Anaerobic Digestion: Factors Effecting Odor Generation

Nitin Verma

Thesis submitted to the faculty of
the Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Master of Science
in
Environmental Engineering

John T. Novak, Ph.D., Chair
Gregory D. Boardman, Ph.D.
Clifford W. Randall, Ph.D.

July 19, 2005
Blacksburg, Virginia

Keywords: Anaerobic Digestion, biosolids, odor, organic sulfur, trivalent metals, SRT, advanced digestion processes,

Copyright 2005, Nitin Verma

Anaerobic Digestion: Factors Effecting Odor Generation

Nitin Verma

Abstract

Land application of anaerobically stabilized biosolids is a beneficial method of handling the solid residuals from a wastewater treatment plant. One of the main issues that restrict land application of biosolids is nuisance odors associated with biosolids. Despite its importance, few studies have been done to enhance our knowledge of odor causing processes. This study was conducted to evaluate the effects of some factors that have been thought to be linked to odor generation from biosolids. The first part of this study has looked at the role of metals, iron and aluminum in particular, in determining the odor causing processes. The results showed that iron correlated well with headspace organic sulfur odor. In general, as the iron content of sludge increased greater amounts of odorous sulfur gases were produced from dewatered biosolids cakes. Aluminum did not show any relationship with organic sulfur odors. Parameters commonly used for assessing the performance of anaerobic digesters (volatile solids reduction (VSR), residual biological activity (RBA) and effluent volatile fatty acid (VFA) content) also showed no correlation with odors.

The second part of the study focused on determining the impact of anaerobic digester solids retention time (SRT) on the odor generation from dewatered biosolids cakes and also on elucidating the nature and impact of the various Extracellular Polymeric Substances (EPS) fractions on odors. The results showed that odors decreased with an increase in the anaerobic digester SRT. VSR and RBA correlated with odors; however, as only one type of sludge was assessed, the conclusions about any relationship may not be universal. The results also showed that sulfur gas generation was a function of EPS material bound to iron, again showing that iron plays an important role in odor generation from dewatered sludge cakes.

The third part of the study looked at the effects of advanced digestion processes on odor generation. Digested sludge from acid/gas and temperature phased anaerobic digestion systems were analyzed in the lab. The results show that both acid/gas system and temperature phased digestion had a positive impact on odor generation from dewatered biosolids cake. Comparison of sludge from pancake shaped and egg shaped digesters showed that egg shaped digester was more efficient with regard to odor reduction.

Acknowledgements

I gratefully acknowledge the guidance I have received from Dr John Novak over the period of my masters' education at Virginia Tech. He has given the research group freedom of thought and allowed our growth in various directions while being readily accessible for any doubts and clarifications we have had. I especially thank him for giving me the opportunity to work on this project as it gave me the chance to interact with various other professionals in the Environmental Engineering industry. He has been especially kind to me in keeping me funded and focused on research. I thank my other faculty members –Dr. Gregory Boardman, Dr. Clifford Randall, Dr. Nancy Love and Dr. Linsey Marr for their inputs and timely guidance.

I acknowledge the monetary support that I have received from Water Environment Research Foundation. I thank Los Angeles County Sanitation District and all other utilities that provided me with the sludge samples for this study.

I would also like to acknowledge and thank the timely help and advice I have had regarding lab practices and experimental methods from Julie Petruska and Jody Smiley. Betty Wingate and Sherry Burke have been most co-operative and supportive in administrative issues and I duly acknowledge their help. Lastly, I thank fellow researchers and friends Christopher Muller, Chul Park, David Inman, Sangeetha Subramanian, Rahul Subramanian, Nitin Kumar and Dong Hyun for having innumerable valuable discussions with me throughout the span of this study and maintaining a friendly environment in the laboratory.

Table of Contents

List of Figures

Chapter I - Literature Review

Chapter II - Manuscript 1

Chapter III - Manuscript 2

Chapter IV - Manuscript 3

List of Tables

Chapter II - Manuscript 1

Chapter IV - Manuscript 3

I Literature Review

Introduction

Anaerobic digestion is a process which breaks down organic matter into simple chemical components without oxygen. This process has been extensively used to treat organic waste such as sewage sludge, organic farm waste and municipal solid wastes. Primary advantages of anaerobic digestion are:

- Stabilization of organic waste with low energy consumption,
- Biogas production – good renewable source of energy,
- Stabilized matter that can be land applied,
- Pathogen reduction,
- Relatively small footprint, and
- Comparatively lower odor nuisance

The anaerobic digestion occurs in 3 steps: hydrolysis, acidogenesis, and methanogenesis. Hydrolysis is the step during which insoluble organic matter and large molecular organic compounds are broken down to soluble and smaller organic compounds. In acidogenesis, anaerobic microorganisms break down the products of the first step into hydrogen and simple organic acids. In the final step of anaerobic digestion, known as methanogenesis, methanogenic bacteria convert acetic acid and hydrogen into methane and carbon dioxide. It is also believed that one third of methane is produced from the pathway using hydrogen and the rest of methane is from the acetic acid. Methanogens are strict anaerobes and have very slow growth rate. Consequently, their metabolism is usually considered rate-limiting and a long detention time is required for slow growth (Metcalf and Eddy, 1991).

The production of methane, a useful end product, is the great advantage that that other sludge stabilization methods do not possess. Relatively higher pathogen inactivation can also be accomplished due to the harsh conditions in the anaerobic process (Grady et al., 1999). In comparison to aerobic digestion, anaerobic digestion is a very complex process and various groups of microorganisms in the absence of oxygen and nitrate are involved

in syntropic relationships. Conversion of organic matter into methane after several steps of biochemical reactions accounts for removing COD in anaerobic digestion [Metcalf and Eddy, 1991].

Land application of anaerobically stabilized sludge (i.e. biosolids) is a beneficial method of handling the solid residuals from a wastewater treatment plant. It is a good way to recycle nutrients and organics that enhance the properties of the soil for agriculture use and land reclamation. To reduce the hauling and handling costs of the stabilized sludge, the sludge is dewatered and then hauled to land application sites. Nuisance odors have been reported as a major problem with land application and it is cited as a significant concern of many treatment plant operations. The transportation, storage and land application of odorous biosolids generate complaints from neighbors and activists. These complaints can eventually result in bans on land application which in turn can reduce land available for recycling and increased biosolids management costs. [Murthy et al., 2002].

Recent studies [Adams et al., 2002, Murthy et al., 2003, Muller et al., 2004] have shown that odor production from biosolids is dependent on the dewatering process. High odor nuisance conditions have been reported by utilities that recently upgraded to high-solids centrifuges. Biosolids are exposed to high shear conditions in the presence of polymer in a high-solids centrifuge. This renders un-stabilized materials bioavailable. Proteins in biosolids have shown to have direct correlation with odor production [Higgins et al., (in press)]. These materials upon degradation produce volatile sulfur compounds (VSCs) such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide. A recent study showed a good correlation between olfactometry results and VSCs, showing a linear correlation for odors and sulfur gases from biosolids [Adams et al., 2003].

The following sections discuss the causes, processes and factors that cause and influence odor generation from biosolids.

Volatile sulfur compound odors

VSCs produced by biosolids are generally hydrogen sulfide, methyl mercaptan or methanethiol (MT), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS). Recent research has implicated volatile sulfur compound (VSCs) as one of the key groups of compounds associated with odors during biosolids cake storage [Higgins et al., 2002]. A good correlation is reported with olfactometry results which show that VSCs have direct correlation with odors from biosolids [Adams et al. 2003].

Much of the literature on Volatile Organic Sulfur Compounds (VOSCs) synthesis is found in research related to oral bacteria as they produce VSCs associated with oral malodor and periodontal diseases [Oho et al., 2002 Persson et al. 1990, Persson, 1992], as well as research related to sulfur cycling in freshwater sediments.

Formation of VOSCs in Biosolids

Higgins et al. (2003) suggest that VOSCs production from biosolids occurs through several pathways which include degradation of proteins and amino acids to form H_2S and MT. Biosolids which have high protein content (up to 50%) serve as a good source for the formation of VOSCs. The proteins are broken down into constituent sulfur containing amino acids (cysteine and methionine), which further degrade to form H_2S and MT, respectively. The sequential mechanism for the breakdown of proteins into MT is shown in Figure I-1. As similar pathway is expected for the production of cysteine and its degradation to H_2S.

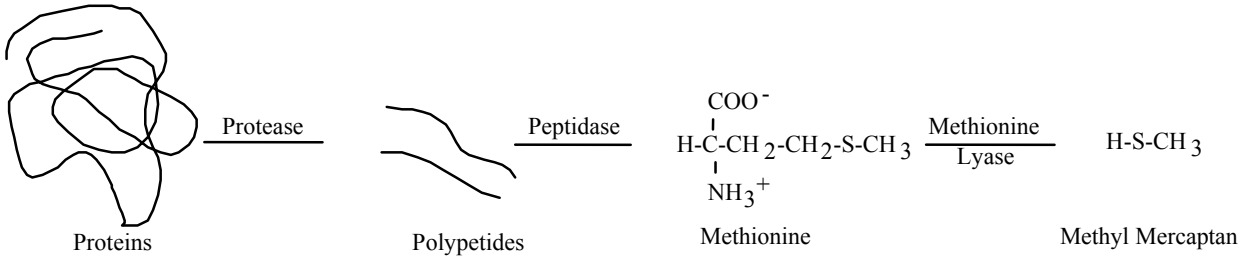


Figure I-1: Formation pathway of MT by the degradation of proteins [Higgins et al., 2003]

Anaerobic bacteria found in freshwater sediments, soils, and water have been shown to methylate H_2S and MT to produce MT and DMS, respectively [Drotar et al., 1987, Bak et

al, 1992, Lomans et al., 1997 and 2001]. The H_2S methylation reaction is thought to occur in two sequential reactions with MT as an intermediate. For this methylation reaction, H_2S is produced by Sulfur Reducing Bacteria (SRBs) as well as degradation of cysteine and the source of methyl groups is often methoxylated aromatic compounds [Bak et al., 1992]. Biosolids have a significant amount of humic acid type material [Frølund et al., 1996], which are a source of methyl group donors. This reaction is suggested to be an important mechanism for VOSC formation in biosolids. Higgins et al. (2004) carried out a set of experiments to compare the effects of syringate addition (source of methyl groups from its methoxylated groups [Bak et al., 1992, Lomans et al., 2001], cysteine or methionine to determine if methylation occurred in biosolids cake. DMS production during the experiments suggested that methylation did occur as DMS formation would not be expected from degradation of methionine or cysteine [Perssson et al., 1990].

No microbial pathways for formation of DMDS have been reported in literature, although it is often found as an odorant in many systems. Persson et al.(1990) demonstrated that when MT producing cultures are grown under anaerobic conditions no DMDS is formed and they also suggested that researchers reporting direct formation of DMDS as a microbial product were likely measuring DMDS as a result of MT oxidation. In another study DMDS formation from MT did not occur under anaerobic conditions but did in the presence of oxygen [Chin and Linday, 1994]. Literature suggests abiotic formation of DMDS through polymerization of MT and this reaction is catalysed by several agents including light and metal surfaces. Higgins et al. (2004) showed formation of DMDS when MT was added to clean serum bottles. Greater amounts of DMDS were formed in bottles which were exposed to light. These results suggest the formation of DMDS can occur through abiotic mechanisms and presence of light catalyses the formation[Higgins et al., 2004]. Experiments to study the catalytic effects of metals on oxidation of MT to DMDS demonstrated that addition of $FeCl_3$ had a significant positive impact on the oxidation reaction. It is speculated that this could be due to the oxidation capability of $FeCl_3$ or possible surface phenomena that increase oxidation.

Addition of amino acids methionine and cysteine to biosolids samples also results in the formation of DMDS. Greater amounts of DMDS were recorded in the methionine amended biosolids samples; this supports the abiotic reaction since this amino acid produced much greater amounts of MT. It is also shown that DMDS formation from MT occurred only in the presence of oxygen, and when the oxygen in a serum bottle exhausted formation of DMDS ceased. As MT is readily produced by biosolids, it can be readily oxidized to form DMDS and this would be enhanced by number of different catalysts. However, the absence of oxygen in laboratory serum bottles prevents the formation of DMDS from biosolids. [Higgins et al., 2004]

Cycling of VOSCs

During biosolids storage, it has been shown that VOSCs can be consumed after their production [Higgins at al., 2003]. Research has shown that methanogens can degrade or demethylate MT, DMS and DMDS to form H_2S [Lomans et al., 1999a,b,c and 2001]. Lomans et al. (1999a) demonstrated that methanogens were the primary degraders of MT and DMS in freshwater sediments with low sulfate concentrations (conditions similar to anaerobic digestion). In freshwater sediments a balance typically exists between the production and degradation of VOSCs resulting in little emission of these compounds unless the system is disturbed [Lomans et al., 2001]. Typically, MT, DMS and DMDS are not emitted from anaerobic treatment units. However, under conditions that cause stress to methanogenic bacteria MT emissions from anaerobic digesters is reported [Zitomer and Speece, 1995]. This suggests that a similar balance between the producers and consumers of VOSCs exists in well operated anaerobic units [Higgins et al., submitted].

Higgins et al. (2003) summarized the different reactions that could take place in the cycling of VOSCs. A diagram of these pathways is shown in Figure I-2.

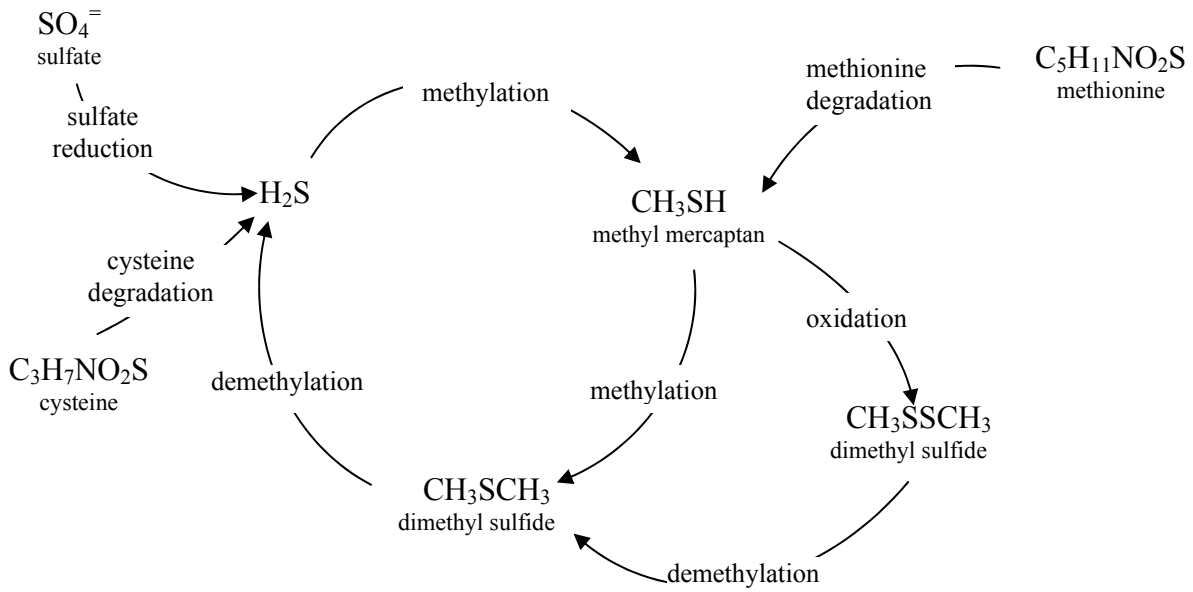


Figure I-2: Proposed pathways and cycle for VSC production and degradation in biosolids (Higgins et al., 2003)

From Figure I-2, it is seen that three main inputs or substrates exist for producing VSCs: sulfate, methionine, and cysteine. Reductions in concentrations of these substrates or enhancing intermediate reactions such as demethylation and sulfide precipitation could aid in controlling odors associated with VSCs.

Anaerobic degradation of methylated sulfur compounds is accomplished through activity of methylotrophic methanogens. Higgins et al. demonstrated that when Bromo Ethane Sulphonic Acid (BESA), a strong inhibitor of methanogenesis, is added to biosolids, there is no degradation of MT in a static headspace. This is in contrast to samples without BESA addition, where MT increases then declines over time. Similar results were reported for the degradation of DMS by Lomans et al. (1999c).

Curve-A in Figure I-3 shows a typical plot of VOSCs concentration in a static headspace with incubation time for dewatered anaerobic biosolids samples kept in sealed serum bottles. The left side of the curve shows the initial build up of VOSCs, after which the total concentration of VOSCs peaks. Following the peak, the concentrations of VOSCs starts to decrease suggesting their consumption. If a methanogenic inhibitor such as

BESA is added to the sample, then a curve similar to curve B is obtained. From a plot of concentration of VOSCs with time like shown in Figure I-3 the following occurs:

- Initial formation of VOSCs due to degradation of proteins in biosolids, due to methylation of H_2S and MT and also due to abiotic formation of DMDS,
- After a certain period the VOSC consumers start degrading the VOSC in the headspace (research has shown that methanogens are actively involved in this reaction)[Lomans et al.],
- When methanogenic activity is inhibited, VOSC concentration peaks and stays at the peak level – suggesting the important role of methanogens in degrading VOSCs.

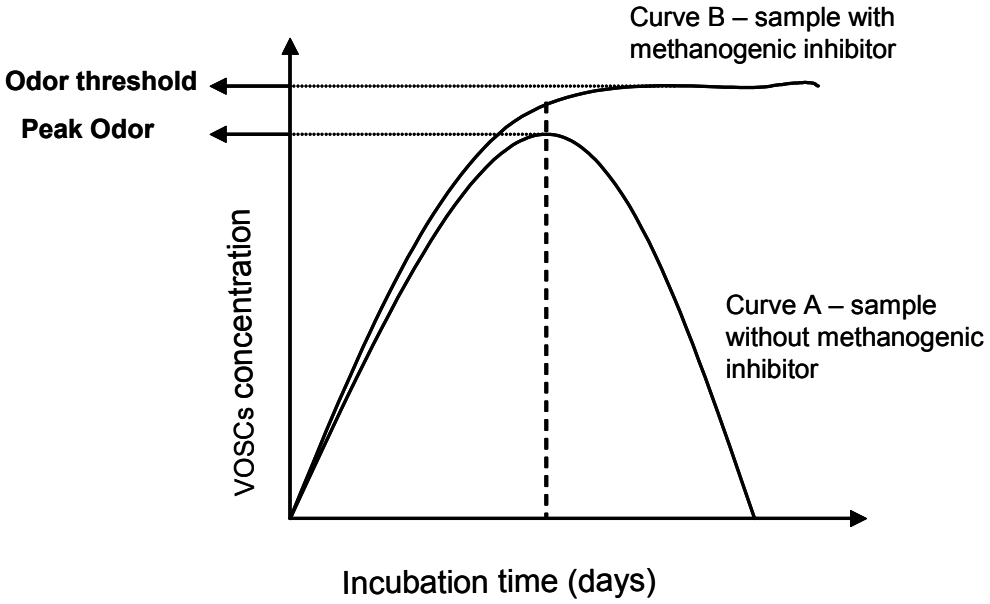


Figure I-3: Typical VOSC concentration versus incubation time plot. Curve A – with BESA (strong inhibitor of methanogens) and, Curve B- without BESA.

It is also typically seen that peak odor (i.e. VOSC concentration) in samples without methanogen inhibition is lower than the peak in samples to which methanogenic inhibitor is added. Higgins et al. (2003) showed that near stoichiometric amounts of VSCs are produced when the methanogens are inhibited. Hence, the peak value in these samples can be treated as the "odor threshold or odor potential" for those biosolids samples [Higgins et al., 2003].

Effects of biofloc and EPS on Odors from biosolids and role of cations

Proteins are directly linked to odor production from biosolids [Adams et al., 2003]. Hence, the bioavailability of proteins is considered to be the key process in release of odorous compounds from wastewater sludges/biosolids. Proteins containing amino acid groups as monomeric building blocks are considered to be the primary precursors for formation of odor compounds. Cysteine and methionine (precursors of VOSCs) are known to be present in proteins extractable from activated and anaerobically digested sludges [Chul Park, personal communication]. This extracted protein remains unmetabolized as long as the digestion/stabilization process does not make them available for degradation.

Biofloc is comprised of microbial consortium, organic and inorganic matter held together in a matrix formed by exocellular biopolymer and cations [Higgins et al., 1997]. Microbial metabolism and cell lysis release biopolymers (proteins and polysaccharides) in wastewater sludges (Grady et al., 1999). As much as 40% of volatile solids remaining after digestion as part of residual biological activity are speculated to be comprised of undegraded proteineceous material. Frølund et al. (1996) have shown that up to 50% of the extracellular polymeric substance (EPS) in sludge is comprised of proteins. The presence of polysaccharides is also known to influence exocellular characteristics of sludge, although its effect on odor generation is not known at this time.

Because the majority of exocelluar biopolymers carry negatively charged functional groups at typical pH of wastewater, the cations become an important structural component as a binding agent within the biopolymeric matrix. (Bruus et al., 1992, Urbain et al., 1993, Higgins and Novak, 1997). Novak et al. (2003) showed that flocs are composed of different types of exocellular biopolymer with different cation bindings and their degradation is dependent on the digestion environment. The important exocellular biopolymer fractions are: Lectin like material-protein where Ca^{2+} and Mg^{2+} and polysaccharide are cross-linked, and iron-bound biopolymer

It was shown that materials associated with Ca^{2+} and Mg^{2+} are degraded under aerobic conditions while the latter was the main organic constituent that was degraded under anaerobic conditions [Park et al., 2004].

Aluminum also plays a significant role in bioflocculation but its specific relation to EPS and the fate of its binding organic matter during digestion remains unclear. This biofloc model can be used to explain dewatering characteristics of biosolids and possibly effects on odor production.

Effects of the dewatering process on odors

Murthy et al. (2003) showed that the type of dewatering equipment impacts the VSC production characteristics. They showed that for similar cake solids content obtained from different dewatering equipment (high-solids, low-solids centrifuge and belt filter press), the samples obtained from high-solids centrifuge yielded the highest VSCs concentrations. Murthy et al. (2002) and Higgins et al. (2002b) suggested that the VSC production characteristics are influenced by a combination of factors:

- Shearing of biosolids cakes during centrifugation results in making proteins bioavailable,
- This bioavailable protein is degraded during storage to form VSCs, and
- If proteins are not made bioavailable then VSC production would not occur.

Murthy et al. (2003) also showed that variation of high-solids centrifuge parameters resulted in substantial variation in VSC production characteristics. Muller et al. (2004) showed that shear plays a critical role in the generation of nuisance odors. It was also shown that shear was not the only factor that influenced VSC production. Odors from samples which had dewatering polymer generated maximum odors; also increase in cake solids concentrations increased odor production.

Rosenfeld et al. (2001) showed significant differences in the odor compounds generated from centrifuged, pressed-biosolids and dried biosolids. Odors from centrifuged and pressed biosolids were similar to each other, with similar physical, chemical, and

microbial properties. The dried-biosolids however, produced the most odors and volatilized a more complex array of odorants.

Polymer addition to sludge in the dewatering process is documented to increase odor (Higgins et al., 2002b; Muller et al., 2004). This is thought to be due to association of proteins from floc with added polymer. Higgins et al. (2002) showed that minimizing polymer demand had a large impact on reducing VSCs and odors by minimizing the amount of protein that was made bioavailable in the cake. Muller et al. (2004) showed that polymer over dosing did not increase VSC production beyond that generated at optimum polymer dose. Muller et al. (2004) also showed an increase in the odors with an increase in the solids content of dewatered biosolids.

Advanced Anaerobic Digestion Processes

Rising transportation, disposal, and handling costs have driven the search for digestion processes that have higher volatile solids reduction and better dewaterability of biosolids. Some alternative anaerobic digestion technologies include thermophilic digestion, acid/gas phased digestion, and temperature-phased digestion. These processes can destroy more volatile solids and produce more methane. In addition to reducing biosolids handling costs, land application laws and public heath concerns have driven the development of technologies to reduce pathogens in digested biosolids. For example, the US EPA implemented standards in 40 CFR Part 503 (1993) that govern biosolids disposal based on the pathogen reduction criteria. The 40 CFR Part 503 regulation is a technology based standard and defines the processes suitable to achieve Class A and Class B biosolids. Class A biosolids, those treated with a process that reduces pathogen levels below detectable limits, have few restrictions for ultimate disposal. Biosolids with pathogen levels above detectable limits, termed Class B biosolids, must be disposed of on restricted sites. Advanced anaerobic digestion processes are being researched and adopted at full scale facilities to enhance the quality of biosolids produced. The following sections discuss some of the new technologies in brief.

Thermophilic Digestion

Thermophilic digestion is one of the alternative technologies, which has been primarily been of great interest due to its pathogen reducing potential. Other advantages of thermophilic digestion over conventional mesophilic digestion include higher reaction rates, better dewaterability, and increase volatile solids destruction [Buhr and Andrews, 1977, Metcalf & Eddy]. Thermophilic digesters have been reported to have higher volatile solids reduction, greater biogas generation even at higher organic loading rates, though the system was more susceptible to instability [Kim et al., 2002].

High volatile fatty acids (VFA) in the effluent are frequently cited as a problem with thermophilic digestion causing malodorous biosolids. Moen et al. (2003) showed that effluent VFA concentration decreased with an increase in thermophilic SRT. Also, higher destruction of organics during thermophilic digestion results in higher ammonia levels in the digester which could cause ammonia inhibition of thermophilic biomass [Sung and Liu, 2003].

Acid/Gas Phased Digestion

In acid/gas phased sequential digestion, the acidogenesis phase and methanogenesis phases are separated. The operators vary the SRT to kinetically select for either acid-forming (low SRT) or methane-forming microorganisms (higher SRT) [Massey and Pohland, 1978]. Methane forming microorganisms are washed out of the reactor if the SRT is kept low. The low SRT and higher organic loading causes an accumulation of organic acids in the first digester. The first digester in the acid/gas system is mostly operated at a low SRT of around 12 to 36 hours to promote the growth of acid-forming microorganisms, while the following digester, termed the Gas phase digester, is operated at a higher SRT (typically $\geq$18 days) to allow for the formation of methane.

The principal advantage of acid/gas phased digestion is the ability to optimize hydrolysis and acidogenesis reactions in the first reactor and methanogenesis in the second reactor. Fox et al. (1994) reported that the acid/gas system makes pH control easier, improves the ability of the system to absorb shock loads and detoxifies influents that may harm the sensitive methane formers. They also reported that the phase separation might also result

in disrupting the syntropic relationship between hydrogen formers and hydrogen consumers. Studies have also suggested great VS reduction, methane production and lower effluent VFA concentrations [Ghosh, 1987]. Acid/Gas systems with both reactors operated at mesophilic temperature do not meet EPA's requirements for Class A biosolids.

Temperature Phased Anaerobic Digestion (TPAD)

Temperature phased digestion seeks to combine the benefits of the thermophilic digestion process and partial phase separation instead of complete phase separation. In a TPAD system, the temperature is varied between sequential digesters to select for mesophilic organisms in one stage and thermophilic organisms in the other. Mesophilic temperatures range from 30-38^{o}C and 50-60^{o}C for thermophilic. Partial phase separation is achieved by lowering the SRT in the first digester. Dichtl et al. (1997) suggested that by operating the first reactor in the TPAD system at thermophilic temperatures and with a SRT of 3 to 5 days could achieve an adequate balance between acid-formers and methane-formers. This helps to minimize acid accumulation.

Combined advantages of thermophilic digestion and phase separation result in class A biosolids production [Vandenburgh and Ellis, 2002]. Han and Dague (1997) demonstrated 18% higher VS reduction and methane production from a TPAD system compared to a conventional single stage mesophilic digester. However, improved VS reduction may cause deterioration of the dewatering properties of biosolids from TPAD systems. Bivins et al. (2001) observed poorer dewatering characteristics in a bench-scale TPAD system. Nevertheless, class A biosolids production capability and higher solids destruction may outweigh the disadvantage of poor dewatering characteristics.

Summary

In summary, thermophilic digestion which demonstrated capability of reducing pathogens to achieve class A biosolids has issues with operational stability [Metcalf and Eddy, 2003]. Acid/Gas phased digestion has certain advantages over single stage digestion. The suitability of acid/gas phased digestion however depends on the nature of waste being treated as certain wastes tend to upset environmental conditions that are important for

methane formation [Fox and Pohland, 1994]. Temperature phased digestion incorporates advantages of both phase separation and thermophilic digestion which produces class A biosolids. Literature on the effects of these advanced digestion processes is limited and no studies have been done to compare VSC odors from these systems.

Headspace analysis procedure for measurement of odor causing compounds produced from biosolids

Measurement of odorous compounds from wastewater has two central components, namely sampling and sample analysis. Sampling methods such as static headspace, flux chamber and purge and trap methods have been previously used for testing odors from biosolids. Fluxing is a slow process that can require hours per sample and results in dilution of odorous compounds.

Headspace analysis has several advantages over flux chambers. The storage conditions in headspace bottles are anaerobic and are thus similar to the anaerobic bulk core of large full-scale cake piles. The headspace vials are closed bioactive systems where the odor compound concentration in the headspace is a function of the odor concentration contained in the cake. The headspace method allows the measurement of odor consumption by the cakes in the bottle and the odor production-consumption over time, unlike flux method where in gases are removed from contact with the biosolids. A major advantage of the headspace method is that it is less cumbersome and time consuming compared to flux chamber analysis. Glindemann et al. (in press) showed that the headspace incubation method was an accurate and reproducible method for assessing the odor generation potential from both liquid and dewatered sludge. They also showed that testing the headspace of a single bottle multiple time produced data similar to sacrificial bottles that were sampled on a one time only basis. This is important to reduce the space required to store samples during the analysis period which can last for several weeks.

Considering the advantages of headspace analysis and nature of this study, the headspace analysis method was considered to be the most suitable method as it gave accuracy and repeatability. For this study the headspace gas analysis was done using GC/MS.

Headspace gas samples from glass vials containing dewatered cake were directly injected into a GC/MS for VOSCs detection and quantification.

Reference:

Adams, G.M., Witherspoon, J., Card, T., Forbes, R., Geselbracht, J., Glindemann, D., Hargreaves, R. Hentz, L., Higgins, M., McEwen, D., and Murthy, S. Identifying and Controlling the Municipal Wastewater Odor Environment Phase 2: Impacts of In-Plant Operational Parameters on Biosolids Odor Quality. 2003, Water Environment Research Foundation: Alexandria, VA.

Bak, F., K. Finster, and f. Rothfub. (1992) Formation of dimethyl sulfide and methanethiol from methoxylated aromatic compounds and inorganic sulfide by newly isolated anaerobic bacteria. Arch. Microbiol., 157, 529-534.

Bivins,J.L., Novak, J.T. (2001) Changes in dewatering properties between the thermophilic and mesophilic stages in temperature-phased anaerobic digestion systems. Water Environ. Res. 73, 4, 444-449.

Bruus, J.H., Nielsen, P.H., and Keiding, K. (1992) On the Stability of Activated Sludge Flocs with implication to Dewatering. Water Res., 26, 1597.

Buhr, H.O., Andrews, J.F. (1977) The thermophilic anaerobic digestion process. Water Res., 11, 129-143.

Dichtl, N. (1997) Thermophilic and mesophilic (two-stage) anaerobic digestion. Water and Env. Mgmt: Journal of CIWEM. 11, 2, 98-104.

Drotar, A., G.A. Burton, J.E. Tavernier, and R. Fall (1987) Widespread Occurrence of Bacterial Thiol Methyltransferases and the Biogenic Emission of Methylated Sulfur Gases. Applied and Env. Microbiol., 53, 1626-1631.

Fox, P., Pohland, F.G. (1994) Anaerobic treatment applications and fundamentals: substrate specificity during phase separation. Water Env. Res. 66, 5, 716-724.

Frølund, B., Palmgren, R., Keiding, K., and Nielsen, P.H. (1996) Extraction of Extracellular Polymers from Activated Sludge Using a Cation Exchange Resin. Water Res., 30, 1749.

Ghosh, S. (1987) Improved sludge gasification by two-phase anaerobic digestion. ASCE J. Environ. Eng., 113, 6, 1265-1284.

Glindemann, D., Murthy S.N., Higgins M.J., Yen-Chih Chen, Eschborn R.,Toffey W., Mittman Michele and Novak J.T. (in press) A Standardized Procedure for Measurement of Odor Causing Compounds Produced by Biosolids. Water Reasech(in press).

Grady L, Diagger G. and Lim (1999) Biological Wastewater Treatment, 2nd Edition. Publishers – Marcel Dekker, USA.

Han, Y., Dague, R.R. (1997) Laboratory studies on the temperature-phased anaerobic digestion of domestic primary sludge. Water Environ. Res., 69, 6, 1139-1143.

Hartree, E.F. (1972) Determination of Protein: A Modification of the Lowry Method That Gives a Linear Photometric Response. Anal. Biochem., 48, 422.

Higgins, M.J. and Novak, J.T. (1997) Characterization of Exocellular Protein and Its Role in Bioflocculation. J. Environ. Eng., 123, 479.

Higgins, M. J. and Novak, J.T. (1997a) The Effect of Cations on the Settling and Dewatering of Activated Sludges. Water Environ. Res., 69, 215.

Higgins, M.J. and Novak, J.T. (1997b) Characterization of Exocellular Protein and Its Role in Bioflocculation. J. Environ. Engr. ASCE, 123, 479-485.

Higgins, M. J. and Novak, J. T. (1997c) Dewatering and Settling of Activated Sludges: The Case for Using Cation Analysis. Water Environ. Res., 69, 225.

Higgins, M.J., S.N. Murthy, B. Striebig, S. Hepner, S.Yamani, D.P. Yarosz, W. Toffey. (2002) Factors affecting odor production in Philadelphia Water Department Biosolids. Proceedings Water Env. Fed. Odors and Toxic Air Emissions 2002, Albuquerque, NM.

Higgins, M.J., Yarosz, D.P., Chen, Y.C., Murthy, S.N., Maas, N., Cooney, J., Glindemann, D., Novak, J.T., Cycling of Volatile Organic Sulfur Compounds in Anaerobically Digested Biosolids and its Implications for Odors. Water Environment Research, 2003 (Submitted, November 2003).

Higgins, M.J., Yarosz, D.P., Chen, Y., Murthy, S.N., Maas, N.A., Cooney, J.R. and Glindemann, D. (2002a): 'Mechanisms of Volatile Sulfur Compound and Odor Production in Digested Biosolids', 2003 Residuals and Biosolids, Baltimore, MD.

Higgins, M.J., Murthy S.N., Yarosz, D.P., Novak, J.T., Glindemann, D., Toffey, W.E. and Abu-Orf, M. (2002b): 'Effect of Chemical Addition on Production of Volatile Sulfur Compounds and Odor from Anaerobically Digested Biosolids', WEFTEC 2002 Annual Conference, Chicago, IL.

Kim, M., Ahn, Y.H., Speece, R.E. (2002) Comparative process stability and efficiency of anaerobic digestion; mesophilic vs. thermophilic. Water Res. 36, 4369-4385.

Lomans, B.P., H.J.M. Op Den Camp, A. Pol, C. Van Der Drift, and G.D. Vogels (1999a) Role of Methanogens and Other bacteria in Degradation of Dimethyl Sulfide and

Methanethiol in Anoxic Freshwater Sedimetns. Applied Env. Microbio., 65, 2116-2121

Lomans, B.P., R. Mass, R. Luderer, H.J.M. Op Den Camp, A. Pol, C. Van Der Drift, and G.D. Vogels (1999b) Isolation and Characterization of Methanomethylovorans hollandica gen.nov., sp. Nov., Isolater from Freshwater Sediment, A Methylotrophic Methanogen Able to Frow on Dimethyl Sulfide and Methanethiol. Applied Env. Microbiol., 65, 3641-3650.

Lomans, B.P., H.J.M. Op Den Camp, A. Pol, and G.D. Vogels (1999c) Anaerobic versus Aerobic Degradation of Dimethyl Sulfide and Methanethiol in Anoxic Freshwater Sediments. Applied and Env. Microbiol., 65, 438-443.

Lomans, B.P., R. Luderer, P. Steenbakkers, A. Pol, C. Van Der Drift, G.D. Vogels, and J.J.M. Op Den Camp (2001) Microbial Populations Involved in Cycling of Dimethyl Sulfide and Methanethiol in Freshwater Sediments. Applied and Env. Microbiol., 67, 1044-1051.

Lowry, O.H., Rosebrough, N.J., Farr, A.L., and Randall, R.J. (1951) Protein Measurement with the Folin Phenol Reagent. J. Biol. Chem., 193, 265.

Metcalf and Eddy Inc. (2003) Wastewater engineering: Treatment and reuse. 4th Edition. McGraw-Hill, New York, NY.

Moen, G.H., Stensel, D., Lepisto, R., Ferguson, J.F. (2003). Effects of solids retention time on the performance of thermophilic and mesophilic digestion of combined municipal wastewater sludges. Water Env. Res. 75, 6, 539-548.

Muller, C.D., Nitin Verma, Matthew J. Higgins and John T. Novak. The role of shear in the generation of nuisance odors from dewatered biosolids. WEFTEC 2004 Conference and Exhibition Proceedings, October, 2004, New Orleans, LA.

Murthy, S.N., Forbes, B., Burrowes, P., Esqueda, T., Glindemann, D., Novak, J.T., Higgins, M.J., Mendenhall, T. and Toffey, W. (2002): Impact of High Shear Solids Processing on Production of Volatile Sulfur Compounds from Anaerobically Digested Biosolids, WEFTEC 2002 Annual Conference, Chicago, IL.

Murthy, S.N., Higgins, M.J., Chen, Y., Toffey, W. and Golembeski, J. (2003): Influence of Solids Characteristics and Dewatering Process on Volatile Sulfur Compound Production from Anaerobically Digested Biosolids, Biosolids Conference 2003.

Novak J.T., C. D. Muller and S. N. Murthy (2001) Floc Structure and the Role of Cations Wat. Sci. Tech. 44:10, 209 – 213.

Novak, J.T., Sadler, M.E., and Murthy, S.N. (2003) Mechanisms of Floc Destruction During Anaerobic and Aerobic Digestion and The Effect on Conditioning and Dewatering of Biosolids. Water Res., 37, 3136 - 3144.

Novak, J., D. Glindemann, S.N. Murthy, S.C. Gerwin, C. Peot. Mechanisms for Generation and Control of Trimethyl Amine and Dimethyl Disulfide from Lime Stablilized Biosolids. in WEF Odors and Toxic Air Emissions 2002 Conference. 2002. Albuquerque, NM: WEF.

Novak J.T., C. Park and M.M. Abu-Orf (2004) Conditioning and Dewatering of Digested Waste Activated Sludges. Jour Res. Sci. Tech. 1, 47 – 53.

Oho, T., Saito, T., Koga, T. (2000) Formation of Methyl Mercaptan from L-Methionine by Porphyromonas gingivalis. Infect. Immun. 68, 6912-6916.

Park C., Mohammad M. A., Novak J.T. (2004) Predicting the Digestibility of Waste Activated Sludges. Wat Environ Res. (in Press).

Persson, S et al. (1990) The formation of hydrogen sulfide and methyl mercaptan by oral bacteria. Oral microbiology and immunology. 5, 52.

Persson, S (1992) Hydrogen sulfide and methyl mercaptan in periodontal pockets. Oral microbiology and immunology. 7, 378.

Pohland, F.G., Ghosh, S. (1971) Developments in anaerobic stagilization of organic wastes—the two-phase concept. Env. Letters, 1, 4, 255-266.

Rosenfeld P.E., Henry C.L., Dills R.L. and Harrison R.B. Comparison of Odor Emissions from Three (2001). Different Biosolids Applied to Forest Soil. Water, Air, and Soil Pollution 127: 173-191, 2001

Sung, S., Liu, T. (2003) Ammonia inhibition on thermophilic anaerobic digestion. Chemosphere, 53, 43-52.

Urbain, V., Block, J.C., and Manem, J. (1993) Bioflocculation in Activated Sludge: An Analytic Approach. Water Res., 27, 829.

U.S. Environmental Protection Agency (1993) Standards for the disposal of sewage sludge. Fed. Regist., 58, 32, 40 CFR Part 503.

Vandenburgh, S.R., Ellis, T.G. (2002) Effects of varying solids concentration and organic loading on the performance of temperature phased anaerobic digestion process. Water Env. Res. 74, 2, 142-148.

II Manuscript 1

Odor Generation from Anaerobically Digested Sludge: Role of Iron & Aluminum

Nitin Verma, Chul Park, John T. Novak, Zeynep Erdal* and Bob Forbes*

*CH2M Hill

Abstract

This study was conducted to determine the effect of iron and aluminum on odor generation from anaerobically digested and dewatered sludge cakes. A blend of primary and waste activated sludge obtained from 12 different wastewater utilities was batch digested in the laboratory for 30 days at 37^{o}C, conditioned, dewatered and the organic sulfur odor generation potential measured. In addition to sulfur gas analysis, all sludge samples were analyzed for total and volatile solids, metal (Fe and Al) concentrations, mono and divalent cations in solution and soluble biopolymers (proteins and polysaccharides). A correlation between iron content with peak organic sulfur gas concentration in the headspace of incubation vials was found. Following anaerobic digestion, a significant increase in solution protein occurred and correlations between solution protein, ammonium production, percentile volatile solids reduction and iron content in sludge were observed. These data suggested that iron plays an important role in anaerobic digestion and in odor generation from dewatered sludge cakes. Aluminum, unlike iron is not reduced in anaerobic digester, and showed no apparent relationship with odors. Parameters commonly used for assessing the performance of anaerobic digesters, VS reduction, residual biological activity or digester effluent volatile fatty acid content, also showed no apparent relationship with organic sulfur odors.

Introduction

Anaerobic digestion is the most widely practiced wastewater sludge stabilization process used in the United States. It has numerous advantages over other stabilization processes such as lower operating costs, pathogen reduction and generation of useful by-products. Significant odor reduction from sludge is reported after anaerobic digestion [Murthy et al., 2002, Metcalf and Eddy, 2003]. However, complete stabilization of odorous materials in sludge is not achieved and hence the sludge still has a potential for odor generation [Murthy el al., 2002]. The transportation, storage and land application of odorous biosolids generates complaints from neighbors and environmental activists. These complaints have the potential to result in bans on land application which, in turn, can reduce land available for recycling and increase biosolids management costs [Murthy et al. 2002]. Nuisance odors have been reported as a major obstacle to the beneficial uses of biosolids and they are cited as a significant concern of many treatment plant operations.

The primary odor-causing compounds belong to one of the following three groups:

- sulfur compounds (hydrogen sulfide, methanethiol, dimethylsulfide, dimethyldisulfide, carbon-sulfide and carbon-disulfide),
- nitrogen compounds (trimethylamine, indole and skatole), and
- volatile fatty acids.

Recent research has implicated volatile organic sulfur compounds (VOSCs) as one of the key groups of compounds associated with odors during biosolids cake storage [Higgins et al., 2002]. A good correlation is reported with olfactometry results and VSCs, showing a linear correlation for odors and sulfur gases from biosolids [Adams et al., 2003].

Solids handling comprises a significant fraction of operational costs for wastewater treatment plants. Operational costs in the range of 30 to 50% of the total expenses have been found to result from solids handling (Mikkelsen and Keiding, 2002). Hence, process modifications in solids management can lead to major reductions in operational

and maintenance costs of wastewater facilities. High-solids centrifuges which produce a drier cake than low-solids centrifuges and belt-presses are being adopted at numerous facilities. It has been shown that the type of dewatering equipment impacts the VOSCs production characteristics [Murthy et al., 2003, Rosenfeld et al., 2001]. Murthy el al. (2003) showed that dewatered biosolids cakes obtained from high-solids centrifuge, low-solids centrifuge and belt filter press, possess different properties with regard to odor generation. Dewatered cakes from high-solids centrifuges were shown to produce the highest VOSC concentrations while those from belt presses are lowest. Murthy et al. (2002) and Higgins et al. (2002) suggested that the VOSC production characteristics were influenced by a combination of several factors. They suggested shearing of biosolids cakes during centrifugation make proteins bioavailable and degradation of bioavailable protein during storage forms VOSCs. Therefore, if proteins are not made available then VOSC production is minimal.

Muller et al. (2004) showed that shear plays a critical role in the generation of nuisance odors. It was also shown that shear was not the only factor that influenced VOSCs production. Both an increase in the cationic polymer dose and the cake solids concentration increased the production of sulfur gases. The authors further suggested that degradation of the released materials, the majority of which are proteins, is a cause of odor generation from dewatered biosolids. Proteins in sludge cakes have been shown to correlate with biosolids odors [Adams et al., 2003].

If shear plays a significant role in odor generation from dewatered biosolids, a better understanding of floc structure / role of cations could be usefully linked to the study of odor generation from digested sludges. Cations have been shown to play a key role in the formation of bioflocs and are known to affect the settling and dewatering properties of biosolids [Higgins and Novak, 1997a and b]. Multivalent cations play an important role in the binding biopolymers (mainly proteins and polysaccharides) within the floc, which could likely influence their availability to the microorganisms [Higgins and Novak 1997a].

It is known that extracellular polymeric substances (EPS) compose major organic fractions of biosolids floc. It has been postulated that there are different pools of EPS that are bound with different metal ions in floc and degradation of those materials are associated with different digestion conditions [Novak et al., 2003]. Important biopolymer fractions are divalent cation-associated, Fe-linked, and Al-bound EPS.

The role of metals such as iron and aluminum that are also present in wastewater in high concentrations has been little studied. Recent research at Virginia Tech has shown that sludges contain materials bound to different cations. It was thought that degradation of protein associated with the trivalent cations, Fe and Al contributed to odors when exposed to high shearing forces such as those encountered in a high solids centrifuge [Muller et al., 2004]. It has been reported that ferric iron has high affinity for the binding of protein[Novak et al., 2003] and it has been suggested that reduction of Fe^{+3} to Fe^{+2} releases iron-bound material that is degraded under anaerobic conditions. However, not all protein that is associated with iron degrades and this material was thought to be the source of odors from anaerobically digested sludges. Al, which exists in (+III) state in sludge, is also expected to bind protein, but since it is not reduced in an anaerobic digester, its protein may be relatively unavailable and therefore contribute little to odors.

It is clear from previous research findings that biodegradable proteins remain after conventional anaerobic digestion. These proteins are “released” or “made bioavailable” by shear in centrifuges and upon degradation cause odors. It is also believed that trivalent metals, especially iron, influence both digestion efficiency and odor generation. Keeping in mind the factors discussed above this research was focused to elucidate our knowledge on the role of cations, in particular Fe and Al, in determining bioavailability of proteins for odor generation following centrifugation/shear.

Materials and Methods

Experimental approach

This study was conducted using sludges from a variety of utilities. Raw sludges were obtained from different wastewater treatment plants (WWTPs) and batch digested in the laboratory under controlled conditions. Sludges when received were put in 20 liter glass containers that were sealed with rubber stoppers. Tedlar bags were connected to each digester to collect gases generated during anaerobic digestion. All sludges were batch digested at 37^{o}C for 30 days and the analysis was carried out as discussed in the following sub-sections. The contents of the digester were manually mixed once a day for the complete duration of the 30 days digestion period.

Preparation of Incubation Vials

Dewatered cakes of anaerobically digested sludges for odor analysis were prepared using a method that mimics the processes occurring in a centrifuge. Under shearing conditions, designed to mimic the shear in a high solids centrifuge, the optimum polymer dose for all sludge samples was determined using the capillary suction time (CST) test [Muller et al., 2004]. The optimum dose was determined by finding the dose which produces the minimum CST. A Triton Type 304-M and Triton Type 165 CST apparatus were utilized with Whatman 17-CHR as the chromatography paper. Liquid cationic polymer solution was prepared for dosing. Clarifloc 3275 – a high molecular weight polymer was used for all sludges to minimize the affects of conditioning polymer on odors from biosolids.

The overall approach to mimic the actions of centrifuge to generate odors was to provide shear that was similar to that occurring in the centrifuge, to dewater cakes to solids concentration that was similar to high-solids centrifuge and to provide polymer for conditioning at a dose similar to the centrifuge. A Warring Blender was used to shear the sludge. Liquid sludge was sheared for 30 seconds in 100 mL increments. The optimum dose of cationic polymer for each sample was determined by conducting a polymer dose test for 30 seconds shearing.

Sludge dewatering using the optimum polymer dose was accomplished using a laboratory centrifuge. The centrifuge was operated at 17,700 xG for 15 minutes at 25^{o}C. Sludge cakes obtained from centrifuge were further dewatered to increase solids content using a hydraulic piston press constructed at Virginia Tech, with Whatman 41 paper serving as the filter media.

Cake storage experiments were performed on multiple odor vials containing dewatered cake. To accomplish this, 25g ± 1g of wet cake were placed in glass bottles (250 mL). The bottles were sealed with Teflon septa and stored at a room temperature of about 22^{o}C for the duration of the experiments.

Multiple odor vials containing dewatered cake samples with low and high solids content were prepared for each sludge for GC/MS analysis. Low-cake solids cake refer to cake samples that were dewatered only using the laboratory centrifuge and having solids content similar to dewatered cake achieved low-solids centrifuges. Whereas, high-solids cake refer to cake samples that were further dewatered using the hydraulic piston to achieve solids concentrations similar to those derived from high solids centrifuges.

For high-solids and low-solids cakes, samples both with and without the addition of Bromoethane-sulphonic acid (BESA), a methanogen inhibitor, were prepared. Five milliliters of BESA solution (0.127 mmole) was added to about 400 mL of liquid sludge before dewatering it using the lab centrifuge.

Odor Profiling and Qualification

The characterization of odors was accomplished using the method described by Novak et al. (2002). This method was modified by using glass containers (250 mL, I-CHEM glass bottles) with Teflon lined septa rather than PET bottles. The compounds of interests were MT, DMS and DMDS. H_2S was of secondary interest since it is a metabolic waste product of methylotropic methanogenesis and will react chemically iron. The variability of this parameter resulted in its exclusion from consideration in this study.

The headspace in the incubation vial was analyzed periodically for odorous gases by cryo-trapping and gas-chromatography and mass spectrometry. This method was the same as that used in previous research conducted by Glindemann et al. (2005).

The headspace in the incubation vial was sampled periodically to produce a time response profile. Peak sulfur odor is the maximum concentration of headspace organic sulfur achieved over the incubation period. A typical odor profile for cake without BESA will consist of two phases; the first phase in which sulfur odors are generated and the second phase when they are consumed. The point of inflection between these two phases represents the peak sulfur odor for that particular sample. For cake samples to which BESA was added, the consumption phase did not occur. After attaining the peak, when BESA is added, the total sulfur concentration stays at the peak concentration. Peak organic sulfur gas concentration for all the cake samples was measured and used to compare the odor generation potential for various SRTs.

Metals Analysis

Total concentration of metals (Fe and Al) were measured in the incoming raw sludge on a Perkin Elmer 5100PC Atomic Adsorption Spectrophotometer, following acid digestion per USEPA Method 3050B (EPA 1996). Resultant concentrations are expressed as mg-metal per gram total solids (TS) basis.

In addition to the odor and cation analysis, the following tests were conducted:

a. Total and volatile solids
b. pH
c. Volatile fatty acids (VFA) in the digested biosolids
d. Soluble cations (Na^{+}, K^{+}, Ca^{+2}, Mg^{+2} and NH_4^{+})
e. Residual biological activity
f. Solution proteins and polysaccharides

Solids and pH were conducted according to Standard Methods (APHA, 1999). In order to prepare samples for cation and VFA analyses, a 500mL sample for digester biosolids was centrifuged at 17,700 xG for 15 minutes. Supernatant liquid was filtered through a

0.45 micron syringe filter. From this filtered sample, dilutions were made for cation and VFA analysis. VFA samples were acidified in their individual GC vial by adding concentrated acid at a ratio of 1:10. The VFA samples were analyzed on a GC (Model: Shimadzu, GC-14A) using a flame ionization detector.

Liquid phase cations were measured on a Dionex D-120 ion chromatograph utilizing a CS-12 column and conductivity detector with self generating suppression of the eluent (Dionex Corp., Sunnycale, CA). 20mM methanesulfonic acid was used for eluent at a flow rate of 1mL/min.

The residual biological activity test (RBA) was a simplified modification of the additional digestion test method outlined by EPA (1993). It was conducted by incubating 100mL digester samples in serum vials at 37°C for at least 40 days. During the incubation period, the vials were periodically degassed and weighed. The weight lost from each vial was assumed to be from gasification of the VS in each sample. RBA was calculated by dividing the weight lost from each sample at the end of incubation by the weight of its VS content (analyzed prior to incubation) and is reported as percent VS lost.

Soluble proteins were determined by the modified Lowry et al. (1951) method described by Frølund et al. (1996) using bovine serum albumin as the standard. Soluble polysaccharides were measured by the Dubois et al. (1956) method utilizing glucose as the standard. Laboratory centrifuge was used to separate the solution from majority of solids in sludge. The supernatant after centrifuge was filtered through a 1.5 μm membrane filter and then analyzed separately for proteins and polysaccharides. The values obtained were termed as solution protein and solution polysaccharide.

Results and Discussions

In order to study the influence of cations on odor generation from anaerobically digested biosolids, raw sludges from 12 different WWTPs were anaerobically batch digested for 30 days at 37^{o}C. The mix of primary and secondary sludge was generally the same as generated at the treatment plants. The feed sludge was analyzed for total and volatile solids (TS and VS), solution cations, total Fe and Al, and also for solution biopolymer

(proteins and polysaccharides). The composition of the raw feed sludge including mono and divalent cations in solution and total iron and aluminum are listed in Table II-1. Feed sludge from all plants except 11W and 12W received a blend of primary and waste activated sludge (WAS). Feed sludge from 11W and 12W contained thickened waste activated sludge only.

Anaerobic digestion and metals

Recent studies by have shown that cations play an important role in biofloc formation and destruction during digestion [Novak et al. (2003), Park et al. (2004)]. It is known that extracellular polymeric substances (EPS) compose a major organic fractions of biosolids floc [Frølund et al., 1996]. It has been postulated that there are different pools of EPS that are bound with different metal ions in floc. Degradation of those materials are associated with different digestion conditions [Novak et al. 2003]. Important biopolymeric fractions are: divalent cation-associated EPS, Fe-linked EPS, and Al-bound EPS.

It was observed in previous studies conducted at Virginia Tech that anaerobic and aerobic digestion of a waste activated sludge, from several different wastewater treatment plants (WWTPs), resulted in different cation and biopolymer releases and different degrees of volatile solids (VS) destruction [Park et al., 2004]. It has also been shown that each type of digestion is accompanied by increases in solution biopolymer with proteins being the major component that increases in anaerobic digesters and polysaccharides in aerobic digesters. Park et al. (2004) showed that a large amount of protein was recovered from the sludge solution following anaerobic digestion. Furthermore, there was a correlation between the % VS reduction by anaerobic digestion and Fe concentration in feed sludges. These results suggested that lectin-like proteins (associated with Ca and Mg) are mainly degraded under aerobic conditions while exopolymers associated with Fe are readily degraded under anaerobic conditions [Park et al. 2004]. It was also shown that Al plays a significant role in bioflocculation by improving effluent quality with higher Al content in floc but the impact of Al and its binding organic matter on sludge digestion is unclear [Park et al. 2004].

Studies have shown that iron is immediately reduced under anaerobic conditions and as a result the sludge becomes deflocculated [Park et al., 2004]. Muller (2001) compared the efficiencies of iron (III) and iron (II) salts for coagulation of solution protein and found that iron (III) was more effective in binding proteins. Novak et al. (2003) and Park et al. (2004) observed that a large amount of proteins was always found in the solution phase of anaerobically digested sludges. Therefore, iron reduction under anaerobic conditions can be linked to the release of proteins into solution. Park et al. (2004) showed that solution protein in anaerobically digested waste activated sludge and the percent VS reduction were strongly affected by the iron content in sludge. They showed that as the floc iron concentration increased, greater VS reduction occurred during digestion and more protein was released into solution.

After 30 days of anaerobic digestion, each sludge was analyzed for the TS, VS , solution cations, total metals (Fe and Al), solution biopolymers, dewatering (measured by the CST test) and odors. Table II-2 lists the composition of digested biosolids.

Since VS reduction is one of the key parameters used to assess the performance of an anaerobic digester, it was carefully examined with various other parameters during the study. As shown in Figure II-1, the percent VS reduction was a function of the iron content in feed sludge. These data are in accordance with previous observations that VS destruction increased with an increase in the Fe concentration in feed sludge. However, the correlation was not strong. This could be due to the form of iron in the primary sludge, some of which is probably inert and is not associated in the biofloc. Park et al. (2004) conducted their study with only WAS.

Table II-3 lists the solution biopolymer concentrations measured in the feed and digested sludges. These data are in accordance with previous observations that a large amount of proteins are released into solution during anaerobic digestion and a smaller amount of polysaccharides are released.

Protein has been reported as the major organic compound degraded during anaerobic digestion. While some of the released protein remains in solution, most of the protein is degraded accounting for much of the VS destruction in anaerobic digestion. Figure II-2(a) shows the plot of solution proteins in digested sludge as a function of VS reduction. It can be seen that higher solution proteins were observed in samples that had higher VS destruction. The increase in ammonium ion concentration (Figure II-2) serves as an indication of the degradation of nitrogen containing organic matter, primarily proteins. Figure II-2(b) shows that ammonium production is also associated with VS reduction during anaerobic digestion. These data are in accordance with those reported by Park et al. (2004) for anaerobic digestion of WAS. These data show the trends observed by Park et al. (2004), however the correlation is not strong (r^2 = 0.61). The observed weak correlation is likely to be due to the use of a blend of primary and waste activated sludge, instead of only waste activated sludge as was done in previous research [Park et al., 2004]. Primary sludge is not homogeneous and the characteristic of primary sludge typically differs substantially from one utility to another. The difference in primary sludge is likely the reason for the variability observed.

Sulfur gas production and role of methanogens

Headspace gas in vials containing dewatered cake was periodically analyzed using GC/MS for sulfur gases to generate a sulfur gas concentration versus time plot for each sample. Figure II-3 is an example of a typical organic sulfur odor profile generated using the static headspace method. The data in Figure II-3 is from the different vials prepared for sludge from WWTP No. 1.

Research has shown that methanogenic bacteria are able to degrade VOSCs. For example, in fresh water sediments a balance typically exists between the production of VOSCs and their degradation resulting in little emission of these compounds unless the system is disturbed [Lomans et al., 2001]. A similar balance likely exists in anaerobic digesters since VOSCs are typically not emitted except under conditions that cause stress to methanogenic bacteria. Higgins et al. (2004) have shown that methanogens play an important role in cycling of VOSCs from biosolids. Higgins et al. (2004) also showed

that near stoichiometric amounts of VOSCs are produced to the amount of substrate available when the methanogens are inhibited.

As shown in Figure II-3 dewatered cakes which were amended with BESA, to reduce the methanogenic activity, produced a greater amount of VOSCs. VOSC concentration from cakes which were not amended with BESA did not peak as high and also the concentration decreased rapidly due to degradation by methanogens. These data are in agreement with those reported by Higgins et al. (2004), suggesting that methanogens play an important role in cycling of VOSCs.

The headspace sulfur concentration was normalized to the initial quantity of volatile solids added to the incubation vial. The normalized concentration was then plotted as a function of the incubation time as shown in Figure II-3(b) for sludge from WWTP No. 1.

Figure II-3 shows that the concentration of sulfur gas in headspace of cakes with low solids concentration was lower than that for high solids cake, suggesting that solids concentration of the dewatered cake affect the cycling of VOSCs. These data are in agreement with recent results reported by Muller et al. (2004). It is thought that as the cake moisture is reduced, the methanogens are inhibited, either by exposure to oxygen or lack of moisture. However, although the methanogens are inhibited, other organisms in the sludge cake, many of which are facultative, continue to degrade protein to produce sulfur gases. As a result, the syntropy between sulfur gas production and consumption is lost leading to accumulation of sulfur gases in the headspace.

Similar to Figure II-3, organic sulfur versus time plots for each sludge sample were prepared (data not shown). The formation of organo-sulfur gases for all the samples followed a similar pattern. Odor production differed from one dewatered cake to another in terms of the day in which the sulfur gas reached its peak concentration.

Sulfur odor and cations

In order to compare the odor generation potential of different sludges and correlate them with metal concentrations, the peak organic sulfur concentration were computed. Table 5

and Table 6 list the peak organic sulfur concentration measured in different headspace incubation vials and solids concentration of the dewatered cake in the odor vials respectively.

Figure II-4 shows the peak-organic sulfur gas concentration generated from high-solids concentration cake as a function of Fe concentration in the feed sludge. Peak sulfur gas concentration values fit well with Fe in the sludge solids except those from plants 3 and 4. WWTPs No. 3 and 4 are known to receive water plant sludge containing high amounts of Fe in the influent of the WWTP. It is expected that iron present in these sludges was present in $Fe(OH)_3$ form and hence iron was not able to bind with the proteins. As the fraction of iron bound with proteins is dependent on the concentration of Fe which is available to bind with biopolymer in sludge, the total iron concentration for these sludges not considered to be indicative of odor-causing proteins. Sludges from plants 11W and 12W were different from sludges from other plants as they consisted only of thickened waste activated sludge. No clear relationship could be drawn from the plot (Figure II-5) of peak organic sulfur gas concentration for high-cake solids with Al in feed or with the Fe/Al ratio (data not shown).

Peak organic sulfur gas concentration generated from dewatered cake with low cake solids was plotted as a function of Fe content in feed sludge (figure not shown). A trend similar to that observed for high solids cake samples was observed. The organic sulfur gas concentration increased with an increase in the Fe content of sludge.

It is clear from Figure II-4 that peak organic sulfur concentration in the headspace increases with an increase in the iron content of sludge. Data obtained is consistent with previous research findings that biopolymer associated with Fe is not completely degraded during anaerobic digestion [Adams et al., 2003 and Muller et al., 2004] and when these biopolymers, primarily proteins, are made bioavailable by shear in the presence of polymer they undergo degradation to produce VSCs. Figure II-5 shows the data for peak sulfur gas concentration versus the aluminum in feed sludge. These data show that Al

associated organic matter is not associated with the production of organic sulfur gases from dewatered sludge cake.

Figure II-6 shows the peak organic sulfur concentration in the headspace for the sludges digested in the lab along with four field digested sludges. The field digested sludges are from anaerobic digesters operated at mesophilic temperatures. These data suggest that the amount of organic sulfur gas produced by sludge batch digested in the lab as well as field digested sludge had a strong correlation with the iron content of sludge. These data show that the Fe content of sludge plays a crucial role odor generation from dewatered cake. The relationship between generation of sulfur gases and iron provides a method for predicting prior to anaerobic digestion if a sludge will be likely to generate odors if dewatered by a high solids centrifuge. This provides a tool to help in the selection of dewatering equipment and to select the overall sludge handling process.

The relationship between the monovalent to divalent ration (M/D) and the peak organic sulfur gas concentration in the headspace of vials containing high-solids cake amended with BESA is shown in Figure II-7. The concentrations of cations for this plot are reported in meq/meq basis. The monovalent cations considered were Na, K and NH_4 and the divalent cations considered were Mg, Ca. A weak correlation of peak organic sulfur with M/D ratio is observed, hence, no conclusions about the role of monovalent and divalent cations can be drawn.

Volatile solids destruction and sulfur odors

VS destruction in anaerobic digestion is one of the key parameters for regulatory compliance with the Vector Attraction Reduction (VAR) requirements of the 503 rule. Based on previous research it was anticipated that higher VS reduction would have a beneficial impact on digested biosolids quality and odor from dewatered biosolids cake. The VS destruction data was plotted with the peak organic sulfur data as shown in Figure II-8. There is no apparent correlation between the two parameters. The results indicate that the 38% VS destruction requirement for VAR compliance is not a useful parameter for predicting odor quality of dewatered biosolids. These data are in accordance with those reported by Adams et al. (2003). Since greater VS reduction does not correspond to

lower sulfur odors, these data suggest that the odor causing materials (proteins) in the biosolids cake are different from those degraded in the anaerobic digester.

Effluent VFA

A high concentration of volatile fatty acids in the digested solids has historically been an indicator of poor digester performance, which is often thought as a precursor of biosolids odor. However, as shown in Figure II-9, no clear relationship can be drawn from the data obtained from this study. Figure II-9 illustrates the variability in the peak organic sulfur gas concentration from dewatered cake when plotted with digester effluent VFA concentration as acetic acid (reported in mg/L). Peak sulfur gas concentration values for this plot are those for high solids cake which were amended with BESA. VFA data showed no relationship with organic sulfur odor data.

VFA concentration observed in the effluent are high when compared to those reported in literature, suggesting the digestion was incomplete even after 30 days. This could be due to the limitation of batch digesting blend of primary and WAS, as primary sludge contains readily degradable organics which lead to acid accumulation and potential inhibition of methanogenic activity leading to incomplete digestion.

Residual biological activity (RBA) and sulfur odors

RBA is considered to be a measure of the biological stability of digested biosolids, since RBA represents the potential for biological activity in digested biosolids. Figure II-10 shows the plot between dewatered biosolids RBA measured at 40 days and peak organic sulfur in headspace of dewatered cake. In general, higher peak organic sulfur gas concentration was observed from dewatered cake of digested samples which had higher RBA. However, the correlation was poor. RBA data was also plotted with the VS destruction as shown in Figure II-11. A poor correlation is observed, suggesting that the materials degraded during the additional 40 days incubation are different from the materials degraded in the anaerobic digester. Higher organic sulfur gas concentrations were observed from samples having higher RBA. Further study is required to ascertain the relationship of RBA with sulfur odors.

Organic sulfur odor: Implications for dewatering and biosolids odors

Since liquid anaerobic digested sludges (not exposed to toxicity) generally have low odor and VOSC generation compared to dewatered cake which produce significant odors, this suggests that dewatering process can cause imbalance between the production and consumption rates of VOSCs. Recent research has suggested that the factors like shear in the dewatering equipment, polymer dose, and cake handling and transportation affect VOSC generation from dewatered biosolids cake [Novak et al., (in press)].

For example, high solids centrifuges produce greater cake odors and VOSCs than other dewatering equipment [Novak et al., (in press)]. The results from this study can be used to explain differences in odors from different dewatering equipment. In general, factors that either increase the substrate (primarily protein) for VOSC production or decrease VOSC degradation through methanogen inhibition result in greater net VOSC production from dewatered cake. Large amount of shear is imparted during centrifugation of sludge, which leads to greater floc disintegration and hence greater amounts of bioavailable proteins. It has been shown that high-solids centrifuges which impart greater shear than low-solids centrifuges led to higher VOSC generation [Higgins et al., 2002, Murthy et al., 2003]. Results from this study show that in addition to higher shear, higher cake solids concentration of the dewatered cake also influences odor.

The results from this study clearly show that sludges with higher iron content produced higher amounts of sulfur gases, suggesting that Fe bound material in sludge are highly sensitive to shear. Thus in sludge with higher iron content, iron binds a greater amount of material, part of which is released into solution due to reduction of Fe^{+3} to Fe^{+2} and then degraded during anaerobic digestion. However, complete degradation of iron associated material is not achieved. And, when this high iron anaerobically digested sludge is exposed to high shear conditions in presence of dewatering polymer the material bound to iron is made bioavailable. Degradation of these released materials causes generation of sulfur gases.

The results from this study show that only iron content of sludge has a correlation with organic sulfur odors from dewatered biosolids cake. None of the parameters, like VS reduction, RBA and effluent VFA concentration, showed an apparent relationship with odors. The relationship between iron and odor generation provides a useful tool for predicting if a sludge will be likely to generate odors if dewatered by a high solids centrifuge.

Summary

This study was conducted to improve our knowledge of the role of metals, in particular iron and aluminum, in anaerobic digestion of wastewater sludge and also their role in generation of sulfur odors from dewatered sludge cake. A blend of primary and waste activated sludge was obtained from twelve different wastewater treatment plants. Sludge obtained was batch digested in the laboratory for 30 days at 37^{o}C. Anaerobically digested dewatered sludge cakes were evaluated for their sulfur odor generation potential. Digested biosolids were tested for odor generation with the centrifuge simulation method developed at Virginia Tech. In addition to sulfur gas analysis, all sludge samples were analyzed for total and volatile solids, metal (Fe and Al) concentrations, cations in solution and soluble biopolymers (proteins and polysaccharides).

Odor analysis was conducted on batch digested biosolids samples. Since reduced sulfur gases are the primary odor causing compounds, only concentrations of the reduced sulfur compounds are shown. Headspace vials for odor testing were prepared; biosolids cake with low and high cake solids concentration were prepared to compare the odor generation potential of different dewatered sludges.

All headspace organic sulfur data show a good relationship with the iron content of sludge. In general, higher sulfur gas concentrations were observed in headspace of cakes with higher iron content. These data suggest that iron plays an important role in anaerobic digestion and in odor generation from dewatered cake. Parameters commonly used to assess the performance of anaerobic digesters like volatile solids reduction, volatile fatty acid content and residual biological activity were measured and plotted with the organic sulfur gas potential of dewatered sludge cakes. VS destruction increased with an increase

in the iron content of sludge. In general, greater VS destruction and higher organic sulfur gas concentration was observed for sludge with high iron content. Significant increases in solution protein occurred and correlations between solution protein, ammonium production, volatile solids reduction and iron content in sludge were observed. Aluminum, unlike iron is not reduced in anaerobic digester, showed no apparent relationship with VS destruction or sulfur odors.

Conclusions

The main conclusions that can be drawn from this study are:

1. Organic sulfur gas production correlated well with iron content of sludge. In general, organic sulfur gas concentration increased with an increase in the iron content of sludge. No relationship of sulfur odor was observed with aluminum content of sludge.
2. Volatile solids reduction, residual biological activity and volatile fatty acid showed no apparent correlation with sulfur odors. These parameters are good indicators of the performance of anaerobic digesters; however, they are not good indicators of odor generation from dewatered sludge cakes.
3. Methanogenic bacteria play an important role in the cycling of organic sulfur compounds. Cake samples, to which a strong methanogen inhibitor was added, produced greater amount of sulfur gases and there was no decrease in sulfur gas concentrations even after several weeks of incubation.

Reference:

Adams, G.M., Witherspoon, J., Card, T., Forbes, R., Geselbracht, J., Glindemann, D., Hargreaves, R. Hentz, L., Higgins, M., McEwen, D., and Murthy, S. Identifying and Controlling the Municipal Wastewater Odor Environment Phase 2: Impacts of In-Plant Operational Parameters on Biosolids Odor Quality. 2003, Water Environment Research Foundation: Alexandria, VA.

Frølund, B., Palmgren, R., Keiding, K., and Nielsen, P.H. (1996) Extraction of Extracellular Polymers from Activated Sludge Using a Cation Exchange Resin. Water Res., 30, 1749.

Glindemann, D., Murthy S.N., Higgins M.J., Yen-Chih Chen, Eschborn R.,Toffey W., Mittman Michele and Novak J.T. (in press) A Standardized Procedure for Measurement of Odor Causing Compounds Produced by Biosolids. Water Reasech(in press).

Higgins, M. J. and Novak, J.T. (1997a) The Effect of Cations on the Settling and Dewatering of Activated Sludges. Water Environ. Res., 69, 215.

Higgins, M.J. and Novak, J.T. (1997b) Characterization of Exocellular Protein and Its Role in Bioflocculation. J. Environ. Engr. ASCE, 123, 479-485.

Higgins, M.J., Yarosz, D.P., Chen, Y.C., Murthy, S.N., Maas, N., Cooney, J., Glindemann, D., Novak, J.T., Cycling of Volatile Organic Sulfur Compounds in Anaerobically Digested Biosolids and its Implications for Odors. Water Environment Research, 2004 (Submitted, November 2003).

Higgins, M.J., Murthy S.N., Yarosz, D.P., Novak, J.T., Glindemann, D., Toffey, W.E. and Abu-Orf, M. (2002): 'Effect of Chemical Addition on Production of Volatile Sulfur Compounds and Odor from Anaerobically Digested Biosolids', WEFTEC 2002 Annual Conference, Chicago, IL.

Lomans, B.P., R. Luderer, P. Steenbakkers, A. Pol, C. Van Der Drift, G.D. Vogels, and J.J.M. Op Den Camp (2001) Microbial Populations Involved in Cycling of Dimethyl Sulfide and Methanethiol in Freshwater Sediments. Applied and Env. Microbiol., 67, 1044-1051.

Lowry, O.H., Rosebrough, N.J., Farr, A.L., and Randall, R.J. (1951) Protein Measurement with the Folin Phenol Reagent. J. Biol. Chem., 193, 265.

Metcalf and Eddy Inc. (2003) Wastewater engineering: Treatment and reuse. 4th Edition. McGraw-Hill, New York, NY.

Mikkelsen L.H. and K. Keiding (2002), Physico-chemical characteristics of full scale sewage sludges with implications to dewatering. Wat. Research 36, 2451–2462

Muller, C.D., Nitin Verma, Matthew J. Higgins and John T. Novak. The role of shear in the generation of nuisance odors from dewatered biosolids. WEFTEC 2004 Conference and Exhibition Proceedings, October, 2004, New Orleans, LA.

Murthy, S.N., Forbes, B., Burrowes, P., Esqueda, T., Glindemann, D., Novak, J.T., Higgins, M.J., Mendenhall, T. and Toffey, W. (2002): Impact of High Shear Solids Processing on Production of Volatile Sulfur Compounds from Anaerobically Digested Biosolids, WEFTEC 2002 Annual Conference, Chicago, IL.

Murthy, S.N., Higgins, M.J., Chen, Y., Toffey, W. and Golembeski, J. (2003): Influence of Solids Characteristics and Dewatering Process on Volatile Sulfur Compound Production from Anaerobically Digested Biosolids, Biosolids Conference 2003.

Novak, J.T., Sadler, M.E., and Murthy, S.N. (2003) Mechanisms of Floc Destruction During Anaerobic and Aerobic Digestion and The Effect on Conditioning and Dewatering of Biosolids. Water Res., 37, 3136 - 3144.

Novak, J., D. Glindemann, S.N. Murthy, S.C. Gerwin, C. Peot. Mechanisms for Generation and Control of Trimethyl Amine and Dimethyl Disulfide from Lime Stablilized Biosolids. in WEF Odors and Toxic Air Emissions 2002 Conference. 2002. Albuquerque, NM: WEF.

Park C., Mohammad M. A., Novak J.T. (2004) Predicting the Digestibility of Waste Activated Sludges. Wat Environ Res. (in Press).

Rosenfeld P.E., Henry C.L., Dills R.L. and Harrison R.B. Comparison of Odor Emissions from Three (2001). Different Biosolids Applied to Forest Soil. Water, Air, and Soil Pollution 127: 173-191, 2001

U.S. Environmental Protection Agency (1993) Standards for the disposal of sewage sludge. Fed. Regist., 58, 32, 40 CFR Part 503.

Table II-1: Solution mono and divalent cations and total Fe and Al in feed sludge

Plant	TS (g/L)	VS (g/L)	Na^{+} (mg/L)	NH_4^{+} (mg/L)	K^{+} (mg/L)	Mg^{+2} (mg/L)	Ca^{+2} (mg/L)	Fe (mg/gTS)	Al (mg/gTS)
1	14.4	10.7	53.1	10.2	20.3	13.6	41.9	16.7	5.3
2	6.9	5.5	60.1	13.0	11.3	5.4	27.7	7.6	6.9
3	39.2	29.2	72.8	618.4	227.3	75.4	156.2	35.0	2.9
4	40.9	25.7	56.5	414.0	53.4	65.8	179.7	96.9	5.1
5	41.9	32.6	67.5	280.0	83.9	54.0	115.7	27.6	5.6
6	42.9	36.7	158.0	85.4	98.6	68.7	205.1	10.9	3.1
7	47.8	38.2	98.0	146.3	438.6	121.8	211.4	25.9	6.3
8	33.9	25.1	~	~	~	~	~	49.1	3.8
9	37.5	31.7	67.7	105.1	151.3	51.0	137.9	28.5	5.5
10	39.5	31.8	58.1	278.6	199.1	85.1	129.4	15.3	8.5
11W	10.4	8	35.74	19.75	35.82	22.33	48.01	13.7	9.8
12W	52.0	41	25.8	367.0	221.2	15.9	48.5	11.8	8.6

~: did not measure

Table II-2: Chemical content of sludge following anaerobic digestion for 30 days

Plant	pH	TS (g/L)	VS (g/L)	VSR* (%)	Na^{+} (mg/L)	NH_4^{+} (mg/L)	K^{+} (mg/L)	Mg^{+2} (mg/L)	Ca^{+2} (mg/L)	Fe (mg/gTS)	Al (mg/gTS)
1	~	1.04	0.72	33.1	54.4	229.9	37.9	16.9	14.9	12.4	4.0
2	6.7	0.45	0.30	44.5	61.9	210.7	40.4	13.8	16.5	12.1	16.8
3	7.6	2.50	1.50	48.7	71.1	1516.4	209.6	64.9	87.1	61.3	4.0
4	7.3	2.16	1.01	60.5	59.4	716.0	62.9	46.3	70.8	134.0	5.5
5	6.5	3.14	2.19	32.8	64.7	981.6	171.8	36.4	78.9	43.0	13.6
6	6.4	2.76	2.15	41.5	141.5	962.5	296.4	83.7	137.6	19.1	10.2
7	6.8	2.97	2.09	45.3	97.2	1217.9	433.2	118.9	109.7	41.7	10.1
8	6.9	2.36	1.50	40.2	253.4	895.2	157.1	60.1	28.9	70.6	5.5
9	7.2	2.94	1.75	44.6	3047.5	950.0	108.0	15.3	18.1	38.2	9.0
10	6.9	3.08	2.07	35.0	1912.7	1361.1	352.2	21.0	nd	13.8	7.8
11W	7.4	0.72	0.48	39.4	37.9	300.5	76.3	22.7	43.8	20.0	14.3
12W	7.7	3.68	2.54	38.0	46.0	1844.0	482.1	15.5	8.6	15.2	8.6

*VSR – Volatile solids reduction, nd: not detected, ~: did not measure

Table II-3: Solution biopolymers in feed and digested sludge

Plant	Feed-Proteins (mg/L)	Digested-Proteins (mg/L)	Feed Polysaccharides (mg/L)	Digested-Polysaccharides (mg/L)
1	56.6	413.1	10.0	41.0
2	43.5	192.3	5.4	15.7
3	904.4	1407.2	160.6	168.3
4	693.6	906.2	97.1	59.4
5	604.0	2411.3	145.6	435.8
6	728.8	2315.4	134.4	372.9
7	1934.4	2995.9	341.5	430.2
8	~	1189.6	~	115.6
9	634.5	1303.8	106.7	44.4
10	745.6	1734.2	200.1	41.8
11W	51.2		~	23.9
12W	968.8	2848.7	130.3	47.1

~: did not measure

Table II-4: Peak organic sulfur concentration for dewatered cake

Plant	High solids (mg/m^3)	High solids with BESA (mg/m^3)	Low solids (mg/m^3)	Low solids with BESA (mg/m^3)
1	101.2	322.5	50.0	-
2	4.7	59.0	1.8	33
3	178.7	330.7	~	294.0
4	274.3	1015.3	~	589.4
5	996.9	1000.0	~	925.3
6	11.0	19.0	~	46.6
7	758.4	872.6	~	816.7
8	922.1	1148.7	852.0	1098.1
9	160.0	178	~	156.1
10	201	306	~	290
11W	4.6	277	~	~
12W	513.1	493.3	59.4	450.6

~: did not measure

Table II-5: TS and VS of dewatered cake analyzed for headspace sulfur gases

Plant	High solids		Low solids	
	TS	VS	TS	VS
1	22.0%	14.7%	11.9%	7.9%
2	11.8%	8.3%	10.6%	7.5%
3	24.3%	14.1%	20.6%	11.4%
4	36.4%	16.7%	24.3%	11.5%
5	20.4%	13.0%	17.8%	11.4%
6	24.0%	18.4%	19.2%	13.9%
7	17.9%	12.7%	16.7%	11.7%
8	27.4%	15.1%	19.6%	11.3%
9	27.6%	19.1%	19.0%	13.0%
10	15.8%	11.5%	13.4%	8.8%
11W	19.0%	14.4%	~	~
12W	19.2%	13.3%	15.2%	10.7%

~: did not measure

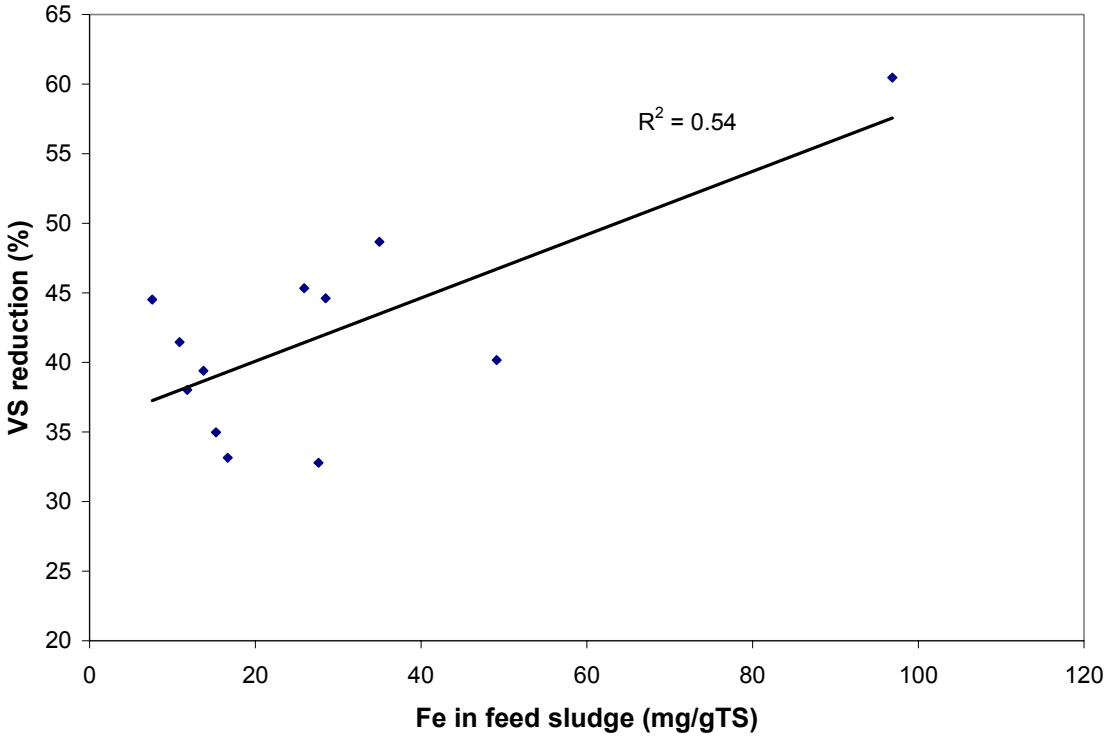


Figure II-1: VS destruction versus iron in feed sludge.

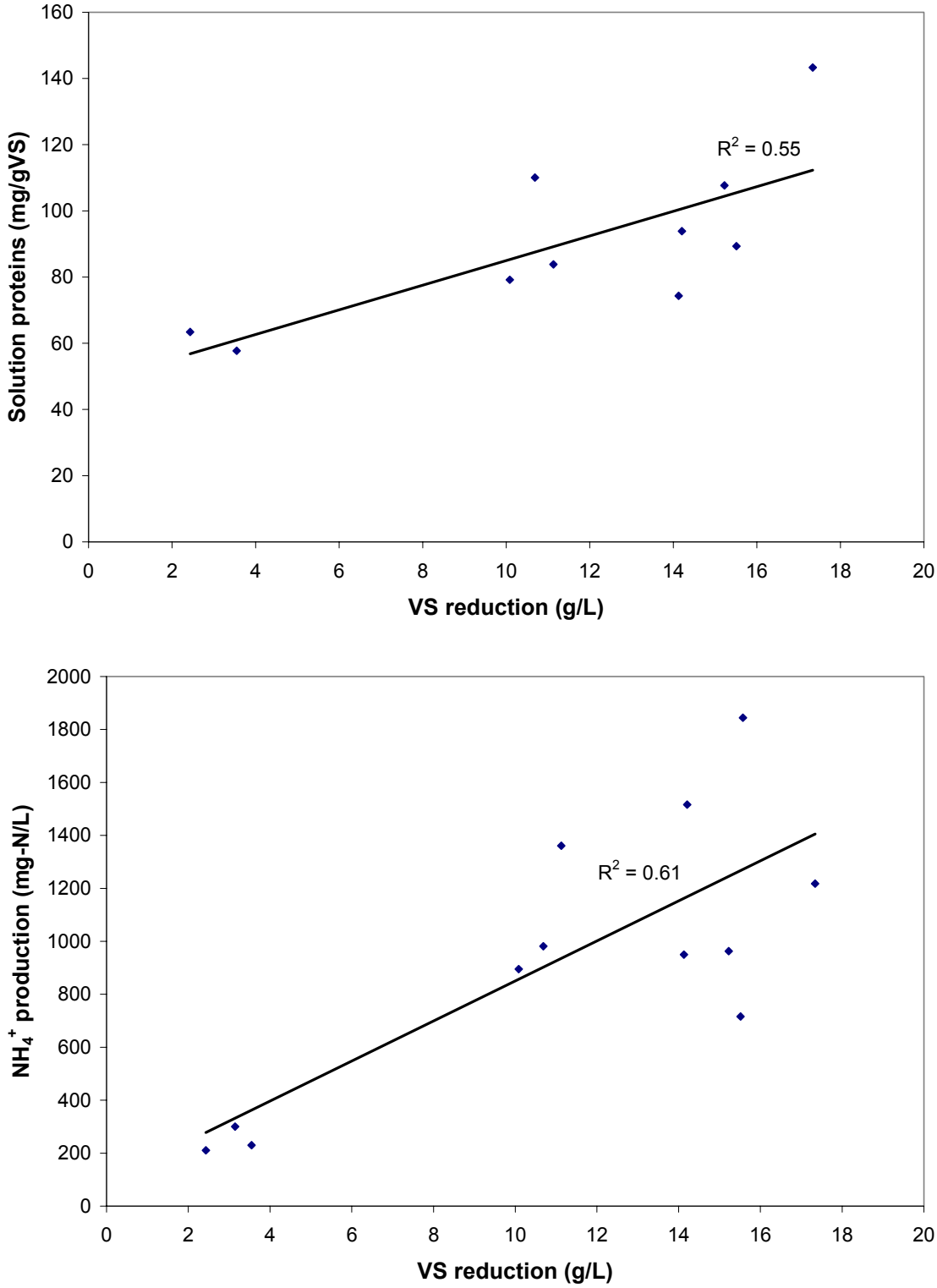
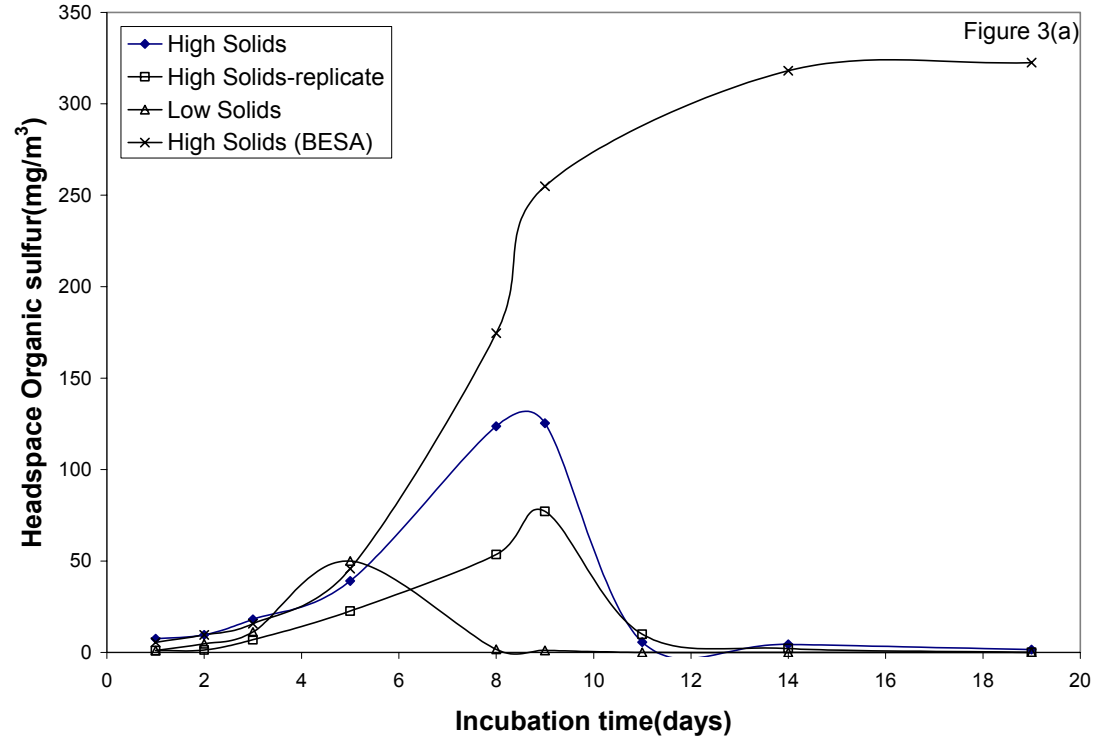


Figure II-2:a) Solution proteins versus VS reduction, b) Ammonium ion concentration in digested sludge as a function of VS reduction.



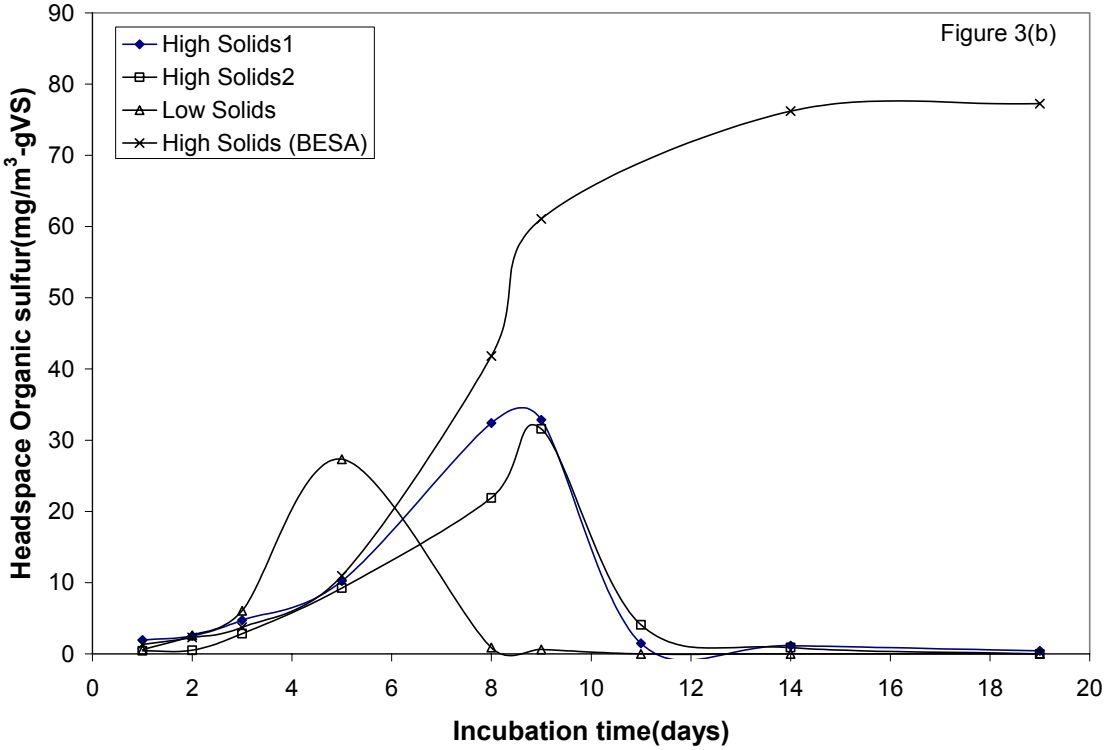
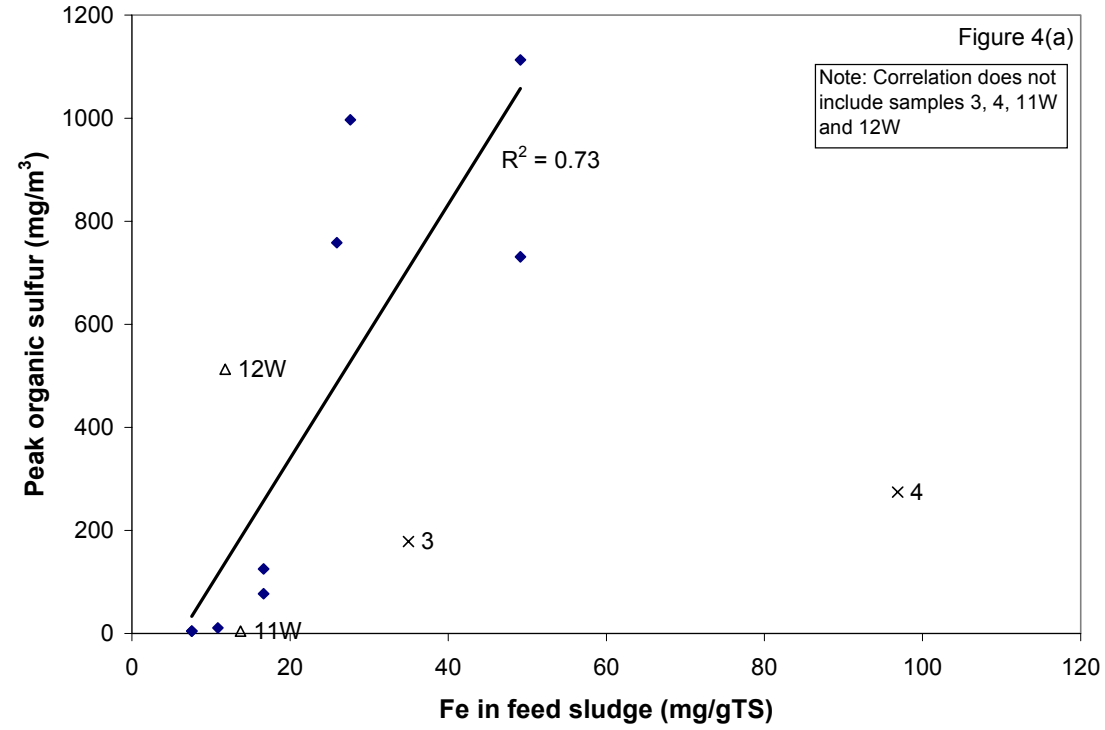


Figure II-3: a) Changes in headspace organic sulfur concentration under static headspace incubation of cakes solids for dewatered sludge from WWTP No. 1. Organic sulfur reported in mg/m3. b)Organic sulfur concentrations normalized to volatile solids content of cake in incubation vial.



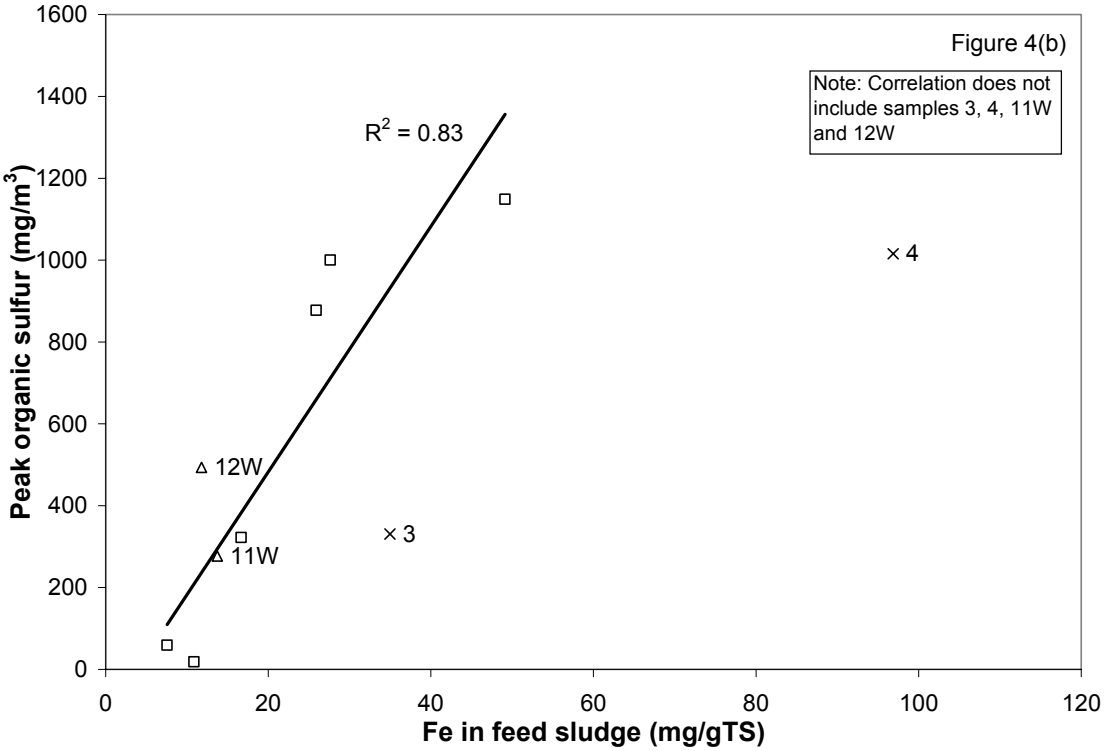


Figure II-4: Peak headspace organic sulfur gas concentration for high-solids cake as a function of iron content of feed sludge a) without BESA, b) with BESA

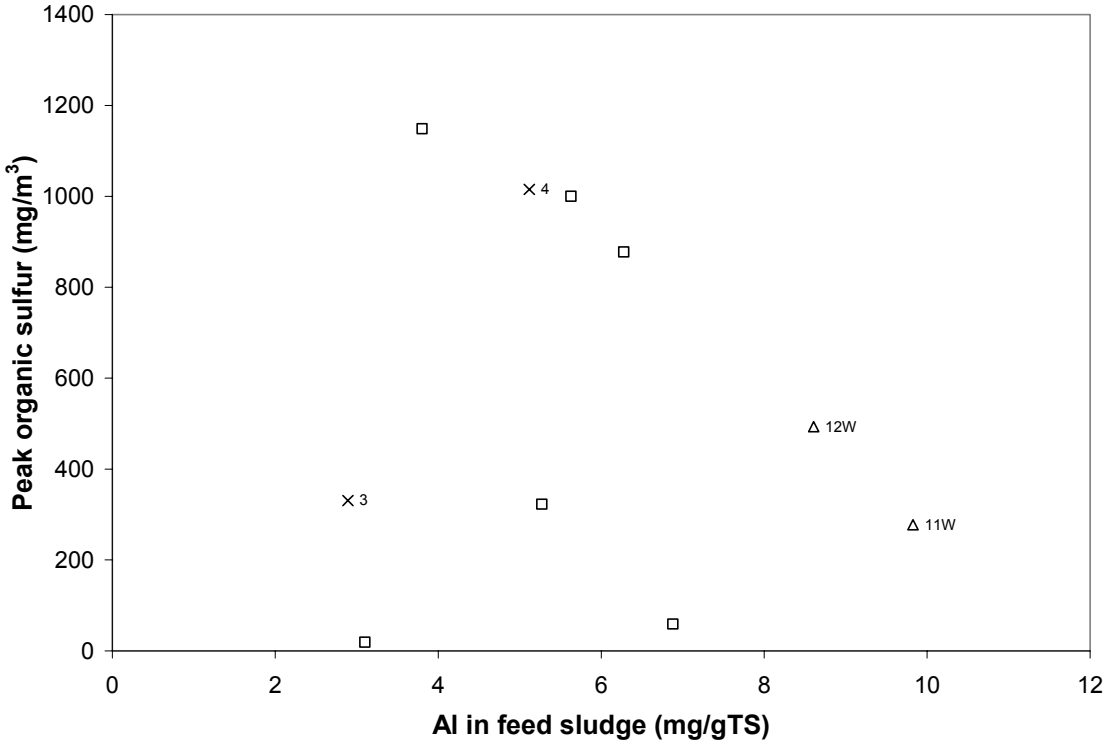


Figure II-5: Peak headspace organic sulfur gas concentration for high-solids cake as a function of aluminum content of feed sludge with BESA

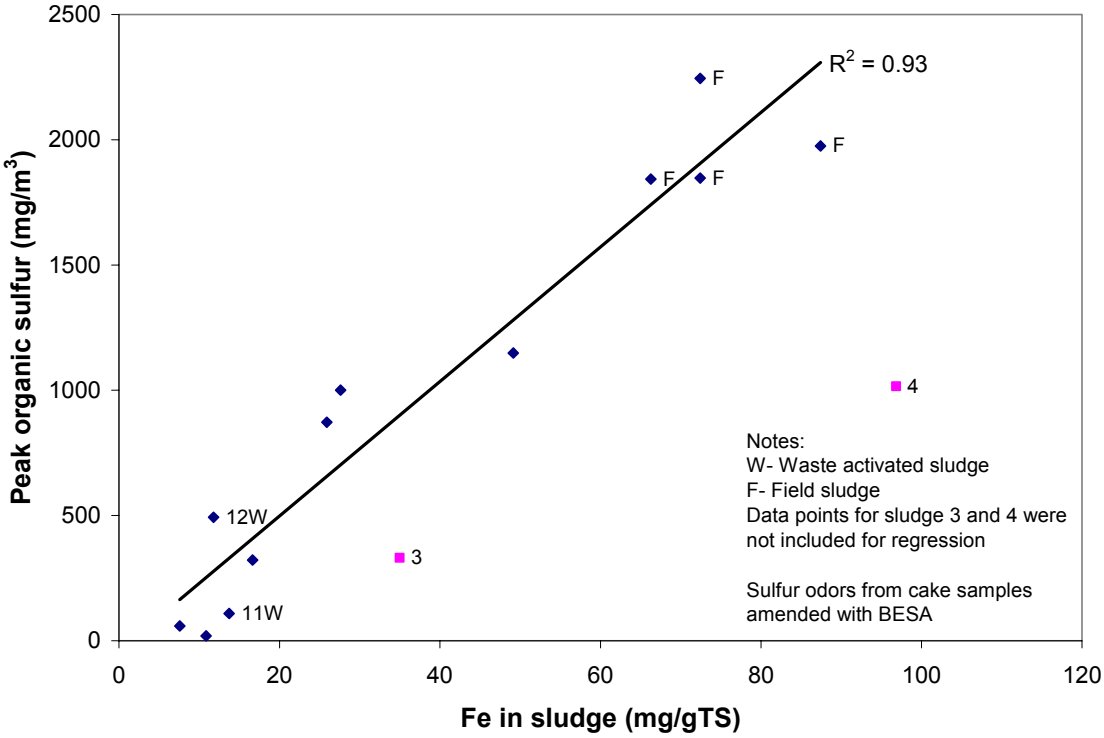


Figure II-6: Peak headspace organic sulfur gas concentration for high solids cake amended with BESA as a function of iron in sludge.

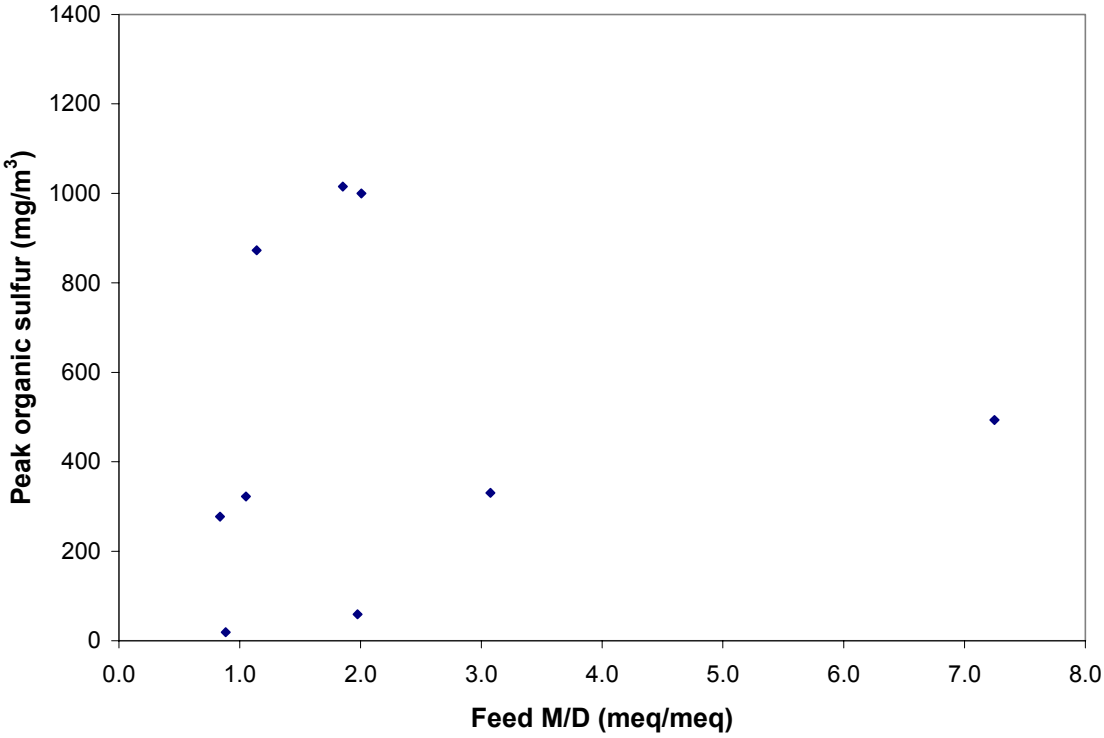


Figure II-7: Peak organic sulfur gas concentration in the headspace of vials containing high-solids cake amended with BESA as a function of feed M/D ratio.

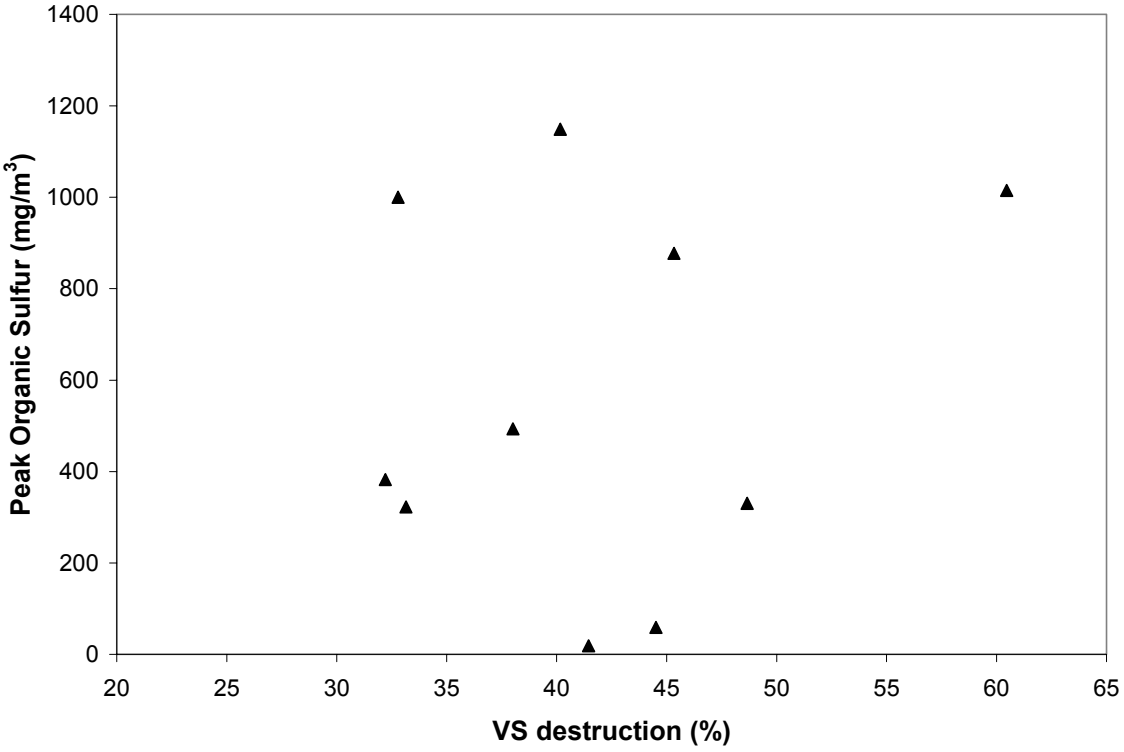


Figure II-8: Peak organic sulfur gas concentration in the headspace of vials containing high-solids cake amended with BESA as a function of the VS destruction during anaerobic digestion.

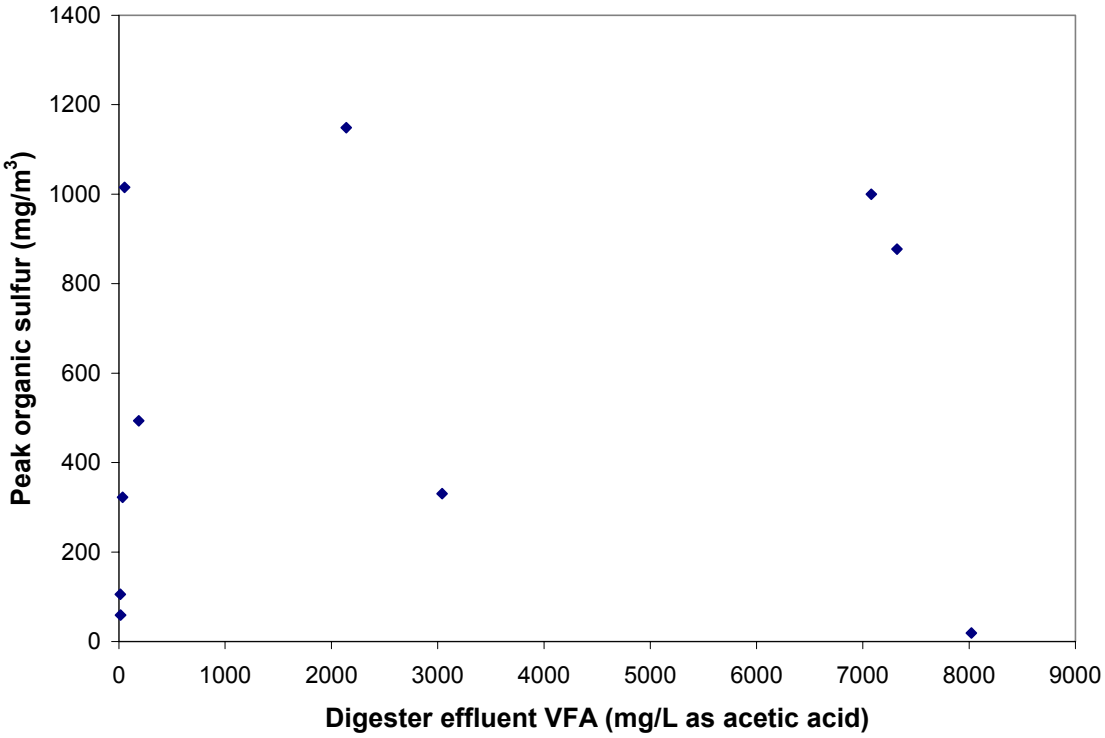


Figure II-9: Peak organic sulfur gas concentration win the headspace of vials containing high-solids cake amended with BESA as a function of the digester effluent VFA concentration.

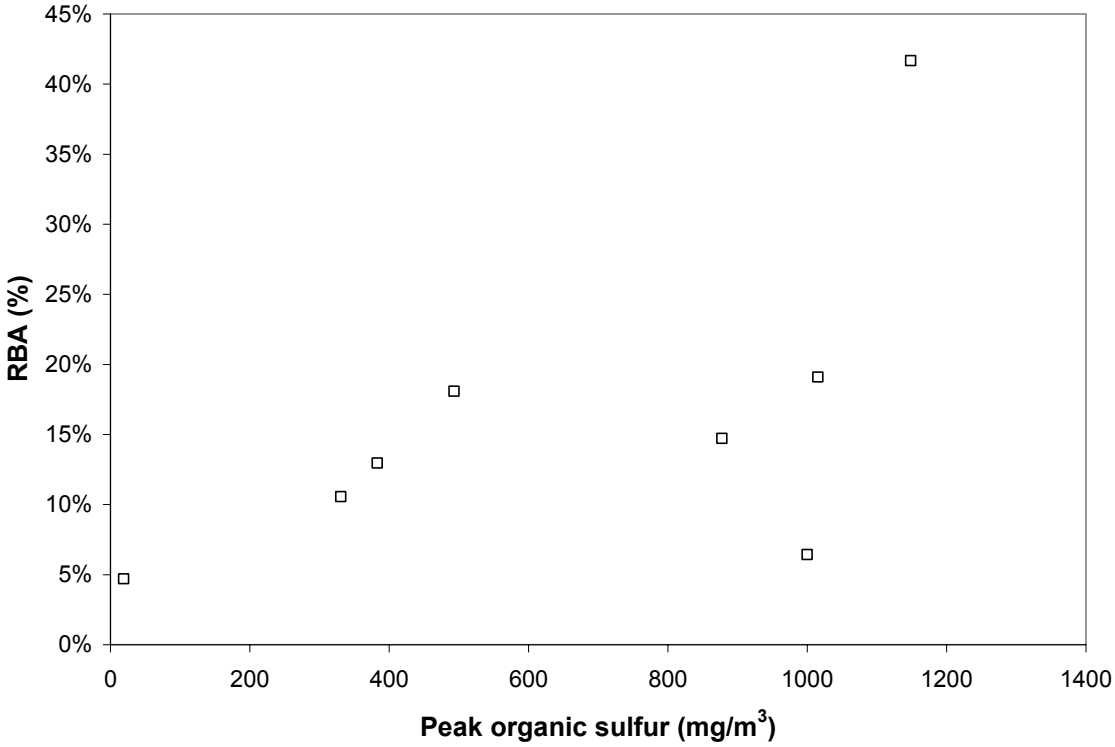


Figure II-10: Impact of residual biological activity (40days) on peak organic sulfur odor. For this plot the peak organic sulfur concentration data is for high-solids cake samples amended with BESA.

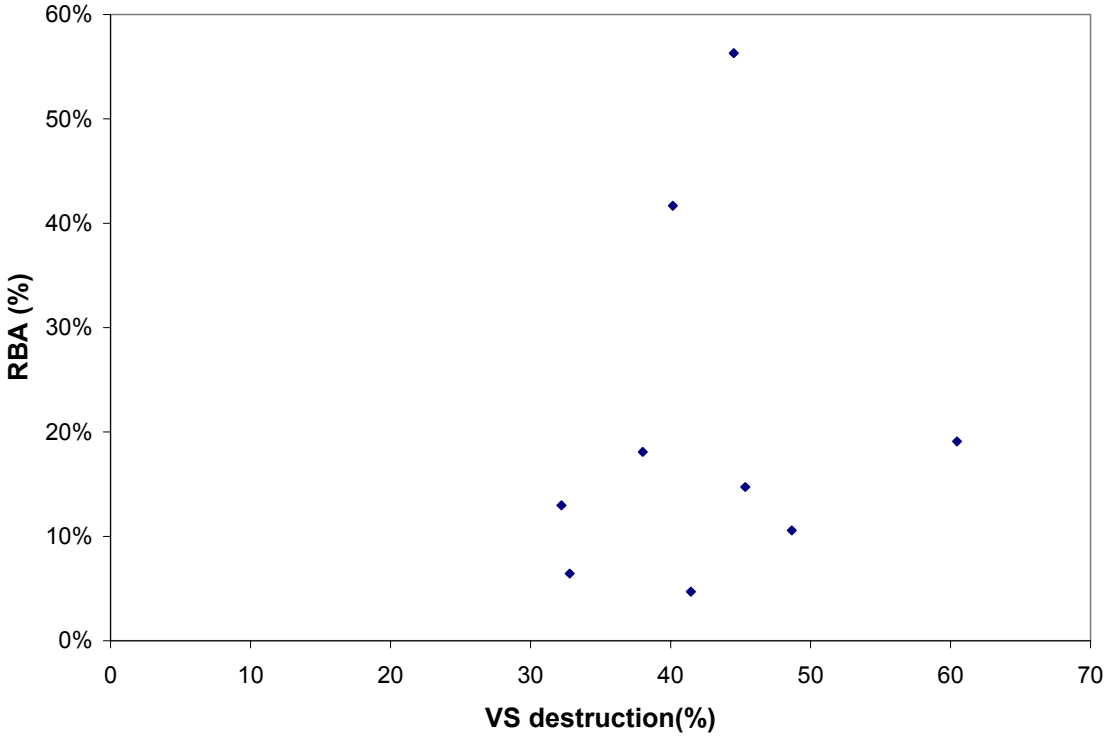


Figure II-11: Residual biological activity versus VS destruction.

III Manuscript 2

Effects of Anaerobic Digester Sludge Age on Odors from Dewatered Biosolids

Nitin Verma, Chul Park, John T. Novak, Zeynep Erdal* and Bob Forbes*

*CH2M Hill

Abstract

Dewatered sludge cakes from bench scale anaerobic digesters operated at mesophilic temperatures and solids retention times (SRT) ranging from 10 days to 40 days were evaluated for their sulfur odor generation potential. Extracellular Polymeric Substances (EPS) extraction for digested sludge samples was also carried out. Static headspace sulfur gas analysis was successfully used to compare different sludge digestion SRTs for their odor potential. Higher volatile solids destruction was observed at higher SRTs and also the quantity of sulfur gases was found to decrease with an increase in the SRT of the anaerobic digesters. Results also showed that the cake solids concentration affected the odor generation from dewatered sludge cakes. Three different EPS extraction techniques were used to selectively extract materials bound to Fe, Al and Ca-Mg in sludge. It was found that Fe-associated proteins correlated well with sulfur gas production. As the Fe-associated protein content declined, the odor potential declined. Operating anaerobic digesters at higher SRTs seem to provide benefit with regard to odor generation. However, even after 40 days of anaerobic digestion, the odor potential remained high.

Introduction

Odor produced from dewatered biosolids is a major cause of concern at many wastewater treatment plants and land application sites. Recent studies have shown that most odors are associated with volatile sulfur compounds (VSCs) and that the odor generation was largely influenced by the dewatering equipment [Adams et al. 2002, Muller et al. 2004]. The solids retention time (SRT) of anaerobic digesters was also reported by Adams et al. (2003) to affect the odor potential of digested biosolids. A recent WERF study [Adams et

al., 2002], the odor threshold decreased with an increase in digester SRT, however, the data were for a variety of sludges so the results were not entirely clear. The mechanisms responsible for reduction in odor potential with longer SRT have not been evaluated.

A recent study by Muller et al. (2004) showed that when biosolids in the presence of conditioning polymer are exposed to high shearing forces, proteins are released from sheared sludge particles and rendered bioavailable. The authors further suggested that degradation of this released material is a cause of odor generation from dewatered biosolids. If this reasoning is true, a better understanding of floc structure could be usefully linked to the study of odor generation from digested sludges. It is known that extracellular polymeric substances (EPS) compose a major organic fraction of biosolids floc [Frølund et al., 1996]. It has been postulated that there are different pools of EPS that are bound with different metal ions in floc. Degradation of those materials are associated with different digestion conditions [Novak et al. 2003]. Important biopolymeric fractions are:

- divalent cation-associated EPS,
- Fe-linked EPS, and
- Al-bound EPS

It was observed in previous studies conducted at Virginia Tech that anaerobic and aerobic digestion of a waste activated sludge, from several different wastewater treatment plants (WWTPs), resulted in remarkably different cation and biopolymer releases and different degrees of volatile solids (VS) destruction [Park, 2002]. A large amount of protein was recovered from the sludge solution following anaerobic digestion but the release of divalent cations was not observed. Furthermore, there was a correlation between the VS reduction by anaerobic digestion and the Fe concentration in feed sludges. These results further suggested that lectin-like proteins (associated with Ca and Mg) are mainly degraded under aerobic conditions while exopolymers associated with Fe are readily degraded under anaerobic conditions [Park et al. 2004]. It was also shown that Al plays a significant role in bioflocculation by improving effluent quality with higher Al content in

floc but the impact of Al and its binding organic matter on sludge digestion is unclear (Park et al. 2004).

Park et al. (2004) showed that three components of floc EPS can be selectively extracted by different chemical extraction methods, as discussed below:

Cation exchange resin (CER) extraction to target Ca^{2+} and Mg^{2+}-bound EPS

Addition of the strong Na^{+} form of a cationic resin is thought to remove multivalent cations that participate in cross-linking EPS within flocs, thereby releasing floc-bound EPS to the bulk solution. However, Wilen et al. (2003) suggested that this exchange mechanism mainly occurs between divalent cations and resin-Na^{+}. As evidence, CER-extracted EPS had strong correlation with Ca^{2+} and Mg^{2+} in sludge floc, but not with either Al or Fe (Wilen et al. 2003). This led the use of the CER procedure to extract divalent cation-bound EPS.

Addition of sulfide to extract Fe-linked EPS

Nielsen and Keiding (1996) reported that the addition of sulfide into activated sludge removed Fe^{2+}/Fe^{3+} from floc matrix by formation of FeS, simultaneously resulting in a significant disintegration of activated sludge floc. This study led to the use of addition of strong reductant, sulfide, to selectively remove Fe-associated exopolymers from activated sludge floc.

Base extraction to remove Al-associated EPS

Based on the solubility water chemistry of Al as a function of pH, Al can be solubilized at either high pH or low pH conditions. Since much of biopolymer could be protonated and re-flocculated under acidic conditions, base treatment at pH 10.5 was chosen to dissolve Al from solid floc and release Al-linked EPS.

The objective of this study was to determine the impact of anaerobic digester SRT on the sulfur gas generation from dewatered biosolids cakes. The relationship between SRT and odors is an important conceptual issue. If additional solids destruction is possible at higher sludge ages and this leads to lower odors, then this would suggest that improvements in digestion process are likely to reduce odors. On the other hand, if at higher SRT substantial reduction in odor is not observed, that will indicate that post

digestion processes are likely to be the best approach for reducing odors from dewatered biosolids cake. This study was also aimed at elucidating the nature and impact of the various EPS fractions on odors. The results of this study are also expected to help determine the floc composition with changing SRT and its impact on odor generation from dewatered biosolids.

Materials and Methods

This study was conducted at Los Angeles County Sanitation District (LACSD) and Virginia Tech using pilot scale anaerobic digesters operated over a range of SRTs (10, 15, 20, 30 and 40 days). The pilot scale digesters were operated by the LACSD. The reactors were fed with a 75% primary and 25% waste activate sludge blend, the same mixture as in the treatment plant. Feed and digested sludge samples were periodically sent to Virginia Tech for odor testing and EPS extraction. Multiple odor vials were set up and odor thresholds were determined using the centrifuge simulation technique described below and Gas Chromatography/Mass Spectrometry for sulfur compound idenfication. The extraction methods described previously were used to determine the floc fraction that gives different characteristics of sludges between different SRTs and maybe associated with odors in biosolids.

Preparation of Incubation Vials

Dewatered cakes of anaerobically digested sludges for odor analysis were prepared using a method that mimics the processes occurring in a centrifuge. Under high shear conditions, the optimum polymer dose for all sludge samples was determined using the capillary suction time (CST) test [Muller et al. 2004]. The optimum polymer dose was determined by finding the polymer dose that produces the minimum CST. A Triton Type 304-M and Triton Type 165 CST apparatus were utilized with Whatman 17-CHR as the chromatography paper. Liquid cationic polymer solution was prepared for dosing. Clarifloc 3275 – a high molecular weight cationic polymer was used for all sludges to minimize the affects of varying polymer types on odors from biosolids.

The overall approach to mimic the actions of centrifuge to generate odors was to provide shear that was similar to that occurring in the centrifuge, to dewater cakes to solids

concentration that was similar to high-solids centrifuge and to provide polymer for conditioning at a dose similar to the centrifuge. A Warring Blender was used to shear the sludge. Liquid sludge was sheared for 30 sec at in 100 mL increments. The optimum dose of cationic polymer for each sample was determined by conducting a polymer dose test using 30 seconds shearing.

Sludge dewatering using the optimum polymer dose was accomplished using a laboratory centrifuge followed by a mechanical filter press. The centrifuge was operated at 17,700 xG for 15 minutes at 25^{o}C. Sludge cakes obtained from centrifuge were further dewatered to increase the solids content using a hydraulic piston press developed at Virginia Tech, using Whatman 41 paper as the filter media.

Cake storage experiments were performed on samples of the dewatered cake in odor vials. To accomplish this, 25g ± 1g of dewatered cake were placed in glass bottles (250 mL). The bottles were sealed with Teflon septa and stored at a constant temperature of 22^{o}C for the duration of the experiments.

Multiple odor vials containing dewatered cake samples with low and high solids content were prepared for each sludge for GC/MS analysis. Low-cake solids cake refer to cake samples that were dewatered using the laboratory centrifuge and having a solids content similar to dewatered cake achieved using a low-solids centrifuge. High-solids cake refer to cake samples that were further dewatered using the hydraulic piston to achieve solids concentrations similar to those derived from high solids centrifuges.

For high-solids and low-solids cakes, samples both with and without the addition of Bromoethane-sulphonic acid (BESA), a methanogen inhibitor, were prepared. Five milliliters of BESA solution (0.127 mmole) was added to about 400 mL of liquid sludge before dewatering it using the lab centrifuge.

Odor Profiling and Qualification

The characterization of odors was accomplished using the method described by Novak et al. (2002). This method was modified by using glass containers with Teflon lined septa

rather than PET bottles. The compounds of interests were MT, DMS, DMDS with H_2S being of secondary interest since it is a metabolic waste product of methylotropic methanogenesis and will react chemically with iron. Since the LACSD adds iron salts to the digester feed to reduce hydrogen sulfide, little H_2S was found.

The headspace in the incubation vial was analyzed periodically for sulfur gases by cryo-trapping and gas-chromatography with mass spectrometry. This method was adopted from previous research conducted by Glindemann et al. (2005).

The headspace in the incubation vial was sampled periodically to produce a time response profile. Peak sulfur odor is the maximum concentration of headspace organic sulfur achieved over the incubation period. A typical odor profile for cake without BESA consists of two phases; a first phase in which organic sulfur gases are generated and a second phase when organic sulfur gases are consumed. The point of inflection between these two phases represents the peak sulfur odor for that particular sample. For cake samples to which BESA was added, the second phase does not occur. After attaining the peak, when BESA is added, the total sulfur concentration stays at the peak concentration. Peak organic sulfur gas concentration for all the cake samples was measured and used to compare the odor generation potential for various SRTs.

Metals Analysis

Metals were measured in the incoming raw sludge on a Perkin Elmer 5100PC Atomic Adsorption Spectrophotometer, following acid digestion per USEPA Method 3050B (EPA 1996). The metal concentrations were expressed as mg-metal per gram total solids (TS) basis.

In addition to the odor and cation analysis the following tests were conducted:

a. Total and volatile solids
b. Soluble cations (Na^+, K^+, Ca^{+2}, Mg^{+2} and NH_4^+)
c. Residual biological activity
d. Solution proteins and polysaccharides

All solids analyses were conducted according to Standard Methods (APHA, 1999). In order to prepare samples for cation and VFA analyses, a 500mL sample for digester biosolids was centrifuged at 17,700 xG for 15 minutes. The supernatant liquid was filtered through a 0.45 μm syringe filter. From this filtered sample, dilutions were made for cation testing.

Liquid phase cations were measured on Dionex D-120 ion chromatograph utilizing a CS-12 column and conductivity detector with self generating suppression of the eluent(Dionex Corp., Sunnycale, CA). Twenty millimolar methanesulfonic acid was used for eluent at a flow rate of 1mL/min.

The residual biological activity test (RBA) was a simplified modification of the additional digestion test method outlined by the EPA (1993). It was conducted by incubating 100mL digested sludge samples in serum vials at 36.5°C for at least 40 days. During the incubation period, the vials were periodically degassed and weighed. The weight lost from each vial was assumed to be from gasification of the VS in each sample. The RBA was calculated by dividing the weight lost from each sample at the end of incubation by the weight of its VS content (analyzed prior to incubation) and is reported as percent VS lost.

Soluble and the extracted proteins were determined by the modified Lowry et al. (1951) method described by Frølund et al. (1996) using bovine serum albumin as the standard. Soluble and extracted polysaccharides were measured by the Dubois et al. (1956) method utilizing glucose as the standard. Laboratory centrifuge was used to separate the solution from majority of solids in sludge. The supernatant after centrifuge was filtered through a 1.5 μm membrane filter and then analyzed separately for proteins and polysaccharides. The values obtained were termed as solution protein and solution polysaccharide.

Results and Discussions

Multiple incubation vials for dewatered sludge cake samples from the different bench scale digesters were prepared using the methods previously described. The headspace in the incubation vial was sampled periodically to produce a headspace gas versus time

profile. Total organic sulfur concentrations were calculated by summing the individual concentration of methanethiol, dimethylsulfide, and dimethyldisulfide as sulfur. Figure III-1 is an example of a typical organic sulfur odor profile generated using the static headspace method. The data in Figure III-1 is from the different vials prepared for a sample from the lab anaerobic digester operated at 10 days. The non-BESA amended samples differed little from the high-solids BESA amended cakes. This indicated that the methanogenic bacteria in the dewatered sludge cakes were inhibited. This could be due to toxicity associated with industrial waste discharges. This facility received refinery wastewater among the industrial wastes discharged to this facility.

Sulfur gas production and role of methanogens

The peak organo-sulfur gas concentration is the maximum concentration of headspace sulfur achieved over the incubation period. Samples to which BESA was added were expected to achieve a maximum organic sulfur concentration and remain near the maximum level. The small amount of organic sulfur gas reduction in samples to which BESA was added, as seen in Figure III-1, was thought to be due to leakage due to pressure buildup in the odor vials.

Research has shown that methanogenic bacteria are able to degrade VOSCs to sulfide. For example, in fresh water sediments a balance typically exists between the production of VOSCs and their degradation, resulting in little emission of these compound unless the system is disturbed [Lomans et al., 2001]. A similar balance likely exists in anaerobic treatment processes since VOSCs are typically not emitted except under conditions that cause stress to the methanogenic bacteria. Higgins et al. (in press) have shown that methanogens play an important role in cycling of VOSCs from biosolids. Higgins et al. (2004) also showed that near stoichiometric amounts of VOSCs are produced to the amount of available sulfur containing substrate when the methanogens are inhibited.

As shown in Figure III-1 dewatered cakes that were amended with BESA to reduce the methanogenic activity produced greater amounts of VOSCs. The VOSC concentration from cakes which were not amended with BESA did not peak as high and also the concentration decreased, especially for the low solids cake sample. These data are in

agreement with those reported by Higgins et al. (2004), indicating that methanogens play an important role in cycling of VOSCs.

Variation in Sulfur gas production with anaerobic digester SRT

The headspace peak organic sulfur concentration plotted as a function of SRT of the laboratory anaerobic digesters is shown in Figure III-2. The sulfur gas concentration from the dewatered cake of the feed sludge is shown as SRT = 0 days. The data shows the peak organic sulfur concentration in headspace vials both with and without BESA. As suggested by Adams et al. (2002), the head space peak organic sulfur decreased as the SRT increased. The non-BESA amended samples with high-solids content differed little from high-solids cake samples amended with BESA; indicating BESA addition did not have much effect. These data suggest some other form of toxicity is likely present in the dewatered cake samples. Further study is required to improve our knowledge of toxicity effects on sludge and odor generation from dewatered cakes.

The peak organic sulfur gas concentration in the headspace of the odor vials ranged from about 2000 to 2500 mg/m^3 for the feed sludge and from about 800 to 1000 mg/m^3 for the 40 day SRT sludge. These concentrations are much higher than those reported by Adams et al. (2003). For 11 sludges tested in their study none of the 11 sludges tested by Adams et al. (2003) produced an organic sulfur concentration exceeding 1000 mg/m^3. These data show that sludge used from LACSD has a very high odor potential.

Figure III-3 shows the average headspace peak VOSC concentration in incubation vials containing dewatered cake sample having low(TS = 17.0%, VS= 12.3%) and high solids content(TS = 28.3%, VS= 21.0%). All values for this plot were generated from samples which were amended with BESA. This plot also shows that the organic-sulfur gas concentration decreased with an increase in SRT of the laboratory anaerobic digesters. Moreover, these data also suggest that low-solids cake produced lower sulfur gas concentration compared to high-solids cake, suggesting that the cake solids concentration also influences the sulfur gas concentration in the headspace vials. The difference in concentrations of sulfur gas in headspace of high-solids and low-solids cake was about 400 - 450 mg/m^3. These data are in agreement with the results recently reported by

Muller et al. (2004). As the headspace gas represents only a portion of the organo-sulfur (the rest is in the liquid phase), the variation in organo-sulfur with cake solids could be due to the difference in the sludge cake water content alone.

As shown in Figure III-2 and Figure III-3, the headspace sulfur gas concentration decreased with increase in digester SRT. The peak headspace sulfur gas concentration for low-solids cake varied from 1000 mg/m^3 to 2500 mg/m^3 and for high-solids it varied from 1500 mg/m^3 to 3000 mg/m^3. Greater reductions in sulfur gas concentration were observed in samples which were not amended with BESA. This is due to the important role methanogens play in cycling of VOSCs. Lower peak concentrations of sulfur gases was observed in headspace of cakes that were not amended with BESA. These results are in accordance with those reported by Higgins et al. (in press). Higgins et al. (in press) also observed higher peak concentration of methanethiol and dimethylsulfide in headspace of vials which contained anaerobically digested, dewatered sludge cake to which BESA was amended.

It is also worth noting that the sludge used for this study was a highly odorous sludge and even after several weeks of incubation the odors did not subside. These observations suggest partial inhibition of methanogens. The reasons for inhibition are speculated to be either because of presence of some chemical inhibitor in sludge or the high iron content of sludge. The high iron content could promote the growth of iron reducing bacteria which can out compete methanogens [Lovley et al., 1987]. Iron is injected into the digester feed to control sulfide in the gas and this could be the source of oxidized iron in the sludge.

Figure III-4 shows the percentage reduction in odors as a function of digester SRT. Odor vials which contained low solids samples without BESA showed a greater odor reduction (Figure 4b) and greater variability. Results from most dewatered cakes containing low or high solids content sludge cake samples amended with BESA show that the odors are consistently reduced with increase an in SRT. Organic sulfur gas analysis for incubation vials with higher cake solids content, both with and without BESA, were more consistent.

For the low-solids concentration cake samples, a much greater reduction (about 75%) in peak headspace organic-sulfur gas concentration was observed for low solids without BESA, even at 10 days. These results suggest that cake solids content influences odor generation and also that methanogens play an important role in cycling of VOSCs. These data clearly show the odor problems that utilities have seen when switching from a low to high solids centrifuge. It is believed that methanogenic activity [Lomans et al. 2001] maybe somewhat inhibited due to the dryness of cakes.

Volatile solids destruction and odors

Figure III-5 shows the average VS destruction versus digester SRT. The data show that VS destruction increases with an increase in digester SRT. About 50% VS reduction was observed in the 10 days digester. Evaluation of the data showed that VS destruction in anaerobic digestion for 10 days or more was greater than 38%, which is one of the major parameters for regulatory compliance with the Vector Attraction Reduction (VAR) requirement of 503 rule. On average, about 6% additional VS destruction from 20 days to 30 days and 8% from 30days to 40 days was observed. It is clear that the 30% VS reduction does not guarantee low odor sludge.

VS reduction is used as a design parameter and also for the classification of biosolids as Class A or B. It was believed that higher VS destruction in the digester should have a beneficial impact on digested biosolids quality and dewatered biosolids odors. To investigate this relationship, peak headspace organic sulfur gas concentrations were plotted against digester VS destruction as shown in Figure III-6. The organic sulfur concentration in the headspace of incubation vials containing high-solids cake varied from 1000 to 2500 mg/m^3 for a 50 to 58% VS destruction range. Lower sulfur gas concentrations were observed for cake samples from digesters with higher VS destruction suggesting that VS destruction results in the degradation of odor generating organic matter. The percentage change in VS is small in comparison to the drop in organic sulfur concentration, indicating that the extra VS that is destroyed is highly odorous. However, the VS range for the samples analyzed during this study is very small and also the characteristics of feed sludge were the same. Hence, the conclusion that VS destruction

measurement can be a good indication for sulfur odor may not apply on a wider range of VS or for sludges with different characteristics.

Residual biological activity with VS reduction and odors

Residual biological activity is considered to be a measure of the biological stability of digested biosolids, since it represents the potential for further biological activity through endogenous decay and consumption of the substrate available in the form of volatile acids and proteins. Figure II-7(a) illustrates the correlation between biosolids RBA measured at 40 days post digestion and VS reduction in the digester. The RBA test for each SRT digester was similar to the VS reduction pattern observed. The 40 day SRT digester had the lowest RBA of about 20%. Figure III-7(b) shows the plot of RBA versus peak headspace organic sulfur gas concentration for sludge sample set four. The RBA varied from about 15% to 28% and headspace sulfur concentration varied from 1500 mg/m^3 to 2800 mg/m^3. These data suggest that as RBA increased the organic sulfur gas concentration increased. It is worth noting that the characteristics of sludge for this study were the same, hence, the conclusion that RBA correlates well with sulfur odor generation might not be a valid conclusion for sludges with different characteristics.

Variation of dewatering rate and solution biopolymer concentration with SRT

Figure III-8 shows the variation in the dewatering rate of digested sludge (Capillary Suction Time - CST) as a function of anaerobic digester SRT. The CST for the feed sludge was highest and the CST decreased with increase in digester SRT. Figure III-9 shows the variation in the concentration of solution proteins and polysaccharides respectively in the digester effluent as a function of digester SRT. Both solution protein and polysaccharide concentrations decreased with an increase in SRT. These data suggest that within the first 10 days most of the organic material in feed sludge is hydrolyzed. This results in solubilization of proteins and polysaccharides, some of the constituents are colloidal and interfere with sludge filtration, resulting in a high CST. From 10 to 40 days much of the soluble and colloidal material and a smaller amount of solids are degraded. After 10 days the soluble material and a smaller amount of solids are degraded.

Extracellular Polymeric Substances (EPS) and odors

The data from the first set of samples for odor and EPS extraction study are shown in Figure III-10. Consistent with previous findings [Adams et al. 2003], the headspace peak organic sulfur concentration decreased as SRT increased. It was observed that protein extracted by addition of sulfide decreased while the CER extractable protein did not vary with SRT. These data suggest that decrease of odor potential with an increase in SRT was accompanied by the degradation of Fe-associated protein. The importance of Fe-bound protein in anaerobic digestion is in accordance with a previous study [Novak et al., 2003] showing that release of Fe-bound protein by reduction of Fe under anaerobic conditions and its further degradation is related to the digestibility of sludge by anaerobic digestion. The sulfide extraction data from the study further imply that there are still proteins bound with reduced Fe in anaerobically digested sludges and this material leads to the generation of odor.

Figure III-11 shows the protein concentration extracted from the feed sludge and the sludge following 40 days digestion using the three extraction techniques. The data in Figure III-11 illustrates that anaerobic digestion of feed sludge was closely related to the degradation of Fe-bound protein (sulfide extractable protein). While proteins extracted by CER and base extractions did not change before and after digestion, almost 45% of the Fe-associated protein was removed after 40 days of anaerobic digestion. These data provide a strong indication that Fe-linked proteins were selectively and continuously degraded under anaerobic conditions. This result is also in accordance with earlier studies that iron and the proteins associated with iron play an important role in determining the digestibility of sludge under anaerobic conditions [Park et al., 2004]. It is believed that this is most likely because Fe^{+3} undergoes reduction under anaerobic conditions, making Fe-linked proteins bioavailable.

Figure III-12 shows the plot of peak organic sulfur against sulfide extracted proteins for two sets of samples. For sludge from both set 2 and set 4, the extracted protein concentrations correlated well with the peak headspace organic sulfur gas concentrations. Headspace sulfur gas concentration increased with an increase in the amount of proteins

bound to iron, extracted by sulfide extraction method. These data suggest that sludges with high iron content have a greater potential for odor generation.

Figure III-13 shows the plot of sulfide extracted proteins for set 4 sludge samples with the RBA values. These data suggest that the sulfide extraction protein correlated with the RBA suggesting that the materials associated with iron that are left un-degraded after anaerobic digestion are degraded during the extended digestion of 40days. These data are preliminary and only for one sludge, hence any universal relationship is subject to speculation.

Summary

This study was conducted to elucidate the effect of anaerobic digester SRT on the odor generation potential of dewatered biosolids cakes. A blend of primary and waste activated sludge, 75% primary and 25% WAS – the same mixture as in the treatment plant, was digested in lab scale anaerobic digesters operated at SRT ranging from 10 days to 40 days. Digested biosolids were tested for odor generation using a centrifuge simulation method developed at Virginia Tech along with EPS extraction studies which were aimed at improving our understanding of the odor generation and what fractions of EPS are related to odor production.

It was observed that VS destruction increased with increase in SRT. This was corroborated with higher lower solution proteins and greater ammonium ion concentrations in solution for samples from digesters operated at higher SRT. Residual biological activity was measured by digesting biosolids samples for additional 40 days. RBA results showed a reasonable correlation with VS reduction and also correlated well with headspace organic sulfur gas concentration.

Headspace gas analysis was conducted on dewatered cake samples with and without addition of BESA, a strong methanogenic inhibitor. It was observed that sulfur gas concentration decreased with increase in SRT. All headspace vials showed this trend. However, better reproducibility of headspace gas concentration data was observed for high solids content cake samples or for cakes that were amended with BESA. Lower

sulfur gas concentrations were consistently observed from cake samples which had a lower cake solids concentration. These data suggest that solids concentration influences the generation of sulfur gases, hence odors. Peak sulfur gas concentration data showed a good correlation with VS destruction. It was seen that higher VS destruction resulted in lower odors.

Three EPS extraction techniques were used to extract organic materials bound to different cations (Fe, Al, Ca and Mg). It was observed that proteins extracted by different chemical methods behaved in considerably different manner as anaerobic digestion proceeded and it is Fe-associated proteins that were primarily associated with VS destruction and sulfur gas generation.

Conclusions

The main conclusions that can be drawn from this study are:

1. Higher volatile solids destruction is achieved by operating anaerobic digesters at higher SRT.
2. Sulfur gas concentration in headspace on dewatered cakes of anaerobically digested biosolids decreased with increase in digester SRT.
3. A good correlation of VS destruction with sulfur gas concentration in headspace was observed, suggesting that VS destruction can be used as a tool to estimate sulfur gas generation from dewatered biosolids. Reduction in sulfur odors with increase in SRT was observed, however, quite high concentrations of sulfur gases were observed even for biosolids cake from the digesters operated at 40 days detention time.
4. Headspace gas analysis on dewatered cake samples is a tool used to estimate the odor generation from biosolids cakes. Amending samples with a methanogenic inhibitor produced better repeatability of results, suggesting that methanogenic activity has a key role in reducing sulfur odors.
5. Sulfur gas generation was found to be a function of the EPS material bound to Fe. Good correlation of sulfur gas concentration with extracted Fe-bound protein was observed. However, the data was not consistent for multiple trials; suggesting that

iron in sludge was found to be linked to sulfur production but the EPS extraction method may not be a universal tool to estimate odor generation.

Further research needs to be done to elucidate on the processes involved in sulfur gas generation and degradation from dewatered biosolids cake. The extraction data suggests iron associated EPS material is degraded during anaerobic digestion, however, all iron bound material is not degraded in anaerobic digestion and this iron-bound material is rendered bioavailable in the presence of shear. Once bioavailable these materials, primarily proteins, degrade to generate odor. The role of iron and aluminum needs to be explored further along with what changes in properties of anaerobically digested biosolids occurs when it is subject to high shear.

Reference:

Adams, G.M., Witherspoon, J., Card, T., Forbes, R., Geselbracht, J., Glindemann, D., Hargreaves, R. Hentz, L., Higgins, M., McEwen, D., and Murthy, S. Identifying and Controlling the Municipal Wastewater Odor Environment Phase 2: Impacts of In-Plant Operational Parameters on Biosolids Odor Quality. 2003, Water Environment Research Foundation: Alexandria, VA.

American Public Health Association; American Water Works Association; and Water Environment Federation (1995) Standard Methods for the Examination of Water and Wastewater. 19th Ed., Washington, D.C.

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., and Smith, F. (1956) Colorimetric Methods for Determination of Sugars and Related Substances. Analytical Chem., 28, 350.

EPA (1999) Environmental regulations and technology: Control of pathogens and vector attraction in sewage sludge. Office of Research and Development, Washington, D.C.

Frølund, B., Palmgren, R., Keiding, K., and Nielsen, P.H. (1996) Extraction of Extracellular Polymers from Activated Sludge Using a Cation Exchange Resin. Water Res., 30, 1749.

Hartree, E.F. (1972) Determination of Protein: A Modification of the Lowry Method That Gives a Linear Photometric Response. Anal. Biochem., 48, 422.

Lomans, B.P., R. Luderer, P. Steenbakkers, A. Pol, C. Van Der Drift, G.D. Vogels, and J.J.M. Op Den Camp (2001) Microbial Populations Involved in Cycling of Dimethyl Sulfide and Methanethiol in Freshwater Sediments. Applied and Env. Microbiol., 67, 1044-1051.

Lovley D.R. and Phillips E.J.P (1987) Competitive Mechanisms for Inhibition of Sulfate Reduction and Methane Production in the Zone of Ferric Iron Reduction in Sediments. Applied and Environmental Microbiology, 1987, p. 2636-2641.

Lowry, O.H., Rosebrough, N.J., Farr, A.L., and Randall, R.J. (1951) Protein Measurement with the Folin Phenol Reagent. J. Biol. Chem., 193, 265.

Muller C.D., Nitin Verma, Matthew J. Higgins and John T. Novak. The role of shear in the generation of nuisance odors from dewatered biosolids. WEFTEC 2004 Conference and Exhibition Proceedings, October, 2004, New Orleans, LA.

Nielsen, P.H., Frølund, B., and Keiding, K. (1996) Changes in the Composition of Extracellular Polymeric Substances in Activated sludge during Anaerobic Storage. Appl. Microbiol. Biotechnol., 44, 823-830.

Novak, J., D. Glindemann, S.N. Murthy, S.C. Gerwin, C. Peot. Mechanisms for Generation and Control of Trimethyl Amine and Dimethyl Disulfide from Lime Stablilized Biosolids. in WEF Odors and Toxic Air Emissions 2002 Conference. 2002. Albuquerque, NM: WEF.

Novak, J.T., Sadler, M.E., and Murthy, S.N. (2003) Mechanisms of Floc Destruction During Anaerobic and Aerobic Digestion and The Effect on Conditioning and Dewatering of Biosolids. *Water Res.,* **37,** 3136 - 3144.

Park, C. Abu-Orf, M.M and Novak, J.T. Analysis of Floc Structure and Predicting Sludge Digestibility Using Different Cation-Associated EPS Extraction Methods. WEFTEC 2004 Conference and Exhibition Proceedings, October, 2004, New Orleans, LA

U.S. Environmental Protection Agency (1996), Method 3050 Acid Digestion of Soils, Sediments, and Sludges. U.S. E.P.A., 2000.

U.S. Environmental Protection Agency (1993) Standards for the disposal of sewage sludge. Fed. Regist., 58, 32, 40 CFR Part 503.

Wilén, B.-M., Jin, B., and Lant, P. (2003) The Influence of Key Chemical Constituents in Activated Sludge on Surface and Flocculating Properties. Water Res., 37, 2127-2139.

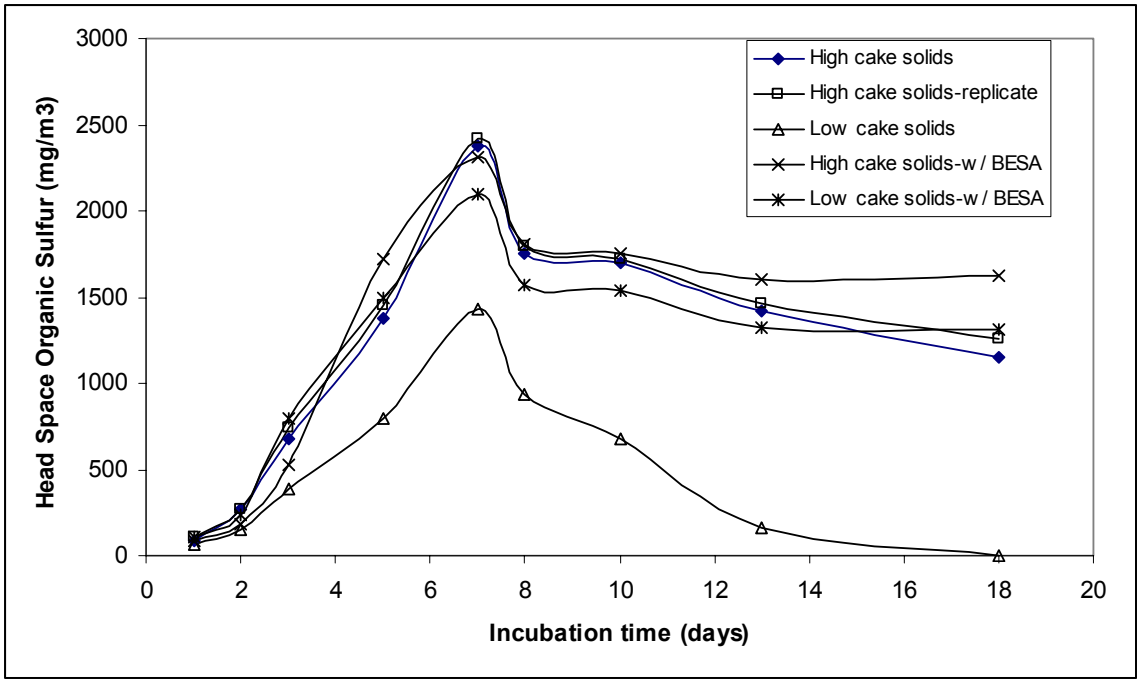


Figure III-1: Changes in headspace organic sulfur content under static headspace incubation of cakes obtained after dewatering liquid sludge sample from 10day bench scale digester

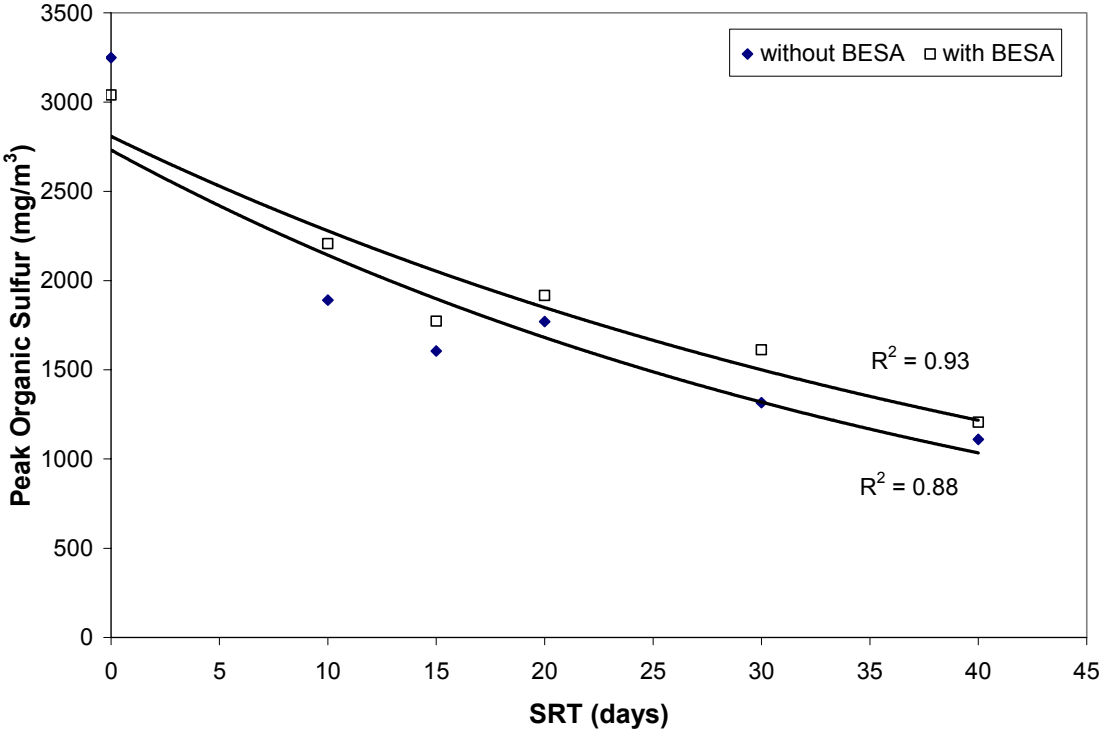


Figure III-2: Variation of peak headspace organic sulfur gas concentration for high-solids cake (for sample set 4) with anaerobic digester SRT.

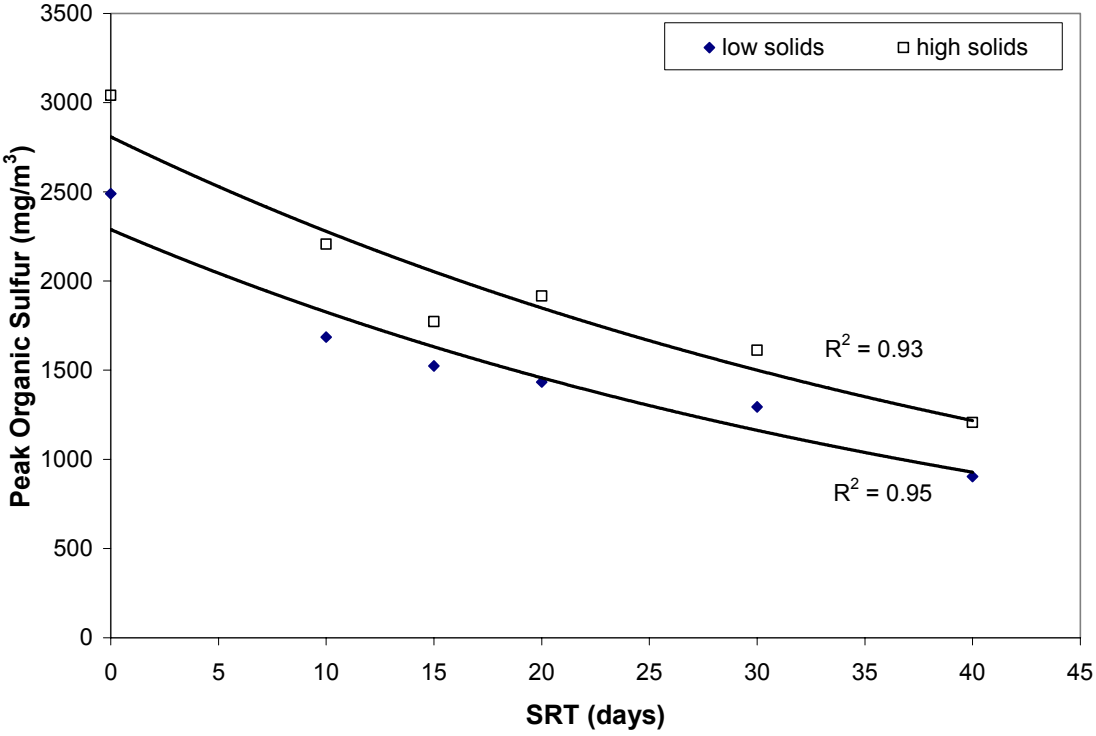
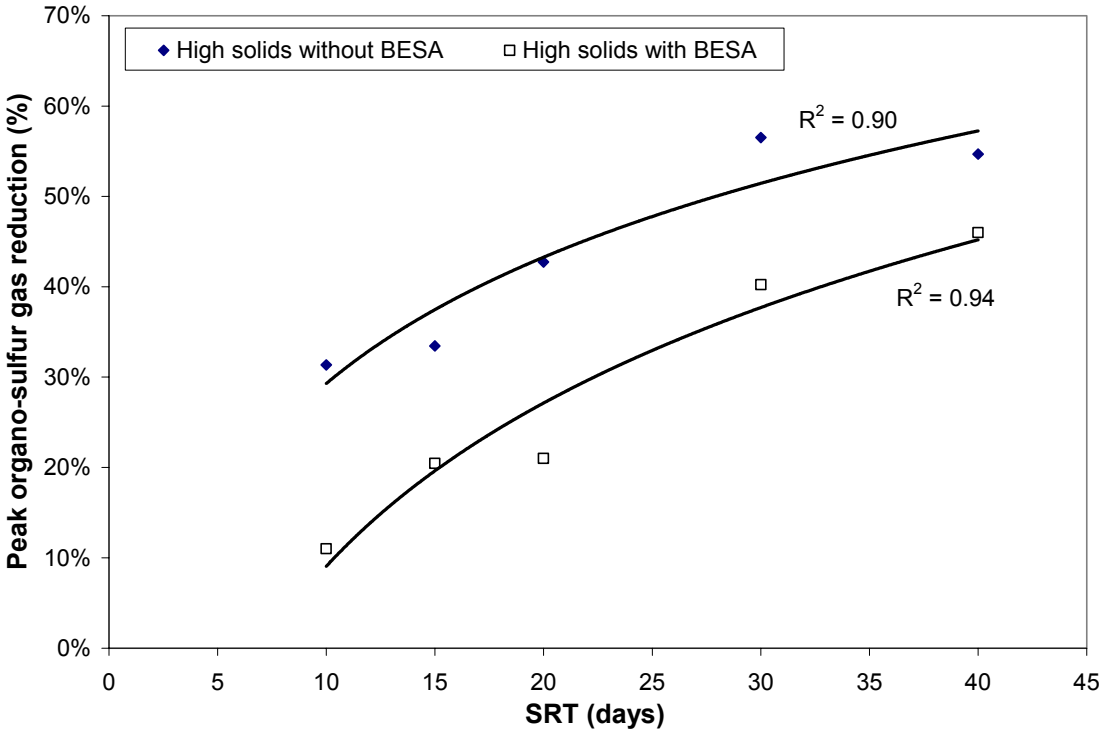


Figure III-3: Effect of cake solids concentration and SRT of anaerobic digester on peak headspace organic sulfur concentration for cake samples amended with BESA. Peak organic sulfur gas concentrations shown are for that obtained for sample set 4.



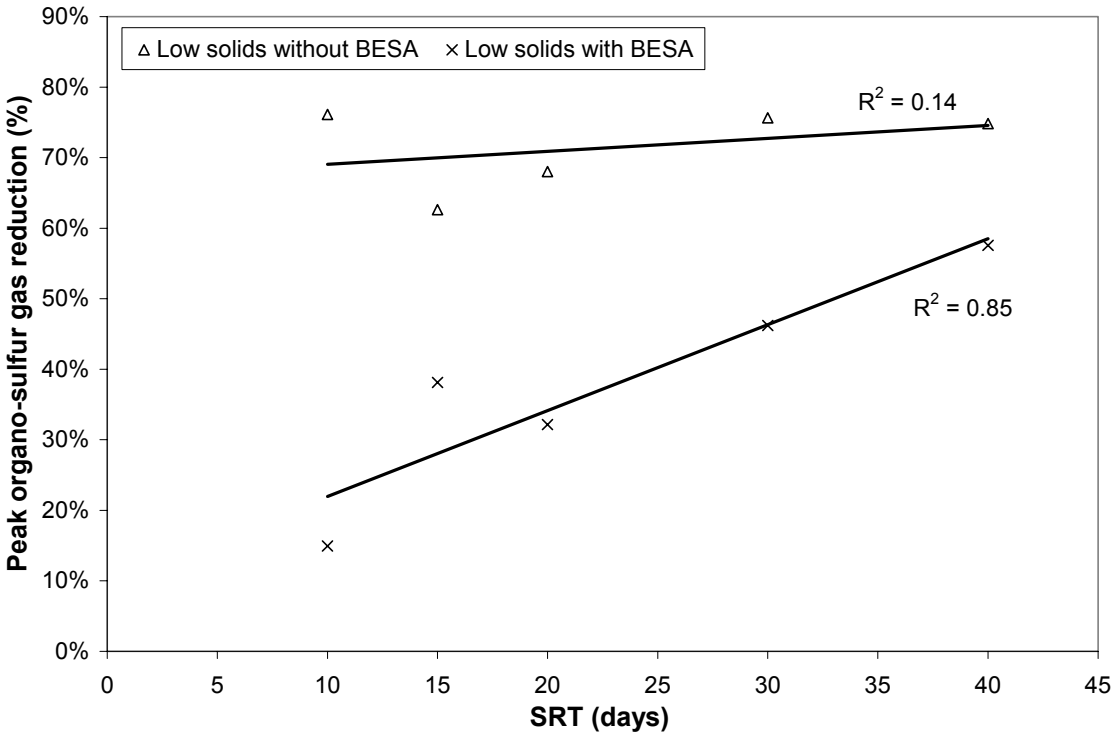


Figure III-4: Reduction in peak headspace organic sulfur gas concentrations for dewatered biosolids cakes compared to feed sludge a) high cake solids biosolids cake, b) low cake solids biosolids cake.

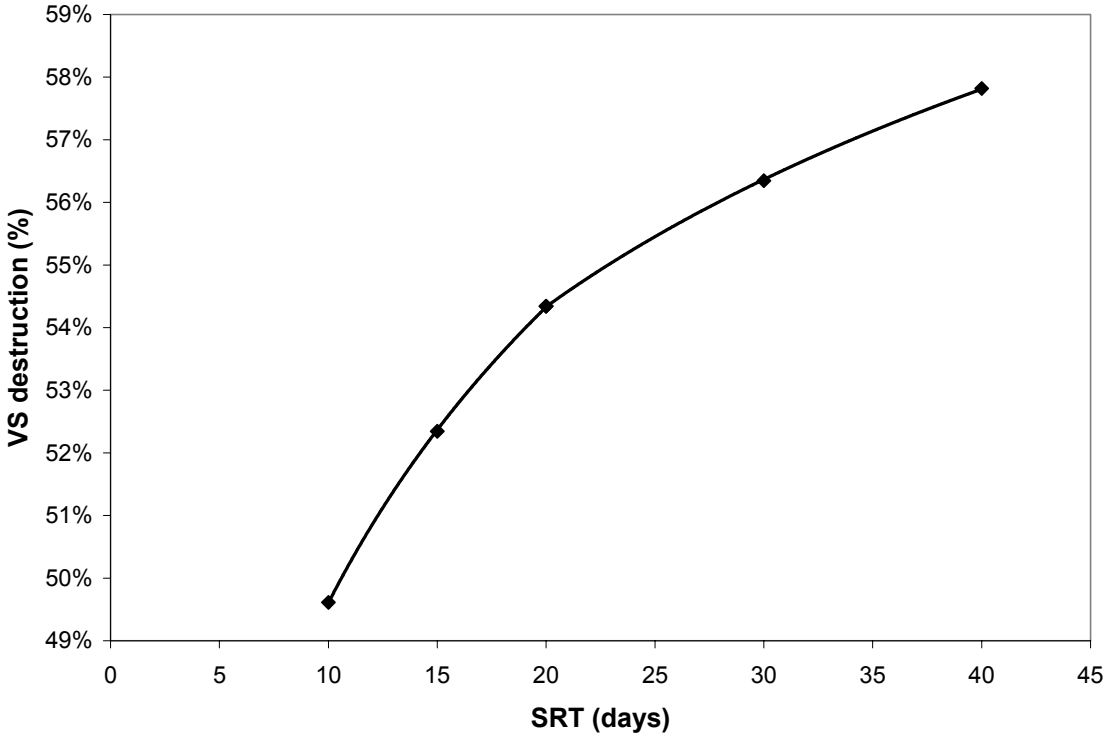


Figure III-5: VS reduction as a function of digester SRT.

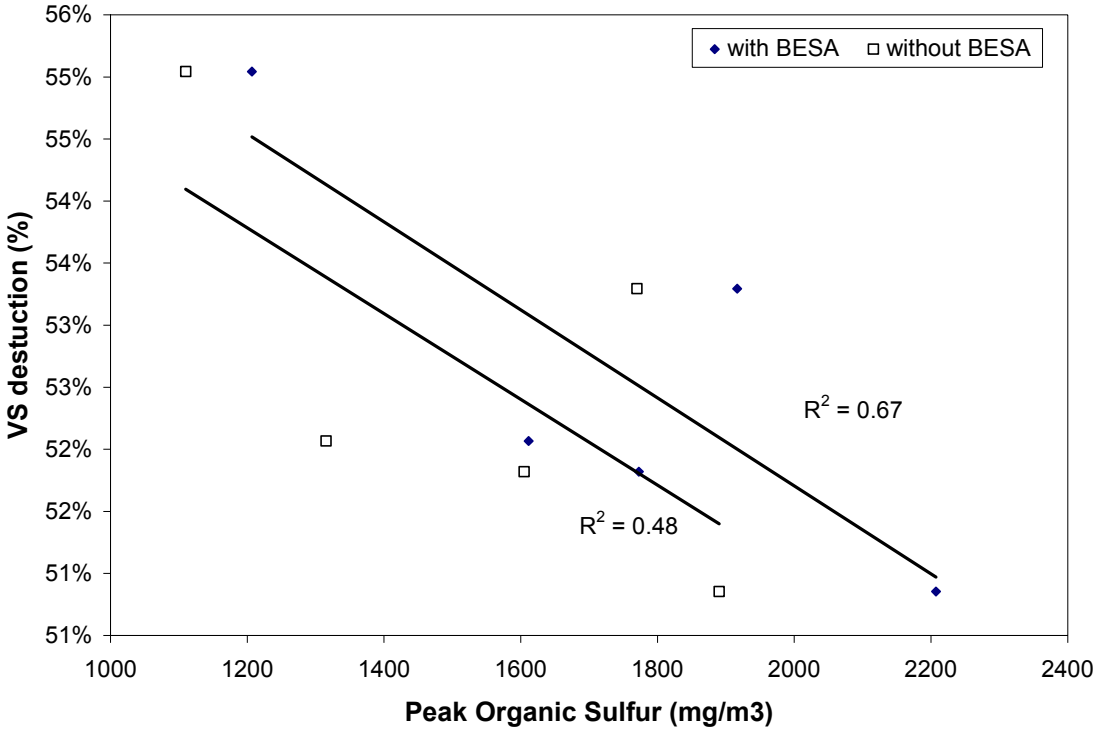
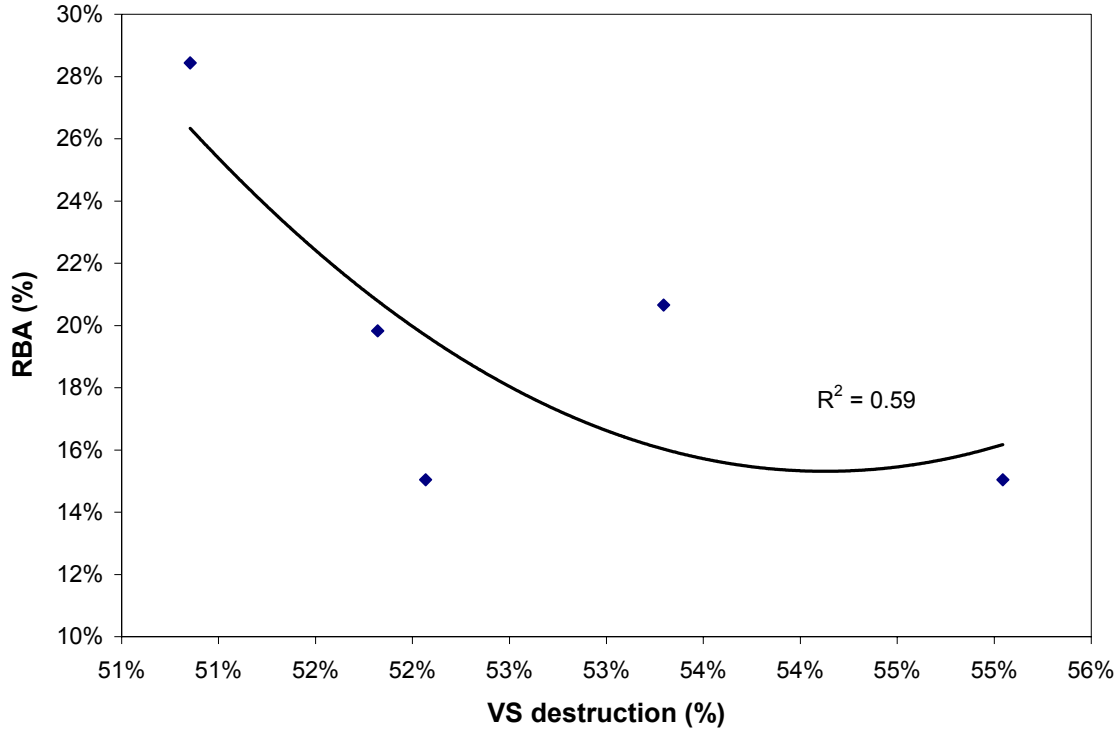


Figure III-6: Odor as a function of VS destruction.



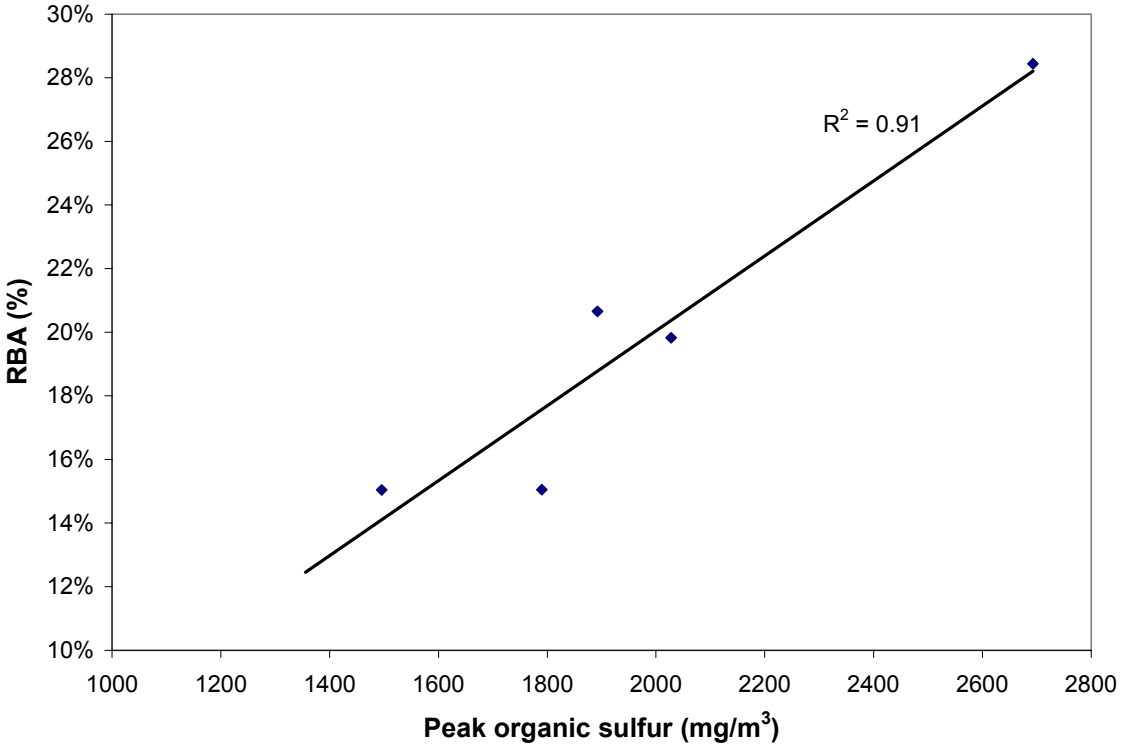


Figure III-7: a) Relationship of Residual Biological Activity with VS destruction in anaerobic digester for biosolids from digesters operated at different SRT. b) Relationship of RBA with peak headspace organic sulfur concentration. (Data for sample set 4).

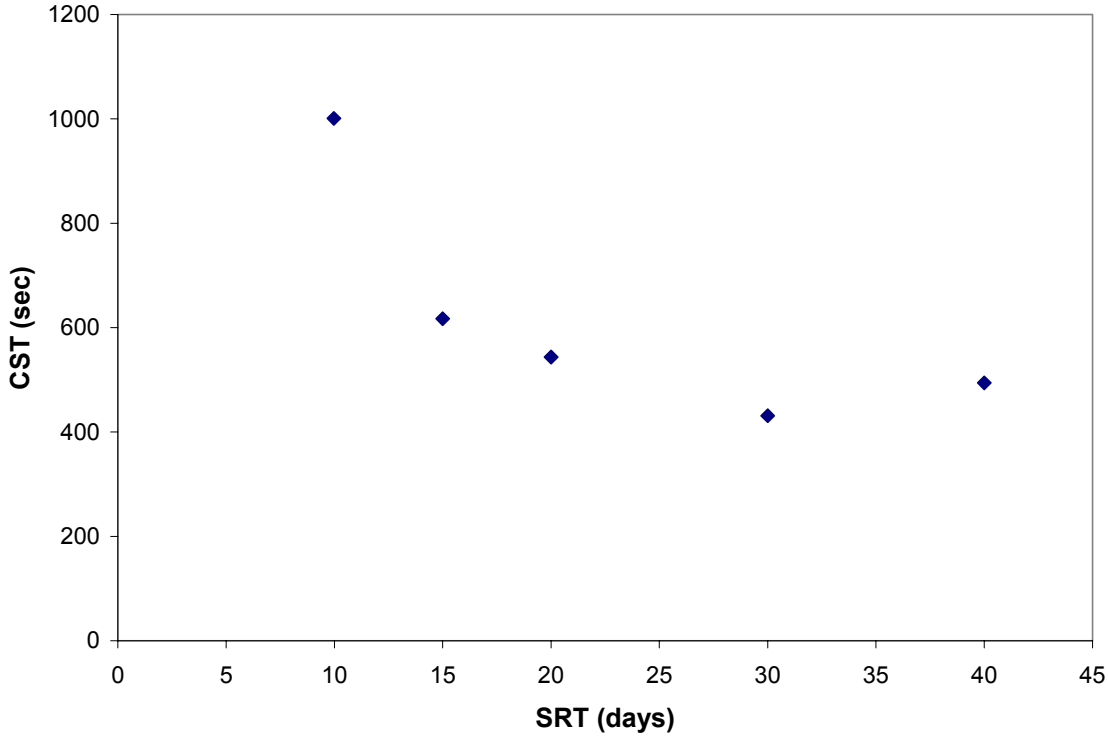


Figure III-8: Dewatering measured as CST as a function of digester SRT. (Data for sample set 4)

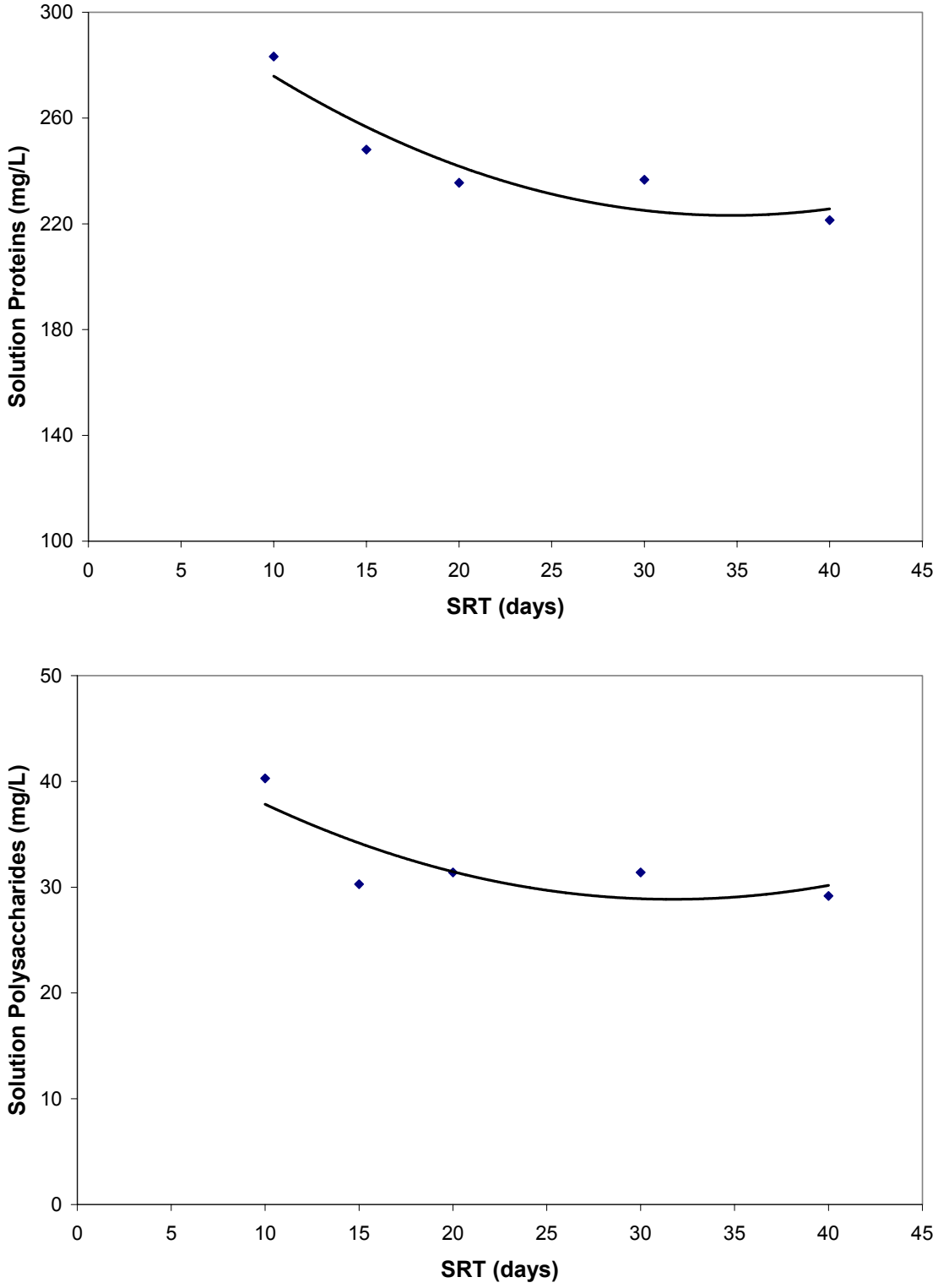


Figure III-9: Biopolymer concentration in solution as a function of anaerobic digester SRT. a) Proteins, b) Polysaccharides. (Data for sample set 4)

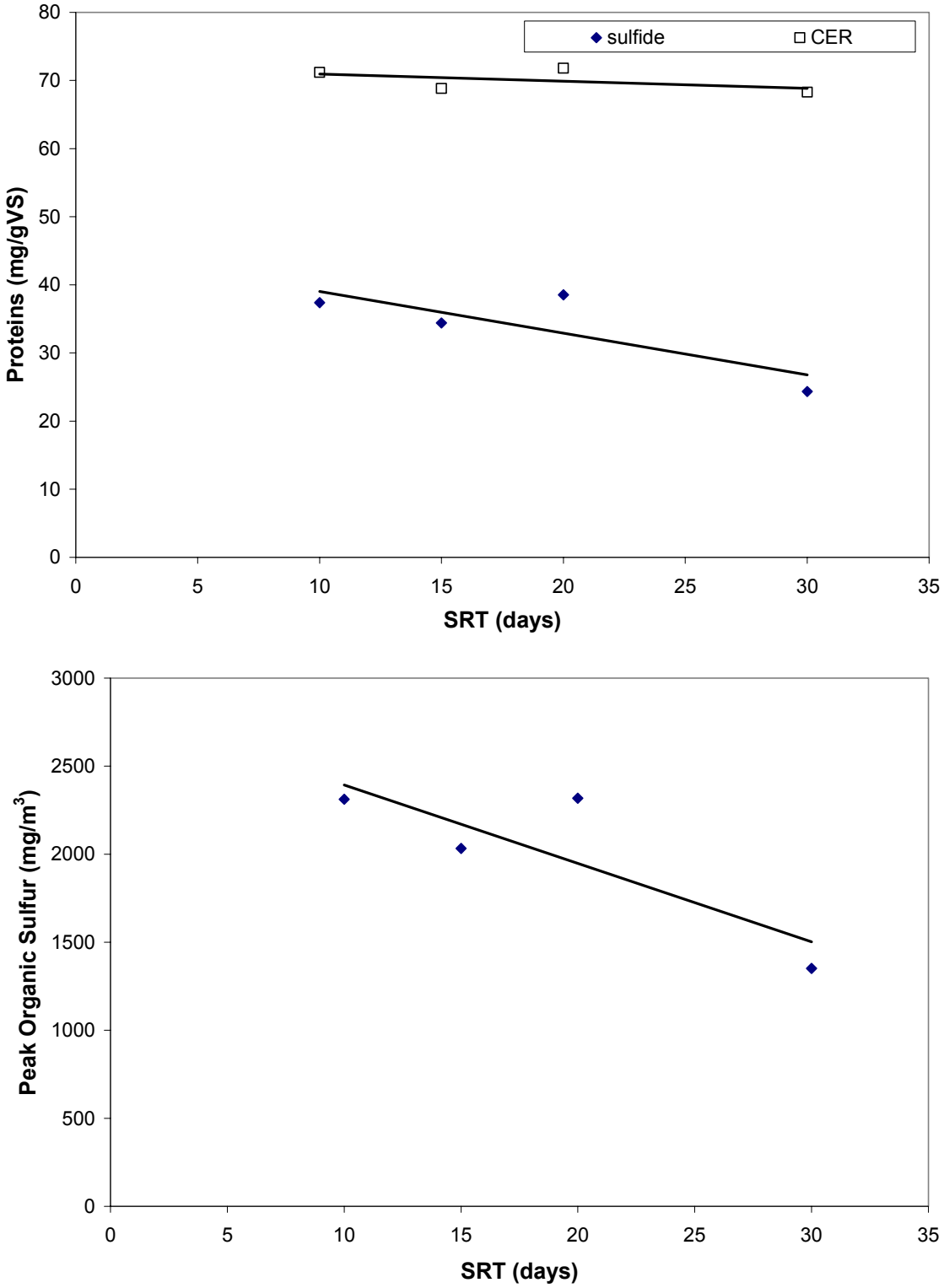


Figure III-10: a) Protein extracted by CER procedure and sulfide extraction technique with SRT and b) Variation of peak organic sulfur. (Data for sample set 1)

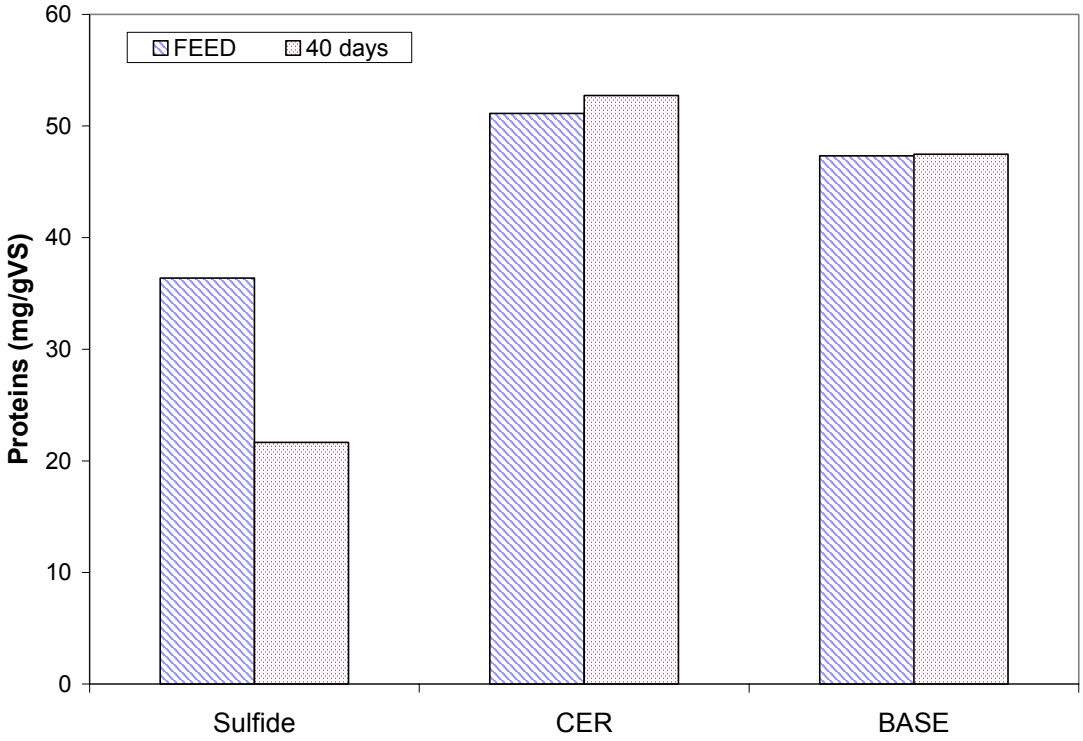


Figure III-11: Proteins extracted from feed sludge and 40 day SRT anaerobic sludge by different extraction methods. (Note: Sulfide – extraction of Fe-bound material using sulfide extraction, CER – extraction of Ca-Mg bound material using cation exchange resin(CER), BASE – extraction of Al-bound material using strong base.)

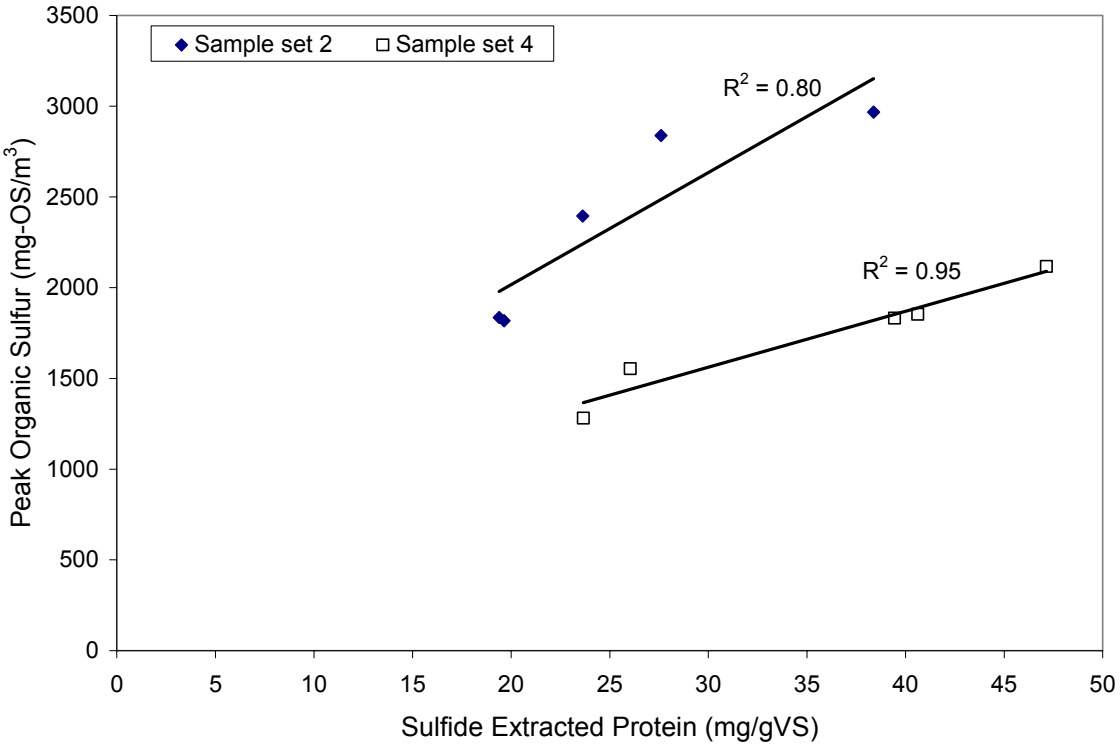


Figure III-12: Sulfide extracted protein versus peak organic sulfur odor.

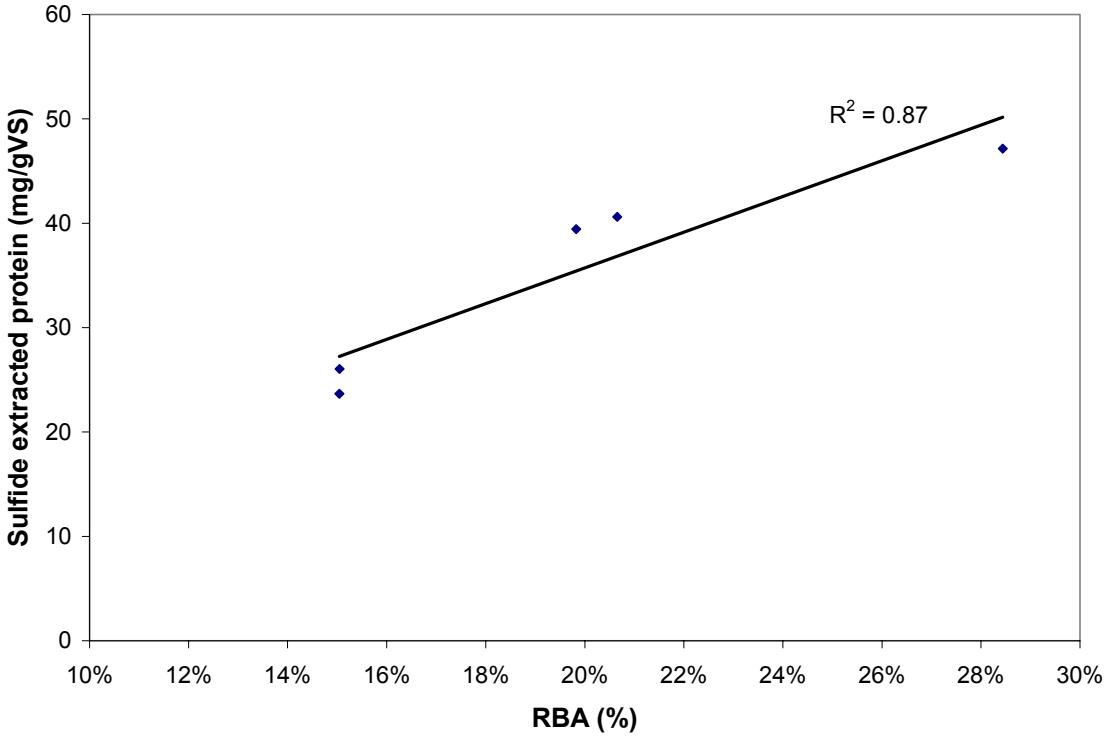


Figure III-13: Sulfide extracted protein versus RBA. (Data for sample set 4)

IV Manuscript 3

Effects of Advanced Digestion Processes on Odors from Dewatered Biosolids

Nitin Verma, Chul Park, John T. Novak, Zeynep Erdal* and Bob Forbes*

*CH2M Hill

Introduction

Anaerobic digestion is a common method used to stabilize municipal wastewater treatment residuals. Single stage conventional anaerobic mesophilic digestion is the most widely used digestion technology to stabilize municipal sludges. Rising transportation, disposal and handling costs have driven the search for improvements in digestion processes and improvised digestion techniques. Phased digestion is a recent technology for improving efficiency of anaerobic digestion. Metcalf and Eddy (2003) list four digestion phasing configurations: staged mesophilic digestion, temperature-phased digestion, acid/gas phased digestion, and staged thermophilic digestion. These processes can destroy more volatile solids (VS), produce greater amount of methane gas and result in better dewaterability of sludge. Little is known about the effects these advanced digestion processes have on the quality of biosolids in regard to odor generation.

Acid/Gas Phased Digestion

In acid/gas system, the SRT of two sequential digesters is varied to kinetically select either acid forming or methane forming organisms. First digester in the sequence is maintained at a low SRT. The first digester in an acid/gas system is operated at a low SRT of about 12 hour to 1.5 days to promote growth of acid forming organisms. The low SRT and high organic loading causes an accumulation of organic acids in the first digester. Methane forming organisms have a slow growth rate and thus are washed out of the first digester as the SRT is very low. The second digester is operated at a higher SRT, typically SRT $\geq$ 18 days, to allow for the growth of a substantial population of methane forming organisms. Studies suggest greater volatile solids destruction in an acid/gas

system compared to single stage digestion [Ghosh, 1985]. Inman (2004) showed comparable volatile solids destruction for acid/gas system operated at mesophilic temperatures to single stage mesophilic digesters. Previous studies are unclear whether acid/gas phased digestion enhances anaerobic digestion and no studies have been reported on the odor generation potential from dewatered sludge cakes from acid/gas system.

Temperature Phased Digestion

In temperature phased digestion, the operation temperature is varied between digesters to select for mesophilic or thermophilic organisms. Mesophilic digesters are typically operated at temperatures ranging from 30-38^{o}C and thermophilic digesters from 50-60^{o}C. Thermophilic digestion is of interest as it reduces the pathogens in sludge, hence making sludge available for unrestricted land application. In addition to the pathogen reducing potential, other advantages of thermophilic digestion include higher VS reduction and improved dewaterability. Thermophilic digestion is thought to have enhanced performance due to increased biochemical reaction rates of thermophilic organisms (Buhr and Andrews, 1977). Faster biochemical rates translate to smaller digester volumes. However, thermophilic digestion process is instable due to fluctuations in pH and odor problems caused by high volatile fatty acids (VFA) in the effluent.

Temperature-phased anaerobic digestion (TPAD) incorporates the advantages of phased digestion and thermophilic digestion. Typically, the first digester is operated at thermophilic temperatures to achieve higher VS reduction and better dewaterability and the second digester is operated at mesophilic temperatures to increase process stability and decrease the odor potential of thermophilically digested biosolids [Han and Dague, 1997].

Objectives

The objective of this study was to evaluate the impact of advanced anaerobic digestion processes namely, acid/gas anaerobic digestion and TPAD on the odor generation processes and potential of dewatered biosolids cake. If substantial benefits are observed,

that will indicate that these process can be successfully employed to achieve better quality sludge and also control odor nuisance from dewatered biosolids cake.

Materials and Methods

This study was conducted with sludge samples collected from wastewater treatment plants operating anaerobic digesters in acid/gas or TPAD configuration. Three wastewater treatment plants were sampled for this study. The configuration and sampling procedure for each treatment are briefly discussed below.

Treatment Plant A

Figure IV-1 illustrates the treatment scheme at wastewater treatment plant A. This facility uses a two-stage anaerobic digestion process. In the first stage (thermophilic stage), wastewater solids are heated to 55^{o}C for 5 days. The second stage (mesophilic stage) digester is operated at temperature in the range of 35^{o}C to 48^{o}C for 15 days. The second phase digester (mesophilic digester) when sampled was being operated at 48^{o}C. As this temperature was above the normal mesophilic temperature range, it was thought that the benefits of mesophilic digestion were reduced. To assess the effect of operating the second stage digester at a temperature higher than the typical mesophilic temperature on odor generation the thermophilic sludge was batch digested in the lab at 37^{o}C for 30 days.

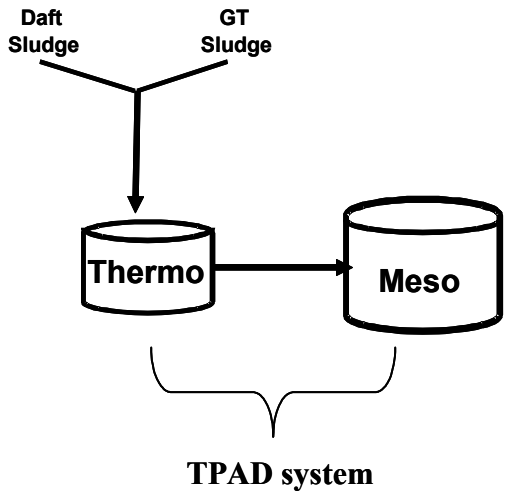
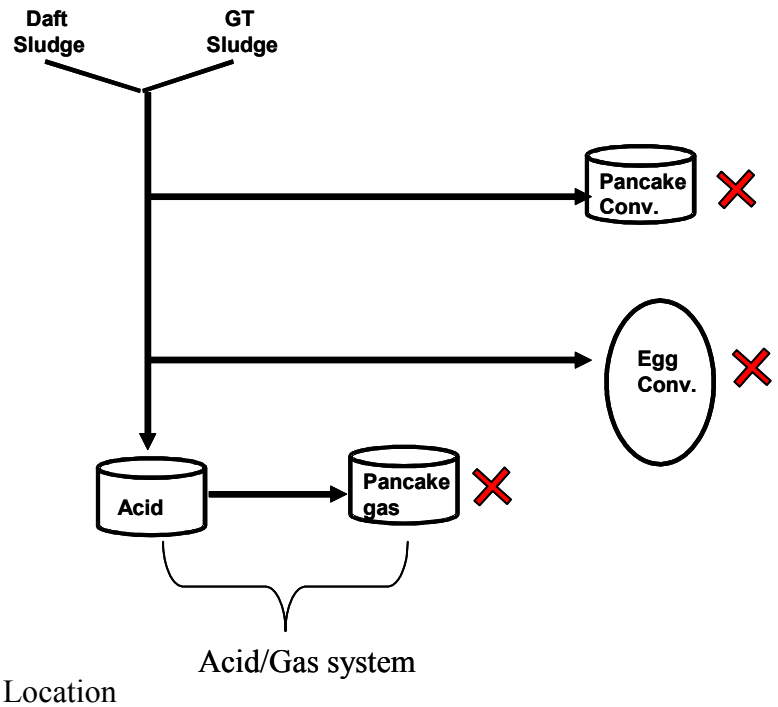


Figure IV-1: Treatment schematic at wastewater treatment plant A.

Treatment Plant B

Figure IV-2 illustrates the treatment scheme at wastewater treatment plant B. This facility uses a two stage anaerobic digestion process. The configuration of the digesters at this facility is similar to an acid/gas system. The acid phase digester is fed with a blend of gravity thickened (Gt) primary sludge and thickened waste activated sludge. The waste activated sludge is thickened in a dissolved air flotation (Daf) unit.

The first stage digester is operated at a low SRT (acid phase) and the second stage at a high SRT (gas phase). This plant has digesters which are either traditional pancake shaped or more efficient egg shaped. As shown in Figure IV-2, effluent from the acid digester is used to feed a pancake shaped digester, which is the gas phase of the acid/gas system. The facility also operates two conventional mesophilic digesters, one of which is pancake shaped (one with a flat bottom) and the other being egg shaped. In order to evaluate the effect of acid/gas system, samples from the conventional digesters were also sampled and analyzed for odor potential. The conventional egg shaped digester was also sampled to evaluate the effect of the egg-shape digester on odor generation potential of dewatered sludge cakes.



: Sampling Location

Conv. : Conventional

Figure IV-2: Treatment schematic at wastewater treatment plant B.

Treatment Plant C

This facility was sampled as anaerobic digesters at this facility are being operated in such a way that allowed side-by-side evaluation of three advanced digestion technologies.

1. Three-phase (acid- gas mesophilic-thermophilic-mesophilic)
2. Two-phase (acid-gas mesophilic -thermophilic)
3. Two-phase (acid-gas mesophilic - mesophilic)

Figure cc illustrates the facility layout and operation modes, while Table cc summarizes these modes of digestion and each digester shown on Figure cc. The manure digestion train was not included in the study.

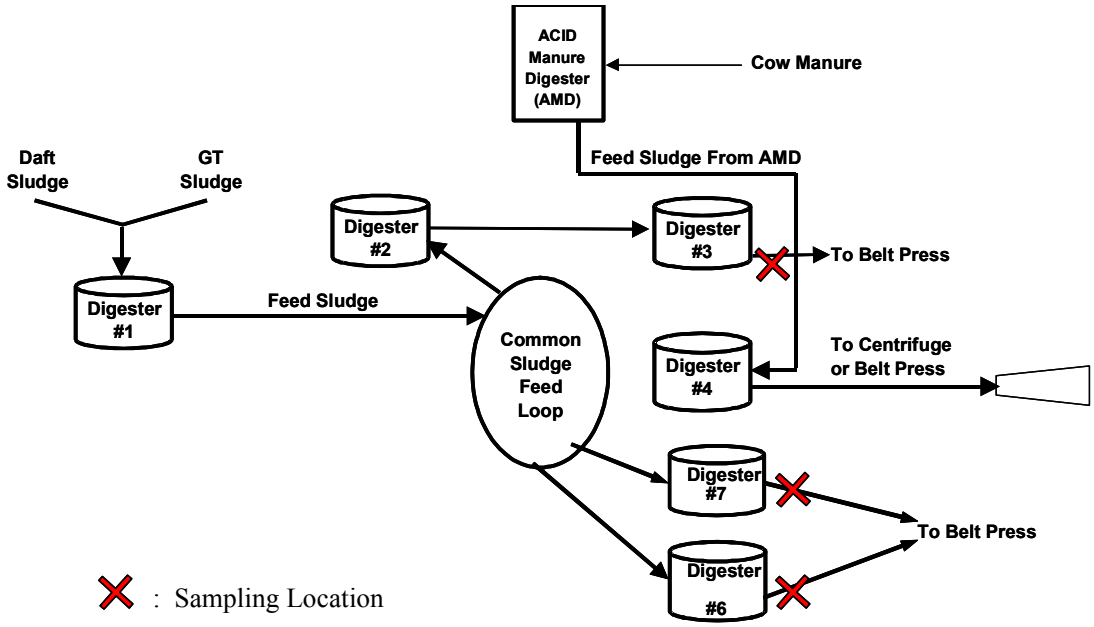


Figure IV-3: Treatment schematic at wastewater treatment plant B.

Wastewater Treatment Plant C - Advanced Digestion Facility Digester Operation Modes

Train No.	Acid	Gas 1	Gas 2
1. Biosolids	Dig. #1, meso	Dig. #2, thermo	Dig. #3, unheated
2. Biosolids	Dig. #1, meso	Dig. #7, thermo	-
3. Biosolids	Dig. #1, meso	Dig. #6, meso	-
4. Manure	-	Dig. #4, thermo	-

In order to compare the odor potential of the advanced digestion technologies, feed sludge was collected from the facility and batch digested in the lab for 30 days at 37^{o}C mesophilic temperature. The batch digested sludge was considered as a conventional digester and the data for this batch digested sludge was used to compare the advanced digestion technologies.

All digested sludges were analyzed for odor generation using the method used by Verma (2005). All sludges were also analyzed for total and volatile solids, residual biological activity, metals, cations and solution biopolymer.

Results and Discussions

Table IV-1 summarizes the samples that were collected from treatment plants A, B and C.

Table IV-1: Sample summary table

Plant	Digesters sampled	Comments
A	• Thermophilic • Mesophilic	Thermophilic and mesophilic digester operated at 5days and 15 days SRT respectively
B1*	• Acid • Gas • Conventional	Shape of acid, gas digesters is like a pancake. Conventional digester is egg shaped.
B2*	• Gas • Conventional(p) • Conventional(e)	Shape of gas and Conventional (p) is like a pancake and Conventional (e) digester is egg shaped.
C	• Feed • AGMM - Acid/Gas Mesophilic-Mesophilic • AGMT - Acid/Gas Mesophilic-Thermophilic • AGMTM - Acid/Gas mesophilic-thermophilic-mesophilic	AGMM and AGTM had a total SRT equal to 19days and AGMTM had a total SRT of 26day

* Treatment plant B was sampled 2 times. Number following "B" refers to the sample set.

The experimental results for sludge from different treatment plants are discussed separately in the following sub-sections.

Analysis of Sludge from Treatment Plant A

Thermophilic and mesophilic digesters were sampled at this treatment facility. It was observed at the treatment facility that the even after mesophilic digestion the sludge was fairly odorous. It was thought that the high odors could be due to the inefficient performance of the second phase (mesophilic) digester which was operated at a high

temperature (about 45-48^{o}C). In order to evaluate the effect of operating the mesophilic digester at elevated temperature, thermophilic sludge was batch digested in the lab for 30 days at 37^{o}C(mesophilic temperature). Odor analysis of thermophilic and mesophilic sludge from field and lab digested mesophilic sludge, henceforth referred as TPAD-lab digested was carried preformed. Figure IV-4 shows the variation in organic sulfur gas concentrations in the headspace of vials containing dewatered sludge cakes amended with BESA. It can be clearly seen that the sulfur gas concentration in the headspace of vials containing dewatered thermophilic sludge was the highest. Both field mesophilic and TPAD-lab digested sludges had lower organic sulfur concentration than the field thermophilic sludge.

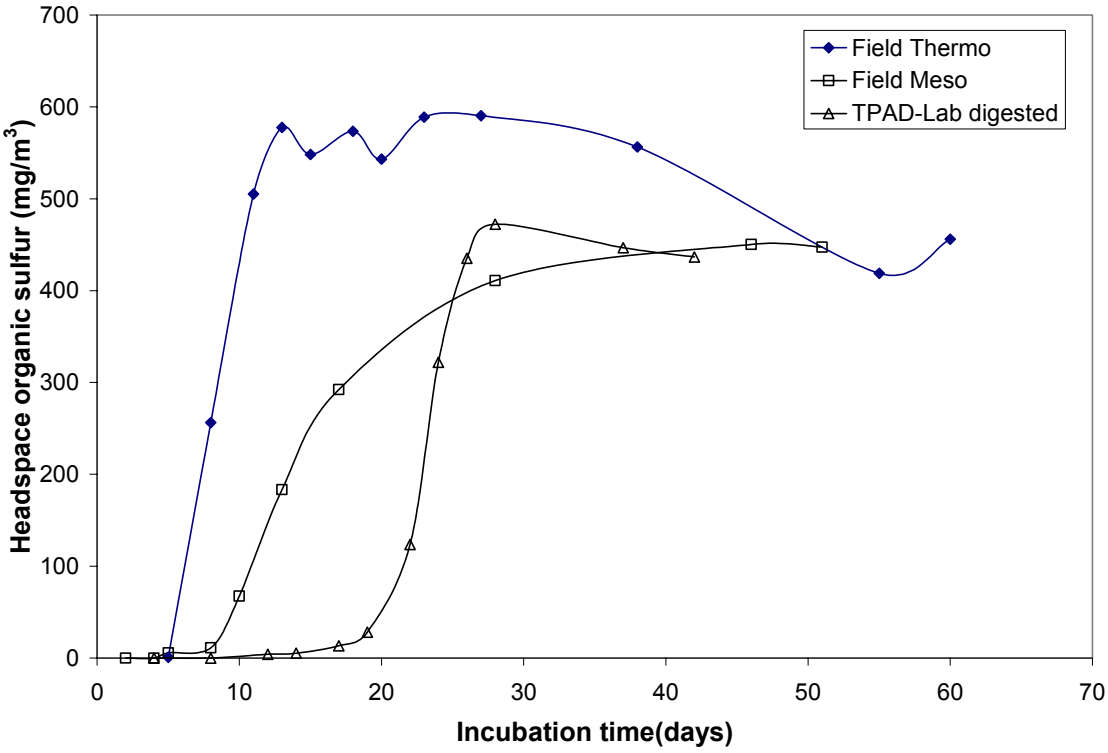


Figure IV-4: Variation in headspace sulfur organic gas content over time. Data for high-solids cakes amended with BESA.

The peak organic sulfur gas concentration in the headspace of vials containing dewatered cake for field-meso and TPAD-lab digested sludges were similar. These data suggest that TPAD digestion reduced the odor generation potential of sludge. However, not much difference in odors was observed from TPAD with a total SRT of 20days from that with a

total SRT of 35 days. Little difference was observed in odor generation from dewatered cakes from the field mesophilic (operated at higher temperature) and TPAD-lab digested (operated at 37^{o}C). These data suggest that odor generation potential of sludge was not affected by the operating temperature of the second phase digester. As there was no control, no statement can be made about the comparison of TPAD system with a conventional single-stage mesophilic digester.

Figure IV-5 shows the residual biological activity (RBA) for the three sludges. As expected, the RBA for Field thermo was highest. The RBA data shows the same trend as the organic sulfur data. The RBA for field-meso and TPAD-lab digested differed little, suggesting that RBA is also not affected by the operating temperature of the second phase digester.

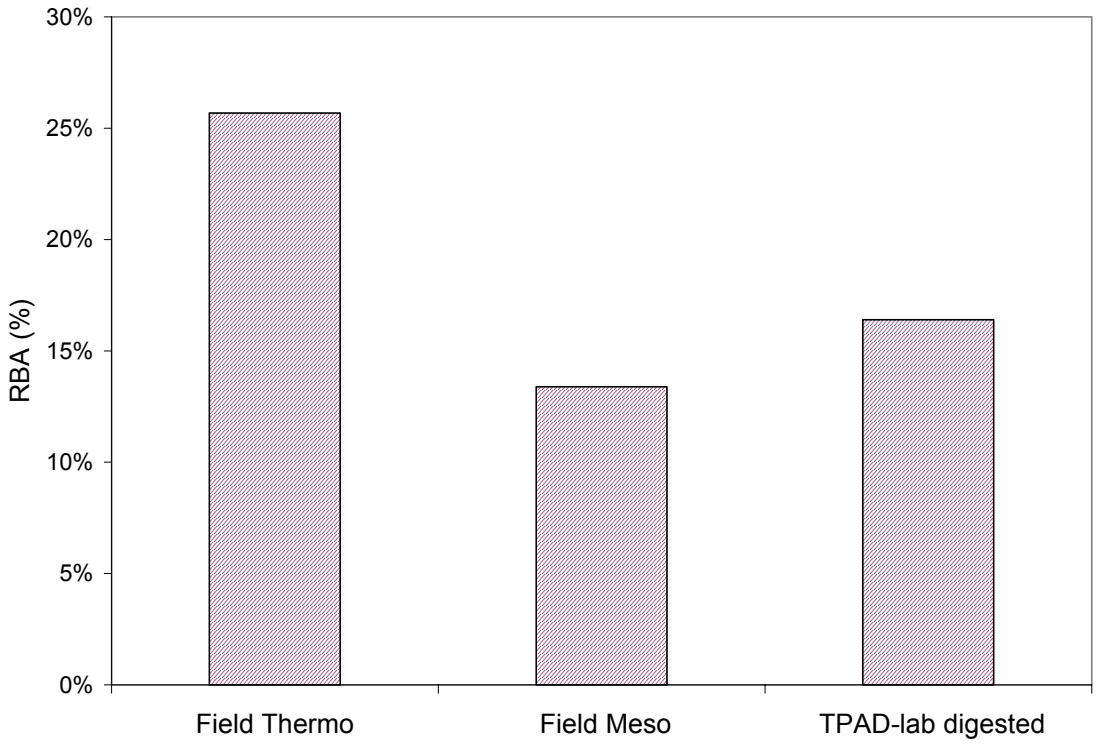


Figure IV-5: Residual biological activity for sludges from treatment plant A.

Analysis of Sludge from Treatment Plant B

Treatment plant B was sampled two times. First set of samples included sludge from the acid, gas (pancake shaped) and conventional (egg shaped) digesters. Figure IV-6 shows the variation in organic sulfur gas concentration in headspace of vials containing

dewatered cake for acid, gas (pancake shaped) and conventional (egg shaped) sludges as a function of incubation time. These data suggest that acid/gas system did not have much benefit with regard to organic sulfur odor generation. The conventional digester had the lowest sulfur gas concentrations in the headspace.

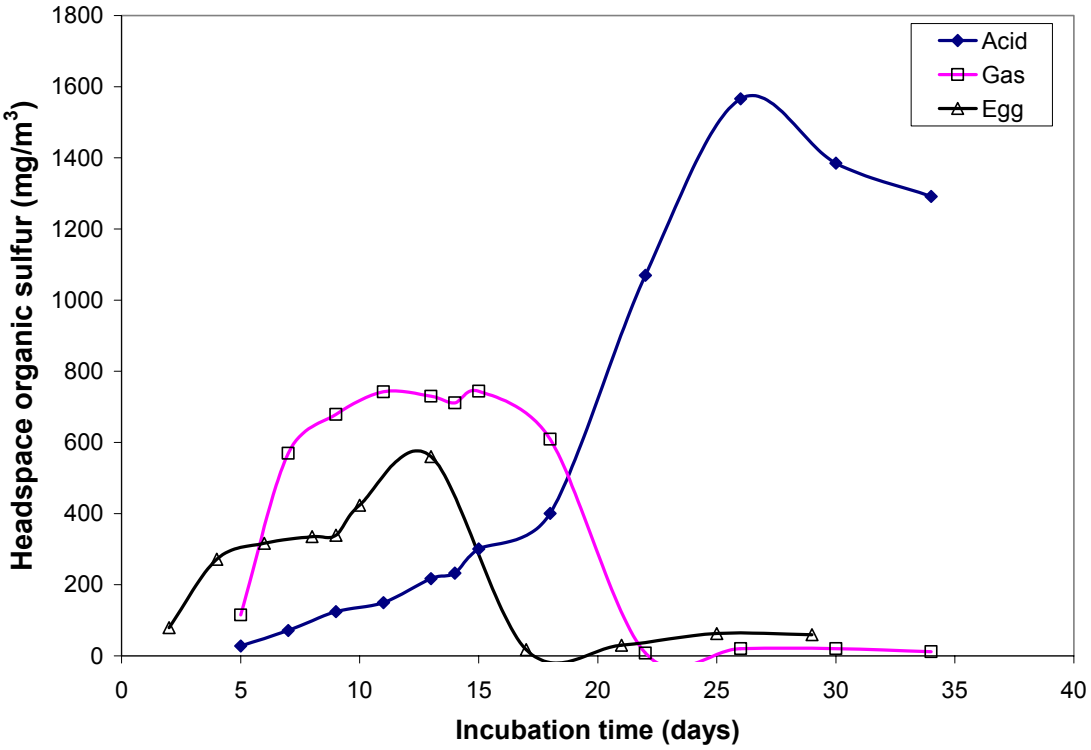


Figure IV-6: Headspace organic sulfur gas concentration versus incubation time for sample set 1 from treatment plant B.

The data from sample set 1 for the acid/gas system and the conventional digester could not be used to justly compare the two systems as the conventional digester was egg-shaped, whereas, the digesters of the acid/gas system were pancake shaped. It was thought that the lower odors from the conventional digester were because of efficient digestion achieved in the egg shaped digester due to better mixing. In order to have a suitable comparison of acid/gas system with conventional single-stage digestion and also to evaluate the odor reducing potential of egg shaped digesters a second set of samples was collected from the treatment plant.

The second set of samples comprised of sludge from the gas (pancake shaped), conventional (pancake shaped) and conventional (egg shaped) digesters. Figure IV-7 shows the variation in organic sulfur gas concentration in the headspace of dewatered sludge cakes as a function incubation time for the three sludges. The sludge from conventional (pancake shaped) generated the highest amount of organic sulfur in the headspace. These data suggest that acid/gas system produce sludge with lower organic sulfur odor generation potential compared to conventional mesophilic digestion.

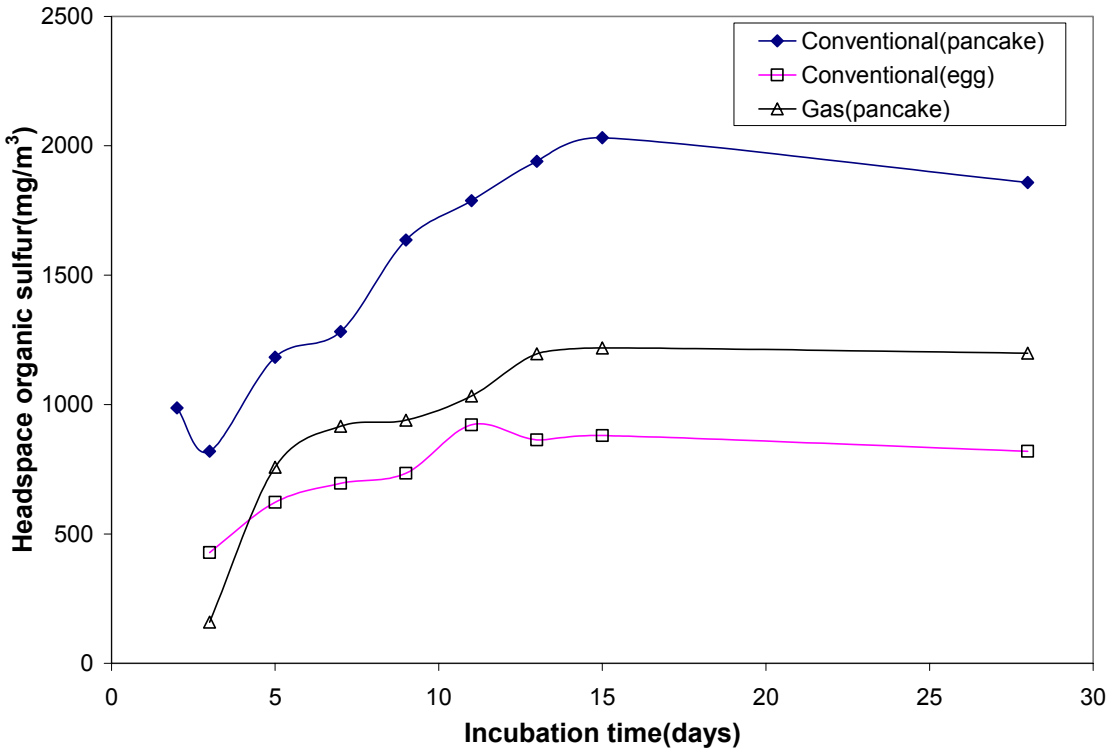


Figure IV-7: Headspace organic sulfur gas concentration versus incubation time for sample set 2 from treatment plant B. Organic sulfur data for high-solids cakes amended with BESA.

The sludge from egg shaped digester, operated as a conventional mesophilic digester, had the lowest organic sulfur gas concentrations, suggesting that the efficient mixing in the egg shape digester is beneficial for odor reduction.

Analysis of Sludge from Treatment Plant C

The AGMM and AGMT systems had a total SRT of 19 days and the AGMTM had a total SRT of 26days. The lab batch digestion was carried out for retention time of 30 days.

Three anaerobic treatment schemes were compared for odor generation from dewatered biosolids cake. Figure IV-8 shows the variation in organic sulfur gas concentration in the headspace of a dewatered high-solids cake from sludge from the three-phase (acid- gas mesophilic-thermophilic-mesophilic, two-phase (acid-gas mesophilic -thermophilic) and two-phase (acid-gas mesophilic - mesophilic) anaerobic digestion schemes. Figure IV-8 also shows the variation in the headspace organic sulfur gas concentration for batch digested sludge.

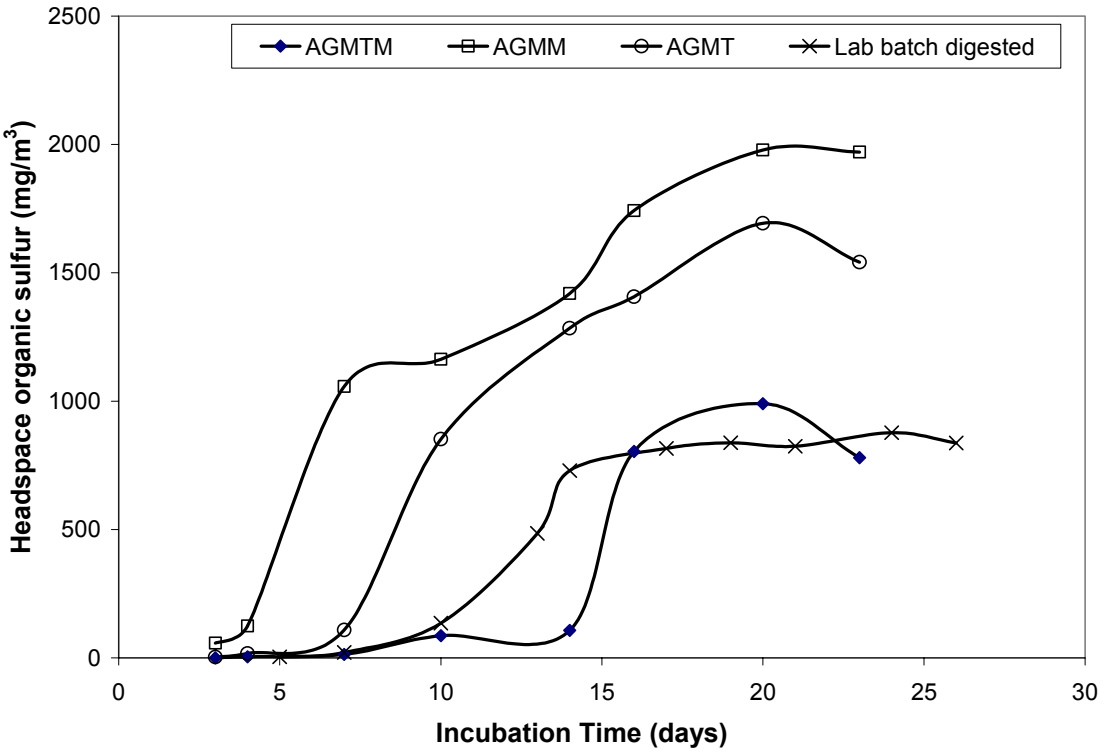


Figure IV-8: Headspace organic sulfur gas concentration as a function of incubation time for samples from treatment plant C. Headspace organic sulfur data for high-solids cakes amended with BESA.

The AGMM system had higher odor in comparison to AGMT, suggesting that a combination of mesophilic and thermophilic digestion is a more efficient technique to reduce odors from dewatered biosolids cake. The three phase digestion, AGMTM had the least odor. This could be due to the longer SRT coupled with meso-thermo digestion. Headspace organic sulfur gas concentration from dewatered cake from batch digested sludge was low and comparable to that obtained fro the AGMTM system. However, it was observed that the H2S gas concentration for the two sludges was very different. The

lab digested sludge cake produced much higher amount of hydrogen sulfide. Figure IV-9 shows the variation in headspace total sulfur gas concentration. These data also suggest that the AGMM sludge had the highest sulfur gas concentration followed by AGMT and AGMTM had the least sulfur gas production.

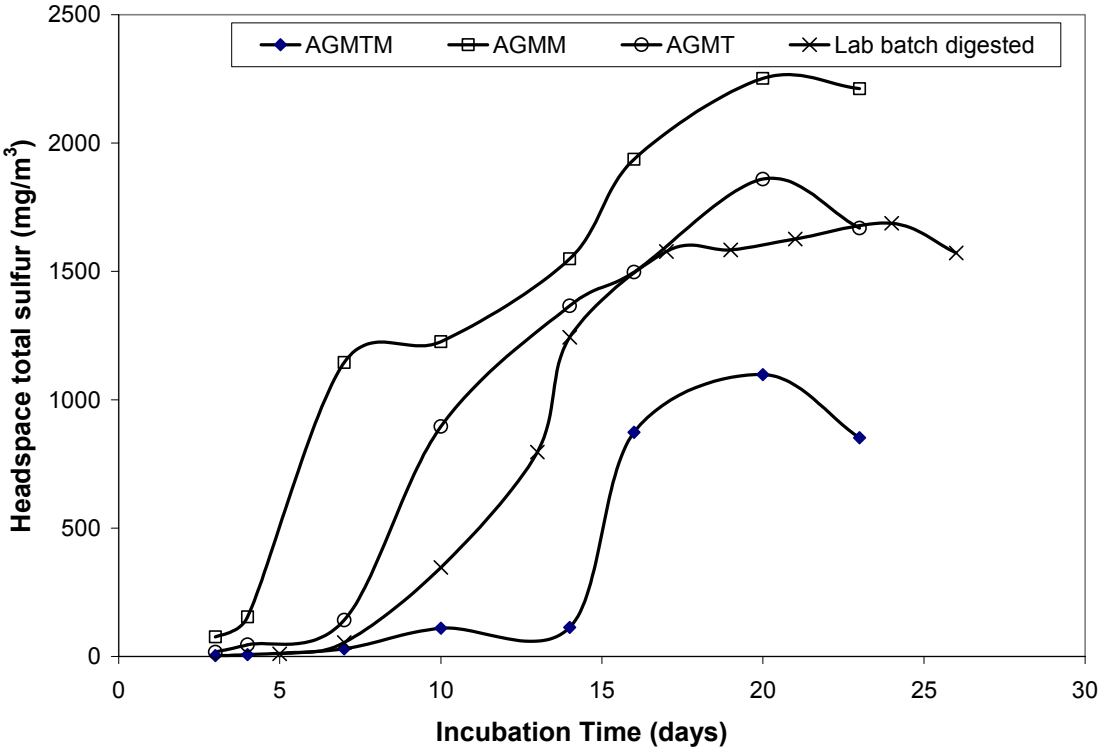


Figure IV-9: Headspace total sulfur gas concentration as a function of incubation time for samples from treatment plant C. Headspace organic sulfur data for high-solids cakes amended with BESA.

Sulfur gas concentration from cakes prepared with batch digested sludge produced odors comparable to AGMT system. This was thought to be due to the difference in the SRT of the two systems, the AGMT system had a total SRT of 19days whereas the batch digestion was done for 30days. AGMTM operated at a total SRT of 26days had the least sulfur gas concentration in the headspace showing that operating digesters in a temperature phased configuration in beneficial with regard to odor generation from dewatered biosolids cakes.

Conclusions

This study was conducted to evaluate advanced digestion techniques for their effects on odor generation from dewatered biosolids. The acid/gas and temperature phased anaerobic digestion systems were evaluated. Dewatered sludge cakes were prepared, for sludges from three different utilities, using the centrifuge simulation technique developed at Virginia Tech. The headspace of cake stored in incubation vials was analyzed for sulfur gases using GC/MS.

The main conclusions that can be drawn from this study are:

1. Acid/gas system had a beneficial impact on odors from dewatered sludge cake compared to conventional single-stage mesophilic digestion.
2. Efficient mixing of contents in egg-shaped digesters seems to be beneficial for reducing odor generation from dewatered sludge cake.
3. For acid/gas system, the odors in terms of high to low were AGMM, AGMT AGMTM. The AGMTM had the longest SRT.

Reference

Buhr, H.O., Andrews, J.F. (1977) The thermophilic anaerobic digestion process. Water Res., 11, 129-143.

Ghosh, S. (1987) Improved sludge gasification by two-phase anaerobic digestion. ASCE J. Environ. Eng., 113, 6, 1265-1284.

Han, Y., Dague, R.R. (1997) Laboratory studies on the temperature-phased anaerobic digestion of domestic primary sludge. Water Environ. Res., 69, 6, 1139-1143.

Inman D.C. (2004) Comparative Studies of Alternative Anaerobic Digestion Techniques. Master's Thesis at Virginia Polytechnic Institute and State University.

Metcalf and Eddy Inc. (2003) Wastewater engineering: Treatment and reuse. 4th Edition. McGraw-Hill, New York, NY.

Verma N. (2005) Anaerobic Digestion: Factors Effecting Odor Generation. Master's Thesis at Virginia Polytechnic Institute and State University.

Filename: NitinVerma-Thesis-etd
Directory: C:\Documents and Settings\Nitin Verma\Desktop\Nitin\Masters\Research-WERF3\Thesis
Template: C:\Documents and Settings\Nitin Verma\Application Data\Microsoft\Templates\Normal.dot
Title: Digestion Processes and Their Effect on Dewatering and Bound Water Content of Sludge
Subject:
Author: Nitin Verma
Keywords:
Comments:
Creation Date: 7/20/2005 1:31 PM
Change Number: 3
Last Saved On: 8/4/2005 9:18 AM
Last Saved By: user
Total Editing Time: 70 Minutes
Last Printed On: 8/11/2005 6:44 AM
As of Last Complete Printing
Number of Pages: 102
Number of Words: 23,811 (approx.)
Number of Characters: 135,728 (approx.)