Factors Contributing to Trimethylamine Generation from Limed and Polymer Conditioned Sludges

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Abstract

Trimethylamine, $(CH_3)_3N$, (TMA), odors are often associated with limed and polymer conditioned sludges. This odor has a fishy smell and can be a nuisance to the community surrounding a wastewater treatment plant or land application site. Several factors are thought to determine the amount of TMA generated from limed biosolids. These are, the presence of cationic polymer, the polymer dose, the time between addition of polymer and lime stabilization, shear imparted on the sludge in the dewatering process and dewatered cake solids concentration. All of these were investigated in this study. The results showed that TMA could be generated from sludge that did not contain polymer but the concentrations were low compared to sludge conditioned with cationic polymer. As the polymer dose increased, the TMA increased. Shear also showed to play an important role for TMA production. In addition to higher shear increasing the polymer demand, shear in itself can increase TMA generation. However, the most important factor in generating TMA was the time between conditioning and liming. If this time was minimized, little TMA was produced, even at high polymer doses. Data also suggests that methanogens play an important role in the breakdown of TMA.

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Dr. Novak and Dr. Murthy are coauthors in Chapter 3 of this thesis. Dr. Novak served as the principal investigator of the research discussed in this thesis and has contributed equally to Chapter 3.

Chapter 1
Introduction

The treatment of wastewater generates odors that are considered offensive. Different kinds of odors arise at different parts of the treatment process. This study investigates the factors contributing to trimethylamine (TMA) odors during the process of sludge dewatering. Sludge dewatering is an important process that allows for further use of the biomass generated by of either incineration or land application. Dewatering follows the general procedure of cationic polymer addition for improved thickening, followed by mechanical dewatering such as done by centrifuges or belt press.

Several key aspects of the dewatering process are believed to contribute to the generation of TMA odors. These include time between cationic polymer conditioning and lime stabilization, shear imparted on the sludge, biosolids concentration, and polymer dose. In addition, it is believed that methanogens break down TMA. Therefore methanogenic activity is also of interest in the study of TMA generation.

It is believed that the generation of TMA odors is based on biological processes where both naturally occurring polymers and synthetic polymers are broken down. As long as these polymers contain the amine functional groups as the basis for the generation of the precursors to TMA, such as choline, glycine betaine, trimethylamine-N-oxide, or aminopropyltrimethylammonium, TMA can be generated.

Chapter II reviews the literature of studies dealing with TMA. Specifically, work that investigated the mechanisms of the generation of TMA odors, especially in wastewater treatment, as well as TMA destruction and effective odor detection methods for TMA was reviewed. Works by different investigators show that the generation as well as the destruction of TMA seems to be a common process, especially in the marine environment.

The study of this thesis is presented in Chapter III. A detailed description of the methods used for the investigation, the results of the experiments, as well as the interpretation of the results are explained. The study was comprehensive, as it looked at all major factors contributing to TMA generation; therefore a fairly complete picture is given how each aspect of sludge dewatering influences the generation of this specific odor, as well how these aspects influence each other. Finally, what stands out is a very practical insight that can limit the generation of TMA. The factor that time plays between the addition of cationic polymer and lime stabilization is the most easily controlled aspect of all other factors investigated and also the most effective in TMA control.

The conclusion of the thesis explains the significance of the study. The study is a very relevant contribution to the understanding of odor mechanisms in wastewater treatment. The knowledge gained can help engineers and wastewater treatment plant operators to adjust dewatering procedures to minimize TMA odor production.

CHAPTER 2

Literature Review

Introduction

Treating wastewater or sewage results in the generation of sludge. Sludge, also known as biosolids, is comprised of microbial organisms that have removed much of the significant nutrients and biochemical oxygen demand initially present in the sewage. Biosolids that have been digested for longer periods have reduced biological activity, as readily degradable organics are no longer present in high concentrations. With the reduced biological activity and sludge being generated in large amounts at wastewater treatment plants (WWTP), this represents an attractive source of fertilizer.

Typical options for sludge processing from municipal WWTP are land application or incineration. In either case, the sludge must be dewatered before it can be further processed. Dewatering is aided by the addition of cationic polymer, that allows for much improved flocculation and thickening of the sludge. At this stage however, sludge still emits significant odors, including volatile reduced sulfur compounds, nitrogen based compounds, such as TMA and volatile organic fatty acids (Hwang *et al.* 1995, Kim *et al.* 2003). In addition to very unpleasant odors being emitted that reduce the acceptability for land application, a threat from possible pathogens still active in the sludge remains. To abate this odor and pathogen problem biological activity in the sludge must be limited. Therefore it has become typical practice to stabilize dewatered sludge by lime addition. In this practice powdered lime is added to dewatered sludge and mixed.

Although sludge stabilization by liming has been proven to be successful for reducing many odor emissions including sulfur odors, new odor problems have arisen. Volatilization of trimethylamine results as an unwanted consequence of raising the pH during lime stabilization (Novak *et al.* 2002). Trimethylamine (TMA) is an odor that is characteristic of a fishy smell and is considered unpleasant by many. TMA generation in WWTP has gained attention recently as more research has focused on this topic.

Trimethylamine (TMA)

TMA is a weak base and has a pKa of 9.80 (Perrin *et al.* 1981). In its non-protonated form it volatilizes and can be noticed by its characteristic fishy smell. Even at very low concentrations TMA can be noticed by humans. An odor threshold of 0.48 ppmv has been reported (Amoore and Hautala 1983). While Ruth (1986) reports a human detection limit of 0.11 micro g/m^3 and Novak (2002) 0.4 ppb.

Generation of TMA odors

Mechanisms for TMA generation during lime stabilization have not been studied in detail. However the primary source of TMA is believed to the result of enzymatic breakdown of cationic polymer and proteins (Kim *et al.* 2001). TMA odors have been noticed primarily during and after lime stabilization (Novak *et al.* 2002). Under conditions prior to liming, dewatered sludge cakes have pH values below the pKa of TMA of 9.81. This prohibits TMA to volatilize as it remains in the protonated form, trimethylammonium, and is therefore bound to the sludge cake. Lime stabilization raises the pH above the pKa of TMA and thus drives off significant portions of the chemical and a significant fishy odor can be observed.

Dentel (2005) has studied the relationship between alkylamine odors and the degradation of cationic polymers in sludge. By comparing polymers with different structures, he suggests the nature of the formation of TMA. The polymers that were found to generate TMA in polymer conditioned sludge had either ester functional groups or functional groups with an amide linkage. The necessary amines for TMA are present in each of these functional groups. Thus it is believed that TMA generation is preceded by an initial ester hydrolysis step or the hydrolysis of the amide linkage, followed by subsequent enzymatic hydrolysis of the resulting choline or aminopropyltrimethylammonium to generate the protonated form of TMA, trimethylammonium (Dentel *et al.* 2005).

That TMA generation is mediated by biological activity is further supported by studies in microbiology. *Escherichia coli* for example has been found to have several terminal reductases that catalyze the reduction of N-oxide compounds. Sambasivarao and Weiner (1991) report that in *E. coli* an inducible trimethylamine oxide reductase is expressed. The enzyme reduces trimethylamine oxide to TMA. Microbial organisms, especially in

marine environments, produce the precursors to TMA abundantly. These precursors include choline, glycine betaine, and trimethylamine-N-oxide (Summons *et al.* 1998).

Experiments have shown that abiotic degradation of cationic polymers does not occur and does not produce TMA (Subramanian 2004). Subramanian (2004) found while polymer conditioned activated sludge samples produced TMA upon liming, control samples with cationic polymers added but without sludge had no detectable TMA after liming.

TMA Odor Potential

As TMA has a very low odor threshold of 0.00012 mg/m^3, small amounts of TMA in sludge cakes have the potential for significant odor generation upon liming. A partitioning coefficient of TMA of about 300 was determined (Novak *et al.* 2002). The interpretation by the authors of the study is that one cubic meter of digested and polymer conditioned sludge cake with a TMA concentration of 46 mg/L can release TMA at the odor threshold concentration to 376 million cubic meters of air. In addition, air in contact with limed sludge cake becomes saturated at 1/300 of the potential total TMA released. Thus, limed sludge cake has the potential to release TMA odors for extended periods of time.

TMA Destruction

Long term anaerobic storage of polymer conditioned and dewatered sludge suggests that TMA destruction happens. Novak *et al.* (2002) found that conditioned sludge cake stored anaerobically for five weeks prior to lime addition had almost no TMA detected. In contrast, experiments where similar sludge cake was stored under anoxic conditions prior to lime addition showed TMA generation but no TMA destruction. The experiments suggest that anaerobic demethylation of TMA occurs in anaerobic conditions. It is believed that similarly to organosulfur destruction, methylotrophic methanogens play a role in TMA destruction and the formation of ammonia. Summons *et al.* (1998) have found methane production by methanogens utilizing TMA as their principal carbon source, where *Methanosarcina barkeri*, and *Methanococcoides burtonii* showed conversion of TMA to methane and biomass.

Odor Detection Methods

Odor detection methods include subjective as well as quantitative methods. Olfactometry is a subjective method that uses human subjects to evaluate the type and the concentration of an odor (Persaud *et al*. 1996). This method is often useful as it requires few or in many cases no technical apparatus. Another advantage this method has when panel sizes are large enough ($n > 10$) is that one obtains useful information how a general population perceives a particular odor. Quantitative odor detection methods are more useful in many cases. When gas samples contain multiple odorants that interfere with the human ability to focus on a target smell, olfactometry often looses its ability to be a useful method of odor detection. In cases where the concentration of particular chemicals in gas samples have to be determined with high degrees of accuracy the human sensation of different levels of intensity also no longer provides the accuracy needed. In scientific research odor detection is usually performed according to the accepted methods for analyzing the composition of gases and liquids. These methods include liquid chromatography, phase microextraction, polymer arrays, and the static head-space method used in this study.

Liquid Chromatography (LC) can be a useful tool for quantitatively analyzing water and wastewater samples. Pericas *et al*. (2004) demonstrated how this method was used in analyzing various water samples for TMA. This method generated results with good linearity, accuracy and reproducibility.

Solid phase microextraction (SPME) is another method that has been used for TMA detection in wastewater, thickened sludge, and dewatered sludge (Kim et al. 2002). A small, coated fiber that absorbs volatile organic compounds is used for sampling the gas. The analysis is then proceeded by gas chromatography. SPME can be used for sampling the gas phase over the headspace of sludge samples. The detection limits are near the odor threshold by humans.

Static head-space method was used by Novak *et al.* (2002) for the analysis of TMA odors. In these studies sludge was incubated in bottles with volumes ranging 200 to 700 mL and made up 5-10% of the bottle volume. Gas was withdrawn from the head-space using a gas-tight GC syringe, followed by the injection into the gas chromatograph column. The static head-space method was explained to have several advantages. The method gives investigators the ability to run multiple samples in a short time period. Another advantage is that the relation between sludge volume and head-space volume is not very sensitive to the head-space concentration.

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Chapter 3
Manuscript

Factors Contributing to Trimethylamine Generation from Limed and Polymer Conditioned Sludges

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Abstract Trimethylamine, $(CH_3)_3N$, (TMA), odors are often associated with limed and polymer conditioned sludges. This odor has a fishy smell and can be a nuisance to the community surrounding a wastewater treatment plant or land application site. Several factors are thought to determine the amount of TMA generated from limed biosolids. These are, the presence of cationic polymer, the polymer dose, the time between addition of polymer and lime stabilization, shear imparted on the sludge in the dewatering process and dewatered cake solids concentration. All of these were investigated in this study. The results showed that TMA could be generated from sludge that did not contain polymer but the concentrations were low compared to sludge conditioned with cationic polymer. As the polymer dose increased, the TMA increased. Shear also showed to play an important role for TMA production. In addition to higher shear increasing the polymer demand, shear in itself can increase TMA generation. However, the most important factor in generating TMA was the time between conditioning and liming. If this time was minimized, little TMA was produced, even at high polymer doses. Data also suggests that methanogens play an important role in the breakdown of TMA.

Keywords

biosolids, lime stabilization, odor, trimethylamine, polymer conditioning, sludge cake, dewatering, shear, methanogens

INTRODUCTION

Trimethylamine (TMA) odors are often associated with limed and polymer conditioned sludges. This odor has a fishy smell and can be a nuisance to the community surrounding a wastewater treatment plant or land application site. Primary and secondary waste activated sludge is collected from settling tanks and may undergo treatment to thicken the sludge. Cationic polymer is often mixed with the sludge to improve thickening. Primary sludge can be thickened in several ways including gravity or centrifugal thickening. Thickening using dissolved air flotation for waste activated sludge may or may not use polymers. After thickening and dewatering, the sludge can be stabilized by the addition of lime. Following lime addition, fishy odors are sometimes noted.

This study was undertaken to determine the cause of fishy odors from lime stabilized sludge generated by DC Water and Sewer Authority (DCWASA) and the Washington Suburban Sanitary Commission (WSSC). Lime stabilization is practiced at DCWASA and at several of the WSSC plants. There is no "standard" sludge processing flow scheme so a variety of thickening processes were of interest in this study.

It is thought that the production of TMA is due to biological activity that transforms proteins in sludge and polymers added for conditioning into TMA. TMA is dissolved in the liquid phase of the sludge in an ionic form and is released into the gaseous phase when the pH of the dewatered sludge is raised above 10, which happens when lime is added to the sludge. The addition of lime causes TMA to be released rather quickly, creating a concentrated odor.

The study focuses on determining the significance of each of the factors believed to contribute to TMA generation in primary and waste activated sludges. These factors include the solids concentration of sludge cakes, amount of polymer added, shear imparted on the sludge during the dewatering process, and time between polymer conditioning and lime stabilization. The study also investigated TMA decomposition by methanogenic microorganisms.

METHODOLOGY

Gravity thickened activated sludge from the Blacksburg, VA and Pepper's Ferry, VA wastewater treatment plants were used in this study. These are municipal plants near Blacksburg and Radford, Virginia. The obtained sludge was allowed to further thicken by gravitational settling prior to polymer conditioning in the laboratory.

Polymer solutions were made up from dry polymer and distilled water. Polymer was added to water in a beaker and magnetically stirred overnight. The optimum polymer dose was determined by the capillary suction time (CST) test using a Triton Type 304-M type apparatus with Whatman 17-CHR chromatography paper. Polymer was added to sludge in a 1/2 HP Waring blender, sheared, and then the CST was measured. The polymer dose at the lowest CST was considered to be the optimum dose. The polymers were likewise added to the sludge prior to shearing in the blender for the preparation of samples and subsequently transferred to 440 mL centrifuge bottles. The sludge was then thickened in a laboratory centrifuge. The typical solids concentration from the laboratory centrifuge was between 7 and 10 %. The centrifuge operated up to 10,000 rpm for up to 10 minutes, depending on the desired solids concentration. When higher solids concentrations were needed, additional thickening was done using a sludge press. The sludge press operated at a pressure of 30 psi and thickened 10 to 15 g of centrifuge cake to a solids concentration of up to 25%, depending on the time the sludge was allowed to press. This procedure is shown in Figure 1.

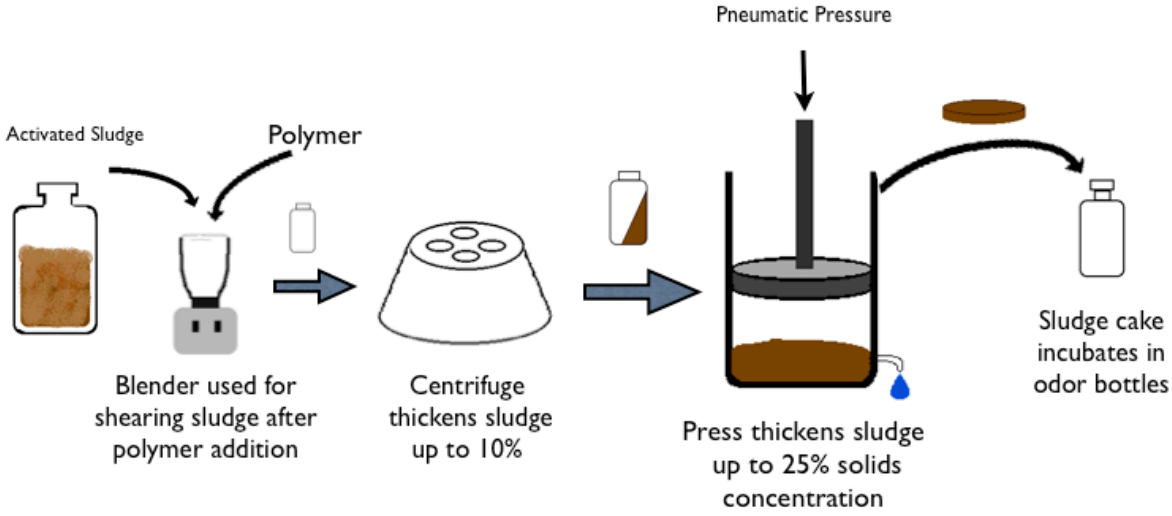


Figure 1 Method used for simulating odor production to mimic high-solids centrifugation.

After incubation, for the desired time, distilled water and dry lime were added directly to the odor bottles to cover all the sludge cake with liquid and to raise the pH to above pH 11 and to maintain it at that level. At this pH, trimethyl ammonium is converted to the gaseous form, trimethylamine, a volatile gas. After hand shaking the bottle and allowing for equilibrium to be attained, the gas was removed and sampled using a syringe and analyzed using a cryo-trapping gas-chromatography and mass spectrometry. This method was the same as that used in previous research conducted by Novak et al. (2002).

Experimental Plan

Investigating Time as a Factor in TMA Generation. For these experiments, activated sludge from the Blacksburg wastewater treatment plant was used. The sludge was allowed to further thicken by settling. The thickened sludge was polymer conditioned using the optimum dose and half optimum dose determined from CST tests. The optimum dose was 0.04g of polymer in 100 mL of sludge. The samples were sheared for 30 seconds. After shearing the conditioned sludge was dewatered by a centrifuge and

obtained a solids concentration of 10%. A control sample was not polymer conditioned but was sheared, dewatered and incubated in an identical method as the polymer conditioned sludge. Samples were limed after 2, 6, 12, 22, 34, and 46 hours of sitting in the laboratory at room temperature (~23^{o}C).

Investigating Methanogenic Activity and TMA Decomposition. Waste activated sludge from the Pepper's Ferry wastewater treatment plant near Radford, Virginia was used for these experiments. The sludge was polymer conditioned at the optimum dose at 0.12g for 400mL of sludge. After the addition of polymer, six samples received 5.0 mL of a 0.127 M solution of BESA and six did not. The sludge was then thickened to three different solids concentrations, 5.4, 7.7, and 10.7 %. The samples were limed 24 hours after polymer conditioning.

Investigating Biosolids Concentration as a Factor in TMA Generation. Waste activated sludge was obtained from the Blacksburg waste water treatment plant, thickened by settling and then polymer conditioned using the optimum polymer dose determined under conditions of high shear using the CST test. After conditioning, the sludge was thickened using a laboratory centrifuge, followed by additional dewatering using a laboratory filter press. The final solids concentrations ranged from 7.5 to 20 %. The samples were incubated for 30 hours, at which point they were limed.

Investigating the Effect of Polymer Dose. Waste activated sludge was obtained from the Blacksburg wastewater treatment plant and was further thickened by settling. Using a jar test apparatus, six different polymer doses were applied. A control sample did not receive any polymer. The other samples received 0.7, 3.0, 10.0, 30.0, and 70.0 mL of cationic polymer solution in 450 mL of sludge. The polymer solution was made up of 1.5g of polymer in 500 mL of distilled water. The optimum polymer dose determined by CST tests was around 1.5 mL. The shearing consisted of one minute of mixing at 100 rpm followed by five minutes at 30 rpm. These shearing conditions reflect conditions that might be expected for a dissolved air flotation unit used in treatment plants. Following mixing, the sludge was thickened using a laboratory centrifuge. The supernatant liquor was then decanted and the remaining sludge was incubated in odor bottles. The solids

concentrations of the final samples were 5.0 ± 0.5 %. After incubating seven hours the samples were limed and the TMA in the headspace measured.

Investigating the Effect of Shear. In order to investigate the role of shear in generating TMA odors, two experiments were conducted to determine the amount of TMA generated in sludge that received a constant polymer dose but had varying shearing times. The first experiment was conducted using a polymer dose that was optimized for 15 seconds of shearing time. This corresponded to a 15 mL polymer solution in 100 mL of sludge. The second experiment used a polymer dose optimized for 45 seconds, which was 18 mL of polymer solution in 100 mL of sludge. Both experiments used polymer solutions made up of 1.0 g of dry polymer in 500 mL of distilled water. The samples were prepared using different shearing time in the blender after addition of cationic polymer. In the first experiment, where the optimum polymer dose was for 15 seconds of shearing, samples were prepared receiving shearing ranging from 0 seconds to 25 seconds in 5 second intervals. The second experiment, where the polymer dose was optimized for 45 seconds, samples were sheared for 0, 15, 30, 45, 60, and 75 seconds. The samples of both experiments were limed after 24 hours of incubation.

RESULTS

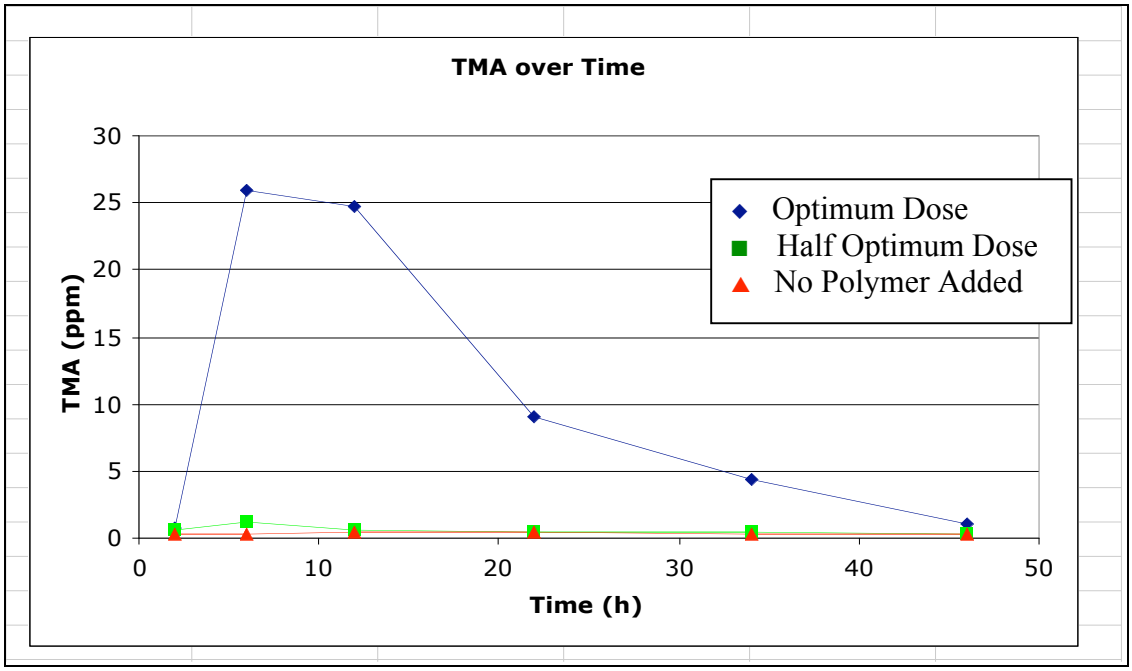
Time as a Factor in TMA Generation

The influence of incubation time (the time between addition of polymer and the addition of lime) on the generation of TMA was investigated. TMA generation is believed to come from biological cleavage of the TMA group from the structure of certain cationic polymers or from amino acids in sludge (Kim, et al., 2003). Chang et al. (2005) have proposed that an initial biologically mediated ester hydrolysis step occurs in the generation of TMA from cationic polymers. Therefore it was hypothesized that the longer the sludge sat between polymer addition and liming, the more TMA would increase.

The data revealed that time plays a critical role in TMA generation. Further, it was evident that after an initial increase in TMA generation, the TMA headspace

concentration decreased with extended incubation time (Figure 2). These results give a clear indication that TMA generation requires incubation time to be generated. All three samples, the sludge conditioned with the optimum polymer dose, the sludge with half the optimum dose, and the sludge without any polymer added showed an initial increase in TMA production followed by a significant decrease (Figure 2). The polymer conditioned sludges reached a peak in headspace TMA concentration quite rapidly, between 6 and 12 hours of incubation time, while the sludge without polymer addition reached a peak after 22 hours of incubation. After 46 hours TMA concentrations decreased to levels similar to those at the beginning of the incubation.

This behavior of an increase of TMA followed by a decrease reflects a similar behavior found with organic sulfur odors in dewatered and incubated sludge cakes (Novak, et al., 2006). The removal of TMA in waste gas has been observed in conjunction with biofilters, and digestion of TMA by bacteria has been proposed (Krumbiegel 1996). Although polymer conditioning is an important part in TMA generation, it is also seen in Figure 2 that TMA will be produced in sludge that was not polymer conditioned. In addition, it was seen that fresh activated sludge contained very little TMA. Polymer conditioning and shearing did not add TMA directly. Incubation was still required and incubation for 1 hour was insufficient to generate much TMA.



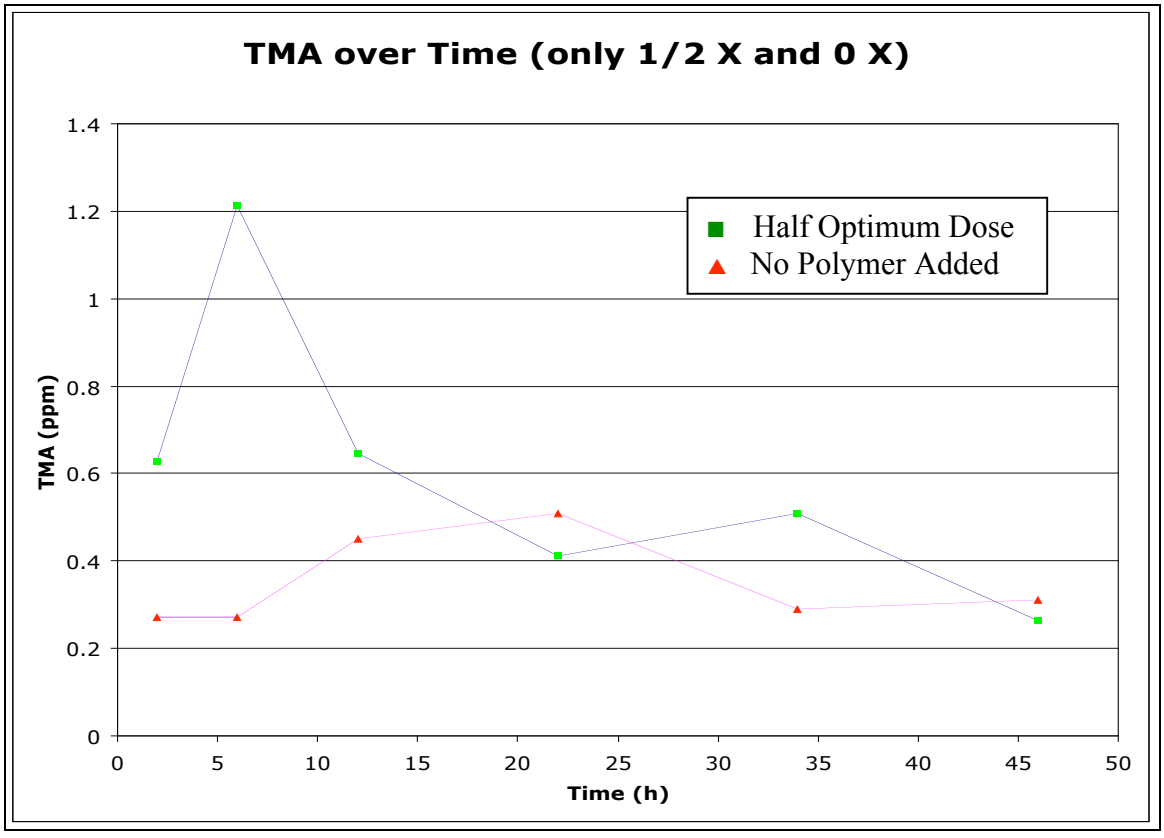


Figure 2. Effect of incubation time on TMA production for different polymer conditioned sludges. at optimum dose, half optimum dose, and no polymer added

(control). (a) shows data for the optimum dose, half optimum dose, and no polymer added. (b) compares half optimum dose to sample with no polymer added.

Methanogenic Activity and TMA Decomposition

At the beginning of incubation the sample bottles were purged with nitrogen, to establish anaerobic conditions. The incubation time experiments showed that extended incubation times produced samples with low TMA headspace concentrations (Figure 2). TMA utilization as the main carbon source by methanogens in marine environments has been well established (Summons et al. 1998). To test if methanogens are responsible for the decreased TMA concentrations at longer incubation times, an experiment was conducted to compare cationic polymer-conditioned sludge cake with conditioned sludge cake where methanogens were inhibited. The methanogen inhibitor, bromoethanesulphonic acid (BESA) was used to determine if methanogens play a role in breaking down TMA.

The data indicate that methanogens may play a role in the breakdown of TMA. TMA concentrations increased as the solids concentration increased and decreased for samples where BESA was added (Table 1). The data also show that there was considerable variation in the duplicate samples. These data indicate that methanogens can play a role in the amount of TMA that will be generated from limed sludges. This is similar to the role played by methanogens in the generation of organic sulfur odors from sludges (Higgins, et al., 2006)

Table 1. Effect of BESA on TMA production. Samples incubated for 24 hours and showed higher TMA headspace concentrations where methanogens were inhibited as well as samples with higher solids concentrations.

% Solids	TMA (in ppm for samples with BESA)	TMA (in ppm for samples without BESA)
5.4	5.4	2.4
	5.8	3.6

% Solids	TMA (in ppm for samples with BESA)	TMA (in ppm for samples without BESA)
7.7	2.5	2.7
	8.3	1.7
10.7	524	13.5
	254	348

Biosolids Concentration as a Factor in TMA Generation

The data from experiment investigating the role of methanogens indicated that the biosolids concentration may be an important factor in TMA production. In order to investigate this, sludge cakes at different cake solids concentration were prepared to determine how cake solids impacted TMA generation.

The TMA concentrations were found to increase linearly with increasing cake solids concentration (Figure 3). The data suggests that doubling the solids concentration from 10 to 20 % almost doubles the TMA generation, from about 20 to 35 ppm. The range of solids concentrations reflects that which is commonly found at treatment plants for dewatered solids. The mechanism for the increase in TMA is not known. There could be a dilution effects since TMA partitions between water and air so more water would allow more TMA to remain in solution, even in its unionized form. Another possibility is that drier cakes interfere with the consumption of TMA by methanogenic bacteria.

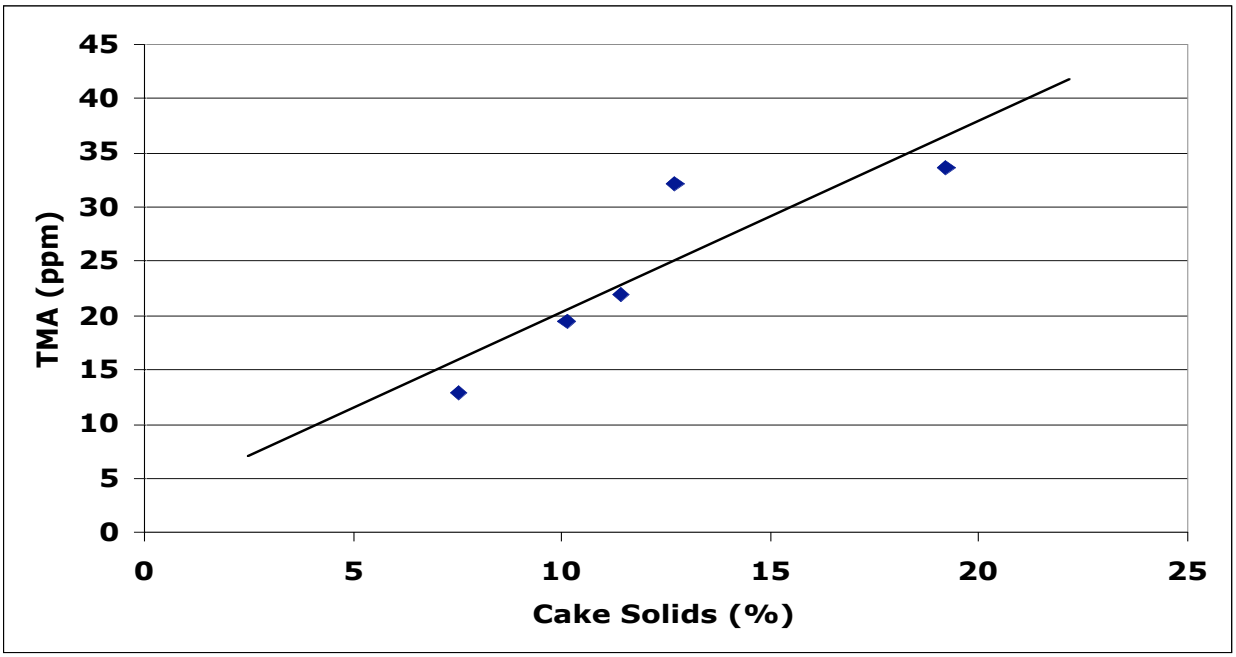


Figure 3. Effect of cake solids on TMA generation form polymer conditioned sludge.

A similar effect of cake solids on gas generation has been seen for sulfur gases (Muller, et al., 2004). Both sulfur gas and TMA can be consumed by methanogenic bacteria so a reduction in moisture in the cakes may expose the methanogens to more aerobic conditions, thereby reducing their ability to convert TMA to ammonia. However, based on the linear response to cake solids, it is likely that dilution also plays a role in the production of TMA odors.

The Effect of Polymer Dose

The portion of the study was set up to investigate the role of polymer dosing on TMA generation under identical shearing conditions so that the only variable was the polymer dose. A linear relationship was found to exist between the polymer dose and TMA concentration (Figure 4). The data shows that doubling the polymer dose doubles the TMA generation. When no polymer was added, a small amount of TMA was still produced. This is believed to be the result of degradation of proteins found in the extracellular polymers associated with activated sludge. Dignac et al. (1998) have shown

that extracellular proteins make up the major portion of extracellular polymers in activated sludge. Therefore precursors to TMA exist even without polymer conditioning. However, it is clear that the primary precursor for TMA is cationic polymer.

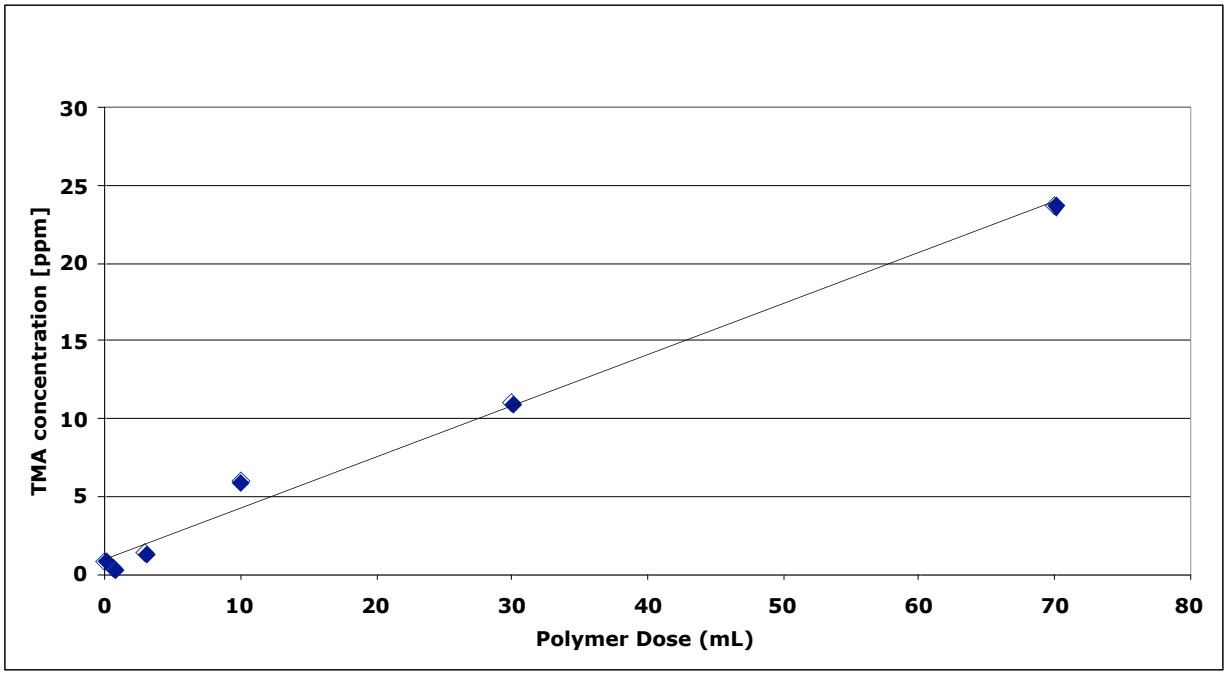


Figure 4. Effect of polymer dose on TMA generation. Incubation time was for 7 hours prior to lime addition.

The amount of TMA generated was also influenced by the incubation time. For the data presented in Figure 4, the incubation time was 7 hours. The lower dosed samples may have been further away from their TMA concentration peak than higher dosed samples. The data from the incubation time experiment (Figure 2) suggests that lower dosed samples reach their TMA peak much later than higher dosed samples. The data in Figure 4 was also conducted for conditions of both optimal dose and sub-optimal polymer dose. When excess polymer is added, odors were not increased to the degree expected because much of the excess polymer is removed in the dewatering process and ends up in the filtrate and is therefore, not degraded in the cake.

Shear

Dewatering processes can impart varying amounts of shear to sludge. It has been found that the shear in high solids centrifuges leads to increased organic sulfur odors from dewatered sludge cakes (Novak, et al., 2006). Subramanian, et al. (2005) found that increased shear resulted in greatly increased TMA production from polymer conditioned limed sludges. The optimal polymer dose for sludge conditioning depends directly on the shear imparted on sludge (Werle, et al., 1984). In general, as the intensity of shear increases or the shearing time increases, more polymer is needed for optimal conditioning (Dentel 2001).

As can be seen in Figure 5, the TMA generation remained relatively low until the optimum shear time for the polymer dose was reached. At the optimum mixing or shear time, the TMA concentration increased sharply. Mixing beyond the optimum mixing time did not result in increased TMA production, but rather, resulted in a small decrease. This was somewhat surprising. It was expected that mixing above the optimum mixing time would increase TMA production. At the lower mixing times, the sludge could be considered overdosed. Under overdosed conditions, excess polymer would remain in the liquid phase and not be incorporated into the sludge solids. When dewatered, the excess polymer is likely removed with the centrate or filtrate so it is does not remain in the sludge cake.

It appears that when polymer is incorporated into the sludge matrix, it is available for biodegradation and leads to TMA production. Shear seems to lead to increased TMA odors primarily because at higher shear more polymer is needed for optimal conditioning and when this polymer is degraded, TMA is produced.

Similar results were seen for the higher optimal mixing time (Figure 6), which also corresponds to a higher polymer dose. The higher polymer dose leads to much higher TMA generation, 6 ppm for the lower dose, lower shear time compared to 77 ppm for the higher dose, higher shear time. As with the lower polymer dose, when the mixing time was increased beyond optimum, the TMA production did not increase significantly. Both sets of data indicate that the primary effect of shear is to increase the polymer dose. At

the higher polymer dose, more TMA is produced. However, prior investigations have shown that samples without polymer addition still had higher TMA concentrations with higher shear (Subramanian, 2004). Increased shear yields more extra cellular proteins in suspension (Frølund 1996). The enhanced availability of extracellular proteins most likely leads to their biodegradation and formation of TMA.

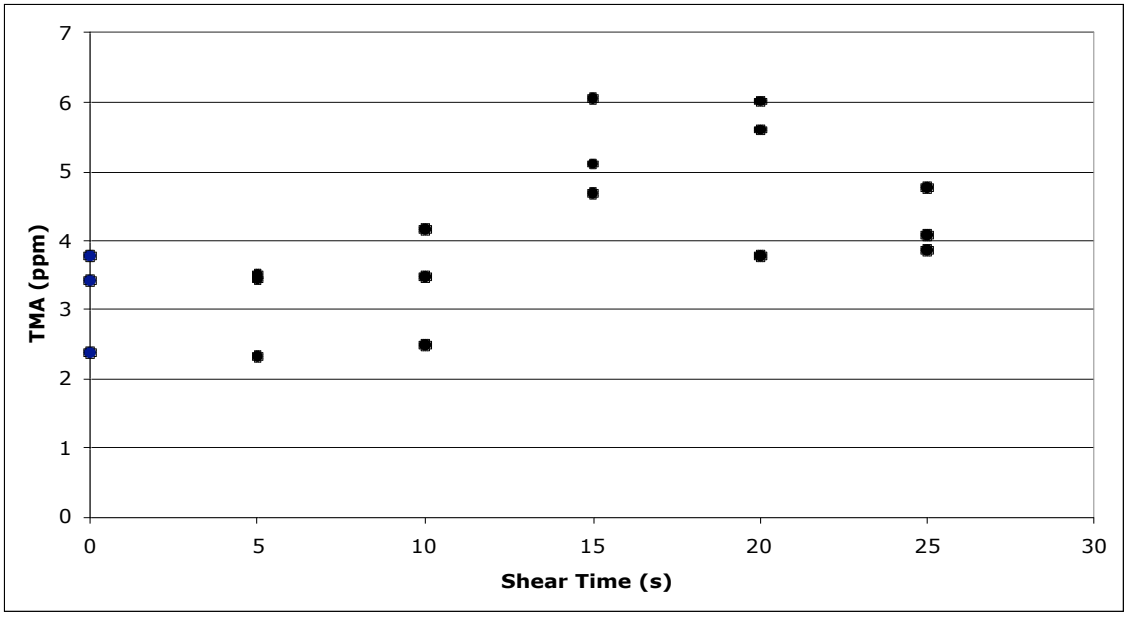


Figure 5. Effect of shearing time on TMA generation. Polymer dose is optimized at a mixing time of 15 seconds.

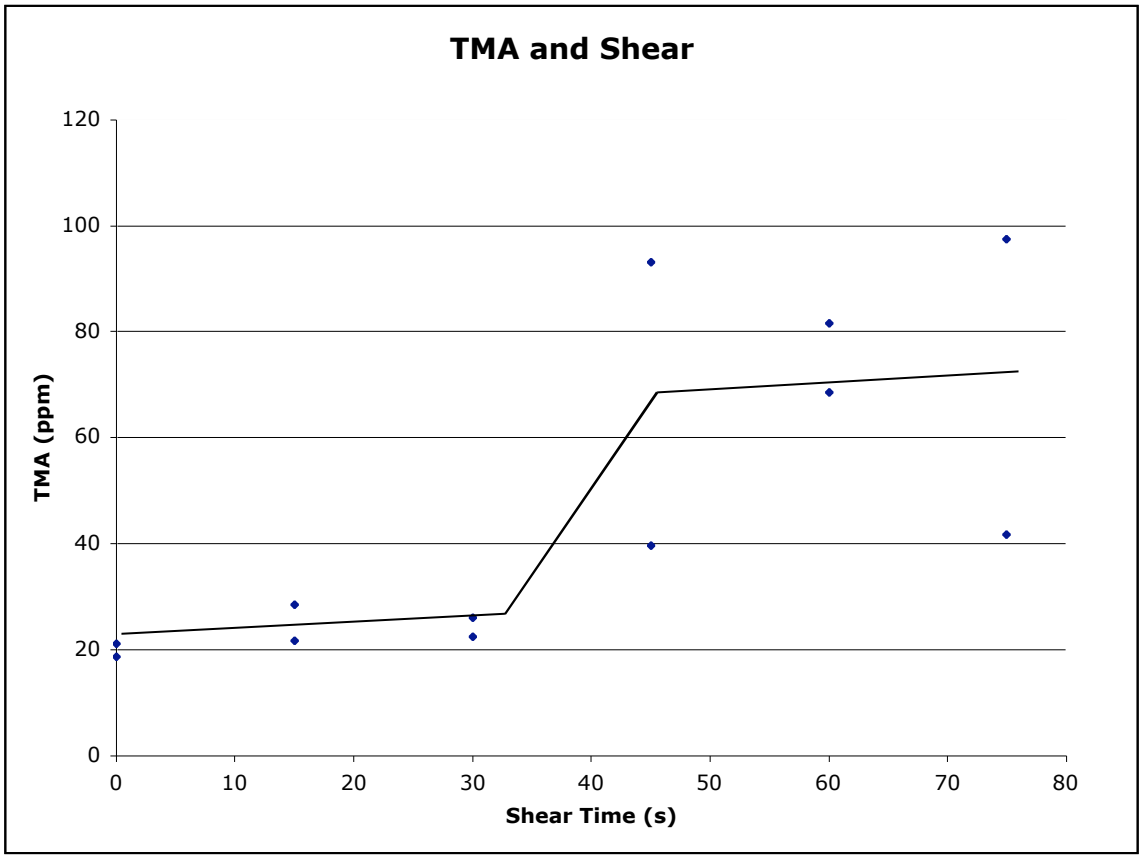


Figure 6. Effect of shearing time on TMA generation. Polymer dose is optimized at a mixing time of 45 seconds.

DISCUSSION

The generation of TMA from limed biosolids was found to depend on many features associated with conditioning and dewatering. Most of the TMA appears to come from degradation of cationic polymer used for sludge conditioning. A direct relationship between the amount of TMA produced and polymer dose was found. It was also found that the type of polymer used may play a role in TMA generation. A plot of two different polymers is shown in Figure 7. It can be seen that the two polymers, one, a manich polymer used for the dissolved air flotation of waste activate sludge and the other, a dry polymer used for conditioning of the combined primary and secondary sludge for centrifugal dewatering, showed the centrifuge polymer producing more TMA. However, further study would be needed to evaluate the TMA potential of different polymers. It

can also be seen in Figure 2 that TMA can be generated from sludge without polymer addition, although the amount is much smaller than when polymer is added.

The most critical factor associated with TMA generation is the incubation time or time between polymer addition and lime addition. If this time is small, very little TMA is produced, even at high polymer doses. Since TMA can be produced from sludge without polymer addition, finding a polymer that is not amine based will reduce TMA but it could still be a problem if the incubation time is long. The most likely spot for TMA odor generation is from waste activated sludge that has been thickened by dissolved air flotation and then allowed to sit prior to dewatering and liming.

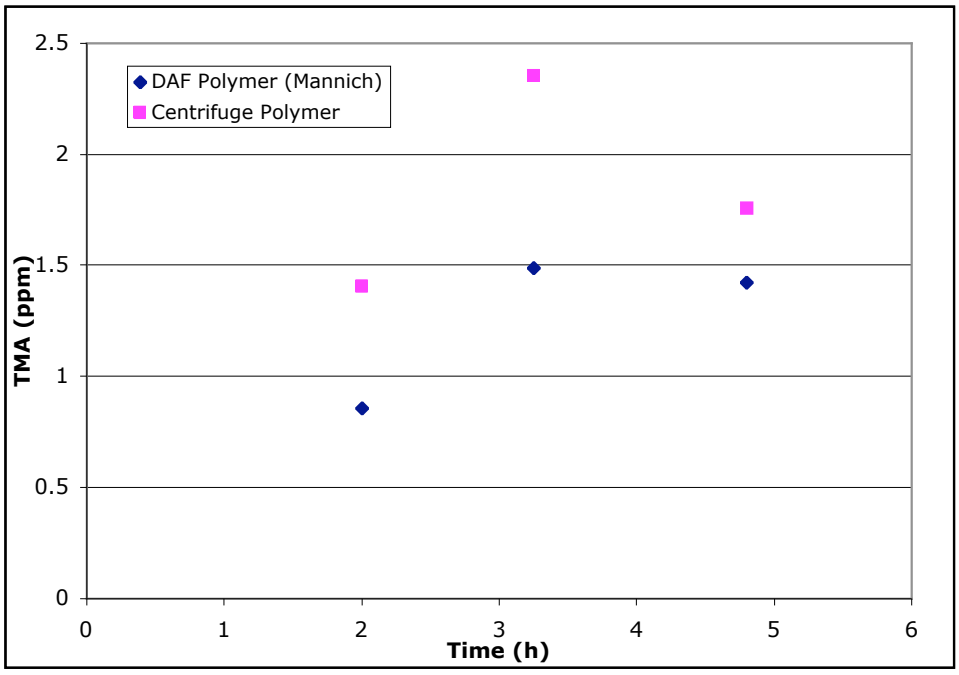


Figure 7. Effect of polymer dose on TMA generation for two different cationic polymers.

It was found that inhibition of methanogenic activity using BESA also increased the amount of TMA that was produced. TMA is thought to be converted to ammonia by methanogens. Therefore when methanogens are inhibited, TMA can increase. In Figure 4, higher cake solids were observed to increase TMA. This might reflect less dilution but

could also be due to the effect on methanogens. It has been shown for generation of organic sulfur odors that higher cakes solids leads to higher organic sulfur odors and it is thought that this is due to reduced methanogenic activity. The same effect might lead to increased TMA and higher cake solids. Therefore, if liming is inadequate, dewatered cakes may allow degradation of polymer and allow production of TMA.

CONCLUSION

The data in this study show that elevated trimethylamine (TMA) generation is caused by a set of variables. These variables include incubation time, biosolids concentration, polymer dose, and shear.

Of the factors contributing to TMA generation that were investigated, the time between dewatering and liming the sludges can be singled out as the most easily controlled cause of high TMA odors. Liming the sludges quickly after polymer addition and dewatering will result in low TMA concentrations. Although other factors can be manipulated as well, making significant changes to the biosolids concentration, polymer dose and shear would be impractical since they optimized to produce an acceptable dewatered sludge cake.

ACKNOWLEDGEMENTS

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Chapter 4
Engineering Significance

Treating wastewater has become an integral part of developed societies. Throughout time people treating wastewater were confronted with odors that were part of the sewage and of the treatment process itself. Today most sewage systems emit few odors until they meet the wastewater treatment systems. The problem of odor emissions is very prevalent today and plays a major role in the placement of water treatment plants as well as it plays a role for people where they want to reside. In addition, fertilizer gained from water treatment processes also are constrained for their use with respect to the odors they emit.

Trimethylamine (TMA) is one of the constituents that contribute to the unpleasantness of odors from wastewater treatment plants as well as odors emitted from land applied fertilizers from these plants. This study has led to insights of the mechanism that influence the generation of TMA. Wastewater treatment can be considered as a combination of unit processes and each process has its unique influence on TMA generation. Specifically, this study investigated TMA generation during conditioning of waste activated sludge, dewatering and lime stabilization. These have been identified as the most relevant unit operations that contribute to TMA generation and release into the atmosphere.

The study investigated specifically what role time plays between polymer addition and lime stabilization, methanogenic activity that may play a role in breaking down TMA, biosolids concentration of the produced sludge, polymer dose added to the sludge to be dewatered, and shear imparted on the sludge after polymer addition during the dewatering process. This study has led to a comprehensive understanding of the influence of TMA odors during the mentioned unit processes and allows for recommendations that allow treatment processes to limit their generation of TMA.

The most significant knowledge that has been gained is the influence of time between polymer addition and lime stabilization. TMA generation is a biological process that takes places as cationic polymer is added to the sludge that is to be dewatered. Cationic polymers contain functional groups that are broken down enzymatically to finally release TMA upon liming. As this enzymatic process is kinetically driven, the time between the addition of the substrate, the cationic polymer as well as extracellular proteins, and the forced inactivity to the enzymatic process by lime stabilization is key in limiting TMA generation. The release of this odor can be simply limited by quickly liming sludge after the dewatering process.

The study has also showed evidence that suggest that methanogenic activity influences TMA being released. The findings that suggest methanogens breaking down TMA have been supported by previous studies. This may have practical implications that wastewater treatment plants may want to store their dewatered sludge in conditions that promote methanogenic activity prior to lime stabilization. If done properly this would reduce the generation of TMA odors if enough time for TMA decomposition were given.

Solids concentration has also showed to play a role in TMA generation. The solids concentration is an important factor in desirability of land application as it plays a role in the total mass of sludge that has to be carried around and therefore plays a role in total energy that has to be used and therefore greenhouse gas emissions that are generated for the use of sludge for land application. The studies show that TMA generation is higher at higher solids concentration.

Polymer dose was also very relevant to the generation of TMA generation. Essentially one can say that cationic polymers added to sludge is the substrate for microbes to generate TMA. High cationic polymer concentration in the dewatered sludge will provide for much TMA generation potential.

Shear imparted on the sludge during the dewatering process plays a key role in the generation of TMA. First it determines the amount of cationic polymer added. Second

shear itself seems to increase the ability for TMA to be generated. This conclusion seems especially evident at the point where the optimum polymer dose and shearing time lies. Just prior to the shearing time of the optimum dose a sample produces much less TMA then it does right after the shearing time of the optimum dose. The exact reasons behind these observations could not be explained in this study.

The most significant finding for this study that would limit the effects of TMA generation without conflicting with the processes of generating sludge at the most desired solids concentration, conditioned at any polymer dose experiencing the appropriate shear, is that TMA generation can be limited by simply reduced by limiting the time between polymer addition and lime stabilization.

This research has shown that an array of factors exist that influence each other with the generation of TMA odors. Yet, a simple procedural care could allow for all unit operations to function at their most efficient, while TMA odors can be limited most effectively. Further study can be recommended to gain a better understanding of the sudden rise of TMA generation for samples around to point of optimum polymer dose when samples are over sheared compared to under shearing.