEDS) (Muezzinoglu, 2003; Ras et al., 2008; Sivret et al., 2016). To date, the variability in the VSC speciation throughout WWTPs, as well as between different sites has not been reported.

H<sub>2</sub>S can be generated from reduction of sulfate in the wastewater as well as the degradation of organic matter. While the degradation of the sulfur containing amino acids, methionine and cysteine, can produce MeSH, DMS and H<sub>2</sub>S (Lomans et al., 2002). VSCs are also known to be transformed into other compounds, via the oxidation of mercaptans to sulfides or degradation of mercaptans to H<sub>2</sub>S (Higgins et al., 2006).

The generation and emission of VSCs throughout biosolids processing are dependent on both microbial activity and the chemical and physical properties of the sludge. Such properties are influenced by the wastewater composition and WWTP performance. Therefore, the compositions of odour emissions are expected to vary throughout WWTPs. The inlet works, primary sedimentation tanks, thickening, biosolids dewatering and biosolids storage locations have all been identified as locations of intense odour emissions (Dincer and Muezzinoglu, 2008; Frechen, 1988; Lehtinen and Veijanen, 2011; Ras et al., 2008; Zarra et al., 2008). To minimise these impacts, odour emissions from the inlet works and primary sedimentation tanks may be controlled by chemical dosing, frequent desludging and the installation of odour abatement units (Gostelow et al., 2001). However, nuisance emissions from biosolids produced at the WWTPs can still affect the community during onsite processing and storage, transportation and land applications. Therefore, in order to prevent nuisance odour emissions sources of odours throughout biosolids processing should be identified. Furthermore, identification of key odorants and understanding why they are present will aid odour mitigation of both onsite and offsite emissions.

Previous research into the impact of biosolids processing on VSC emissions from biosolids has identified anaerobic digestion, dewatering and chemical dosing as key factors affecting odour emissions from biosolids (Adams, 2004). As VOSCs are produced from the degradation of proteins, the odour potential of biosolids can be reduced by decreasing the protein content with longer anaerobic digestion durations (Muller et al., 2007). In addition, the use of pre-treatments, thermophilic digestion or multistage digestion has been either shown or suggested to reduce odours from biosolids (Kim et al., 2011; Wilson et al., 2006; Wilson et al., 2009).

It has also been shown that greater shear during dewatering releases bound proteins, making them bioavailable. Their inevitable degradation as the dewatered biosolids are stored has been shown to produce VSCs (Muller et al., 2004; Murthy et al., 2003b). Shearing during dewatering can be affected by factors such as polymer type, dosage, conditioners, dewatering method and set-up (Higgins et al., 2005; Higgins et al., 2002; Johnston et al., 2009).

Complexes of metal salts with proteins and other organic matter may be formed from the addition of Fe and Al based salts (Fe and Al). Such complexes limit the degradation of bound proteins in anaerobic digesters (Novak, 2010). However, shearing has been shown to release the Fe complexes more easily than the Al complexes. Therefore, higher ratios of Fe to Al are suggested to result in more bioavailable organic matter in the biosolids, in turn resulting in greater odours.

The storage duration of the biosolids after dewatering is another factor that has been shown to affect odour emissions. Microbial activity changes as the dewatered biosolids are stored affecting the generation and emission of VSCs (Higgins et al., 2006; Kacker et al., 2011). Microbial activity in dewatered biosolids is influenced by the dewatering process as well as anaerobic digestion (Adams et al., 2007). As variations in wastewater influent composition, anaerobic digester and dewatering can affect the generation of VSCs, it is difficult to predict VSC emissions throughout biosolids processing at different WWTPs.

In this study, VSCs emitted throughout biosolids processing at 6 WWTPs were measured. VOCs throughout biosolids processing at these 6 WWTPs were reported in Fisher et al. (2017b). The importance of VSCs compared to VOCs was compared based on the odorants OAVs. In addition, operational parameters and sludge properties were monitored at each site to explore the variability in emissions throughout and between the different WWTPs. The identification of key odorants emitted from different locations throughout biosolids processing will aid in pinpointing the origin of nuisance odours and support plant operators in mitigating potential odour impacts on surrounding communities.

### 2. Methodology

### 2.1. Sample collection

Large samples (~10 L) of sludge or biosolids were transported directly to UNSW Sydney for emission assessment. The time between sampling from the WWTPs and emission assessment was at most 6 h. Sludge and biosolids were collected from various locations within the 6 WWTPs. Sampling locations include the primary sludge (PS), thickened primary sludge (TPS), WAS, thickened WAS (TWAS), mixed TWAS and TWAS (MTS), digested sludge (DS), centrate, dewatered biosolids (DWS) and stored biosolids (SS). The specific sampling locations used at each WWTP are listed in Appendix A and were also reported in Fisher et al. (2017b). Samples were taken on at least four days within a three week period. In total 26, 67, 66, 30, 33 and 36 sludge/biosolids samples were taken from Sites 1–6, respectively.

#### 2.2. Emission generation and measurement

Emissions from the sludge or biosolids were captured using a US EPA endorsed dynamic fluxhood according to AS/NZS 4323.4:2009. The samples were spread out in a plastic tray, then the fluxhood was pushed into the sludge or biosolids to a depth of about 10 cm. A 5 L/min sweep of high purity N<sub>2</sub> gas (BOC, Australia) was applied to the fluxhood, with an initial purge time of 30 min prior to emission sample collection. Emission sampling was conducted in ambient conditions (20–25 °C). Emissions were collected in duplicate freshly prepared nalophan bags using the lung method at flowrate of 2 L/min. All gas samples were analysed within 6 h of collection in order to reduce potential compound loss via diffusion through the bags or transformation (Le et al., 2015).

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