STEADY-STATE SLUDGE DIGESTION MODEL WITH AUTO-CALIBRATION

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ABSTRACT

STEADY-STATE SLUDGE DIGESTION

MODEL WITH AUTO-CALIBRATION

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Anaerobic digestion is a wastewater treatment technology used to treat sludge. One of the main benefits of this technology is the production of biogas that can be used as fuel for energy production. This process is extremely complex with many different steps and parallel reactions occurring simultaneously. These steps require highly specific environmental conditions that must be maintained for anaerobic digestion to occur. Modeling for anaerobic digestion began in the late 1960s to better understand and streamline the anaerobic digestion process. Many years of research were combined by the International Water Association to develop the Anaerobic Digestion Model No. 1 (ADM1), which was published in 2002 and no widely accepted updates have been published since. This model has repeatedly been proven to be a complete and accurate model for anaerobic digestion, but it is extremely complex and requires many estimated parameters. This complexity results in the model not being used by currently operating wastewater treatment plants due to the lack of data that is required for the ADM1. Creating a simple steady-state model to predict the concentration of methane in the biogas produced that does not require as many parameters would be beneficial for wastewater treatment plants to repurpose the biogas. Using full-scale solids data, a steady-state model that auto-calibrates to a specific wastewater treatment was developed by creating simple relationships between volatile solids, metabolism factors, and hydraulic retention times. This resulted in methane concentrations ranging from 55 – 71% of the biogas. These values are within expected ranges for

mesophilic operations, but due to lack of measured methane data from wastewater treatment plants, it is not possible to know if this is accurate for the specific plant. This poses the need for wastewater treatment plants to routinely monitor methane concentrations to successfully develop a steady-state anaerobic digestion model. Despite its limitations, the steady-state model is successful in terms of providing a way for wastewater treatment plants to easily predict the methane concentration within the biogas.

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1.0 Introduction

Anaerobic digestion is a wastewater treatment technology that has great potential for processing organic waste. It is one of the main processes currently used for stabilizing sludge, but it is a very complex and sensitive process. One of the benefits of anaerobic digestion is the generation of biogas that can be captured and used for energy production, reducing plant costs and fossil fuel consumption. The biogas, made up of mostly methane and carbon dioxide, is not typically measured by wastewater treatment plants, so it is rarely used to its full potential [1, 2]. Creating a way to estimate the production of methane within the biogas without sampling would greatly improve the efficiency of using it for energy production. Therefore, creating a generic model that can easily implement full-scale anaerobic digestion data is needed for efficient biogas utilization.

Modeling for anaerobic digestion began in the late 1960s, but these models were very simple and did not account for all the biochemical processes that occur [3]. Since then, there has been an increase in development of more complex models, but none have been widely accepted as the basis for generic anaerobic digestion modeling for operating wastewater treatment plants. The Anaerobic Digestion Model No. 1 (ADM1) is a model that was developed in 2002 by the International Waster Association [4] to act as the generic model for anaerobic digestion at a full-scale level, but it is very complex due to the many steps and parallel reactions that occur during anaerobic digestion. The ADM1 is still the most widely used model today for anaerobic digestion, but it has never been used to its full potential by current operating wastewater treatment plants due to the large number of required parameters, and there has not been a widely accepted update in the past 20 years. This lack of use by wastewater treatment plants indicates the need for a review of the current state of anaerobic digestion models and their availability.

The purpose of this thesis is to develop a steady-state model for anaerobic digestion and provide recommendations for a generic model that can be used to auto-calibrate to most wastewater treatment plants. By creating a mathematical relationship between methane production, metabolism factors, and volatile solids destruction in full-scale sludge digestion processes, it is intended to provide wastewater treatment plants with a less complicated model that can be more widely used. This model will aid wastewater treatment plants in understanding how their anaerobic digesters work and to promote improved routine monitoring of digester gas at new or existing plants.

The manuscript chapters included in this thesis were written to appear as articles in specific journals. This results in some redundancy when combined to meet the university format requirements.

2.0 Literature Review of Anaerobic Digestion and its Modeling

2.1.0 Anaerobic Digestion Processes

Anaerobic digestion is a wastewater treatment technology that is used to process organic waste. It consists of five steps called disintegration, hydrolysis, acidogenesis, acetogenesis, and methanogenesis. These processes have a number of parallel reactions that occur, making anaerobic digestion a very complex process. A basic flow chart of the processes is shown in Figure 2.1 with the different processes separated by color [4]. The intermediate acids produced during acidogensis are propionic acid (HPr), butyric acid (HBr), and valeric acid (HVr). The percentages shown are typical values for municipal sludge.

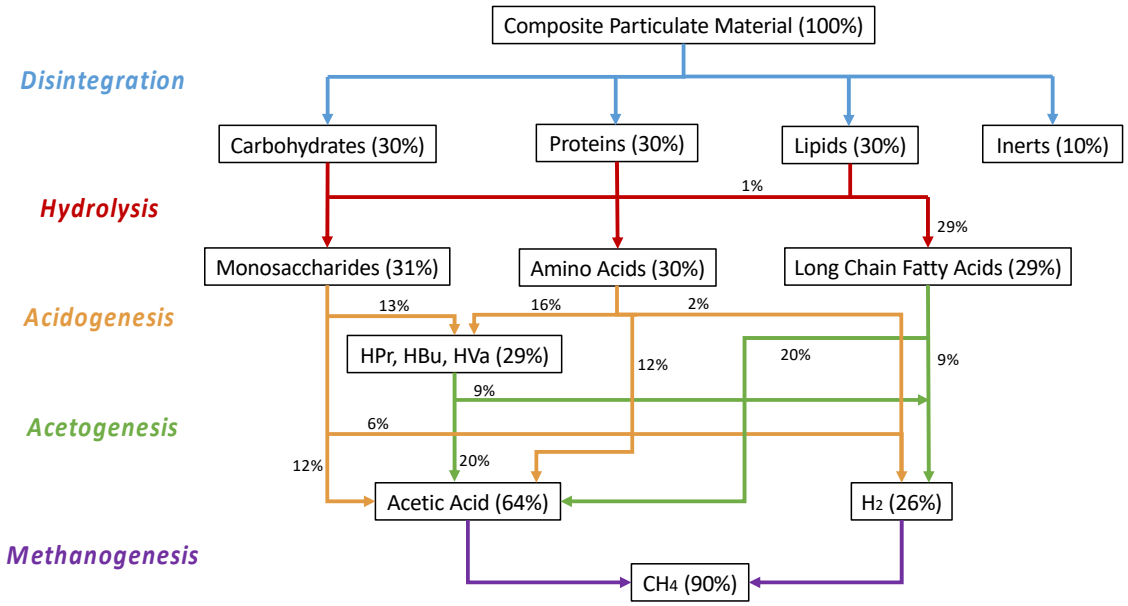

Figure 2.1: Anaerobic Digestion Processes [4]

Each step is important in breaking down the composite material into soluble components that eventually leads to methane and carbon dioxide as the end products. The methanogens, which are responsible for most of the waste stabilization during anaerobic digestion grow slow compared to other organisms and require a longer adjustment period to changes in environmental conditions [5]. Therefore, in order to achieve efficient treatment, it is

recommended to strive for optimum environmental conditions. These environmental conditions include temperature, pH, nutrient concentration, concentration of toxic substances, and the mixing that occurs [6]. The ideal environmental conditions are discussed in detail in the Section 2.2. Overall, these environmental conditions ensure that all steps of anaerobic digestion occur, and the optimum amount of methane and carbon dioxide are produced as end products. The individual steps of anaerobic digestion are described in more detail in the following sections.

2.1.1 Disintegration and Hydrolysis

Disintegration and hydrolysis are extracellular processes that help break down complex organic material into soluble substrates. Disintegration is used to represent a pool of composite particulate matter being broken down into carbohydrates, proteins, lipids, and inert solids. This step is not represented in every model but is beneficial for waste-activated and primary sludge digestion because it represents the lysis of whole cells and separation of composites [4]. The steps for disintegration and hydrolysis are shown in Figure 2.2.

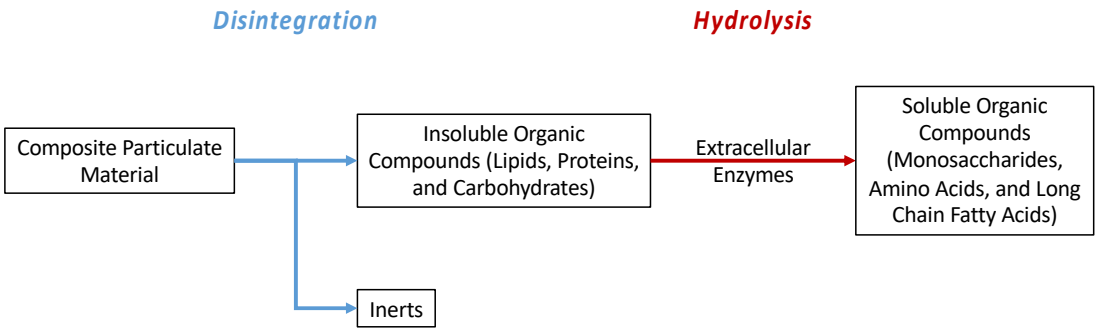

Figure 2.2: Step Diagram of Disintegration and Hydrolysis

Hydrolysis includes transforming complex insoluble organic matter, such as carbohydrates, proteins, and lipids, into a soluble form that can be used by acidogenic

bacteria. Hydrolysis can either be enzymatic process or take place due to physiochemical reactions, making it a very complex process [5]. The solubilization of complex insoluble substrate depends on many factors including particle size, pH, production of enzymes, diffusion, and adsorption of enzymes to particles. During hydrolysis, carbohydrates are transformed into monosaccharides, proteins are transformed into amino acids, and lipids are mostly transformed into long chain fatty acids (LCFAs), with a small percentage going into monosaccharides [5]. These transformations are typically accomplished by the enzymes that are released by the microorganisms. The products of hydrolysis are then able to diffuse through the cell membranes of the acidogenic microorganisms, which is necessary for the next step in anaerobic digestion.

These processes can be described as a first order kinetic model as the enzymatic activity that occurs is not directly coupled with the bacterial growth. However, some researchers have found that hydrolysis could be tied to microbial growth, and in that case is often recommended to use a Monod-type equation that depends on a hydrolytic constant to estimate the rate of substrate consumption as shown in Equation 2.1 [5].

Equation 2.1: Monod-Type Kinetics for Hydrolysis

$$\frac{dS}{dt} = K_h \times S$$

Where:

- dS/dt = Substrate consumption rate (kg/m^3 day)
- K_h = Hydrolytic constant (1/day)
- S = Concentration of substrate (kg/m^3)

The hydrolytic constant depends on many factors including the temperature, origin of substrate, and the solids retention time used. It also differs between carbohydrates, proteins, and lipids, resulting in wide range of possible values [5]. Hydrolysis or methanogenesis can be the rate determining step for the anaerobic process, which one depends on the ratio of hydrolytic to methanogenic microorganisms [7].

2.1.2 Acidogenesis

During acidogenesis, the dissolved organic matter is further biodegraded into volatile fatty acids (VFAs) and alcohols by the acidogenic bacteria, this process is shown in Figure 2.3.

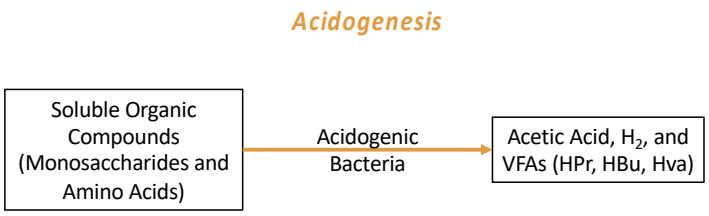

Figure 2.3: Step Diagram of Acidogenesis

The VFAs are mostly made up of acetic acid and larger organics such as propionate, butyrate, and valerate [7]. It is often reported that VFA concentration can fluctuate significantly for digesters operating at a different pH, which can affect the concentration of the products of acidogenesis. Acidogenesis is also believed to be the fastest stage of anaerobic digestion, with acidogenic bacteria having a regeneration rate of only 36 hours. The rapidity of this step is beneficial because it creates compounds directly used in later steps, however acidification of VFAs is largely reported to cause digester failure, so it important that the VFAs are being used up as rapidly as they are produced [7].

In most cases, Monod kinetics is assumed for the acidogenesis for carbohydrates, while the kinetics for the degradation of amino acids is more complex [5]. When dealing with protein-rich wastewater, it is important to look at the formation of VFAs from amino acids. Amino acids typically degrade into VFAs in pairs and produce ammonia in the process. If ammonia is present in high concentrations it is known to be an inhibitor of anaerobic digestion [7]. The factors that can influence this production are the hydrogen transfer, pH, dilution rate, and previous acclimation of the anaerobic culture [5]. After acidogenesis, the acetic acid is ready for methanogenesis, but the larger VFAs and LCFAs still need to be broken down to be made accessible to the methanogens during the next step.

2.1.3 Acetogenesis

Acetogenesis is the processes of breaking down larger VFAs and LCFAs into acetic acids while also producing hydrogen [7]. The steps for acetogenesis are shown in Figure 2.4.

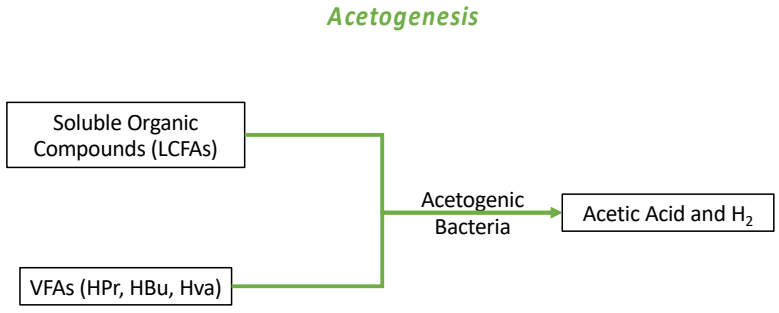

Figure 2.4: Step Diagram of Acetogenesis

The purpose of acetogenesis is to oxidize the VFAs and LCFAs into methanogenic substrate such as acetic acid, hydrogen, and carbon dioxide [8]. The hydrogen produced during acetogenesis can lead to excessive hydrogen partial pressure, which can be

harmful to acetogenic microorganisms. This is because acetogenic microorganisms require longer adjustment periods to changes in environmental conditions [8]. This issue is typically resolved with the rapid consumption of hydrogen during hydrogenotrophic methanogenesis [7].

2.1.4 Methanogenesis

Methanogenesis involves converting the acetic acid and hydrogen into methane. About 65-70% of the methane is produced during acetoclastic methanogenesis from acetic acid, while the rest comes from the hydrogen during hydrogenotrophic methanogenesis, as shown in Figure 2.5 [7].

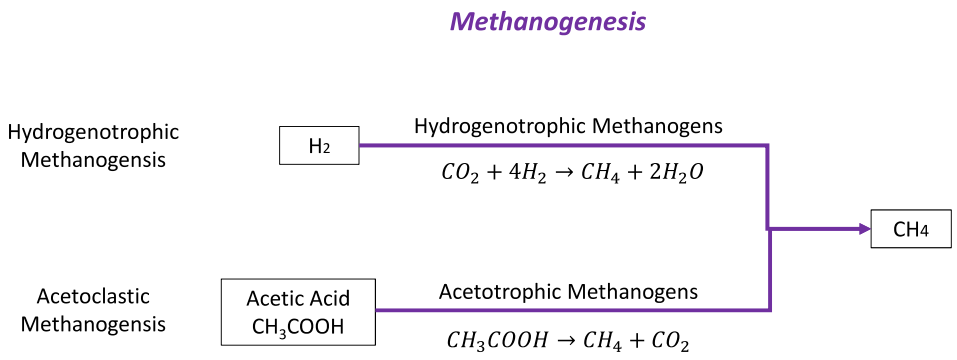

Figure 2.5: Step Diagram of Methanogenesis [9]

Acetoclastic methanogenesis is accomplished by the cleavage of the acetate methyl group to generate methane [8]. The hydrogenotrophic methanogenesis helps to keep a low hydrogen pressure by removing the H_2 produced during acidogenesis and acetogenesis. During hydrogenotrophic methanogenesis the methane is produced by a reduction of carbon dioxide using the hydrogen gas [10].

Methanogenic microorganisms, called methanogens [11], typically require a higher pH than the previous stages of anaerobic digestion and have a significantly lower

regeneration rate, which can be between 5 and 16 days [7]. The methanogens are extremely sensitive and can be affected by temperature, pH fluctuations, and high loading rates. A high loading can lead to increased concentration of volatile acids because the methane bacteria cannot break down the acids as fast as they are being produced, which can lead to digester imbalance and inhibit methanogenesis [6]. There are also many other factors that inhibit methanogens such as intermediate products and high concentration of substrate [5]. For these reasons, methanogens are likely to be the most sensitive out of all of the anaerobic digestion processes [7]. These factors cause methanogenesis to be difficult to model and the amount of methane produced is often unknown.

2.2.0 Environmental Conditions

Due to the sensitivity of the bacteria associated with the anaerobic digestion process, it is important to strive for ideal environmental conditions within the digester. These environmental conditions include temperature, pH, nutrient concentration, concentration of toxic substances, and the mixing that occurs. In general, the conditions for anaerobic digestion that lead to optimum processes performance include [6]:

- Anaerobic conditions
- Mesophilic temperatures in the range of 30°C to 38°C
- pH range of 6.6 to 7.6
- Sufficient biological nutrients
- Absence of toxic substances
- Adequate mixing

Anaerobic conditions must be maintained for anaerobic treatment because the methane forming organisms could die in the presence of oxygen, hindering the operation of the digester. This environmental condition causes the need for a closed digestion tank, which is also beneficial for collecting the methane gas produced [6]. If small amounts of oxygen entered the tank, it is most likely that the surface level would only be affected while the rest of the tank would continue the digestion, but it is best to avoid this if possible.

Anaerobic digestion can be operated at psychrophilic (20-25°C), mesophilic (30-38°C), and thermophilic (49-57°C) temperatures [12]. Mesophilic temperatures are recommended as the ideal temperature range for anaerobic digestion because they result in the most efficient operation. When temperatures are higher than the mesophilic range, large amounts of additional heat are required to maintain the temperature. This heat requirement may offset any advantages obtained by faster rate reactions, therefore most treatment plants are not designed to operate higher than the mesophilic range [6]. When temperatures are lower than the mesophilic range, operation is not very efficient, methane production decreases, and detention times increase significantly [7].

Maintaining a pH range of 6.6 to 7.6 is one of the most important anaerobic conditions to maintain due to the extreme sensitivity of the methanogenic bacteria [12]. The optimum range from methanogenesis is from 7.0 to 7.2, digestion can occur outside this range but it is less efficient. If the pH drops below 6.6, the conditions become too acidic and are toxic for the methanogenic bacteria [6]. Acid-forming bacteria, used for hydrolysis and acidogenesis, are less sensitive to acidic conditions and can tolerate a pH range of 4.8 to 8.5, but optimal conditions are from 5.5 to 6.5. At the beginning of acidogenesis, acids and CO_2 are produced which decrease the overall pH of the system. Then, the methanogenic bacteria consume the

acids, which raises the pH and stabilizes the digester [12]. Therefore, the difference in pH ranges between steps is not a large concern because the bacteria stabilize it without outside influence.

Since anaerobic digestion is dependent on bacteria, sufficient amounts of nitrogen and phosphorus are required for the bacteria to achieve optimal growth. Municipal solid waste typically contains these nutrients, so it typically provides an ideal nutrient environment without alterations. Waste from other sources, such as industrial waste, might need nitrogen and phosphorus added for optimum conditions [6]. For the average biological cell, the nitrogen requirement is roughly 11% of the volatile solids weight, and the requirement for phosphorus is roughly 2% of the volatile solids weight [6].

Another important environmental condition is the absence of toxic substances. These substances can include sulfides, heavy metals, salts, volatile acids, and high concentrations of ammonia [6, 13]. Sulfides can be present in anaerobic digestion due to entering with the raw waste, or from biological production in the digester due to the reduction of sulfates and sulfur-containing compounds. Sulfides can either be in the insoluble, soluble, or gaseous hydrogen sulfide form. Insoluble sulfides precipitate from the solution and are typically not harmful to the microorganisms. Soluble sulfides form a weak acid, which could ionize depending on the pH of the system. The gaseous hydrogen sulfide will escape with the digester gas produced [14]. The distribution of sulfides in dependent on the pH and the amount of gas produced, with the higher the gas production, the higher the number of sulfides that will leave the solution as a gas, and the lower the concentration remaining in the solution. The concentrations of soluble sulfides that can be tolerated is from 50 to 100 mg/L, with concentrations greater than 200 mg/L being extremely toxic [14, 13].

Heavy metals have caused many digesters to fail, with even low concentrations of copper, zinc, and nickel being very toxic to the microorganism present during anaerobic treatment. Heavy metals are non-biodegradable and have the potential to accumulate to toxic concentrations [13]. The concentrations of these heavy metals that can be tolerated is dependent on the concentration of sulfides available because of the sulfides ability to combine with the heavy metals and form very insoluble sulfide salts. These salts are inert and do not have a large effect on the bacteria within the reactor [14]. When the sulfide concentration is low, only a small number of heavy metals can be tolerated, but when sulfide concentration is high, large amounts of heavy metals can be handled. Although both heavy metals and sulfides are toxic on their own, when combined they can have no detrimental effect. One mole of sulfide is required per mole of heavy metals for precipitation. Due to the molecular weights of copper, zinc, and nickel, about 0.5 mg/L of sulfide is required to precipitate 1 mg/L of these heavy metals [14]. If sufficient sulfide is not produced during waste treatment, sodium sulfide of sulfate salt can be added before anaerobic digestion to ensure efficient precipitation of heavy metals.

High concentrations of salts such as sodium, potassium, calcium, and magnesium are frequently the cause of inefficiency or failure in anaerobic treatments [14]. For municipal solid waste the concentration of these salts is typically rather low so they would not inhibit anaerobic digestion. It has been reported that the cation part of the salt is typically associated with toxicity, rather than the anion. The concentrations of salts, shown in mg/L, that are considered stimulatory or inhibitory are shown in Table 2.1 [14].

Table 2.1: Stimulatory and Inhibitory Concentrations of Salt Cations in mg/L [14]

Cation	Stimulatory	Moderately Inhibitory	Strongly Inhibitory
Sodium	100 – 200	3,500 – 5,500	8,000
Potassium	200 – 400	2,500 – 4,500	12,000
Calcium	100 – 200	2,500 – 4,500	8,000
Magnesium	75 – 150	1,000 – 1,500	3,000

The stimulatory concentrations are desirable as they allow optimum efficiency of the system. Moderately inhibitory concentrations are those that can be tolerated, but the organisms require an acclimation period. If these concentrations are introduced suddenly, they will significantly inhibit the anaerobic digestion process. The concentrations listed as strongly inhibitory are those that will significantly slow down the process, resulting in lower efficiency and higher detention times [14]. Reducing salt concentrations in anaerobic digestion can be difficult, so it is typically recommended to dilute the waste to remove this inhibition [14].

Volatile acids represent the intermediate products that are most important in anaerobic digestion, as most of the methane produced during this process is a result of the fermentation of these acids by the methane bacteria. In optimum steady-state conditions, the methane bacteria will use up the volatile acids as quickly as they are being produced. If there is an imbalance of methane bacteria or inadequate environmental conditions that slow down the bacteria, they will not use the acids as rapidly as they are produced [6]. This causes a build-up of volatile acids, which is one of the first indicators of an unbalanced digester. It is important to note that a high concentration of volatile acids is not necessarily toxic, and it is not the cause of digester imbalance, but instead is the result of an imbalanced digester [6]. If

there is a high concentration of volatile acids, methanogenesis can also be inhibited, resulting in inefficient biogas production. High volatile acid concentration also decreases the pH of the system, which will cause further issues in the digester [6]. For this reason, the concentration of volatile acids is important to monitor.

Ammonia is typically formed from the degradation of waste containing proteins. Toxic concentrations may be reached in highly concentrated municipal waste sludge. Ammonia can be present as either the ammonium ion (NH_4^+), or as ammonia gas (NH_3). These two forms are in equilibrium with each other, while the concentration of each is dependent on the pH [14]. When the pH is 7.2 or lower, the equilibrium is shifted toward so that the NH_4^+ concentration is the inhibitory factor. At higher pH levels, the equilibrium shifts so that the NH_3 gas concentration is the inhibitory factor. The NH_3 gas is inhibitory at a much lower concentration, therefore lower pH levels are typically favored [14]. The ammonia nitrogen concentration is the sum the ammonium ion and the ammonia gas concentrations. Table 2.2 shows ammonia nitrogen concentrations and the effect they have on anaerobic treatment [14].

Table 2.2: Effect of Ammonia on Anaerobic Treatment [14]

Ammonia Nitrogen Concentration (mg/L)	**Effect on Anaerobic Treatment**
50 – 200	Beneficial
200 – 1,000	No adverse effect
1,500 – 3,000	Inhibitory at higher pH values
Above 3,000	Toxic

Concentrations between 1,500 and 3,000 mg/L can be inhibitory if the NH_3 gas is favored but can be tolerated if the NH_4^+ is favored. At concentrations greater than 3,000 mg/L the ammonia nitrogen is toxic regardless of the pH level [14].

Adequate mixing is also very important to maintain ideal environmental conditions. Mixing has many benefits including providing efficient utilization of full digester volume and preventing stratification such as floating and sedimentation. It also prevents buildup of foam, scum, and crust. Thorough mixing helps to avoid gradients in pH or temperature and effectively disperses end products and toxic material contained in the influent. Finally, mixing ensures contact between bacteria and the substrate and facilitates the release of biogas from the substrate [15]. If a digester has inadequate mixing, there is typically less contact between the bacteria and substrate, leading to low volatile solids reduction and biogas production [15]. The quality of mixing depends on the equipment used, the shape of the digester, and the speed of mixing [16]. Adequate mixing helps to ensure most of the optimum environmental conditions discussed are met are maintained within the digester.

The large number of environmental conditions that must be maintained for effect anaerobic treatment contribute to the complexity of the process. If only one environmental condition is not within the ideal range, steps in the anaerobic digestion process can be affected and efficiency of the digester will significantly decrease. Therefore, monitoring and maintaining ideal environmental conditions is one of the most important aspects of anaerobic digestion.

2.3.0 Early History of Anaerobic Digestion Modeling

Anaerobic digestion as a controlled technology has been implemented for over one hundred years. In the mid-1800s, anaerobic digestion facilities that produced methane were

used to fuel things such as streetlights in parts of Asia and Europe. The technology became more sophisticated in the 1900s, when anaerobic treatment was moved to airtight tanks that were heated and stirred independently [17]. Interest in this technology continued to grow as it became more efficient, but use of anaerobic digestion really expanded during World War II as anaerobic digestion was used in Europe in response to energy shortages. Around the same time, municipal solid waste in the United States started to be treated by anaerobic digestion. However, difficulty of maintaining the proper environment for bacterial growth soon became evident when anaerobic digesters were repeatedly failing [3]. This repeated failing led to increased research on anaerobic digestion to better understand the technology, which then led to the first model for anaerobic digestion to be developed in 1969.

Modeling the anaerobic digestion processes was a solution to understand the complexity of the system and reduce digester failure. The first mathematical model of anaerobic digestion was published in 1969 by John F. Andrews [3]. His model used ordinary differential equations to build upon empirical and theoretical research of pioneers in mathematical biology, such as Lotka, Volterra, Haldane, and Monod [3]. Andrews combined enzymatic inhibition with microbial growth to develop non-liner ordinary differential equations to simulate the continuous culture dynamics of microorganisms under rate limiting inhibition. This model considered acetoclastic methanogens as the only bacterial population and assumed all VFAs could be represented in acetic acid units [5]. This model takes into consideration the liquid, gas, and biological solid phase. The methane is considered to be completely insoluble while the carbon dioxide is considered to be partly dissolved while the rest escapes as gas. This model was successfully used to simulate digester start up and was able to predict digester failure due to temporary buildup of VFAs [5]. Andrews later

extended his model to include changes in pH which introduced time dependent and predictive characteristics. This allowed for the assessment of model uncertainty which helped to pave the way for other model-based process control of engineered systems [3].

Andrews's model considered the degradation of acetate to be the limiting step of organic matter digestion, which is the slowest step and would cause the process to fail under conditions of kinetic stress [18, 19]. During the next decade, other groups continued to build on his work to further extend anaerobic digestion models to include additional stages and processes, while still maintaining the same mass-balanced, reaction kinetics approach [3]. The models were built around the rate limiting step, although the rate limiting step was not the same for every model [19]. Hill and Barth worked to include hydrolysis and acidogenesis processes to reflect inhibition from VFAs on the methanogenesis rate. Their model considered two microbial groups, the acid formers and the acetoclastic methane formers [5]. From this, a mathematical description of the gas-liquid transfer of carbonate and ammonia and charge balancing to calculate temperature-corrected pH was developed and included in the model. This led to increased model complexity and reliance on high specification computers and programming languages [3]. The structuring of their model, which is based on a combination of microbial functions, provided a basis for mathematical modeling of biologically engineered systems that became well established in the following two decades.

Several models were then developed that provided important steps and improvements towards an overall dynamic anaerobic digestion model. This work included new inhibitions from VFAs, ammonia, and hydrogen, pH, and temperature regulations, and reducing the overall rate order for process control. All these models contributed to the development of the Activated Sludge Model No. 1 (ASM1), which was published in 1987 [3]. This model

contributed greatly to the generation of future models, including the Anaerobic Digestion Model No. 1 (ADM1).

Increased research in empirical microbiology contributed to a better characterization of anaerobic growth kinetics and understanding of principle reaction pathways. This helped improve modeling and increased development in parallel modeling [3]. Gujer and Zehnder performed an extensive study on anaerobic digestion which helped create a more structured approach at modeling [3]. Their research was built on a previously purposed structure that described substrate flux from particulate matter to methane and carbon dioxide. Their work was further developed and structured into a matrix formulation for constructing biochemical reaction models, which led to the framework for active sludge modeling. Although this was a decade before the ADM1 was published, this work contributed greatly to understanding the general structure of a complex biological model [3]. The International Water Association (IWA) Task Group for Mathematical Modeling of Anaerobic Digestion Processes used this research, as well as the work from previous models, to consolidate the anaerobic digestion process into five steps that comprise the ADM1 [4]. The ADM1 was published in 2002 and has not been updated in the past 20 years.

3.0 Anaerobic Digestion Model No. 1

3.1.0 Introduction

In 2002 the International Water Association (IWA) published the Anaerobic Digestion Model No. 1 (ADM1) to serve as a comprehensive and generic model that can be used to predict concentrations of end products in anaerobic digestion. The IWA task group has established a basic platform for modeling anaerobic digestion processes and is now considered the most accepted and widely used model [20]. The IWA describes the benefits of this model to be [4]:

- Increased model application for full-scale plant design, operation and optimization
- Further development work on process optimization and control, aimed at direct implementation in full-scale plants
- Common basis for further model development and validation studies to make outcomes more comparable and compatible
- Assisting technology transfer from research to industry

One of the main benefits that was expected to come from this model was its ability to be used in practical, industrial applications. For this reason, the model uses the main relevant processes that occur in anaerobic digestion to be as simple as possible, while still being a complete model. This model is likely to not be as accurate as some other models that were developed for specific applications, but instead is intended to be more widely applicable to anaerobic digestion in general [4].

The ADM1 uses chemical oxygen demand (COD) as the component base unit due to its use as a wastewater characterization measure in concentrated streams [4]. It is broken up into

four steps: disintegration and hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The full structure is shown in Figure 3.1 [4].

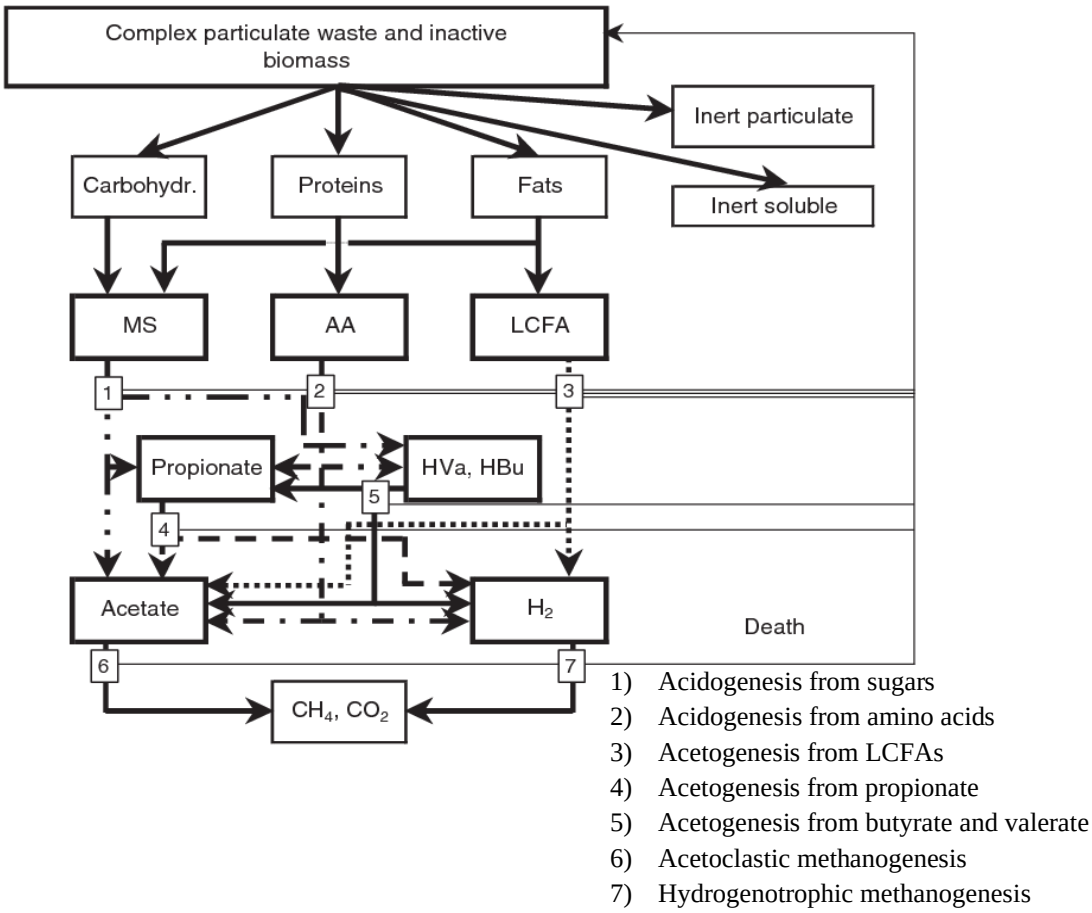

Figure 3.1: Anaerobic Digestion Processes in the ADM1, Reproduced IWA T ask Group for Mathematical Modelling of Anaerobic Digestion Processes, 2002. *Anaerobic Digestion Model No.1 (ADM1),* with permission from the copyright holders, IWA Publishing

There are a total of 29 processes, 37 fractions, and over 100 parameters required in the ADM1 [21]. The parameters, equations and coefficients for soluble and particulate components are shown in Appendix C. The large number of parameters makes the calibration of the model extremely difficult [21]. This model handles the biochemical and physico-chemical processes that take place in anaerobic digestion, as well as information on how to implement the model into a continuous-flow stirred-tank reactor (CSTR) [4].

3.2.0 Biochemical Processes

The ADM1 is broken up into three biochemical processes (acidogenesis, acetogenesis, and methanogenesis) and an extracellular disintegration and hydrolysis step. Some of these processes also have parallel reactions, making them very complex to model [4]. The cellular kinetics are described by expressions of growth, uptake, and decay. The key rate equation is substrate uptake, which is based on Monod-type kinetics to decouple growth from uptake [4]. The Monod substrate uptake is shown in Equation 3.1.

Equation 3.1: Monod-Type Substrate Uptake

$$\rho_j = \frac{K_m S_c}{K_s + S_c} X$$

Where:

- ρ_j = Kinetic rate of process (kgCOD S m^{-3} d^{-1})
- K_m = Monod maximum specific uptake rate (kgCOD S kgCOD X^{-1} d^{-1})
- S_c = Soluble component (kgCOD m^{-3})
- K_s = Half saturation value (kgCOD S m^{-3})
- X = Particulate component (kgCOD m^{-3})

Disintegration and hydrolysis are the first steps that take place in anaerobic digestion. The non-biological disintegration step is included as the first process to allow for more diversity of application, and to include a lysis of biological sludge and complex organic material [4]. Most anaerobic digestion models do not include a disintegration step, but the IWA task group chose to include it to represent a pool of composite organic material, which is beneficial for waste-activated and primary sludge digestion [4]. The complex composite particulate waste is assumed to be homogenous, which would disintegrate into carbohydrates,

lipids, and proteins. Adding the disintegration step allows for the primary substrate to be represented with lumped kinetic and biodegradability parameters [4]. The products of disintegration include carbohydrates, proteins, lipids, inert particulate material, and inert soluble material. These products of disintegration are then used as substrate for the hydrolysis step.

The hydrolysis is catalyzed by enzymes that are produced from the organisms within the system. These enzymes break down carbohydrates, proteins, and lipids into soluble monomers, such as monosaccharides, amino acids, and long chain fatty acids (LCFAs) [4]. For this model, hydrolysis occurs when the organisms attach to a particle, produce enzymes in the vicinity of the particles and benefit from soluble products released by the enzymatic reaction [4]. Both disintegration and hydrolysis are described by first order kinetics in the ADM1 [22].

The next step that occurs is acidogenesis, which is an acid-producing microbial process without an additional electron acceptor. This process includes the degradation of monosaccharides and amino acids into simpler products [4]. The degradation of LCFAs is an oxidation reaction with an external electron acceptor, and therefore is included in the next step, acetogenesis. Since acidogenesis can occur without an additional electron acceptor, the reactions can occur at high hydrogen or formate concentrations [4]. The IWA task group broke acidogenesis up into two parts, separating into the acidogenesis from monosaccharides, and acidogenesis from amino acids.

Glucose was used at the monomer to model acidogenesis from monosaccharides. Other monomers, such as fructose and pentoses will have similar stoichiometric yields if used [4].

The products formed from the degradation of monosaccharides and their respective stoichiometric reaction is shown in Table 3.1 [4].

Table 3.1: Products from Glucose Degradation [1]

	Products	**Reaction**
(i)	Acetate	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$
(ii)	Propionate	$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$
(ii')	Acetate, Propionate	$3C_6H_{12}O_6 \rightarrow 4CH_3CH_2COOH + 2CH_3COOH + 2CO_2 + 2H_2O$
(iii)	Butyrate	$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$
(iv)	Lactate	$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$
(v)	Ethanol	$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$

Reaction (ii) was included because it has been used in several other models, but the IWA task group recommends using reaction (ii') instead. This is because no organism that produces only propionate has been cultured, all organisms produce both propionate and acetate with CO_2 as a by-product. Also, oxidizing formate is thermodynamically unfavorable except at high H_2 partial pressure and is therefore inconsistent with the release of formate by organisms fermenting monosaccharides [4].

The yield of amino acids from hydrolysis of proteins is directly dependent on the protein primary structure. There are 20 common amino acids that be produced. These amino acids go through fermentation during acidogenesis [4]. The main pathway for amino acid fermentation is Strickland oxidation-reduction reactions but amino acid fermentation can also occur from oxidation of a single amino acid with hydrogen ions or carbon dioxide as the external

electron acceptor. This is useful in modeling amino acid acidogenesis because the stoichiometric yields of products can be predicted based on the amino acid mixture. These products are typically normal organic acids [4]. Figure 3.2 shows a coupled Strickland reaction of alanine and glycine [23].

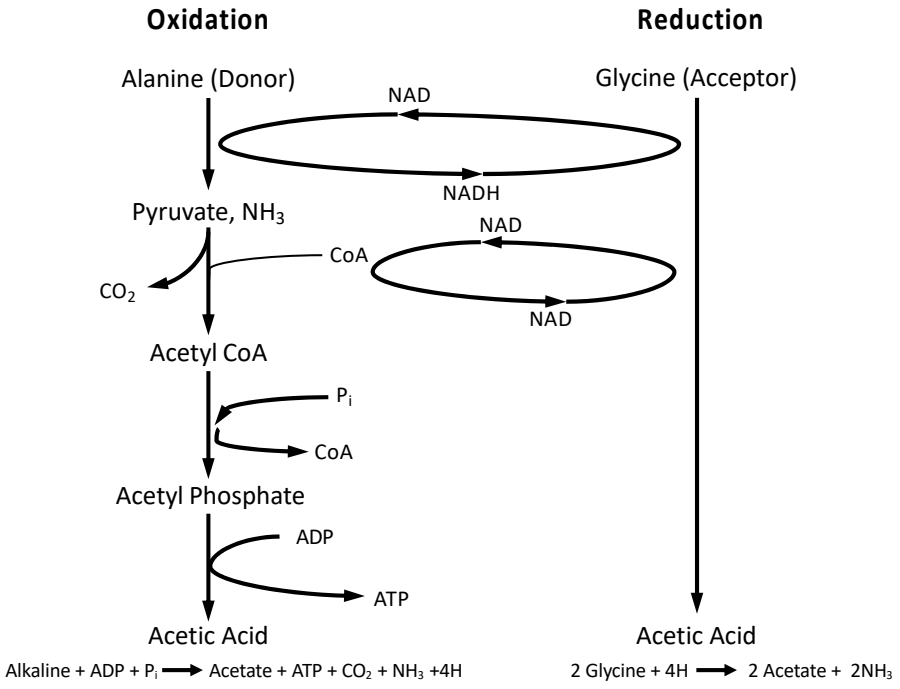

Figure 3.2: Couple Strickland Reaction of Alanine and Glycine

Where:

- NAD is nicotinamide adenine dinucleotide
- NADH is nicotinamide adenine dinucleotide with hydrogen
- CoA is coenzyme A
- Pi is inorganic phosphate
- ADP is adenosine diphosphate
- ATP is adenosine triphosphate

After acidogenesis, the higher organic acids and LCFAs are degraded into acetic acid and hydrogen by acetogenesis. Acetogenesis requires an additional electron acceptor such as hydrogen ions to produce hydrogen gas. These electron carriers are required to be kept at a low concentration for the reaction to be thermodynamically possible [4]. Formate can also be an electron carrier for acetogenesis, but the ADM1 does not include it because formate has different influences on the physico-chemical system than hydrogen [4]. The hydrogen gas that is produced is consumed by the methanogenic organisms during hydrogenotrophic methanogenesis, which occurs simultaneously with acetogenesis [4]. The reaction for hydrogenotrophic methanogenesis is shown in Equation 3.2 [8].

Equation 3.2: Hydrogenotrophic Methanogenesis Reaction

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

The carbon dioxide is reduced with the hydrogen gas to produce methane. Acetoclastic methanogenesis is the final biochemical step in the ADM1, where acetate is cleaved to form methane and carbon dioxide. The reaction is shown in Equation 3.3 [4].

Equation 3.3: Acetoclastic Methanogenesis Reaction

$$CH_3COOH \rightarrow CH_4 + CO_2$$

About two thirds of the methane produced during anaerobic digestion come from acetoclastic methanogenesis, while the rest is produced during hydrogenotrophic methanogenesis [7]. There are two genera used in the model that utilize acetate to produce methane, *Methanosarcina* and *Methanosaeta*. *Methanosarcina* dominates above 10^{-3} M acetate while *Methanosaeta* dominates below this acetate level. When comparing the two, *Methanosaeta* has lower yields, higher Monod uptake rate values, lower half saturation values, is more sensitive to pH, and requires two moles of ATP while *Methanosarcina*

requires only one. For these reasons, *Methanosarcina* has a higher growth rate and requires a shorter detention time [4]. Methanogenesis is the last biochemical process that takes place during anaerobic digestion, and the ADM1 then goes on to describe the physico-chemical processes that occur.

3.3.0 Physico-chemical Processes

Physico-chemical processes are described as the non-biological processes that occur during anaerobic digestion. There are three types of processes including liquid-liquid, liquid-gas, and liquid-solid processes. The processes are listed in order of relative kinetics rates with liquid-liquid being rapid and liquid-solid being slow [4]. Liquid-solid processes are not included in the ADM1 because of difficulties in implementing them, but this does not have a large impact on the model because only a limited number of systems have high levels of inorganic solids. The other physico-chemical processes are extremely important to model in anaerobic digestion for three reasons. One reason is because a number of biological inhibition factors can be expressed. Another reason is due to the fact that major performance variables, such as gas flow and carbonate alkalinity, are dependent on correct estimation of physico-chemical processes. And lastly, pH control is typically a major operating cost, and in this case the control set point and inputs are calculated from physico-chemical estimation [4].

The liquid-liquid processes include association and dissociation with hydrogen and hydroxide ions, often called acid-base reactions. There are a number of compounds that have a dissociation coefficient (pK_a value) close to the operating pH of anaerobic systems that can be used [4]. Since the association/dissociation processes are so rapid, they are often referred to as equilibrium processes and can be represented as either differential equations or with an implicit set of algebraic equations. There are two different approaches that can be used to

formulate the equations: the charge balance and the tableau method. The IWA task group recommended using the charge balance method because it is easier to understand [4]. The charge balance method in the ADM1 is shown in Equation 3.4.

Equation 3.4: ADM1 Charge Balance [4]

$$S_{Cat^+} + S_{NH_4^+} + S_{H^+} - S_{HCO_3^-} - \frac{S_{Ac^-}}{64} - \frac{S_{Pr^-}}{112} - \frac{S_{Bu^-}}{160} - \frac{S_{Va^-}}{208} - S_{OH^-} - S_{An^-} = 0$$

Where:

- S represents the soluble components
- S_{Cat^+} and S_{An^-} represent metallic ions such as Na^+ and Cl^-

If using the algebraic set of equations, the combined concentration of the acid-base pair should be expressed as a dynamic state variable, meaning the free form and ionic form are lumped together. The differential equational method and the algebraic method of solving acid-base reactions can be used separately or as a combination of both. The method chosen does not have a large effect on the end results of the ADM1 but does affect how subsequent equations are calculated [4].

The gas components considered in the ADM1 are H_2, CH_4, and CO_2, all of which have relatively low solubility. The liquid and gas phases in contact will reach steady-state with respect to each other [4]. The resistance to transfer of insoluble gases is mainly in the liquid phase, therefore dynamic gas transfer equations are required to describe the liquid-gas transfer [4]. Equation 3.5 shows the liquid-gas transfer used in the ADM1.

Equation 3.5: Dynamic Liquid-Gas Transfer [4]

$$\rho_{T,i} = k_L a(S_{liq,i} - K_H p_{gas,i})$$

Where:

- $\rho_{T,i}$ = Specific mass transfer rate of gas i (kgCOD m^{-3} d^{-1})
- $k_L a$ = Overall mass transfer coefficient multiplied by the specific transfer area (d^{-1})
- $S_{liq,i}$ = Liquid phase concentration of gas I (kgCOD m^{-3})
- K_H = Henry's law coefficient (M bar^{-1})
- $p_{gas,i}$ = Gas phase partial pressure of gas I (bar)

Since the transfer of all three gases is liquid-film controlled, and the diffusivities are similar, the k_La values should be similar in magnitude. Values of k_La depend greatly on mixing, temperature, and liquid properties. In order to simplify this process, the IWA task group recommends using the same k_La value for all three gases [4].

3.4.0 Model Implementation in a Single Stage Continuous-Flow Stirred-Tank Reactor

The ADM1 provides model implementation for a single stage CSTR, which is the most common type of reactor used for anaerobic digestion. Single stage anaerobic digestion means that there is one treatment stage that is operated at a one temperature, typically in the mesophilic range. The alternative to this is two-stage anaerobic digestion that separates the process into a thermophilic pre-treatment followed by the mesophilic main treatment, which increases the efficiency of the system [24]. A schematic of a typical CSTR is shown in Figure 3.3 [4]. The subscripts of the soluble and particulate variables correspond to the component shown in the ADM1 matrices in Appendix C.

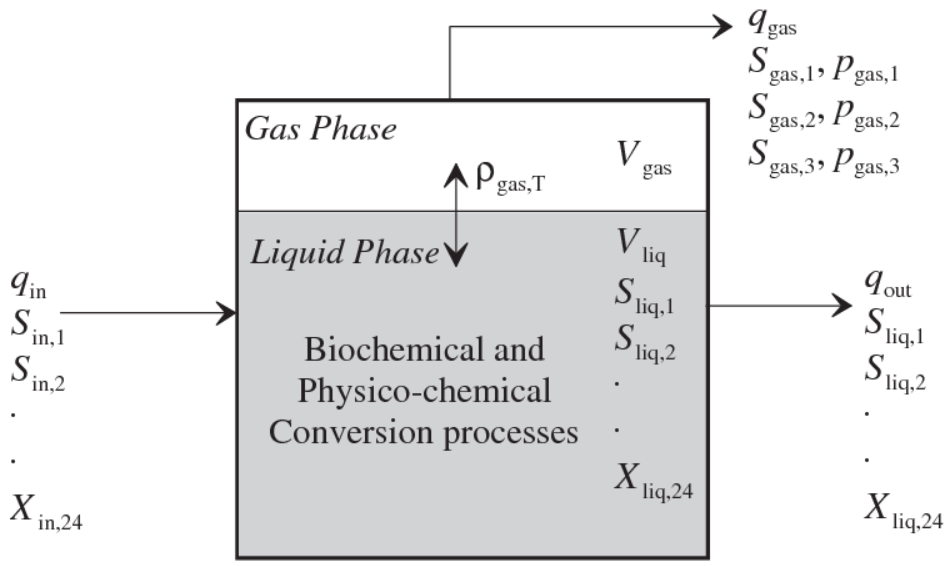

Figure 3.3: Schematic of CSTR, Reproduced IWA T ask Group for Mathematical Modelling of Anaerobic Digestion Processes, 2002. *Anaerobic Digestion Model No.1 (ADM1),* with permission from the copyright holders, IWA Publishing

In the schematic, q is the flow rate, S is the concentration of soluble components, X is the concentration of particulate components, and V is the volume. Typical anaerobic digestion systems consist of a stirred-tank reactor with liquid volume and a sealed gas headspace, with the gas removed for downstream utilization [25]. Any equations presented for the CSTR implementation can also be used for batch and semi-batch mixed reactors [4]. The equations formed depend on whether the acid-base reactions were implemented as implicit algebraic equations or as differential equations. If implicit algebraic equations, the solution requires a differential and algebraic equation solver. If differential equations were used then only a differential equation solver is required, but an increased number of errors are introduced if using this method [4].

For the liquid phase, the mass balance can be written as in Equation 3.6.

Equation 3.6: Liquid Phase Mass Balance [4]

$$\frac{dVS_{liq,i}}{dt} = q_{in}S_{in,i} - q_{out}S_{liq,i} + V\sum_{j=1-19}\rho_j v_{i,j}$$

Where:

- $\sum_{j=1-19} \rho_j v_{i,j}$ is the sum of the specific kinetic rates for process j multiplied by $v_{i,j}$
- ρ_j = Kinetic rate of process j (kg soluble COD/m^3 d)
- $v_{i,j}$ = Rate coefficient for component i on process j (kg COD/m^3)

This equation includes all factors that cross the boundary of the system to determine the accumulation of liquid soluble material over time. The gas phase equation is similar, except it does not contain an influent flow. The gas phase mass balance is shown in Equation 3.7.

Equation 3.7: Gas Phase Mass Balance [4]

$$\frac{dS_{gas,i}}{dt} = -\frac{S_{gas,i} q_{gas}}{V_{gas}} + \rho_{T,i} \frac{V_{liq}}{V_{gas}}$$

This equation includes all components of the gas that cross the system boundary to determine the accumulation of soluble material in the gas phase over time.

3.5.0 Limitations

In order to reduce the complexity of the ADM1, some processes were excluded from the model. These processes include [24]:

- Production of lactate from glucose fermentation
- Sulfate reduction and sulfide inhibition
- Nitrate reduction
- LCFA inhibition
- Competitive uptake of H_2 and CO_2 between hydrogenotrophic methanogens and homoacetogenic bacteria

- Solids precipitation due to high alkalinity or other chemical precipitation reactions

Lactate is an intermediate produced from the fermentation of glucose, and most of the monosaccharide substrate degrades via lactate. This degradation occurs very quickly so lactate is typically one seen in the digester when there is a significant overload of substrate. Lactate also has the same stoichiometry as glucose so omitting this does not affect the biological reaction stoichiometry. For these reasons the production of lactate from glucose fermentation was not included in the ADM1 [4].

Sulfate reduction, sulfide inhibition, and nitrate reduction were not included because of their complexity. When sulfur reduction compounds are present in anaerobic digestion they compete with hydrogenotrophic, acetogenic, and aceticlastic organisms and almost all biological and physico-chemical processes are affected by this competition for substrate, which occurs at low levels of sulfate and sulfide. The ADM1 should not be used to model systems with low amount of sulfide in the substrate, but this should not be a significant problem for modeling sewage waste [4]. Nitrate reduction occurs during denitrification, which is performed by a number of anaerobic bacteria. This can cause a decrease in the overall production of methane, and instead produce N_2 and more CO_2. This process also introduces competition for substrate with other microbial groups and inhibition of methanogenesis due to nitrogen oxides. Although nitrate reduction can have a significant impact on the system, the interactions that occur were deemed too complex to include in the ADM1 [4].

LCFA inhibition occurs when the substrate is lipid-rich, which is common for manure and oil waste. This inhibition is complex and is not considered to be a significant concern for

sewage waste, so it is not included in the ADM1. Adaptation to high concentration of LCFAs can occur which also reduces the concern of this inhibition, but an acclimation period is required to avoid digester failure [4].

Homoacetogens reduce carbon dioxide with hydrogen to produce acetate and therefore compete with the methanogens for this substrate. At mesophilic temperatures, homoacetogens are considered non-dominant in anaerobic conditions because they have higher H_2 thresholds than methanogens [4]. However, at lower operating temperatures the homoacetogens play a significant role in hydrogen oxidation because methanogens have low activity at low temperatures. Since most anaerobic systems are not operated lower than mesophilic temperatures this was not included in the ADM1, but it is recommended to include this inhibition in extended models [4].

Solids precipitation involves transforming cations and anions into neutral inorganic forms, with the most important precipitates being $CaCO_3$ and $Mg(OH)_2$. Solids precipitation is not included in the ADM1 because of its complexity, the large number of precipitation cations, and systems with high levels of calcium and magnesium are not common for sewage sludge. However, it is recommended to include solids precipitation in future models in order to accurately model the physico-chemical processes [4].

Some other limitations have emerged when trying to integrate the ADM1 with additional wastewater treatment plant models. The Activated Sludge Models (ASMs) use different states than the ADM1, and therefore slightly different variables. When using the ASM with the ADM1, a translator must be used to translate ASM states to ADM1 states [26]. Also, the ASMs do not include the acid-base equilibrium equations that the ADM1 does. In order to combat these differences, it is recommended to use equations based on the total of the acid

and base components, rather than having different equations for each acid and base. This method was used in the development of the Benchmark Simulation Model No. 2 (BSM2) [27].

In 2014, the BSM2 was published to act as a plant-wide model, that integrated the ASM and ADM1 to model the activated sludge and anaerobic digestion sections, respectively [27]. The development of this model identified an issue with the complex organic state (X_c) being used as a primary input in the ADM1. This is because combining the nitrogen content, carbon oxidation state, and degradability into one value removes the ability to separate these values for primary and activated sludge, which has the potential to disrupt plant-wide modeling [26]. This X_c value is used in the disintegration step in the ADM1, which is a step that is often not included in other anaerobic digestion models. The BSM2 uses carbohydrates, proteins, and lipids as primary inputs instead, which changes the two-step process of disintegration followed by hydrolysis into one-step that involves both processes [26]. This is considered a limitation of the ADM1 because one of the goals stated by the IWA was to be able to integrate the ADM1 with other models to serve as a complete model for full-scale wastewater treatment.

These limitations in the ADM1 become an issue when trying to expand the model to include broader purposes and integrate it with other models, but they do not have a large impact on the results of the model when using it alone. Other issues arise when currently operating wastewater treatment plants attempt to use this model. This is because of the complexity of the ADM1 and a lack of data at a typical wastewater treatment plant. The long list of required inputs is not easily available to wastewater treatment plants without additional testing. Therefore, this limitation has the greatest impact on the applicability of this model, as

it is not being used by wastewater treatment plants to determine operating parameters, which was one of the intended uses of the model.

3.6.0 Updates to the ADM1

Although there has been no widely accepted generic update to the ADM1 since its original publication, there has been some updates that provide improvements to the ADM1. These updates include modifications of specific parameters to simplify the modeling process [28]. There have also been modifications done that stress different components of anaerobic digestion modeling, such as focusing on the evolution of hydrogen and methane within the system [1, 29], stressing specific operative steps [30], or including new inhibitions [31]. In many cases, hydrogenotrophic methanogenesis has been omitted in simplified models since it only produces around 30% of the methane [28]. There has also been research to expand the ADM1 to process different substrates, such as waste from olive mills [22], maize silage [32], and plant matter [2].

Some updates to the ADM1 have focused on simplifying parameters to be more applicable to full-scale wastewater treatment plant operation [30], but most models developed are still based on experimental data which creates limitation when using the model for practical applications [28]. Although these updates have provided important steps and research regarding simplifying the model, the application that results in the greatest simplification is applying the model to steady-state conditions. A review of steady-state anaerobic digestion models is described the following chapter.

3.7.0 Conclusions

The ADM1 is comprehensive model of the entire anaerobic digestion process designed to predict end products and be used as the basis for full-scale anaerobic digestion modeling. The

model is broken up into biochemical and physico-chemical processes in order to be as complete as possible, but this makes the model extremely complex with a long list of required parameters. Despite its complexity, the ADM1 has been repeatedly proven to be an accurate and complete way to model anaerobic digestion and is a very good model in terms of its functionality.

Although this model includes all processes of anaerobic digestion, there are still some limitations of the ADM1. These limitations impact the ability of the model to be used at full-scale wastewater treatment plants due to the complexity of the system. No other complete anaerobic digestion models have been widely accepted as a generic model since the release of the ADM1 in 2002, but there have been updates to the ADM1 that provide simplifications. These updates include focusing on specific aspects of the anaerobic digestion processes, reducing required parameters, or changing the substrate used. Although these updates do simplify the overall model, the ADM1 is still used as the basis for anaerobic digestion modeling despite its limitations. Simplifying the ADM1, while still maintaining the completeness of the model would greatly increase the ability of it to be used by current wastewater treatment plants.

4.0 Simple Steady-State Anaerobic Digestion Model

4.1.0 Introduction and Rationale for a Steady-State Model

A simple steady-state model for anaerobic digestion is possible due to the desire to model optimum environmental anaerobic conditions. The environmental conditions that lead to optimum performance are discussed in detail in Section 2.2. Steady-state means that the digester is at a constant volume, and does not change over time. In other words, the flow rate into the digester is equal to the flow rate out of the digester. Therefore, the concentration of substrate leaving the digester is equal to the concentration of substrate within the digester and there is no accumulation of substrate over time. Steady-state modeling assumes that all processes are working as efficiently as possible and there is a constant production of biogas.

In order to maintain the desired environmental conditions, such as temperature, pH, sufficient nutrients, and absence of toxic materials, it is important that the digester remains balanced [6]. This means that there should not be any abrupt changes to any part of the system to ensure the bacteria remains stable. The environmental conditions and bacteria are directly related to one other, meaning that if an environmental condition is altered, the bacteria population will be affected, and if the bacteria population is affected, other environmental conditions will be disrupted. If the digester is not operated at steady-state, there will be an accumulation of substrate within the digester, which will lead to environmental conditions being altered. Since optimum environmental conditions lead to the best yield of biogas, every anaerobic digester operation should strive for these conditions. The digester with the best yields will be the digester that is operated at steady-state, or as close to steady-state as possible. Therefore, modeling the anaerobic digestion system at steady-state is an appropriate assumption and will greatly simplify the modeling process.

Steady-state modeling does not give a lot of information about the short-term behavior of the digester [33]. This means that daily fluctuations within the digester will not be as clearly shown with this model, as they would with a more complex model such as the Anaerobic Digestion Model No. 1 (ADM1). However, in many cases this behavior is not of interest because it does not have a large impact on digester performance. Therefore, steady-state modeling is sufficient in most cases [33]. The simple methane prediction from volatile solids data that is possible with steady-state modeling is sufficient for most wastewater treatment plants.

4.2.0 Published Steady-State Anaerobic Digestion Models

The purpose of creating an anaerobic digestion model that runs at steady-state conditions is to simplify implementing the modeling process. One of the reasons the ADM1 is so complex is because it requires a large number of parameters, operating at steady-state reduces the number of parameters required. The ADM1 has been applied to steady-state conditions in some cases, which results in the following equations [34].

Equation 4.1: Steady-State ADM1 Soluble Component Model

$$S = \frac{D k_s}{\mu_m - D}$$

Where:

- S = Outlet concentration (kg/m^3)
- D = Dilution rate (1/day)
- k_s = Saturation constant (kg/m^3)
- μ_m = Maximum specific growth rate (1/day)

Equation 4.2: Steady-State ADM1 Particulate Component Model

$$X = Y\left(S_{in} - \frac{Dk_s}{\mu_m - D}\right)$$

Where:

- X = Concentration of particulate components leaving the digester (kg/m^3)
- Y = Yield of biomass on substrate (kg X/kg S)
- S_{in} = Inlet concentration (kg/m^3)

The equations presented are based on Monod kinetics, which is consistent with the non-steady-state model. These equations results are much simpler when compared to the non-steady-state model. The presented equations do not directly calculate the production of methane, but it can be determined using the gas flow rate and the molar fraction of methane in the gas phase [34]. The parameters required for this model include the inlet substrate concentration, the yield coefficient, the specific growth rate, the saturation constant, and the dilution rate which is dependent on flow rate and volume of the liquid. This steady-state model was determined to successfully reproduce the results of the ADM1 [34].

A steady-state model can also be developed assuming first-order kinetics. The resulting equations for operating in a continuous-flow stirred-tank reactor (CSTR) are shown below [35].

Equation 4.3: Steady-State Estimation of Outlet Concentration

$$S = \frac{S_{in}}{1 + k_h\theta}$$

Equation 4.4: Steady-State Estimation of Methane Yield

$$B = B_o \frac{k_h \theta}{1 + k_h \theta}$$

Where:

- B = Methane yield (m^3 CH_4/kg VS)
- B_0 = Ultimate methane yield (m^3 CH_4/kg VS)
- k_h = Kinetic coefficient (1/day)
- θ = Hydraulic retention time (HRT) (days)

These equations use a simple kinetic coefficient in order to estimate the production of methane. The kinetic coefficient depends of experimental conditions and biomass to substrate ratios. The ultimate methane yield depends on composition of the sludge and is equal to the total amount of methane that could be produced at optimum conditions [35]. This model is beneficial because it includes fewer parameters, but some of the parameters are difficult to obtain such as the ultimate methane yield because it depends on many different sludge conditions [36].

Another steady-state model was introduced in order to predict the volumetric methane production. The equations used for this analysis are based on Contois kinetics and are shown below [36].

Equation 4.5: Estimation of Methane Yield

$$B = B_0 \left(1 - \frac{K}{\mu_m \theta - 1 + K}\right)$$

Equation 4.6: Volumetric Methane Production

$$\gamma_V = B_0 L\left(1 - \frac{K}{\mu_m \theta - 1 + K}\right)$$

Where:

- K = Kinetic parameter
- γ_V = Volumetric methane production (m^3 CH_4/m^3)
- L= Volatile solids loading rate (kg VS/m^3)

This model estimates the methane production by finding the methane yield conversion factor based on the growth rate and HRT using pig manure as the substrate. This will cause some differences when compared to models used for municipal sludge, but the procedure used is the same [36]. From this analysis it was determined that the kinetic parameter, K, is consistent around 0.6 for low influent volatile solids concentrations, but increases sharply for higher volatile solid concentrations [36]. The ultimate methane yield and maximum specific growth rate are the same as previously presented. This model is more complex than the proposed first-order model, but it is still significantly less complex than non-steady-state models.

4.3.0 Modeling Optimum Steady-State Conditions

The desired outcome of creating a model that runs at steady-state conditions is to create a simple relationship to easily calculate the concentration of biodegradable volatile solids flowing through the digester, since these are the components that eventually become methane and the maximum methane yield of substrate depends on the biodegradability of the substrate [37]. The biodegradable volatile solids are assumed to be equal to the volatile solids destroyed, since these are the solids are that are being degraded in the digester. Data on

volatile solids are used as a parameter to estimate the volatile solids destroyed because these data are routinely collected by wastewater treatment plants. In order to determine the volatile solids destruction, a steady-state model must be created to predict the volatile solids leaving the digester. The proposed steady-state model for anaerobic digestion in a CSTR is shown in Equation 4.7.

Equation 4.7: Simple Steady-State Model

$$0 = QS_{in} - QS - k_m VS$$

Where:

- Q = Flow rate (m^3/day)
- S_{in} = Concentration of volatile solids entering the digester (kg/m^3)
- S = Concentration of volatile solids leaving the digester (kg/m^3)
- k_m = Metabolism factor (1/day)
- V = Volume of the digester (m^3)

Substituting $Q\theta$ for V and rearranging Equation 4.7 to solve for the concentration of volatile solids leaving the digester results in Equation 4.8 [35].

Equation 4.8: Volatile Solids Leaving the Digester

$$S = \frac{S_{in}}{1 + k_m \theta}$$

For a steady-state digester, the time in which the volatile solids stabilized is equal to the time in which the solids are destroyed, which is the HRT. This equation uses a metabolism factor that is dependent on the specific digester to estimate the volatile solids leaving the digester. This is the same as the first order steady-state model that was previously explained.

The volatile solids destroyed, which are equal to the biodegradable volatile solids, can then be found from the Equation 4.9.

Equation 4.9: Volatile Solids Destroyed

$$VSD = S_{in} - S$$

Where:

- VSD = Volatile solids destroyed (kg/m^3)

These volatile solids destroyed will then be used to estimate the production of methane during anaerobic digestion, discussed in the following section. When comparing this steady-state model to the other steady-state models discussed, there are the most similarities with the first-order model. The equation for the solid concentration leaving the digester is exactly the same both models, and the methane production estimation is similar but uses a slightly different approach. The full input parameters and intended application of each introduced steady-state model is shown in Table 4.1 [34, 35, 36].

Table 4.1: Comparison of Steady-State Models

	Proposed Steady-State Model	**Steady-State ADM1 – Monod Kinetics [34]**	**Steady-State Volumetric Methane Model – Contois Kinetics [36]**	**Steady-State Digestion Model – First Order Kinetics [35]**
Input Parameters	Flow rate, HRT, volatile solids in, metabolism factor	Inlet substrate concentration, yield coefficient, specific growth rate, saturation constant, flow rate, volume of the liquid.	Ultimate methane yield, specific growth rate, HRT, kinetic parameter, volatile solids loading rate	Ultimate methane yield, kinetic coefficient, HRT, volatile solids in
Application	Municipal sludge for HRTs greater than 10 days	Municipal sludge	Pig manure	Municipal sludge

All of these models require the concentration of substrate into the digester as well as some kind of kinetic coefficient. The Monod and Contois kinetic equations require the specific growth rate of the microorganisms, which introduces some complexity in determining this factor. It is also interesting to note that the Monod kinetics is not dependent on HRT, while all of the other models are [34]. Overall, all of the presented models follow the same general structure for determining solids leaving the digester and the methane production. From the similarities between models, it can be determined that the proposed steady-state model follows first-order kinetics. The proposed CSTR steady-state model will be used to predict the concentration of methane produced.

4.4.0 Methane Production and Metabolic Conversion of Biodegradable Solids

The methane produced during anaerobic digestion is mainly generated from the volatile acids within the system. These acids are produced from the volatile solids entering the digester, which can also be referred to as the biodegradable volatile solids. This relationship allows for a simple way to predict the steady-state methane production in the system based on the number of volatile solids destroyed within the digester since these are equal to the biodegradable volatile solids. The relationship is shown in Equation 4.10 [37, 38].

Equation 4.10: Methane Prediction from Volatile Solids

$$\frac{dCH_4}{dt} = K\frac{dS}{dt}$$

Where:

- dCH_4/dt = Methane production rate (m^3/day)
- K = Conversion factor (m^3 CH_4/kg VS)

- dS/dt = Volatile solids destroyed (kg/day)

The amount of volatile solids destroyed over time can be determined from the loading of volatile solids entering and leaving the digester, which is found by multiplying the flow rate with the concentration of volatile solids. The conversion factor, K, is typically estimated based on the relationship between methane production and the chemical oxygen demand (COD) of the sludge. Determining the COD is dependent on the composition of the sludge within the digester. Therefore, the COD content for the specific sludge is not typically known without performing lab analyses and most wastewater treatment plants do not know this information based on observed data. Typical values of K range from 0.2-0.6 m^3 CH_4/kg VS for municipal solid waste [12]. A K value of 0.6 m^3 CH_4/kg VS is used for optimum conditions, where the most amount of methane possible is generated from volatile solids destruction.

Being able to estimate the methane content of the biogas produced is extremely beneficial for wastewater treatment plants due to the ability to use it for energy production. Since anaerobic digestion is a closed process, it is very easy to capture the biogas generated, which is mostly carbon dioxide and methane with small amounts of other trace gases [39]. The biogas can then be used as an electricity or heat source for other parts of the wastewater treatment plant. It has been reported that approximately 78% of the total energy used in wastewater treatment plants could be potentially recovered by anaerobic digestion [20]. Utilizing the biogas is beneficial for the environment because it offsets the need to use fossil fuels to generate electricity [40]. It could also have cost saving benefits because less energy would need to be purchased from other sources if the biogas is being used to for energy. For these reasons, knowing the composition of the biogas is beneficial for estimating its potential

for energy production. However, most wastewater treatment plants do not measure methane content of the biogas, and therefore the biogas is not being used to its full potential. The simple relationship of estimating methane from volatile solids destruction, shown in Equation 4.6, would create an easier way to know the methane percentage in the biogas, without performing additional tests, which is the goal of a steady-state model.

4.5.0 Metabolism Factor and Auto-Calibration Method

The metabolism factor, k_m, is a generic factor that describes the metabolic rate in which the bacteria are breaking down the volatile solids. This factor is influenced by many different conditions including temperature, retention time, and biodegradability of the waste. The specific k_m value for different temperatures can be determined by Equation 4.11, where a standard temperature of 35°C is used because anaerobic digesters are typically operated near this temperature [38].

Equation 4.11: Metabolism Factor Temperature Correction

$$k_T = k_{35}(1.072)^{T-35}$$

Where:

- k_T = Metabolism factor at temperature T (1/day)
- k_{35} = Metabolism factor at 35°C (1/day)
- T= Temperature (°C)

The effect of the HRT and the biodegradability of the volatile solids is shown in Figure 4.1. The retention is dependent on the digester temperature and composition of the sludge, with average retention times being 15-30 days.

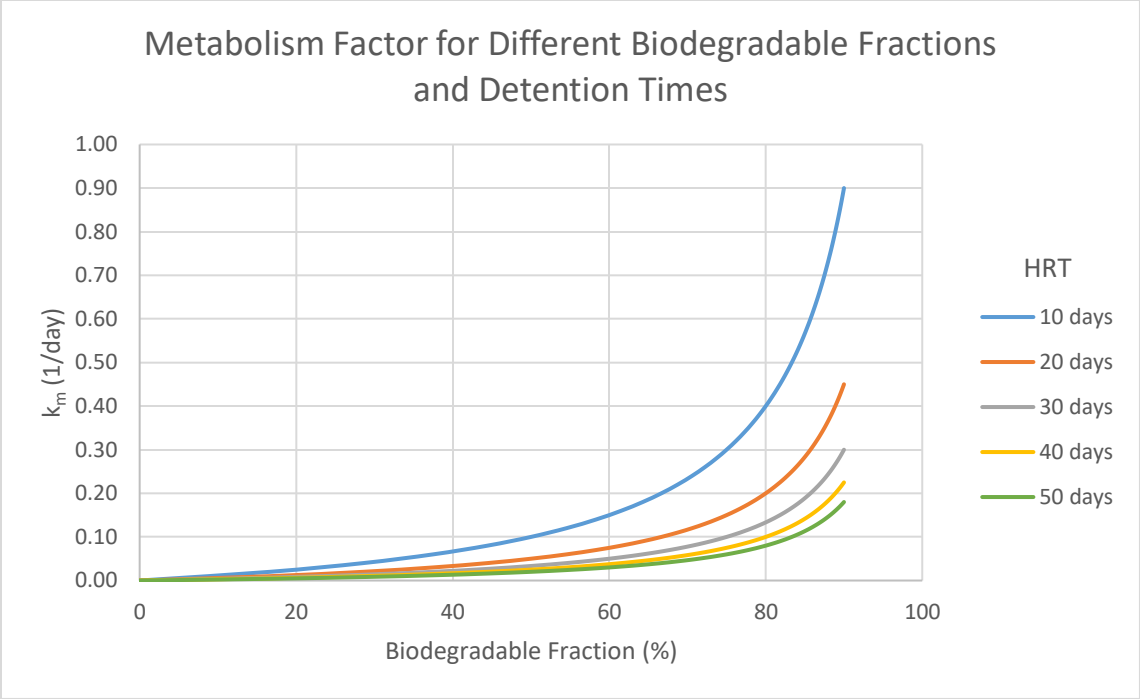

Figure 4.1: Metabolism Factor for Different Biodegradable Fractions and Hydraulic Retention Times

The graph shows the k_m values associated with HRTs between 10 and 50 days. Although the plot shows higher k_m values for an HRT of 10 days, retention times less than 10 days are typically not recommended because it results in low methane productivity. This is because as the HRT decreases, the percentage of microorganisms wasted from the digester increases. At some minimum HRT the microorganisms are wasted faster than they can be reproduced, for this reason it is recommended that the design HRT be 2.5 times the minimum value [41]. The graph shows that as the HRT increases, the values of k_m decrease and get closer together. Therefore, the digester typically reaches stability between 30-40 days, and having an HRT longer than that typically does not have a large impact on the system [12]. The fraction of biodegradable solids is shown on the x-axis. Typical values for biodegradability range from 50-70%, with a higher biodegradable fraction resulting in larger k_m values.

Not only does the value of k_m differ due to these conditions, it also varies within individual systems as well as between separate systems, making it difficult to assume specific values. The value for k_m can be determined from either the volatile solids or from gas production data. Calculation of k_m based on methane gas data is considered to be more reliable because the precision of measuring gas production is greater than that for solids measurements [38]. However, it is not common for wastewater treatment plants to have the necessary gas data.

Determining k_m from the methane produced is done by using Equation 4.10 to convert the methane produced to its volatile solids equivalence. Then, using these volatile solids estimation and the HRT in Equation 4.8 to solve for k_m. This k_m value can then be used to predict future production of methane within the model. If the methane content is unknown, which is typical for wastewater treatment plants, k_m can be estimated using the actual volatile solids data in Equation 4.8. Rearranging Equation 4.8 to solve for k_m results in Equation 4.12.

Equation 4.12: Model Metabolism Factor Estimation

$$k_m = \frac{dS/dt}{S\theta}$$

Determining a linear relationship between the volatile solids destroyed (dS/dt) and the HRT full-scale data creates a way for the k_m value to be auto-calibrated to a specific wastewater treatment plant. The linear equation generated from this relationship is then used to predict model dS/dt values for a range of different HRTs. This linear relationship is shown in Equation 4.13.

Equation 4.13: Linear Relationship Between VSD and HRT

$$\frac{dS}{dt} = m\theta + b$$

Where:

- m = Slope of VSD and HRT (g/L)
- b = Intercept of VSD and HRT (g/L/day)

After model dS/dt values are found, the model volatile solids entering the digester can then be estimated from the average percent reduction of full-scale volatile solids data at the specific plant. The percent reduction is determined using Equation 4.14.

Equation 4.14: Percent Reduction of Volatile Solids

$$Percent\ Reduction = \frac{dS/dt}{S_{in}}$$

The volatile solids leaving the digester than then be determined using Equation 4.9. Once these values are known, Equation 4.12 can then be used to estimate model k_m values at each model dS/dt values. Plotting these model k_m values with the model dS/dt and HRT values results in the relationship shown in Figure 4.2, but the exact relationship differs for each anaerobic digester. It can be seen that there is a linear relationship between the k_m and volatile solids destroyed at higher HRTs, with this relationship showing the optimum range of HRTs to use for the specific digester. The linear portion of the plot is determined by the percent difference between the slope values. A slope with a percent difference less than 2% is considered to be the linear portion of the plot. In the case the linear relationship exists between 22 and 40 days, and this is shown with red lines on the plot.

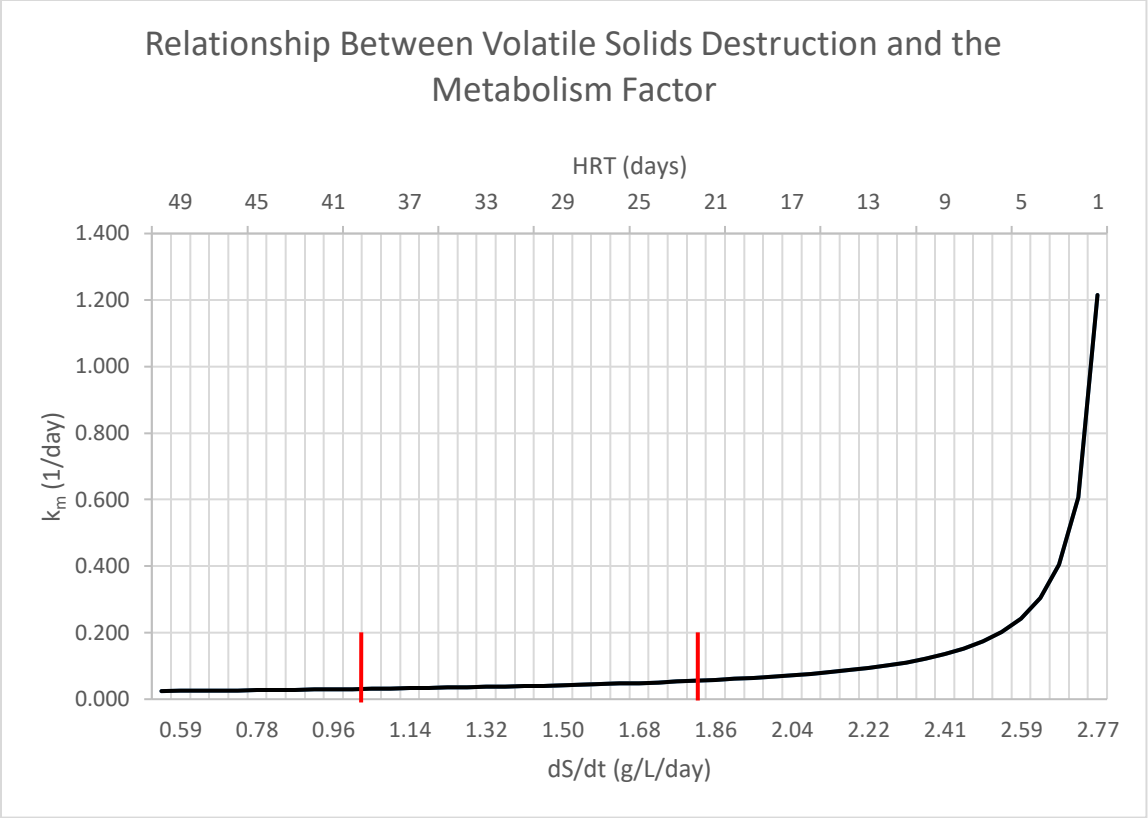

Figure 4.2: Relationship for Auto-Calibrating the Metabolism Factor

Since the period of linearity differs between different anaerobic digesters, a generic relationship cannot be made to apply to all wastewater treatment plants, instead this linear relationship changes from plant to plant, which is one of the benefits of a model that auto-calibrates to a wastewater treatment plant. In general, the relationship found between the metabolism factor and the volatile solids destroyed is shown in Equation 4.15.

Equation 4.15: Linear Relationship between Metabolism Factor and Volatile Solids Destroyed

$$If\ \frac{dS}{dt} > \frac{dS}{dt}_{max} \qquad k_m = k_{m,max}$$

$$If\ \frac{dS}{dt} \leq \frac{dS}{dt}_{max} \qquad k_m = m \times \frac{dS}{dt}$$

Where:

- $\frac{dS}{dt}_{max}$ = The maximum volatile solids destroyed for the linear relationship (g/L/day)
- $k_{m,max}$ = The maximum metabolism factor for the linear relationship (1/day)
- m = The slope of the linear relationship (L/g)

Once the steady-state k_m is determined, the estimated steady-state volatile solids leaving the digester can be found using Equation 4.8 and the average full-scale HRT for the specific digester. The conversion factor between methane production and volatile solids destroyed, K, can then be used in Equation 4.10 to estimate the volume of methane produced per day. The amount of methane can be compared to the volume of biogas produced to determine the percent of methane. An example of this auto-calibration is shown in Appendix D.

This auto-calibration of the metabolism factor is based on a limited number of parameters. These parameters include flow rate, total solids in and out of the digester, volatile solids in and out of the digester, HRT, and biogas production. When compared to the ADM1, this is a significantly smaller number of parameters. This is beneficial for implementing models at currently operating wastewater treatment plants because the parameters required are ones that are typically monitored, and do not require any additional analyses besides the biodegradable fraction and the methane content of biogas.

Although the end goal of the model is to estimate methane, the methane content is based on the volatile solids destroyed. Therefore, the percent difference between predicted volatile solids destruction and actual volatile solids destruction can be found to determine the accuracy of the auto-calibration method.

4.6.0 Conclusions

Modeling anaerobic digestion at steady-state is a much simpler way to predict digester behavior and biogas production than complex models, such as the ADM1. Steady-state conditions assume that there is no build-up of substrate in the digester and it is operating at ideal environmental conditions. This is a valid assumption to make because all wastewater treatment plants will strive for optimum conditions in order to increase the efficiency and stability of the system. Modeling at steady-state also results in less inputs needed when compared to the ADM1 due to the simple relationships that can be created. This is beneficial for wastewater treatment plants because typically only a small number of parameters are routinely monitored, making the ADM1 difficult to use without performing additional analyses on the data.

The proposed simple steady-state model needs only seven inputs in order to auto-calibrate to a wastewater treatment plant and predict methane production. These inputs include the flow rate, the percent of total solids and volatile solids entering the digester, percent of total solids and volatile solids leaving the digester, the HRT, and the volume of biogas produced. Knowing the percent of methane in the produced biogas would also be beneficial, but if the percent methane is not known, the model will be calibrated based on the volatile solids destruction rather than the gas data. All of these parameters, except for biodegradable volatile solids, are data that wastewater treatment plants regularly collect to monitor digester performance. The biodegradable fraction of the volatile solids can be assumed to be equal to the percent reduction of volatile solids, but the actual fraction must be determined with a special study which is a limitation of this model. Comparing this constraint with the constraints of the ADM1, the steady-state model requires one extra parameter to be determined while the ADM1 required over one hundred additional

parameters. Therefore, it is reasonable to assume that most wastewater treatment plants would be able to effectively use this model to predict methane production.

The benefit of auto-calibrating the model to specific wastewater treatment plants is that the metabolism factor changes when necessary. Since the k_m is dependent on the volatile solids destruction of a specific digester, determining a relationship between these parameters is a simple way to estimate methane production. The fact that the relationship auto-calibrates based only on the solids data and HRT allows the model to easily be used by most wastewater treatment plants without knowing information about the sludge composition or methane content of the biogas. For this reason, a simple steady-state model is more user friendly and readily implemented than the ADM1 for currently operating wastewater treatment plants.

5.0 Auto-calibration of a Steady-State Anaerobic Digestion Model Using Full-Scale Data

5.1.0 Introductions and Significance of Auto-calibration

Wastewater treatment plants have a limited amount of data that is regularly monitored. The parameters that are easily available to wastewater treatment plants include flow rate, percent of total solids entering and leaving the digester, percent of volatile solids entering and leaving the digester, hydraulic retention time (HRT), and volume of biogas produced, although not all wastewater treatment plant measure biogas production. Therefore, most wastewater treatment plants will not have data required for the inputs of the Anaerobic Digestion Model No. 1 (ADM1). This is one reason that the ADM1 is currently not used to its full potential. Wastewater treatment plants could perform additional analyses to obtain this data, but most will not because this requires additional time and costs. In order for a model to be effectively used by currently operating wastewater treatment plants, it would be beneficial for the model to auto-calibrate to the specific wastewater treatment plant based on the data that are readily available. This auto-calibration would allow for typically monitored data to be input in the model without having to know additional information such as the composition of the sludge or the metabolic degradation rate.

In order to determine the best way to auto-calibrate a model, full-scale data was received from four different wastewater treatment plants from 2022 in the Hampton Roads Sanitary District, which is located in Southeast Virginia. The wastewater treatment plants analyzed are the Atlantic plant, James River plant, York River plant, and Nansemond plant. None of the wastewater treatment plants analyzed monitored the percent methane of their biogas for 2022, and only the Atlantic plant measured biogas production. The remaining wastewater treatment plants estimate their biogas production using a constant that is dependent on

volatile solids destruction within the digester. Since no methane data were available, the auto-calibration done is based on the volatile solids destruction for each wastewater treatment plant. Between the four wastewater treatment plants, a total of seven digesters were analyzed using the auto-calibration method described in Section 4.4. The seven digesters analyzed are shown in Table 5.1.

Table 5.1: Digesters from the Hampton Roads Sanitary District Wastewater Treatment Plants

Wastewater Treatment Plant Digesters
Atlantic – Dig 1
Atlantic – Dig 2
Atlantic – Dig 3
James River
York River
Nansemond – Dig 1
Nansemond – Dig 2

For the Atlantic and Nansemond plants the multiple digesters are operated in parallel with one another. This means that the total incoming flow is separated into the different digesters and each digester completes the full anaerobic digestion process. The York River plant also has two digesters, but they are operated in series, meaning that the flow enters one digester and is processed, then goes to the second digester to be further processed. The data for each York River digester was combined to result in the total data for the full anaerobic digestion process.

5.2.0 Method for Validating Full-Scale Data

In order to validate the solids data received from wastewater treatment plants, an inert solids mass balance is performed. Inert solids are the non-volatile solids that enter the digester as part of the total solids. Since inert solids are non-volatile, they are not degraded

by the bacteria in the system. Therefore, assuming the digester is operated at steady-state and there is adequate mixing, the inert solids entering the digester should equal the inert solids leaving the digester. There is an additional flow rate associated with the gas leaving the digester, but there is no inert solids present in this flow rate, and therefore it can be eliminated from the mass balance. Having a digester that is well-mixed validates the assumption that the HRT is close to the average value found when dividing the digester volume by the flow rate. The mass balance of inert solids at steady-state is shown in Equation 5.1.

Equation 5.1: Steady-State Inert Solids Mass Balance

$$0 = Q_{in}S_{in,i} - Q_{out}S_{out,i}$$

Where:

- Q_{in} = Flow rate into the digester (L/day)
- Q_{out} = Flow rate out of the digester (L/day)
- $S_{in,i}$ = Concentration of inert solid entering the digester (mg/L)
- $S_{out,i}$ = Concentration of inert solids leaving the digester (mg/L)

For each wastewater treatment plant, the daily data for an entire year was averaged for each month. The average values were used because daily fluctuations in the system should not have a large effect on the model. Then, the average values of actual inert solids leaving the digester was compared to the inert solids that should be leaving the digester at steady-state by finding the percent difference between the values. Data with a percent difference less than 15% are considered to be valid, and the digester is assumed to be operating at optimum conditions. Only the York River plant had an average percent difference greater than 15% for

the inert solids data, but this digester was still analyzed because of lack of better data. The results for inert solids percent difference for all of the seven digesters in shown in Table 5.2.

Table 5.2: Results for Inert Solids Percent Difference

Digester	Inert Solids Percent Difference
Atlantic – Dig 1	9.1%
Atlantic – Dig 2	13.8%
Atlantic – Dig 3	9.0%
James River	8.6%
York River	22.3%
Nansemond – Dig 1	13.9%
Nansemond – Dig 2	13.5%

One possible reason that the inert solids data from the York River plant has a large percent difference is because that data are from two digesters that are operated in series. This results in higher errors in the data because any errors from the individual digesters must be added together to determine the total error for the entire anaerobic digestion process. Another reason for possible differences in inert solids data could be due to the method of sampling. If sampling methods differ from sample to sample, this would affect the accuracy of the data. Also, it is often difficult to get a representative sample of the digester sludge due to the differing environmental conditions outside of the digester as well as the pipe system used to sample at some wastewater treatment plants. If samples are taken from pipes that contain stagnant sludge it is important to let the sludge flow for a couple minutes before taking the sample in order to ensure an accurate sample of the sludge within the digester is taken. The other digesters have an acceptable difference between the inert solids.

5.3.0 Analysis of Auto-Calibration Method

The auto-calibration method that is described in Section 4.4 was applied to the data from all four wastewater treatment plants. Data from the Nansemond wastewater treatment plant was deemed as invalid because of a reporting error in the gas production values for both digesters, this resulted in two digesters being removed from the analysis. The remaining five digesters were successfully auto-calibrated using the steady-state model, with an example of digester 1 from the Atlantic plant shown in Appendix D. The yearly average of auto-calibrated metabolism factors found for each of the analyzed digesters is shown in Table 5.3.

Table 5.3: Auto-Calibrated Metabolism Factors

Digester	k_m (1/day)
Atlantic – Dig 1	0.0472
Atlantic – Dig 2	0.0514
Atlantic – Dig 3	0.0459
James River	0.0564
York River	0.0588

The metabolism factors found for each digester are within the expected range for anaerobic digestion operated at mesophilic temperatures. These values were then used in the model to predict volatile solids destroyed within the digester to estimate the methane production. The yearly average for percent difference between estimated and actual volatile solids destruction, percent difference between inert solids entering and leaving the digester, and the estimated percent methane is shown in Table 5.4.

Table 5.4: Results of Full-Scale Data from the Steady-State Model

Digester	Inert Solids Percent Difference	Volatile Solids Destroyed Percent Difference	Percent Methane of the Biogas
Atlantic – Dig 1	9.1%	5.7%	68.1%
Atlantic – Dig 2	13.8%	4.9%	71.1%
Atlantic – Dig 3	9.0%	3.9%	65.9%
James River	8.6%	5.5%	55.4%
York River	22.3%	14.0%	54.7%

The digester from the York River plant has a relatively high percent difference between the inert solids and volatile solids destroyed. Therefore, these data are not considered to be valid and realistically should not be used to develop a steady-state model. The reasons for a high percent difference in inert solids is explained in the previous section.

Since the methane content in the biogas produced is unknown for 2022 at all of the wastewater treatment plants analyzed, there is no way to compare the methane content predicted to what is actually being produced. The Atlantic plant is the only plant that has available methane data, which is from 2020 and 2021. At this time, the wastewater treatment plant was implementing a new thermal hydrolysis pretreatment (THP) before the anaerobic digester. THP is an alternate why to handle the hydrolysis step that treats the sludge a higher temperature, increasing the efficiency and methane percentages [42]. This pretreatment could be a reason that the model predicted higher methane percentages for the Atlantic plant when compared to the other plants. The average methane content for the digesters from the Atlantic plant is shown in Table 5.3.

Table 5.5: Methane Content of Biogas from Atlantic Plant

Digester	2020	2021
Dig 1	60.0%	58.7%
Dig 2	58.4%	58.1%
Dig 3	-	61.9%

The methane values found by the model are somewhat higher than the data found for previous years, but this is expected because as the THP system continues to stabilize, methane production will become more efficient. Typical methane percentages of biogas range from 50-75% for municipal solid waste anaerobic digestion [43]. Since the values of percent methane from the model are within that range, this model is a reasonable approach to estimating methane production although limitation exist and improvement could be made. Ideally, having measured methane data to compare the model results to would allow further analysis to improve the model.

The monthly methane production model results for the James River plant are shown in Figure 5.1. The York River plant shows a similar pattern, shown in Appendix E.

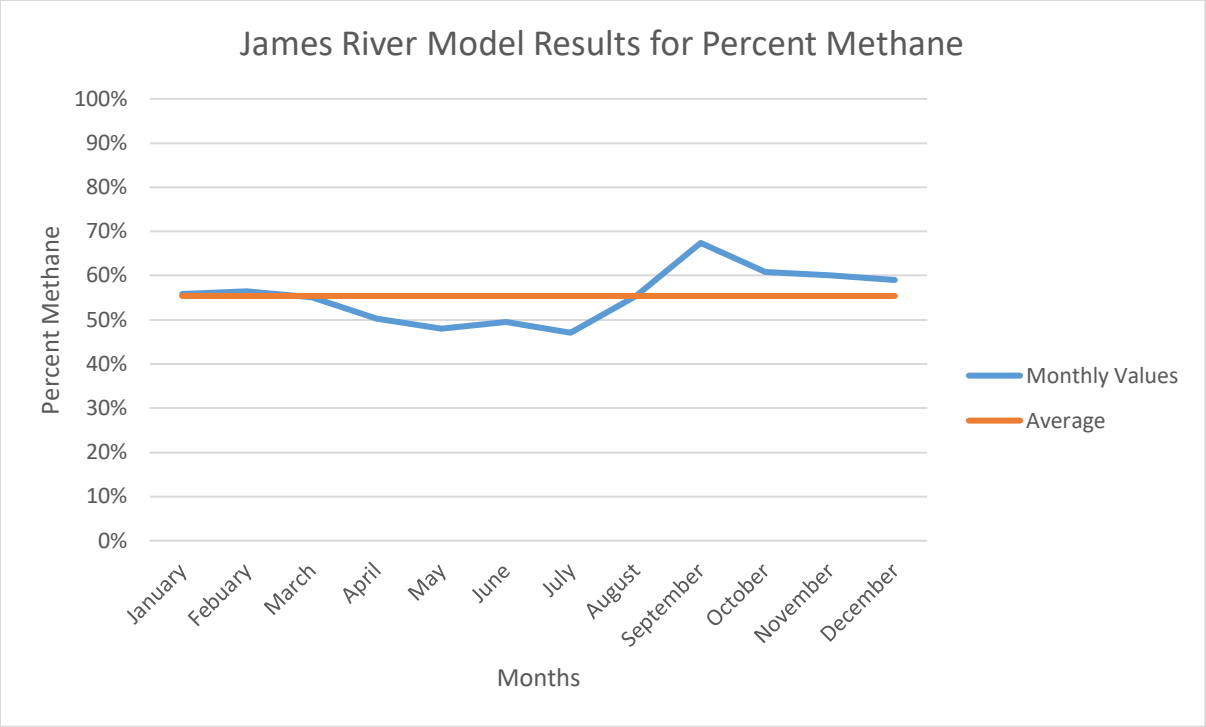

Figure 5.1: Monthly Percent Methane for the James River Plant, average values shown in Table 5.4

The percent methane in the biogas differs from month to month, but the difference between the high values and the average is relatively equal to the difference between the low values and the average. This shows that the digester is most-likely operating near steady-state, and the average value of methane found is an acceptable value to report.

The monthly data from Atlantic – Dig 1 is shown in Figure 5.2. The remaining Atlantic digesters follow a similar pattern and are shown in Appendix E.

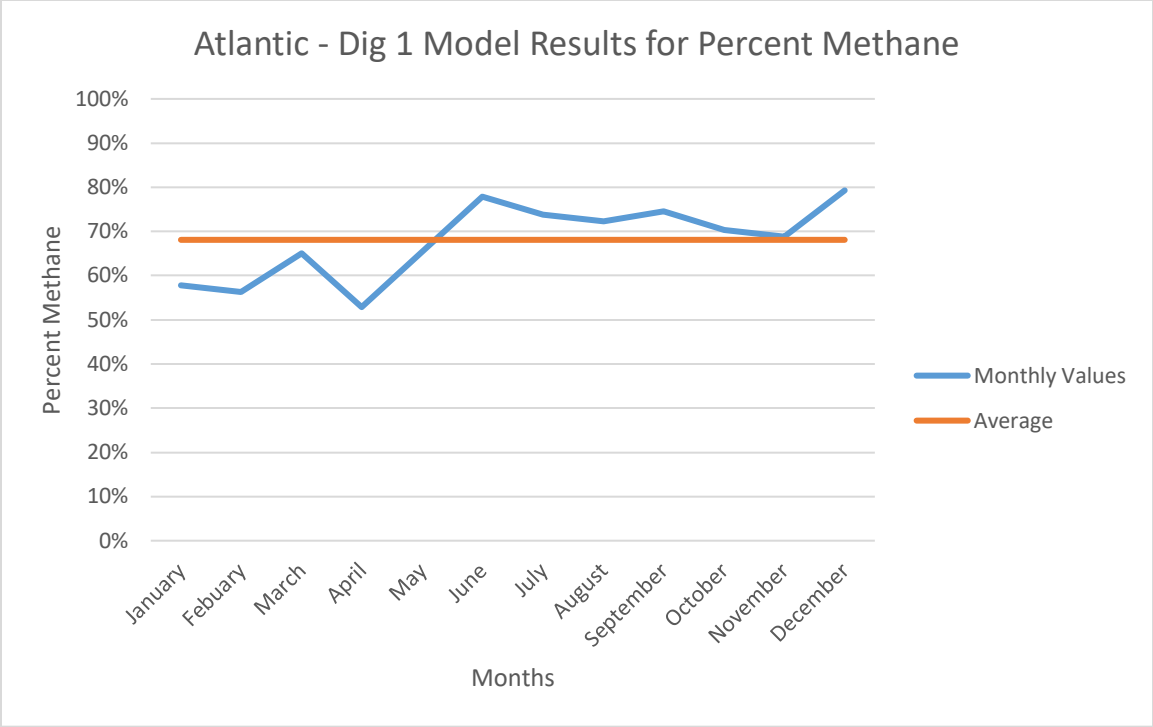

Figure 5.2: Monthly Percent Methane for Atlantic - Digester 1, average values shown in Table 5.4

This digester shows an upward trend in the percent methane produced. This is expected because the THP system is most likely still reaching stability since it was implemented. This means that the efficiency of the system will continue to increase as the THP continues to stabilize [42]. Therefore, the digester has most likely not operated at steady-state over the entire year, but it is expected that it operated near steady-state from month to month. This suggests that the yearly average values for the Atlantic plant are not an accurate representation of the percent methane, and instead the monthly values should be used.

5.4.0 Discussion of Model Development and Modification Recommendations

Implementation of full-scale data into the simple steady-state model helped to show that it is common for wastewater treatment plants to have incomplete or inaccurate data associated with anaerobic digestion. This could be due to differing sampling methods, inefficient mixing, or many other reasons that would not be known without additional

analyses of the data. This is one of the main limitations for developing a steady-state model based on full-scale data. The inert solids balance for all of the full-scale data evaluated showed that there is great variability between model operations from month to month, resulting in averages that could be inaccurate. It is recommended that any steady-state model is based on full-scale data with smaller percent difference between inert solids to ensure that that digester is being operated as close to steady-state as possible.

With only a small amount of wastewater treatment plants measuring biogas production, and an even smaller amount measuring methane content, it is very difficult to create a model based on this data. Steady-state models can be created based on volatile solids data, but it is difficult to determine the accuracy of the model if there is no gas data to compare the model output to. Creating models based on lab analysis can allow for comparison between model estimations and actual methane produced, but this is not ideal for creating a model for full-scale operation. Routinely measuring biogas production and composition is strongly recommended for a more accurate development of a simple steady-state model.

5.5.0 Conclusions

Since currently operating wastewater treatment plants only have a small number of parameters routinely monitored for the anaerobic digestion process, it is ideal to create a model that can be auto-calibrated to a specific plant based on this data. This auto-calibration method creates a simple relationship between HRT, volatile solids destruction, and the metabolism factor to predict future volatile solids destruction and estimate methane content of biogas. Using full-scale anaerobic digestion data resulted in a simple-steady model that predicted methane concentrations within the expected range for anaerobic digestion operated at mesophilic temperatures.

The inert solids entering and leaving the digester were analyzed in order to validate the full-scale data. From this, it was determined that it is common for wastewater treatment plants to have large variabilities between digester operation from month to month. This impacts the model because some months are not operated near steady-state conditions. In order to create a reliable steady-state model, these data should not be used in future development and instead only steady-state data should be used. It also became evident that the lack of biogas data impacts the evaluation of a steady-state model because it is not possible to compare values to real values obtained in full-scale digestion.

The large variability in inert solids data as well as the lack of biogas production and composition data create limitations for the simple steady-state model. Although these limitations differ from the limitations in the ADM1, they impact the development of a simple steady-state model. It is recommended that a simple steady-state model be developed based on a plant that has more accurate inert solids data, as well as composition and production of biogas easily available.

6.0 Overall Discussion of Results and Conclusions

6.1.0 Status of Advanced but Complex Models

The status of anaerobic digestion models has not significantly changed in the past 20 years. The Anaerobic Digestion Model No. 1 (ADM1) is one of the only models currently available that includes the full anaerobic digestion process and considers all biological and physico-chemical pathways. This model has been repeatedly proven to accurately model anaerobic digestion in full-scale processes, so this could be a potential reason there has not been any widely accepted improvements or changes to the model. However, this model is extremely complex and requires many different parameters as inputs that are not easily obtainable by wastewater treatment plants. These parameters require additional lab analyses that wastewater treatment plants are not required to do. Therefore, the ADM1 is not being used to its full potential as the parameters are not easily accessible for most wastewater treatment plants.

Other models have been developed since the ADM1, but none have been as widely accepted as a generic model as the ADM1. Most models published since the ADM1 are variations of the ADM1 that include the same steps but model different processes. For example, many two-stage anaerobic digestion models have been created based on the ADM1, which is single stage anaerobic digestion. These models do not typically differ in terms of parameters evaluated, but instead add on to the ADM1 which only increases its complexity [24]. Other models that include the entire wastewater treatment process have been developed that include the ADM1 for the anaerobic digestion step of the treatment, such as the Benchmark Simulation Model No. 2 (BSM2). These models have had to change inputs of the ADM1 in order to be compatible with a full wastewater treatment plant model, but the overall structure of the model has not changed [26]. Since newer models have had to adjust

the ADM1 to be compatible with other wastewater treatment processes, this shows that the ADM1 is not as easily applied to treating wastewater as originally intended.

Potential development of other models that are simpler than the ADM1 could help to make the application more accessible to wastewater treatment plants in general, including the ability to combine it with models for other wastewater treatment processes. In order to be used to its full potential by wastewater treatment plants, the overall model would need to be greatly simplified. The International Water Association (IWA) task group for the ADM1 claims that the model is already simple and it is a generic model meant to be as widely applicable as possible [4]. This claim has been proven to not be true when it comes to implementing the ADM1 with other models or in existing wastewater treatment plants. Since anaerobic digestion is such a complex process, there are many limitations when it comes to simplifying the model, but it could be greatly simplified if applied to steady-state anaerobic digestion conditions.

6.2.0 Applicability of Simple Steady-State Modeling

Simple steady-state modeling is applicable to anaerobic digestion because if a digester is stable, the production of biogas should be consistent and there would be no accumulation of substrate within the digester. An anaerobic digester will be stable if ideal environmental conditions are met. The environmental conditions that have an impact on the digester include temperature, pH, nutrient concentration, and concentration of toxic substances. Adequate mixing is extremely important to maintain because the environmental conditions cannot remain uniform if the system is not mixed well enough [15]. Therefore, the environmental conditions depend directly on the type of mixing that is occurring within the digester. Ensuring that these environmental conditions are met will help the bacteria population to

become stable, which will in turn help to keep environmental conditions ideal. Due to the desire to have optimum efficiency in an anaerobic digester, it is safe to assume that wastewater treatment plants will strive to maintain these ideal conditions. Therefore, wastewater treatment plants are striving to operate at steady-state conditions. This allows for steady-state modeling to be used to predict methane concentration of the biogas generated.

Steady-state modeling is favored over non-steady-state because it is less complex and reduces the number of parameters required as inputs. During steady-state anaerobic digestion modeling, relationships between methane production, metabolism rates, and volatile solids destruction can be determined in order to create simple ways to estimate these parameters. This is beneficial for current operating wastewater treatment plants because they only routinely collect data for a limited number of parameters, such as flow rate, total solids, volatile solids, and hydraulic retention time. Due to this, complex models that include a large number of parameters, such as the ADM1, are not able to be used by wastewater treatment plants because the necessary inputs require additional lab analyses. Creating a generic steady-state model that could be more easily usable for wastewater treatment plants would be extremely helpful in estimating methane concentration within the biogas.

When the steady-state model was applied to full-scale data, the results for methane content for the wastewater treatment plants with accurate solids and gas data were within the expected range. The percent methane found was consistent with typical values for anaerobic digestion operated at mesophilic temperatures. The model also predicted volatile solid destruction at steady-state accurately, with an average of 5.2% difference between predicted and actual values. The full-scale results further justify the applicability of a simple steady-state model for anaerobic digestion.

6.3.0 Significance of Using Anaerobic Digestion Models

Utilizing modeling for anaerobic digestion has many benefits for operating wastewater treatment plants. One benefit is the estimation of methane content within the biogas. This would allow the biogas to be better used in a wastewater treatment plant for energy production because the composition of the biogas can be predicted. This has potential to generate energy and cost savings for the wastewater treatment plant if it is done efficiently. Creating a model that estimates the required information would help to increase this efficiency by reducing the steps and costs needed to measure gas composition. Once a reliable model is created, measuring gas composition would only need to be done occasionally to perform ongoing calibration checks and adjustments as needed. This is an alternative to routinely measuring gas composition in order to effectively utilize the production of biogas.

Another benefit of anaerobic digestion modeling is its ability to predict digester failure and gain an understanding of the process dynamics, which is one of the greatest benefits of the ADM1. This is possible because any significant changes in the digester operation will show up in the model as increased errors and differences in model outputs. Anaerobic digestion modeling also allows for easy estimation of future digester operation because of the ability to easily edit model inputs. This allows wastewater treatment plant operators to estimate how a digester will respond if any parameters of the feed change. This is significant because it could help to better understand how to use the digester more efficiently, but also allow possible changes to operation to be analyzed without having to actually make those changes. This allows wastewater treatment plants to be better prepared if there is a change and potential upsets within the digester can be avoided. Overall, the development of a steady-state anaerobic digestion model would greatly benefit currently operating treatment plants by

creating an easy way to estimate biogas production with only the data that is routinely monitored.

7.0 References

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8.0 Appendices

8.1.0 Appendix A: List of Abbreviations

ADM1 – Anaerobic Digestion Model No. 1

ASM – Activated Sludge Models

ASM1 – Activated Sludge Model No. 1

BSM2 – Benchmark Simulation Model No. 2

COD – Chemical Oxygen Demand

CSTR – Continuous-flow stirred-tank reactor

HRT – Hydraulic retention time

IWA – International Water Association

LCFA – Long chain fatty acid

TS – Total solids

VFA – Volatile fatty acid

VS – Volatile solids

8.2.0 Appendix B: List of Notations

B = Methane yield (m^3 CH_4/kg VS)

B_0 = Ultimate methane yield (m^3 CH_4/kg VS)

D = Dilution rate (1/day)

dCH_4/dt = Methane production rate (m^3/day)

dS/dt = VS destroyed (kg/day)

$\frac{dS}{dt}_{max}$ = The maximum volatile solids destroyed for the linear relationship (g/L/day)

ρ_j = Kinetic rate of process (kgCOD S m^{-3} d^{-1})

$\rho_{T,i}$ = Specific mass transfer rate of gas i (kgCOD m^{-3} d^{-1})

K = Conversion factor (m^3 CH_4/kg VS)

k_h = Kinetic coefficient (1/day)

K_H = Henry's law coefficient (M bar^{-1})

$k_L a$ = Overall mass transfer coefficient multiplied by the specific transfer area (d^{-1})

k_m = Metabolism factor (1/day)

$k_{m,max}$ = The maximum metabolism factor for the linear relationship (1/day)

K_m = Monod maximum specific uptake rate (kgCOD S kgCOD X^{-1} d^{-1})

K_s = Half saturation value (kgCOD S m^{-3})\

k_T = Specific factor at temperature T

k_{35} = Specific factor at 35°C

L= Volatile solids loading rate (kg VS/m^3)

m = The slope of the linear relationship (L/g)

$p_{gas,i}$ = Gas phase partial pressure of gas I (bar)

Q = Flow rate (m^3/day)

S = Concentration of biodegradable volatile solids leaving the digester (kg/m^3)

S_c = Soluble component (kgCOD m^{-3})

S_{in} = Concentration of biodegradable volatile solids entering the digester (kg/m^3)

$S_{in,i}$ = Concentration of inert solid entering the digester (mg/L)

$S_{out,i}$ = Concentration of inert solids leaving the digester (mg/L)

$S_{liq,i}$ = Liquid phase concentration of gas I (kgCOD m^{-3})

T= Temperature (°C)

V = Volume of the digester (m^3)

X = Particulate component (kgCOD m^{-3})

Y = Yield of biomass on substrate (kg X/kg S)

θ = Hydraulic retention time (day)

μ_m = Maximum specific growth rate (1/day)

γ_V = Volumetric methane production (m^3 CH_4/m^3)

8.3.0 Appendix C: Anaerobic Digestion Model No. 1 Parameters

Table C 1: Kinetic Parameters and Rates, Reproduced IWA T ask Group for Mathematical Modelling of Anaerobic Digestion Processes, 2002. *Anaerobic Digestion Model No.1 (ADM1),* with permission from the copyright holders, IWA Publishing

Symbol	Description	Units
$k_{A/Bi}$	Acid base kinetic parameter	$M^{-1}d^{-1}$
k_{dec}	First order decay rate	d^{-1}
$I_{inhibitor, process}$	Inhibition function	
$k_{process}$	First order parameter	d^{-1}
k_La	Gas-liquid transfer coefficient	d^{-1}
$K_{I, inhibit, substrate}$	50% inhibit coefficient	kgCOD m^{-3}
$k_{m, process}$	Monod maximum specific uptake rate	kgCOD_S kgCOD_X^{-1} d^{-1}
$K_{S, process}$	Half saturation value	kgCOD_S m^{-3}
ρ_j	Kinetic rate of process j	kgCOD_S m^{-3} d^{-1}
$Y_{substrate}$	Yield of biomass on substrate	kgCOD_X kgCOD_S^{-1}
μ_{max}	Monod maximum specific growth rate	d^{-1}

Table C 2: Dynamic State Variables, Reproduced IWA T ask Group for Mathematical Modelling of Anaerobic Digestion Processes, 2002. *Anaerobic Digestion Model No.1 (ADM1),* with permission from the copyright holders, IWA Publishing

Name	i	Description	Units
X_c	13	composite	kgCOD m^{-3}
X_{ch}	14	carbohydrates	kgCOD m^{-3}
X_{pr}	15	proteins	kgCOD m^{-3}
X_{li}	16	lipids	kgCOD m^{-3}
X_I	24	particulate inerts	kgCOD m^{-3}
S_I	12	soluble inerts	kgCOD m^{-3}
S_{su}	1	monosaccharides	kgCOD m^{-3}
S_{aa}	2	amino acids	kgCOD m^{-3}
S_{fa}	3	total LCFA	kgCOD m^{-3}
S_{va}	4	total valerate	kgCOD m^{-3}
S_{bu}	5	total butyrate	kgCOD m^{-3}
S_{pro}	6	total propionate	kgCOD m^{-3}
S_{ac}	7	total acetate	kgCOD m^{-3}
S_{h2}	8	hydrogen	kgCOD m^{-3}
S_{ch4}	9	methane	kgCOD m^{-3}
S_{IC}	10	inorganic carbon	M
S_{IN}	11	inorganic nitrogen	M
X_{su-h2}	17-23	biomass	
S_{cat}		cations	M
S_{an}		anions	M

Table C 3: Biochemical rate coefficients and kinetic rate equations for soluble components, Reproduced IWA T ask Group for Mathematical Modelling of Anaerobic Digestion Processes, 2002. *Anaerobic Digestion Model No.1 (ADM1)*, with permission from the copyright holders, IWA Publishing

Component (i) →		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**Rate (ρ_j, kg COD.m^{-3}d^{-1})**
j	Process ↓	S_{su}	S_{aa}	S_{fa}	S_{va}	S_{bu}	S_{pro}	S_{ac}	S_{h2}	S_{ch4}	S_{IC}	S_{IN}	S_I	
1	Disintegration												$f_{sI,xc}$	$k_{dis}X_c$
2	Hydrolysis Carbohydrates	1												$k_{hyd,ch}X_{ch}$
3	Hydrolysis of Proteins		1											$k_{hyd,pr}X_{pr}$
4	Hydrolysis of Lipids	1- $f_{fa,li}$		$f_{fa,li}$										$k_{hyd,li}X_{li}$
5	Uptake of Sugars	-1				(1-Y_{su}) $f_{bu,su}$	(1-Y_{su}) $f_{pro,su}$	(1-Y_{su}) $f_{ac,su}$	(1-Y_{su}) $f_{h2,su}$			- (Y_{su}) N_{bac}		$k_{m,su}\frac{S_{su}}{K_S+S}X_{su}I_1$
6	Uptake of Amino Acids		-1		(1-Y_{va}) $f_{bu,aa}$	(1-Y_{aa}) $f_{bu,aa}$	(1-Y_{aa}) $f_{pro,aa}$	(1-Y_{aa}) $f_{ac,aa}$	(1-Y_{aa}) $f_{h2,aa}$			N_{aa} - (Y_{aa}) N_{bac}		$k_{m,aa}\frac{S_{aa}}{K_S+S_{aa}}X_{aa}I_1$
7	Uptake of LCFA			-1				(1-Y_{fa}) 0.7	(1-Y_{fa}) 0.3			- (Y_{fa}) N_{bac}		$k_{m,fa}\frac{S_{fa}}{K_S+S_{fa}}X_{fa}I_2$
8	Uptake of Valerate				-1		(1-Y_{c4}) 0.54	(1-Y_{c4}) 0.31	(1-Y_{c4}) 0.15			- (Y_{c4}) N_{bac}		$k_{m,c4}\frac{S_{va}}{K_S+S_{va}}X_{c4}\frac{1}{1+S_{bu}/S_{va}}I_2$
9	Uptake of Butyrate					-1		(1-Y_{c4}) 0.8	(1-Y_{c4}) 0.2			- (Y_{c4}) N_{bac}		$k_{m,c4}\frac{S_{bu}}{K_S+S_{bu}}X_{c4}\frac{1}{1+S_{va}/S_{bu}}I_2$
10	Uptake of Propionate						-1	(1-Y_{pro}) 0.57	(1-Y_{pro}) 0.43			- (Y_{pro}) N_{bac}		$k_{m,pr}\frac{S_{pro}}{K_S+S_{pro}}X_{pro}I_2$
11	Uptake of Acetate							-1		(1-Y_{ac})		- (Y_{ac}) N_{bac}		$k_{m,ac}\frac{S_{ac}}{K_S+S_{ac}}X_{ac}I_3$
12	Uptake of Hydrogen								-1	(1-Y_{h2})		- (Y_{h2}) N_{bac}		$k_{m,h2}\frac{S_{h2}}{K_S+S_{h2}}X_{h2}I_1$
13	Decay of X_{su}													$k_{dec,Xsu}X_{su}$
14	Decay of X_{aa}													$k_{dec,Xaa}X_{aa}$
15	Decay of X_{fa}													$k_{dec,Xfa}X_{fa}$
16	Decay of X_{C4}													$k_{dec,Xc4}X_{c4}$
17	Decay of X_{pro}													$k_{dec,Xpro}X_{pro}$
18	Decay of X_{ac}													$k_{dec,Xac}X_{ac}$
19	Decay of X_{h2}													$k_{dec,Xh2}X_{h2}$
		Monosaccharides (kgCOD m^{-3})	Amino Acids (kgCOD m^{-3})	LCFAs (kgCOD m^{-3})	Total valerate (kgCOD m^{-3})	Total butyrate (kgCOD m^{-3})	Total propionate (kgCOD m^{-3})	Total acetate (kgCOD m^{-3})	Hydrogen gas (kgCOD m^{-3})	Methane gas (kgCOD m^{-3})	Inorganic Carbon (kgCOD m^{-3})	Inorganic Nitrogen (kgCOD m^{-3})	Soluble inerts (kgCOD m^{-3})	Inhibition factors: $I_1 = I_{pH}I_{IN,lim}$ $I_2 = I_{pH}I_{IN,lim}I_{h2}$ $I_3 = I_{pH}I_{IN,lim}I_{NH3,Xac}$

Table C 4: Biochemical rate coefficients and kinetic rate equations for particulate components, Reproduced IWA Task Group for Mathematical Modelling of Anaerobic Digestion Processes, 2002. *Anaerobic Digestion Model No.1 (ADM1)*, with permission from the copyright holders, IWA Publishing

Component (i) →		**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**Rate (ρ_j, kg COD.m^{-3}d^{-1})**
j	Process ↓	X_c	X_{ch}	X_{pr}	X_{li}	X_{su}	X_{aa}	X_{fa}	X_{c4}	X_{pro}	X_{ac}	X_{h2}	X_I	
1	Disintegration	-1	$f_{ch,xc}$	$f_{pr,xc}$	$f_{li,xc}$								$f_{sI,xc}$	$k_{dis}X_c$
2	Hydrolysis Carbohydrates		-1											$k_{hyd,ch}X_{ch}$
3	Hydrolysis of Proteins			-1										$k_{hyd,pr}X_{pr}$
4	Hydrolysis of Lipids				-1									$k_{hyd,li}X_{li}$
5	Uptake of Sugars					Y_{su}								$k_{m,su}\frac{S_{su}}{K_S+S}X_{su}I_1$
6	Uptake of Amino Acids						Y_{aa}							$k_{m,aa}\frac{S_{aa}}{K_S+S_{aa}}X_{aa}I_1$
7	Uptake of LCFA							Y_{fa}						$k_{m,fa}\frac{S_{fa}}{K_S+S_{fa}}X_{fa}I_2$
8	Uptake of Valerate								Y_{c4}					$k_{m,c4}\frac{S_{va}}{K_S+S_{va}}X_{c4}\frac{1}{1+S_{bu}/S_{va}}I_2$
9	Uptake of Butyrate								Y_{c4}					$k_{m,c4}\frac{S_{bu}}{K_S+S_{bu}}X_{c4}\frac{1}{1+S_{va}/S_{bu}}I_2$
10	Uptake of Propionate									Y_{pro}				$k_{m,pr}\frac{S_{pro}}{K_S+S_{pro}}X_{pro}I_2$
11	Uptake of Acetate										Y_{ac}			$k_{m,ac}\frac{S_{ac}}{K_S+S_{ac}}X_{ac}I_3$
12	Uptake of Hydrogen											Y_{h2}		$k_{m,h2}\frac{S_{h2}}{K_S+S_{h2}}X_{h2}I_1$
13	Decay of X_{su}	1				-1								$k_{dec,Xsu}X_{su}$
14	Decay of X_{aa}	1					-1							$k_{dec,Xaa}X_{aa}$
15	Decay of X_{fa}	1						-1						$k_{dec,Xfa}X_{fa}$
16	Decay of X_{C4}	1							-1					$k_{dec,Xc4}X_{c4}$
17	Decay of X_{pro}	1								-1				$k_{dec,Xpro}X_{pro}$
18	Decay of X_{ac}	1									-1			$k_{dec,Xac}X_{ac}$
19	Decay of X_{h2}	1										-1		$k_{dec,Xh2}X_{h2}$
		Composites (kgCOD m^{-3})	Carbohydrates (kgCOD m^{-3})	Proteins (kgCOD m^{-3})	Lipids (kgCOD m^{-3})	Sugar degraders (kgCOD m^{-3})	Amino acid degraders kgCOD m^{-3})	LCFA degraders (kgCOD m^{-3})	Valerate and butyrate degraders (kgCOD m^{-3})	Propionate degraders (kgCOD m^{-3})	Acetate degraders (kgCOD m^{-3})	Hydrogen degraders (kgCOD m^{-3})	Particulate inerts (kgCOD m^{-3})	Inhibition factors: $I_1 = I_{pH}I_{IN,lim}$ $I_2 = I_{pH}I_{IN,lim}I_{h2}$ $I_3 = I_{pH}I_{IN,lim}I_{NH3,Xac}$

8.4.0 Appendix D: Example of Steady-State Model Auto-Calibration Calculation

Raw wastewater treatment plant data:

Table D 1: Data from Atlantic Wastewater Treatment Plant - Digester 1

Date	Flow Rate	TS in	VS in	TS out	VS out	HRT	Gas Produced
	MGD	%	%	%	%	day	ft^3/day
January	0.048	9.18	83	4.55	73	23	281,100
February	0.047	9.72	85	4.63	73	23	306,300
March	0.036	9.39	86	4.49	73	37	201,300
April	0.040	9.89	85	5.05	73	29	290,700
May	0.035	9.00	85	4.87	74	42	109,700
June	0.045	9.72	84	5.28	74	25	212,600
July	0.042	9.03	84	5.13	74	27	196,100
August	0.040	8.62	82	4.81	72	28	178,200
September	0.038	8.57	83	4.78	71	29	165,600
October	0.039	8.55	83	4.68	71	28	179,600
November	0.038	9.13	85	4.61	71	29	195,900
December	0.034	8.78	86	4.47	71	29	148,000
Average	0.040	9.13	84.3	4.78	72.5	29	205,425

1) Estimate concentration of VS in and out using the relationship between percent solids and concentration of solids for municipal solid waste: 1% solids = 10,000 mg/L and find VSD

Equation D 1: Volatile Solids Destruction

$$VSD = VS_{in} - VS_{out}$$

Table D 2: Concentration of Solids

Date	TS in	VS in	TS out	VS out	VSD	VSD
	mg/L	mg/L	mg/L	mg/L	mg/L	g/L/day
January	91800	76194	45500	33215	42979	1.869
February	97200	82620	46300	33799	48821	2.123
March	93900	80754	44900	32777	47977	1.297
April	98900	84065	50500	36865	47200	1.628
May	90000	76500	48700	36038	40462	0.963
June	97200	81648	52800	39072	42576	1.703
July	90300	75852	51300	37962	37890	1.403
August	86200	70684	48100	34632	36052	1.288
September	85700	71131	47800	33938	37193	1.283
October	85500	70965	46800	33228	37737	1.348
November	91300	77605	46100	32731	44874	1.547
December	87800	75508	44700	31737	43771	1.509
Average	91317	76961	47792	34666	42294	1.497

2) Determine relationship between HRT and VSD

Equation D 2: Linear Relationship between VSD and HRT

$$\frac{dS}{dt} = -0.045\theta + 2.813$$

3) Use previous relationship to find dS/dt at average HRT

$$\frac{dS}{dt} = -0.045(29) + 2.813 = 1.50\ g/L/day$$

4) Use slope and intercept to estimate dS/dt for range of HRTs

Table D 3: Estimated Volatile Solids Destruction

HRT	dS/dt	HRT	dS/dt
days	g/L/day	days	g/L/day
1	2.768	26	1.636
2	2.723	27	1.591
3	2.678	28	1.546
4	2.632	29	1.500
5	2.587	30	1.455
6	2.542	31	1.410
7	2.496	32	1.365
8	2.451	33	1.319
9	2.406	34	1.274
10	2.361	35	1.229
11	2.315	36	1.184
12	2.270	37	1.138
13	2.225	38	1.093
14	2.180	39	1.048
15	2.134	40	1.002
16	2.089	41	0.957
17	2.044	42	0.912
18	1.998	43	0.867
19	1.953	44	0.821
20	1.908	45	0.776
21	1.863	46	0.731
22	1.817	47	0.685
23	1.772	48	0.640
24	1.727	49	0.595
25	1.682	50	0.550

5) Determine percent reduction

Equation D 3: Percent Reduction of Solids

$$Percent\ Reduction = \frac{VSD}{VS_{in}}$$

Table D 4: Percent Reduction of Volatile Solids

Date	VS Reduction
January	56.4%
February	59.1%
March	59.4%
April	56.1%
May	52.9%
June	52.1%
July	50.0%
August	51.0%
September	52.3%
October	53.2%
November	57.8%
December	58.0%
Average	54.9%

6) Use average percent reduction to estimate S_{in} and find S_{out} for new dS/dt values

Equation D 4: Biodegradable Volatile Solids Entering Digester Estimation

$$S_{in} = \frac{dS/dt}{Percent\ Reduction}$$

Table D 5: Biodegradable Volatile Solids Entering and Leaving Digester

HRT	S in	S out	HRT	S in	S out
days	g/L/day	g/L/day	days	g/L/day	g/L/day
1	5.046	2.278	26	2.983	1.346
2	4.963	2.241	27	2.900	1.309
3	4.881	2.203	28	2.818	1.272
4	4.798	2.166	29	2.735	1.235
5	4.716	2.129	30	2.653	1.197
6	4.633	2.092	31	2.570	1.160
7	4.551	2.054	32	2.487	1.123
8	4.468	2.017	33	2.405	1.086
9	4.386	1.980	34	2.322	1.048
10	4.303	1.942	35	2.240	1.011
11	4.221	1.905	36	2.157	0.974
12	4.138	1.868	37	2.075	0.937
13	4.056	1.831	38	1.992	0.899
14	3.973	1.793	39	1.910	0.862
15	3.890	1.756	40	1.827	0.825
16	3.808	1.719	41	1.745	0.788
17	3.725	1.682	42	1.662	0.750
18	3.643	1.644	43	1.580	0.713
19	3.560	1.607	44	1.497	0.676
20	3.478	1.570	45	1.415	0.639
21	3.395	1.533	46	1.332	0.601
22	3.313	1.495	47	1.250	0.564
23	3.230	1.458	48	1.167	0.527
24	3.148	1.421	49	1.084	0.490
25	3.065	1.384	50	1.002	0.452

7) Find metabolism factor values

Equation D 5: Metabolism Factor Estimation

$$k_m = \frac{dS/dt}{S_{out}\theta}$$

Table D 6: Metabolism Factor Values

HRT	k_m	HRT	k_m
days	1/day	days	1/day
1	1.215	26	0.047
2	0.608	27	0.045
3	0.405	28	0.043
4	0.304	29	0.042
5	0.243	30	0.041
6	0.203	31	0.039
7	0.174	32	0.038
8	0.152	33	0.037
9	0.135	34	0.036
10	0.122	35	0.035
11	0.110	36	0.034
12	0.101	37	0.033
13	0.093	38	0.032
14	0.087	39	0.031
15	0.081	40	0.030
16	0.076	41	0.030
17	0.071	42	0.029
18	0.068	43	0.028
19	0.064	44	0.028
20	0.061	45	0.027
21	0.058	46	0.026
22	0.055	47	0.026
23	0.053	48	0.025
24	0.051	49	0.025
25	0.049	50	0.024

8) Determine slope (m) values from new data using relationship between k_m and dS/dt and find percent difference between slope values

Equation D 6: Slope of Metabolism Factor and VSD Relationship

$$m = \frac{k_m}{dS/dt}$$

Table D 7: Model Slope and Percent Difference

HRT	Slope	Percent Difference	HRT	Slope	Percent Difference
1	0.439	49.17%	26	0.029	0.96%
2	0.223	32.21%	27	0.028	0.75%
3	0.151	23.71%	28	0.028	0.53%
4	0.115	18.60%	29	0.028	0.33%
5	0.094	15.18%	30	0.028	0.12%
6	0.080	12.73%	31	0.028	0.09%
7	0.070	10.88%	32	0.028	0.30%
8	0.062	9.44%	33	0.028	0.51%
9	0.056	8.27%	34	0.028	0.72%
10	0.051	7.31%	35	0.028	0.94%
11	0.048	6.51%	36	0.029	1.17%
12	0.045	5.81%	37	0.029	1.40%
13	0.042	5.21%	38	0.029	1.65%
14	0.040	4.69%	39	0.030	1.90%
15	0.038	4.22%	40	0.030	2.18%
16	0.036	3.80%	41	0.031	2.47%
17	0.035	3.42%	42	0.032	2.78%
18	0.034	3.07%	43	0.033	3.11%
19	0.033	2.75%	44	0.034	3.48%
20	0.032	2.45%	45	0.035	3.89%
21	0.031	2.17%	46	0.036	4.34%
22	0.030	1.90%	47	0.038	4.84%
23	0.030	1.65%	48	0.040	5.41%
24	0.029	1.42%	49	0.042	6.07%
25	0.029	1.19%	50	0.044	

9) Determine linear portion of relationship between k_m and dS/dt

   Slope with percent difference less than 2% is considered to be the linear portion. This introduces a maximum value for k_m and dS/dt for the specific digester. Then find the slope of the linear portion.

Table D 8: Linear Portion of Model

HRT	k_m	dS/dt
days	1/day	g/L/day
22	0.055	1.817
23	0.053	1.772
24	0.051	1.727
25	0.049	1.682
26	0.047	1.636
27	0.045	1.591
28	0.043	1.546
29	0.042	1.500
30	0.041	1.455
31	0.039	1.410
32	0.038	1.365
33	0.037	1.319
34	0.036	1.274
35	0.035	1.229
36	0.034	1.184
37	0.033	1.138
38	0.032	1.093
39	0.031	1.048

Equation D 7: Linear Relationship between Metabolism Factor and VSD

$$If\ \frac{dS}{dt} > 1.817 \qquad k_m = 0.055$$

$$If\ \frac{dS}{dt} \leq 1.817 \qquad k_m = m \times \frac{dS}{dt}$$

m = 0.0305 L/g

Since dS/dt = 1.50 g/L/day, k_m = 0.0305 x 1.50 = 0.046 1/day

10) Find loading of VS out and dS/dt

$$VS_{out} = \frac{VS_{in}}{1 + k_m\theta} = \frac{11722.7\ kg/day}{1 + (0.046\ 1/day)(29\ days)} = 5041.1\ kg/day$$

$$\frac{dS}{dt} = VS_{in} - VS_{out} = 11722.7 - 5041.1 = 6681.6\ kg/day$$

11) Estimate methane production

$$\frac{dCH_4}{dt} = K\frac{dS}{dt} = 0.6\frac{m^3CH_4}{kg\ VS} \times 6681.6\ \frac{kg\ VS}{day} = 4009\ \frac{m^3CH_4}{day}$$

12) Divide methane production by overall gas production to estimate percent methane

$$\frac{4009\ \frac{m^3CH_4}{day}}{5817\ \frac{m^3\ TG}{day}} = 68.9\%\ CH_4$$

8.5.0 Appendix E: Model Results

Table E 1: Model Results for Atlantic - Dig 1

Date	k_m (1/day)	Inert Solids Percent Difference	Volatile Solids Destroyed Percent Difference	Percent Methane of the Biogas
January	0.0540	21.28%	1.8%	58%
February	0.0540	14.26%	6.3%	56%
March	0.0347	7.78%	5.4%	65%
April	0.0457	8.09%	1.5%	53%
May	0.0278*	6.21%	1.8%	105%*
June	0.0512	11.73%	7.7%	78%
July	0.0484	7.68%	13.5%	74%
August	0.0471	13.20%	11.5%	72%
September	0.0457	4.85%	9.0%	75%
October	0.0471	6.63%	6.9%	70%
November	0.0457	2.38%	1.4%	69%
December	0.0457	5.46%	1.7%	79%
Average	0.0472	9.13%	5.7%	68%

*There is an error in the raw data for this month, so it was not included in the average calculation.

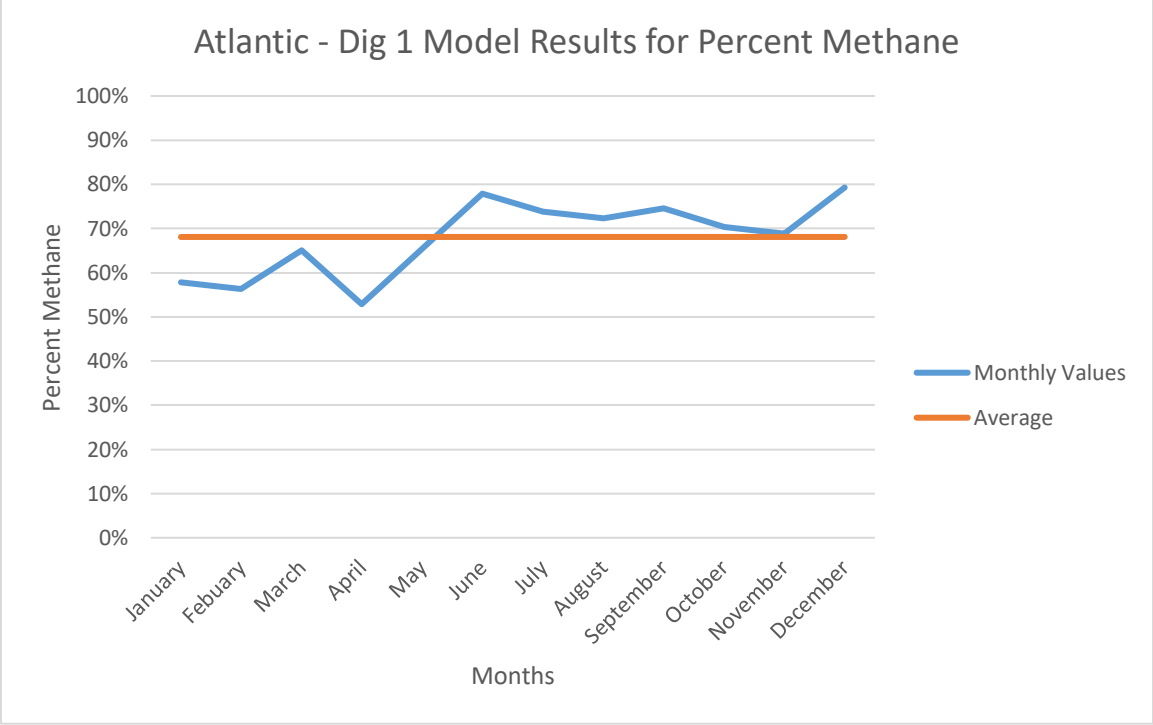

Figure E 1: Monthly Percent Methane for Atlantic - Dig 1

Table E 2: Model Results for Atlantic - Dig 2

Date	k_m (1/day)	Inert Solids Percent Difference	Volatile Solids Destroyed Percent Difference	Percent Methane of the Biogas
January	0.0595	21.97%	1.7%	59%
February	0.0595	16.67%	4.1%	59%
March	0.0375	15.79%	7.7%	63%
April	0.0516	15.92%	1.3%	72%
May	0.0312	9.00%	16.9%	75%
June	0.0579	15.10%	3.3%	76%
July	0.0532	14.60%	5.3%	70%
August	0.0516	18.88%	4.8%	75%
September	0.0532	8.78%	4.5%	77%
October	0.0595	10.22%	5.1%	73%
November	0.0501	12.29%	1.6%	73%
December	0.0516	5.92%	2.5%	83%
Average	0.0514	13.76%	4.9%	71%

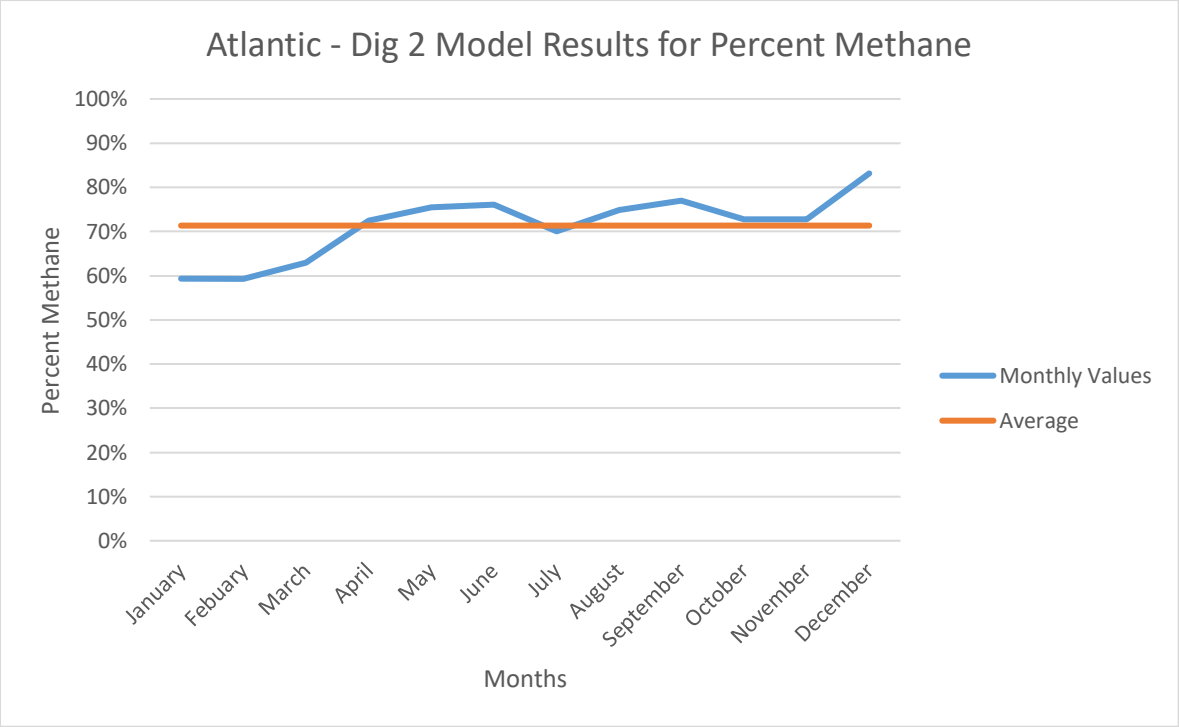

Figure E 2: Monthly Percent Methane for Atlantic - Dig 2

Table E 3: Model Results for Atlantic - Dig 3

Date	k_m (1/day)	Inert Solids Percent Difference	Volatile Solids Destroyed Percent Difference	Percent Methane of the Biogas
January	0.0524	20.59%	2.5%	55%
February	0.0524	13.52%	7.0%	54%
March	0.0352	11.79%	4.3%	61%
April	0.0463	8.27%	0.4%	68%
May	0.0279	4.00%	0.6%	69%
June	0.0512	8.68%	4.1%	69%
July	0.0475	5.07%	9.9%	69%
August	0.0463	16.75%	6.5%	70%
September	0.0475	5.65%	6.6%	69%
October	0.0524	4.43%	4.9%	64%
November	0.0450	5.13%	0.5%	66%
December	0.0463	3.87%	0.1%	81%
Average	0.0459	8.98%	3.9%	66%

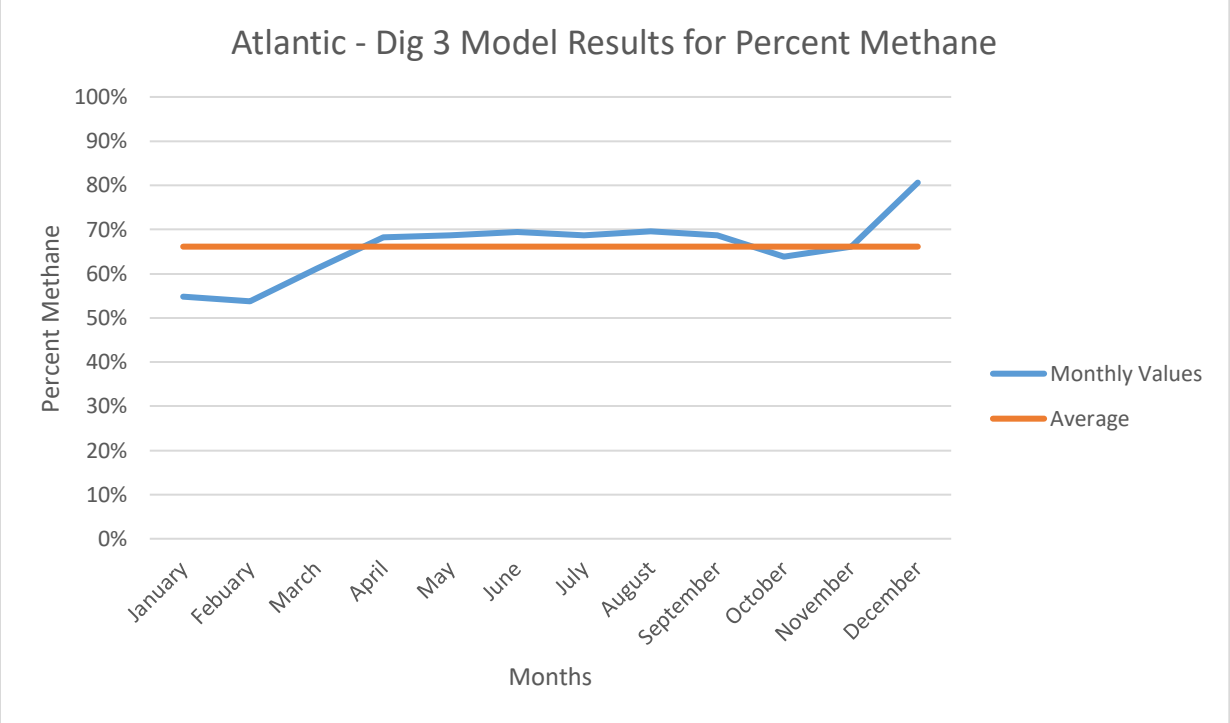

Figure E 3: Monthly Percent Methane for Atlantic - Dig 3

Table E 4: Model Results for James River

Date	k_m (1/day)	Inert Solids Percent Difference	Volatile Solids Destroyed Percent Difference	Percent Methane of the Biogas
January	0.0558	12.9%	10.4%	56%
February	0.0604	8.7%	7.7%	56%
March	0.0604	12.5%	1.3%	55%
April	0.0583	0.8%	5.2%	50%
May	0.0558	2.1%	0.5%	48%
June	0.0533	8.2%	1.9%	50%
July	0.0458	9.4%	0.0%	47%
August	0.0533	1.9%	11.5%	55%
September	0.0583	9.3%	8.7%	67%
October	0.0583	13.0%	11.3%	61%
November	0.0583	11.7%	5.5%	60%
December	0.0583	12.6%	1.8%	59%
Average	0.0564	8.6%	5.5%	55%

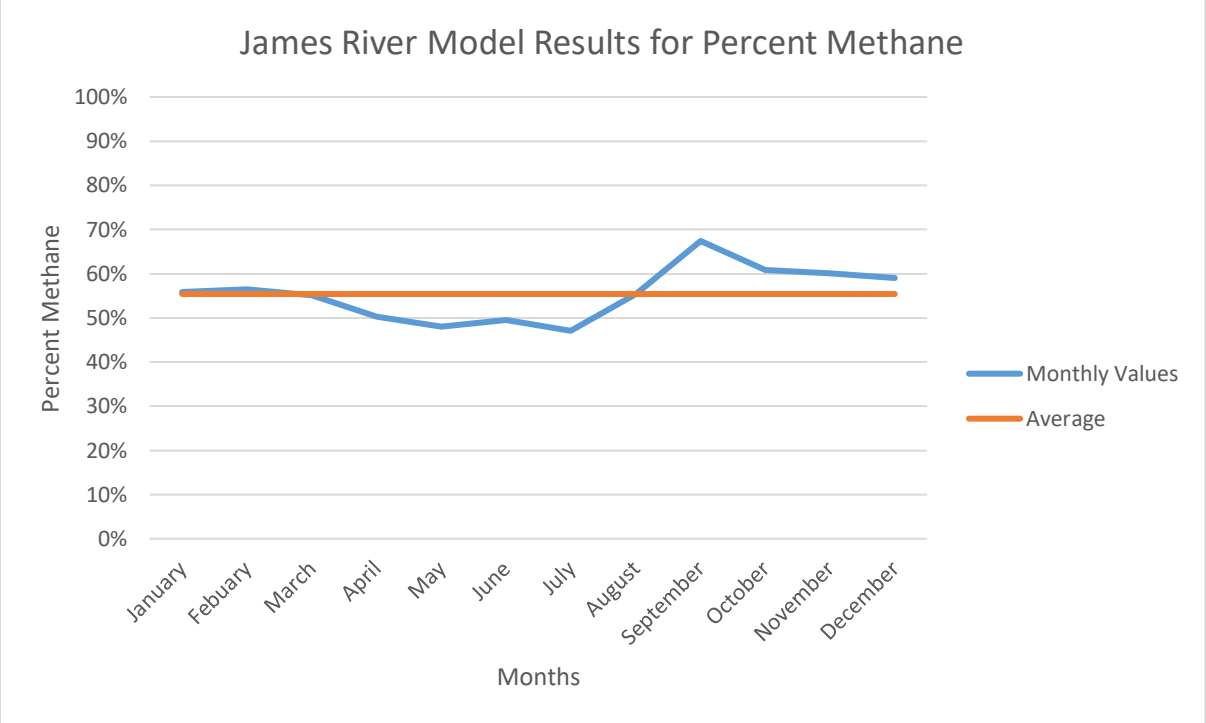

Figure E 4: Monthly Percent Methane for James River

Table E 5: Model Results for York River

Date	k_m (1/day)	Inert Solids Percent Difference	Volatile Solids Destroyed Percent Difference	Percent Methane of the Biogas
January	0.0593	41.58%	4.2%	56%
February	0.0602	36.68%	8.9%	56%
March	0.0620	21.66%	13.9%	53%
April	0.0457	26.89%	1.9%	47%
May	0.0611	12.64%	25.9%	53%
June	0.0593	22.35%	15.4%	55%
July	0.0593	11.97%	13.5%	57%
August	0.0611	1.00%	21.0%	58%
September	0.0593	19.71%	18.4%	55%
October	0.0593	18.30%	20.1%	50%
November	0.0575	20.89%	17.2%	51%
December	0.0611	34.32%	7.8%	58%
Average	0.0588	22.33%	14.0%	54%

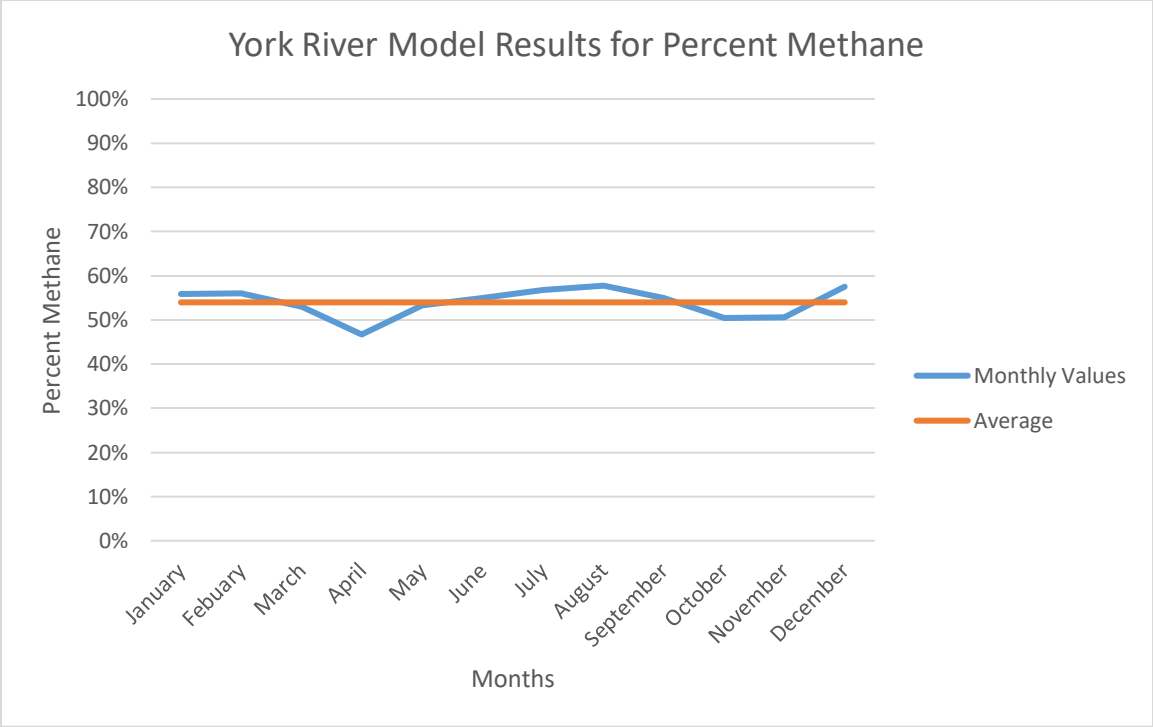

Figure E 5: Monthly Percent Methane for York River

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