Reduction of Odour in Biosolids

Literature Review

CWQRC Report No: CWQRC-2011-003

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Prepared for
Water Corporation of Western Australia

Executive Summary

Introduction

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

The aim of this literature review was to survey the available literature on various aspects of biosolids odours such as compounds associated with odours, process factors that affect odours, odour measurement and how treatment processes impact odour production, especially during storage of biosolids.

Odour Formation in Biosolids

Based on the literature surveyed, many different compounds have been associated with odours from biosolids facilities. Some of the most prevalent include volatile organic sulphur compounds (VOSCs) such as methanethiol (MT, also called methyl mercaptan), dimethyl sulphide (DMS) and dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS), as well as inorganic sulphur compounds such as hydrogen sulphide (H_2S), nitrogenous compounds such as trimethylamine (TMA) and ammonia and potentially volatile fatty acids (VFA) (Adams, *et al.*, 2003a; Higgins, *et al.*, 2003, 2006, 2008a). Other organic compounds such as terpenes, acids, aldehydes, alcohols and ketones have also been reported (Adams, *et al.*, 2003a; Forbes, *et al.*, 2004; Rosenfeld and Suffet 2004) and several odorous volatile aromatic compounds (OVACs) have been identified in headspace samples from stored biosolids (Chen, *et al.*, 2004, 2006). The generation of VOSCs, reduced inorganic sulphur compounds and OVACs has been associated with proteins, in particular the biodegradation of proteins to amino acids which then degrade further to give a product that is an odorant itself or undergoes further biochemical reactions to form odour causing compounds (Higgins, *et al.*, 2003, 2004, 2006, 2008b; Chen, *et al.*, 2004, 2006). For example, the sulphur containing amino acid methionine, is degraded by enzymes to methanethiol which can then be methylated to form dimethyl sulphide or oxidised to dimethyl disulphide (Section 3.1).

Several factors affect the odour production in biosolids. These include: (1) the role of protein, amino acids and enzyme activity; (2) the relationship between odours and concentrations of odorants (3) impact of processes upstream of anaerobic digestion; (4) anaerobic digestion and various enhancements to the anaerobic digestion process; (5) impact of biosolids dewatering and conveyance process; (6) polymer addition; (7) chemical addition and (8) storage of biosolids cake (Adams, *et al.*, 2008). It has been reported that a strong correlation exists between the odours produced by biosolids from anaerobic digestion and the concentration of volatile sulphur compounds in the headspace of biosolids samples (Adams, *et al.*, 2003b, 2008; Higgins, *et al.*, 2008a). Similarly, protein concentration and, in particular, the concentration of methionine have been found to be well correlated with the production of odorous VSCs (Adams, *et al.*, 2003b; Higgins, *et al.*, 2003, 2004, 2006, 2008b). A more detailed discussion of the factors affecting odour generation in biosolids is presented in Section 3.2.

Odour Reduction/Control Strategies

The most cost effective approach to odour control may be the examination of the operational and maintenance practices at the biosolids processing facility. The level of control required for biosolids processing plants should be based on site-specific characteristics such as: the proximity of a processing site to residential or commercial development; local wind patterns, air mixing and dispersion factors; temperature and humidity; seasonal variations; and the amount and of type of biosolids being processed (US EPA, 2000c).

Since proteins have been identified as the major precursors to odorous compounds in biosolids, odour reduction strategies could be aimed at reducing the amounts of bioavailable protein in the cake. Some of the reported examples for achieving this include more complete degradation of protein during digestion which should reduce the available substrate for odour production. Greater SRTs and pre-digestion treatments, which aim to improve digestibility of solids, may aid in removing protein (Higgins, *et al.*, 2006). Advanced digestion processes such as multi-phased digestion, egg-shaped digesters, thermophilic digestion or a series operation of digesters could also contribute to better degradation of proteins (Adams, *et al.*, 2008). Shear created by centrifugal dewatering may release protein, providing substrate for odorant production (Higgins, *et al*., 2003, 2006, 2008a). Therefore, dewatering processes should be operated and designed to minimize shear thereby reducing the amount of bioavailable protein (Higgins, *et al.*, 2008a; Adam, *et al.*, 2008).

Research has shown that methanogens play a key role in removing VOSCs and reducing odours, and methane production was related to reduced VOSC generation (Chen, *et al.*, 2005). It has been reported that the abundance of the overall methanogenic population is more important than the presence of a certain bacterium (Chen, *et al.*, 2005) and factors affecting the growth of methanogens such as shear during dewatering and storage temperature showed a strong impact on net odour production. Thus, one possible odour control strategy could be the protection and improvement of the methanogenic population during biosolids storage (Chen, *et al.*, 2005).

The use of statistical models to predict odour formation can help WWTP managers to better forecast odours and minimise the "odour footprint". For example, a multiobjective model that incorporates the reduction of biosolids odours as well as processing and distribution costs can help managers at WWTPs to proactively handle odour complaints at reuse sites close to populations while being cost effective in their operations (Gabriel, *et al*., 2007). A more detailed discussion of odour control strategies is presented in Section 4.

Odour Measurement
Odour measurements can be divided into two classes: (1) Analytical measurements, which characterise odours on the basis of their chemical composition, however they provide little information about the perceived effect of odours; and (2) Sensory measurements, which use the human nose to characterise odours in terms of their perceived effect (Gostelow and Parsons, 2000).

The reported analytical techniques range from onsite measurements with electrochemical equipment and colorimetric sorption tubes to offsite analysis using gas chromatographs and mass spectrometers (Adams, *et al.*, 2003a). A variety of sampling methods are available for sampling volatile compounds. The static headspace sampling method has been reported to be a practical and comparative method for chemical and olfactometric analyses (Adams, *et al.*, 2003b; Glindemann, *et al.*, 2006). This method has been used in several biosolids odour projects (Murthy, *et al.*, 2002; Adams, *et al.*, 2003b; Higgins, *et al.*, 2004, 2006; Glindemann, *et al.*, 2006) and offers several advantages over other methods. Solid phase microextraction (SPME) has emerged as a relatively simple, inexpensive, solvent-free method to extract organic compounds from various sample matrixes. Coupled with gas chromatography-mass spectrometry, this method has been successfully applied to several biosolids projects for the analysis of volatile sulphur compounds, nitrogen containing compounds and volatile fatty acids (Kim*, et al.*, 2002a, 2002b, 2003, 2005; Visan and Parker, 2004; Turkmen, *et al*., 2004).

Sensory measurement techniques can be divided into two classes: (1) Subjective measurements in which the nose is used without any other equipment and (2) Objective measurements which use the nose together with some form of dilution instrument (Gostelow, *et al.*, 2001). Subjective measurements have poor repeatability and difficulties in comparing results but can be useful for preliminary identification and ranking of odour sources and also for awareness raising (Gostelow, *et al.*, 2001). Objective measurements include threshold olfactometry and suprathreshold olfactometry.

Threshold olfactometry expresses odour strength in terms of number of dilutions of odour-free air required to reduce sample to threshold concentration and is currently the method of choice for sensory odour measurement. Suprathreshold olfactometry measures odour intensity by comparing with reference odorant at known concentration and is claimed to be more repeatable than threshold olfactometry (Gostelow, *et al.*, 2001). Olfactometry methods have frequently been used to measure odorous emissions from biosolids and biosolids processing plants (Williams, 1995; Lambert, *et al.*, 2000; Adams, *et al.*, 2003a). The most common method for measuring odour emissions involves measuring the number dilutions required to eliminate a perceived odour. A standard method has been developed for sampling and analysing odours using a panel of trained persons who determine the number of dilutions needed to eliminate the odour. This panel can also determine the intensity and character of the odour and the rate at which the intensity decreases with dilution (Adams, *et al.*, 2003a).

Although olfactometry methods are useful and reflect actual human response to odours, they do not provide information on the chemical components of a gas mixture and the data provided is often insufficient to determine the cause of odour emissions (Kim, *et al.*, 2002a; Adams, *et al.*, 2003a). Also there are many external factors that influence the perception of an odour. The main factor being, the variability in the sense of smell between different people. Therefore, care should be taken in equipment design, panel selection, test procedure and interpretation of panel results. Differences in these parameters can lead to poor repeatability (Gostelow, *et al.*, 2001). A more detailed analysis of odour measurement techniques is given in Section 5.

Recommendations for Odour Reduction
A summary chart of potential odour reduction measures is presented in Figure 15 (Section 4.3). The potential measures for reducing odours in biosolids can be divided into two categories: (1) design changes that could be implemented during the design of new WWTPs, development of new unit processes for existing WWTPs or engineering modifications to existing processes and (2) operational changes that could be made at an existing WWTP, either by adjusting operational parameters of processes or equipment, or *via* chemical addition (Adams, *et al.*, 2008).

Due to the inherent differences in biosolids characteristics, treatment processes and operating conditions between different wastewater treatment plants, 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 will probably be required to optimise odour quality of biosolids cake (Adams, *et al.*, 2008). The overall amount of odour reduction required should be determined prior to implementing any odour reduction schemes (Adams, *et al.*, 2008). Odour measurements before and after process modifications should be performed to give a more accurate evaluation of the scheme's true odour reduction potential. The chosen strategies for odour reduction should be focussed on approaches that have the highest chance of success in each case (Adams, *et al.*, 2008). A more detailed summary of findings and recommendations for odour reduction is presented in the Appendix.

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Acronyms and Abbreviations

AETAC	Acryloyloxyethyltrimethylammonium Chloride
AM	Acrylamide
AS	Activated Sludge
ASTM	American Society for Testing and Materials
ATAD-Air	Auto Thermal Aerobic Digestion using air
ATAD-Oxygen	Auto Thermal Aerobic Digestion using oxygen
AVSR	Additional Volatile Solids Reduction
AWWA	American Water Works Association
BOC	Bio-Organic Catalyst
BOD	Biological Oxygen Demand
CEBAs	Chemical, Enzymatic & Biological Agents
CFR	Code of Federal Regulations
CLND	Chemiluminescence Nitrogen Detector
COS	Carbonyl Sulphide
CS_2	Carbon Disulphide
d	day
DADMAC	Diallyldimethylammonium Chloride
DAF	Dissolved Air Flotation
DMA	Dimethylamine
DMDS	Dimethyl Disulphide
DMS	Dimethyl Sulphide
DMTS	Dimethyl Trisulphide
DT	Detection Threshold
Epi	Epichlorohydrin
Eqn.	Equation
GC-MS	Gas Chromatography-Mass Spectrometry
GC-FID	Gas Chromatography with Flame Ionisation Detector
GC-FPD	Gas Chromatography with Flame Photometric Detector
GT	Gravity Thickeners
HPLC	High Performance Liquid Chromatography
H_2S	Hydrogen Sulphide
Hg	Mercury
in.	Inch
JWPCP	Joint Water Pollution Control Plant
MAD	Mesophilic Anaerobic Digestion
MAPTAC	Methacrylamidopropyl Trimethylammonium Chloride
MEK	Methyl Ethyl Ketone
MMA	Methyl Methacrylate
MT	Methanethiol (also known as methyl mercaptan)
ORP	Oxidation-Reduction Potential
OVACs	Odorous Volatile Aromatic Compounds
PAM	Polyacrylamide
ppb	parts per billion
ppm	parts per million
ppmv	parts per million per volume
PWD	Philadelphia Water Department
RBA	Residual Biological Activity
RVS	Residual Volatile Solids
SCD	Sulphur Chemiluminescence Detector
SIM	Selective Ion Monitoring

SPME	Solid Phase Microextraction
SRT	Solids Retention Time
STP	Sewage Treatment Plant
STW	Sewage Treatment Works
TAD	Thermophilic Anaerobic Digestion
TMA	Trimethylamine
TPAD	Temperature-Phased Anaerobic Digestion
TRS	Total Reduced Sulphur
TVOSCs	Total Volatile Organic Sulphur Compounds
UNEP	United Nations Environment Programme
US EPA	United States Environmental Protection Agency
VFA	Volatile Fatty Acids
VOSCs	Volatile Organic Sulphur Compounds
VS	Volatile Solids
VSCs	Volatile Sulphur Compounds
VSD-ATAD-Air	ATAD-Air using a vertical shaft reactor for aeration/digestion
VSD-ATAD-Oxygen	ATAD-Oxygen using a vertical shaft reactor for oxidation/digestion
VSR	Volatile Solids Reduction
WAS	Waste Activated Sludge
WCS	Wastewater Collection System
WEF	Water Environment Federation
WEFTEC	Water Environment Federation Technical Exhibition and Conference
WERF	Water Environment Research Foundation
WWTP	Wastewater Treatment Plant

1.0   Introduction

Biosolids are the stabilised, nutrient rich, organic solid residues generated from wastewater treatment processing, which in most cases can be used beneficially. Biosolids are carefully treated and monitored and they must be used in accordance with regulatory requirements. Only those biosolids that meet strict quality standards for pollutants and pathogens can be land-applied for beneficial purposes.

Beneficial reuse of biosolids using land application is a viable and important practice to the wastewater industry and the agricultural community. Land application offers a low-cost disposal option for biosolids and a low-cost nutrient source and soil amendment for farmers and other land application sites, such as mine reclamation projects. According to a recent survey, approximately 60% of biosolids in the USA is land applied (Higgins, *et al.*, 2006). Biosolids are also widely used in Europe and several other countries.

Biosolids produced from Western Australian sewage treatment plants (STPs) are currently being used as organic humus and as fertiliser substitute on some agricultural properties; incorporated into commercial composts at licensed facilities and are also being trialled for mine site rehabilitation and forestry application (WA Guidelines for Direct Land Application of Biosolids and Biosolids Products, 2002).

One of the main issues that may restrict land application programs is nuisance odours associated with biosolids. Surveys of the wastewater industry have listed biosolids odour as a top concern (Higgins, *et al.*, 2006, 2008a). As such, considerable research has been carried out to understand the causes of odour formation in biosolids. For example, the Water Environment Research Foundation (WERF) has funded a multi-phase study to better understand odours in biosolids as well as to develop management practices to minimize these odours (Adams, *et al.*, 2003a; Adams, *et al.*, 2003b, 2008). Sydney Water Corporation (Sydney Water) has conducted a study to understand the relationship between various stability indicators and biosolids odour (Miller, *et al.*, 2006; Davis, *et al.*, 2008). South East Water in Victoria has conducted studies on odour emission rates from dewatered sludges (Carsen, *et al*., 2008). Various other researchers have carried out research on compounds associated with odours, process factors that affect odours, odour measurement and how treatment processes impact odour production, especially during storage of biosolids.

This literature review will survey the available literature focusing mainly on the causes of odour production in biosolids, odour reduction/control strategies and odour measurement techniques. Due to the plethora of literature available, this survey has been mainly limited to literature published in the last 15 years and reviews literature that was able to be obtained either through Curtin University library's on-line literature searching capabilities or from Water Corporation researchers.

2.0   Processing of Biosolids from Municipal Sludge

2.1   Wastewater Treatment

Figure 1 shows an example of a typical wastewater treatment process (UNEP, 2002). Coarse solids and grit are removed during preliminary wastewater treatment using screens and other filtering equipment. This is followed by primary wastewater treatment which usually involves gravity sedimentation of the screened wastewater to remove the settled solids. Approximately half of the solids suspended in the wastewater are removed during primary treatment. Secondary wastewater treatment uses a biological process to remove biodegradable material. In this process microorganisms in the wastewater consume the dissolved and suspended organic matter producing carbon dioxide and other by-products. The organic matter also provides nutrients needed to sustain the microorganisms. As the microorganisms feed, their density increases and they settle at the bottom of the processing tanks, separating from the clarified water as a concentrated suspension called secondary sludge, biological sludge, waste activated sludge (WAS) or trickling filter humus (UNEP, 2002).
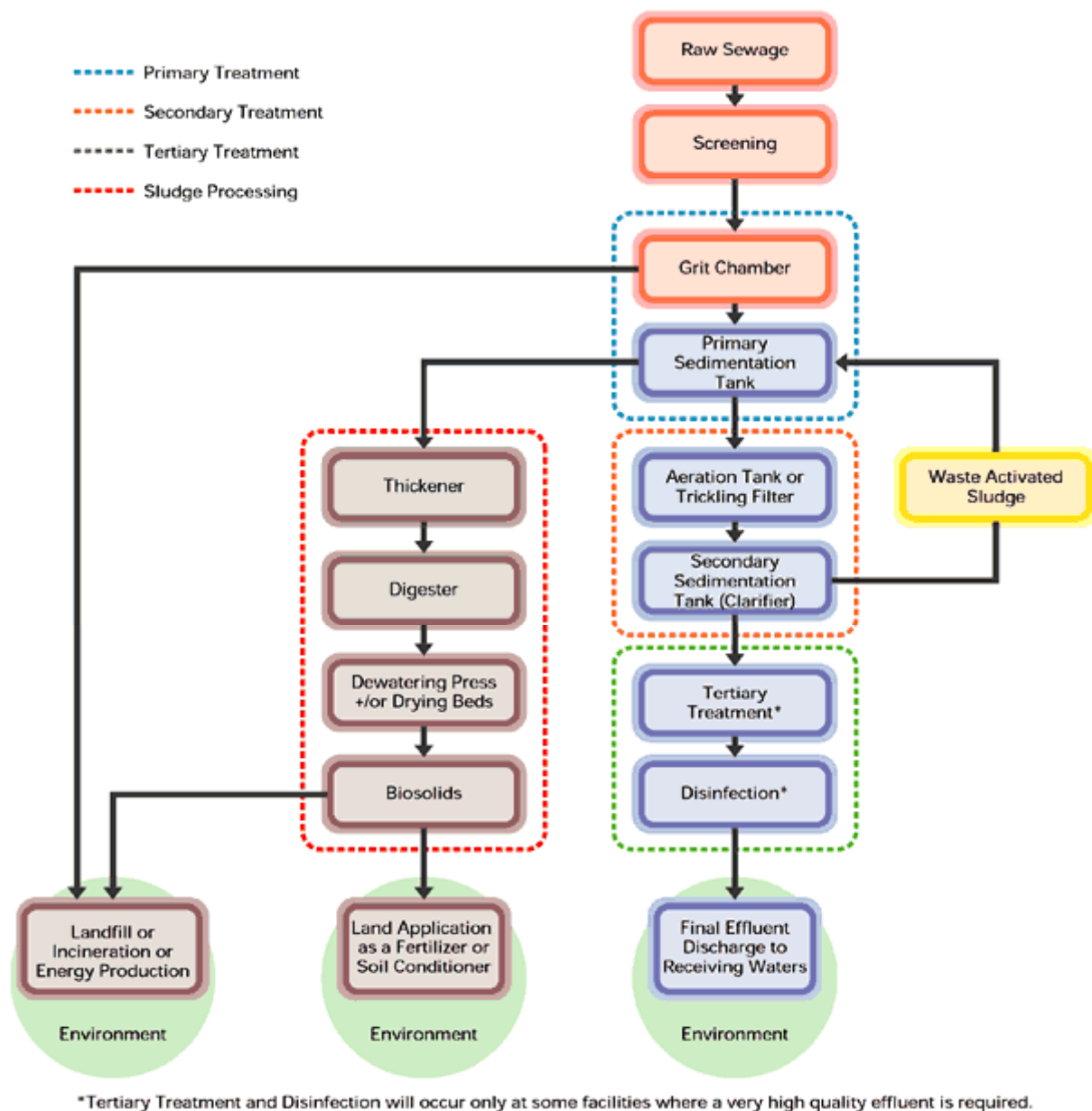
Figure 1: Typical Wastewater Treatment Process (adapted from UNEP, 2002)
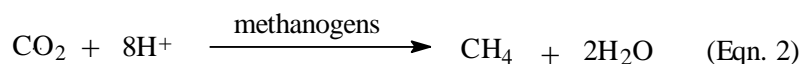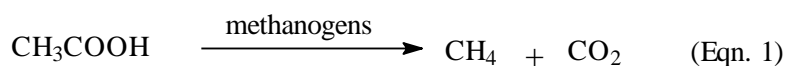
2.2   Stabilisation

The combined primary and secondary sludge then undergoes a stabilization process which accelerates the biodegradation of organic compounds, reduces the microbial population including pathogens and renders the material microbiologically safe for land application (UNEP, 2002). Some of the most common stabilization methods include:

- Biological stabilization – uses aerobic or anaerobic digestion to reduce the organic content of solids through controlled biodegradation (the aerobic and anaerobic processes will be discussed in more detail below) (UNEP, 2002).

- Chemical stabilization – this process does not reduce the quantity of biodegradable organic matter of solids, instead it creates conditions that inhibit microorganisms, thereby slowing down the degradation of organic materials and reducing odours. The most common method of chemical stabilization is to increase the pH level of the solids by adding lime or other alkaline materials (UNEP, 2002). The most commonly used alkaline materials used are slaked lime ($Ca(OH)_2$) and quicklime (CaO) (Andreasen, 2001).

- Thermal drying and composting can also be used to stabilize biosolids (UNEP, 2002).

- Pasteurization – involves an increase in temperature for an appropriate period of time to either inactivate microorganisms or decrease their numbers to a specific level (Spinosa and Vesilind, 2001). Full pasteurization of biosolids is not necessary when the primary use is for agricultural application (UNEP, 2002).

2.2.1 Anaerobic Digestion

Anaerobic digestion of wastewater sludges is a controlled process in which an orderly degradation of the organic material occurs by a variety of bacteria in the absence of free oxygen, resulting in the production of gases, mainly methane, carbon dioxide with trace amounts of hydrogen, hydrogen sulphide and stable innocuous biosolids (Dohányos and Zábranská, 2001). The process is thought to be at least a two-stage biological reaction, involving at least two different groups of microorganisms, acid-forming bacteria (saprophytic) and methane forming bacteria (methanogens) (Taricska, *et al.*, 2007). The first step (acid phase) of the process is thought to involve the conversion of complex organic compounds into simpler soluble compounds, e.g. carbohydrates into sugars, proteins to amino acids and lipids into fatty acids (Dohányos and Zábranská, 2001; Taricska, *et al.*, 2007). These soluble organic compounds are then converted to a relatively small group of end products, including, formate, acetate, propionate, butyrate, lactate, succinate, ethanol, carbon dioxide and hydrogen gas by acid-forming bacteria (Dohányos and Zábranská, 2001; Taricska, *et al.*, 2007). Methanogens then convert these intermediate products into methane and carbon dioxide. The methanogenic bacteria produce methane *via* two major pathways (Dohányos and Zábranská, 2001; Taricska, *et al.*, 2007):

$$CH_3COOH \xrightarrow{\text{methanogens}} CH_4 + CO_2 \qquad \text{(Eqn. 1)}$$

$$CO_2 + 8H^+ \xrightarrow{\text{methanogens}} CH_4 + 2H_2O \qquad \text{(Eqn. 2)}$$

About 70% of the methane produced during the digestion process is formed by degradation of the acetate (Eqn.1) and the remainder is obtained from the reaction between carbon dioxide and hydrogen (Eqn. 2) (Dohányos and Zábranská, 2001). The second process is critical to the entire digestion process as it is responsible for removing hydrogen and maintaining the low hydrogen pressure needed for acetate production (Dohányos and Zábranská, 2001). The methanogenic bacteria are sensitive and slow-growing, thus it is important to maintain optimum environmental conditions such as temperature and pH (Dohányos and Zábranská, 2001).

Two general temperature ranges have been investigated and utilized for anaerobic sludge digestion in current wastewater treatment practices (Taricska, *et al.*, 2007):
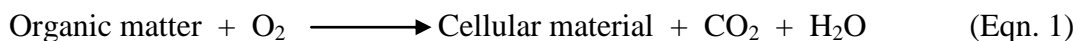
- Mesophilic anaerobic digestion (MAD) at temperature ranges from 30 to 37.7°C is most commonly employed with the majority of facilities operating at approximately 35°C (Taricska, *et al.*, 2007).

- Thermophilic anaerobic digestion (TAD) at temperature ranges from 49 to 57°C has been used on a limited basis, with the optimum thermophilic temperature being 55°C (Dohányos and Zábranská, 2001; Taricska, *et al.*, 2007). TAD offers several advantages over traditional MAD, such as increased rates of methane production, decreased fluid viscosity, decreased biomass formation, increased conversion of organic matter from waste to biogas and increased pathogen inactivation (Dohányos and Zábranská, 2001).

2.2.2 Aerobic Digestion

There are several primary variations of the aerobic digestion process (Shammas and Wang, 2007a):

- Conventional aerobic digestion using air or oxygen.
- Auto thermal aerobic digestion using air (ATAD-Air) or oxygen (ATAD-Oxygen) – this process operates in the thermophilic temperature range (>45°C) using either air or pure oxygen to aerate/oxidise the sludge. The process is autothermal as the heat required for the increase in temperature in supplied from the exothermic breakdown of organic and cellular material occurring during aerobic digestion. The increase in temperature reduces the required retention time for a given amount of solid reduction (Shammas and Wang, 2007a).

- ATAD-Air and ATAD-Oxygen processes using a vertical shaft reactor for oxidation/digestion (VSD-ATAD-Air and VSD-ATAD-Oxygen) – newer generation of the ATAD-Air and ATAD-Oxygen processes. The vertical shaft reactor is typically 350ft in depth and 2.5-10ft in diameter, offers very high oxygen transfer efficiency and very small foot print for construction, shorter retention times (3-6 d for obtaining 35-45% volatile solids reduction) and reduction in power costs in comparison to conventional ATAD-Air or ATAD-Oxygen processes (Shammas and Wang, 2007a).

- Cryophilic aerobic digestion – involves operation of aerobic digestion systems in lower temperature ranges (<20°C). Particularly relevant in some treatment facilities in countries with colder climate. Longer solid retention times are required at lower temperatures. It has been reported that at lower temperatures (5-20°C) a processing time of 250-300 d is required to obtain reasonable volatile solids destruction (Shammas and Wang, 2007a).

The theory and principles of all of the above aerobic digestion processes are similar. Each of the processes is a "suspended-growth biological treatment" process for the stabilization of biosolids produced at wastewater treatment plants. (Shammas and Wang, 2007a). Aerobic digestion involves the direct oxidation of biodegradable matter and the oxidation of microbial cellular material by organisms. These two steps are represented in the equations below (Shammas and Wang, 2007a):

$$\text{Organic matter} + O_2 \longrightarrow \text{Cellular material} + CO_2 + H_2O \qquad \text{(Eqn. 1)}$$

$$\text{Cellular material} + O_2 \longrightarrow \text{Digested sludge} + CO_2 + H_2O \qquad \text{(Eqn. 2)}$$

The process described by Eqn. 2 is referred to as endogenous respiration, where in the absence of suitable substrate food, microorganisms digest their own protoplasm to obtain energy. The cell tissue is aerobically oxidized to carbon dioxide, water, ammonia or nitrates. Some of the energy released the

microbial degradation is used to form new cellular material, but most is released as heat making aerobic digestion an exothermal process (Shammas and Wang, 2007a).

2.3 Dewatering

The dewatering of sludges is carried out to reduce sludge volumes and improve handling properties (Novak, 2001). The choice of dewatering technique and conditioning chemicals impact dewaterability as well as the potential for odour during further processing or recycling to land (US EPA, 2000a). The major dewatering processes used in dewatering are the belt filter press, centrifuge and recessed chamber filter press. Other methods include sand drying beds and lagoons (Novak, 2001). This review will briefly discuss belt filter presses and centrifuges.

2.3.1 Belt Filter Presses

Belt filter presses (BFPs) dewater by applying pressure to the biosolids to squeeze out the water. Biosolids are sandwiched between two tensioned porous belts and are passed over and under rollers of various diameters. Increased pressure is created as the belt passes over rollers which decrease in diameter (US EPA, 2000a; Shammas and Wang, 2007b). Many designs of the belt filtration process are available, but all incorporate the following basic features: polymer conditioning zone, gravity drainage zones, low pressure and high pressure squeezing zones (US EPA, 2000a; Shammas and Wang, 2007b). Some BFPs include the added feature of vacuum boxes in the free drainage zone. About 6 in. Hg vacuum are applied to obtain higher cake solids. A "second generation" of belt filters have extended shearing or pressure stages that produce substantial increases in cake solids, but are more expensive (Shammas and Wang, 2007b). Advanced designs provide a large filtration area, additional rollers and variable belt speeds that can increase cake solids by 5% (US EPA, 2000a; Shammas and Wang, 2007b).

Good chemical conditioning is the key to successful and consistent performance of the belt filter press, as it is for other dewatering processes (Shammas and Wang, 2007b). The primary effect is to ensure that the free drainage phase works well and dose and polymer type can usually be determined from a simple free drainage test where the rate of drainage and clarity of the filtrate can be determined (Novak, 2001). It has been reported that the polymer dose for optimizing a filter cake solids is often lower than that for achieving minimal filtrate solids. The data has shown that the optimum polymer dose of producing the highest solids cake was lower than that needed for the highest quality filtrate (Novak, 2001). Polymer feed points should be designed at several locations to ensure flexibility and optimum performance. The solids/polymer mixture should be subject to gentle mixing as turbulent conditions can shear the floc, minimizing polymer effectiveness. Polymer dilution and aging system should be large enough to optimize polymer usage (Shammas and Wang, 2007b). Potassium permanganate or other oxidizing agents are often added to solids before dewatering. These have been shown to reduce odour caused by sulphides, reduce the amount of polymer needed and increase cake solids content (Shammas and Wang, 2007b).

Although biosolids produced using belt filter presses may be odorous, recent reports have shown that cake solids produced using belt presses produced much less odorants compared to centrifuge cakes (Adams, *et al.*, 2008; Murthy, *et al.*, 2006; Higgins, *et al.*, 2008a) however the dryness of the cake from the belt filter press was not as good as that of the centrifuge cake (Adams, *et al.*, 2008).

2.3.2 Centrifuges

Centrifuges operate as continuous feed units which remove solids by a scroll conveyor and discharge liquid over the weir. The bowl is conical in shape which helps to lift solids out of the liquid allowing them to dry on an inclined surface before being discharged (US EPA, 2000b). Centrifuge performance is mainly controlled by the feed rate to the machine, the polymer dose, torque and bowl speed (Adams, *et al.*, 2008; Novak, 2001).

High-solids centrifuges are a leading edge dewatering technology and produce an approximately 5% increase in cake solids compared to low solids centrifuges and belt filter presses (Murthy, *et al.*, 2006). However, studies have shown that biosolids cakes processed using high-solids centrifuges have higher odorant production potential than those dewatered using low-solids centrifuges or belt filter presses (Murthy, *et al.*, 2006; Higgins, *et al.*, 2008a; Adams, *et al.*, 2008).

3.0   Odour Formation in Biosolids

The constituents of biosolids that are thought to most strongly influence odours are proteins, which comprise 50 to 70% of the volatile solids in wastewater sludges (Adams, *et al.*, 2003b; Forbes, *et al.*, 2004). Proteins are made up of amino acids that contain life-essential elements of carbon, hydrogen, nitrogen and sulphur. The most volatile, odorous gases are derived from amino acids containing nitrogen and sulphur that comprise a portion of all cell material (Forbes, *et al.*, 2004). Other odorous components that also have biological origins include acids, aldehydes and ketones. In addition, the normal biological processes that are a part of the wastewater treatment are also suspected culprits of odour generation (Forbes, *et al*., 2004). Figure 2 shows a simplified diagram of the biosolids treatment and handling processes that are believed to influence the characteristics and intensity of odours produced by biosolids (Forbes, *et al.*, 2004).
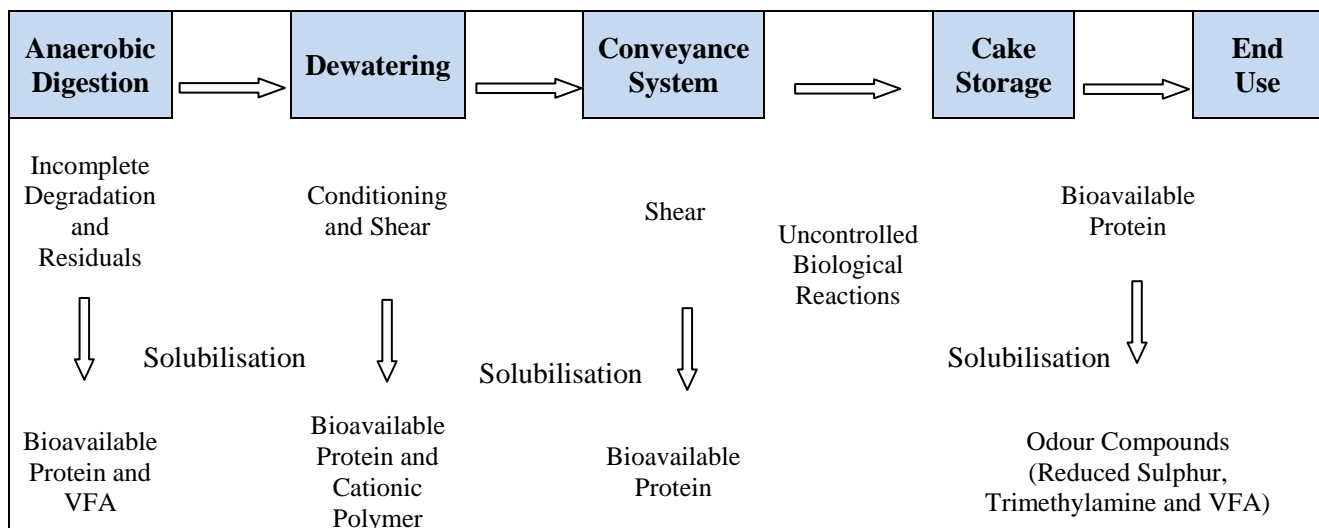

Figure 2: Suspected Mechanisms Creating Odours in Biosolids Handling (adapted from Forbes, *et al.*, 2004)

The common elements in the process illustrated above are solubilisation reactions that occur during biological activity and produce bioavailable protein. When the protein becomes available as food for microbes, the products of their biological activity produce a range of volatile, organic chemicals that have been associated with odours in biosolids (Forbes, *et al.*, 2004).

3.1   Compounds Associated with Odours

Many different compounds have been associated with odours from biosolids facilities. Some of the most prevalent are thought to include volatile organic sulphur compounds (VOSCs) such as methanethiol (MT, also called methyl mercaptan), dimethyl sulphide (DMS), dimethyl disulphide (DMDS) and dimethyl trisulphide (DMTS), as well as inorganic sulphur compounds such as hydrogen sulphide (H_2S), nitrogenous compounds such as trimethylamine (TMA) and ammonia and potentially volatile fatty acids (VFA) (Adams, *et al.*, 2003a; Higgins, *et al.*, 2003, 2006, 2008a). Other organic compounds such as terpenes, acids, aldehydes, alcohols and ketones have also been reported (Adams, *et al.*, 2003a; Forbes, *et al.*, 2004; Rosenfeld and Suffet 2004). Several odorous volatile aromatic compounds (OVACs) have been identified through GC-MS analysis of headspace samples from stored biosolids (Chen, *et al.*, 2004, 2006).

Table 1 shows some of the most common organic compounds associated with biosolids odour along with their odour threshold concentrations.

Table 1: Most Common and Intense Odorous Compounds Found in Biosolids (adapted from Forbes, *et al.*, 2004)

Compound Name	Formula	Odour Character	Threshold Conc., (ppm)
Hydrogen sulphide	H_2S	Rotten eggs	0.008
Dimethyl sulphide	$(CH_3)_2S$	Rotten vegetables	0.001
Dimethyl disulphide	$(CH_3)_2S_2$	Putrification, decay	0.00003
Methanethiol (methyl mercaptan)	CH_3SH	Rotten cabbage, garlic	0.002
Trimethylamine	$(CH_3)_3N$	Rotten fish	0.0004
Indole	C_8H_6NH	Faecal, nauseating	0.0001
Skatole	C_9H_8NH	Faecal nauseating	0.001
Butyric acid	C_3H_7COOH	Rancid	0.0003
Butyraldehyde	C_3H_7CHO	Rancid, sweaty	0.005

3.1.1 *Volatile Sulphur Compounds (VSCs)*

Recent research has shown that the main odour causing chemicals produced by biosolids were volatile sulphur compounds which include H_2S, MT, DMS, DMDS and dimethyl trisulphide (DMTS) (Higgins, *et al.*, 2003, 2006, 2008b). Some of these VSCs can be produced by various microorganisms (Kadota and Ishida, 1972). For example, simple alkyl thiols such as MT can be produced by bacteria, molds and unicellular algae. MT is often produced by microorganisms during the decomposition of methionine (Kadota and Ishida, 1972). Dimethylsulphide is produced by higher plants, multicellular and unicellular algae and rumen microorganisms (Kadota and Ishida, 1972). Some limited groups of microorganisms also produce H_2S *via* the desulphydration of organic sulphur compounds or the reduction of sulphate (Kadota and Ishida, 1972). For example, H_2S is often produced by sulphate-reducing bacteria and most of the chemoorganotropic bacteria in paddy soil, bottom sediments and waters of estuaries (Kadota and Ishida, 1972). Table 2 shows the various microorganisms which produce volatile sulphur compounds using methionine as a substrate.

Twenty four strains of bacteria from activated sludge with high DMDS forming ability have been identified to the genus level and genera, and include *Lactobacillus*, *Corynebacterium*, *Pseudomonas*, *Alcaligenes* and *Achromobacter* (Tomita, *et al.*, 1987; Rosenfeld and Suffet, 2004). DMDS and DMS have also been identified as products of the following five fungal species: *Aspergillus versicolor*, *Penicillium commune*, *Cladosporium cladosporioides*, *Paecilomyces variotii* and *Phialophora fastigiata* (Sunesson, *et al.*, 1995; Rosenfeld and Suffet, 2004).

Table 2: Volatile Sulphur Compounds Produced by Microorganisms (adapted from Kadota and Ishida, 1972)

Microorganism	Substrate	Compounds produced
A soil fungus	methionine	MT
Aspergillus oryzae	methionine	MT
Micromonospora sp.	methionine	MT
Fusarium culmorum	methionine	MT
Candida albicans	methionine	MT
Pseudomonas fluorescens	methionine	MT
Proteus vulgaris	methionine	MT
Sarcina lutea	methionine	MT
Streptomyces griseus	methionine	MT
Streptomyces lavendulae	methionine	MT
Pseudomonas sp.	methionine	MT
Escherichia coli	methionine homocysteine and cysteine	MT H_2S
Pseudomonas aeruginosa	methionine	MT
Clostridium tetani	methionine	MT
Clostridium pefringens	methionine	MT
A Gram-negative motile rod	methionine	MT
Pseudomonas sp. NCMB 1521	methionine	MT
Pseudomonas sp. NCMB 1520	methionine cysteine	MT and DMS H_2S
Schizophylum commune	methionine SO_4 + glucose	MT and DMS MT
Micromonospora gypseum	methionine	MT
Scopulariopsis brevicaulis	methionine	MT
Aspergillus niger	methionine	MT

Recent studies have shown that three key mechanisms are responsible for the formation of the VSCs (Higgins, *et al.*, 2003, 2004, 2006, 2008b):

(1) Biodegradation of the sulphur-containing amino acids, cysteine and methionine to H_2S and MT, respectively, by proteolytic enzymes,
(2) Methylation of H_2S and MT to from MT and DMS, respectively and
(3) Oxidation of MT to form DMDS.

Figure 3 shows the pathways for production of methyl mercaptan (MT) from the biodegradation of protein to methionine and the production of H_2S from the degradation of protein to cysteine (Higgins, *et al.*, 2004). The mechanism entails the breakdown of proteins to form peptides which are then degraded to form the free amino acids, methionine and cysteine, which then breakdown to form VOSCs (Higgins, *et al.*, 2003, 2006). In particular, the degradation of methionine to form methanethiol appears to be a key pathway for the production of odorants (Higgins, *et al.*, 2008b). Methanethiol is the odorant that has been measured in the highest concentrations in a number of studies (Higgins, *et al.*, 2008, 2006; Murthy, *et al.*, 2004; Novak, *et al.*, 2004, 2006) and thus is of significant importance in understanding odours from biosolids.
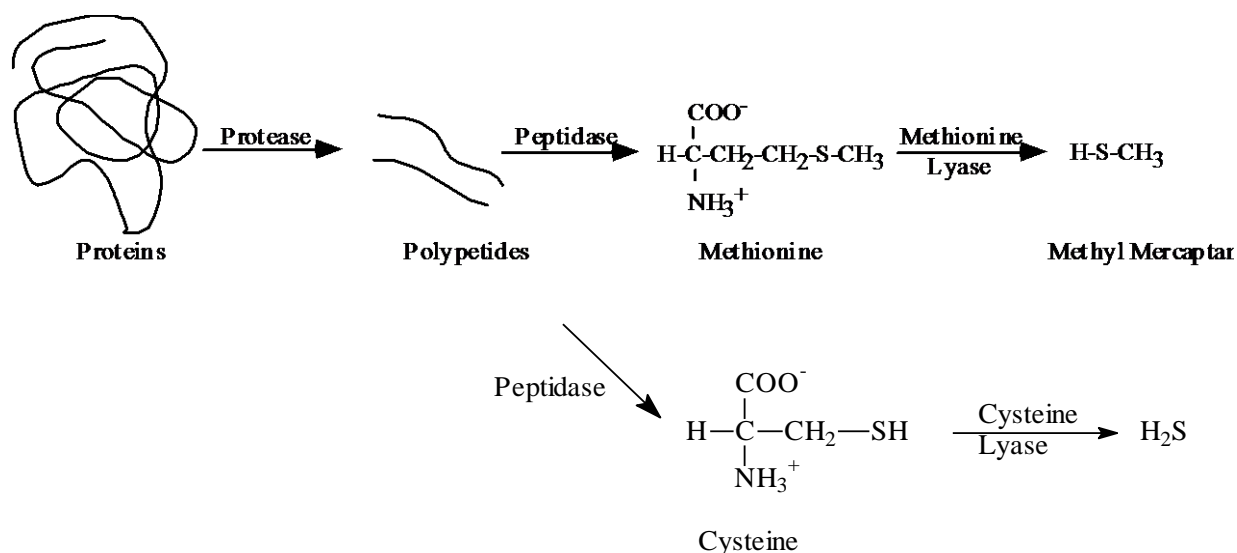
Figure 3: Formation Pathways for MT and H_2S by the Degradation of Proteins (adapted from Higgins, *et al.*, 2004)

The second mechanism for the formation of VSCs involves the methylation of H_2S and MT and is represented in the reactions below (Higgins, *et al.*, 2003, 2006).

$$R\text{-}O\text{-}CH_3 + H_2S \longrightarrow R\text{-}OH + CH_3SH \qquad \text{(Reaction 1)}$$

$$R\text{-}O\text{-}CH_3 + CH_3SH \longrightarrow R\text{-}OH + CH_3SCH_3 \qquad \text{(Reaction 2)}$$

Hydrogen sulphide is methylated to form MT which can then undergo further methylation to produce DMS. This methylation process has been reported to occur in freshwater sediments, soils and water under both aerobic and anaerobic conditions and methyl donor groups have been shown to include humic-like materials with methoxy groups (Higgins, *et al.*, 2003, 2006). Since biosolids contain a significant amount of humic acid type material which can act as a source of methyl group donors, this may also be an important mechanism for VSC production in biosolids (Higgins, *et al.*, 2003, 2006). It should be noted that H_2S can also be produced by sulphate reducing bacteria (SRBs) as well as the degradation of cysteine, however, direct production of MT (excluding methylation) will mainly arise from the degradation of methionine (Higgins, *et al.*, 2003).

$$CH_3SH + CH_3SH + 1/2O_2 \longrightarrow CH_3S\text{-}SCH_3 + H_2O$$
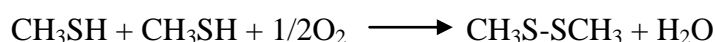
The third mechanism for the formation of VSCs involves the oxidation of MT to dimethyl disulphide (DMSD), as shown above, and can be catalysed by light and certain constituents of biosolids, such as metals (Higgins, *et al.*, 2003, 2006).
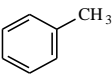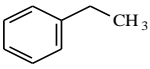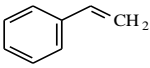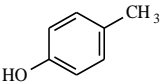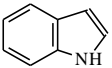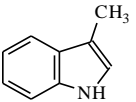
3.1.2 *Odorous Volatile Aromatic Compounds (OVACs)*
Research has shown that one of the major causes of odours during the first 1-2 weeks of biosolids storage is due to the production of VOSCs *via* the microbial degradation of sulphur-containing amino acids (Higgins, *et al.*, 2003, 2006; Chen, *et al.*, 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). Thus, some other odorous compounds with low odour detection threshold are responsible for the malodour after the VOSCs have abated (Chen, *et al.*, 2006).

Six odorous volatile aromatic compounds (OVACs) have been identified through GC-MS analysis of headspace samples from stored biosolids (Chen, *et al.*, 2004, 2006). The compounds identified are

listed in Table 3 along with their chemical structures and odour detection thresholds (Chen, *et al.*, 2004, 2006). These 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 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).

Table 3: Chemical Structures and Odour Detection Thresholds for the Six OVACs (adapted from Chen, *et al.*, 2006)

Name	Chemical Structure	Odour Detection Threshold	Odour Descriptor
Toluene		2.9 ppm	Sweet, pungent
Ethylbenzene		2.3 ppm	Gasoline
Styrene		320 ppb	Sweet
p-cresol		0.011-5.4 ppb	Medicine
Indole		0.13-1.5 ppb	Faecal nauseating
Skatole		0.065-0.15 ppb	Faecal nauseating

Based on the chemical structures of the OVACs and past research, these compounds are likely to be the degradation products of aromatic amino acids (Chen, *et al.*, 2004, 2006). Indole and skatole are thought to be derived from tryptophan; *p*-cresol has been reported to be the degradation product of tyrosine; and toluene, ethylbenzene and styrene are thought to be derived from phenylalanine (Chen, *et al.*, 2004, 2006). Figure 4 summarises the OVACs formation pathways based on research carried out by Chen, *et al.* (2004, 2006).
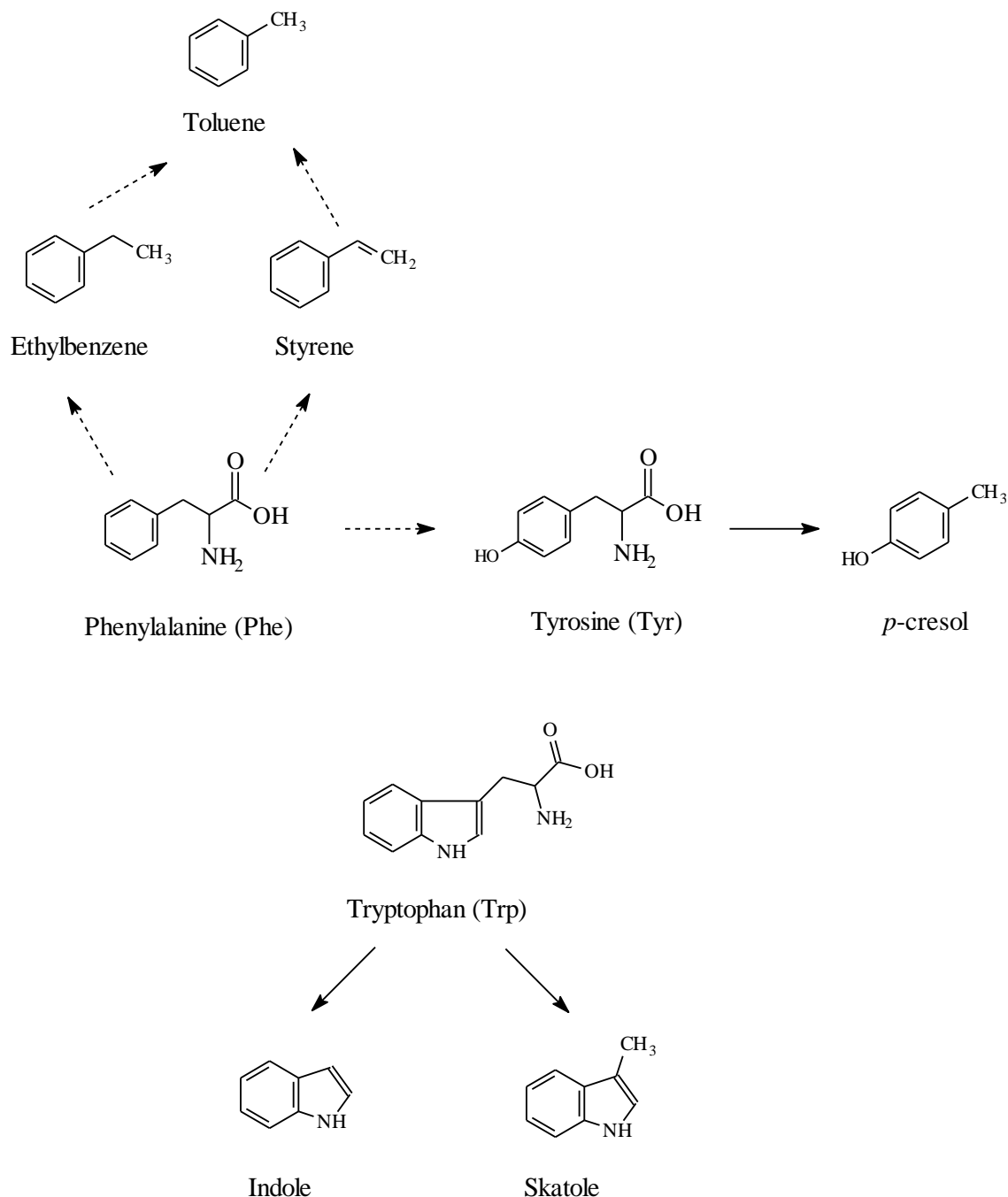
Figure 4: Possible Mechanisms of Formation of OVACs *via* Degradation of Aromatic Amino Acids. Solid arrows represent pathways confirmed experimentally. Dashed arrows represent proposed or reported pathways but not confirmed experimentally (adapted from Chen, *et al.*, 2004, 2006)

Indole can be produced directly from tryptophan using tryptophanase, while skatole is formed through decarboxylation of the intermediate indole-3-acetic acid (Chen, *et al.*, 2004, 2006). Tryptophan degradation was found to be pH dependant with high pH values (e.g. pH 8) promoting the formation of indole, while low pH promotes skatole production (Chen, *et al.*, 2004, 2006). The formation of *p*-cresol from tyrosine occurs *via p*-hydroxyphenylacetic acid as the intermediate. Toluene is expected to be produced from phenylalanine *via* transamination followed by a series of decarboxylations (Chen, *et al.*, 2004, 2006). The formation of ethylbenzene is similar to toluene with one less decarboxylation. No literature was found as to how styrene could be formed from aromatic amino acids except for the possible double bond formation from ethylbenzene (Chen, *et al.*, 2004, 2006).

In order to confirm that the proposed degradation pathways shown in Figure 4 exist in biosolids during storage conditions, Chen, *et al.* performed a series of experiments. In these experiments, individual amino acids were added to biosolids and the headspace was monitored for VOSCs and OVACs (Chen, *et al.*, 2004, 2006). The results from these experiments are summarised below:

- *p*-cresol accumulated immediately after the addition of tyrosine.

- The production of indole was immediate in biosolids treated with tryptophan, while skatole production occurred after 5-6 days of storage. It is possible that this delayed production of skatole was due to the two-step degradation of tryptophan. Also the experiments were performed at pH 7.2, which is closer to the high pH range which promotes indole formation (Chen, *et al.*, 2004, 2006).

- The dramatic increase of indole and skatole suggested a substrate-limited condition and the presence of degradation microorganisms.

- Among all the OVACs, indole and skatole had the highest percent conversion from the parent amino acids.

- The lack of significant increase of toluene, ethylbenzene and styrene after the addition of phenylalanine, indicated that: the formation of these compounds in biosolids is not substrate limited; only a limited amount of phenylalanine degrading bacteria were present in biosolids and it is possible that these compounds may be derived from non-biological sources (Chen, *et al.*, 2004, 2006).

3.1.3 *Other Odorous Compounds*

Reduced sulphur compounds, such as carbonyl sulphide (COS) and carbon disulphide (CS_2), trimethylamine (TMA) and volatile fatty acids (propionic acid and butyric acid) have been associated with heat-dried biosolids products (Murthy, *et al.*, 2003c). Aldehydes and ketones have been also been detected in thermal conditioning facilities (Adams, *et al.*, 2003a).

TMA was also found in lime stabilised biosolids along with DMDS, DMS and CS_2, although DMS and CS_2 were present in lower concentrations (Kim, *et al.*, 2003). Emissions from lime stabilisation facilities have also been reported to contain significant amounts of ammonia (Adams, *et al.*, 2003a). Biosolids treated with polymers such as acryloyloxyethyltrimethylammonium chloride (AETAC) and methacrylamidopropyltrimethylammonium chloride (MAPTAC) have also been reported to release TMA after the addition of lime (Chang, *et al.*, 2005).

Compounds such as terpenes, alcohols, aldehydes, ketones and volatile fatty acids have been identified in emissions from biosolids composting facilities (Adams, *et al.*, 2003a; Rosenfeld and Suffet, 2004). Aldehydes and ketones generally have sweet pungent odours that result from the incomplete decomposition of organic matter during composting or biosolids production. They can be formed during anaerobic degradation of cellulose, starch, hemicellulose and pectins (Rosenfeld and Suffet, *et al.*, 2004). Acetone and methyl ethyl ketone (MEK) have been identified as odorants in composting of biosolids (Rosenfeld and Suffet, *et al.*, 2004). Acetone can be produced by *Clostridium* sp. bacteria which has been identified in wastewater biosolids (Rosenfeld and Suffet, *et al.*, 2004).

Volatile fatty acids have a rancid, vinegar and body odour-like stench and are formed from the breakdown of starch, cellulose and hemicelluloses by acid forming bacteria (Rosenfeld and Suffet, *et al.*, 2004).

A summary of the odorous compounds that have been associated with compost, biomass facilities and land application of biosolids along with their odour character and odour detection thresholds in air and water is presented in Table 4.

Table 4: Summary of Odorous Compounds Associated with Biosolids (adapted from Rosenfeld and Suffet, 2004; Chen, *et al.*, 2004, 2006)

Compound	Odour Character	Air odour threshold (ppmv)	Water odour threshold (ppm)
Nitrogen Compounds			
Ammonia	Pungent	0.038	1.5
Methylamine	Fishy	3.2	2.4
Triethylamine	Fishy	0.48	0.42
Trimethylamine	Fishy	0.00044	0.0002
Sulphur Compounds			
Ethyl mercaptan	Rotten cabbage	0.00001	0.0000075
Hydrogen sulphide	Rotten eggs	0.0005	0.000029
Carbon disulphide	Disagree, sweet	0.0077	0.00039
Dimethyl sulphide	Rotten cabbage	0.001	
Dimethyl disulphide	Rotten cabbage	0.000026	
Dimethyl trisulphide	Rotten cabbage	0.0012	
Methyl mercaptan	Rotten cabbage	0.00002	0.000024
Allyl mercaptan	Garlic coffee	0.0001	
Propyl mercaptan	Unpleasant	0.0001	
Amyl mercaptan	Putrid	0.00002	
Benzyl mercaptan	Unpleasant	0.0003	
Sulphur dioxide	Irritating	0.449	
Volatile Fatty Acids			
Formic acid	Biting	0.024	
Acetic acid	Vinegar	1.019	97
Propionic acid	Rancid, pungent	0.028	
Isobutyric and butyric acid	Rancid	0.0003	
Isovaleric acid	Unpleasant	0.0006	
Valeric acid	Unpleasant	0.0006	
Aldehydes and Ketones			
Formaldehyde	Unpleasant	1.199	0.6
Acetaldehyde	Green sweet	0.0001	0.034
Acetone	Sweet, minty	20.6	
Acreolin	Burnt, sweet	0.0228	20
Propionaldehyde	Sweet, ester	0.011	
Crotonaldehyde	Pungent, suffocating	0.037	
Methyl ethyl ketone	Sweet, minty	0.25	8.4
Butyrladehyde	Sweet, rancid, sweaty	9.5	
Valeraldehyde	Pungent	0.028	
Odorous Volatile Aromatic Compounds			
Inodole	Faecal nauseating	0.13-1.5 ppb	
Skatole	Faecal nauseating	0.065-0.15 ppb	
p-cresol	Medicine	0.011-5.4 ppb	
Toluene	Sweet, pungent	2.9 ppm	
Ethylbenzene	Gasoline	2.3 ppm	
Styrene	Sweet	320 ppb	

3.2 Factors Affecting Odour Production in Biosolids

The Water Environment Research Foundation (WERF) funded a multi-phase collaborative project investigating the factors that impact odour formation in biosolids (Adams, *et al.*, 2003a; Adams, *et al.*, 2003b, 2008). The study was based on an in-depth sampling and analysis of biosolids and headspace samples from 11 different WWTP facilities across North America (Adams, *et al.*, 2003b, 2008). All of the facilities used anaerobic digestion for biosolids stabilisation, with 10 of the digestion systems operating in the mesophilic temperature range and one operating in the thermophilic temperature range. The WWTPs used various technologies for biosolids thickening, dewatering, and conveyance of dewatered cake and end use or disposal (Adams, *et al.*, 2003b).

A detailed sampling of the 11 different WWTPs was performed in which nearly every location within the liquid and solids handling process was sampled and the samples were analysed for a number of different constituents. Although the process configuration varied from plant to plant, a general schematic of sampling locations (A to I) is illustrated in Figure 5 (Adams, *et al.*, 2003b; Higgins, *et al.*, 2008a).
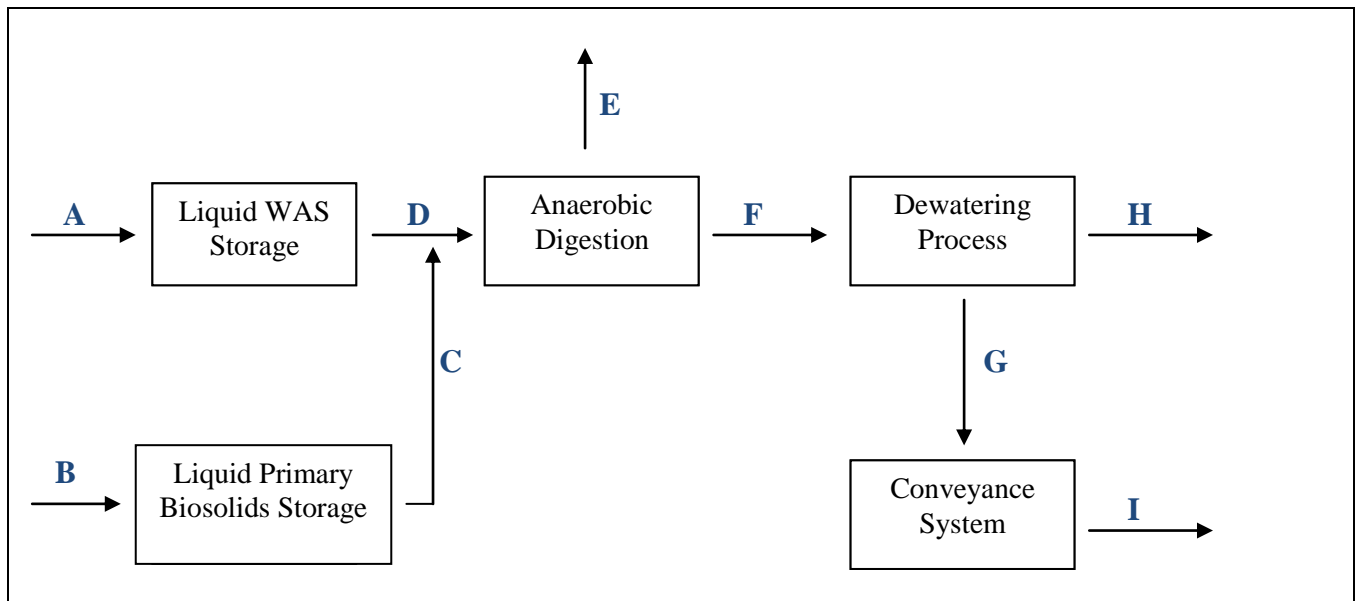

Figure 5: Generalised Test Facility Schematic Showing Sample Locations (adapted from Adams, *et al.*, 2003b)

The above WERF study looked at the following factors impacting on biosolids odours:

- Role of protein, amino acids and enzyme activity.
- The relationship between odours and concentrations of odorants.
- Impact of processes upstream of anaerobic digestion.
- Effects of anaerobic digestion and various enhancements to the anaerobic digestion process.
- Impact of biosolids dewatering and conveyance process.
- Effects of polymer addition.
- Effects of chemical addition.
- Impact of biosolids cake storage.

3.2.1 Role of Protein, Amino Acids and Enzyme Activity on Biosolids Odour Production

It has been hypothesised that the concentration of bioavailable protein in biosolids would be related to the amount of odorants that are produced during the storage of biosolids (Adams, *et al.*, 2003b, Higgins, *et al.*, 2008b). In addition, protein-degrading enzyme activity may also be an indicator of VSC production, as these enzymes are responsible for the degradation of proteins to the amino acids which then degrade to form the VSCs (Adams, *et al.*, 2003b; Higgins, *et al.*, 2008b).

To understand the role of protein, amino acids and enzyme activity in odour production from anaerobically digested and dewatered biosolids, samples taken from the 11 test WWTPs were analysed for protein, amino acids and enzyme activity (Adams, *et al.*, 2003b; Higgins, *et al.*, 2003, 2004, 2006, 2008b). The conclusions from this study were as follows:

- Protein and amino acid content varied significantly from WWTP to WWTP.
- Protein concentration and, in particular, the concentration of methionine were well correlated with the production of odorous VSCs.
- No significant relationships were found between cysteine content of the biosolids cake and any of the VSCs or odour panel measurements.
- Protein-degrading enzyme activity measured in cake and digester samples did not correlate well with the production of odorous VSCs.
- Protein-degrading enzyme activity did not appear to be a good predictor of digester performance and it was not correlated with digester performance parameters such as SRT, VS destruction or digester loading rates and should not be used as a tool for measuring the odour production potential of dewatered biosolids samples.
- The results supported the hypothesis that protein is the main precursor for VSCs, which are associated with odours generated from stored biosolids cake.

3.2.2   *Relationship Between Odours and Concentrations of Odorants*

To determine if there was any correlation between the concentration of odorous compounds and the quality and quantity of odours, the headspace samples of biosolids from the 11 test WWTPs were analysed chemically (GC-MS) for the following compounds (Adams, *et al.*, 2003b, 2008):

- Volatile Sulphur Compounds (VSCs) such as H_2S, MT, DMS, DMDS, DMTS, COS and CS_2.
- Nitrogen compounds: TMA, indole and skatole.
- Fatty acids – these are odorous but difficult to measure in headspace and thus were analysed by direct liquid analysis and the results compared with olfactometry measurements.

The odours themselves were measured by olfactometry (in terms of detection threshold (DT)), using human test panels that analysed the same headspace gas samples used for chemical analysis. However, the olfactometry measurements were undertaken with head space gas samples on Day 6 of incubation, as this has been established as the required time period to generate maximum odour levels from biosolids samples (Adams, *et al.*, 2003b).

The results of the above analyses showed that:

- For most of the odour samples analysed from the test WWTPs there was a strong correlation between the olfactometry measurements (DT) and the total volatile sulphur compound (TVOSC) concentrations (Adams, *et al.*, 2003b, 2008; Higgins, *et al.*, 2008a).
- The concentrations of nitrogenous odour compounds (TMA, indole and skatole) measured in the headspace were not high enough to indicate a correlation (Adams, *et al.*, 2003b).
- There was no correlation between olfactometry measurements on post-digestion samples and fatty acids concentrations in the liquid phase of the digester effluent (Adams, *et al.*, 2003b).

It should be noted that the strong relationship between biosolids odour levels and headspace TVOSC observed in the WERF study is based on biosolids that have undergone anaerobic digestion and mechanical dewatering and may not apply to biosolids that undergo other stabilisation processes (Adams, *et al.*, 2008).

Carsen and Anderson (2008) investigated odour emission rates from sludges that have undergone different stabilisation processes and were subjected to low shear dewatering and then stored over a

period of time in open containers. The headspace odour levels and a suite of both chemical and physical parameters (gas and solid phase) were measured at time intervals. The researchers found that:

- Odour emission rate and the variation with time was dependent on the stabilisation process the sludge had undergone (Carsen and Anderson, 2008).

- The peak odour emission rate was highest for waste activated sludge, followed by aerobically digested sludge, then anaerobically digested sludge and the lowest odour emission rate was observed for lagoon digested sludge (Carsen and Anderson, 2008).

- No correlations were observed between odour and any of the measured chemical or physical parameters in the gas or solid phase (Carsen and Anderson, 2008).

- Speciated sulphur gases were non-detectable (<50ppb) in all samples from all sludges, with odour concentrations varying up to 2500OU. Total mercaptans (detection limit 5ppb) measured in two samples with odour concentrations of 120OU and 180OU were also not detected (Carsen and Anderson, 2008).

The last finding is in contrast with the WERF study findings which reported that the concentration of VOSCs strongly correlated with odour from anaerobically-digested sludges. The explanation for this difference was not apparent (Carsen and Anderson, 2008).

3.2.3   Impact of Processes Upstream of Anaerobic Digestion

A number of upstream process parameters were investigated to determine if they were correlated to biosolids odour production (Higgins, *et al.*, 2008a). One set of parameters examined was influent characteristics such as metal concentrations (Na, K, Mg, Ca, Al and Fe), sulphate concentration, sulphide, ammonia, TKN, alkalinity and pH. None of these parameters showed any significant correlation with any of the odour measurements including peak TVOSC, peak total reduced sulphur (TRS) or the odour panel results (Higgins, *et al.*, 2008a). The influent iron concentration was negatively correlated with peak total organic sulphur concentration in the cake. However, iron was added during the process in 8 of the 11 test WWTPs either for nutrient removal or odour control, thus it is difficult to determine the impact of iron on odours at these plants since the addition points varied between the plants (Higgins, *et al.*, 2008a).

The impact of upstream operational parameters such as activated sludge SRT, storage of primary solids and the ratio of WAS/primary solids entering the digester on odours and VOSC concentration was also examined and the following results were obtained (Adams, *et al.*, 2003b; Higgins, *et al.*, 2008a):

- Peak organic sulphur concentration measured during cake storage correlated well with the percentage of WAS added to the digester on a mass basis, i.e. as the fraction of WAS increased compared to the primary sludge fed to the digester, the VOSC concentration decreased (Higgins, *et al.*, 2008a).

- SRT of activated sludge was negatively correlated with cake odour detection threshold and cake peak organic sulphur concentration (Higgins, *et al.*, 2008a).

- Increased storage time of primary solids did not appear to increase odour emissions from pre-digestion processes or digested biosolids (Adams, *et al.*, 2003b).

Chemical addition to the primary or secondary treatment processes was investigated and it was found that depending on the chemical added and the process point at which it was applied, biosolids odour emissions may be decreased or increased by chemical addition (Adams, *et al.*, 2008). The impact of chemical addition on biosolids odours is discussed in more detail in Section 3.2.7.

3.2.4 *Effects of Anaerobic Digestion and Various Enhancements to the Anaerobic Digestion Process on Biosolids Cake Odours*

Anaerobic digestion is the method of choice for the stabilisation of biosolids by many large scale water treatment plants due to its lower operation costs and its general effectiveness in meeting regulatory requirements regarding volatile solids (VS) and pathogen destruction, as well as the added benefit of methane production (Adams, *et al.*, 2003b; Subramanian, *et al.*, 2007). However, the anaerobic digestion process is not well understood with respect to its impact on odours from digested biosolids, and especially with respect to biosolids cake after dewatering (Adams, *et al.*, 2003b). To better understand the process of anaerobic digestion and its impact on biosolids odour production, the researchers involved in the WERF study examined digester operation data collected from the test WWTPs and evaluated parameters such as: digester effluent VFAs, solids retention time (SRT), residual biological activity (RBA) and volatile solids (VS) destruction (Adams, *et al.*, 2003b; Adams, *et al.*, 2008). The following conclusions were reached:

- No relationship was apparent between the digester effluent VFA (acetic acid) concentration and dewatered cake odour (Adams, *et al.*, 2003b).

- Longer SRT during mesophilic anaerobic digestion resulted in lower TVOSC emissions from dewatered cakes. Lab data showed 1/3 reduction in TVOSC could be obtained by increasing digestion SRT from 15 to 30 days (Adams, *et al.*, 2008).

- VS destruction during digestion of the same feed sludge under identical conditions, except for SRT, increased as the SRT during digestion increased. This finding was confirmed by lower protein concentrations found in samples taken from digesters operating at higher SRTs (Adams, *et al.*, 2008).

- RBA results showed a reasonable correlation with VS reduction and also correlated well with headspace TVOSC concentrations. Lower RBA consistently resulted in lower TVOSC concentrations in headspace of biosolids cake (Adams, *et al.*, 2008).

- In general, an increase in cake solids concentration resulted in increased TVOSC emissions from biosolids cake, suggesting that solids concentration itself may influence the production of TVOSCs from dewatered biosolids and that there may be an optimum solids concentration range with respect to TVOSC generation (Adams, *et al.*, 2008).

- In most cases, higher VS destruction and lower RBA resulted in lower TVOSC production (Adams, *et al.*, 2008).

The effects of various enhancements to the anaerobic digestion process, such as pre-digestion conditioning, thermophilic anaerobic digestion, sequential anaerobic/aerobic digestion and advanced digestion processes, on biosolids cake odours were also examined. A summary of the findings for each enhancement process is presented below.

Pre-digestion Conditioning – The MicroSludge[TM] Process

The MicroSludge[TM] process is a patented chemical and pressure pre-treatment that liquefies WAS to improve the rate and extend of its degradation by conventional mesophilic anaerobic degradation (Rabinowitz and Stephenson, 2005, 2006; Novak, *et al.*, 2007; Adams, *et al.*, 2008). The process uses caustic pre-treatment to weaken activated sludge floc and then uses a high pressure homogeniser or "cell disruptor" to provide a large and sudden pressure drop to burst the cells (Rabinowitz and Stephenson, 2005, 2006; Novak, *et al.*, 2007; Adams, *et al.*, 2008). The first full-scale prototype of the MicroSludge process was commissioned at the Chilliwack WWTP, located approximately 100km east of Vancouver, in January 2004 (Rabinowitz and Stephenson, 2005, 2006).

The second full-scale unit was operated at the Los Angeles County Sanitation District's Joint Water Pollution Control Plant (JWPCP) from October 2005 to August 2006 to evaluate the performance of this technology in enhancing anaerobic digestion and to determine its effect on odour generation from

dewatered sludge cakes (Novak, *et al.*, 2007; Adams, *et al.*, 2008). The following observations were made from this evaluation:

- The MicroSludge processed sludge produced lower TVOSC compared to sludge from the Control digester (Novak, *et al.*, 2007; Adams, *et al.*, 2008).

- The greatest difference in TVOSC levels was observed for sludges dewatered using an emulsion polymer and operational conditions that would create the highest shear. Under these conditions, the TVOSC emissions from the MicroSludge processed material were less than half of those produced by the Control sludge (Novak, *et al.*, 2007; Adams, *et al.*, 2008).

- For sludges dewatered by belt filter presses, the differences in TVOSC generation between the MicroSludge processed material and the control were relatively small (Novak, *et al.*, 2007; Adams, *et al.*, 2008).

- The additional VS reductions using the MicroSludge process were in the range of 3 to 6%, suggesting that something other than additional VS reduction accounted for the benefits of the MicroSludge process in reducing TVOSC concentrations (Novak, *et al.*, 2007; Adams, *et al.*, 2008).

- The reduction of peak TVOSC by more than 50% suggests that the sludge homogenisation technology may alter the degradation ability of the precursors of VOSCs, reducing their build up in the headspace (Novak, *et al.*, 2007; Adams, *et al.*, 2008).

Thermophilic Anaerobic Digestion

- Biosolids associated with digestion temperatures greater than 53°C yielded an 83% reduction in total headspace VOSCs compared to mesophilic biosolids, and a 71% reduction when compared to low temperature thermophilic (49°C) biosolids (Wilson, *et al.*, 2006, 2008).

- Treatment at higher temperatures (55°C, 57.5°C) showed evidence of inhibition of methanogenic activity (Wilson, *et al.*, 2006, 2008).

- The optimal digestion temperature that minimised both the production of odours and H_2 accumulation was approximately 53°C (Wilson, *et al.*, 2006).

- Biosolids digested at high temperatures are advantageous when considering land application and other storage disposal options (Wilson, *et al.*, 2006, 2008).

- Thermophilic digestion produced a different pattern and timing of odour release in its dewatered biosolids (Wilson, *et al.*, 2006, 2008; Adams, *et al.*, 2008).

Sequential Anaerobic/Aerobic Digestion

- Sequential anaerobic/aerobic digestion assisted in obtaining more than 60% volatile solids removal, with minimum of 3 days aerobic digestion (Kumar, *et al.*, 2006).

- Thermophilic anaerobic-aerobic digestion showed better overall biopolymer removal during digestion than the mesophilic anaerobic-aerobic sequence. Total biopolymer removal was approximately 80% after 6 days of post-aerobic SRT in the thermophilic sequence, compared to a maximum removal of 70% for the mesophilic sequence after 9 days of post-aerobic SRT (Kumar, *et al.*, 2006).

- Using sequential anaerobic/aerobic digestion, it was observed that sludges digested under thermophilic anaerobic conditions produced approx 30% less odorants than mesophilic digested biosolids and the additional aerobic digestion step reduced odorants by a further 40%.

- Improvement in biosolids dewatering properties was also observed - polymer conditioning requirements could be reduced by up to 50% compared to anaerobic digestion alone (Kumar, *et al.*, 2006; Subramanian, *et al.*, 2007).

Advanced Digestion Processes

To determine how advanced digestion processes influenced odour potential from centrifugally dewatered sludges, the WERF study examined three WWTPs that had operational advanced digestion processes, either at pilot or full-scale, (Adams, *et al*., 2008). Results of this study for each of the WWTPs containing advanced digestion processes are summarised below.

WWTP 1 – Phased Digestion

This waste water treatment plant had 3 distinct treatment trains:

- Acid-gas mesophilic-thermophilic (AGMT)
- Acid-gas mesophilic-mesophilic (AGMM)
- Acid-gas mesophilic-thermophilic-mesophilic (AGMTM)

The AGMT and AGMM systems had a total SRT of 19 days and the AGMTM system had a total SRT of 26 days (Adams, *et al.*, 2008). A comparison of these three anaerobic treatment schemes with respect to odour generation from dewatered biosolids cake showed that, the three phase digestion system (AGMTM) resulted in the lowest TVOSC generation of the three digestion systems tested. The headspace peak TVOSC of the AGMTM system was reduced by 50% compared to the AGMT dewatered cake, indicating that the three phase acid-gas system with a combination of mesophilic-thermophilic-mesophilic temperatures could be an effective scheme for reducing odour potential of dewatered biosolids (Adams, *et al.*, 2008). This could be attributed to the longer SRT coupled with an extra digestion step or from the MTM configuration, or both (Adams, *et al.*, 2008).

WWTP 2 – Phased Digestion

This WWTP had the following system configurations:

- Conventional mesophilic digestion (pancake-shaped digesters)
- Conventional mesophilic digestion (egg-shaped digesters)
- Acid-gas mesophilic-mesophilic (AGMM) digestion

Experimental results from this treatment plant showed that the acid-gas system reduced the TVOSC odour potential from dewatered cakes by 40-50% compared to the conventional pancake digester, and the egg-shaped digester in a conventional mode reduced TVOSC by about 30% compared to the acid-gas system (Adams, *et al.*, 2008). A comparison of TVOSC concentrations suggested that the conventional mesophilic egg-shaped digester could reduce TVOSC generation by approximately 70% compared to the conventional mesophilic pancake-shaped digester (Adams, *et al.*, 2008).

WWTP 3 – Temperature-Phased Digestion

This study was performed using sludge samples from a temperature-phased anaerobic digestion system (TPAD). In the course of this study, this WWTP was employing a second stage mesophilic digester that operated in a higher temperature range (42-48°C) than is usual for a TPAD system (Adams, *et al.*, 2008). To determine if operating the second mesophilic digestion stage at a "normal" mesophilic temperature could reduce TVOSC generation in dewatered biosolids cake, lab-scale testing was performed on a sample from the first digestion stage that was digested in the laboratory for an additional 30 days at 37°C, and compared to the dewatered cake from the second stage full-scale process operating at 42°C at the time of testing (Adams, *et al.*, 2008). The results showed that there was little difference in the peak TVOSC between the sample from the second stage full-scale process and the laboratory second stage digestion (Adams, *et al.*, 2008). Based on these findings the WERF researchers concluded that although the second stage mesophilic digestion practice at this particular WWTP was not at the standard mesophilic temperature, it did not pose a problem with respect to biosolids odour potential (Adams, *et al.*, 2008).

3.2.5 Impact of Biosolids Dewatering and Conveyance Process

The results of the WERF study showed that odours produced from dewatered biosolids were generally much greater than the odours produced from other locations sampled throughout the WWTPs (Higgins, *et al.*, 2008a). Comparisons of dewatering equipment showed the following:

- Biosolids cakes produced using high-solids centrifuges had the highest odorant production potential (Murthy, *et al.*, 2003a, 2003b, 2006; Higgins, *et al.*, 2008a; Adams, *et al.*, 2008).

- TVOSC emissions from cakes dewatered by medium-solids centrifuges (1800rpm bowl speed) were about half of the emissions from cake dewatered by high-solids centrifuges (2200rpm) (Adams, *et al.*, 2008).

- Dry solids concentration of biosolids dewatered by medium-solids centrifuges was slightly lower than those dewatered by high-solids centrifuges but the reduction in TVOSC was greater in proportion to reduction in solids concentration (Adams, *et al.*, 2008).

- A 10% reduction in centrifuge bowl speed (2200 to 2000rpm) 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).

- 15% reduction in torque resulted in almost 40% reduction in TVOSC emissions from dewatered cake but solids concentration was also reduced by 15-20% (Adams, *et al.*, 2008).

- TVOSC emissions from digested biosolids dewatered by belt filter presses or rotary presses were significantly lower than TVOSC emissions from same biosolids dewatered by high-solids centrifuges, but the dry solids concentrations of biosolids dewatered by belt filter presses or rotary presses were lower than the centrifuged cake (Adams, *et al.*, 2008).

- It has been shown that desiccation of BFP cakes (using a desiccant) or air-drying cakes to 35% dry solids content followed by anaerobic storage, did not generate VOSC emissions (Murthy, *et al.*, 2003).

Although this study found that most of the shear on biosolids after digestion occurred during centrifugal dewatering, one experiment showed that screw conveyance of the dewatered cake increased bioavailable protein and headspace TVOSC emissions (Adams, *et al.*, 2008). Since increasing the shear on dewatered cake may increase its odour potential, conveyance devices that are lower in shear should be considered. For example, belt conveyors are generally preferred over screw conveyors or cake pumps (Adams, *et al.*, 2008).

3.2.6 Effects of Polymer Addition

The cationic organic polymers used to enhance thickening and dewatering processes are potential sources of odours in biosolids (Kim, *et al.*, 2003; Abu-Orf, *et al.*, 2005; Subramanian, *et al.*, 2005; Chang, *et al.*, 2005). This has been reported to be attributed to association of proteins from floc with added polymer (Subramanian, *et al.*, 2005). Polymer has been shown to bind soluble protein during dewatering and deposit this protein in the cake. This protein can then contribute to greater odorant generation (Higgins, *et al.*, 2005). Polymer dose can also influence odour production. Studies have shown that an increase in polymer dose can result in increased odour production (Murthy, *et al.*, 2002; Adams, *et al.*, 2008). It has been suggested that partial degradation of certain type of cationic polyelectrocytes can result in generation of amine odours such as TMA (Chang, *et al.*, 2001; Chang, *et al.*, 2005; Abu-Orf, *et al.*, 2005). For example, TMA formation was observed from the enzymatic breakdown of a polyacrylamide (PAM) cationic polymer with amine functional groups (Kim, *et al.*, 2003; Abu-Orf, *et al.*, 2005; Chang, *et al.*, 2005).

The polymers vary in chemical structure and some may be more susceptible to degradation then others. Figure 6 shows the monomeric chemical structures of some of the commercially available polymers (Chang, *et al.*, 2005).
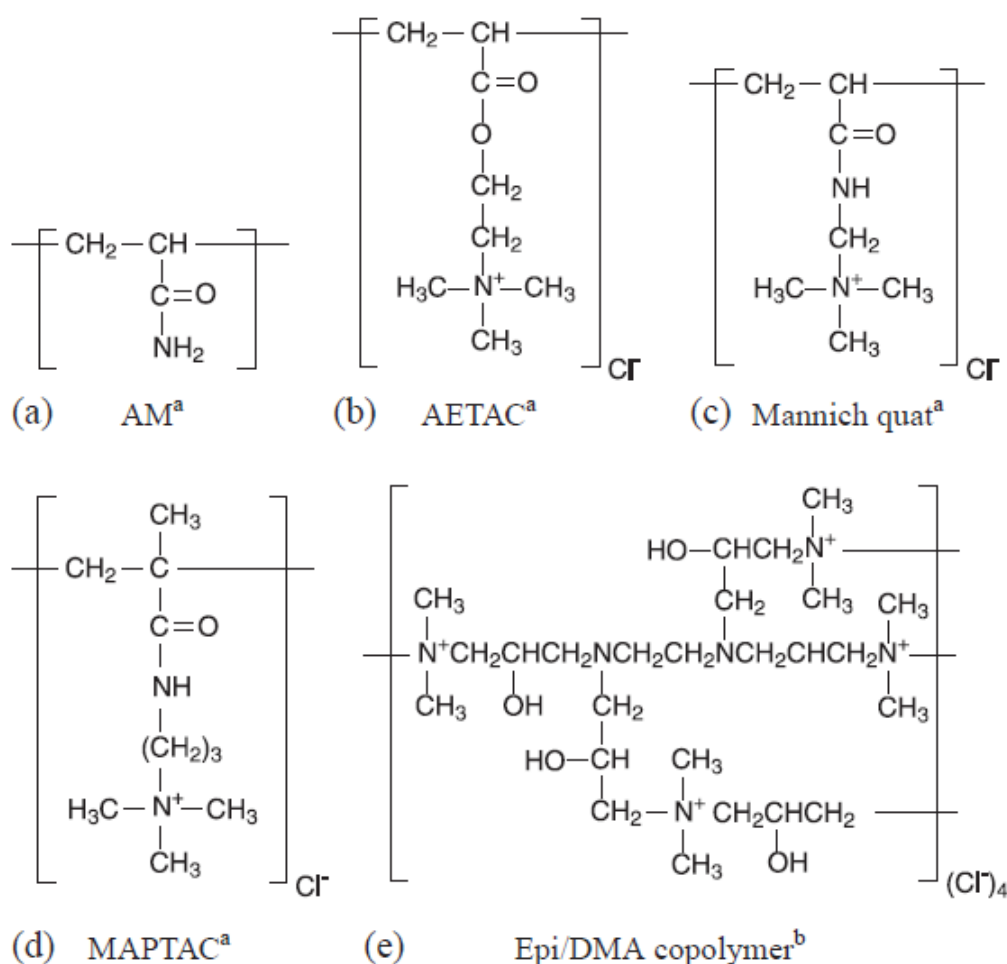
Figure 6: Monomeric Chemical Structures of Selected Cationic Polymers. [a]Acrylamide-based (AM) polymers. [b]Formed by reacting epichlorohydrin (Epi) with dimethylamine (DMA) (adapted from Chang, *et al.*, 2005).

Chang, *et al.* (2005) conducted a study to determine the effect of polymer structure on TMA generation. Of the four polymers tested, two were acrylamide based (AETAC/AM copolymer and MAPTAC/AM copolymer) and two were the Epi/DMA copolymers. The AETAC/AM polymer contains an ester linkage and the MAPTAC/AM polymer has an amide linkage, both of which are susceptible to biological and chemical hydrolysis (Chang, *et al.*, 2005; Chang, *et al.*, 2001). The two Epi/DMA polymers contained different degrees of branching to test if this had any effect on conditioning, gas production or TMA formation (Chang, *et al.*, 2005). The results of this study were as follows:

- Of the 4 different cationic polymers added to anaerobically digested sludge, only the two acrylamide-based polymers (AETAC/AM and MAPTAC/AM) generated measurable amounts of TMA after lime addition to the sludges (Chang, *et al.*, 2005).

- The TMA formation may be attributed to hydrolysis of the ester linkage of the AETAC monomer in the AETAC/AM polymer or hydrolysis of the amide linkage of MAPTAC monomer in the MAPTAC/AM polymer, followed by degradation of the resulting product (choline or aminopropyltrimethylammonium, respectively) as shown in Figure 7 (Chang, *et al.*, 2005). The first step appears to be biologically mediated, while subsequent steps are the result of the alkaline conditions rather than anaerobic microbial activity (Chang, *et al.*, 2005).

- The cross-linked Epi/DMA polymers did not generate TMA and were suitable for sludge conditioning but the optimum doses were considerably higher than for the two AM-based polymers (Chang, *et al.*, 2005).
- Significant concentrations of TMA were not generated in the absence of an AM-based polymer, suggesting that sludge constituents such as protein did not act as direct precursors of TMA formation under the conditions tested (Chang, *et al.*, 2005).
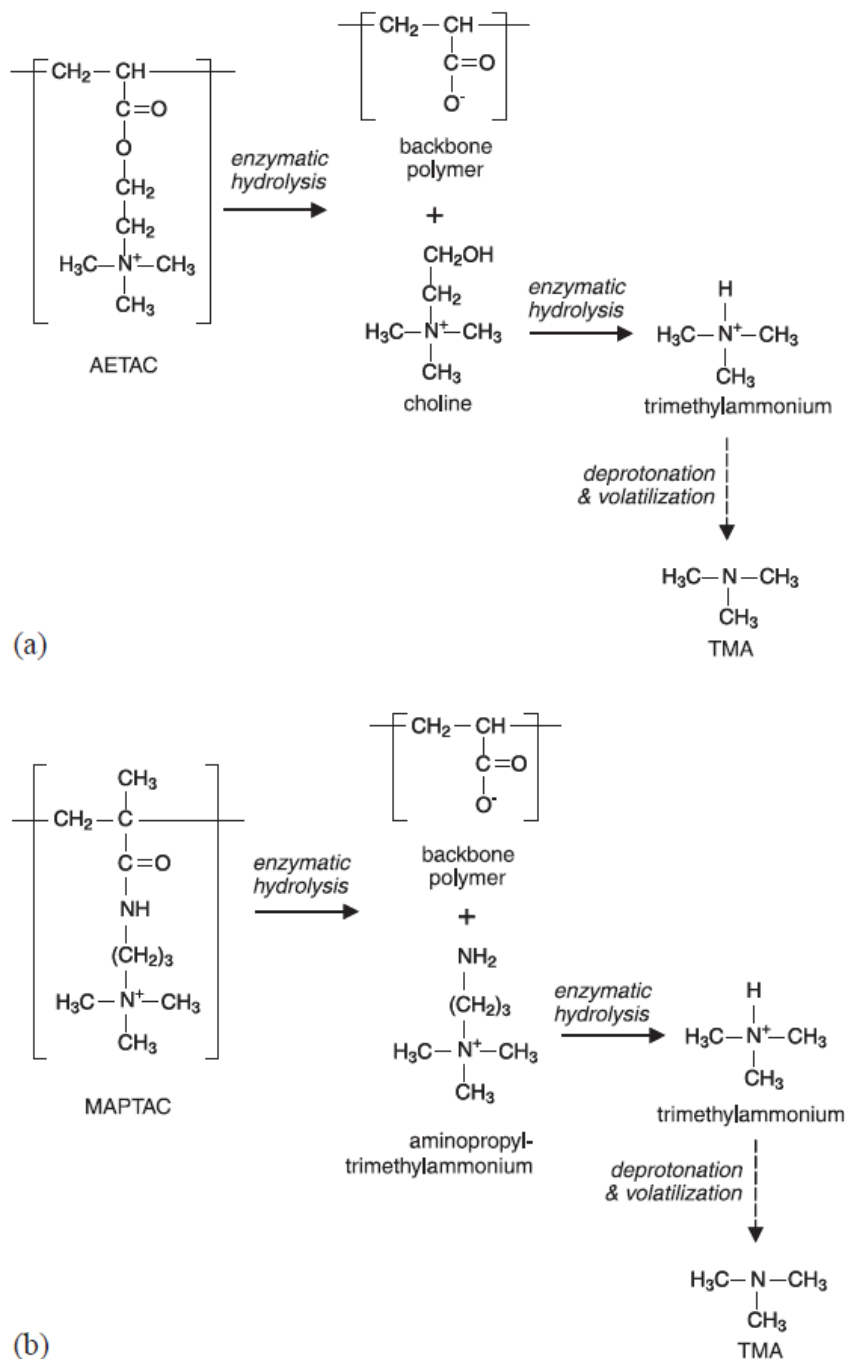

Figure 7: Proposed TMA formation pathways from AETAC (a) and MAPTAC (b) polymers (adapted from Chang, *et al.*, 2005).

In another study, Abu-Orf, *et al.* (2005) also investigated the effect of polymer structure on odour formation in dewatered biosolids. The polymers used in this study included 2 acrylamide-based

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polymers, MAPTAC/AM and AETAC/AM which contain functionalities which are subject to hydrolysis, and two non-AM based polymers, DADMAC and Epi/DMA/MMA, which incorporate a more enclosed structure around the amine nitrogen which was expected to provide chemical stability. The conclusions from this study were as follows:

- The optimum polymer dose of the non-acrylamide polymers, DADMAC and Epi/DMA/MMA, for biosolids dewatering was approximately double that of the optimum dose for MAPTAC/AM and AETAC/AM polymers (Abu-Orf, *et al.*, 2005).

- After lime addition, biosolids containing the acrylamide-based polymers, MAPTAC/AM and AETAC/AM produced significant amounts of TMA (Abu-Orf, *et al.*, 2005).

- The Epi/DMA/MMA polymers did not generate any TMA, even after lime addition (Abu-Orf, *et al.*, 2005).

- The structural differences of the polymers did not affect the production of the sulphur odorants (Abu-Orf, *et al.*, 2005).

- Lime addition almost eliminated H_2S, but organic sulphide odours appeared after lime addition (Abu-Orf, *et al.*, 2005).

- Pilot scale tests with one non-acrylamide polymer did not produce biosolids cake during centrifugal dewatering (Abu-Orf, *et al.*, 2005).

Rosenfeld, *et al.* (2001) investigated the odour emissions and microbial activity associated with biosolids dewatered using seven different polyacrylamide cationic polymers. Nitrogen, sulphur, ketone and odour unit emissions, as well as the biosolids microbial metabolic profiles were measured for biosolids containing each of the polymers (Rosenfeld, *et al.*, 2001). The following conclusions were made from this study:

- Biosolids odours were not affected by the different dewatering polymers (Rosenfeld, *et al.*, 2001).

- Ammonia represented more than 98% of total nitrogen flux for all polymers, with small amounts of TMA (Rosenfeld, *et al.*, 2001).

- DMDS and CS_2 emissions represented 87-97% of the sulphur flux for all polymers, with smaller concentrations for DMS (Rosenfeld, *et al.*, 2001).

- Maximum DMDS, ammonia and TMA concentrations were approximately 3.4, 3.2 and 13.5 times greater than published detection limits, respectively. While maximum DMS, CS_2, acetone and MEK concentrations were approximately 0.028, 0.007, 0.002 and 0.0006 times lower than the published detection limits, respectively (Rosenfeld, *et al.*, 2001).

- All treatments were found to volatilise equal odour unit emissions (except for one polymer) and polymers did not dramatically affect odour emission from biosolids application (Rosenfeld, *et al.*, 2001).

- Although there were no statistical differences in the overall microbial metabolic potential for the seven polymers tested, metabolic fingerprints showed differences in the ability of microbial communities from certain polymer treatments to degrade amino acids as a sole carbon substrate (Rosenfeld, *et al.*, 2001).

- Odour unit emissions correlated well with potential for amino acid decomposition (Rosenfeld, *et al.*, 2001).

3.2.7 *Effects of Chemical Addition*

A brief discussion of the effects of lime, iron and aluminium additions as well as the addition of chemical, enzymatic and biological agents (CEBAs) on the odour potential of biosolids is presented in this section.

Lime Addition

As part of the WERF study on odours in biosolids, the impact of hydrated lime addition on the production of TVOSCs was examined. In this study the lime dosage ranged from 0 to 5% by mass of lime to dry mass of biosolids. The lime was added directly to the cake in a form of a slurry after dewatering. In general, it was found that as the lime dosage increased the concentration of TVOSC emissions from the cake also increased, as shown in Figure 8 (Adams, *et al.*, 2008). This trend was attributed to the increase in pH associated with lime addition. It was found that as the pH increased above 8, the TVOSC headspace concentrations also increased (Adams, *et al.*, 2008). Also, as the lime dosage increased, methanogenic activity decreased. The microbial organisms that produce TVOSC emissions did not appear to be as affected by the increase in pH (Adams, *et al.*, 2008).
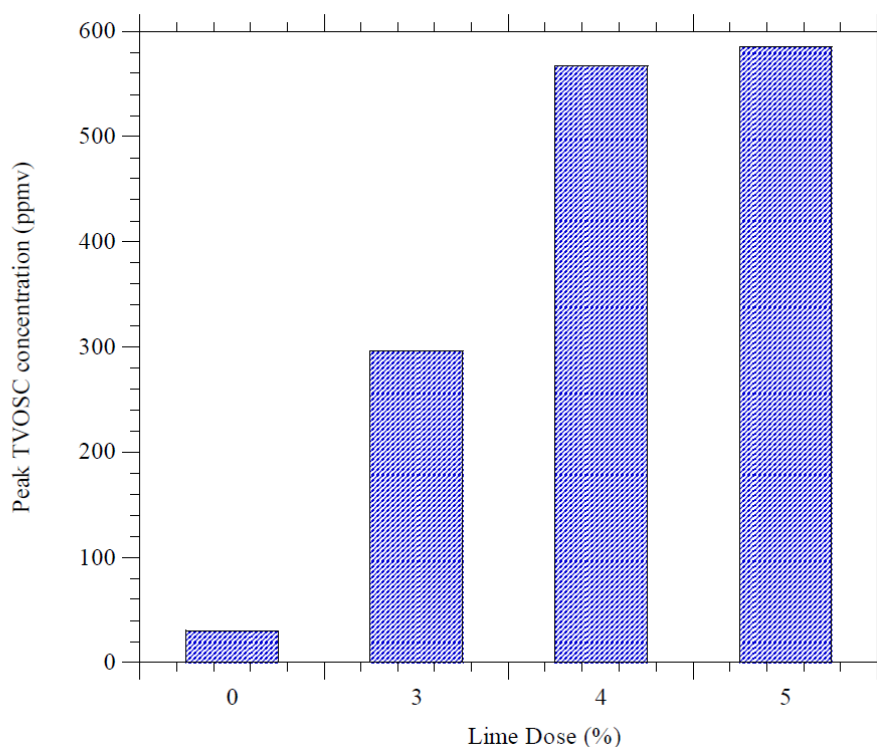

Figure 8: Peak TVOSC Concentrations for Cakes with Different Lime Dosages (adapted from Adams, *et al.*, 2008)

Murthy, *et al.* (2000, 2001) have reported that the optimum lime dose required for biosolids stabilisation is affected by blending and proper incorporation of lime into the biosolids, as well as the storage time. An increase in storage time and a decrease in lime dose can promote biological activity thereby increasing the production of odorants (Murthy, *et al.*, 2000, 2001). A study of one particular WWTP showed that a biosolids product with a 15% lime dose still produced substantial odours after four days of storage and the odours increased over time, while biosolids products stabilised with 30% and 40% lime dose were very stable and the odours appeared to decrease with increased storage time (Murthy, *et al.*, 2001).

Iron Addition

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 found that, addition of ferric chloride ($FeCl_3$) to anaerobically digested solids before dewatering did not reduce TVOSC emissions from cake until $FeCl_3$ dose was at least 8% on a dry mass-mass basis and also required additional lime addition to maintain near neutral pH (Adams, *et al.*, 2008). However, a full-scale trial at a different WWTP showed that iron addition at lower dosage rates may be effective in reducing odours in some biosolids. Thus, it was concluded

that the effectiveness of iron addition in reducing odours seemed to be dependent on the characteristics of biosolids as well as other factors (Adams, *et al.*, 2008).

Aluminium Addition (added as alum)

Two laboratory-scale trials were performed with aluminium sulphate (alum) addition to the feed of laboratory centrifuges. In the first trial (Trial 1) the polymer dose was kept constant and in the second trial (Trial 2), the optimum polymer dose was determined for each alum dose. The trial used a high-solids centrifuge simulation method to produce cake that had similar TVOSC production as cake samples obtained from full-scale high solids centrifuges. The alum was added before polymer addition, the samples were mixed and then dewatered using the laboratory centrifuge (Adams, *et al.*, 2008). The conclusions from these lab trials were as follows:

- *Trial 1* – addition of alum significantly reduced the production of TVOSCs compared to the control sample with no alum. A dose of 0.5% alum resulted in an 83% reduction of peak TVOSC concentration and did not affect the methanogenic activity (Adams, *et al.*, 2008).

- *Trial 2* – it was found that as the alum dose increased the optimum polymer dose decreased. Alum addition again resulted in a significant reduction in the peak TVOSC concentration. It was also found that the methane production increased compared to the control for the 0.5% and 2% alum doses, and decreased slightly at the highest dose of 4% compared to the control, suggesting that alum addition in the dosage range of 0.5% to 4% appears not to adversely affect beneficial methanogenic activity (Adams, *et al.*, 2008).

Based on the results of the lab-scale trials, a full-scale study was performed to determine if alum addition would reduce the generation of odorous compounds under field conditions. The field trial was performed using digested sludge from two different WWTPs (Adams, *et al.*, 2008). The conclusions from this trial were as follows:

- *Alum trial from WWTP 1* – lower dosages of alum resulted in a slight decrease in the peak TVOSC, however at the higher dosages of 2% and 4% an increase in TVOSC was observed (Adams, *et al.*, 2008). The higher dosages were accompanied by a significant decrease in the pH of the feed, which could have had a detrimental effect on methanogenic activity which has been shown to be advantageous in reducing TVOSCs. It was observed that as the alum dosage increased, methane production decreased (Adams, *et al.*, 2008).

- *Alum trial from WWTP 2* – the peak TVOSC decreased as alum dose increased. At the highest dosage of 4% a peak TVOSC reduction of more than 50% was observed compared to the control sample (Adams, *et al.*, 2008). At the higher dosages of 2% and 4%, the methane production was lower which would be expected to increase TVOSC production. Thus, the reduction in TVOSCs may indicate some success in removing odour precursors without being impacted by the reduction in methanogens (Adams, *et al.*, 2008).

- Although the field trial of alum addition did reduce odour production, it did not achieve the same level of TVOSC reduction as the laboratory trials. This could be partly attributed to the period of chemical contact time, where the contact time between alum and biosolids in the laboratory trials was longer than in the field trials (Adams, *et al.*, 2008). Therefore improvements to the field application protocol were recommended in order to achieve better odour reduction in biosolids.

Aluminium – vs – Iron

It has been reported that trivalent metals help to bind labile proteins within the floc structure of sludge/biosolids (Subramanian, *et al.*, 2005). It has also been shown that binding of protein by aluminium is different than the binding by iron. This is partly because iron can undergo reduction from Fe(III) to Fe(II) as the oxidation/reduction conditions change during the process, while aluminium is unaffected by oxidation/reduction (Subramanian, *et al.*, 2005). At higher Al/Fe ratios the odour potential was observed to be low irrespective of shear conditions, suggesting that aluminium

forms tighter bonds with the protein precursors than iron, especially under the reduced conditions of anaerobic digestion, therefore organic material bound with aluminium will not be released as easily as iron-bound material when biosolids are sheared during centrifuge dewatering (Subramanian, *et al.*, 2005; Adams, *et al.*, 2008).

Chemical, Enzymatic and/or Biological Agents (CEBAs)

The Philadelphia Water Department (PWD) has conducted trials of a number of commercial CEBA products to enhance anaerobic digestion and reduce odour intensity of digested cake (Toffey and Higgins, 2006). In these trials three products were added directly to conventional anaerobic digesters, three products were added into the liquid sludge just prior to centrifuge dewatering and two products were incorporated into biosolids cake prior to land application. Product performance was measured by tracking the concentration of odorant emissions from field gathered samples over time (Toffey and Higgins, 2006). The results of this study were as follows:

- A commercial nutrient product added to the digester showed a significantly lower profile of odour emissions of biosolids from the treated digesters and a reduction of peak TVOSC of about half compared to the control sample (Toffey and Higgins, 2006).

- Of the three products used as centrifuge additives, a metallic salt (ferric chloride) showed a reduction in odour intensity but the effective dosage was 10% addition on a dry weight basis, which is not economically viable. Lower dosages were not effective in odour reduction. A Bio-Organic Catalyst (BOC) added ahead of the digester and then sprayed on the cake, did not reduce the odour intensity to a great extend (Toffey and Higgins, 2006). The third product to be trialled was alum, which in pilot scale trials was shown to be a cost-effective replacement for polymer as well as being effective in reducing odours. However, no details from the full scale trial involving centrifuges were available to the authors at the time of writing the report (Toffey and Higgins, 2006).

- Ashes have been the most successful cake additives for odour control. Both of the ashes tested in this trial showed significant reductions in peak TVOSC concentrations. An 80% reduction of peak TVOSC was observed for one of the ashes tested at the lower dosage (10% w/w,), while the second ash showed a 70% reduction of peak odorant at a similar dose (Toffey and Higgins, 2006).

- A humate product added to cake on the discharge belt reduced TVOSC emission by more than half compared to the control sample (Toffey and Higgins, 2006).

As part of the WERF study, extensive laboratory testing of eight commercially available CEBAs was performed to determine their effect on cake odours. Four of the CEBAs (designated as CEBA Nos. 1, 4, 5, and 6) were added to sludge prior to laboratory anaerobic digestion, two CEBAs (Nos. 7 and 8) were added post-digestion and two CEBAs (Nos. 2 and 3) were tested as post-dewatering agents (Adams, *et al.*, 2008). The following conclusions were made regarding the eight CEBAs tested:

- Of the four pre-digestion agents tested, the headspace TVOSC results from three CEBAs (Nos. 4, 5, and 6) were essentially the same as the controls at the dosages tested. Addition of CEBA No. 5 to the digester sludge feed resulted in an improvement in volatile solids reduction (VSR), suggesting improved digestion, however this was not accompanied by subsequent reduction in TVOSC (Adams, *et al.*, 2008).

- Application of CEBA No. 1 resulted in sludge that inhibited methanogenic activity due to reduced pH. As a result, VS reduction was decreased and little gas was produced. The TVOSC generation was low after addition of CEBA No. 1, but the level of digestion was not adequate. Thus, the observed TVOSC reduction was due to inhibition of the overall digestion process (Adams, *et al.*, 2008).

- Headspace analysis of cake derived from sludge dosed with CEBA Nos. 7 and 8 which were applied post-digestion showed an increase in TVOSC emissions (about 70% for CEBA No. 7 and a 33% increase for CEBA No. 8 compared to the controls) (Adams, *et al.*, 2008).

- CEBA Nos 2 and 3, added to dewatered sludge, showed little change in peak TVOSC concentrations compared to the control cake samples (Adams, *et al.*, 2008).

- None of the eight CEBAs investigated had any overall beneficial effect on the sludge samples tested. In this study, each of the CEBAs was only tested at one particular dosage, thus additional testing at different dosages and conditions may be required to investigate the impact these agents may have on reducing odorants in more detail (Adams, *et al.*, 2008).

3.2.8 *Impact of Biosolids Cake Storage*

Research has shown that VSC production from biosolids cake is time dependant over more than a week of storage (Murthy, *et al.*, 2002; Murthy, *et al.*, 2003; Higgins, *et al.*, 2003; Adams, *et al.*, 2008). Thus, a product that may be relatively non-odorous at the WWTP or immediately after dewatering can become odorous during storage. It has also been shown that the emission of VSC is temperature dependant, with an increase in temperature resulting in higher VSC emissions (Adams, *et al.*, 2008).

The WERF study examined the impact of time on odour production for the 11 test WWTPs (Adams, *et al.*, 2003b). Figure 9 illustrates the volatile sulphur compounds (H_2S, MT, DMS and DMDS) released after anaerobic storage of biosolids from test WWTP No. 6. This pattern was found to be representative of most of the test WWTPs (Adams, *et al.*, 2003b). The major emissions during storage were MT and DMS, with MT production usually peaking before DMS peak production (Adams, *et al.*, 2003b).
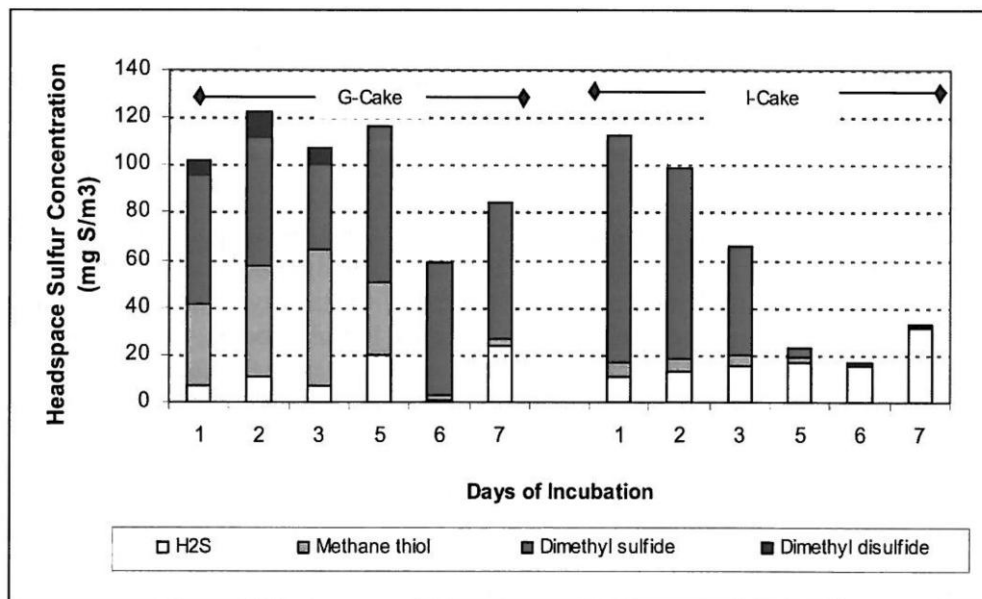

Figure 9: Profile of Sulphur Compounds Measured in Post-Dewatering Biosolids Headspace for WWTP No. 6 (adapted from Adams, *et al.*, 2003b).

Figure 10 shows the time-to-peak for VSCs. Most biosolids cake samples for the test WWTPs emitted maximum VSCs within the first 14 days of storage (Adams, *et al.*, 2003b). VSC emissions at WWTP No. 8 peaked around 35 days, possibly attributed to a shift in the microbial population during storage (Adams, *et al.*, 2003b). This plant employs thermophilic digestion which has been reported to produce different pattern and timing of odour release (Adams, *et al.*, 2003b; Wilson, *et al.*, 2006). The median time-to-peak occurred seven days after storage for dewatered cakes (Adams, *et al.*, 2003b).
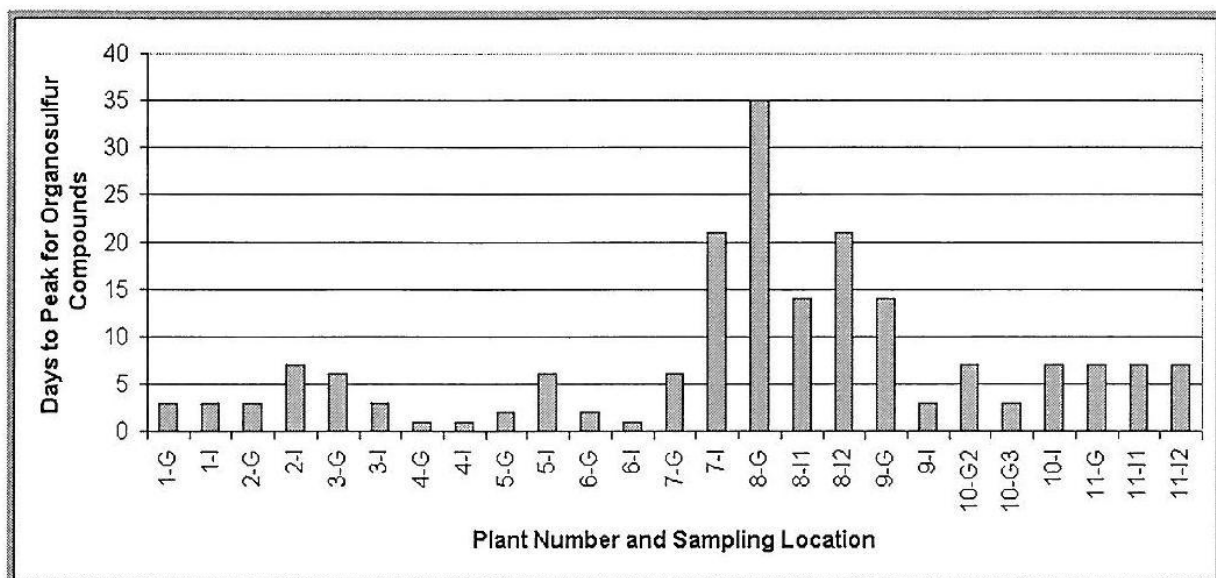
Figure 10: Days to Peak for VSC Compounds Measured in Bottle Headspace in Post-Digestion Samples of the Test WWTPs (adapted from Adams, *et al.*, 2003b).

Figure 11 shows the overall peaking patterns for reduced sulphur emissions. The peak VSC generation varied from plant to plant, with maximum emissions greater than 1800mg S/m^3 and minimum emission of less than 10 mg/m^3 (Adams, *et al.*, 2003b).
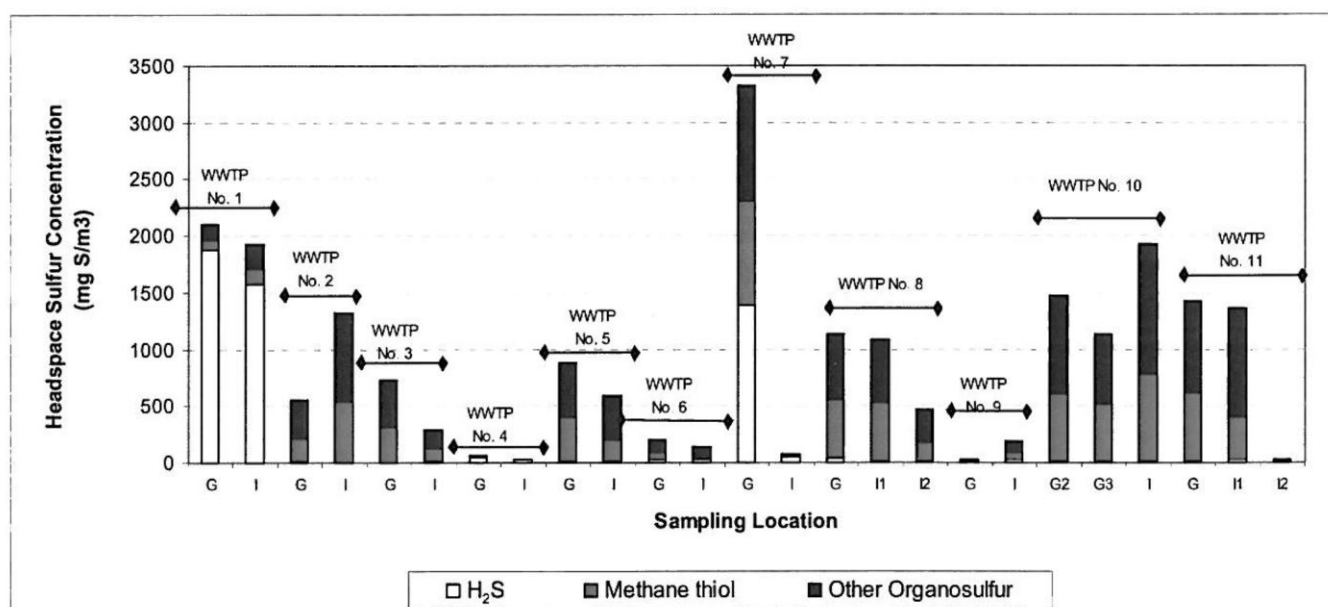

Figure 11: Peaking Patterns of Volatile Sulphur Compounds from Dewatered Biosolids Cakes For All the Test WWTPs (adapted from Adams, *et al.*, 2003b).

Experiments have shown that odours from dewatered biosolids can be reduced during product storage due to growth of odour consuming methanogenic bacteria in stored biosolids cake (Adams, *et al.*, 2003b; Higgins, *et al.*, 2003; Chen, *et al.*, 2005; Adams, *et al.*, 2008) as shown by the rise and fall in TVOSC concentrations in sample bottle headspaces when analysed over bottle incubation period of 2 to 4 weeks (Adams, *et al.*, 2008). Figure 12 shows a typical profile of MT and DMS production during anaerobic storage of digested and dewatered cakes.
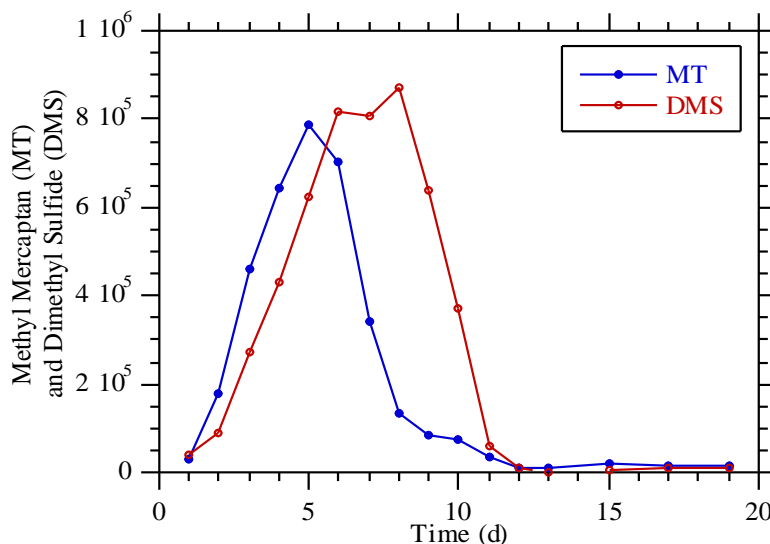
Figure 12: MT and DMS Profile During Storage (adapted from Higgins, *et al.*, 2003).

In most experiments involving mesophilic anaerobic digestion, peak TVOSC concentrations occurred after a storage period of 5-9 days and then decreased to levels of only 20% of peak after 15-20 days (Adams, *et al.*, 2003b; Adams, *et al.*, 2008). Thus, it has been recommended to make provisions for onsite storing and aging of dewatered biosolids for a period of two to four weeks prior to transport and land application. Given the variability in the storage and odour characteristics of biosolids from the different plants, it was also recommended to conduct bottle storage and headspace analyses of dewatered biosolids daily over a 3-4 wk period in order to determine the rise and fall characteristics of TVOSC for each type of biosolids from each WWTP (Adams, *et al.*, 2008).

Biosolids that have been stored for several weeks have a methanogenic population that has recovered from the stress of dewatering and are actively degrading VOSCs. Therefore, spiking fresh biosolids with these stored biosolids can support early establishment of a methanogenic population which can reduce net odour generation (Chen, *et al.*, 2005). Figure 13 shows an almost 50% reduction of methanethiol when an additional 50% of "old" biosolids was mixed into the sample compared to the control. Thus, the incorporation of "old" biosolids into freshly prepared biosolids before storage may be a possible method of reducing odour production. However, additional research to determine the optimum ratio of stored/fresh biosolids may be required to achieve the best odour quality (Chen, *et al.*, 2005).
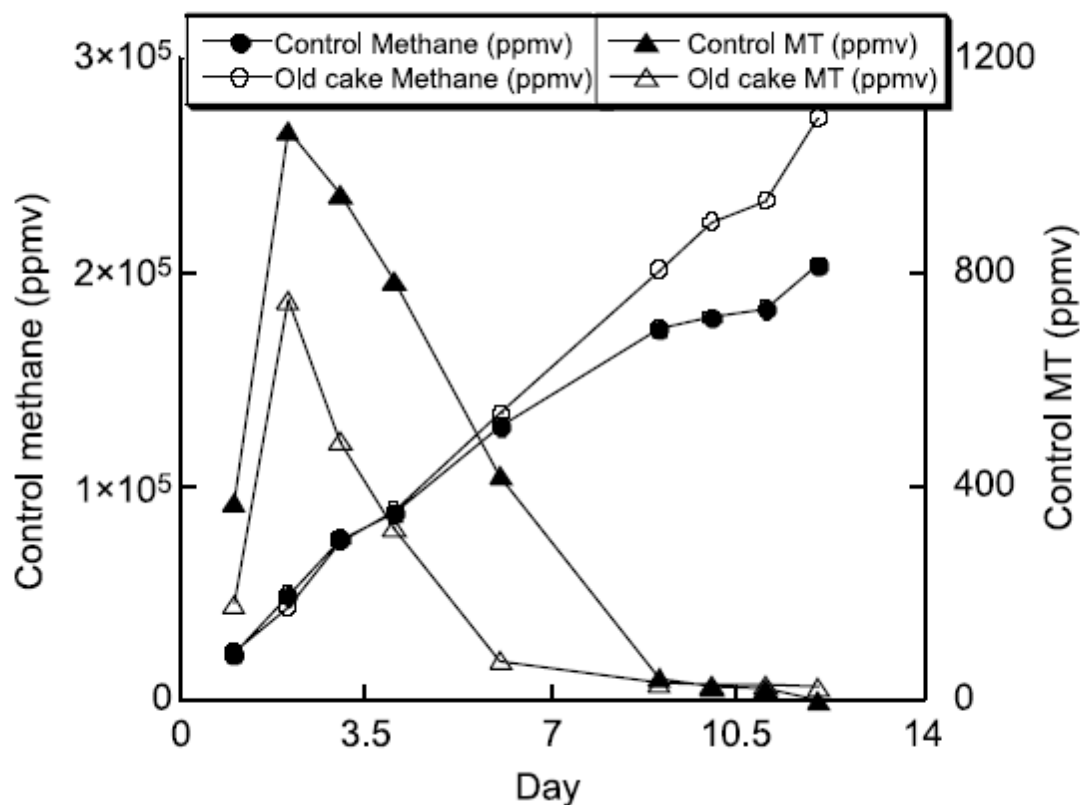
Figure 13: Odour Production Profile of Biosolids With and Without the Addition of "Old" Biosolids (adapted from Chen, *et al.*, 2005).

3.2.9 *Other Factors Influencing Odours in Biosolids*

Sydney Water conducted a study to understand the relationship between various stability indicators and biosolids odour. The stability indicators used in this study were: Volatile Solids Reduction (VSR), Additional Volatile Solids Reduction (AVSR), Residual Volatile Solids (RVS) in the final product, microbial analysis (faecal coliforms and *E. coli*) and odour measurements (Davis, *et al.*, 2008). In this study, 12 sewage plants have been assessed for these parameters. Six plants used aerobic digestion and six used anaerobic digestion (Davis, *et al.*, 2008). The results of this study were as follows:

- There was little correlation between VSR and odour in all plants, suggesting that VSR may not be a suitable indicator of biosolids stability (Davis, *et al.*, 2008).

- In general, aerobic digestion performed better than anaerobic digestion in terms of VSR, odour, RVS and pathogen reduction, indicating that aerobic digestion may produce more stable biosolids (Davis, *et al.*, 2008).

- For anaerobic treatments alone, a significant positive correlation was observed between AVSR and odour (Davis, *et al.*, 2008).

- The anaerobic treatment also had a significant correlation between indicator organisms and odour. The correlation coefficient for *E. coli* was 0.923 and correlation coefficient for faecal coliforms was 0.924 (Davis, *et al.*, 2008).

- The aerobic treatment did not show any significant correlation between stability indicators and odour (Davis, *et al.*, 2008).

- Overall, the results showed that there was an inconsistency between various indicators in predicting the stability of biosolids, making it difficult to identify the best stability indicator (Davis, *et al.*, 2008).

- AVSR was found to be the most representative stability indicator of odour for anaerobic digestion, while further investigation is required to determine the most suitable stability indicator for aerobic digestion (Davis, *et al.*, 2008).

4.0 Odour Reduction/Control Strategies

Biosolids processing facilities are faced with odours during thickening, digestion, dewatering, conveying, storage, truck loading, air drying, composting, heat drying, alkaline stabilisation and/or incineration (US EPA, 2000c). These odours may be derived from point sources or be present in ambient air from area sources (US EPA, 2000c). Good management practices or modifications to the processing operations may reduce odour emissions, however, odour containment and treatment at the biosolids processing plant may be required to control downwind effects (US EPA, 2000c). The following sections describe some potential odour reduction strategies that can be applied to biosolids processing facilities.

4.1 Degradation of Odorous Compounds

In a digester, a balance exists between VSC production and degradation (Higgins, *et al.*, 2003; Higgins, *et al.*, 2006). This balance has also been reported for freshwater sediments, where it has been shown that methanogens were the main degraders of MT and DMS in freshwater sediments with low sulphate concentrations (conditions similar to anaerobic digesters) (Higgins, *et al.*, 2003; Higgins, *et al.*, 2006). Figure 14 summarises the different reactions that could take place during the cycling of VSCs (Higgins, *et al.*, 2003; Higgins, *et al.*, 2006). The methanogens demethylate MT, DMS and DMDS to form H_2S which could then be bound by metals in the biosolids or potentially removed by other microbial processes, resulting in deodorisation of the biosolids (Higgins, *et al.*, 2006). Thus, these reactions are important in maintaining low levels of VOSCs in anaerobic digesters and inhibition of methanogens (e.g. due to poor digester performance) could result in greater VOSC production (Higgins, *et al.*, 2006).

Research into the roles of methanogens on odour production in biosolids has shown that methanogens play a key role in removing VOSCs and reducing odours, and methane production was related to reduced VOSC generation (Chen, *et al.*, 2005). Examination of the microbial communities of both bacteria and archaea suggested that the role of methanogens on VOSC degradation is most likely quantitative rather than qualitative, i.e. the abundance of the overall methanogenic population is more important than the presence of a certain bacterium (Chen, *et al.*, 2005). Factors affecting the growth of methanogens such as shear during dewatering and storage temperature showed a strong impact on net odour production, therefore one possible odour control strategy is the protection and improvement of the methanogenic population during biosolids storage (Chen, *et al.*, 2005).

While methanogens have been shown to be effective in degrading VOSCs (Higgins, *et al.*, 2003; Higgins, *et al.*, 2006; Chen, *et al.*, 2005), they were not effective in degrading OVACs (Chen, *et al,*. 2004, 2006).
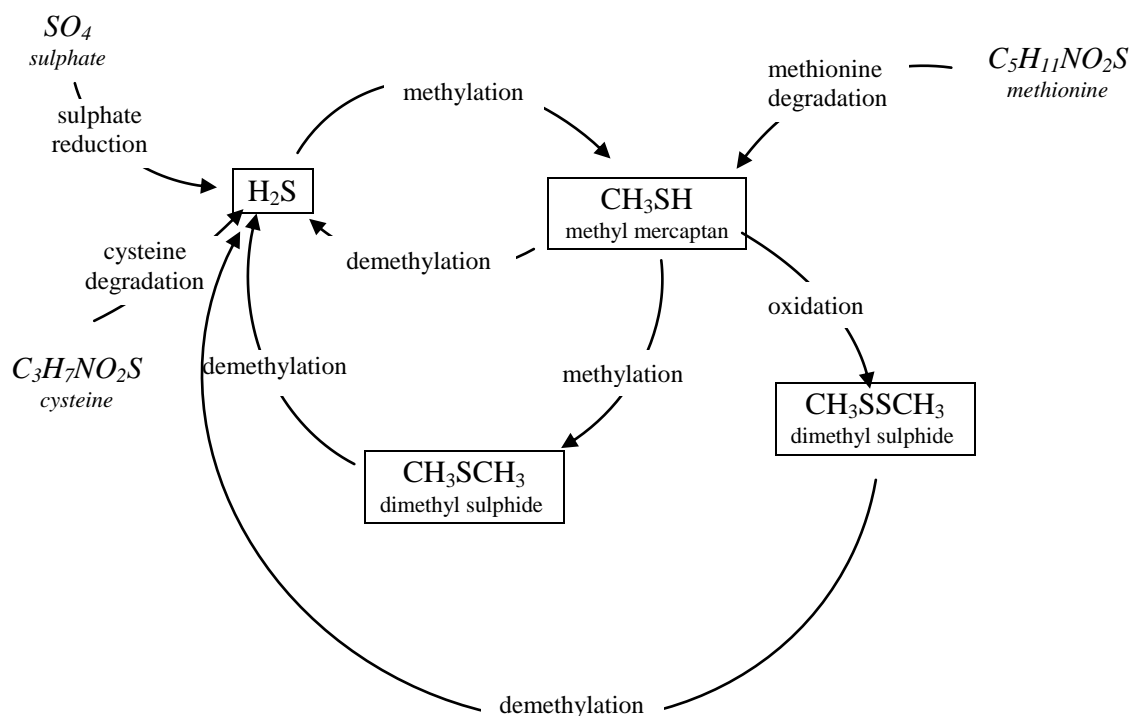
Figure 14: Cyclic Pathway Proposed to Describe the Production and Degradation of Volatile Sulphur Compounds in Biosolids. Key substrates for odour production are in italics and key odour causing compounds are shown in boxes (adapted from Higgins, *et al.*, 2006).

4.2   Reducing Concentration of Precursors to Odorous Compounds

Proteins have been identified as the major precursors to odorous compounds in biosolids (Higgins, *et al.*, 2003, 2004, 2006, 2008b; Forbes, *et al.*, 2004; Adams, *et al.*, 2008; Chen, *et al.*, 2004, 2006), so odour control strategies could be aimed at reducing the amounts of bioavailable protein in the cake. For example, more complete degradation of protein during digestion would reduce the available substrate for odour production. Greater SRTs and pre-digestion treatments, which aim to improve digestibility of solids may aid in removing protein (Higgins, *et al.*, 2006). Shear created by centrifugation may release protein, providing substrate for odorant production (Higgins, *et al.*, 2003, 2006, 2008a). Therefore, dewatering processes should be operated and designed to minimize shear thereby reducing the amount of bioavailable protein (Higgins, *et al.*, 2008a; Adam, *et al.*, 2008).

4.3   Process Evaluation

The most cost effective approach to odour control may be to examine the operation and maintenance practices at the biosolids processing facility (US EPA, 2000c). The level of control required for biosolids processing plants should be based on site-specific characteristics such as: the proximity of a processing site to residential or commercial development; local wind patterns, air mixing and dispersion factors; temperature and humidity; seasonal variations; and the amount and of type of biosolids being processed (US EPA, 2000c). The quantity and intensity of odorous compounds released by biosolids processing facilities can be reduced by:

- Optimising operation and maintenance procedures to prevent anaerobic conditions, which can have dual benefits: (1) Reduce the amount and intensity of odours generated at the site, reducing cost of odour control equipment and (2) Generate a less odorous product which will be easier to store, transport, utilise or market (US EPA, 2000c).

- Addition of oxidizing agents to prevent formation of H_2S (US EPA, 2000c; Lambert and McGrath, 2000; Adams, *et al.*, 2003a).

- Selecting polymers which are resistant to breakdown at high temperatures and pH (US EPA, 2000c).
- Optimizing all stabilisation processes such as anaerobic digestion, aerobic digestion, or alkaline stabilization (US EPA, 2000c.)
- Reducing the amount of shear imparted during dewatering and conveyance (Adams, *et al.*, 2008).
- Evaluating the impacts of blending different types of solids and storage (US EPA, 2000c; Chen, *et al.*, 2005).
- Scrubbing with a properly operated chemical scrubber or biofilter (US EPA, 2000c).

Figure 15 shows the potential reduction measures for biosolids odour control that were explored as part of the WERF study (Adams, *et al.*, 2008). The potential odour reduction strategies represented in Figure 15 are categorised into two types of changes:
- *Design changes* – that could be implemented during the design of new WWTPs, development of new unit processes for existing WWTPs or engineering modifications to existing processes (Adams, *et al.*, 2008).
- *Operational changes* – that would involve modifying process operations at an existing WWTP, either by adjusting operational parameters of processes or equipment, or *via* chemical addition (Adams, *et al.*, 2008).

In most cases, "trial-and-error" laboratory or pilot scale approaches will probably be required when examining any of the odour reduction measures outlined in Figure 15 in order to optimise odour quality of biosolids cake (Adams, *et al.*, 2008). Also, the overall amount of odour reduction required should be determined prior to implementing any of these odour reduction schemes (Adams, *et al.*, 2008). Odour measurements before and after process modifications should be performed to give a more accurate evaluation of the scheme's true odour reduction potential (Adams, *et al.*, 2008). One or two carefully chosen modifications may be all that is required to achieve sufficient odour reduction in a given case. Therefore, a thoroughly planned approach that takes into consideration the level of odour reduction required to satisfy the end use is recommended (Adams, *et al.*, 2008). Thus, the chosen strategies for odour reduction should be focussed on approaches that have the highest chance of success in each case (Adams, *et al.*, 2008).

A more detailed summary of findings and recommendations for odour reduction in biosolids, based on the WERF study, is presented in the Appendix.
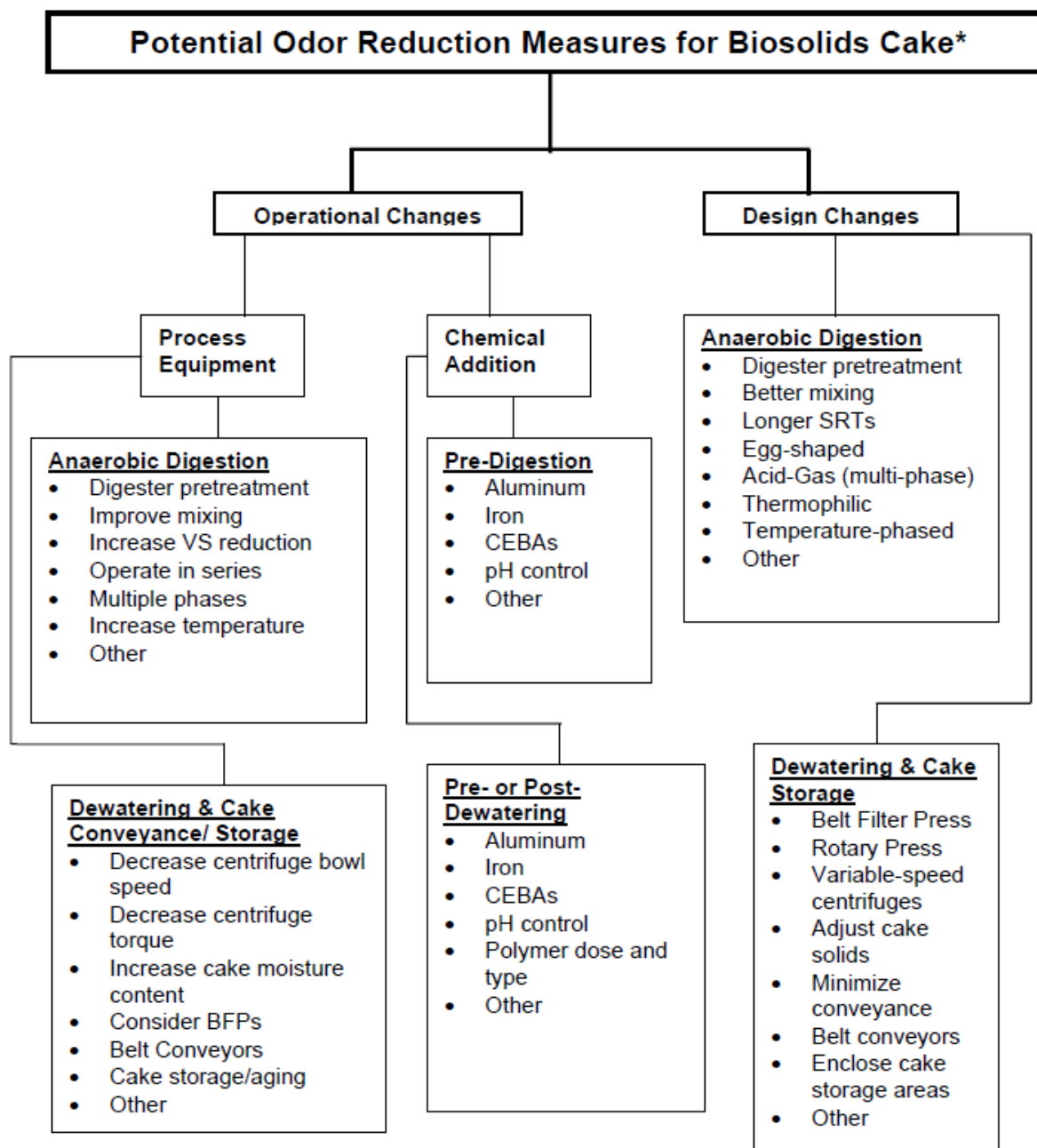
Figure 15: A Summary Chart of Potential Odour Reduction Measures. * **Note:** None of these options should be considered independently of the others. Odour reductions in one area may impact processes and odours in other areas. Therefore, a consolidated and customised approach is required for each WWTP (adapted from Adams, *et al*., 2008).

4.4 Statistical Modelling to Predict Odour Formation

Statistical models used to predict odour formation can be useful tools for WWTP managers in helping them to better forecast odours and minimise the "odour footprint". For example, a computerised air dispersion model that takes into account magnitude, frequency and duration of events, and is calibrated and validated with on-site monitoring can be an effective tool to predict the impact of odour emissions (US EPA, 2000c). This type of model may determine how much and what type of control will be required to prevent or minimise odour impact (US EPA, 2000c). The information obtained from such modelling may result in design changes such as: increasing stack height or velocity, providing heat to increase thermal buoyancy or dilution with ambient air (US, EPA, 2000c).

In this section, examples of some statistical models to forecast odour levels in biosolids as well as models to predict odours in sewage treatment works will be described briefly.

Two statistical models have been reported for the prediction of DMDS levels in biosolids produced by the Blue Plains WWTP in Washington (Gabriel, *et al.*, 2005). This plant concentrates sludge from primary sedimentation basins in gravity thickeners (GT) and sludge from secondary sedimentation basins in dissolved air flotation (DAF) thickeners. The thickened sludge is then pumped into blending tanks and then fed into centrifuges for dewatering. The dewatered sludge is then treated with lime before leaving the plant (Gabriel, *et al.*, 2005). To develop the models, odorants from biosolids produced at this plant and the process variables were measured in headspace samples collected over one year. The control variables used in the models included: oxidation/reduction potential (ORP) values of GT and DAF samples; the amount of sludge dewatered by centrifuges and the blend ratio between GT thickened sludge and DAF thickened sludge in the blending tanks (Gabriel, *et al.*, 2005). The accuracy of the developed regression models was assessed by checking the adjusted R^2 of the regression as well as the signs of the coefficients associated with each variable. In general, both models performed well in predicting DMDS levels, as is illustrated in Figures 16 and 17 (Gabriel, *et al.*, 2005).
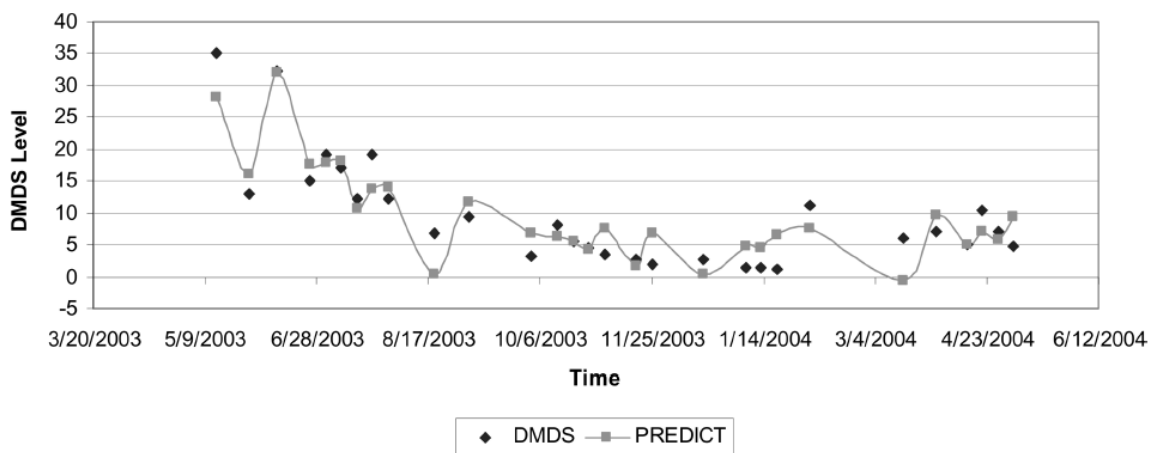

Figure 16: Comparison of Actual – vs – Predicted DMDS Levels for Model 1 (adapted from Gabriel, *et al.*, 2005).
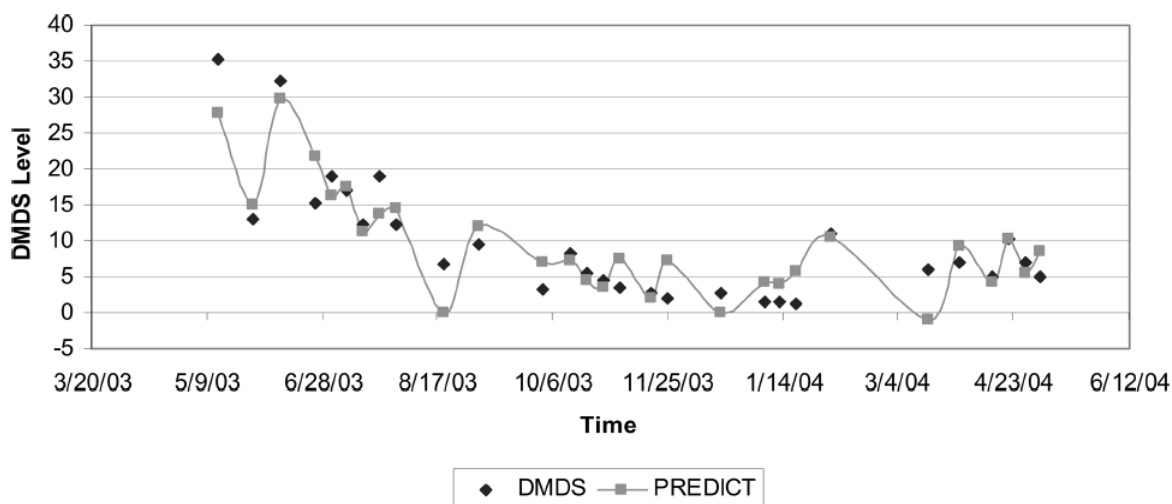

Figure 17: Comparison of Actual – vs – Predicted DMDS Levels for Model 2 (adapted from Gabriel, *et al.*, 2005).

Gabriel, *et al.* (2006) also developed several statistical models for predicting odour levels of biosolids applied to reuse sites. These models were based on data from the Blue Plains WWTP and took into account processing and management variables, such as amount of polymer used, number of centrifuges used, amount of lime added, as well as ambient conditions (e.g. temperature). These models can be used as a guide by managers at WWTPs to predict when particularly odorous biosolids will be produced based on the levels of processing and ambient variables (Gabriel, *et al.*, 2006). Thus, when highly odorous biosolids were expected, the distribution of these biosolids could be diverted to more isolated sites or immediately incorporated into the soil after application, thereby reducing the odour impact among the intended population (Gabriel, *et al.*, 2006). These models can also be used to more equitably distribute the biosolids among the intended reuse sites and to vary the processing parameters to produce fewer biosolids when required (Gabriel, *et al.*, 2006).

While statistical model such as those described above are useful in predicting odour level, the inherent tradeoffs between resulting biosolids odours and the associated operational and distribution costs should be considered (Gabriel, *et al.*, 2007). To this end, using the statistical models described above, Gabriel, *et al.* (2007) developed a multiobjective model to jointly minimise the biosolids odours as well as processing and distribution costs. The model employed linear odour function and bilinear costs (Gabriel, *et al.*, 2007). It is envisaged that managers at WWTPs could make use of this model to proactively handle odour complaints at reuse sites close to populations while being cost effective in their operations. The model has been validated using case studies from the Blue Plains WWTP and successfully demonstrated tradeoffs between odour levels and associated costs (Gabriel, *et al.*, 2007).

Witherspoon, *et al.* (2004) have developed a computer-based model, the Interceptor Model, that can assist in evaluating the odour and corrosion potential of wastewater collection systems (WCS). The model can predict the generation, transport and fate of H_2S in WCS. The major parts of WCS that can be modelled include gravity-flow sewers, force mains, inverted siphons with and without air jumpers and drop structures (Witherspoon, *et al.*, 2004). The model was developed using a mass-balance approach and used a simultaneous solution of liquid- and gas-phase steady-state mass balances to accurately represent several important reactions/processes such as: liquid-phase based generation of sulphides; temperature and BOD impacts on sulphide generation; liquid-phase bulk transport of sulphides; liquid-phase oxidation of sulphides; pH dependent sulphide species distribution; liquid-vapour mass transfer of H_2S; liquid-drag induced natural ventilation rates and vapour-phase bulk transport of H_2S (Witherspoon, *et al.*, 2004).

This model was applied to an operating WCS with known odour and corrosion problems to demonstrate the applicability of modelling in odour and corrosion assessments. The WCS examined had a location that was corroded to the point that the pipe collapsed 23 years after construction (Witherspoon, *et al.*, 2004). The model was used to predict liquid-phase sulphide and vapour-phase H_2S concentrations, corrosion rates and pipe life expectancies. The model predicted a pipe life of 26 years in the same vicinity of the system as the pipe failure (Witherspoon, *et al.*, 2004). The model also predicted that the majority of sulphide generation was present within the force main and that prevention of this generation would reduce odour and corrosion problems. The model was also used to assess liquid-phase treatment, and the results were used to recommend the appropriate treatment chemical, the location of dosing and the annual quantity as well as the cost of the chemical used. With a liquid-phase treatment in place, the model predicted that the pipe life for the WCS could be extended beyond 75 years (Witherspoon, *et al.*, 2004).

Gostelow, *et al.* (2004) reported the development of integrated odour models for annoyance prediction. The models described the liquid-phase transformations and emissions of H_2S from sewage treatment processes. The outputs from these models can then be integrated with dispersion models, which can then be used to predict odour annoyance (Gostelow, *et al.*, 2004). The models have been applied to hypothetical and real sewage treatment works. Results from simulation studies have emphasised the potential importance of emission rate variations on odour impact assessments

(Gostelow, *et al.*, 2004). Although the model only considered H$_2$S as the odour marker compound, future inclusion of other odorants is possible. The authors believe that with the incorporation of improved odour markers and improved dose-response functions, an improved odour modelling package could be developed, resulting in better assessments of odour impact (Gostelow, *et al.*, 2004).

4.5 Other Odour Control Strategies

Longhurst, *et al.* (2004) reported a risk-based approach to developing odour management plans. In this approach, odour mitigation procedures were assessed and prioritised on the basis of the likely frequency and intensity of odour exposure (Longhurst, *et al.*, 2004). A key aspect of this approach was the use of knowledge from data obtained from key stakeholder groups such as customers, staff and regulators. Development of clear communications between these groups was highlighted as it can help in raising awareness among operators about the significance of odour problems as well as managing the expectations of customers and regulators (Longhurst, *et al.*, 2004). The practical application of this approach was demonstrated by successful development of odour management plans for wastewater treatment sites by Yorkshire Water Services Ltd., which used data from staff, customers and regulators to develop risk grids which were then used to prioritise remediation measures. The end result was the implementation of low-cost emission reductions through improved housekeeping (Longhurst, *et al.*, 2004).

Winter, *et al.* (2004) studied the impact of air stripping on the odour of liquid sludge and on the quality of the dewatered product at a full-scale treatment facility. Continuous and batch air stripping modes were tested. The odour samples were collected during air stripping from the liquid sludge and from the biosolids surface during long term storage. The biosolids were also analysed for hedonic tone and for their odour potential expressed as an odour unit per unit mass (Winter, *et al.*, 2004). The following conclusions were reached:

- Dispersion modelling showed a significant reduction in overall odour impact from the sludge centre when air stripping was applied (Winter, *et al.*, 2004). The reduction was mainly related to reduction of odour emissions from stored biosolids produced from aerated sludge (Winter, *et al.*, 2004).

- The continuous air stripping mode appeared to give the highest benefits in terms of odour impact from site operations (Winter, *et al.*, 2004).

- Air stripping showed important operational advantages for the storage of biosolids. The cake dry solids were increased by approximately 5% compared to unaerated cake with an earthy appearance (Winter, *et al.*, 2004).

Bowker (2000) conducted a review of wastewater treatment plants that were using activated sludge (AS) diffusion as a means of odour reduction. The process is illustrated in Figure 18.
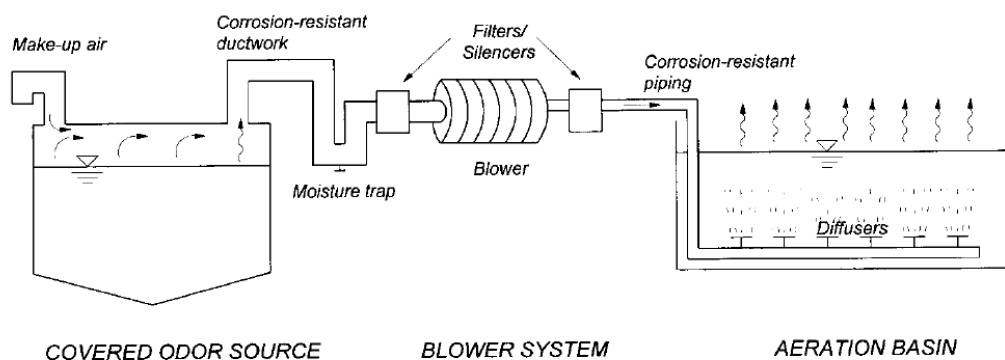

Figure 18: A Schematic of Activated Sludge Scrubbing System (adapted from Bowker, 2000).

It involves odorous air being drawn from under tight-fitting corrosion-resistant covers or enclosures by the vacuum induced by the blower. In some cases, a booster fan may be required to compensate for head losses between the odour course and the blower inlet. A moisture trap removes acidic condensate and the odorous air then is diffused into the aeration basins through standard coarse- or fine-bubble diffusers (Bowker, 2000). Several mechanisms are thought to be responsible for removing odorous compounds:

- *Absorption* – odorous compounds are transferred from the gas phase into the bulk liquid. Water-soluble compounds, such as hydrogen sulphide, are readily absorbed into the liquid. The mass of material transferred is a function of the surface area of the bubbles, the contact time, and the diffusivity coefficient (Bowker, 2000).

- *Adsorption* – high molecular weight compounds with lower solubility may be physically adsorbed onto the biological floc that is generally present at concentration levels of 1,000 to 2,000 mg/L in the liquid (Bowker, 2000).

- *Condensation* – warm, odorous air that is transferred into a liquid of lower temperature will result in condensation of volatile organic compounds (Bowker, 2000).

- *Biological oxidation* – because of the high concentration of active, aerobic microorganisms, biological oxidation is thought to be responsible for a significant conversion of odorous compounds that are initially absorbed by the liquid, adsorbed onto the floc, or condensed (Bowker, 2000).

Based on the evaluation of published and unpublished data, telephone surveys of WWTPs and experience with alternative odour reduction measures, Bowker concluded that:

- A significant number of WWTP practiced activated sludge diffusion for the treatment of odorous air (Bowker, 2000).

- The process appeared to be very effective for treatment of moderate to high strength odours and was very economical in facilities where diffused aeration was already practiced (Bowker, 2000).

- Fine bubble diffusers were more efficient in removing odours than coarse bubble diffusers when handling high strength odours, such as from sludge holding tanks (Bowker, 2000).

The performance of activated sludge diffusion as a bioscrubber for the removal of H_2S at concentrations of 25, 75 and 150 ppmv was studied by Barbosa, *et al.* (2004). The experiments were conducted on pilot scale using parallel 60-L aeration tanks and 20-L clarifier reactors at the Bedford Sewage Treatment Works, Carington, UK. Olfactometry measurements were also performed to determine whether there was any increase in odour concentration owing to H_2S diffusion (Barbosa, *et al.*, 2004). The following conclusions were reached:

- Hydrogen sulphide removal rates of 100% were obtained, with no noticeable increase in odour concentration throughout the trials as determined by olfactometry (Barbosa, *et al.*, 2004).

- Odour concentration was highest at the beginning of the trials and lowest during the high H_2S dosing period, with similar values being obtained for test and control (Barbosa, *et al.*, 2004).

- Acclimatisation of the sludge to low concentrations of H_2S improved its ability to remove peak loads (Barbosa, *et al.*, 2004).

- It was found that most of the sulphide input was degraded mainly to sulphate (SO4), and the concentration of S in SO4 corresponded to the concentration of total S (Barbosa, *et al.*, 2004).

- Assimilation of S by the biomass was also observed, with increases in the total S in the mixed liquor solids when H_2S loading increased (Barbosa, *et al.*, 2004).

- AS diffusion is an effective bioscrubber for the removal of H_2S odour and the degree of removal is dependent on the origin of the sludge (Barbosa, *et al.*, 2004).

5.0 Odour Measurement

Complaints due to odours are of significant concern to wastewater treatment facilities. In order to develop effective odour reduction strategies, accurate and objective measurement techniques are required to monitor the odorous emissions (Kim, *et al.*, 2002a, 2002b). Odour measurements can be divided into two classes: (1) Analytical measurements, which characterise odours on the basis of their chemical composition, however they provide little information about the perceived effect of odours; and (2) Sensory measurements, which use the human nose to characterise odours in terms of their perceived effect (Gostelow and Parsons, 2000). Whichever measurement technique is chosen, appropriate sampling methods should be used.

5.1 Sampling Methods

Many sampling methods have been used to determine the presence and concentration of odorous compounds. These methods usually involve collecting the sample and then using appropriate instrumentation to measure and identify the odorants (Adams, *et al.*, 2003a). Sampling devices include Tedlar bags, canisters and glass tubes filled with a variety of solid adsorption media (Adams, *et al.*, 2003a). For example, air sampling uses sampling bags or adsorption tubes to measure odour concentration at the WWTP directly. Using chemical analysis, this method measures the concentration of odorants in air at a given time, however, it is not useful for measuring the changes in biosolids odours over time (Adams, *et al.*, 2003b). Flux chamber (Kim, *et al.*, 2002a; Rosenfeld, 2001) and purge and trap (Winter and Duckham, 2000) methods have previously been used for bench-scale and full scale measurement of biosolids odours. However, these methods are slow requiring hours per sample and result in dilution of the odorants. The purge and trap method also removes the gases from contact with the biosolids, reducing the opportunity for the microbes in the biosolids to transform the odorous compounds over time (Adams, *et al.*, 2003b; Glindemann, *et al.*, 2006).

The static headspace sampling method has been reported to be a practical and comparative method for chemical and olfactometric analyses (Adams, *et al.*, 2003b; Glindemann, *et al.*, 2006). This method has been used in several biosolids odour projects (Murthy, *et al.*, 2002; Adams, *et al.*, 2003b; Higgins, *et al.*, 2004, 2006; Glindemann, *et al.*, 2006) and offers several advantages over air sampling, flux chamber and purge and trap methods. The headspace method has been reported to be representative of the biosolids storage pile interior, easier to use and highly reproducible. This method also has the advantage of continuous contact between the headspace and biosolids, ease of sampling and less equipment needs (Adams, *et al.*, 2003b; Glindemann, *et al.*, 2006). The method uses gas tight bottles for the combined purposes of sampling of biosolids at the WWTP, transport to the laboratory and static headspace analysis of odorants during storage. The method also enables comparison of the odorous samples from different treatments plants and process locations, and mimics the aging of large biosolids storage piles in both the odour generation and consumption cycles (Adams, *et al.*, 2003b; Glindemann, *et al.*, 2006).

5.2 Analytical Measurements of Odorants

It has already been established that compounds which are responsible for the odorous emissions from biosolids and biosolids processing facilities include volatile sulphur compounds, nitrogenous compounds as well as other volatile organic compounds (Section 3.1). Thus, appropriate analytical methods are required to accurately measure these compounds. The reported analytical techniques range from onsite measurements with electrochemical equipment and colorimetric sorption tubes to offsite analysis using gas chromatographs and mass spectrometers (Adams, *et al.*, 2003a).

Examples of onsite measuring devices include the Jerome Analyser, which uses a gold film sensor to adsorb hydrogen sulphide. The amount of adsorbed H_2S is measured as a proportional change in electrical resistance (Adams, *et al.*, 2003a). This instrument also has a response curve for organic sulphur compounds, however, there is no specific method for determining the individual organic sulphur compound being measured. Other electrochemical instruments have also been effective in measuring H_2S concentrations onsite (Adams, *et al.*, 2003a).

Colorimetric sorption tubes have also been used for field measurements of organic sulphur compounds. In this method, a fixed volume of air is drawn through the tube where a chemical reaction takes place, changing the colour of the adsorbent (Adams, *et al.*, 2003a). These tubes can be used to measure H_2S, DMS, mercaptans, ammonia and other odorous compounds. Sorption tubes can provide a quick indication of the odorants present in the air, even though their accuracy may vary from source to source. However, the detection limits of these devices are relatively high (>1ppmv) and other compounds may interfere with the results (Adams, *et al.*, 2003a).

Several standard analytical methods are available to industry for the measurement of sulphur compounds in air emissions and petroleum products (Sulphur Measurement Handbook; 40 CFR Part 60, Appendix A; Adams, *et al.*, 2003a). For example, US EPA Methods 15 and 16 describe methods to sample and measure sulphur in air emissions (Adams, *et al.*, 2003a; 40 CFR Part 60, Appendix A). Both methods use a gas chromatograph with a flame photometric detector (GC-FPD). Method 15 is applicable to light molecular weight compounds, such as H_2S, COS and CS_2, while Method 16 is suitable to heavier molecular weight compounds such as MT, DMS and DMDS (Adams, *et al.*, 2003a; 40 CFR Part 60, Appendix A). However, these methods are subject to interference from moisture and carbon dioxide, which may be a problem for biosolids application as biosolids emissions usually contain significant concentrations of these interferents (Adams, *et al.*, 2003a).

The use of sulphur chemiluminescence detector (SCD) has been reported for the separation, identification and quantification of sulphur compounds in the petroleum and petrochemical industry (ASTM, 1998; Yan, 2002; Adams, *et al.*, 2003a; Hua, *et al.*, 2004; Choi, *et al.*, 2004). The use of SCD has potential for application to the biosolids industry as it gives a linear response and is not as susceptible to interference from moisture and carbon dioxide (Adams, *et al.*, 2003a; Choi, *et al.*, 2004). Yan (2002) also reported the use of a chemiluminescence nitrogen detector (CLND) for the analysis of nitrogen containing compounds in the food industry and detecting ultratrace levels of nitrosamines in ground water. Thus, while there are several standard analytical methods available to industry, no standard method has been adopted by the biosolids industry for sampling and analysis of organic sulphur compounds in air samples (Adams, *et al.*, 2003a).

An analytical technique for the detection and quantification of trace levels (ng/L) of polysulphide sulphur has been reported by Heitz, *et al.* (2000). The method involved *in-situ* methylation of polysulphides with methyl iodide, followed by analysis of the resulting dimethylpolysulphides (e.g. DMDS and DMTS) by GC-MS. The method was shown to be quantitative from 0.15µg/L to 370µg/L and was not subject to interference from other sulphur compounds (Heitz, *et al.*, 2000; Franzmann, *et al.*, 2001).

Schmidt, *et al.* (1997) documented several sampling and analytical techniques to measure nonsulphur compounds. Majority of the reported techniques were based on US EPA, ASTM or other standard methods. Tedlar bags and summa canisters were most frequently used to collect gas samples from biosolids and biosolids processing plants. The nonsulphur compounds were mainly analysed by GC-MS methods (Adams, *et al.*, 2003a). For example, Chen, *et al.* (2004; 2006) have used headspace GC-MS for the analysis of odorous volatile aromatic compounds in stored biosolids.

Solid phase microextraction (SPME) has emerged as a relatively simple, inexpensive, solvent-free method to extract organic compounds from various sample matrixes, such as aqueous (Eisert and Levsen, 1995; Müller, *et al.*, 1997; Magbanua, *et al.*, 2000), headspace (Fromberg, *et al.*, 1996; Kim, *et al.*, 2002b; Huang, *et al.*, 2004) and ambient air (Haberhauer-Troyer, *et al.*, 1999). This method provides an alternative to the traditional extraction methods for the analysis of volatile compounds, for example, liquid-liquid extraction, headspace and purge and trap for aqueous samples (Hwang, *et al.*, 1995; Hauser and Popp, 2001) or porous polyurethane foam or multiple adsorbent tube traps for air sampling (Islam, *et al.*, 1998; Ma, *et al.*, 1997; Kim, *et al.*, 2002a).

Unlike other conventional methods, which require extensive sample preparation, SPME integrates sampling and preconcentration in one step. In this procedure, the compounds of interest are absorbed by a thin polymer film or by porous carbonaceous materials that are bonded to a fused silica fibre (SUPELCO, Bulletin 923, 1998; Kim, *et al.*, 2002a; Visan and Parker, 2004). Ideally, equilibrium is reached between the odour matrix and fiber, but for accuracy and precision, consistent sampling time, temperature and fiber immersion depth are more important than equilibrium (SUPELCO, Bulletin 923, 1998; Visan and Parker, 2004). SPME is compatible with analyte separation/detection by gas chromatography or HPLC and gives linear results for wide concentrations of analytes. By controlling the polarity and thickness of the coating on the fiber, 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).

The solid phase microextraction method has several applications in the water and wastewater treatment industry. For example, Kristiana, *et* al. (submitted) developed a headspace SPME-GC-MS method for the analysis of sulphide and polysulphides in drinking water distribution systems. The SPME technique has also been successfully applied to several biosolids projects. For example Kim, *et al.* (2002a, 2002b, 2003, 2005) have used SPME and GC-MS for the analysis of trimethylamine, propionic and butyric acids, and sulphur compounds (CS_2, DMS, methyl and butyl mercaptans and DMDS) in wastewater influent, thickened sludge and dewatered sludge and biosolids. Visan and Parker (2004) have used SPME-GC-MS for the analysis of TMA, DMS, DMDS and methyl mercaptan in stored biosolids. Turkmen, *et al.* (2004) have reported the use of SPME coupled with GC-MS (using selective ion monitoring (SIM)) for the analysis of DMS, DMDS, methyl merceptan, H_2S, CS_2, trimethylamine and dimethylamine in anaerobically digested wastewater sludge.

5.3   Sensory Measurements

Sensory measurements use the human nose as the odour detector and thus they relate directly to the properties of odours as experienced by humans. The problems of complex mixtures, interactions between components and detectability below the threshold of smell become irrelevant as the total effect of the overall odour is measured (Gostelow and Parsons, 2000; Gostelow, *et al.*, 2001). Sensory measurement techniques can be divided into two classes: (1) Subjective measurements in which the nose is used without any other equipment and (2) Objective measurements which use the nose together with some form of dilution instrument (Gostelow, *et al.*, 2001). Table 5 summarises the main sensory techniques.

Table 5: Summary of Sensory Odour Measurement Techniques (adapted from Gostelow, *et al.*, 2001)

Technique	Comments/Applications	Sensitivity
Subjective intensity measurement	Provides a crude indication of odour intensity, needing no equipment other than trained observers. Poor repeatability and difficulties in comparing results. Useful for preliminary identification and ranking of odour sources and also for awareness raising.	Poor
Threshold olfactometry (Objective measurement)	Expresses odour strength in terms of number of dilutions of odour-free air required to reduce sample to threshold concentration. Currently the method of choice for sensory odour measurement. Care is required in equipment design, panel selection, test procedure and interpretation of panel results. Differences in these parameters can lead to poor repeatability. The development of standards will improve repeatability, but can still expect up to factor of three difference in measured concentration between identical samples measured in the same laboratory. Insufficiently sensitive for measurement down to `nuisance' concentrations in field samples. Relatively accurate at high odour concentrations and more suited to source measurement.	20–50 oum^{-3}
Suprathreshold olfactometry (Objective measurement)	Measures odour intensity by comparing with reference odorant at known concentration. Claimed to be more repeatable than threshold olfactometry, but little evidence of dynamic suprathreshold olfactometry use for sewage odours. Suitable for field assessment?	Intensity equivalent to ~1ppm butanol

Olfactometry methods have frequently been used to measure odorous emissions from biosolids and biosolids processing plants (Williams, 1995; Lambert, *et al.*, 2000; Adams, *et al.*, 2003a). Several standard methods are available for measuring odours in air (McGinley, 2002). The most common method for measuring odour emissions involves measuring the number dilutions required to eliminate a perceived odour. ASTM Method E-697-91 has been developed for sampling and analysing odours using a panel of trained persons who determine the number of dilutions needed to eliminate the odour. The panel can also determine the intensity and character of the odour and the rate at which the intensity decreases with dilution (Adams, *et al.*, 2003a). Thus, olfactometry methods provide information to rank the intensity and persistence of emissions from various sources. For example, Hobson (1995) used olfactometry methods to determine the odour potential of different biosolids sources by bubbling air through liquids from primary clarifiers, gravity thickeners and dewatering facilities (Adams, *et al.*, 2003a). Lambert, *et al.* (2000) reported the use of descriptive terms to develop characteristic odour profiles for the comparison of fresh and stored liquid and cake sludges derived from different sites, following different treatment or dewatering processes. Olfactometry methods have also been used to measure the efficacy of odour control methods (Williams, 1995; Adams, *et al.*, 2003a) and process improvements (Hentz, *et al.*, 1996; Adams, *et al.*, 2003a).

Although olfactometry methods are useful and reflect actual human response to odours, they do not provide information on the chemical components of a gas mixture and the data provided is often insufficient to determine the cause of odour emissions (Kim, *et al.*, 2002a; Adams, *et al.*, 2003a). Also there are many external factors that influence the perception of an odour. The main factor being the variability in the sense of smell between different people. This can be minimised by using a panel of several observers and averaging individual results. Thus, great care must be taken in the presentation of samples to observers to give reproducible results. Also factors such as the order in which the samples are presented, the environment in which the testing takes place and the flow rate of the carrying gas stream are all important (Gostelow and Parsons, *et al.*, 2000; Gostelow, *et al.*, 2001). In a study of variability and method uncertainty in odour perception research, Jardine and Hrudey (1999) showed that the major source of uncertainty was panellist response and detection thresholds for pre-selected panellists, with detection limits for trained panellists ranging up to 60-fold for certain compounds (Adams, *et al.*, 2003).

5.4   Other Odour Measurement Technologies

The development of an electronic nose has been reported in the literature (Ziegler, *et al.*, 1998; Gostelow, *et al.*, 2001; Bos, 2004; Mahmoudi, 2009). The electronic nose is designed to detect and discriminate among complex odours using an array of sensors. This array of sensors consists of a number of broadly tuned (non-specific) sensors that have been treated with a variety of odour sensitive biological or chemical materials (Mahmoudi, 2009). A variety of different sensors are currently used in the electronic noses including metal oxides, conductive polymers, piezoelectric crystal and fibre optics (Gostelow, *et al.*, 2001; Mahmoudi, 2009). The number of sensors used in a sensor array typically varies between 5 and 20 (Gostelow, *et al.*, 2001). An odour stimulus generates a characteristic fingerprint from this array of sensors. Patterns of fingerprints from known odours are then used to construct a database and train a pattern recognition system so that unknown odours can then be classified and/or identified (Mahmoudi, 2009). An electronic nose usually consists of three key elements: a sensor array which is exposed to the volatiles, conversion of the sensor signal to a readable format and software analysis of the data to give characteristic outputs related to the odour. The output from the sensor array can be interpreted using a variety of methods such as pattern recognition algorithms, principal component analysis, discriminant function analysis, cluster analysis or artificial neural networks to discriminate between samples (Mahmoudi, 2009). The choice of technique will depend on the amount and nature of information available on the range of different test samples that could potentially be measured by the sensor array and the type of information required from the analysis (i.e. quantitative or qualitative) (Gostelow, *et al.*, 2001). The outputs can range from a simple yes/no response to ascertain the presence of a certain odour, estimates of concentration levels

or characterisation in terms of organoleptic properties such as used in the food, beverage and perfume industries (Gostelow, *et al.*, 2001).

The electronic nose provides a rapid, simple and non-invasive sampling technique for the detection and identification of a range of volatile compounds and is thought to mimic the human olfactory system (Muhmoudi, 2009). These devices can identify simple or complex gas mixtures and have been used to detect odorous chemicals, in particular amines, volatile fatty acids, alcohols and sulphurs from food (Paolesse, *et al.*, 2006; Casalinuovo, *et al.*, 2006; Vestergaard, *et al.*, 2007), and cattle, pig and chicken slurries (Persaud, *et al.*, 1996; Hobbs, *et al.*, 1995; Misselbrook, *et al.*, 1997; Gallmann, *et al.*, 2004). This technology has also been applied to odour measurements from sewage treatment works (STWs) (Stuetz, *et al.*, 1998, 1999a) and characterisation and monitoring of wastewater and potable water (Stuetz, *et al.*, 1999b; Fenner and Stuetz, 1999; Stuetz, *et al.*, 2000; Bourgeois, *et al.*, 2001; Di Francesco, *et al.*, 2001; Bourgeois and Stuetz, 2002; Canhoto and Magan, 2003; Bourgeois, *et al.*, 2003a, 2003b). Based on the available literature, this technique may also be applicable to the biosolids industry.

6.0   Conclusions and Recommendations

This literature review examined various aspects of odour formation in biosolids, odour reduction/control strategies and odour measurement. Based on the literature surveyed, the following conclusions and recommendations can be made:

- Compounds associated with odours include volatile organic sulphur compounds such as MT, DMS and DMDS, as well as inorganic sulphur compounds such as H_2S, nitrogenous compounds such as TMA and ammonia and potentially volatile fatty acids. Other organic compounds such as terpenes, acids, aldehydes, alcohols and ketones have also been reported and odorous volatile aromatic compounds such as skatole, indole, toluene, ethylbenzene, styrene and *p*-cresol have been identified in headspace samples from stored biosolids.

- Proteins are thought to be the precursors to the volatile organic sulphur compounds, inorganic reduced sulphur compounds, nitrogenous compounds and the odorous volatile aromatic compounds.

- Volatile fatty acids are formed from the breakdown of starch, cellulose and hemicelluloses by acid forming bacteria.

- Aldehydes and ketones can be formed during anaerobic degradation of cellulose, starch, hemicellulose and pectins.

- A strong correlation exists between the odours produced by biosolids from anaerobic digestion and the concentration of volatile sulphur compounds in the headspace of biosolids samples.

- Protein concentration and, in particular, the concentration of methionine have been found to be well correlated with the production of odorous VSCs.

- The most cost effective approach to odour control may be the examination of the operational and maintenance practices at the biosolids processing facility.

- Due to the differences in biosolids characteristics, treatment processes and operating conditions between different wastewater treatment plants, the chosen odour reduction strategies need to be based on the site-specific conditions at each WWTP.

- Odour reduction measures may include design changes that could be implemented during the design of new WWTPs, development of new unit processes for existing WWTPs or engineering modifications to existing processes. Odour reduction strategies may also incorporate operational changes that involve modifying process operations at an existing WWTP, either by adjusting operational parameters of processes or equipment, or *via* chemical addition.

- Since proteins have been identified as the major precursors to odorous compounds in biosolids, odour control strategies could be aimed at reducing the amounts of bioavailable protein in the

cake. For example, more complete degradation of protein during digestion would reduce the available substrate for odour production. Greater SRTs and pre-digestion treatments, which aim to improve digestibility of solids may aid in removing protein.

- Based on the WERF study which examined the operational parameters of 11 different WWTPs, the highest concentrations of headspace odorous gases were generated by samples taken after dewatering compared to other locations within the plants.

- 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).

- Shear created by centrifugation may release protein, providing substrate for odorant production. Therefore, dewatering processes should be operated and designed to minimize shear thereby reducing the amount of bioavailable protein.

- Methanogens can degrade VOSCs, thus one possible odour control strategy is the preservation and enhancement of methanogenic population during biosolids storage. The methanogenic bacteria are sensitive and slow-growing, thus it is important to maintain optimum environmental conditions such as temperature and pH.

- Advanced digestion processes such as multi-phased digestion, egg-shaped digesters, thermophilic digestion or a series operation of digesters all appeared to be effective to some extend in reducing biosolids odour emissions.

- A pre-digestion treatment such as the MicroSludge^{TM} process reduced the peak TVOSC emissions of digested and dewatered biosolids cake by 50% compared to conventional mesophilic digestion.

- Addition of alum to a high-solids dewatering centrifuge resulted in lower TVOSC emissions from dewatered biosolids.

- Statistical models used to predict odour formation can help WWTP managers to better forecast odours and minimise the "odour footprint".

- Analytical measurements characterise odours on the basis of their chemical composition and thus can help determine the cause of odour emissions, however they provide little information about the perceived effect of odours.

- Sensory measurements (i.e. olfactometry) use the human nose to characterise odours in terms of their perceived effect.

- Several sampling and analytical techniques are available for the analysis of odorous compounds in biosolids. For example, the static headspace sampling method has been described as a practical and comparative method for chemical and olfactometric analyses. This method has been applied to several biosolids odour projects and offers several advantages over other sampling methods. Solid phase microextraction has been reported to be a relatively simple, inexpensive, solvent-free method for the extraction of organic compounds from various sample matrixes. Coupled with gas chromatography-mass spectrometry, this method has been successfully used in several biosolids projects for the analysis of volatile sulphur compounds, nitrogen containing compounds and volatile fatty acids.

- Olfactometry methods have frequently been used to measure odorous emissions from biosolids and biosolids processing facilities.

- A standard method has been developed for sampling and analysing odours using a panel of trained persons who determine the number of dilutions needed to eliminate the odour. This panel can also determine the intensity and character of the odour and the rate at which the intensity decreases with dilution.

- Several external factors, such as the variability in the sense of smell between different people, can influence the perception of an odour. Therefore, care should be taken in selecting the panel, the presentation of samples to observers to give reproducible results and ensuring optimal environmental conditions for testing of samples.

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APPENDIX

Summary of Findings and Recommendations for Odour Reduction

SUMMARY OF FINDINGS AND RECOMMENDATIONS FOR ODOUR REDUCTION IN BIOSOLIDS

- Proteins have been identified as the major precursors to odorous compounds in biosolids, so odour control strategies could be aimed at reducing the amounts of bioavailable protein in the cake. For example, more complete degradation of protein during digestion would reduce the available substrate for odour production. Greater SRTs and pre-digestion treatments, which aim to improve digestibility of solids may aid in removing protein.
- Based on the WERF study, the highest concentrations of headspace odorous gases were generated by samples taken after dewatering compared to other locations within the plants.
- 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). Shear created by centrifugation may release protein, providing substrate for odorant production.
- Methanogens can degrade VOSCs, thus one possible odour control strategy is the preservation and enhancement of methanogenic population during biosolids storage. The methanogenic bacteria are sensitive and slow-growing, thus it is important to maintain optimum environmental conditions such as temperature and pH.

The table below summarises the findings and recommendations for odour reduction in biosolids. The findings and recommendations are mainly based on the multi-phase study funded by WERF in which 11 WWTP across the USA participated.

PROCESS	FINDING	DESIGN RECOMMENDATION	REFERENCE
Anaerobic digestion	• Longer SRT during mesophilic anaerobic digestion resulted in lower TVOSC emissions from dewatered cakes. Lab data showed 1/3 reduction in TVOSC could be obtained by increasing digestion SRT from 15 to 30 days.	• Could do minimum SRT of 20 days during peak loading periods and 30 days SRT for average loading rates.	• Adams, G.A., *et al.* (2008)
Thermophilic Anaerobic digestion	• Biosolids associated with digestion temp >53°C yielded an 83% reduction in total headspace VOSCs compared to mesophilic biosolids and a 71% reduction when compared to low temperature thermophilic (49°C) biosolids. • Treatment at higher temperatures (55°C, 57.5°C) showed evidence of inhibition of methanogenic activity. • The optimal digestion temperature that minimised both the production of odours and H_2 accumulation was approx. 53°C.	• Investigate increasing digestion temperature to the thermophilic range, if possible.	• Wilson, C.A., *et al.* (2006) • Wilson, C.A., *et al.* (2008)
Sequential Anaerobic/Aerobic Digestion	• Using sequential anaerobic/aerobic digestion, volatile solids removal was more than 60%. • Improvement in biosolids dewatering properties was also observed (less polymer was required). • Combined soluble protein and polysaccharides present in anaerobic digester were reduced by 85% after aerobic digestion. • Using sequential anaerobic/aerobic digestion, it	• Sequential anaerobic/aerobic digestion is a promising technology for waste water sludges.	• Kumar, N., *et al.* (2006) • Subramanian, S., *et al.* (2007)

PROCESS	FINDING	DESIGN RECOMMENDATION	REFERENCE
	was observed that sludges digested under thermophilic anaerobic conditions produced approx 30% less odorants than mesophilic digested biosolids and the additional aerobic digestion step reduced odorants by a further 40%.		
Pre-Digestion Treatments: The MicroSludge™ Process	• The MicroSludge process reduced the peak TVOSC emissions of digested and dewatered biosolids cake by 50% at one WWTP, compared to conventional mesophilic digestion. • It appeared that destruction of odour precursors such as bioavailable protein during digestion was enhanced by the MicroSludge treatment of waste activated sludge prior to digestion.	• Consider piloting the MicroSludge™ process of similar type of pre-digestion treatment instead of conventional mesophilic digestion at longer SRTs. • By breaking down the digester feed sludge and making it more amenable to anaerobic digestion, a pre-treatment process such as Microsludge™ may be more cost effective than increasing SRT , depending on the site-specific conditions of the plant.	• Adams, G.A., *et al.* (2008) • Rabinowitz, B. and Stephenson, B. (2005a). • Rabinowitz, B. and Stephenson, B. (2005b) Rabinowitz, B. and Stephenson, B. (2006) • Novak, J.T., *et al.* (2007) WERF Odour

Advanced Digestion Processes	• Multi-phased digestion, egg-shaped digesters and thermophilic digestion appear to be effective to some degree in reducing biosolids TVOSC emissions when compared with conventional mesophilic digestion.
	• TVOSC reduction was related to more complete degradation of proteins as odour precursors.
	• In addition to longer SRTs, the following factors could contribute to better protein destruction:
	  ➢ More efficient and vigorous mixing (egg-shaped digesters)
	  ➢ Higher digestion temperatures speed up anaerobic biological activity
	  ➢ Phased digestion in various forms, e.g. two-phased (acid-gas) or temperature phased (thermophilic followed by mesophilic) digestion
	  ➢ Series operation of digesters is more effective at protein degradation than single-stage digestion.
	• In general research of advanced digestion processes indicated that VS destruction of >50% could be achieved with most advanced digestion processes and even 55% to 60% VS destruction
		• Consider potential advantages of implementing a more advanced digestion process that incorporates one or more of the odour reduction measures, particularly if a new anaerobic digestion system is required, rather than modifying an existing system.
		• Site-specific bench-scale testing and evaluations of advanced digestion processes, followed by onsite piloting of the chosen process are recommended prior to design of full-scale facilities.
			• Adams, G.A., *et al.* (2008)

PROCESS	FINDING	DESIGN RECOMMENDATION	REFERENCE
	has been observed in some cases. • Proportionately higher % of odour precursors are destroyed when VS destruction in digestion is >50%.		
Chemical addition (Iron and Aluminium)	• In general, increase in Fe concentration in sludge or biosolids resulted in higher TVOSC concentrations in the dewatered biosolids headspace, especially if Fe was added prior to or during digestion. • Addition of ferric chloride ($FeCl_3$) to anaerobically digested solids before dewatering did not reduce TVOSC emissions from cake until $FeCl_3$ dose was at least 8% on a dry mass-mass basis and also required additional lime addition to maintain near neutral pH. • Effectiveness of Fe addition in reducing odours seemed to be dependent on the characteristics of biosolids and other factors. • Higher concentrations of aluminium in raw sludge of digested biosolids resulted in lower TVOSC emissions from dewatered biosolids. • In lab trials, the lowest dosage examined of 0.5% alum reduced the peak TVOSC concentration by about 83%. • Field trials of alum (aluminium sulphate) addition improved odour quality, but not to the same extend as the laboratory trials. • Aluminium forms tighter bonds with organic sulphur compounds than iron, especially under the reduced conditions of anaerobic digestion, therefore organic material bound with aluminium will not be released as easily and iron-bound material when biosolids are sheared during centrifuge dewatering.	• The relationship between iron, aluminium and TVOSC generation may provide a useful tool for predicting if a raw sludge is likely to generate odours after anaerobic digestion and thus is worth investigating further. • Further investigation of an improved field application of alum is recommended to achieve better odour control of biosolids.	• Adams, G.A., *et al.* (2008) • Subramanian, *et al.* (2005)
Dewatering	• TVOSC emissions from cakes dewatered by med-solids centrifuges (1800rpm bowl speed) were about ½ of the emissions from cake dewatered by high-solids centrifuges (2200rpm). • Dry solids conc. of biosolids dewatered by med-	• Investigate feasibility of adjusting centrifuge main bowl speed and torque levels and analyse samples for dry solids content and odour characteristics at each of the settings.	• Adams, G.A., *et al.* (2008) • Murthy, S., *et al.* (2006) • Murthy, S., *et al.* (2003) • Murthy, S., *et al.* (2003)

PROCESS	FINDING	DESIGN RECOMMENDATION	REFERENCE
	solids centrifuges was slightly lower than those dewatered by high-solids centrifuges but the reduction in TVOSC was greater in proportion to reduction in solids conc. • A 10% reduction in centrifuge bowl speed (2200 to 2000rpm) on one high-solids centrifuge resulted in 20% reduction of TVOSC emissions from dewatered cake with no observed reduction in cake solids conc. • 15% reduction in torque resulted in almost 40% reduction in TVOSC emissions from dewatered cake but solids conc. was also reduced by 15-20%. • TVOSC emissions from digested biosolids dewatered by belt filter presses or rotary presses were significantly lower than TVOSC emissions from same biosolids dewatered by high-solids centrifuges, but the dry solids conc. of biosolids dewatered by belt filter presses or rotary presses were lower than the centrifuged cake.	Or • Continue using belt filter presses if feasible and cost effective. • If BFP biosolids cakes are not as dry as centrifuged cakes, it has been shown that desiccation of cakes (using a desiccant) or air-drying cakes to 35% dry solids content followed by anaerobic storage, did not generate VOSC emissions.	
Cake conveyance	• Increasing shear on dewatered cake can increase odour potential.	• Use conveyance devices low in shear, e.g. belt conveyors are usually preferred to screw conveyors or cake pumps.	• Adams, G.A., *et al.* (2008)
Cake storage	• Odours from dewatered biosolids can be reduced during storage due to growth of odour-consuming methanogens in stored biosolids cake as shown by rise and fall in TVOSC concentrations in sample bottle headspaces when analysed over bottle incubation period of 2-4 wks. • In most experiments involving mesophilic anaerobic digestion, peak TVOSC conc. occurred after 5-9 days and then decreased to levels of only 20% of peak after 15-20 days. • Biosolids that have been stored to several wks have a methanogenic population that has recovered from the stress of dewatering and are actively degrading VOSCs.	• Make provisions for onsite storing and aging dewatered biosolids for a 2-4 wk period prior to transport and land application. • Conduct bottle storage and headspace analyses of dewatered biosolids daily over a 3-4 wk period in order to determine the rise and fall characteristics of TVOSC for each type of biosolids from each WWTP. • Spike fresh biosolids with the stored biosolids which can provide early establishment of a methanogenic population which can reduce net odour production. • Maintain optimum environmental conditions for good methanogenic population.	• Adams, G.A., *et al.* (2008) • Chen, Y., *et al.* (2005)