

***Investigating the Role of Various Environment and Process Conditions in  
Wastewater Sludge Odor Generation***

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## **ABSTRACT**

Dewatered sludges and biosolids generated from wastewater treatment facilities are known to emit malodorous odors causing public inconvenience. The odors typically comprise of reduced organo sulfur based compounds and nitrogen containing compounds. Lime stabilization is a technique which is commonly used in the wastewater industry to produce biosolids having reduced odors that can be safely land disposed. In this research, odors produced from dewatered sludges and lime stabilized biosolids were investigated.

Lime dosing and incorporation in sludge play an important role in generation of reduced sulfur and trimethylamine (TMA) odor compounds. Results revealed that poor lime dosing can lead to an increase in odors due to biological generation of volatile sulfur compounds (VSCs) during storage. In this study, a belt filter press gave a higher production of sulfur and TMA odors compared to a vacuum filter for the same sludge, which is attributed to the shear imparted to sludge during the dewatering process. Preliminary studies suggested incomplete mixing of lime with sludge led to biological activity. The achievement of the correct pH and its maintenance during storage is considered critical for effective odor management from lime stabilized biosolids.

A positive linear relation was obtained between sulfur based odor production and labile protein content in sludge. Furthermore, as the Al/Fe ratio increased, the labile proteins was observed to decrease. Trivalent metals are found to play an important role in binding of labile proteins thus effecting odor potential contained in sludge/biosolids. This was found true for most sludge irrespective of their liming status and independent of upstream process conditions. Further work in this area is needed to be able to provide a better understanding of odor production to aid in development of odor control techniques.

Trimethylamine odors, having a characteristic fishy odor, are commonly found in lime stabilized biosolids. Cationic polymers used as dewatering aids are the primary precursors for TMA production. Proteins present in sludge are also associated with odor forming compounds but they produce much lower levels than polymers. These two components under the action of shear present in dewatering devices such as centrifuge are more likely to cause an increase in odor production from lime stabilized biosolids. It was also determined that abiotic polymer degradation to produce TMA either does not occur, or the rate is so slow that TMA production in this way is insignificant for actual field situations.

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## Chapter 1: Literature Review

### Introduction:

Biosolids is the term designated for treated municipal wastewater sludge having a reduced biological activity such that it can be land applied. Biosolids typically refer to processed sludge in solid form though the term can be extended to processed sludge in liquid or semi liquid form as well (Evanlyo, 1999). In the United States more than 10 million tons of biosolids are generated each year of which about 65% is recycled. Class A is a designation used to refer to biosolids that can be directly used for land application because of its high quality. Class B biosolids, however, have restrictions to its land application and disposal.

One major concern with the land disposal of biosolids is the generation of objectionable odors. Biosolids are abundant sources of food for microorganisms in the form of proteins, amino acids and carbohydrates (EPA, 2000a). The degradation of these compounds is the cause of malodorous odor emissions. The odors typically identified from a wastewater processing facility or land application site containing biosolids are reduced sulfur compounds, nitrogen based compounds and organic fatty acids (WEF, 1995). Stored sewage sludges continuously release malodorous odors and tend to smell worse during transport and ensuing movement due to sudden release of accumulated odors (Lambert and McGrath, 2000a).

Solving problems related to wastewater sludge/biosolids odors is of increasing interest due to complaints from public residing in the vicinity of wastewater treatment plants and disposal locations for biosolids. Wastewater sludge stabilization involves the use of biological or chemical processes to achieve a reduction in odor potential and eliminate pathogenic activities. Anaerobic and aerobic digestion has been traditionally used for stabilizing sludge generated from wastewater treatment facilities. Other measures include lime/alkaline stabilization or composting following the dewatering process. Lime or alkaline treatment offers extra benefits (NLA, 1999; Mendez et.al, 2002; Akrivos et.al, 2000) in addition to achieving stabilization of sludge. These are lower capital and operational costs, reduced hydrogen sulfide

generation and metals leachability and provision of an environmental-friendly alternative for beneficial reuse of biosolids.

Two classes of malodorous odor compounds are the focus of this research: sulfur based compounds comprising of hydrogen sulfide (HS), methanethiol (MT) (methyl mercaptan), dimethylsulfide (DMS) and dimethyldisulfide (DMDS) and the nitrogen based compound – trimethylamine (TMA). In addition to these, there are other compounds such as carbon disulfide, dimethyltrisulfide (DMTS), ammonia, indole and skatole which contribute to the odor potential contained in dewatered sludges/biosolids.

### **Volatile sulfur compound odors in the environment:**

Characteristic odor compounds having a sulfur base are detected in headspace of dewatered sludge/biosolids, both pre and post stabilization. Winter and Duckman (2000) found significant amounts of sulfide compounds, DMS, DMDS and DMTS in sewage sludge after stabilization. Anaerobically digested sludges are known to emit volatile sulfur compounds (VSCs) comprising mainly of MT (Novak et.al, 2004). VSCs are reported to be by-products from industries like tanneries and paper mills. In addition to being a universal odor problem, VSCs can also contribute to other harmful effects such as causing acid rain and corrosion of steel and concrete structures. HS can be quite lethal when present at high concentrations, but typical emissions from wastewater treatment plants are not a threat to human health (Abalos et.al, 2002). Organic sulfur compounds have been found to build up in a variety of environment such as dentistry, medical areas, chemical industries etc. Sulfur bearing organic compounds are known to first oxidize into sulfur oxides and then be reduced to sulfates in secondary particulate formation (Muezzinoglu, 2003).

**TMA odors in the environment:**

TMA has a pKb of 9.81 (Novak et.al, 2002) with a characteristic fishy odor. TMA odors are known to emanate from lime stabilized biosolids along with DMDS (Kim et.al, 2001). Quicklime and calcium hydroxide (hydrated lime) are commonly used liming agents for stabilizing sludge (NLA, 1999). TMA formation is not due to a chemical breakdown of organic compounds, but is a result of a pH and temperature mediated physico-chemical process (Murthy et.al, 2002c). The same results were obtained by Kim et.al (2002a) who detected TMA along with ammonia in the headspace of only post limed samples. TMA is known to be associated with the sludge matrix in the ionized form with a sludge/headspace partition coefficient of 300 (Novak et.al, 2002). As the pH is raised beyond the pKb for TMA, liquid phase TMA is converted to its un-ionized form followed by gradual emission over storage time (Murthy et.al, 2002c). The authors further reported that TMA emission from limed biosolids is a function of initial ionized TMA concentration in the sludge.

**Properties of select odor compounds of interest:**

<b>Compound</b>	<b>Odor Description</b>	<b>Threshold (ppm)</b>
Hydrogen Sulfide	Rotten Eggs	0.5-10.0
Dimethylsulfide	Decayed Cabbage	2.5-50.8
Dimethyldisulfide	Vegetable Sulfide	0.1-346.5
Methanethiol	Sulfidy	2.10
Trimethylamine	Ammonical, Fishy	0.8

(Source: EPA, 2000b)

## **Proteins as precursors for odor forming compounds:**

Microbial metabolism and cell lysis release biopolymers (proteins and polysaccharides) in wastewater sludges (Grady et.al, 1999). Proteins containing amino acid groups as monomeric building blocks are considered to be the primary precursors for formation of odor compounds. Cysteine and methionine are known to be present in proteins extractable from activated and anaerobically digested sludges. This protein remains unmetabolized as long as the digestion/stabilization process does not make them bioavailable. The bioavailability of proteins is considered to be the key process in release of odor compounds from wastewater sludges/biosolids. As much as 40% of volatile solids remaining after digestion as part of residual biological activity are speculated to be comprised of undegraded proteinaceous material. Frølund et.al (1996) have shown that 50% of the extracellular polymeric substances (EPS) in sludge is comprised of proteins. The protein is known to degrade enzymatically under anaerobic conditions to form odor compounds or their precursors (Kim et.al, 2001).

Exocellular proteins are also known to influence floc structures and settling characteristics of sludge. The cation bridging model postulated by Higgins et.al (1997) explains the role of cations acting as a bridge connecting the negatively charged sites in the biopolymer within sludge. Higher concentrations of divalent cations are responsible for increased bound protein content in the sludge matrix as opposed to higher concentrations of monovalent cations like sodium or potassium which decrease the bound protein levels in sludge. The presence of polysaccharides is also known to influence exocellular characteristics of sludge, although its effect on odor generation profiles is not known at this time. A study by Morgan et.al (1990) showed that activated sludge is more electronegative than anaerobic sludges. On the other hand protein content was estimated to be higher in the latter compared to activated sludge which had a larger fraction of carbohydrate contributing to EPS. Anaerobic conditions also gave a higher protein release into solution than aerobic conditions (Novak et.al, 2003). Dignac et.al (1998) characterized EPS in activated sludge using sonication or a combination of sonication and cation exchange resin (CER) treatment. Proteins were found to be major constituents and they concluded that proteins had a more important role in defining

floc structure because of their predominance in electrostatic bond formation with multivalent cations.

### **Role of shear and polymer:**

Shearing of sludge that occurs in dewatering devices such as centrifuge and belt filter press is known to significantly influence the production of odors. Basu et.al (2004) reported that shear energy enhances the digestibility of a sludge leading to better VS destruction. This is due to proteins being rendered bioavailable under application of shear energy. Muller et.al (2004) further showed that the same explanation could be given for an increase in odor potential when subjected to mechanical shear. Their studies were conducted using a laboratory KADY mill imparting shear to the sludge. High speed centrifuges gave a higher production of VSC compared to low speed centrifuges. Further, a combination of screw conveyance following dewatering by centrifugation produced almost three times more odor than that produced by centrifugation alone (Murthy et.al, 2002a). These workers also developed a model correlating the increase in labile protein content in biosolids to the increase in applied shear. The subsequent degradation of labile proteins under conditions of shear resulted in an increased production of VSCs particularly MT (an order of magnitude of almost 16 times) compared to VSCs production under unsheared conditions.

Polymer added to sludge to aid the dewatering process is documented to increase odor potential (Higgins et.al, 2002b; Muller et.al, 2004). This was reported to be due to association of proteins from floc with added polymer. Murthy et.al (2001, 2002b) have theorized that cationic polymer conditioning of sludge prior to dewatering raises odor potential, especially for production of TMA. Proteins and polymers in biosolids are thought to be enzymatically broken down and on consequent lime addition, cause the release of TMA and DMDS (Kim et.al, 2001; Turkmen et.al, 2004). It is further suspected that the shear could cause breakdown of the polymer linkages which might contribute to an increase in TMA production.

## **Mechanisms of sulfur odor generation and consumption:**

Several pathways are thought to be responsible for the generation of sulfur based odors. Lomans et.al (1999) conducted studies with Bromoethansulfonic (BES) acid and sodium tungstate as methanogenic and sulfate reduction inhibitors respectively and showed that methanogenesis is the major mechanism for DMS and MT consumption in fresh water sediments. Aerobic degradation of DMS occurred at a higher kinetic rate compared to anaerobic degradation especially under conditions when oxygen was rate limiting. In another of their experiments, methylation reactions were found to transform sulfide and MT into MT and DMS respectively. Using syringate as a methyl group donating compound and a sole carbon source, an anaerobic bacterium *methanomethylorans hollandica* was isolated and shown to transform HS and MT through an anaerobic methylation metabolism. They further demonstrated that methanogens and sulfate reducing bacteria in the presence of sulfate can degrade MT and DMS thus continuing the VOSC degradation cycle (Lomans et.al, 2002a). Anaerobic o-demethylation of methoxylated aromatic compounds such as syringate and 3, 4, 5 trimethoxy benzoate is also recognized to yield formation of DMS and MT (Lomans et.al, 2002b). Abiotic production of DMTS is identified to occur under addition of methylating agents, methyl iodide or methyl-*p*-toluene sulfonate. Biomethylation, a commonly used approach by microorganisms as a detoxifying mechanism generates DMDS and DMTS from biofilm oligosulfides (Franzmann et.al, 2001). Biodegradation of *Peridinium gatunense* lysis products under aerobic conditions is known to yield DMS and DMDS (Ginzburg et.al).

These findings were corroborated by Higgins and co workers (2002a) and they summarized the production and consumption cycle for VSCs as follows.

1. Amino acids as odor precursors

Proteins-----> Peptides-----→Methionine-----→MT

2. Methylation reactions with formation of MT as intermediate

Methyl donating group + HS -----→ MT (reaction 1)

Methyl donating group + MT -----→ DMS (reaction 2)

3. Abiotic oxidation reaction

DMS + oxygen -----→ water + DMDS

4. Methanogenic degradation of VSCs

MT, DMS and DMDS -----→ HS

DMS can undergo oxidation in the atmosphere by hydroxyl and nitrate radicals producing degradation products such as carbon dioxide, sulfate, organic oxyacids of sulfur, dimethyl sulfoxide etc. DMS has also been reported to form from storing and crushing broccoli, in dairy products and alcoholic beverages (Bentley et.al, 2004). Cha et.al (1999) successfully isolated strains of *Thiobacillus novellas* SRM from sewage sludge which was able to remove HS, MT, DMS and DMDS at various rates under immobilized conditions. Hirano et.al (1996) developed a bacterial deodorant which simultaneously removed HS and TMA from kitchen garbage. The bacterial deodorant consisted of *Thiobacillus thiooxidans* JCM7814 cells which oxidized HS biologically in presence of sodium citrate buffer. TMA was removed abiotically through a neutralization reaction with citric acid from the buffer.

**Odor detection methods:**

Before the development of analytical procedures, odors were quantified using olfactometry; wherein an odor panel conducts a sensory analysis of odorous air samples. Results are expressed in the form of dilution to threshold ratio indicating the number of dilutions required to reach the odor threshold for a particular analyte. Another method known is the butanol wheel method based on the same principle as olfactometry (EPA, 2000b). Lambert

et.al (2000b) proposed 'odor fingerprints' for characterizing olfactometric profiles of commonly grouped odor compounds based on standard descriptive terms. Other methods include the use of sorbent tubes coupled with gas chromatography and newer techniques like the electronic nose. These methods have not been very successful for wastewater odor analyses either because they are too impractical or too undeveloped at this stage to conveniently assess multiple samples with repeated accuracy (Kim et.al, 2002b).

Pericas et.al (2004) used Liquid Chromatography (LC) for analysis of liquid phase TMA and successfully quantified TMA in water samples amidst presence of other primary and secondary short-chain aliphatic amines. More recently Solid Phase Microextraction (SPME) followed by Gas Chromatography/Mass Spectrometer (GC/MS) has been used for analysis of VSCs from wastewater treatment plants (Hills et.al, 1999; Abalos et.al 1999). Other methods include the use of Gas Chromatography/Flame Photometric Detector (GC/FPD) and Gas Chromatography/Nitrogen Phosphorous Detector (GC/NPD) with a purge and cold trap method (Hwang et.al, 1995). SPME followed by GC/NPD has been used for determination of free volatile amines in wastewater samples giving detection limits in the low to mid ppb levels and the procedure was found to be linear over one order of magnitude (Abalos et.al, 1999; Hill and Smith, 2000). SPME has also been used for measurement of low levels of odorous gases from wastewater, sludge and biosolids due to its advantage over traditional methods like olfactometry because of its convenience and relatively low cost. The method can be used to capture odorous compounds on site with the added benefit of being capable of continuously monitoring samples with some modifications (Kim et.al, 2002a).

The analyses of samples in this project was conducted using a static headspace method in which samples were taken directly from headspace of incubating vials and injected into a GC/MS (Novak et.al., 2002). This method was found to be very convenient for analyzing large number of samples in a relatively short time with reliable accuracy.

### **Role of chemicals in odor production and also as a means for odor abatement:**

The effect of chemical addition like ferric chloride ( $\text{FeCl}_3$ ) on odor generation from dewatered sludge cakes was investigated by Higgins et.al (2002b). Studies revealed that high doses of  $\text{FeCl}_3$  prior to dewatering gave low production of malodorous sulfur odors. The authors thought that this was due to binding of odor compounds or their precursors by iron in the +3 oxidation state. Calcium based compounds when added post the dewatering stage also helped in reducing odors from sludge/biosolids. Other commonly used odor control techniques in wastewater industry include addition of metal salts, nitrates and chemical oxidants like chlorine, hydrogen peroxide, ozone etc. HS can be removed by precipitation using metal ions such as iron and zinc (de Luca et.al, 1996).

Addition of fly ash to sewage sludge during lime stabilization can lower the lime requirement still yielding a class A biosolids product with low odor potential (Abu-Orf, 2004). Solid characteristics upstream of the wastewater treatment process impacts the production of VSC from dewatered sludge downstream. The reason for this solids influence on odor generation is not yet identified and maybe a function of either chemicals present in the sludge or variation in the wastewater treatment process itself (Murthy et.al, 2003). Organo sulfur compounds can be removed chemically by methods like charcoal adsorption, incineration and chemical washing. The use of these methods is however inhibited due to high capital and operational costs.

### **Role of metals:**

Sodium, potassium, ammonium, calcium, magnesium, iron and aluminum are cations commonly found in wastewater sludge (Park, 2002). Trivalent cations are acknowledged to have a greater impact on sludge characteristics than divalent cations due to their stronger association with sludge matrix. Iron is known to undergo reduction from Fe (III) to Fe (II) by iron reducing bacteria (Rasmussen et.al, 1996; Caccova et.al, 1996). Ferric iron has been shown to have a higher affinity for proteins (Novak et.al, 2003). They also concluded that large quantities of proteins are released during anaerobic digestion process which can be attributed to

specific binding of proteins with ferric iron. The influence of aluminum on sludge characteristics is not known. However it is believed that the relative proportions of iron and aluminum can significantly alter the binding of proteins thereby effecting sludge quality and odor production profiles.

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## Chapter 2: Manuscript 1

### **Inter-relation between trivalent cations and labile proteins and its influence on odor production from wastewater sludges and biosolids.**

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### **ABSTRACT**

Odor production from solids handling processes in wastewater treatment has long been a matter of concern. In this study, the production of malodorous odors from lime stabilized biosolids at three wastewater treatment plants in the Washington DC area was investigated along with the role of trivalent cations in odor production.

In phase one, it was found that production of total sulfur and TMA odors over time was influenced by the lime dose and the incorporation of lime into sludge. Shear conditions present in belt filter press produced higher quantities of odors compared to a vacuum filter. Pre liming, used to provide better lime incorporation into sludge, was found to be effective in one case and ineffective in another. Increased biological activity was thought to be the reason for change in odor patterns, with an increase in sulfur odors under poorly limed conditions and a decrease in TMA odors as the pH goes down and TMA becomes less volatile.

In phase two, the inter-relation between trivalent cations, labile proteins and odor potential was investigated. It was determined that odor potential is directly related to the labile protein content in sludge/biosolids. Furthermore, as the Al/Fe ratio increased, the labile proteins was observed to decrease. This indicates that trivalent cations have an important role in binding the proteins thus controlling their bioavailability and hence effecting odor production. This was found true for most sludge irrespective of their liming status and independent of upstream process conditions.

## **KEYWORDS**

sludge, total sulfur odors, trimethylamine, trivalent cations, odor potential, labile proteins, shear

## **INTRODUCTION**

More than ten million tons of biosolids are generated in the United States each year, of which about 65% is recycled beneficially. One of the barriers to the beneficial reuse of biosolids is odor generation. Opposition to land application can be reduced if odors can be minimized.

Wastewater sludges/biosolids are abundant sources of food for microorganisms in the form of proteins, amino acids and carbohydrates (EPA, 2000a). The degradation of these compounds is considered to be the cause of malodorous odor emissions. The odors typically identified from a wastewater processing facility or land application site containing biosolids are reduced sulfur compounds, nitrogen based compounds and organic fatty acids (WEF, 1995). Stored sewage sludges continuously release malodorous odors and tend to smell worse during transport and ensuing movement due to the sudden release of accumulated odors (Lambert and McGrath, 2000).

Various processes are used for stabilizing sludge which include anaerobic and aerobic digestion, lime stabilization and composting. Sulfur based odors are obtained from dewatered sludge both pre and post digestion. Sulfur compounds typically detected in wastewater sludges include hydrogen sulfide (HS), methane thiol (MT), dimethylsulfide (DMS) and dimethyldisulfide (DMDS). Anaerobically digested sludges are known to emit volatile sulfur compounds (VSCs) comprising mainly of MT (Novak et.al, 2004).

Trimethylamine (TMA) odors are typically associated with lime stabilized sludges where the pH is 12 or greater. TMA has a pKa of 9.81 (Novak et.al, 2002) and has a characteristic fishy odor. TMA odors are known to emanate from lime stabilized biosolids along with DMDS (Kim et.al, 2001). TMA formation is due to microbial breakdown of organic compounds coupled with pH and temperature mediated physico-chemical processes (Murthy et.al, year, 2002c). As the pH is raised above the pKa for TMA, liquid phase TMA is converted to its unionized and volatile form followed by gradual emission over time.

Proteins, containing an amino acid group as monomeric building blocks, are considered to be the primary precursors for formation of odor compounds. Cysteine and methionine are known to be present in proteins extractable from activated and anaerobically digested sludges. This protein remains unmetabolized as long as the digestion/stabilization process does not make them bioavailable. The bioavailability of proteins is considered to be the key, but poorly understood, process in the release of odor compounds from wastewater sludges/biosolids. The cation bridging model postulated by Higgins et.al (1997) explains the role of cations acting as a bridge connecting the negatively charged sites of the biopolymer within sludge. Proteins were found to be major constituents in activated sludge and they concluded that proteins had a more important role in defining floc structure because of their predominance in electrostatic bond formation with multivalent cations.

Lomans et.al (1999) showed that methanogenesis is the major mechanism for DMS and MT consumption in fresh water sediments. In another of their experiments, methylation reactions were found to transform sulfide and MT into MT and DMS respectively. They further

demonstrated that methanogens and sulfate reducing bacteria in the presence of sulfate can degrade MT and DMS, thus continuing the VSC degradation cycle (Lomans et.al, 2002a). These findings were corroborated by Higgins and co workers (2002).

Shearing of sludge that occurs in dewatering devices like centrifuge and belt filter press is known to significantly influence the production of odors. Basu et.al (2004) reported that shear increases the digestibility of sludge, leading to more volatile solids (VS) destruction. This is due to exocellular biopolymers being rendered bioavailable under application of shear. Muller et.al (2004) further showed that the proteins in exocellular biopolymer would degrade following shear, leading to odors.

Studies conducted by Murthy et.al (WEFTEC 2002a) revealed that a high solids centrifuge gave a higher production of VSCs compared to a low solids centrifuge. A combination of screw conveyance following dewatering by centrifugation produced almost three times more odor than that produced by centrifugation alone. These workers also developed a model correlating the increase in labile protein content in biosolids to the increase in applied shear. The subsequent degradation of labile proteins upon being subjected to shear resulted in an increased production of VSCs, particularly MT (an order of magnitude of almost 16 times) compared to unsheared conditions.

Polymer added to sludge to aid the dewatering process is documented to contribute towards increasing odor potential (Higgins et.al, 2002; Muller et.al, 2004). This was reported to be due to association of proteins from floc with added polymer. Murthy et.al (2001, 2002b) have theorized that cationic polymer conditioning of sludge prior to dewatering raises odor potential, especially for production of TMA. Proteins and polymers in biosolids are thought to be enzymatically broken down upon consequent lime addition, cause TMA and DMDS to be released (Kim et.al, weftec 2001; Turkmen et.al, 2004).

Trivalent cations (iron and aluminum) are thought to have a major impact on sludge characteristics due to their strong association with sludge matrix (Park et.al, 2004). Iron is known to undergo reduction from Fe (III) to Fe (II) by iron reducing bacteria (Rasmussen et.al,

1996; Caccova et.al, 1996). Ferric iron has been shown to have a higher affinity for proteins (Novak et.al, 2003). They also concluded that large quantities of proteins are released during iron reduction during anaerobic digestion process which can be attributed to specific binding of proteins with ferric iron.

The objectives of this study were

1. To determine the odor profile from limed biosolids
2. To determine effect of lime incorporation in dewatered sludges
3. To determine the inter-relations between trivalent cations, labile proteins and odor potential from wastewater sludges/biosolids.

## **MATERIALS AND METHODS**

### *Study overview*

This study was conducted in two phases. The first phase was an investigation of the odor production from three wastewater treatment plants in the Washington DC area that use lime stabilization for odor control. Wastewater sludge samples were obtained from the Blue Plains, Parkway and Piscataway treatment plants. Samples included both limed as well as unlimed from the three plants. Phase II was comprised of experiments conducted at Virginia Tech to study the interaction between trivalent metals in sludge, labile proteins and odor potential.

### *Sample preparation and analysis*

#### Phase I

Sludge/biosolids samples were shipped directly from the three plants in 260 mL PET bottles on ice through overnight shipping. Two sets of samples were studied. Short term samples were analyzed when received for TMA and sulfur compounds in headspace following which, the bottles were opened for withdrawal of samples for analyses of metals and proteins. The long term samples were monitored for odorous gases in the headspace and analyzed on days 1, 2, 3,

5, 8, 14, 28 and 56 for the analytes of interest. Samples for headspace analysis were incubated at 25 degree C for the duration of experiment. All other samples were stored at 4 degree C for preservation until the start of the experiment.

## Phase II

Wastewater sludges were obtained from two local wastewater treatment plants, Blacksburg, VA and Radford, VA. Samples were collected within 24 hours of start of the experiment, and were stored at 4 degree C for preservation until analyses. Polymer solution for sludge conditioning was prepared fresh each day. The optimum polymer dose was using capillary suction time (CST) [method 2710G of standard methods (APHA 1995)] and noting the dose giving the lowest response time. A triton type CST apparatus [304-M and 165] was used for this purpose with Whatman 17-HCR as the chromatography paper. The optimum polymer dose for each sludge type was determined after addition of polymer to sludge followed by shearing using a 1/5 HP waring blender for five seconds. Once the optimum polymer dose was determined, sludge samples were dewatered using a centrifuge (Beckman J2-HS Centrifuge or Beckman-Coulter Avanti-JE) at 17,600 x g for 15 minutes. A solids content of 14-18% was obtained. Between six and seven grams of cake solids was placed into 40 mL EPA vials (Fisher brand) for incubation under anaerobic conditions at 25 C for the duration of the experiment. Samples were analyzed on days 0.5, 1, 2, 3, 6 and 11.

## *Metals*

Metals were analyzed using an atomic absorption spectrometer after acid digestion by EPA 3050B method. Samples were dried overnight at 105 degree C to completely remove water before acid digestion. Metals were quantified using a calibration curve made for iron and aluminum using respective standards.

## *Labile proteins*

Labile proteins were quantified using the Hartree modification of Lowry et.al method after extraction by the method developed in the WERF II project (**insert ref**). Extraction of samples

was performed by first dewatering the sludge samples in case they were in liquid phase. Ten grams of the dewatered sludge cake or biosolids cake was re-suspended in pH 8 phosphate buffer saline solution (PBS). The suspension was sheared for ten minutes at  $G = 1000/s$  followed by centrifugation at  $3000 \times g$  for 15 minutes. The centrate obtained after filtering through a 1.5  $\mu m$  glass microfiber filter was termed as labile or bound protein. Bovine serum albumin was used as the protein standard.

#### *Total and Volatile Solids Analysis*

Total solids (TS) and total volatile solids (VS) were measured according to Standard Methods (APHA, 1995).

#### *Headspace analysis*

Headspace odor analysis was performed using a capillary column Gas Chromatography/Mass Spectrometry (GC/MS) (Hewlett-Packard 6890). One hundred  $\mu L$  of headspace gas was injected into the column for analysis of each sample. Integration of peak area was carried out using the environmental Chemstation program (G1701 CA). The amount of odor contributing compound in each sample was determined ratiometrically by comparing the sample peak area with the area of a known standard of hydrogen Sulfide, methane thiol, dimethyldisulfide and trimethylamine (Scott Specialty Gases). Dimethyldisulfide was quantified using DMS as a reference.

## **RESULTS AND DISCUSSION**

### **Phase I:**

#### **Analysis of odor potential from limed biosolids at Blue Plains, Parkway and Piscataway Wastewater Treatment Plants.**

In phase I, limed and unlimed samples from Blue Plains, Piscataway and Parkway WWTPs were evaluated to quantify sulfur and TMA odor production. Lime stabilization is used in all of

these facilities. Blue Plains and Parkway do postliming (lime added after dewatering) whereas Piscataway does preliming (lime added prior to dewatering) of sludge to produce biosolids. The objective of this phase of study was to determine the effect of lime addition on dewatered cakes. The effectiveness of lime incorporation under pre and post liming was also monitored. A summary of the odor production results and description of samples is provided in table 1. In addition to determining odor potential, tests were conducted to analyze trivalent metals and labile proteins in these samples to provide a framework for correlating the production of odors with the trivalent metals, iron and aluminum and to determine if lime reduces the labile protein content or simply stops microbial utilization of the labile materials.

Table 1: Sample descriptions and summary results for odor production from Blue Plains, Parkway and Piscataway WWTPs.

<b>WWTP</b>	<b>Sample Description</b>	<b>Peak Total S (mg/cu.m.)</b>	<b>Peak TMA (mg/cu.m.)</b>
Blue Plains	Post limed, full scale, Plant personnel limed	5.1	4.1
Blue Plains	*Lab limed, Plant personnel limed	5.0	5.2
Blue Plains	Post limed, full scale, Contract agency limed	5.7	2.0
Blue Plains	*Lab limed, Contract agency limed	5.0	4.8
Parkway	Post limed, full scale	11.7	12.7
Parkway	Post limed, *lab limed	14.3	6.4
Piscataway	Vacuum Filter Press - pre limed, full scale, no polymer addition, Fe and lime addition	5.9	9.7
Piscataway	Belt Filter Press - pre limed, full scale, polymer addition, no Fe addition	2292.1	43.0

\*Lab liming was done at 20% w/w.

As can be seen in table 1, odor production from the belt filter press for the Piscataway samples were very high compared to all other samples. Of the low odor gas plants, Parkway had the highest total sulfur and TMA odors.

*Blue Plains:*

The flow scheme for solids handling at the Blue Plains treatment plant is shown in figure 1.

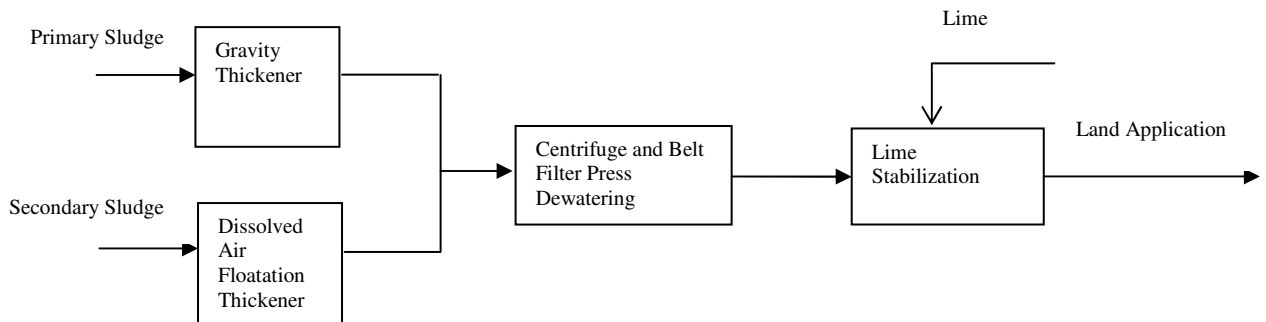


Figure 1: Solids handling process at Blue Plains WWTP

Blue Plains uses a post liming sludge stabilization process following dewatering of the blended primary and secondary sludges. The dewatered cakes are divided into two trains, one of which is limed by plant personnel and the other limed by a contractor. Further, sludge from the two trains was also studied after liming the sludge under lab conditions. For the lab tests, a 20% lime addition followed by two minutes of mixing was carried out. The lab testing was conducted to ensure mixing was complete.

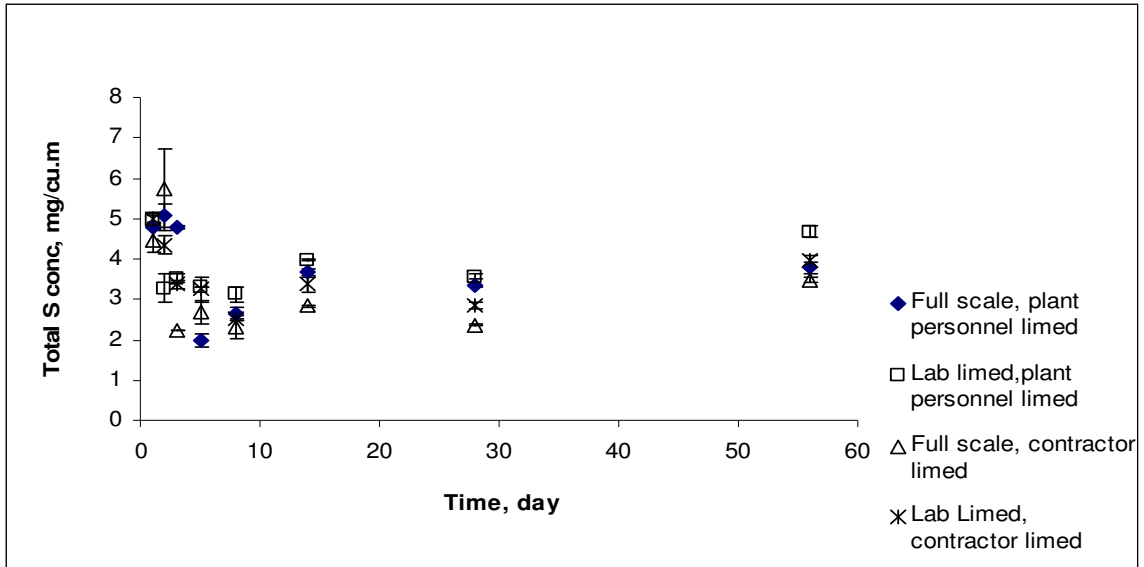


Figure 2a: Headspace Sulfur odor profile: Limed samples from Blue Plains WWTP

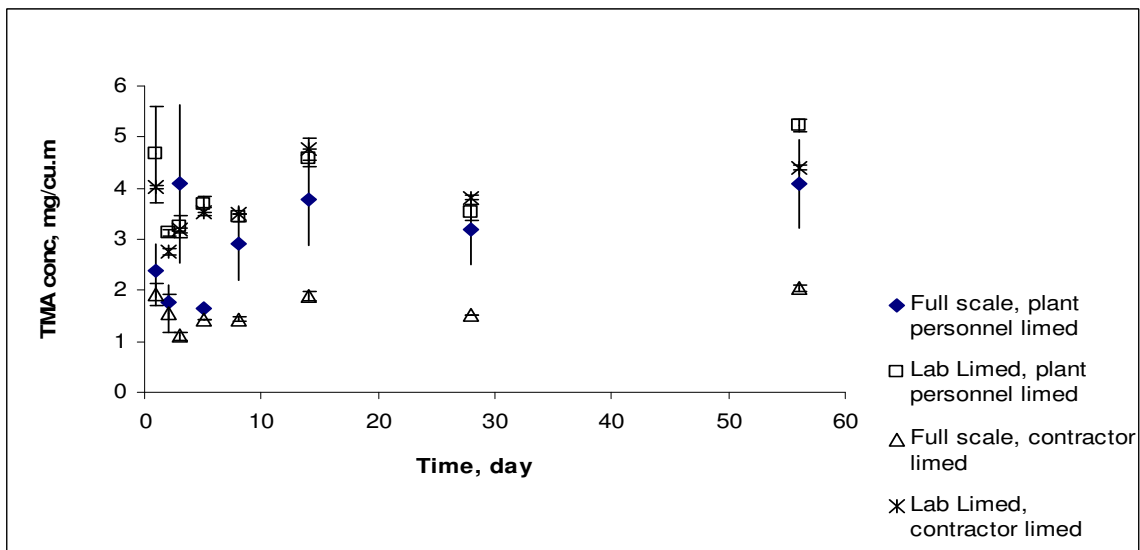


Figure 2b: Headspace TMA odor profile: Limed samples from Blue Plains WWTP

The results show that total sulfur and TMA odors from both trains are similar. This indicates that for Blue Plains, lime incorporation into the sludge is achieved in a homogenous way as there is no increase in total sulfur odor concentration over time. TMA is also stable and does not go down indicating low microbial activity. Similar trends for lab limed samples compared to field conditions for both plant personnel limed and contractor limed conditions show that sulfur odor and TMA production are influenced by lime incorporation. A total sulfur concentration, less than 50 mg/cu.m. and more than 500

mg/cu.m in the headspace are thought to be low and high levels of sulfur odor potential respectively from lime stabilized biosolids. For TMA, these concentration levels are considered to be less than 5 mg/cu.m. and more than 50 mg/cu.m. representing low and high TMA odor potentials respectively. Thus current liming procedures at Blue Plains facility are effective in keeping the odor levels under control.

*Parkway:*

The flow scheme for the Parkway treatment plant is shown in figure 3.

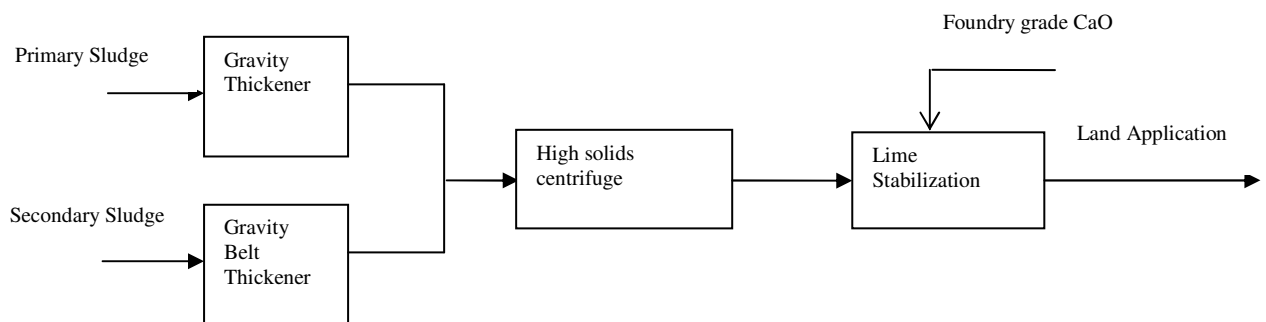


Figure 3: Solids handling process at Parkway WWTP

Parkway uses a post lime stabilization process following blending of primary and secondary sludges. Personnel at the Parkway plant indicated they experience occasional odor problems from their lime stabilization sludge handling process. The plant is currently modifying their sludge handling process to improve the mixing of lime and sludge to reduce odors. In this part of study, the dewatered cake from the facility was lab limed (20% w/w and two minutes mixing) and compared to field samples.

The results for parkway WWTP are shown in Figure 4. It is seen that lab liming gives a lower production of total sulfur and TMA odors than full-scale samples. This suggests that the dose lime added under field conditions could be insufficient or lime is not effectively mixed with the sludge. The increase in odors with passage of time indicates that the pH could be dropping and as a result, microbial activity is resuming and odor production occurs.

Headspace odors for unlimed samples from Blue Plains and Parkway were measured when they arrived (day one). The blended undewatered sludge from Blue Plains had a total headspace sulfur concentration of 23.38 mg/cu.m. while that from Parkway had 130 mg/cu.m. Comparison of these odor values for the unlimed samples to those for the limed samples supports the results for limed samples from Blue Plains which has a lower total sulfur odor production compared to Parkway. Although odor production from Parkway samples is higher than Blue Plains, both plants are considered to be emitting relatively low levels of malodorous odors, thus indicating that liming procedures at both facilities are effective in controlling odors. However, because of odor concerns, Parkway should consider improving their lime/sludge mixing process. This should reduce sulfur and TMA odors to levels about half of what is currently generated.

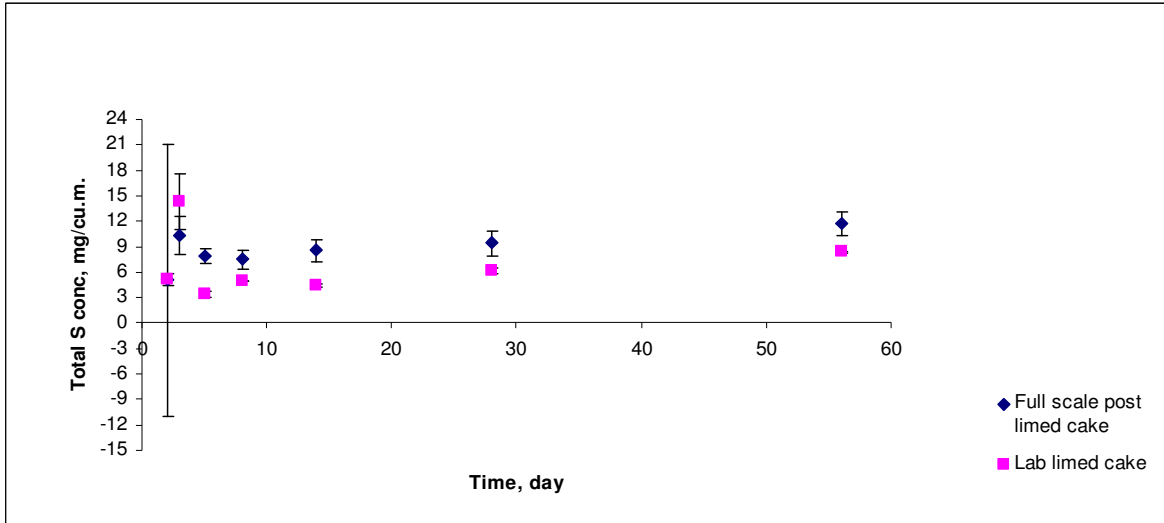


Figure 4a: Headspace Sulfur odor profile: Limed samples from Parkway WWTP

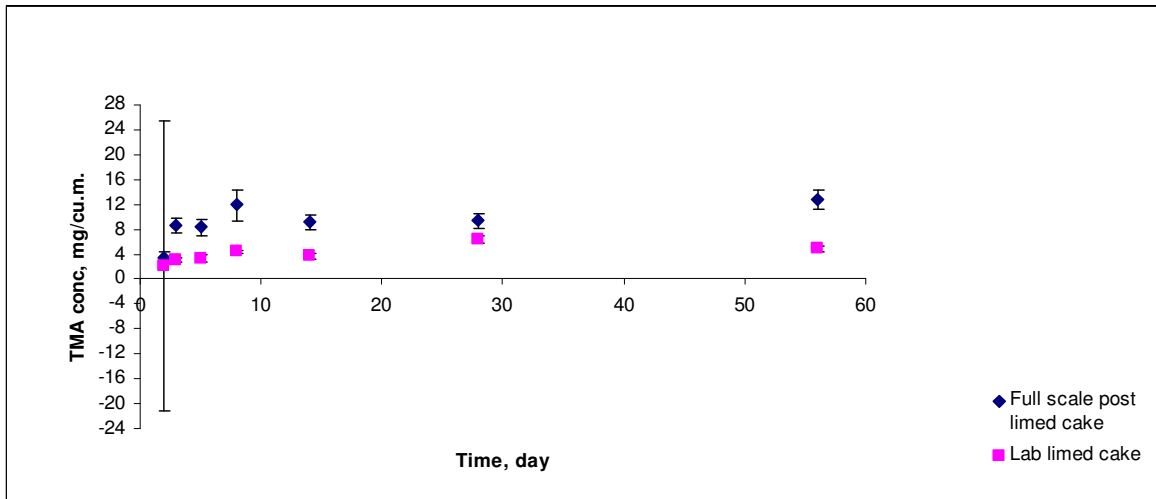


Figure 4b: Headspace TMA odor profile: Limed samples from Parkway WWTP

*Piscataway:*

The flow scheme for the Piscataway treatment plant is shown in figure 5.

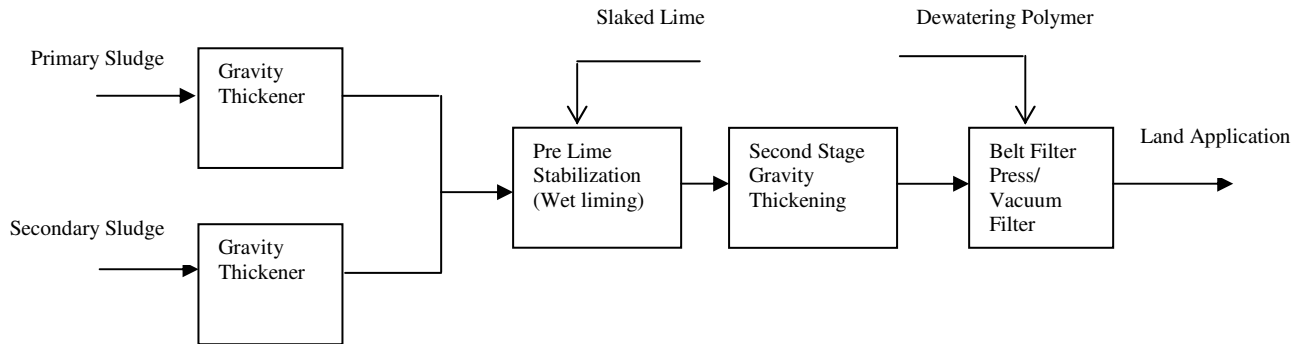


Figure 5: Solids handling process at Piscataway WWTP

Piscataway, a smaller WWTP does pre-liming to its sludge for lime stabilization. This has the advantage of providing more time for lime to get incorporated into the sludge. Lab limed samples were not monitored for this plant. A different dewatering process is practiced than for Blue Plains and Parkway. The blend sludge was dewatered using a belt filter press (BFP) or a vacuum filter (VF) instead of a centrifuge.

Results from the study show that there is a significant difference between the BFP and VF samples. This could be due to shearing of the samples in the BFP as a result, the total sulfur production is very high and shows an increasing trend. Lime incorporation maybe insufficient because the total sulfur from the VF remains fairly constant initially but then gradually starts to rise. After day 16, TMA production also starts to go down. This could possibly be due to a reduction in pH, indicating resumption of microbial activity. The consequences could be either consumption of TMA by biological activity or less TMA in the headspace because the pH is less than the pKa (9.81).

The same could be an explanation for the decrease in TMA production from the belt filter press. The shear causes TMA to be rapidly produced in the beginning and then it starts to

decrease as the pH goes down for reasons cited above. Because the bottles were sealed, the pH could not be measured.

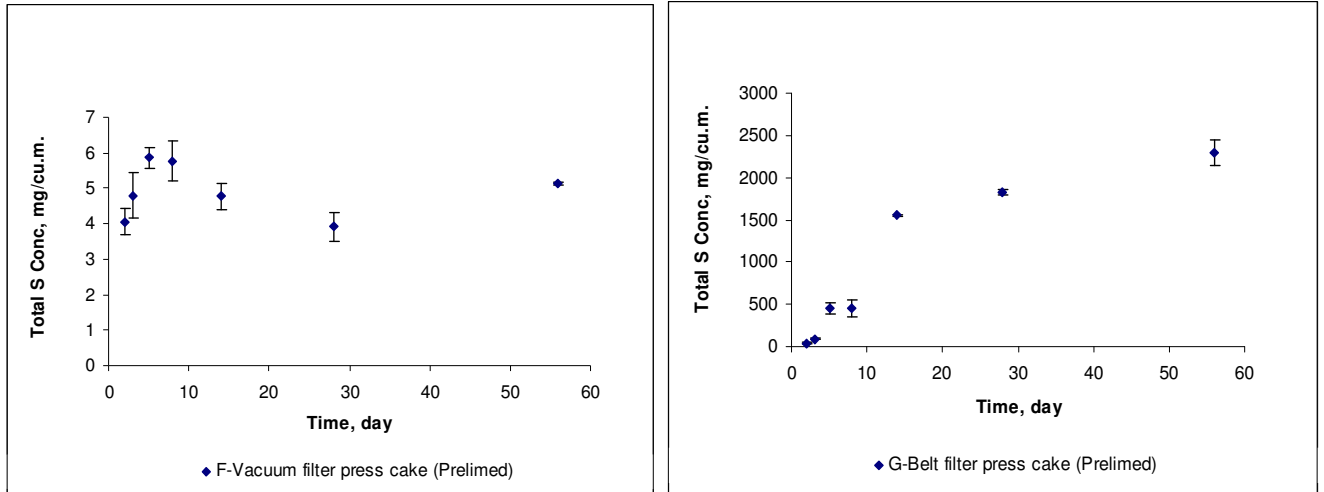


Figure 6a: Headspace sulfur odor profile: Limed samples from Piscataway WWTP

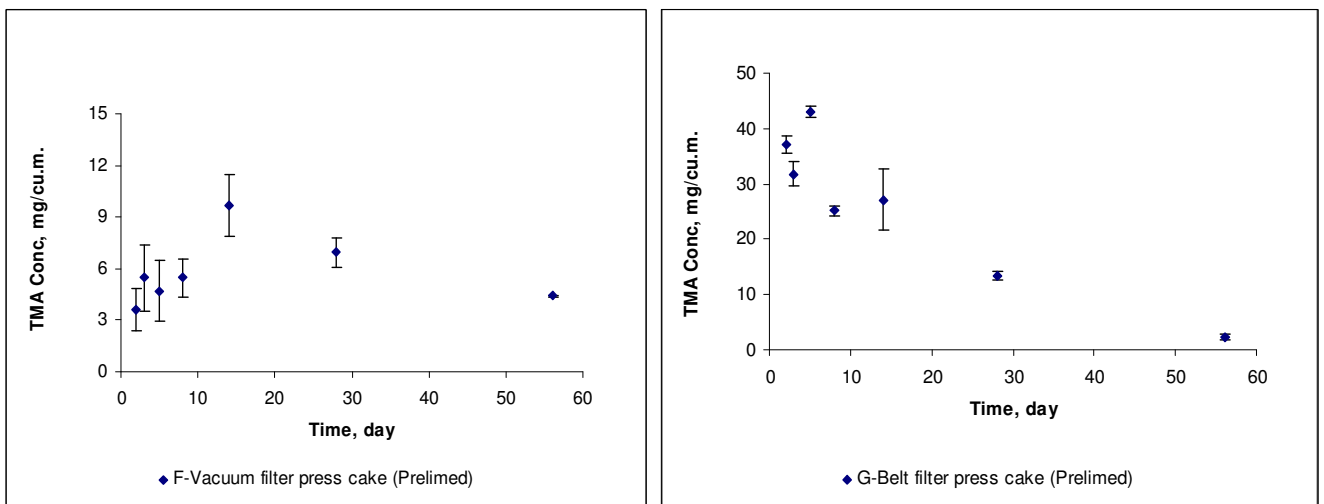


Figure 6b: Headspace TMA odor profile: Limed samples from Piscataway WWTP

Odor production from limed sludges from three wastewater treatment facilities were investigated in phase I. Lime dose and incorporation into sludge was found to influence odor production over time. Pre liming conditions resulted in poor lime incorporation into sludge, compared to post liming. Shear in the BFP produced more odors compared to the VF. Once the odor potential for the limed samples from Blue Plains, Parkway and Piscataway were analyzed it was decided to investigate the interaction between trivalent metals and labile proteins. Proteins are known to be precursors to odor forming compounds. It is hypothesized that trivalent metals such as iron and aluminum could influence the binding of these labile proteins and hence effect odor production. This was especially true for aluminum. Park et.al (2004) showed that high aluminum in sludge reduced its digestibility, so its effect on labile protein and odor production was of interest. The results of this portion of the study are given in phase II.

## **Phase II**

### **Interaction of trivalent metals, labile proteins and odor potential.**

It is theorized that trivalent metals help in binding labile proteins within the floc structure of sludge/biosolids. Recent research by Novak et.al (2003) suggests that biopolymer in floc is comprised of several components, one associated with calcium and magnesium and the other associated with trivalent cations, iron and aluminum. Trivalent iron and aluminum are key metals in association with floc structure. Park et.al (2004) have shown that the binding by aluminum is different than the binding by iron, in part, because iron can undergo oxidation/reduction changing from Fe(III) to Fe(II), while aluminum does not. Novak et.al (2002b) has also shown that under high shear, followed by anaerobic digestion, little calcium or magnesium is released, indicating that the biopolymer associated with these divalent cations is relatively stable and difficult to degrade anaerobically. Therefore, it was thought that biopolymer associated with iron and aluminum, specifically the protein component would be the most important organic associated with odor. Under poorly bound conditions, labile proteins are thought to become readily bioavailable giving rise to higher odor potential.

Higgins (personal communication) has developed a method to assess the labile fraction of proteins in sludge. This labile fraction is the material that can be degraded to yield odors. He found that the labile protein content present in wastewater sludges is well related to methane thiol concentration in the headspace of bottles containing sludge. Therefore in this portion of the study, the labile fraction was measured and compared to iron and aluminum in the sludge floc to determine the relationship between trivalent cations and the protein available for degradation.

Wastewater sludges were obtained from two local WWTPs. In all, six different sludges were studied. Primary and WAS from Blacksburg WWTP and primary, WAS, digested and dewatered cake from Pepper's Ferry WWTP. Optimum polymer doses for all sludges except dewatered cake from the Pepper's Ferry WWTP were obtained under conditions of shear by performing CST on them as described previously. Samples were then set up in 40 mL EPA vials for headspace odor analysis. Dewatered cake from the PF WWTP was put into 40 mL EPA vial directly without any processing. In addition, a second set of samples were set up without the addition of polymer and with no shear. Sludge samples were dewatered and directly put into 40 mL EPA vials. This was done to compare the effect of shear and polymer addition on odor production. All samples were incubated anaerobically at 25 degree C after purging the headspace with nitrogen gas. Analyses were made on days 0.5, 1, 2, 3 and 6. Analytes of interest were HS, MT, DMS and DMDS. Odor analysis of these samples was then conducted using a gas chromatography/mass spectrometer.

Results of these odor analyses is shown in figure 7.

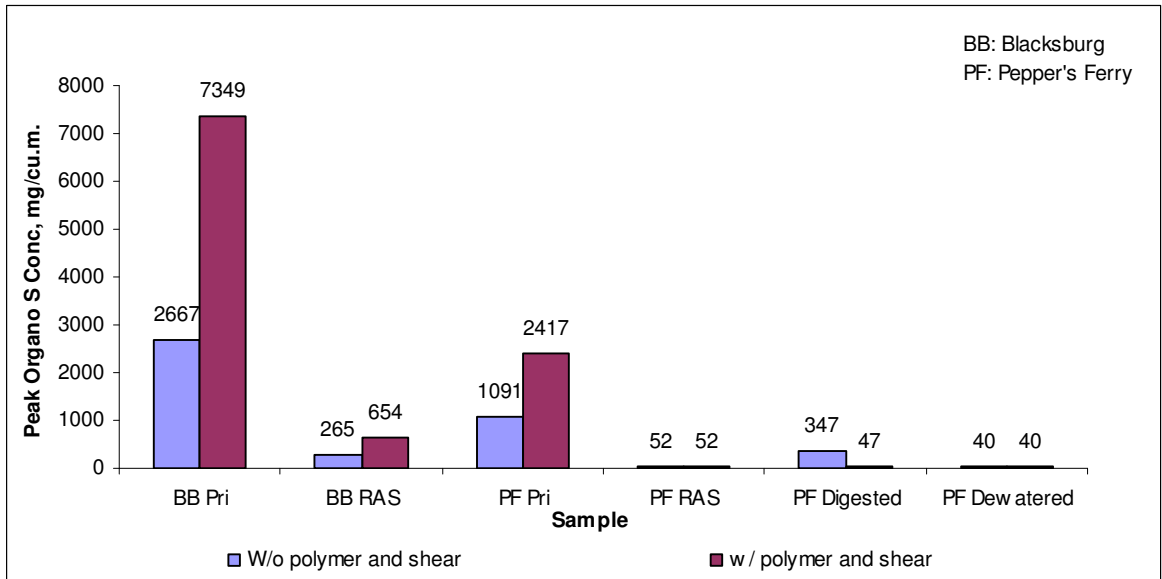


Figure 7: Odor production form six local wastewater sludge samples

It can be seen from figure 7 that peak headspace odor production under shear conditions and with polymer addition is higher than that without shear and polymer addition for primary and WAS from Blacksburg WWTP and primary from Pepper's Ferry WWTP. This shows that shear and polymer addition create favorable conditions for production of nuisance odors. An aberration was observed for the digested sludge from PF WWTP. It showed a higher concentration of reduced sulfur odors under unsheared conditions without polymer addition as compared to conditions with polymer addition and with shear.

Trivalent metals and labile proteins were analyzed after dewatering the samples without addition of polymer and without subjecting the samples to shear.

The relationship between labile proteins, trivalent metals and odor potential is as shown below.

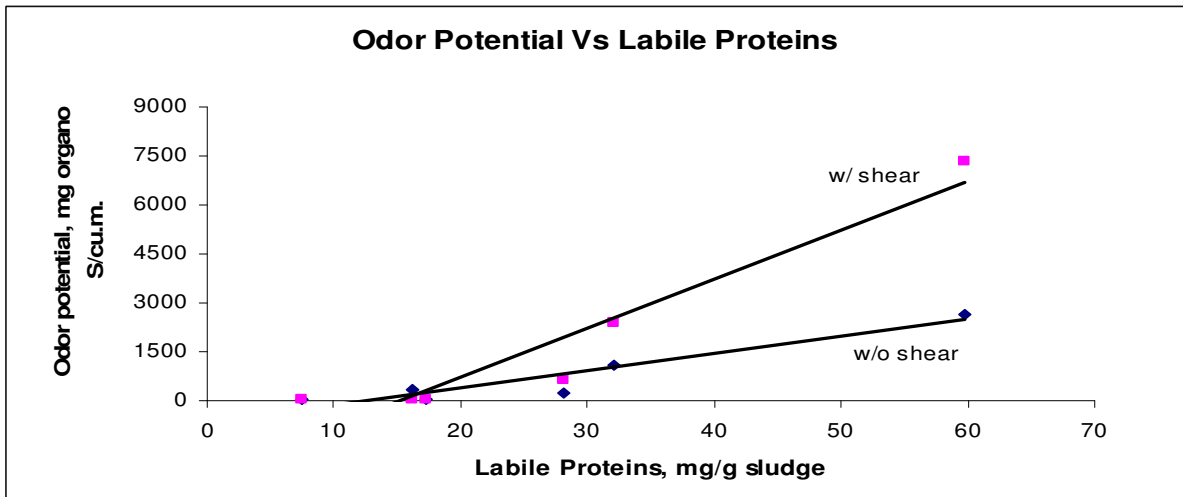
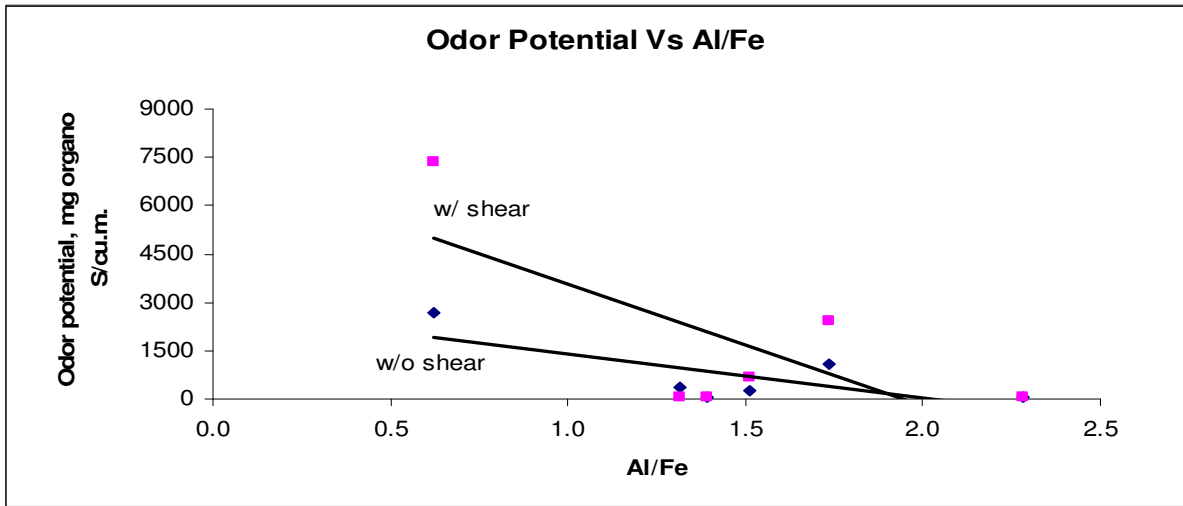
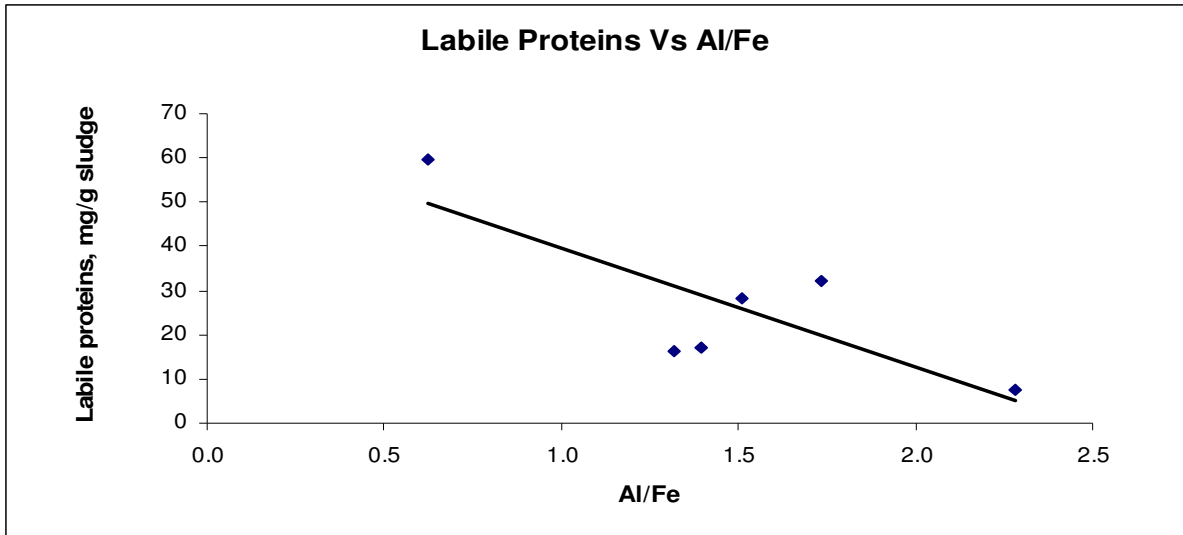


Figure 8a, b and c: Interrelation between trivalent metals, labile proteins and odor potential.

From figures 8a, b and c, we see that as the ratio of Al/Fe decreases, the labile proteins and peak organo S increases. As the labile protein content in sludge goes up, the odor potential also increases correspondingly. The odor potential is represented by reduced organo S species comprised of methane thiol, dimethylsulfide and dimethyldisulfide. It is further observed that the trend in the relationship between odor potential and labile proteins or metals is the same for sheared and polymer dosed samples and samples without polymer and shear. However the odor potential for sheared-polymer dosed and unsheared-without polymer samples tend to converge at high Al/Fe ratios.

It is hypothesized that trivalent cations, iron and aluminum, keep the labile proteins bound to the sludge/biosolids. Labile proteins are important precursors for odor generating compounds. Iron can undergo reduction from Fe (III) to Fe (II) as oxic conditions change through the process. Aluminum is however unchanged in its oxidation state. The relative presence of trivalent cations to divalent is thought to be the influencing factor in generation of nuisance odors due to release of bioavailable labile proteins. At this stage it is difficult to predict the relative importance of iron or aluminum in generation of nuisance odors. At higher Al/Fe ratios the odor potential is low irrespective of shear conditions. This suggests that trivalent metals help in binding the labile proteins to such an extent that even under high shear conditions, odor precursors are not bioavailable.

It is not clear why protein extracted at pH 8 under shear would be odor causing material. However, as a screening method, this procedure seems to be a useful odor indicator. Since the odor causing protein seems to be associated with iron, the mild extraction process seems to be extracting protein weakly bound and therefore subject to release from iron when reducing conditions occur during cake storage.

An interesting point to note from this experiment is the interaction between trivalent metals, odor potential and labile proteins without dependence on the wastewater treatment process. The results from this experiment show the importance of trivalent metals in odor generation. Metals are known to influence sludge floc structure and settling characteristics. They can now be related to odor production mechanisms and more knowledge can lead to better odor

abatement procedures. Additional work is needed to understand the mechanisms by which trivalent cations influence the production of odors from dewatered sludges/biosolids.

*Combining Phase I and Phase II results*

Figure 9 shows the relationship between trivalent metals and labile proteins for limed samples from phase I experiments and unlimed local sludges from phase II.

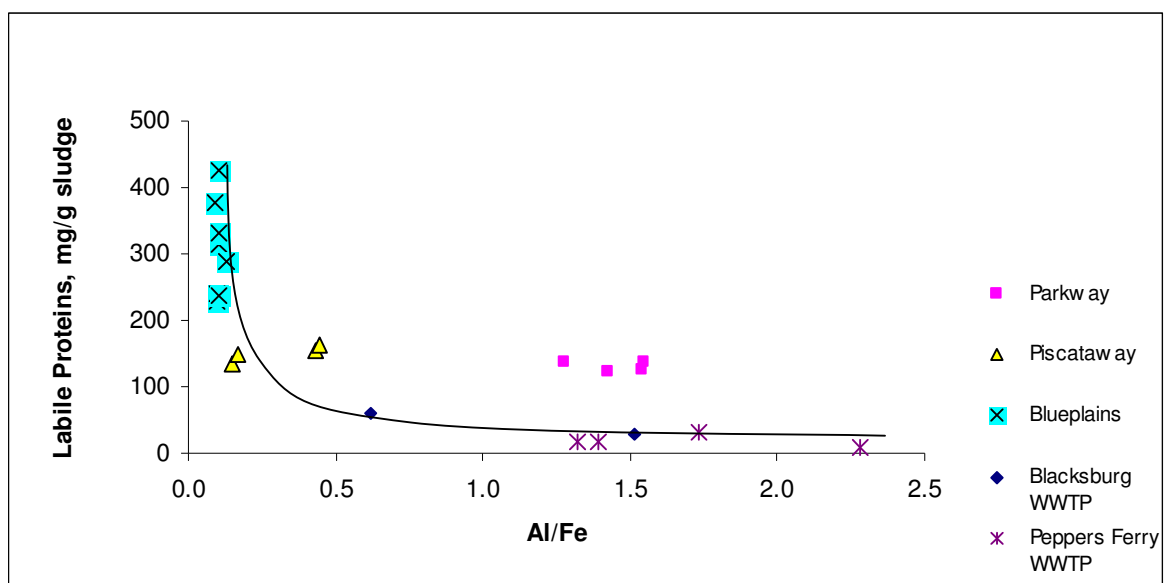


Figure 9. Relationship between trivalent metals and labile proteins for unlimed and limed sludges.

It can be seen that a relationship between trivalent metals and labile proteins obtained from phase II experiments is valid. The plot is consistent with the results obtained from the WERF II odor study (insert ref).

Samples from phase I are all limed. They fit well with the unlimed samples results for the local sludges (Blacksburg and Pepper's ferry WWTPs). The hypothesis that labile protein content in sludge decreases as the ratio of trivalent Al/Fe increases is corroborated

irrespective of the sludge type. The only samples that did not fit the pattern well were those from Parkway. Though the Al/Fe was high for these samples, the labile proteins in these samples were somewhat higher compared to the other samples. One possible explanation could be that the aluminum is present in an inactive form since it is added as alum sludge and it does not bind the labile proteins which become bioavailable, generating odors.

These data suggest that there maybe an important inter-relation between trivalent metals, labile proteins and odor. The control of metal concentration in sludges/biosolids may alter odor production giving better alternatives to odor management practices.

## SUMMARY AND CONCLUSIONS

This two phase study provides an outlook into generation of nuisance odors from domestic wastewater treatment plants. Limed samples from three WWTPs were analyzed for total reduced sulfur compounds and trimethylamine production.

The focus of study in phase I was the role of lime dosing and lime incorporation in odor generation. Lab limed and field samples from centrifuges and filter presses were analyzed to understand the differences in odor generation pattern due to lime incorporation as compared to other factors. Total sulfur and TMA odor generation was mostly low (~ 15 mg/cu.m. and ~ 6 mg/cu.m. respectively) and stable for samples with proper lime dosing. Higher concentrations of odorous compounds are believed to be the result of insufficient lime dosing or poor incorporation of lime into sludge which could lead to a drop in pH over time. This is presumed to lead to resumption of microbial activity and production of sulfur and TMA odors over time. Preliming of sludge to provide better incorporation of lime into sludge was found to be somewhat ineffective especially under shear conditions present in the BFP. Shear in a BFP is considered to be an important factor capable of producing very high levels of nuisance odors. Both total sulfur and TMA odors were detected in high quantities in samples from BFP compared to samples from VF which has less shear. Moreover though the production of total sulfur and TMA odors from the VF was relatively low, they were changing with time, indicating that prelimiting of sludge was not as effective as post liming. It may be that the lime dose was inadequate and if it had been adequate, odor production would have been minimal.

In phase II, the inter-relation between labile proteins, trivalent metals and odor production was investigated. A total of six sludges from two local WWTPs were analyzed in the study. Labile proteins in sludge/biosolids were found to be the link between trivalent metals (iron and aluminum) present in sludge/biosolids and their odor potential. Reduced organo S species was taken as an indicator for odor potential. It was determined that as the ratio of Al/Fe increases, the concentration of labile proteins and the odor potential both go down. Labile proteins are thought to be the precursors for odor forming compounds. This was

confirmed from the fact that as labile proteins concentration increased, so did the odor potential from the sludge/biosolids. It is hypothesized that trivalent metals help in binding the labile proteins. The relative proportion of trivalent to divalent metals controls the release of bioavailable labile proteins thus influencing headspace odor production. At this stage it is difficult to predict the relative importance of iron or aluminum controlling the odor generation process. An interesting observation from the study was the generality of the result applicable to all kinds of sludge irrespective of upstream process conditions. The results show that there exists an inter-relation between trivalent metals and labile proteins for unlimed (raw), stabilized and limed sludges/biosolids. Further studies are required to use this information for improving odor control.

From this two phase study we infer the following specific conclusions.

1. Lime dose and incorporation in sludge plays an important role in generation of total sulfur and TMA odors over storage time. A drop in pH over time is thought to be the reason for increase in production of nuisance odors due to resumption of microbial activities.
2. Belt Filter Press gave very high quantities of total sulfur and TMA odor production compared to Vacuum Filter Press due to shear in BFP. Lime dose is critical. Pre-liming conditions thought to offer better lime incorporation into sludge was found to be not so effective.
3. Shearing under conditions of optimum polymer dose gives higher production of total sulfur odors compared to unsheared conditions with no polymer dose.
4. Reduced organo sulfur odor production was found to increase with higher labile protein content in sludge.
5. Metals were found to play significant role in binding labile proteins irrespective of liming conditions or type of sludge/biosolids. It was determined that higher Al/Fe ratio helps in binding labile proteins in the sludge matrix thus reducing the odor potential.
6. Controlling the concentration of trivalent metals in sludge can offer better alternatives for odor abatement processes.

## **ACKNOWLEDGEMENTS**

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## Chapter 3: Manuscript 2

### Evaluation of Trimethylamine Generation from Biosolids

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#### ABSTRACT

This study was conducted to determine the effect of sludge handling methods on the production of trimethylamine (TMA) odors from limed biosolids. The effect of shear, polymer dose, and oxic state on TMA production was determined. Cationic polymers used to condition wastewater sludges are thought to be precursors for TMA odor production. Proteins contained in sludge may also be associated with odor potential. It is hypothesized that these two components, under conditions of shear, are more likely to cause an increase in odor production from lime stabilized biosolids. Shear studies were conducted to simulate field centrifuge conditions at various polymer doses. Results show that TMA production increased significantly under conditions of high shear and high polymer doses. Unsheared conditions with low polymer doses gave low TMA production as compared to shear in combination with higher polymer doses. Further, polymer overdose conditions produced a delayed TMA peak in which the maximal odor production occurred approximately 48 hours later than conditions of

optimal polymer dosing or overdosing with no shear. In the absence of polymer, TMA was produced under conditions of shear indicating that proteins contained in sludge are also precursors for TMA odor production. In general, TMA production occurs with polymer addition and shear exposure. It was also determined that abiotic polymer degradation to produce TMA either does not happen or the rate constant is so slow that TMA production in this way is insignificant for actual field situations.

## **KEYWORDS**

biosolids, lime stabilization, odor, trimethylamine, protein, polymer, shear

## INTRODUCTION

Odor problems are frequently associated with wastewater treatment. Odors arise from solids processing facilities and from biosolids that are stored for land application. Odor control in such a situation becomes critical to avoid complaints from the public residing around such facilities, near land application areas or transportation routes. Lime stabilization is a method that has been long used for effectively stabilizing sludge because it generates a low cost product with beneficial reuse options (NLA, 1999). In this method calcium oxide (quicklime) or calcium hydroxide (hydrated lime) are added to sludge to inhibit microbial activities and prevent vector attraction, thus meeting EPA requirements for safe disposal of biosolids (40 CFR Part 503). However, researchers have shown that even with lime stabilization, odors in the form of trimethylamine (TMA) and dimethyl disulfide (DMDS) production can be generated (Kim et.al, 2001).

Odors from biosolids can be both organic and inorganic in nature, and are mainly comprised of reduced sulfur and nitrogen based compounds (WEF, 1995). Sulfur containing compounds include hydrogen sulfide, methane thiol, dimethylsulfide, dimethyldisulfide, dimethyltrisulfide and carbon disulfide. Nitrogen containing compounds can be either aliphatic in nature e.g. TMA or heterocyclic which include indole and skatole. Sulfur based compounds are typically not detected from limed biosolids though abiotic production of DMDS has been reported in literature.

This study focuses on limed stabilized biosolids and investigates the conditions under which TMA is produced. TMA is a weak base with a pKa of 9.81 (Novak et.al 2002). It has a decaying or fishy odor and can be produced as a degradation product of cationic polymers used for sludge conditioning/dewatering (Murthy et.al, 2001, 2002a). TMA, along with ammonia, has been found to be present in the headspace of limed sludges (Kim et.al, 2002). Murthy et.al (year, 2002c) theorize that TMA is not a product of abiotic transformation of chemicals present in the sludge but is a result of a pH and temperature mediated physico-chemical release of liquid phase TMA.

TMA is known to be associated with the sludge matrix in ionized form with a sludge/headspace partition coefficient of 300 (Novak et.al, 2002). When the pH is raised above the pKa for TMA, liquid phase TMA is converted to its unionized form followed by gradual emission over storage time (Murthy et.al, year, 2002c). These authors further reported that TMA emissions from limed biosolids are a function of the initial ionized TMA concentration in the sludge. Proteins and polymers in biosolids are thought to be enzymatically broken down and upon lime addition, cause the release of TMA and DMDS (Kim et.al, 2001; Turkmen et.al, 2004).

Frølund et.al (1996) have shown that approximately 50% of the extracellular polymeric substances in sludge are comprised of proteins. This protein remains unmetabolized as long as the digestion/stabilization process does not make them bioavailable. The bioavailability of proteins is considered to be the key process in release of odor compounds from wastewater sludges/biosolids. Muller et.al (2004) have shown that shear enhances the release of extracellular proteins causing an increase in odor potential, mainly due to reduced sulfur compounds. A combination of screw conveyance following dewatering by centrifugation produced almost three times more odor than that produced by centrifugation alone (Murthy et.al, 2002b). It is hypothesized that shear would have a similar effect on the production of TMA. It is further suspected that the shear could cause breakdown of the polymer linkages which might contribute to an increase in TMA production.

Cationic polymers used to dewater sludge in the wastewater industry can be of Polyacrylamide or Mannich type. These cationic polymers are known to contain amino groups in their structure. It is hypothesized that the degradation of these polymeric structures makes the amino groups liberated which can lead to formation of amine based odors.

The objectives of this study were to:

1. determine the effect of polymer addition at various doses on TMA production
2. determine the conditions and environment (aerobic versus anaerobic) more favorable to TMA formation
3. determine if polymer can be degraded abiotically by chemical reaction with lime
4. determine the effect of shear intensity on TMA production

## **MATERIALS AND METHODS**

### *Sample Preparation:*

Wastewater sludge was obtained from Pepper's Ferry Region Wastewater Treatment Authority in Radford, VA. Waste activated sludge (WAS) was used for sample preparation. Samples were collected within 24 hours of the start of each experiment, and were stored at four degree C for preservation.

Sludges were conditioned using polyacrylamide polymer. Since one of the objectives of the study was to determine the effect of polymer dose on TMA production, it was necessary to estimate the optimum polymer dose. Based on this optimal dose, overdosing and underdosing were done. The optimum polymer dose was determined using the capillary suction time (CST) test according to method 2710G of Standard Methods (APHA, 1995) by measuring the minimum CST at various doses of polymer added to sludge. Whatman 17-CHR Chromatography paper was used with a Triton type CST apparatus (304-M and 165). The optimal polymer dose selected was that dose producing the lowest CST response, corresponding to the best dewaterability of the sludge for each polymer. Polymer solution was prepared fresh on the day each experiment was begun.

Once the optimum polymer dose was obtained, samples were set up according to a matrix developed for each experiment (see individual sections for description of sample matrices). The sludge was dewatered in the laboratory by centrifugation using a Beckman J2-HS Centrifuge or Beckman-Coulter Avanti-JE Centrifuge at 17,600 x g for 15 minutes. Typically a

cake solids content of 14-18% was obtained. For each sample, between seven and eight grams of dewatered sludge were placed into 40 mL EPA vials which were then incubated under anaerobic/aerobic conditions at 25 degrees C for the duration of the experiment.

In order to measure the amount of TMA present in each sample, the sludge pH was raised above the pKa for TMA to drive the TMA from liquid phase to the headspace. This increase in pH was accomplished by adding lime to the samples through the addition of a supersaturated slurry solution of CaO (Fisher Scientific) followed by thorough mixing with hand, resulting in a final pH over 11.5. Increasing the pH to this level resulted in inhibition in the biological activity of the samples. Thus each sample that was limed and analyzed for TMA was sacrificed after analysis. At the lime dose incorporated in the experiments, the pH was well above the pKa for TMA and this pH was sustained over the length of the experiment.

#### *TMA Headspace Analysis:*

The analysis of samples in this study was conducted using a static headspace method in which samples were taken directly from the headspace of incubating vials and injected into a Gas Chromatography/Mass Spectrometer (GC/MS) (Novak et.al., 2002). This method was found to be very convenient for analyzing large number of samples in a relatively short time with reliable accuracy. To determine the amount of TMA present in the headspace of each vial, 100 microliters of headspace volume were removed by syringe and injected into a capillary column GC/MS (Hewlett-Packard 6890). Between injections, the syringe was cleaned by heat and vacuum using a syringe cleaner (Hamilton). Integration of peak area was performed using the environmental Chemstation program (G1701 CA). The amount of TMA in each sample was determined ratiometrically by comparing the sample peak area with the area of a known standard, 100 ppm (Scott Specialty gases)

#### *Experimental approach:*

Four different experiments were conducted to understand the role of polymer and shear in TMA production from limed biosolids. These are described in the following paragraph.

- The first experiment was performed using undewatered sludge and without the application of shear to understand the role of cake solids concentration in odor production. Both anaerobic and aerobic incubation conditions were used over a range of pH levels.
- The second experiment focused on polymer as precursors to TMA formation. Extreme polymer overdose conditions were used to confirm the role of polymer in TMA production.
- Once the significance of polymer in odor generation was determined, the third experiment was targeted on the possibility of abiotic degradation of cationic polymers.
- Finally, the fourth set of experiments studied the influence of mixing and shear on TMA production because of the real time shear conditions existing in field centrifuges.

## **RESULTS AND DISCUSSION**

### *The influence of oxic conditions and pH on TMA production*

In this portion of the study, the effect of oxic conditions at various pHs on TMA production was evaluated. Undewatered sludge samples were placed in 40 ml EPA vials and incubated. Both aerobic and anaerobic conditions were monitored at pH values of 2, 7 and 12 for production of TMA. Polyacrylamide polymer (5000 ppm stock concentration) was added at the optimum (X) and overdose (3X) conditions, mixed and then the pH adjusted using either 6N HCl to achieve a pH of 2 or a supersaturated solution of lime (CaO) was used to attain pH 12. A control or undosed sample was also incubated. These samples were not sheared or dewatered prior to analysis. The experiment was designed to mimic conditions in a dissolved air floatation (DAF) unit where WAS is thickened after addition of cationic polymer. Samples were also set up under anaerobic environments to study the influence of anaerobic conditions on TMA production. Headspace TMA was analyzed on days 1, 2, and 3 because DAF units typically have a storage time of less than a day before the WAS proceeds to the dewatering unit. Anaerobic conditions were achieved by purging the headspace of samples with nitrogen. For

aerobic conditions, wet air was continuously blown through the samples using an air stone throughout the incubation period.

Figure 1 shows the TMA present in the samples without polymer addition at pH 12 and demonstrates that the peak TMA is higher under anaerobic conditions. For the sample without polymer, it appears that TMA which was detected was produced from proteins present in the sludge. The maximum concentration, 4 mg/cu.m., is a relatively low concentration of TMA, but could be detected by workers near the sludge.

None of the samples at pH of 2 and 7 showed TMA production at any of the polymer doses tested. This was as expected because although TMA can be produced at neutral pH, it is not volatile and thus not likely to be detected in the headspace unless the pH increases to near or above the pKa. Therefore, even if TMA was present in the sludge in the ionized form, it would not be detected in the headspace. This means that even if TMA were present in the sludge in the ionized form, it did not get detected in the headspace. At a pH of 12, TMA was observed in the headspace, albeit in low concentrations. It was thought that TMA would be highest in the samples with the highest amount of polymer. However, the opposite result was observed in this experiment, in that TMA was detected only in the samples without polymer. None of the polymer dosed samples had any TMA in the headspace. It is possible that TMA was produced in these samples but got consumed within the first 24 hours after sample preparation. Since the first run of analysis was made only after 24 hours, any TMA generated prior to that time could have been missed. Another point to be noted was that samples were not dewatered prior to TMA analysis, so the concentration of headspace TMA is low and although present may be below the detectable limits of the instrument.

Thus anaerobic conditions are more favorable for the production of TMA than aerobic environment. Low quantities of odor produced under both anaerobic and aerobic conditions for undewatered sludge indicate that dewatering of sludge is a critical process influencing odor production.

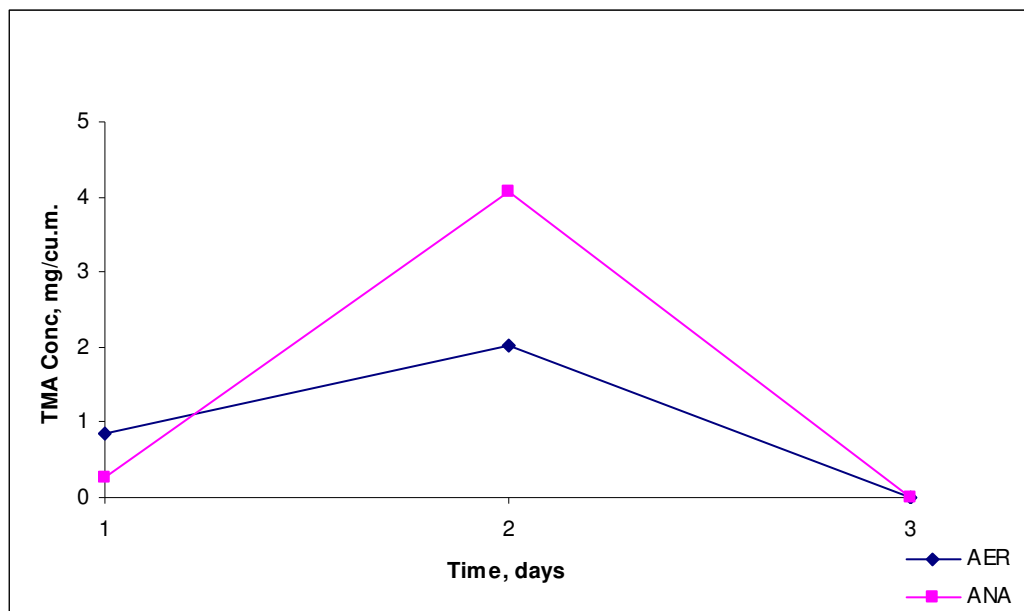


Figure 1: Effect of aerobic and anaerobic conditions on generation of TMA  
(without polymer and at pH-12)

*The impact of polymer biodegradation on TMA production*

The objective of this phase of the study was to determine if polymer could be biologically degraded to yield TMA. The polymer used was NALCO 1404, a high molecular weight cationic polymer at a concentration of 5000 ppm with a Polyacrylamide backbone. Samples were set up according to the matrix shown in table 1.

Table 1: Sample matrix for the evaluation of biological degradation of polymer to yield TMA production.

		1	2	3	4	5
	<b>Sample description</b>	<b>Polymer (ml)</b>	<b>Water (ml)</b>	<b>Sludge (ml)</b>	<b>Polymer conc. (mg/L)</b>	<b>Polymer dose</b>
<b>sample 1</b>	90 ml polymer	90	0	10	4500	90X
<b>sample 2</b>	30 ml polymer	30	60	10	1500	30X
<b>sample 3</b>	10 ml polymer	10	80	10	500	10X
<b>sample 4</b>	3 ml polymer	3	87	10	150	3X
<b>sample 5</b>	no polymer	0	90	10	-	-
<b>sample 6</b>	30 ml polymer & no sludge	30	70	0	1500	-

X indicates the optimum polymer dose.

The optimum dose for polymer was obtained as described previously. To determine the effect of polymer dose on TMA formation, polymer concentrations used to achieve overdosed conditions shown in column 5 of table 1 were used. The samples were prepared by placing the polymer solution into 240 mL serum bottles and then adding the sludge (undewatered) to the bottles. In sample preparation, WAS was dropped into the polymer/water and not mixed so that a blob of sludge was suspended in the polymer solution. The bottle lids were loosely closed, and the headspace of bottle was not purged with nitrogen. The samples were incubated aerobically for eight days. On day six, pure oxygen was injected into the headspace to maintain aerobic conditions. Samples were limed on day eight to raise the pH to approximately 12, the bottles were sealed, and the headspace was analyzed for TMA. Samples were not sheared or dewatered prior to TMA analysis.

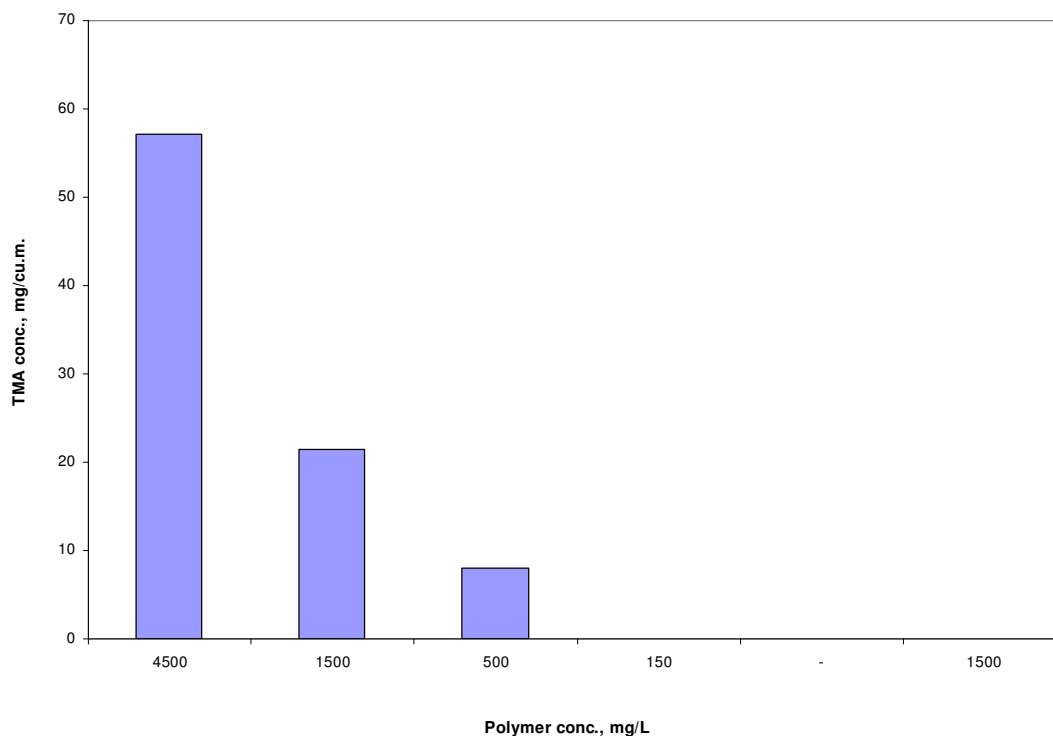


Figure 2: Headspace TMA profile: Effect of polymer dose on TMA production.

The TMA production under varying doses of polymer is shown in figure 2. It is clear that as the polymer dose increases, the TMA production increases correspondingly. A linear increase in TMA was observed with polymer addition. Further, no TMA was detected in either control, one with sludge and no polymer, and the other, a polymer solution without sludge. The occurrence of TMA in samples containing both polymer and sludge, and its absence in the two controls indicates that TMA is produced from the biological breakdown of polymer. No TMA was detected in the headspace of the sample that was three times overdosed with polymer. In this sample, TMA production may have occurred but was likely converted to ammonia and carbon dioxide prior to the analysis on day eight and so was not detected.

As mentioned in the discussion of results for the previous experiment, samples in this experiment were not dewatered prior to inception of incubation. Therefore it is possible that TMA would have been produced for the three times overdosed sample but did not get detected in the headspace because it was present at a low concentration. Furthermore, nothing can be concluded about the critical polymer dose which would produce TMA under the conditions

which form the framework for the design of this experiment. Though the polymer overdose in this experiment do not reflect actual field dosage of such polymers, this experiment provides an important observation that cationic polymer can be biologically degraded leading to formation of TMA. Based on results from the previous experiment, it is hypothesized that under anaerobic conditions the TMA production would be higher than that obtained for aerobic environments. These experimental results show that polymers are important precursors of TMA production in sludge handling and polymer overdosing may be an important contributor to odors.

*Abiotic degradation of polymer to produce TMA.*

Once it was found that polymers could be important precursors for TMA formation, it was necessary to determine whether the microbes in the sludge were responsible for the degradation of polymer to TMA, or whether polymer was interacting with the lime to form TMA abiotically. To make this determination, an abiotic experiment was performed in which polymer and lime was subjected to the same conditions tested in the previous experiment, but without sludge. To determine the correct proportion of polymer to lime, the optimum polymer dose was determined (X mL polymer/L WAS sludge) as described earlier. Though the optimum polymer dose does not have a significant meaning in this experiment due to absence of sludge, some value of polymer dose was needed for comparison, on which the underdosing and overdosing of polymer could be based. Based on CST tests it was determined that 40 mg/L of polyacrylamide polymer added to water would be equivalent to other optimal doses for the other studies. Once this was determined, polymer was added to water at the following approximate doses: control (no polymer), underdose (20 mg/L), optimal dose (40 mg/L), overdose one (80 mg/L) and overdose two (400 mg/L) [Read the polymer dose as X mg polymer /L water]. The overdose conditions in this part of study were designed with the objective of determining the abiotic degradation of polymer. Thus it was thought appropriate to choose a wide range of polymer doses even though the overdose conditions do not represent actual doses implemented at field conditions. Controls for each polymer dosage were set up using polymer only, without addition of lime. A total of 10 samples were prepared to explore the abiotic formation of TMA from polymer and lime as shown in Table 2.

Table 2: Sample matrix for the evaluation of abiotic degradation of polymer.

<b>Control (no lime)</b>		Polymer Dosing				
		0	0.5X	X	2X	10X
	Polymer added (mg/L)	0	20	40	80	400
<b>Lime addition</b>		Polymer Dosing				
		0	0.5X	X	2X	10X
	Polymer added (mg/L)	0	20	40	80	400

X indicates the optimum polymer dose.

Lime was added to increase the pH to greater than 11.5. The purpose of lime addition was to increase the pH and study the abiotic interaction of pH and polymer. Samples were setup in 40 mL EPA vials by adding 55-60 mgs of CaO to 15 ml of water. To perform the experiment abiotically, water and lime were mixed as per the matrix presented in Table 2 and sterilized by autoclaving. Polyacrylamide polymer was sterilized by irradiating it under UV light for five minutes and then adding it to the samples in the granular form. This way of disinfecting was done to prevent any change in the polymer structure. Samples were analyzed for TMA on days 1, 2, 3, 5, 8, 14, 28 and 56. This time schedule for analysis of TMA was thought sufficient to monitor the abiotic production of TMA under site conditions once the biosolids are land disposed. The syringe used for pulling out samples from headspace was sterilized before each run by dipping in alcohol and heating. All apparatus used for setting up the experiment were autoclaved to ensure absence of any biological influence.

None of the samples showed the presence of TMA in the headspace on any of the sampling days. Even after day 56, a lack of TMA indicated that either the abiotic degradation of polymer to yield TMA does not occur or the reaction rate is too slow to have any practical implications. TMA odor production in field sites occurs in shorter time duration, typically within days. From

the results of this experiment, it thus appears that abiotic formation of TMA from polymer has little to no impact on TMA production in plants and sludge disposal locations.

*The Effect of mixing and shear on TMA production:*

As shown previously, under high polymer doses, polymer is degraded biologically to produce TMA. Because sludges are subjected to a range of shear intensities during dewatering and conveyance, the effect of mixing and shear on TMA production was investigated. The optimum polymer dose was obtained as described previously. Sludge samples were prepared for incubation in 40 mL EPA vials. Two doses of polymer were examined: optimum (X) and overdose (3X). Three conditions of mixing were studied: swirling one time, swirling ten times, and shearing for five seconds using a 1/5 HP waring blender. A shearing time of five seconds was found to impart the same amount of shear as a high solids centrifuge and also gave the same optimum polymer dose as obtained after shearing in a KADY Model-L Laboratory Mill, (KADY International, Scarborough ME) (Muller et.al, 2004).

Sludge samples were sheared after addition of polymer. The sample matrix is described below in Table 3. Two controls were used - Control A in which no polymer was added to sludge and no mixing/shear was performed, and Control B in which no polymer was added to sludge but the sludge was sheared for five seconds. All samples were maintained under anaerobic conditions after purging the headspace with nitrogen gas. Incubated samples were limed, and then analyzed for TMA on days 1, 2, 4, 10 and 18. The cationic polymer, NALCO 1404 at 5000 ppm concentration was used.

Table 3: Sample matrix for determination of the effect of mixing and shear on TMA production under varying polymer dosages.

<b>Sample name</b>	<b>Polymer dose and mixing status</b>
Sample A	X,1 swirl mixing
Sample B	X, 10 swirls mixing
Sample C	X, sheared for 5s
Sample D	X,1 swirl mixing
Sample E	X, 10 swirls mixing
Sample F	X, sheared for 5s
Control A	No polymer, no mixing
Control B	No polymer, sheared for 5s

X indicates the optimum polymer dose.

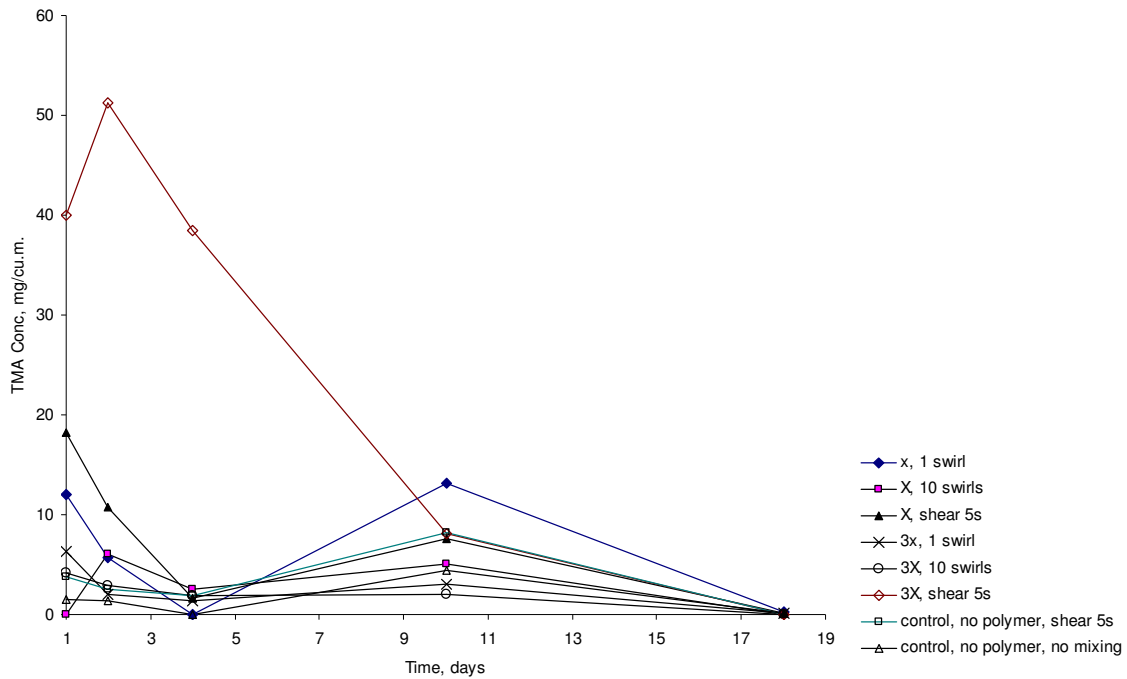


Figure 3. TMA production under various conditions of mixing and shear and dosage of polymer

From Figure 3, it can be seen that TMA production is highest for the sample with highest polymer dose (3X) and high shear conditions. The sample with the optimum dose and high shear also gives high production of TMA relative to samples with little shear. Samples mixed with one swirl and ten swirls did not differ much, which indicates that swirling one time or ten times does not influence TMA production as much as intensive shearing of the samples. However, comparison of unsheared and minimally mixed samples with highly sheared samples demonstrates that shear increases the production of TMA significantly. The two control samples yielded very little TMA and are also similar in TMA production. The low quantity of TMA detected in these control samples could be attributed to the degradation of proteins in the sludge, as discussed earlier. However, there was not much difference observed in the two control samples, in that the sheared and unsheared conditions produce nearly the same amount of TMA in the headspace.

One important observation from the experiment is the time frame during which peaking of TMA occurs. The sample overdosed with polymer and with high shear was found to peak on day two whereas the peak for the sample with the optimum polymer dose and with high shear may have occurred before day one. From the data collected, the peak TMA value and the peaking time for this sample (optimum dose and high shear) cannot be determined. Another interesting observation is the second peaking of the headspace TMA on day ten. It is possible that under optimum polymer dose and high shear conditions, the rate of TMA production exceeds the rate of TMA consumption at a later time, yielding a second peak. Such an occurrence was not observed for overdose condition of polymer (3X) with shear.

This phase of the study demonstrated that shear influences the production of TMA under both optimum polymer dosing and overdosed conditions. However, more data was needed at short incubation times to determine the TMA peak value and production day.

*The effect of shear on TMA production:*

The previous experiment explored the influence of shear and mixing on TMA production. From the data in figure 3, it is evident that mixing by hand, either one swirl or ten swirls, does not have much influence on TMA production, whereas intensive shearing of the samples produced a higher amount of TMA than simple swirling. To simplify the matrix for this experiment, the hand mixing was performed only at the ten swirl level, and more samples for TMA were taken prior to day one. The sample matrix for this experiment is given in table 4. Samples were analyzed after 8, 16, 24, 48 and 72 hrs.

NALCO 1404 at the same polymer strength was used with WAS as in the previous experiment. The optimum polymer dose again represents the dose obtained under shear conditions. The controls were sheared in a separate blender than the samples to prevent possible carry over of polymer into control samples.

Table 4: Phase two sample matrix for determination of the effect of polymer dosage and shear on TMA production

<b>Sample name</b>	<b>Polymer dose and mixing status</b>
Control A	No polymer, no mixing
Control B	No polymer, sheared for 5s
Sample A	X, 10 swirls mixing
Sample B	X, sheared for 5s
Sample C	3X, 10 swirls mixing
Sample D	3X, sheared for 5s

X indicates the optimum polymer dose.

Figure 4 show the results from phase 2 shear experiment.

It can be seen that shearing the sludge clearly increases TMA production. TMA production from the sample dosed at the optimum level with polymer was higher than the sample which was also optimally dosed, but not subjected to shear. On the other hand, comparing the two samples, both of which were overdosed, it is clear that TMA production for sheared sample was much higher than that for unsheared sample. The peak value of TMA for the overdosed sheared sample was almost ten times more than the peak TMA production for the overdosed unsheared sample (Figure 5).

One possible mechanism for the generation of TMA by shearing is that shear breaks the polymer linkages and makes it more readily bioavailable. Thus, at higher doses of polymer, shear influences the TMA production to a larger extent than at optimum dose. Further, the peak TMA production for the overdosed sheared sample occurred at a later time than other samples and the controls. From the two controls in which no polymer was added, it is clear that polymer is an important precursor to TMA production because both the controls yield very low amounts of TMA in the headspace. The control with shear showed slightly more TMA than the control without shear. This is likely due to the breakdown of proteins in the sludge as discussed earlier. It was interesting to note that the difference in the peak TMA values between the two controls and the two optimally dosed samples was almost of the same magnitude. Thus, although shear

enhanced TMA production when polymer was added, the influence was not very significant until the optimal dose was exceeded.

No data is available for polymer overdose in the region between X (optimal) and 3X (overdose). Further work is needed to estimate the critical point beyond which shear influence on TMA production becomes the dominant factor.

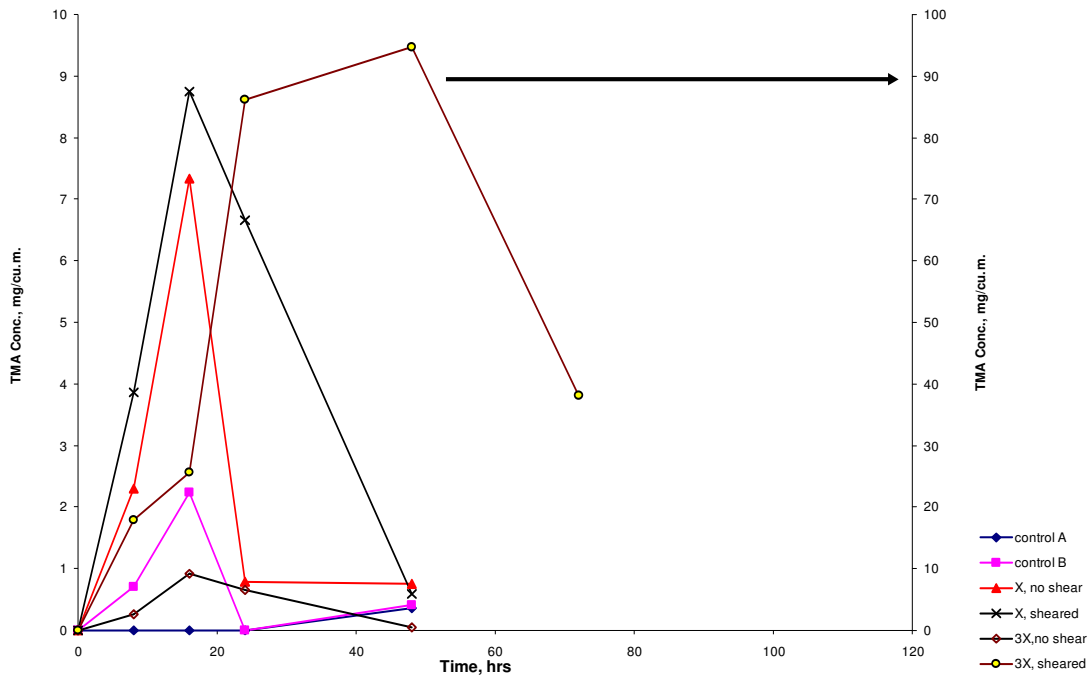


Figure 4: Headspace TMA production with and without shear influence.

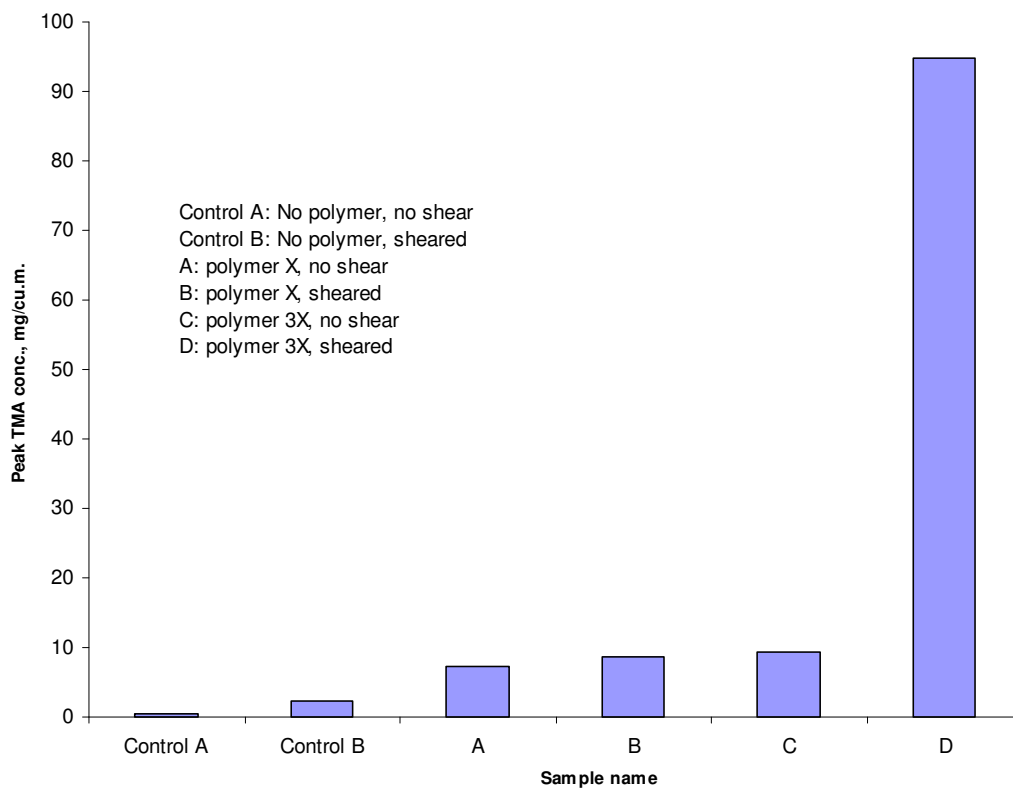


Figure 5. Peak TMA production under different conditions of shear and overdose of polymer

## SUMMARY AND CONCLUSIONS

The purpose of this study was to determine the conditions under which TMA can be produced from sludge. Shearing the sludge was found to be a very important factor influencing TMA production, especially at higher polymer dosages. At optimal polymer dose, shear was found to influence TMA production but the amount of TMA produced was about 10% of that for the overdosed sludge. It is assumed that shear breaks the polymer linkages and makes it more readily bioavailable. As a result biological breakdown of polymer is enhanced giving rise to increased TMA production. Further work is needed to expand the findings about the critical polymer dose beyond which shearing becomes the dominant mechanism of TMA odor production over polymer degradation.

In the absence of polymer, TMA was detected in the headspace, indicating that sludge proteins were also precursors for TMA production. These proteins are thought to become bioavailable upon shearing the sludge, and then contribute towards TMA odor production. However, their headspace concentration was less than 5% of the overdosed and sheared samples. So, while sludge proteins are a source of TMA, they are small in comparison to cationic polymer.

Anaerobic conditions are found to be more conducive for generation of TMA compared to an aerobic environment. The abiotic mechanism of polymer degradation was also studied and indicated that either the polymer does not degrade chemically or the rate is very slow and therefore, is not important.

Specific conclusions are

- Polymer breakdown produces TMA in headspace of stored limed biosolids
- High intensity shear coupled with excess polymer dosing produced greater TMA headspace concentration.
- Proteins in sludge are important precursors for TMA production under conditions of shear.
- Liming alone does not degrade polymer to generate TMA in the headspace
- Anaerobic conditions are more favorable for TMA production over aerobic environments.

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## Chapter 4: Engineering significance

Wastewater treatment plants are an indispensable component of today's society. With the growth of residential areas in the vicinity of treatment plants and land application of biosolids, there has been an increased awareness concerning issues like odor control and management. A variety of factors may contribute to the odor potential of wastewater sludges/biosolids. It is imperative to understand and characterize the odor production cause and patterns for development of better odor abatement and control techniques.

Lime stabilization is a cost-effective method commonly used in the wastewater industry to produce biosolids which can be beneficially reused. The process however is associated with production of trimethylamine and ammonia odors associated with the high pH conditions. Thus, though sulfur based odors are reduced, lime stabilization leads to production of amine based odor compounds. The role of pH and effect of incorporation is known to effect odor production patterns. In addition to these, cationic polymers used in dewatering processes have been found to be important pre-cursors for production of trimethylamine odors. Shear conditions present in certain dewatering devices have also been associated with odor production.

Trivalent metals are known to effect the binding properties of sludge due to their effect on floc associated proteins. Results from this study show a correlation between the protein content in sludge, trivalent cation and odor potential. Specifically, the ratio of Al/Fe has an inverse relation with labile protein in sludge. It is thought that trivalent metals could play an important role in influencing odor production from wastewater sludges/biosolids.

The development of better odor control techniques can be established only with an understanding of odor production mechanisms and cause. This research both increases our understanding and points to future directions.