A Comparative Study of Anaerobic Digestion Processes for Sewage Sludge

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Abstract

The Blue Plains Wastewater Treatment Plant in Washington, D.C. is in the process of updating its anaerobic digesters, with a completion date set for 2008. This research was undertaken to aid designers at Blue Plains by evaluating alternative digestion approaches. The technologies applicable to the plant included thermophilic anaerobic digestion, acid/gas phased digestion, and temperature phased anaerobic digestion. To obtain design data, a year long study was conducted using bench scale digestion systems operating at different solids retention times (SRT) and organic loading rates (OLR). The digesters were fed with mixed primary and secondary waste (50/50 by weight) from the Blue Plains wastewater treatment facility. The digesters were operated until they reached steady state as observed by volatile solids reduction (VSR), methane production, and volatile fatty acid (VFA) levels. At this point, samples of digested waste sludge were analyzed for residual biological activity, dewatering properties and headspace organo-sulfur production. Results from the study demonstrated that the TPAD digestion process had the lowest residual biological activity (RBA) after digestion, and that the single stage thermophilic digesters had the highest RBA. Sludge from single stage mesophilic digestion had the highest odor potential, with headspace gas tests generating over 1400 mg organo-sulfur per m³ of headspace gas, while both single stage thermophilic and TPAD systems generated less than 400 mg/m³ at all SRTs studied.
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Literature Review

Introduction

Primary and waste activated sludges are by-products of municipal wastewater treatment. Prior to their disposal or beneficial re-use, the sludges require further treatment to reduce pathogen levels, organic content, and odor potential. Anaerobic digestion, in particular the mesophilic (35°C) single-stage process, has been designated as a biological treatment process for further degradation and stabilization of municipal sewage sludge. An economic byproduct of this process is the generation of valuable methane gas. Mesophilic digestion usually requires a detention time of 20 days or more, but has been shown to be less efficient than advanced digestion processes at reducing volatile solids and pathogens (Balzonella, 2002).

Due to changing standards for the use and disposal of biosolids, and the need to reduce operational costs, there is increased interest in treating sludges more effectively. The use of a thermophilic temperature regime (55°C) for faster microbial activity, and also separating the anaerobic digestion process into two stages with thermophilic pretreatment followed by a mesophilic treatment stage have shown promise in treating sludges more effectively. Thermophilic and combined thermophilic/mesophilic or temperature phased anaerobic digestion (TPAD) have been shown to reduce pathogens more than mesophilic digestion and therefore are especially attractive (Dague et. al, 1996).

Environmental Health Standards

All sludges formed during the treatment process must be disposed of by the treatment facility. Various stabilization processes that control odor, pathogens,
biodegradable toxins (e.g. hydrocarbons), and that bind heavy metals are used to create biosolids; solids that are suitable for land application. In 1998 an estimated 6.9 million tons of biosolids were generated (E.P.A., 1999), of which 60% were used beneficially by being land applied, composted, or used as landfill cover.

To help make certain that the finalized biosolids were safe to be used beneficially, the United States Environmental Protection Agency (EPA) implemented standards in 40 CFR Part 503 (1993) that govern biosolids disposal based on pathogen reduction criteria. Class A biosolids were deemed those treated by processes that reduce pathogen levels to below detectable limits. These biosolids have few restrictions on the disposal methods used. The digested biosolids with pathogen levels above detectable limits are called Class B biosolids, and must be disposed on restricted sites. Part 503 is a technology based standard and bases its designation of Class A or B only on the specific treatment process (EPA, 2000b).

**Thermophilic Digestion**

Thermophilic digestion processes were first used full-scale in the United States at the Hyperion WWTP in Los Angeles, CA, from 1953 to 1957 (Garber, 1954). The digesters treated a blend of primary and waste activated sludge, with results showing increased volatile solids reduction compared to conventional single stage mesophilic treatment. Subsequent studies showed thermophilic digestion to have better pathogen reduction, faster reaction rates, and the ability to reduce the foaming normally associated with anaerobic digestion (Garber, 1977, Buhr and Andrews, 1977).
Thermophilic digestion has its detractors. Research has shown thermophilic digesters to be sensitive to small changes in temperature and loading rates. The effluent quality and ability to dewater the residual sludge is poor, and the digesters require additional energy to heat the biomass (Fang and Chung, 1999). Higher amounts of volatile fatty acids also are seen in effluent, which cause odor problems (Fisher and Greene, 1945). Kim et al. (2002) compared mesophilic and thermophilic batch reactors using primary waste from the Murfreesboro treatment plant in Tennessee. They found a higher rate of volatile solids removal and methanogenesis in thermophilic reactors that were stirred only before wasting and after feeding. Their results suggest that solubilized compounds such as volatile fatty acids (VFAs) can be converted to methane efficiently in thermophilic reactors when there is closer microbial consortia proximity (Kim et al., 2002).

Temperature-Phased Digestion

Separating anaerobic digestion into a two-phase approach was first suggested by Pohland and Ghosh (1971). They physically separated the two main groups of microorganisms, acid-forming bacteria and methanogenic archaea, into two reactors (Pohland and Ghosh, 1971). This separation provides optimal conditions for each microorganism’s growth. The acid forming, or acidogenic bacteria are favored in the first stage, which then provide food for the methanogenic archaea in the second stage.

The Temperature Phased Anaerobic Digestion (TPAD) process has been studied by Dague and coworkers at Iowa State University (Harris and Dague, 1993). This approach involves a two-stage reactor system with the first stage operated at thermophilic
temperatures (55° C) and the second stage operated at a mesophilic temperature (35° C). The temperature-phased process was able to achieve higher organic removals than either thermophilic or mesophilic single stage reactors (Han and Dague, 1995). Using a mixture of primary and waste activated sludges (50:50, volume ratio), Han was able to show that the temperature-phased system performed better than conventional single stage mesophilic digestion, and was able to reduce the concentration of *fecal coliform* in the effluent to 1000 MPN/g total solids which meets the requirement for Class A sludges (Han, Sung, and Dague, 1997).

By combining thermophilic and mesophilic digestion in series, the benefits of each are maximized while the shortcomings of thermophilic digestion are mediated. The thermophilic reactor has higher VS destruction and pathogen destruction, with high VFA in the effluent (Garber, 1977). The mesophilic reactor is able to decompose those acids and turn them into methane and carbon dioxide. By combining these systems, the solids retention time (SRT) to achieve a specific VS destruction is shorter, with less volume necessary in the thermophilic reactor (Han and Dague, 1995).

Positive results of co-phase mesophilic and thermophilic digestion were also seen by Song et al. (2002) in treating waste from a municipal wastewater treatment plant at B Metro City in South Korea. Their research showed a dependence on the sludge exchange rate in the performance of the co-phase digestion. The conclusion was that this sludge exchange provided for a stable thermophilic digester, selection of the active and higher substrate affinity of anaerobic microorganisms, and sharing the nutrients and intermediates for anaerobic microorganisms (Song et al., 2002).
Enhancing Sludge Treatment

Sludge management has been a crucial part of economic wastewater treatment. Much research has been carried out to reduce the final amount of sewage sludge as well as make the residuals as safe as possible. A key to these studies is the ability to offer real world solutions that can be adapted to wastewater treatment under both time and cost constraints.

Baier and Schmidheiny (1993) worked upon the hypothesis that breaking up the microbial cells in the wastewater prior to anaerobic digestion would allow for better treatment and minimization of the sludge. By using mechanical ball milling on several sludges (primary, secondary, waste activated, anaerobically stabilized sludges, and others), they found that the process can significantly increase the soluble fraction of total chemical oxygen demand (COD). Their research also showed that milling was able to reduce volatile solids in waste activated sludges, with 38-57% enhancement over non-milled sludges (Baier et al., 1993).

Research has also considered the feed characteristics of anaerobic digesters. The major impact of feed depends on the relative amounts and feed concentration of primary and secondary sludges. Balzonella et al. (2004) studied four large Italian wastewater treatment plants that used anaerobic digesters fed with only waste activated sludge. He found that there were problems with the heat balance when using waste activated sludge as the sole substrate. They assumed this came from low biogas production coupled with low volatile solids levels in the feed. The results also showed a relationship between the SRT of digesters and the amount of biogas produced (Balzonella, 2004).
Recommendations from the study were that pre-treatment and thickening of the waste activated sludge can help the biodegradability and heat balance.

**Biosolids**

Biosolids refers to treated municipal sludge that has achieved a certain quality to be land applied. The EPA has designated “classes” of biosolids which designates the type of treated sludge that can be applied to various sites. Class A biosolids undergo advanced treatment to reduce pathogen levels to below-detectable levels. Heat drying, composting, and high-temperature aerobic digestion are treatment processes that typically meet Class A requirements. If Class A biosolids also meet vector reduction requirements along with concentration limits for metals, they can be used as freely as other fertilizer or soil amendment products. Class B biosolids are treated to reduce pathogens to levels protective of human health and the environment, but not to undetectable levels. They require crop harvesting and site restrictions, which minimize the potential for receptor contact until natural attenuation of pathogens has occurred. Class B biosolids cannot be sold or used on sites such as lawns and home gardens, but can be used in bulk on agricultural and forest lands, reclamation sites, and other controlled sites that meet Part 503 vector pollutant and management practice requirements.

Concern over biosolid application has come from both the industry as well as the public. Public response has been due in large part to malodorous odors emitted from the sludges, with additional concerns over the application of Class B biosolids and health risks to those near the application sites. Treatment facilities wish to limit complaints
from the public, as well as reduce costs associated with handling, storing, and transporting the biosolids.

Biosolids serve as a food source for microorganisms with high levels of proteins and carbohydrates (EPA, 2000a). When these microorganisms degrade biosolids under anaerobic conditions, they can release odors. Odors typically identified with wastewater biosolids are reduced sulfur compounds, nitrogen based compounds, and organic fatty acids (WEF, 1995). Anaerobic and aerobic digestion has been traditionally used for stabilizing sludge generated from wastewater treatment facilities. Other measures include lime/alkaline stabilization or composting after dewatering of sludges. Sometimes common sense is all that is needed to control odors at application sites. This includes paying attention to wind speed and direction, weather conditions, prudent locations for stockpiles, and prudent timing of applications. One example is to apply biosolids on weekday mornings, when there are fewer people in the neighborhood to be affected by odor, as well as maximizing the solar drying of surface-applied biosolids (Rynk and Goldstein, 2003).

The biosolids application method used is also an important factor in odor control. Depending on the physical consistency, options for application include subsurface application (injection), irrigation, and surface application with or without soil incorporation (tilling). Methods that incorporate the biosolids into the soil quickest provide the best odor control (EPA, 1999).
Sulfur-based Odors

Odor generation starts with microbial metabolism and cell lyses, which releases biopolymers, mainly proteins and polysaccharides. Up to 50% of extra-cellular polymeric substances (EPS) in sludges are proteins (Frølund et al. 1996). Work by Grady et al. (1999) found both cysteine and methionine in proteins extractable from activated and anaerobically digested sludges. These amino acids remain non-metabolized until they are made bioavailable through digestion. Sulfur based odor compounds can be detected in the headspace of dewatered sludge/biosolids before and after stabilization. These compounds are mainly comprised of hydrogen sulfide, methanethiol, dimethylsulfide, and dimethyldisulfide.

To understand the role of sulfur compounds in odor generation, Lomans et al. (1999) conducted studies with Bromoethansulfonic acid (BESA) and sodium tungstate. The BESA acted as a methanogenic inhibitor, while the sodium tungstate worked as a sulfate reduction inhibitor. Their study showed that methanogenesis is the main mechanism for dimethylsulfide and methanethiol consumption in freshwater sediment. When under anaerobic conditions, DMS degraded at a lower kinetic rate than when oxygen was not rate limiting.

Work also is being done to best analyze headspace gases in liquid and solid phase residuals. Abalos et al. (2000) created an analytical procedure based on headspace solid-phase microextraction (HSPM) to determine levels of VFA derivatives causing odor in urban wastewater. The study used a PDMS-CAR fiber combined with a GC-FID that gave high sensitivity and precise results. Further research showed that a SPME method followed by a GC/MS could determine low molecular mass sulfides and disulfides in
wastewater (Abalos et al. 2002). These volatile sulfur compounds are mainly associated with anaerobic decomposition of organic matter.
References


Comparing Sludges from Acid/Gas-Phased, Thermophilic, Temperature-Phased, and Conventional Mesophilic Anaerobic Digestion

Abstract

During a year long study, laboratory-scale anaerobic digesters were used to treat a blend of primary and secondary sludge from Blue Plains Wastewater Treatment Plant in Washington, D.C. The operating systems in this study included temperature-phased digestion (TPAD), single stage thermophilic (SST), single stage mesophilic (SSM), acid-gas phased digestion (AGMM), and dual phased thermophilic digestion. The study was divided into three phases with different solids retention times (SRT) and organic loading rates (OLR). The acid-gas phased digestion system was only studied during one phase due to its specific loading design, and the dual phase thermophilic digestion was studied during the last phase to provide direct comparison to the TPAD. The TPAD system performed best at each stage of the study, with higher volatile solids destruction and lower residual biological activity than the other digestion systems. The SSM system was shown to produce the most total sulfur in the headspace gas tests, at all SRTs studied. Results of this study show an advantage to the TPAD system for the anaerobic digestion facility to be completed at Blue Plains in 2008.

Keywords

Thermophilic, temperature phased, mesophilic, anaerobic digestion, biosolids, shear, sludge, organosulfur
Introduction

Land application requirements and public opposition due to nuisance odors have pushed the wastewater industry to consider odor potential as part of the digestion process. Single stage mesophilic anaerobic digestion has been an industry standard in trying to meet all parties requirements (Balzonella, 2002). This process is often limited to one reactor and produces methane gas, a useful energy source.

Thermophilic digestion is an old process that is getting new attention due to technological and process-changing advances. Thermophilic range methanogens and other microorganisms have been shown to work better than mesophilic digestion in volatile solids reduction (VSR), produce sludge with better dewaterability, and provide faster reaction rates which results in a shorter solids retention time (SRT) in the reactor (Garber, 1977). Although thermophilic digestion has been shown to meet the E.P.A. Class A biosolids requirements, it has not been approved as an alternative technology to meet the requirements because of short-circuiting and other long-term sludge stability issues (Metcalf and Eddy, 2003).

One way of overcoming these shortcomings is to combine thermophilic and mesophilic digestion into a two-stage configuration. Dague and coworkers at Iowa State University developed a process called Temperature Phased Anaerobic Digestion (TPAD), which uses a short thermophilic phase, followed by a mesophilic stage, utilizing reactors in series (Dague et al., 1995). The thermophilic reactor is able to achieve higher VSD and pathogen destruction, while producing volatile fatty acids that are utilized in the mesophilic reactor to produce methane and carbon dioxide (Han et al., 1997).
Typically, digested sludges are dewatered using belt-press filters or high speed centrifuges. These processes, combined with the use of polymers, help to produce the highest cake solids. Unfortunately, they may also create or magnify odors. The odors typically associated with a wastewater processing facility or land application site containing biosolids are reduced sulfur compounds, nitrogen based compounds, and organic fatty acids (WEF, 1995).

Objectives

The main objective of this study was to compare the performance of TPAD systems with conventional and thermophilic digestion. The performance of the systems and characteristics of the residuals are of interest. Because of the ability to compare digestion techniques with the same feed, an acid-gas phased digestion set-up was tested, as well as single stage thermophilic digestion. This was achieved by collecting samples between the thermophilic and mesophilic reactors in the TPAD configuration. A two stage thermophilic reactor was set up in the third phase of this study to compare with the TPAD system. Both the TPAD system and the two-stage thermophilic were fed from the 7.5-day SRT Thermophilic reactor and had the same SRT in the second reactors. Tests used to measure the steady state levels included volatile solids destruction, methane production, and effluent volatile fatty acid concentrations. The purpose of the study was to aid in the design of an anaerobic digestion facility being constructed at the Blue Plains wastewater treatment facility, with a completion date currently set for 2008.
Methods and Materials

In order to thoroughly test the digestion characteristics of each system, a range of SRT and temperature regimes were used (Table 1). All subsequent figures, tables, and charts refer to the digesters by the acronyms in this table. The digesters were set up in a controlled temperature room at a temperature at 36.5° C. Using a digital thermometer probe it was found that temperatures of the non-insulated mesophilic reactors remained at 35±1 °C. Thermophilic temperatures were achieved by a temperature controlled circulator, pumping 65°C water through 0.95 cm vinyl hose wrapped around the reactor and covered with neoprene foam. This set-up maintained the temperature in the thermophilic reactors at 55±1 °C.

Because batch feeding was required, the digester temperature dropped once each day during feeding. The digesters most affected by this were the thermophilic systems. The feeding resulted in a temperature drop to 45-48 °C, with temperature recovery to 55 °C occurring in two to three hours. The batch feeding was carried out daily at the same time to maintain the SRT of the digesters.

The digesters chosen for this study were conically shaped tanks manufactured for home beer making. They were chosen based on their sturdy and secure design and shape close to the “egg-like” digesters planned for the Blue Plains facility. Two models were used: 1) 24.6 liter stainless steel Fermenator™ manufactured by Blinchmann Engineering; 2) 26.5 gallon plastic Mini-Conical fermentation tank manufactured by Hobby Beverage Equipment Company. Both models were purchased through Grape and Granary in Akron, OH. The rubber gasket seals on the digester lids were covered with silicone caulk to prevent leaks of biogas.
The digesters in phase I were started with thickened waste activated sludge from the Blacksburg-VPI Sanitation Authority, Lower Stroubles Creek WWTP. Previous studies have shown favorable results when starting thermophilic and mesophilic digesters with waste activated sludge (Kim and Speece, 2002). Waste activated sludge equal to one half of the operational volumes was allowed to batch digest in the digesters for approximately 10 days. The digesters were then fed 0.5 liters of combined primary and secondary sludge daily until reaching final operating volume. Once this volume was obtained, daily wasting and feeding operations were started to attain the desired SRT. Digesters in the 2nd and 3rd stages of the study were seeded with the reactor contents from the previous testing phase, except for the 25 day SSM, which was started in an additional Fermentor™ using mesophilically digested sludge from the Pepper’s Ferry WWTP in Dublin, VA.

The digesters were fed with a blend of thickened primary and waste activated sludge from the Blue Plains Wastewater Treatment Plant in Washington, D.C. The sludges were sampled from Blue Plains over several days and shipped overnight bi-weekly in iced coolers. The samples were stored in a 4 °C walk-in storage room until ready to be fed. For the first phase of testing, the sludges were mixed at a 1:1 volumetric ratio, and in the second and third phase they were mixed at a 1:1 weight ratio. Though the feed characteristics remained similar in each phase of the study (Table 2), it is important to note that the proportion of primary sludge to secondary sludge was not calculated in the first phase due to the volumetric mixing. Also of note is that the organic loading rate was not constant between the digesters in each phase as they were operated at different volumes to meet SRT and sampling requirements (Table 3).
The samples were screened at the time of collection, and additional screening took place before feeding. The screening mechanism was a semi-spherical kitchen colander with approximately 3-millimeter diameter holes distributed at approximately 2 holes per square centimeter. Total solids concentration of the feed was diluted to 3% at startup and increased to 4% at 39 days into the first phase of the study. Data used for the first phase came from steady state conditions after the solids increase. In the second and third stages the feed was prepared at 4% total solids. Tap water was used to dilute the feed when necessary to meet the solids condition. Daily batch feeding and wasting was utilized in all three test phases.

The reactors were mixed by circulating gas from the headspace of each digester and injecting it into a valve at the bottom of the digester (Figure 2). This was accomplished by vinyl hoses connected to 6-600 RPM variable speed peristaltic pumps circulating the gas (Cole-Parmer, Vernon Hills, Illinois). The variable speed controllers allowed for desired mixing, which corresponded to 40% of the maximum speed in the pumps. This corresponds to approximately 0.7 liters/minute using Cole-Parmer L/S 18 tubing in the pump heads. At least five minutes before wasting and feeding, the gas flow rate was doubled (1.4 LPM) to ensure that the waste samples were representative of the digester contents. The waste valve was located on the side of the tank and the corresponding drain pipe was situated in the center of the reactor. The flow rate was maintained at 1.4 LPM for around 10 minutes after feeding to disperse feed entering the top of the reactors.

Gas from each digester was collected in Tedlar bags (Fisher Scientific, Hampton, N.H.) attached to the digester gas recirculation set-up (Figure 2) which kept the digesters
from becoming pressurized. The gas flow rate was calculated by measuring the volume of gas in the bags and dividing by the amount of time since the bags were last cleared. Gas composition samples were collected from syringe sampling ports on the Tedlar bags. The thermophilic digesters also required a water trap built into the gas circulation system to keep water vapor from entering the Tedlar bags. The traps collected around 50 milliliters per day of condensate which was then added back to the digester during feeding approximately every other day.

Tests conducted during the study included:

- Total and volatile solids
- Gas production and composition
- Total chemical oxygen demand (COD)
- pH
- Alkalinity
- Effluent volatile fatty acids (acetic, propionic, and butyric/isobutyric)
- Soluble cations (Na⁺, NH₄⁺, K⁺, Mg++, Ca++)

The COD, pH, alkalinity, and solids tests were conducted according to Standard Methods (APHA, 1999).

Gas samples were analyzed with a Shimadzu model GC-14A gas chromatograph (Shimadzu Scientific Instruments, Columbia, MD) using the thermal conductivity detector (TCD). The column used was made from a 1.8 m x 0.635 cm copper tubing. The column was coiled to fit in the GC-14A oven and packed with Haysep Q media (Supelco, Bellefonte, PA). Helium was used as the carrier gas, with column flow set at 17 mL/min.
Standard curves for CH₄ and CO₂ were created using mixtures of 99.1% CO₂ and 99.4% CH₄ at 25, 50, 75, and 100% quantities.

Samples were prepared for cation and effluent volatile fatty acid (VFA) analysis by centrifuging a 500 mL sample of digester biosolids at 13,500 x G for 25 minutes. A 50 mL sample of the supernatant was frozen for storage until the analyses were performed. Samples were typically frozen for no more than 7 days. At the time of analysis, the samples were thawed, centrifuged at 6,000 x G for 15 minutes, and then filtered through a 0.45 micron syringe filter. From these filtered samples, dilutions were made for cation testing and VFA testing.

Diluted VFA samples were arranged and acidified in individual GC vials and acidified by adding concentrated phosphoric acid at a ratio of 1:10. The VFA samples were analyzed on a Hewlett Packard Model 5890 gas chromatograph using a flame ionization detector. A Nukol capillary column (Supelco) was used and samples were injected in the splitless mode. The column flow gas was helium with a flow rate of 17 mL/min. Flow rates for the other gases used were: Nitrogen – 13 mL/min, Hydrogen – 45 mL/min, Air – 450 mL/min.

Diluted cation samples were analyzed on a Dionex D-120 ion chromatograph using a CS-12 column with conductivity detection and self-generating suppression of the eluent (Dionex Corp., Sunnyvale, CA). The eluent used was 20mM methanesulfonic acid at a flow rate of 1 mL/min. Statistical analyses were conducted with SigmaStat 3.10 (SPSS Software Inc., Chicago, IL).

The Residual Biological Activity test (RBA) was conducted by keeping digester waste samples anaerobic in 100 mL serum vials (Fisher brand) at 36.5°C for 40 days.
During the incubation period the samples were periodically degassed and weighed. The resulting weight loss of the samples was assumed to be from gasification of the volatile solids remaining. The RBA value was derived by taking the weight lost by each sample at the end of the incubation period and dividing by the weight of the VS content of the digesters at the start of the test. The RBA is shown as percent VS lost at each degassing.

The method of odor development came from studies conducted by Muller (WEFTEC, 04). Modifications of Muller’s work were made, however, due to a lack of access to a filter press, as well as the addition of Bromoethansulfonic acid (BESA) before centrifugation. Wastes from the digesters were first tested for the optimal polymer dose. The polymer used for this study was Stockholm 650 BC cationic polymer. An optimum dose curve was created for each system using a capillary suction time (CST) test, method 2710G of standard methods (APHA 1995). A triton type CST apparatus (304-M and 165) was used for these tests with Whatman 17-HCR used as the chromatography paper. Using the optimum dose, waste samples were sheared in 100 mL aliquots using a 1.5 hp food service blender. These samples were then dosed with BESA at a concentration of 0.1 mL of BESA per 50 mL of sludge to get a concentration of 0.127 mmol. The samples were then centrifuged in 500 mL tubes at 6,500 RPM for 15 minutes (Beckman J2-HS Centrifuge or Beckman-Coulter Avanti-JE). Supernatant was removed and cake solids were tested for total solids and headspace odor.

The headspace odor samples were placed in 100 mL serum vials (Fisher brand), with 20 grams of cake solids per vial. The vials were placed in a temperature controlled room at 25°C for the duration of the experiment. The analysis was performed using a capillary column Gas Chromatography/Mass Spectrometry (GC/MS) (Hewlett-Packard).
6890) with a cryogenic trap. One hundred µL of headspace gas was injected into the column for each sample. Integration of peak area was done by the environmental Chemstation program (G1701 CA). The amount of each odor contributing compound was derived ratio-metrically by comparing the sample peak area with the area of a known standard of hydrogen sulfide (H₂S), methanethiol (MT), methyl mercaptan, and dimethyldisulfide (DMDS).

Non-parametric statistical methods were employed when comparing the digester data. The Mann-Whitney rank sum method was used when comparing two groups. This was used as a nonparametric equivalent of the student’s t-test. A one-way ANOVA on ranks with Dunn’s method was used for pair wise comparison between three or more groups. This was used as a nonparametric equivalent of the one-way ANOVA. These methods were necessary due to the data not always meeting normality or equal variance requirements of parametric statistical methods. Statistical analysis of the results was conducted with SigmaStat 3.10 (SPSS Software Inc., Chicago, IL).

DIGESTER PERFORMANCE

To provide the best data for evaluating performance of the digestion systems, data analysis was performed once reactors reached steady state conditions. Gas from the digesters was quantified by total volume, percent methane, and percent carbon dioxide. Feed and waste samples were analyzed daily for total and fixed solids. These solids were analyzed for trends with OLR and SRT. Samples from the digesters were also kept anaerobic at mesophilic temperatures and measured for residual biological activity.
Stable Operation and Chemistry

The digesters achieved stable operation within two SRTs. Stable operation was defined by steady pH, gas production, and VS destruction. All the digesters, except for the acid digester, were within typical limits of normal anaerobic treatment for alkalinity, pH, and headspace CO₂ during stable operation (Parkin & Owen, 1986) (Table 3). There were periods when the acid-phase digester operated at higher than optimal, exceeding pH 6. The acid-phase digester experienced several episodes of foaming during the study and these episodes seemed to coincide with periods when the pH levels were above 6.0. To get the best data for the AGMM system, ranges are shown in Table 3 for the period when the system was at steady state. The table also shows that the pH values increased with increasing SRT in the single stage digesters. In the TPAD system, the pH of the 2nd stage mesophilic digester increased when the SRT increased in the 1st stage thermophilic digester.

Ammonia had the highest concentration of any of the cations measured for all digesters (Table 4). This was the result of degradation of proteins during the digestion process. The ammonia concentration ranged from 816 g/L to 1392 g/L during the study and was highest in the SST20 digester (Table 4). The SST20 was significantly higher than all of the other digesters in the study except for the SST5, TPAD5/10, and TPAD7.5/7.5. Although the ammonia was higher, the VS destruction was not, suggesting that the thermophilic digester might preferentially degrade proteins.
**Gas Production and Composition**

Because the OLR varied with each change in SRT during the study (Table 5), it is difficult to consider the effects of SRT on methane production without also considering the OLR. Figure 3 shows the relationships between OLR, SRT, and the specific methane yield. This figure shows that as the OLR increases, the specific methane yield decreases. The specific methane yield increases with an increase in the SRT.

In the first phase of the study, the gas-phase digester of the AGMM system had the highest methane biogas content (Table 6), though the statistical difference was not evaluated. The high methane content from the AGMM system was expected. The acid stage digester only averaged 33% CH₄ in its biogas and the methane data was also highly variable. One factor responsible for this variation may be the problems that occurred with mixing by headspace gas recirculation within the digester. Different gas diffusion devices were used because of clogging. The high loading rate due to the low SRT and foaming may also have contributed to the mixing problem. The methane content of the biogas in the gas-phase digester was expected to be high because the reactor was being fed volatile fatty acids. This feed has higher methane potential than the raw sludge feed where CO₂ is generated in the partial degradation to acetate.

The highest methane biogas content in the second phase of the study was seen in the TPAD5/10 system with 60% CH₄ (Table 6). Both the single stage mesophilic reactors and the SST5 reactor averaged 58% CH₄. In the third phase of the study the TPAD7.5/7.5 reactor averaged 65% CH₄, and SST7.5 was lowest with 57% CH₄.

To compare the reactors methane production, the gas production in liters of methane per day was normalized with the OLR (Figure 3) and with VSD (Figure 4). The
results of the methane normalized with OLR show greater normalized methane production for the TPAD system. TPAD7.5/7.5 produced 12.28 L CH₄/ g VS fed, the highest of all reactors in the study. TPAD10/10 produced the second most methane with 7.19 L CH₄/ g VS fed. However, the TPAD5/10 reactor only averaged 1.84 L CH₄/ g VS fed. This low amount of methane production may be the result of smaller colonies of methanogens due to the short SRT and the high OLR value of 6.08 g VS fed per liter reactor (Table 5). The other SST reactors in the study showed the ability to produce gas over a large SRT range, with SST7.5 averaging 5.03 L CH₄/ g VS fed and SST20 averaging 5.04 L CH₄/ g VS fed. Methane production for SST10 was below the SST reactor average of 3.38 L CH₄/ g VS fed, with 2.82 L CH₄/ g VS fed. Normalizing methane production with OLR for the SSM reactors showed a closer range of production, but well below that of the highest SST and TPAD systems. The highest was SSM25 with 3.40 L CH₄/ g VS fed, and the lowest was SSM15(a) with 2.15 L CH₄/ g VS fed.

The results of the methane production normalized with VSD highlights the total amount of methane produced by the TPAD7.5/7.5 system (Figure 4). The gas trapping system for the SST7.5 reactor was upgraded to two tedlar bags because of the increased flow. The SST7.5 averaged 9.15 L CH₄/ g VSD, and the TPAD7.5/7.5 was able to produce an average of 10.96 L CH₄/ g VSD. Normalizing the methane production with VSD again shows the inconsistency of SST5 and with the associated TPAD5/10 systems. Also there are the same fluctuations in the systems as SRT varied. Although the TPAD7.5/7.5 produced the most of all reactors, the SST processes produced the most methane on average with 6.23 L CH₄/ g VSD. TPAD systems averaged just behind with 6.12 L CH₄/ g VSD, and SSM systems were again lowest with 4.49 L CH₄/ g VSD.
Comparing the systems at 20 day SRTs the TPAD10/10 produced the most methane per OLR, and SST20 produced the most per VSD. TPAD10/10 produced 7.19 L CH$_4$/ g VS fed (Figure 3), and SST20 produced 8.76 L CH$_4$/ g VSD (Figure 4). SSM20 produced the least normalized methane with 2.56 L CH$_4$/ g VS fed and 4.09 L CH$_4$/ g VSD.

**Volatile Solids Reduction**

Due to the fixed solids accumulation in the digesters, the Van Kleeck Method for calculation of volatile solids reduction (VSR) could not be used. The Van Kleeck Method utilizes a total solids and volatile solids mass balance for a digester with decantate and bottom sewage sludge removal (EPA, 1992). Instead, VSR was calculated by the mass balance method. This was achieved by taking the difference in waste VS and feed VS, and dividing by the feed VS. That value was multiplied by 100 to get a percent VSR. This equation assumes that daily flows are steady, fairly uniform, and that the volume and composition of the digesters does not fluctuate substantially on a daily basis (EPA, 1999). These assumptions were deemed reasonable for this experiment.

Comparing the VSR for all reactors in the study shows that all systems were able to destroy at least 50% VS except for the SST5 and SST10 reactors, which all had VSR values above 49% (Figure 6). It must be noted that no other systems were run at a SRT of less than 15 days, and that the SST20 reactor was able to achieve 52.3% VSR, compared to 49.3% for SST5, 49.1% for SST7.5, and 49.4% for SST 10 (Figure 6). The thermophilic reactors also had the lowest VSR of all reactors in the study. When looking at the VSR of the systems at a 20 day SRT, the TPAD10/10 system was significantly
different from the other two digesters with 61% average VSR. The SSM20 and AGMM systems were not significantly different from each other at 54% and 52% VSR respectively (ANOVA on ranks: Dunn’s Method, 95% confidence interval) (Table 7).

The first phase of the study showed a statistically equal VSR between the SSM20 and the TPAD10/10 (Mann-Whitney rank sum, 95% confidence interval). Both the SSM and TPAD systems destroyed at least 7% more VS that the AGMM digesters, and 10% more than the SST10 (Figure 6). In the second and third phases of the study, the TPAD system destroyed more volatile solids compared to the other digesters (ANOVA on ranks: Dunn’s method, 95% confidence interval), with the highest VSR of 67% taking place in the TPAD 7.5/7.5 system (Figure 6). For the second phase, both SSM15 and SSM20 digesters destroyed 7% and 10% less volatile solids than the TPAD5/10, respectively.

The single stage thermophilic reactors all reached approximately 50% VSR, showing no significant difference for SRT (Mann-Whitney rank sum, 95% confidence interval). Due to the feed regimes, the TPAD digesters were operating at a significantly higher OLR than the SSM digesters (ANOVA on ranks: Dunn’s method, 95% confidence interval).

In looking at the reactors VSR versus SRT and OLR the general trend was an increase in VSR with increasing SRT and decreasing VSR with increasing OLR (Figure 7). Interestingly the TPAD systems operated at 15 day total SRT showed a 5% better VSR when using a 7.5 day thermophilic and mesophilic SRT instead of a 5 day thermophilic followed by a 10 day mesophilic. The influence of OLR on VSR cannot be readily determined for these systems because the SRTs were not held constant.
Residual Biological Activity

The residual biological activity test measures the amount of additional volatile solids destroyed over 40 days. This test is used to determine the amount of degradable solids remaining after anaerobic digestion and it is used by the EPA as a major stability parameter in determining whether sludges can be classified as class B biosolids. The residual biological activity test results show the highest additional VSR after digestion are from the single stage thermophilic reactors (Figure 7). Both SST10 and SST5 had results above 42%, with SST20 being the lowest with 27% additional VSR. This value is comparable to the single stage mesophilic reactors. The AGMM and two-stage thermophilic (2ST7.5) systems showed the least RBA activity after digestion with 14.4% and 11.7% VSR, respectively.

In comparing VSR in the digesters with the additional VSR in the RBA test, the single stage thermophilic reactors showed the greatest VSR by RBA, but lowest VSR in the digesters for each phase of the study (Figure 9). The TPAD systems by contrast showed the highest VSR in the digesters and the lowest VSR through RBA. The trend towards a higher VSR by RBA as the VSR in the digesters decreased was observed in all of the systems and indicates that the RBA test is, in fact, measuring material that could be degraded by anaerobic digestion. Volatile solids reduction was also compared by the summation of fractions of VS destroyed in both reactors and the RBA test per VS fed (Figure 10). This data indicates that about 80% of the sludge was degradable under anaerobic conditions.
Summary

All of the reactors were able to reach stable operation and produced levels of alkalinity, pH, and headspace CO₂ consistent with normal anaerobic treatment. The highest methane content of headspace gas was found in the second stage of the TPAD5/10 and TPAD7.5/7.5 systems. When normalizing methane production with OLR and SRT, the SST7.5 and TPAD7.5/7.5 systems produced the most methane. Both SSM and TPAD systems produced VSR above 60%, with the TPAD system averaging the highest VSR over all SRTs studied. The RBA tests showed the ability of SST reactors to continue VSR under anaerobic conditions. The TPAD systems showed the lowest VSR by RBA, consistent with its highest VSR in the reactors.

SLUDGE PROPERTIES

When all the data sets were gathered from each phase of reactors at steady state conditions, tests were conducted on the sludges to evaluate sludge properties. Some of the benefits of the TPAD system’s digestion performance were also expected to be seen in residual properties. With the TPAD system showing the best volatile solids reduction capability, it was also expected that it would show better dewaterability. Dewaterability was measured by capillary suction time. Also, a key to the Blue Plains Wastewater Facility is reducing odors. Organic sulfur levels were measured in cake solid headspace with BESA added to allow organic sulfur to accumulate in the headspace.
Capillary Suction Time (CST)

The results for the CST tests at optimal conditioning dose showed increasing trends with SRT for the SST and TPAD systems, and a decreasing trend with SRT for the SSM reactors. The TPAD system showed the best dewaterability as indicated by the CST, with the exception of the TPAD10/10 digester (Figure 11). It was expected that the CST times after conditioning would be below 50 seconds, but many sludges in the study were above that point. One explanation is that only the negatively charged biopolymers are coagulated by the cationic polymers, leaving positively charged particles in the sludge. Additional research has shown that positively charged chemical precipitates are not influenced by the cationic polymers, and require additional anionic polymers to increase the dewaterability, decreasing the CST.

There was a noticeable trend of increasing CST for increasing SRT in both SST and TPAD reactors. There seemed to be an opposite trend by the SSM reactors, but this may be influenced by the 206 second CST for the SSM15(a) reactor. When compared against the SSM15(b) CST of 77 seconds and the lower times for SSM20 and SSM25, there appears to be a problem with the SSM15(a) reactor at the time of the tests.

Optimum Polymer Dose

The optimal polymer dose curve (Figure 12) created by plotting the amount of polymer dosed versus CST times was used to determine the optimum polymer dose (OPD) for each reactor. The OPD results (Figure 13) show the range of doses in gram of cationic polymer dosed per gram dry solids in the reactors on the day the polymer dose curves were measured. Both SSM and SST systems show an increasing trend with
increasing SRT except for the largest SRT in the study. SSM systems go from a SSM15(a) value of 3.94 $\text{g polymer/ g TS}$ to 7.78 $\text{g polymer/ g TS}$ for the SSM20 reactor, then drops off to 4.13 $\text{g polymer/ g TS}$ in the SSM25. Likewise, the SST systems go from a SST5 value of 3.32 $\text{g polymer/ g TS}$ to 8.62 $\text{g polymer/ g TS}$ for the SST10 reactor, and the SST20 reactor only requires 3.04 grams polymer for OPD. Both TPAD5/10 and TPAD 7.5/7.5 require less polymer for OPD (3.26 and 3.38 $\text{g polymer/ g TS}$, respectively) than the corresponding SST5 and SST7.5 reactors (3.32 and 4.22 $\text{g polymer/ g TS}$ respectively). The largest dose required for TPAD systems was for the TPAD10/10 system with 7.61 $\text{g polymer/ g TS}$.

**Dewatered Cake Solids by Lab Centrifuge**

When preparing the odor samples, total and volatile solids tests were conducted on the cake samples. It was expected that reactors with larger volatile solids reduction would have higher cake solids. Total solid (TS) results were between 13-19% for all test systems (Figure 14). The SST5 and SST20 dewatered to the highest cake solids with 18.4% and 17.1%, respectively. The lowest TS was from the SSM20 reactor with 13.2%, though all other SSM systems had cake TS over 15%. When looking at average TS for the systems, single stage thermophilic averaged 16.6%, single stage mesophilic averaged 15.0%, and the temperature phased digesters averaged 14.7%. The only trend noticeable from the results is in the SST reactors, with a downward trend seen as SRT increased, except for the SST20 reactor. Another note of interest was the relation of the SST to corresponding TPAD reactors. Both TPAD5/10 and TPAD10/10 TS went down in the second stage reactors, while TPAD7.5/7.5 increased. When comparing TS with VSD
(Figure 15), a trend was observed of higher VSD giving lower TS. This was a drawback to the TPAD system.

Volatile solids tests on the lab centrifuged samples showed a range of 4.8-6.8% volatile solids (VS) (Figure 16). A comparison of the performance of the digestion processes showed the highest average for single stage thermophilic digestion at 6.1%. The temperature phased digesters showed similar volatile solids with an average of 6.0%, and single stage mesophilic was lowest with 5.6%. The thermophilic reactors demonstrated the highest cake solids during the study, with an average of 16.6% TS (compared to 15.0% for SSM and 14.7% for TPAD reactors) and 6.1% VS (compared to 6.0% for TPAD and 5.6% for SSM reactors).

**Organic Sulfur Odor Tests w/BESA**

Peak organic sulfur results show a greater production capability for the single stage mesophilic systems compared to the SST or TPAD systems (Figure 17). Both SST and TPAD systems produced less than 400 mg organic S per m$^3$ sludge. A level of 400 mg/m$^3$ is considered low to moderate (Adams et al., 2003) The lowest results are from the SST7.5 at 80 mg/m$^3$ and the TPAD7.5/7.5 utilizing the same SST reactor which produced the 80 mg/m$^3$, just 12 mg/m$^3$ more than the first stage reactor. Comparing the systems on total cake solids and peak organic sulfur highlights the SST systems ability to produce better cake solids and the SSM ability to produce more organic sulfur in headspace gas (Figure 18).

Headspace gas odor tests performed on the first stage of reactors showed a large difference between the reactors, specifically the SSM20 and SST10 (Figure 19). The
SSM20 produced over 600 mg organic sulfur per m$^3$ of sludge, while the other reactors had a maximum organic sulfur concentration of 300 mg/ m$^3$. The decreasing rates towards the end of the study show an underdose of BESA for the sludges as the total organic sulfur levels should have reached a plateau and then remained steady. The organic sulfur content for the TPAD10/10 was still increasing at the end of the test period (day 22), which shows a need for a prolonged test period in future studies. The SSM20 and AGMM2/18 showed similar logarithmic growth curves leveling out between 200 and 300 mg/cu. m organic S. The TPAD process increased the organic sulfur potential of the SST10 from 120 mg/ m$^3$ as a stand alone reactor to 280 mg/ m$^3$ as a dual phase process.

The second stage of the study confirmed the higher organic sulfur concentrations from the single stage mesophilic reactors. The SSM10 reactor reached a concentration of 1490 mg/cu. m, while SST5, SST20, and TPAD5/10 produced organic sulfur levels between 200 and 400 mg/cu. m. (Figure 20). The SST5 produced more organic sulfur than the SST20, showing a reduction in organic sulfur as SRT increased.

The third stage of the study, the only with two single stage mesophilic reactors, showed consistent results. The peak organic sulfur levels of both SSM reactors were almost 500 mg/cu. m higher than SST, dual phase thermophilic, and TPAD systems (Figure 21). The dip in concentrations shown on day 9 in this stage of the study could correspond to higher standards value used for integration.

Results from all three stages of the study show a higher potential for organic sulfur concentrations in SSM reactors. All of the TPAD systems and the SST5 reactor showed an upward trend towards the end of the test period. Other studies have shown that thermophilic reactors may not produce lower organic sulfur than conventional
reactors, but instead delay their formation (Adams et al., 2003). This is consistent with the TPAD and SST5 results. The other SST reactors all showed a downward trend towards the end of the test period which may be the result of underdosing with BESA.

Summary
CST tests showed increasing trends for dewaterability in SST and TPAD systems, with a downward trend for the SSM systems. Increasing trends were also observed in OPD results, with all systems showing a greater polymer dose as SRTs increased except for the highest SRT reactors for SSM and SST. There was not much difference in overall dosing between the systems. Lab centrifuged cake solids also did not show much difference between systems, but there was a trend of reactors with higher volatile solids destruction showing lower total cake solids. Different results for sludge properties of SSM15(a) and SSM15(b) show the influence of different OLRs.

Conclusions
The main purpose of this study was to compare TPAD digestion with single stage mesophilic at different SRTs. However, the ability to sample the thermophilic waste in the TPAD process along with the AGMM and dual phase thermophilic reactors was of significance to the field and provided valuable data and insight for future research. Conclusions of the study are as follows:

• The most stable biosolids values were produced by the TPAD10/10 and TPAD 7.5/7.5 systems.
• Single stage thermophilic digesters with SRT less than 20 days had the lowest VSR in the digesters, and the highest VSR in residual activity.

• Headspace odor tests showed consistently that the single stage mesophilic reactors produced more odors. SSM10 gave the highest peak odors at 1490 mg organo-sulfur/ m³ sludge, followed by SSM25 at 780, SSM20 at 650, and SSM15 at 600.

• Lab centrifuged cake solids and optimum polymer doses did not show any measurable differences between the operating systems.

Due to the changes in organic loading rates (OLR) during the different stages of the study, it was hard to compare the differing SRTs throughout the study. Despite the drawback, it was found that the TPAD digestion system destroyed significantly more VS than the SSM digesters. Also, the TPAD system was shown to have much less sulfur based odor potential than the SSM digesters at all SRTs. Future research with odor potential would benefit by more work on the effects and dosage requirements of Bromoethansulfonic acid.
References


Table 1 -- Operational parameters for digestion systems.

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<th>Volume (L)</th>
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Table 2 -- Feed Characteristics for all study phases.

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Table 3- Average Carbonate Chemistry Conditions.

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<th>s.d.</th>
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*Due to problems with keeping the AGMM system at steady state, the values shown are the range given during the optimal condition period used for analysis.

** Alkalinity as mg/L CaCO3
Table 4- Average Reduced Ammonia (NH₄-N) levels in g/L for the digesters.

<table>
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<th>Digester</th>
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Table 5 -- Organic Loading Rate (OLR, g VS/L*day) during each phase of the study.
Table 6- Methane content of biogas during the study.

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<th>CH$_4$ (%)</th>
<th>s.d. (%)</th>
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<td>SST10</td>
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Table 7 - Statistical Analysis results of Volatile Solids Reduction (VSR) for systems at 20 day SRT.

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*Analysis of Variance (ANOVA) - Dunn's post test compares the difference in the sum of ranks between two columns with the expected average difference (based on the number of groups and their size).*
Table 8 – Capillary Suction Time (CST) test results in (seconds, s) with Optimal Polymer Dose (OPD) curve results in (g polymer/g dry solids).

<table>
<thead>
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<th>Digester</th>
<th>CST (s)</th>
<th>OPD (g/g)</th>
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<td>81.3</td>
<td>4.22</td>
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</table>
Figure 1 – General Flow Diagram for the Temperature-Phased Anaerobic Digestion Systems.
Figure 2 – Gas recirculation design for experimental setup. Water trap was used for thermophilic digesters to prevent condensation from entering the gas accumulation bags.
Figure 3. Methane produced per mass of volatile solids loading (OLR) for mesophilic, thermophilic, and TPAD systems.
Figure 4. Methane produced per mass of volatile solids destroyed for mesophilic, thermophilic, and TPAD systems.
Figure 5. Specific methane yield at STP for each digestion system
Figure 6. Average percent volatile solids reduction (VSR) through mass balance equation.
Figure 7. Volatile solids reduction versus SRT and OLR for the digesters.
Figure 8. Percent volatile solids reduction through residual biological activity (RBA) test.
Figure 9. Percent volatile solids reduction comparison by RBA test and during digestion.
Figure 10. Summation of gram VSD per gram VS fed in both Digesters and RBA.
Figure 11. Capillary Suction Test (CST) times at optimal conditioning dose.
Figure 12. Optimal polymer dose curve test for the SSM15(a) reactor.
Figure 13. OPD Curve test results in gram Stockhausen Cationic Polymer per gram dry solids.
Figure 14. Centrifuged cakes total solids analysis.
Figure 15. Percent volatile solids destruction versus centrifuged cakes total solids.
Figure 16. Centrifuged cakes percent volatile solids analysis.
Figure 17. Peak organic sulfur in headspace gas for the different digestion systems.
Figure 18. Percent total cake solids versus peak organic sulfur in headspace gas for SSM, SST, and TPAD systems.
Figure 19. Total organic sulfur for first phase reactors with BESA.
Figure 20. Total organic sulfur for second phase reactors with BESA.
Figure 21. Total organic sulfur for third phase reactors with BESA.
Vita

Jared Webb was born in Roanoke, VA, on April 25, 1980. He attended Franklin County High School in Rocky Mount, VA, graduating in 1998. He graduated from The College of William and Mary in Virginia in 2002 with a B.S. in both Environmental Studies and Psychology. Deciding to forego law school, he chose to instead focus on the dynamics of natural systems through the department of Environmental Engineering at Virginia Tech.

Jared is currently working as a Project Manager for Earth Environmental Consultants, Inc., in Rocky Mount, VA. In his spare time he enjoys working on old Jeeps, farm work, and spending time with family and friends.