

INVESTIGATING THE ROLE OF PROCESS CONDITIONS IN WASTEWATER SLUDGE ODOR GENERATION

Rahul Subramanian, John T. Novak*, Sudhir Murthy, Dietmar Glindemann, Jason North

Via department of Civil and Environmental Engineering
Virginia Tech, Blacksburg, VA 24061
Phone 540-231-6132
Fax 540-231-7916

ABSTRACT

Odor gas production from solids handling processes in wastewater treatment has long been a matter of concern. In this study, the production of malodorous odors from unlimed sludges and biosolids was investigated along with the role of trivalent cations in odor gas generation. The effect of shear and polymer dose on Trimethylamine (TMA) production was also determined. It was found that production of total sulfur odor gases and TMA 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 odor gases compared to a vacuum filter. 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 were 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. Cationic polymers used to condition wastewater sludges are thought to be precursors for TMA 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. 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, wastewater sludge, malodorous odors, reduced sulfur compounds, trimethylamine, protein, polymer, 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 gas 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 odor gases (Lambert and McGrath, 2000).

Various processes are used for stabilizing sludge which includes 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) comprised mainly of MT (Novak et.al, 2004).

Trimethylamine (TMA) related odors are typically associated with lime stabilized sludges where the pH is 10 or greater. TMA has a pKa of 9.81 (Novak et.al, 2002) and has a characteristic fishy odor. TMA is 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, 2002c). As the pH is raised above the pKa for TMA, liquid phase TMA is converted to its unionized and volatile form.

Shearing of sludge that occurs in dewatering devices such as centrifuges and belt filter presses is known to significantly influence the production of odor gases. 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 odor gas production.

Studies conducted by Murthy et.al (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 causing compounds 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 compared to unsheared conditions.

Polymer added to sludge to aid the dewatering process is documented to contribute to increased 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 prior to lime addition, causing TMA and DMDS to be released (Kim et.al, 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 the 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 as a result of iron reduction during anaerobic digestion.

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 that can lead to formation of amine based odors.

The objectives of this study were to:

1. To determine the effect of polymer addition at various doses on TMA production
2. To determine the effect of shear intensity on TMA production
3. To determine the odor generation profile from limed biosolids
4. To determine effect of lime incorporation in dewatered sludges
5. To determine the inter-relations between trivalent cations, labile proteins and odor potential from wastewater sludges/biosolids.

MATERIALS AND METHODS

Sample Preparation:

Wastewater sludge was obtained from Pepper's Ferry Region Wastewater Treatment Authority in Radford, VA and Blacksburg VPI Sanitation authority in Blacksburg, VA. Primary and recycled activated sludge (RAS) were 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. In addition, sludge/biosolids samples were shipped directly from three wastewater treatment plants in the Washington DC area in 260 mL PET bottles under ice through overnight shipping. Two sets of samples from each plant 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.

Sludges were conditioned using a polyacrylamide cationic 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. 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. Each 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.

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 by Adams et.al (2003). 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 x g for 15 minutes. The centrate obtained after filtering through a 1.5 um glass microfiber filter was termed as labile protein. Bovine serum albumin (BSA) 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).

TMA and reduced sulfur odor compound 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 odor causing gases 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 odor causing gases in each sample was determined by comparing the sample peak area with the area of a known standard, 100 ppm for TMA and 13.5 ppm for reduced sulfur compounds respectively (Scott Specialty gases).

RESULTS AND DISCUSSION

Phase I

Increased reduced Sulfur Odor production comparison under conditions of shear

The flow scheme for the Parkway, Piscataway and Blue Plains treatment plant is shown in figures 1, 2 and 3 and the headspace sulfur and TMA is shown in Table 1.

Blue Plains

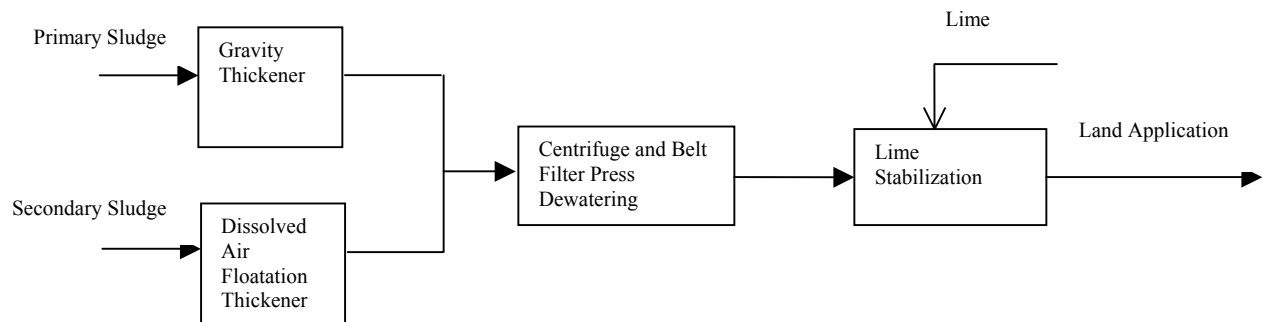


Figure 1: Solids handling process at Blue Plains WWTP

Parkway

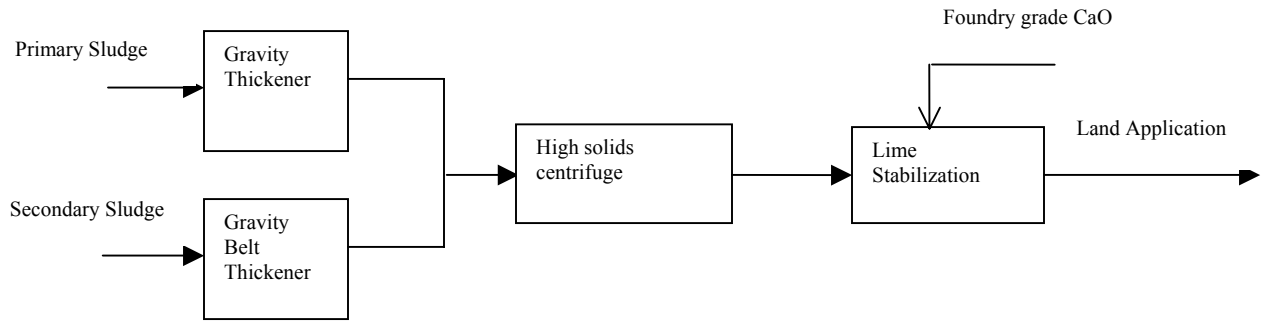


Figure 2: Solids handling process at Parkway WWTP

Piscataway:

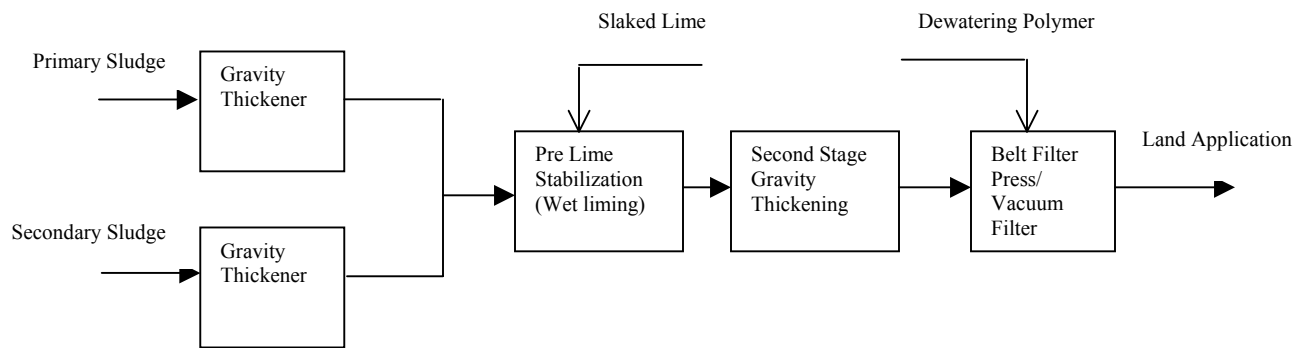


Figure 3: Solids handling process at Piscataway WWTP

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

WWTP	Sample Description	Peak total S (mg/cu.m.)	Peak TMA (mg/cu.m.)
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

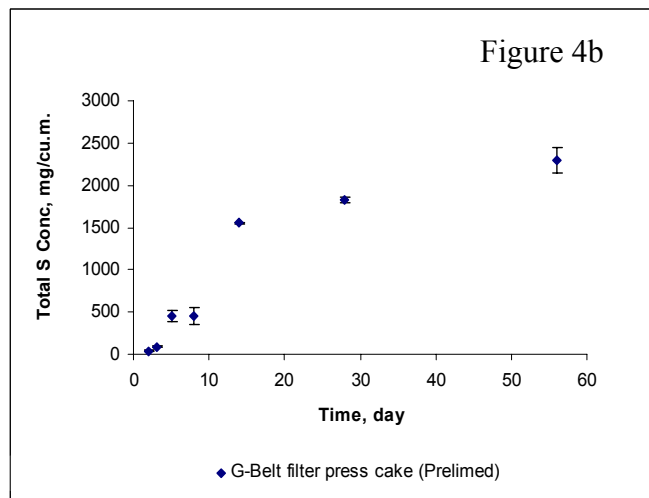
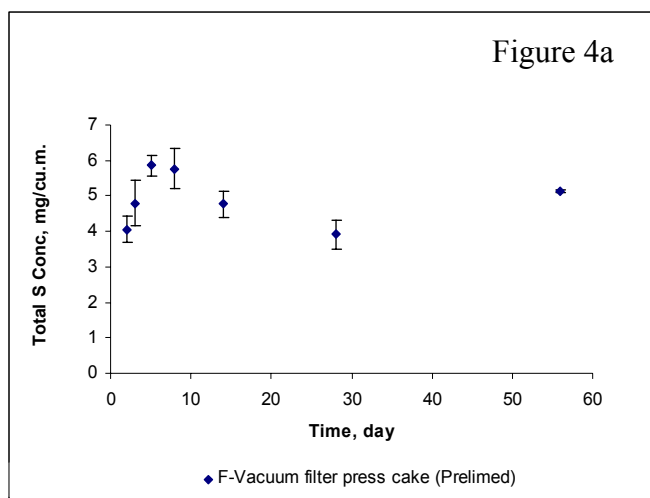
*Lab liming was done at 20% w/w.

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

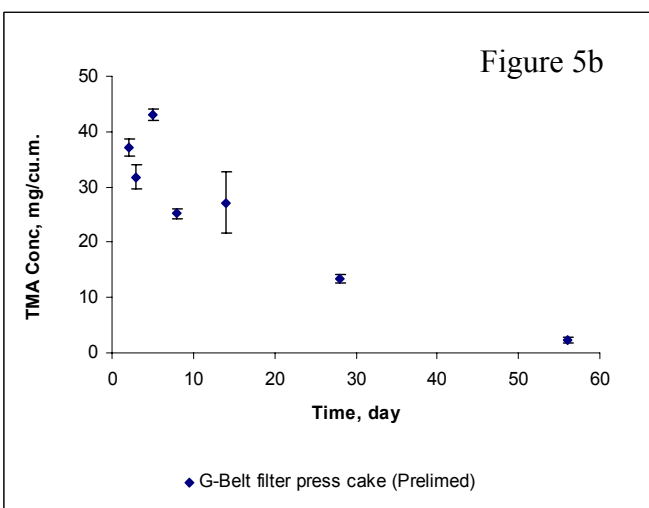
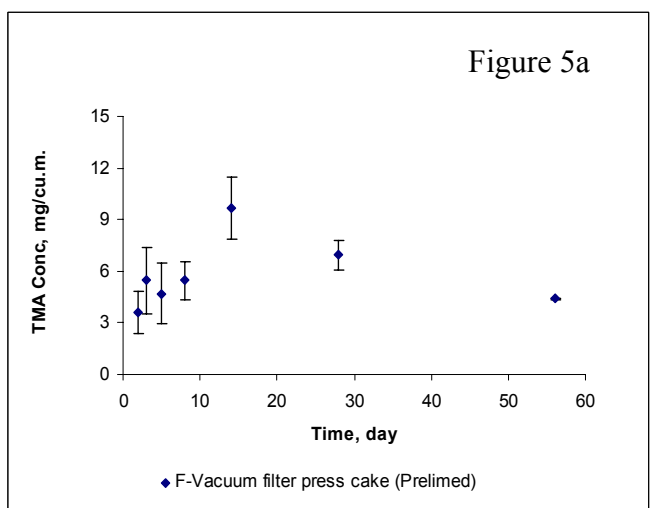
Piscataway, a smaller WWTP than Blue Plains and Parkway uses pre-liming of its sludge for lime stabilization. This has the advantage of providing more time for lime to get incorporated into the sludge. Lab limed samples were not studied for this plant. The blend sludge for Piscataway was dewatered using 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. Lime incorporation appears to be insufficient because the total sulfur from the VF gradually rises, peaking at day 8 and then declines as shown in figure 4a. After peaking at day 16 (figure 5a), TMA production also starts to go down. This could possibly be due to a reduction in pH, indicating resumption of microbial activity and consumption of TMA.

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 and then it decreases as the pH goes. Because the bottles were sealed, the pH could not be measured.



Figures 4a and 4b: Headspace sulfur odor gas profile: Limed samples from Piscataway WWTP



Figures 5a and 5b: Headspace TMA profile: Limed samples from Piscataway WWTP

Odor gas production from limed sludges from the above three wastewater treatment facilities was investigated. Lime dose and incorporation into sludge was found to influence odor gas production over time. Pre liming resulted in poor lime incorporation into sludge, compared to post liming. Shear in the BFP produced more odor gases 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 gas 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 gas 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 to bind 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. 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 correlated to methane thiol concentration in the headspace of bottles containing sludge (Adams et.al, 2003). 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 generation of odor causing gases.

Wastewater sludges were obtained from two local WWTPs. In all, six different sludges were studied. Primary and RAS from Blacksburg WWTP and primary, RAS, 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 by performing CST test on samples being dosed with polymer while being sheared. Samples were then set up in 40 mL EPA vials for headspace odor gas 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 (controls) was 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 gas 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.

Results of these odor gas analyses are shown in figure 6.

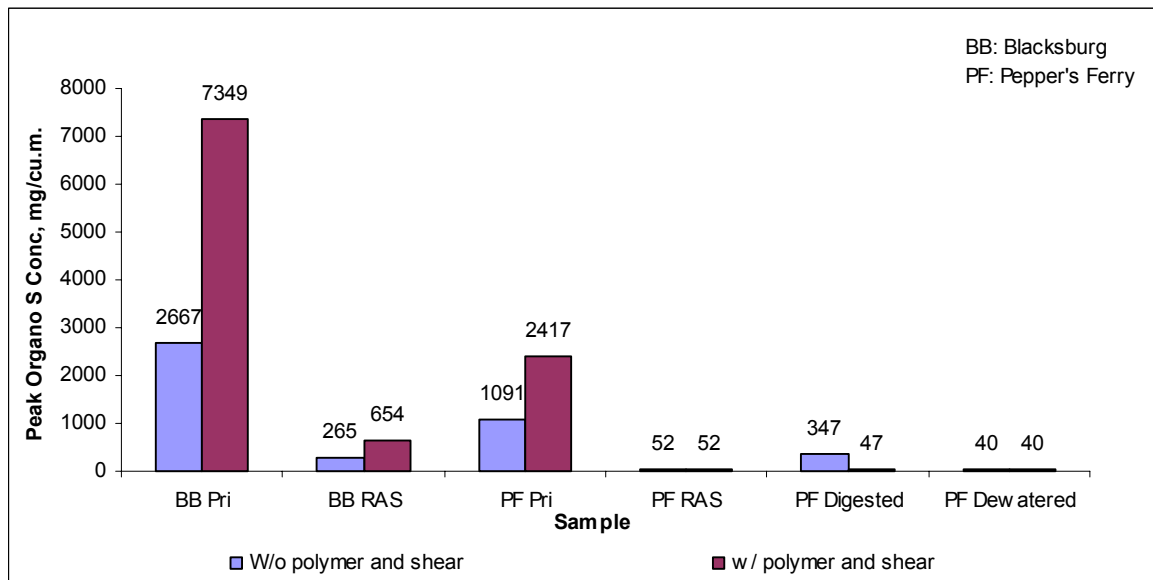


Figure 6: Odor gas production form six local wastewater sludge samples

It can be seen from figure 6 that peak headspace odor gas production under shear conditions and with polymer addition is higher than that without shear and polymer addition for primary and RAS from Blacksburg WWTP and primary sludge from Pepper’s Ferry WWTP. This shows that shear and polymer addition create favorable conditions for production of nuisance odor gases. An aberration was observed for the digested sludge from PF WWTP. It showed a higher concentration of reduced sulfur odor gases 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 in figures 7a and 7b.

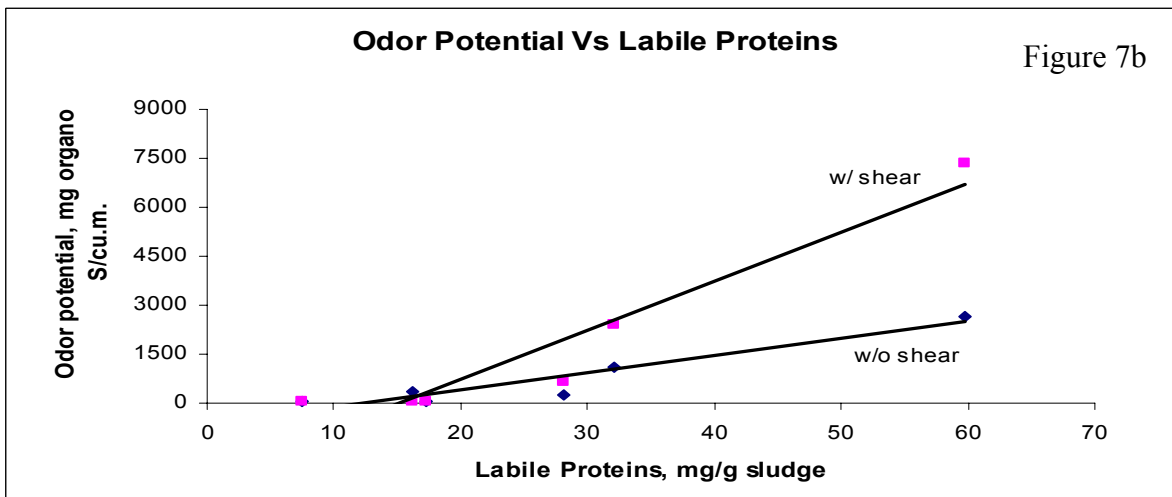
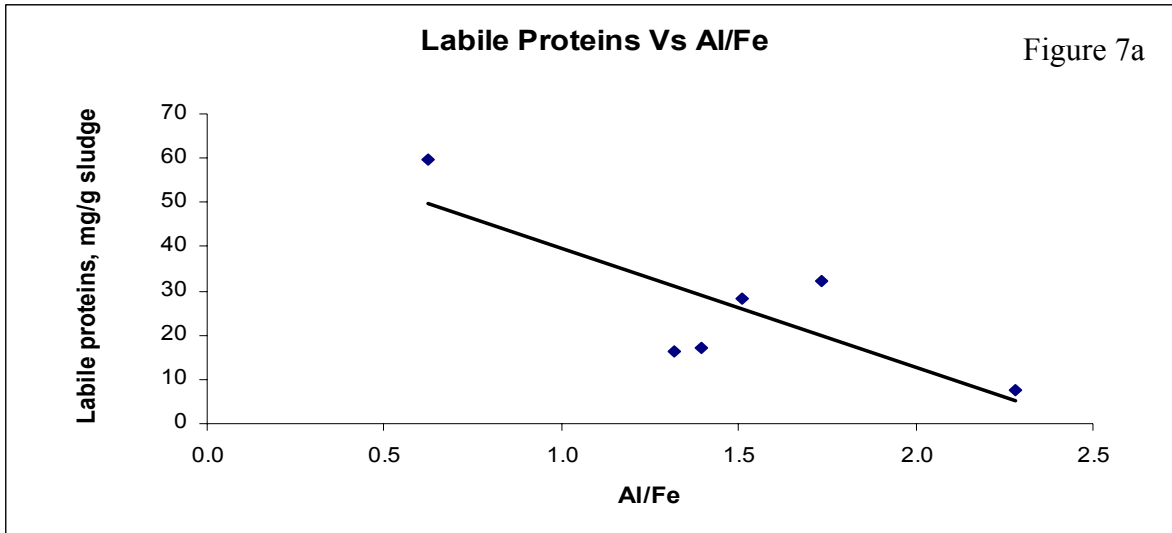


Figure 7a and 7b: Interrelation between trivalent metals, labile proteins and odor potential.

From figures 7a and 7b, it can be seen 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. It is hypothesized that trivalent cations, iron and aluminum bind labile proteins to the sludge/biosolids. Labile proteins are important precursors for odor generating compounds. Iron can undergo reduction from Fe (III) to Fe (II) as oxidation/reduction conditions change through the process, but aluminum is unaffected by oxidation/reduction. The relative presence of trivalent cations to divalent is thought to be the influencing factor in generation of nuisance odor emitting compounds 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 Aluminum helps 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, but it appears that protein associated with iron can be released. As a screening method, this

procedure seems to be a useful odor gas 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 gas generation. Metals are known to influence sludge floc structure and settling characteristics. They can now be related to odor gas 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 odor gases from dewatered sludges/biosolids.

Combining Phase I and Phase II results

Figure 8 shows the relationship between trivalent metals and labile proteins for limed samples from phase I experiments and unlimed local sludges from phase II.

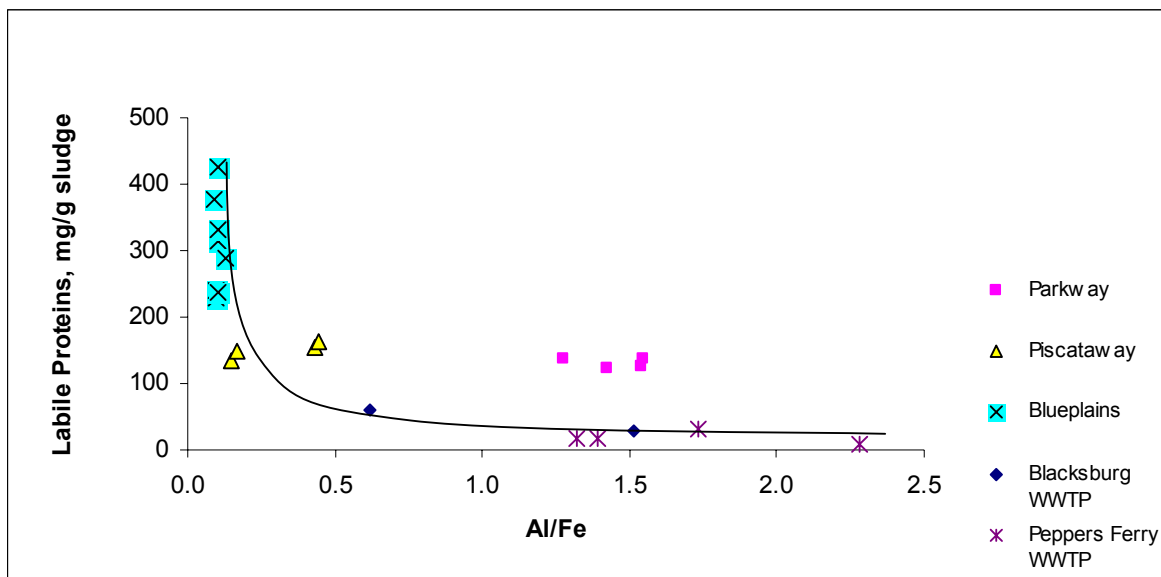


Figure 8. Relationship between trivalent metals and labile proteins for unlimed and limed sludge.

It can be seen that a relationship between trivalent metals and labile proteins obtained from phase II experiments provides useful information concerning odor gas production.

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 is that the aluminum is present in an inactive form since it enters the plant as waste alum sludge and it does not bind the labile proteins.

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

Phase III Production of Trimethylamine from limed biosolids

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 with a Polyacrylamide backbone. Samples were set up according to the matrix shown in table 2.

Table 2: Sample matrix for the evaluation of biological degradation of polymer to yield TMA production.

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

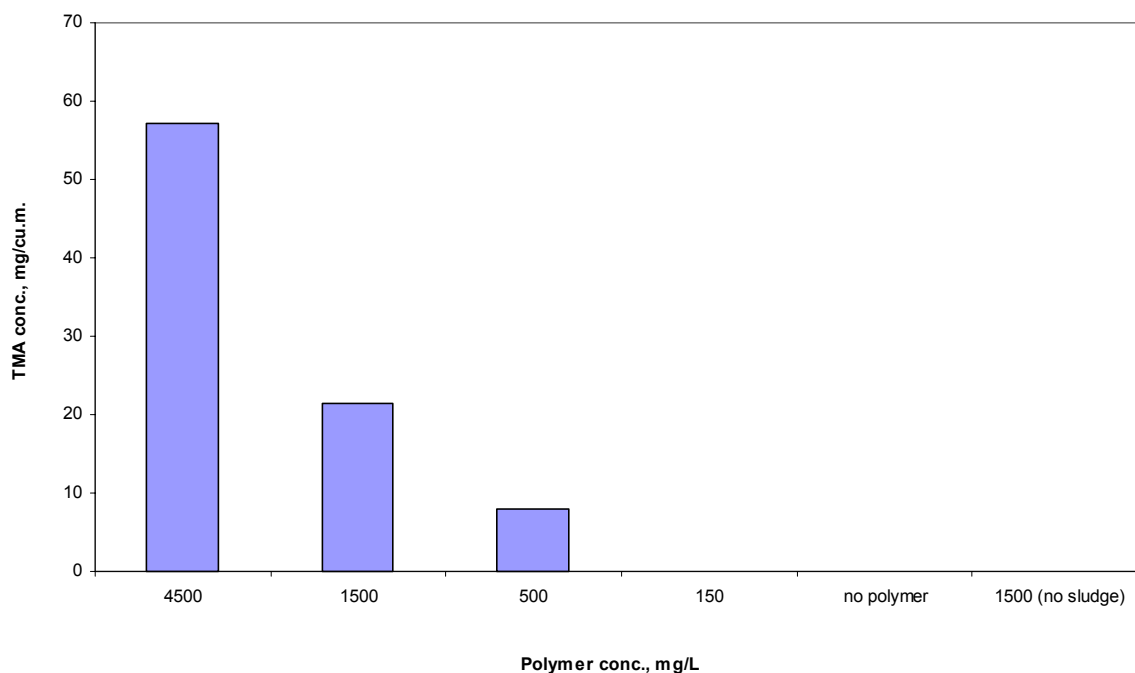


Figure 9: Headspace TMA profile: Effect of polymer dose on TMA production.

The TMA production under varying doses of polymer is shown in figure 9. 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 microbially 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 that 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 and polymer overdosing may be an important contributor to TMA.

Abiotic degradation of polymer to produce TMA.

Once it was found that polymers were 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 a mixture of 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 RAS 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: no polymer, 20 mg/L, 40 mg/L, 80 mg/L and 400 mg/L. 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. A total of 10 samples were prepared to explore the abiotic formation of TMA from polymer and lime as shown in Table 3.

Table 3: Sample matrix for the evaluation of abiotic degradation of polymer.

Control (no lime)	Polymer Concentration (mg/L)				
	0	20	40	80	400
Lime addition	Polymer Concentration (mg/L)				
	0	20	40	80	400

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 production in field sites occurs in shorter time duration, typically within hours or 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 4. 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 day 1. The cationic polymer, NALCO 1404 at 5000 ppm concentration was used.

Table 4: Sample matrix for determination of the effect of mixing and shear on TMA production under varying polymer dosages.

Sample name	Polymer dose and mixing status
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.

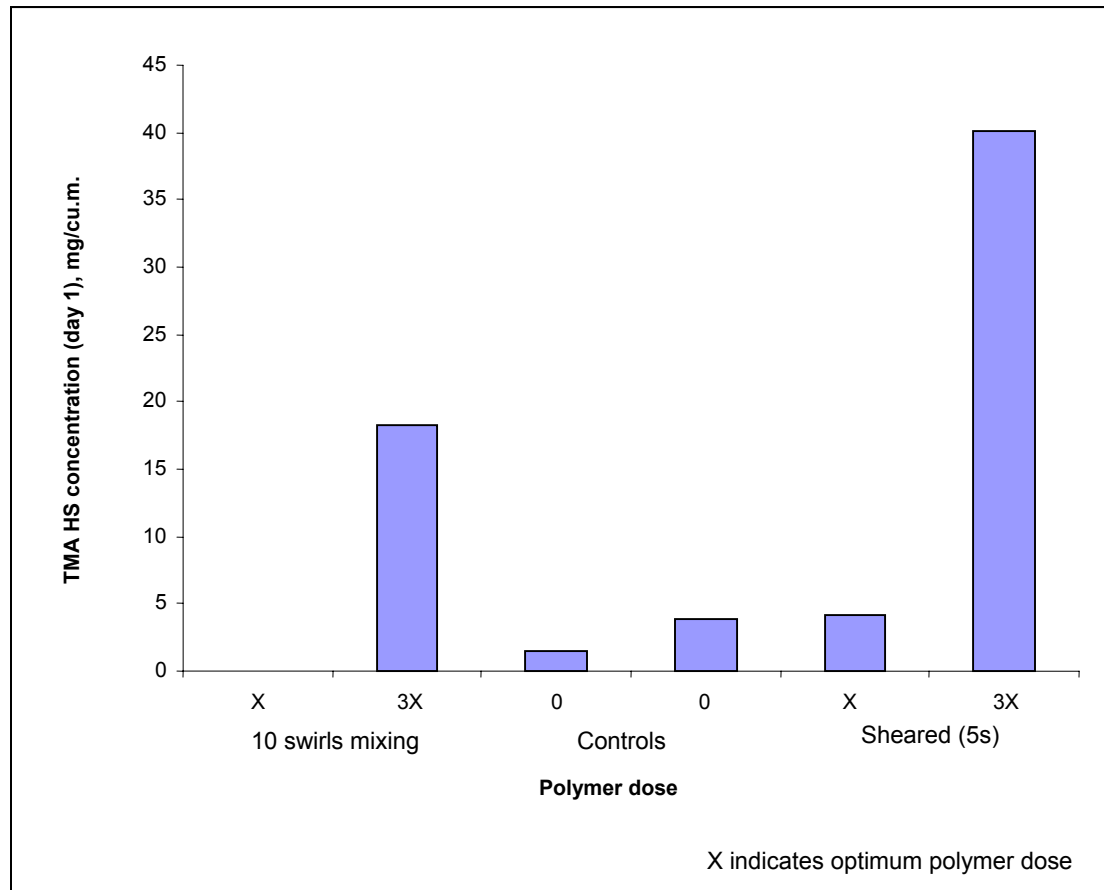


Figure 10. TMA production under various conditions of mixing and shear and dosage of polymer

From Figure 10, 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. 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.

This part 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 10, it is evident that mixing by hand 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 5. Samples were analyzed after 8, 16, 24, 48 and 72 hrs.

NALCO 1404 at the same polymer strength was used with RAS 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 5: Sample matrix for determination of the effect of polymer dosage and shear on TMA production

Sample name	Polymer dose and mixing status
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 11 shows the results from the repeat 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.

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.

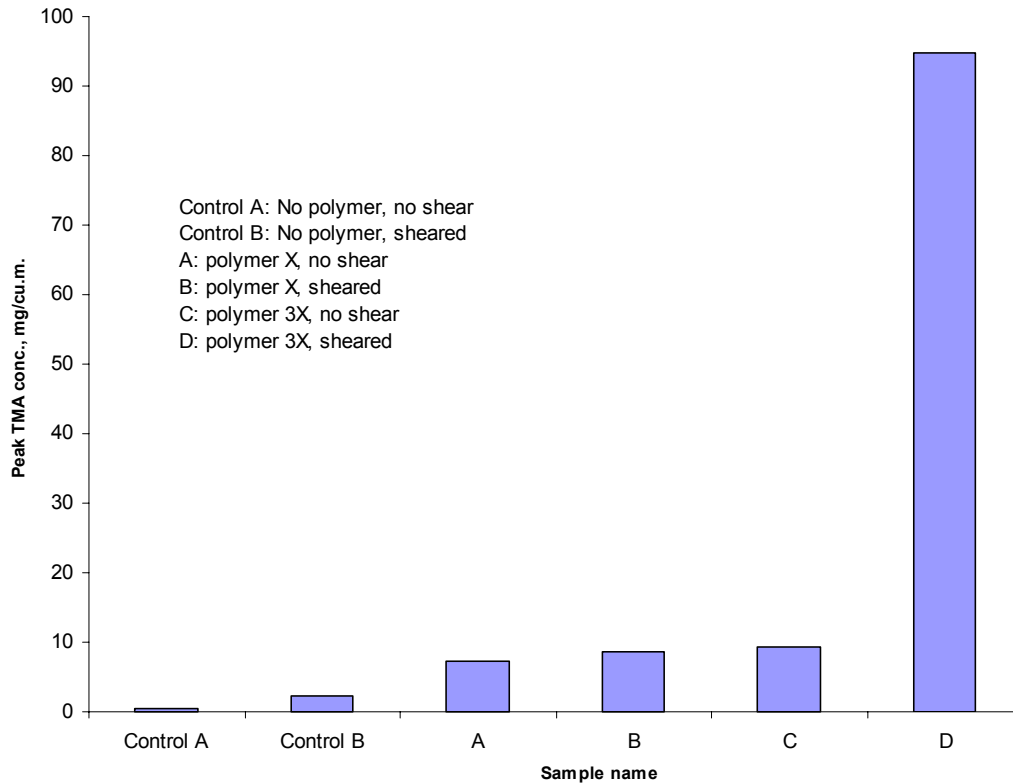


Figure 11. Peak TMA production under different conditions of shear and overdose of polymer

CONCLUSIONS

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 odor gases and TMA 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 odor gases and TMA 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 odor gases compared to unsheared conditions with no polymer dose.
4. Reduced organo sulfur odor gas 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 gas potential.
6. Controlling the concentration of trivalent metals in sludge can offer better alternatives for odor abatement processes.
7. Polymer breakdown produces TMA in headspace of stored limed biosolids
8. High intensity shear coupled with excess polymer dosing produced greater TMA headspace concentration.
9. Proteins in sludge are important precursors for TMA production under conditions of shear.
10. Liming alone does not degrade polymer to generate TMA in the headspace

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