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A STUDY OF HIGH SOLIDS ANAEROBIC DIGESTION OF BUCKNELL

UNIVERSITY FOOD WASTE FOLLOWED BY AEROBIC CURING

by

Margaret F. Drennan

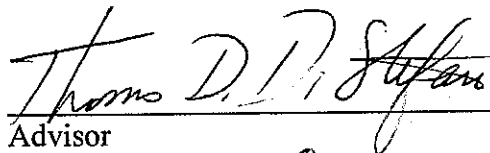
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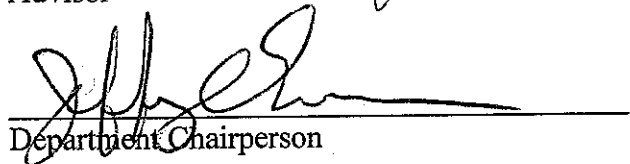
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ABSTRACT

Anaerobic digestion of food scraps has the potential to accomplish waste minimization, energy production, and compost or humus production. At Bucknell University, removal of food scraps from the waste stream could reduce municipal solid waste transportation costs and landfill tipping fees, and provide methane and humus for use on campus.

To determine the suitability of food waste produced at Bucknell for high-solids anaerobic digestion (HSAD), a year-long characterization study was conducted. Physical and chemical properties, waste biodegradability, and annual production of biodegradable waste were assessed. Bucknell University food and landscape waste was digested at pilot-scale for over a year to test performance at low and high loading rates, ease of operation at 20% solids, benefits of codigestion of food and landscape waste, and to provide digestate for studies to assess the curing needs of HSAD digestate. A laboratory-scale curing study was conducted to assess the curing duration required to reduce microbial activity, phytotoxicity, and odors to acceptable levels for subsequent use of humus.

The characteristics of Bucknell University food and landscape waste were tested approximately weekly for one year, to determine chemical oxygen demand (COD), total solids (TS), volatile solids (VS), and biodegradability (from batch digestion studies). Fats, oil, and grease and total Kjeldahl nitrogen were also tested for some food waste samples. Based on the characterization and biodegradability studies, Bucknell University dining hall food waste is a good candidate for HSAD. During batch digestion studies

Bucknell University food waste produced a mean of 288 mL CH₄/g COD with a 95% confidence interval of 0.06 mL CH₄/g COD. The addition of landscape waste for digestion increased methane production from both food and landscape waste; however, because the landscape waste biodegradability was extremely low the increase was small. Based on an informal waste audit, Bucknell could collect up to 100 tons of food waste from dining facilities each year.

The pilot-scale high-solids anaerobic digestion study confirmed that digestion of Bucknell University food waste combined with landscape waste at a low organic loading rate (OLR) of 2 g COD/L reactor volume-day is feasible. During low OLR operation, stable reactor performance was demonstrated through monitoring of biogas production and composition, reactor total and volatile solids, total and soluble chemical oxygen demand, volatile fatty acid content, pH, and bicarbonate alkalinity. Low OLR HSAD of Bucknell University food waste and landscape waste combined produced 232 L CH₄/kg COD and 229 L CH₄/kg VS. When OLR was increased to high loading (15 g COD/L reactor volume-day) to assess maximum loading conditions, reactor performance became unstable due to ammonia accumulation and subsequent inhibition. The methane production per unit COD also decreased (to 211 L CH₄/kg COD fed), although methane production per unit VS increased (to 272 L CH₄/kg VS fed). The degree of ammonia inhibition was investigated through respirometry in which reactor digestate was diluted and exposed to varying concentrations of ammonia. Treatments with low ammonia concentrations recovered quickly from ammonia inhibition within the reactor.

The post-digestion curing process was studied at laboratory-scale, to provide a preliminary assessment of curing duration. Digestate was mixed with woodchips and incubated in an insulated container at 35 °C to simulate full-scale curing self-heating conditions. Degree of digestate stabilization was determined through oxygen uptake rates, percent O₂, temperature, volatile solids, and Solvita Maturity Index. Phytotoxicity was determined through observation of volatile fatty acid and ammonia concentrations. Stabilization of organics and elimination of phytotoxic compounds (after 10–15 days of curing) preceded significant reductions of volatile sulfur compounds (hydrogen sulfide, methanethiol, and dimethyl sulfide) after 15–20 days of curing.

Bucknell University food waste has high biodegradability and is suitable for high-solids anaerobic digestion; however, it has a low C:N ratio which can result in ammonia accumulation under some operating conditions. The low biodegradability of Bucknell University landscape waste limits the amount of bioavailable carbon that it can contribute, making it unsuitable for use as a cosubstrate to increase the C:N ratio of food waste. Additional research is indicated to determine other cosubstrates with higher biodegradabilities that may allow successful HSAD of Bucknell University food waste at high OLRs. Some cosubstrates to investigate are office paper, field residues, or grease trap waste. A brief curing period of less than 3 weeks was sufficient to produce viable humus from digestate produced by low OLR HSAD of food and landscape waste.

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CHAPTER 1: Introduction

The majority of municipal solid waste (MSW) produced in the United States is disposed of in landfills (U.S. EPA, 2010). When organic wastes such as food scraps or yard trimmings are deposited in landfills, methane and carbon dioxide are produced within the landfill by naturally occurring anaerobic digestion. Although greenhouse gas collection is a goal of landfill design, inevitably some of the gases produced will be released into the atmosphere. An alternative for the disposal of organic wastes is composting, which recycles them into a useful end product. However, energy is used for composting (primarily for aeration), and if it is sourced from fossil fuel power plants, greenhouse gases will be produced. If, instead of composting, high-solids anaerobic digestion were used to process organic wastes diverted from landfills, the result would be energy production in addition to waste recycling. Like composting, anaerobic digestion produces a useful end product, with the potential to be a zero-waste process.

The primary goal of this project was to assess the possibility of organics collection at the two main dining facilities at Bucknell University (BU), Bostwick Cafeteria and The Bison. Currently, organics produced at these facilities are collected and transported to the landfill with the rest of the MSW generated on campus. If biodegradable food waste could be diverted from the waste stream, BU could save money on transportation costs and landfill tipping fees. That waste could be used to produce energy and humus that could be used on campus.

Waste characterization

There has been no long-term study of the characteristics of university food waste. In order to assess the possibility of stable anaerobic digestion, it is necessary to know what variability to expect in the substrate during operation. Food waste chemical oxygen demand, total solids, and volatile solids were determined approximately weekly between October 2006 and November 2007. In addition, total Kjeldahl nitrogen and fats, oil and grease were determined for a subset of the food waste samples. Biodegradability was assessed through batch digestion trials using respirometry to record biogas production. Bucknell University landscape waste (currently disposed of by composting on campus) was also characterized because of the possibility that it could be used as a cosubstrate to increase reactor solids content and supply additional carbon for microbial growth.

Reactor operation

Although anaerobic digestion of MSW has become fairly commonplace in Europe, this project presents some novel elements. Digestion of source sorted MSW includes a greater variety of materials and involves much larger reactor volumes than would be the case when digesting food waste generated on campus at Bucknell. To provide a better approximation of results that might be expected from full-scale digestion at high solids, a pilot-scale study was designed to continue previous laboratory-scale research. Research goals were to assess the stability of high-solids anaerobic digestion of BU food waste combined with landscape waste at low and high loading rates and determine the maximum organic loading rate (OLR) at which stable operation could be

sustained. Operation at low and high OLRs was planned in order to compare operation at a low OLR, which would maximize biogas production and waste stabilization, with operation at a high OLR, which would minimize reactor size. The goal of this comparison was to determine whether the increased capital and operating costs of the larger reactor (to accommodate the low OLR) would be compensated by the benefit of increased methane production and waste stabilization. The low OLR digestion study was completed successfully, and the OLR was increased to determine the maximum stable OLR that could be used. During operation at high OLR the reactor became unstable and testing revealed that the cause was ammonia inhibition. A respirometry study was conducted to confirm inhibition by ammonia and study the extent of the inhibition.

Curing study

To produce useful humus from anaerobic digestion, a two- to three-week post-digestion treatment is necessary (Kayhanian and Tchobanoglous, 1993b; 1993a; Vallini et al., 1993; Vermuelen et al., 1993). Digestate from a high-solids process may range from 20-40% solids, too much moisture to be used in the same applications as compost (Sharma et al., 1999; Bidlingmaier et al., 2004; De Baere, 2004; Hartmann and Ahring, 2006). Additionally, although anaerobic digestion is capable of mineralizing much of the organic content of waste, digestate is likely to contain odor-causing and phytotoxic compounds that need to be removed before use. A laboratory-scale curing study was conducted to make a first assessment of the curing needs of digestate from high-solids anaerobic digestion. Study goals were to determine what duration of curing would be

necessary to reduce odors, phytotoxicity, and microbial activity to acceptable levels.

Additionally, the curing study would compare the curing needs of digestate from low and high OLR reactor operation, to allow the size of a potential curing facility to be incorporated into the comparison between operating at low and high OLRs. A curing study was completed using digestate removed during low OLR operation. Because stable operation could not be established at a high OLR, the high OLR curing study was not conducted.

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CHAPTER 2: Literature Review

2.1. Generation and disposal of MSW in the United States

In 2009, 221 million metric tons (MMT) of municipal solid waste (MSW) was produced in the United States. This material went to recycling (55.7 MMT), composting (18.9 MMT), combustion with energy recovery (26.4 MMT), and the remainder was landfilled (120 MMT). Potentially biodegradable materials (paper and paperboard, yard trimmings, and food scraps) composed 56% of MSW generated in 2009 (Table 2.1). The remainder of MSW was plastics, metals, wood, glass, rubber, leather, and textiles (U.S. EPA, 2010).

Table 2.1. Potentially biodegradable components of MSW generated in 2009.

	Paper and paperboard	Yard trimmings	Food scraps
Generated (MMT)	62.2	30.2	31.2
Discarded (MMT)	23.6	12.1	30.4
Discarded (%)	38%	40%	97%

Landfilling as a method of MSW disposal suffers from a number of disadvantages, including methane and other greenhouse gas emissions to the atmosphere, possible soil and groundwater contamination from leachate, and difficulties in siting new facilities (Haight, 2004). Greenhouse gases are produced within landfills when microbes digest biodegradable materials; emissions result from landfill design and operation. It is estimated that half of all landfilled material consists of biodegradable organics

(Verstraete and Vandevivere, 1999). Landfill methane emissions are a serious environmental concern – methane represents 25 times the global warming potential of carbon dioxide over the course of 100 years (Forster et al., 2007). In a typical landfill, biodegradation is limited because of unfavorable conditions. These include low moisture content (often less than 20% inside the landfill) and low pH due to acidogenesis from biodegradable material (Palmisano and Barlaz, 1996). Although leachate recirculation may increase moisture content, leachate tends to flow in channels through the waste, leaving some areas dry (Barlaz, 1996).

Waste-to-energy (combustion with energy recovery) capacity has decreased in the United States since 1990 (U.S. EPA, 2010). The U.S. EPA estimates that in 2009, 26.4 MMT (12% of the total generation) of MSW went to combustion with energy recovery (U.S. EPA, 2010). Generally, food waste is poorly suited for combustion with energy recovery (Hartmann and Ahring, 2006). The high moisture content means that combustion is difficult, and supplemental fuel may be required (Cheng and Hu, 2010). Food waste could, however, provide a high quality substrate for anaerobic digestion; and, although both anaerobic digestion and incineration produce energy, the anaerobic digestion process recovers nutrients and could be used to produce a high-quality humus (Hartmann and Ahring, 2006)

In 2009 there were close to 3,000 yard trimmings composting facilities in the United States (U.S. EPA, 2010). When other components of MSW are included, long processing times, odor problems, difficulty regulating moisture content, difficulties with materials handling, and the lack of a useful end product can adversely affect the

feasibility of composting (Miller, 1996). With anaerobic digestion there is no need for the addition of structural material to maintain pore space for oxygen transport (Verstraete and Vandevivere, 1999; Bidlingmaier et al., 2004). The end product of anaerobic treatment contains fewer weed seeds and pathogens than the end product of aerobic composting, and its odor potential is lower (Verstraete and Vandevivere, 1999). The most significant advantage of anaerobic digestion over composting is energy recovery. Anaerobic digestion can recover 100 to 150 kWh/ton feedstock, whereas composting is a net energy consumer, requiring 30 to 35 kWh/ton feedstock (Hartmann and Ahring, 2006).

2.2. Anaerobic digestion as an alternative for MSW disposal

Anaerobic digestion (AD) of MSW has been employed in Western Europe since the 1990s (De Baere, 2006; De Baere and Mattheeuws, 2010). There were 124 AD facilities operating there in 2006, with a total capacity of 3.9 MMT per year (De Baere, 2006). This represented 28% of the total biological treatment of MSW in Western Europe (the balance was treated through composting) (De Baere, 2006). By 2010 there were 200 AD plants with a total capacity of 6 MMT per year in Western Europe (De Baere and Mattheeuws, 2010). Although AD has not been used extensively in the US for treatment of MSW, research conducted in the 1970s and since has demonstrated that it is feasible (Pfeffer, 1974; DiStefano et al., 2004).

Biogas from AD can be used without treatment for heating, cooking, and running generators or internal combustion engines (Chynoweth and Pullammanappallil, 1996).

After purification, biogas can be added to natural gas pipelines, used as vehicle fuel, or used in any application appropriate for natural gas (Chynoweth and Pullammanappallil, 1996). During full scale operation of a high-solids reactor treating source sorted organic wastes the methane yield from AD was $0.4 \text{ m}^3 \text{ CH}_4/\text{kg}$ volatile solids (VS) fed (Bolzonella et al., 2006).

In order to maximize the methane production from MSW or even green waste, sorting is essential (Hartmann and Ahring, 2006). MSW contains a wide range of different hazardous chemicals, which can be released through microbial, physical, or chemical action (Palmisano and Barlaz, 1996). Source separated waste has a lower proportion of fixed solids and other nondigestible components (Hartmann and Ahring, 2006). Treatment is required at a receiving facility in order to remove contaminants from either source sorted (SS) or mechanically sorted (MS) MSW (Bolzonella et al., 2006). Both SS- and MS-MSW require screening, metals removal, and size reduction, but more extensive treatment is required for MS-MSW, which will affect the net energy production from the AD process (Bolzonella et al., 2006). In a study focused on waste sorting methods, two full-scale high-solids anaerobic digestion (HSAD) systems were compared, treating source sorted and mechanically sorted organic fraction of MSW (OFMSW) (Bolzonella et al., 2006). One reactor was fed a combination of gray waste, MS-OFMSW, and sewage sludge, and the other was fed SS-OFMSW (Bolzonella et al., 2006). The highest biogas yield ($0.4 \text{ m}^3 \text{ CH}_4/\text{kg}$ VS fed) was observed in the reactor fed SS-OFMSW, but each reactor was operated successfully for one year at loading rates of 3 to $8 \text{ kg VS}/\text{m}^3$ reactor volume-day (with MS-OFMSW) and 4 to $6 \text{ kg VS}/\text{m}^3$ reactor

volume-day (with SS-OFMSW) (Bolzonella et al., 2006). Each reactor maintained high biogas methane content during operation (about 55%), and VS removals were 35-40% for MS-OFMSW and 40-45% for SS-OFMSW (Bolzonella et al., 2006). The energy production from SS-OFMSW was 4.3 kWh produced/kWh consumed, while the energy production from MS-OFMSW was only 1.4 kWh produced/kWh consumed (Bolzonella et al., 2006).

Waste biodegradability is determined by waste composition. Biodegradable solid wastes are composed of cellulose, hemicellulose, protein, starch, lignin, and fatty acids (Chynoweth and Pullammanappallil, 1996). Free cellulose is readily hydrolyzed, but in many grasses, woods, and paper products the cellulose is present as part of a lignocellulosic matrix, rather than free (Rittmann and McCarty, 2001). Although the cellulose and hemicellulose present are highly degradable, the lignin sheathing presents a physical barrier to biodegradation – the insolubility, large structure, and complex bonds of lignin make it extremely difficult to break down (Healy and Young, 1979; Komilis and Ham, 2003). In aerobic environments, lignin biodegradation is accomplished by white-rot and brown-rot fungi, and some studies have indicated that unaltered lignin is refractory in anaerobic environments (Komilis and Ham, 2003). However, research using radiolabelled lignocelluloses from grasses and hardwoods, incubated anaerobically with sediments, has confirmed that lignin can be degraded anaerobically, although the process is extremely slow (Benner et al., 1984). For grasses, 3.5 to 16.9% of the lignin and 20.1 to 30% of the polysaccharide components of lignocellulose were degraded during incubations ranging from 280 to 294 days (Benner et al., 1984). In the case of hardwood

samples, 1.5% of lignin and 4.7% of polysaccharide from leaves were degraded and 1.5% of lignin and 4.1% of polysaccharide from wood were degraded over 246 days of incubation (Benner et al., 1984). The lignin content of food and simulated food waste ranges from 0.9 to 12.03% (Verrier et al., 1987; Eklind and Kirchmann, 2000a; Komilis and Ham, 2003). Lignin content in leaves and yard waste ranges from 16.5 to 33.88% (Eklind and Kirchmann, 2000a; Komilis and Ham, 2003). Research on the relationship between waste composition and biodegradability indicates an inverse linear relationship between lignin content and VS destruction efficiency or VS biodegradability (Chandler et al., 1980; Komilis and Ham, 2003). Several studies on this relationship have determined that the maximum biodegradability for a pure cellulose substrate would be about 85% VS destruction, due in part to VS production by microbes (Chandler et al., 1980; Komilis and Ham, 2003).

Analysis to determine the suitability of food waste for AD has not been extensive. Total solids (TS) of 12.38% for Korean food waste, 27.8% for simulated household food waste, and 30.9% for commercial SS-MSW collected in San Francisco have been determined (Eklind and Kirchmann, 2000a; Kim et al., 2006; Zhang et al., 2007). Restaurant, cafeteria, and simulated food waste have VS ranging from 79.4 to 89.6% of TS (Shin and Jeong, 1996; Day et al., 1998; Eklind and Kirchmann, 2000a; Kim et al., 2006; Zhang et al., 2007). Studies of TS and VS of yard or landscape are also rare. One study determined VS of 40.9% of TS for homogenized yard waste arriving at a composting facility (Day et al., 1998). Batch AD of FW produced 300.7 mL CH₄/g TS (Wang et al., 1997) and 435 mL CH₄/g VS (Zhang et al., 2007). The inverse relationship

between lignin content and biodegradable VS (Chandler et al., 1980) has been used to determine biodegradabilities of 81.9% for food waste and 71.5% for yard waste (Kayhanian and Tchobanoglous, 1992).

An ideal C:N ratio for AD is between 25 and 30 (Kayhanian and Hardy, 1994). If the C:N ratio is too high there will not be enough N for microbial growth, while a C:N ratio that is too low allows production of excess ammonia and may result in inhibition or toxicity (McCarty, 1964c; Kayhanian, 1994; Hartmann and Ahring, 2006). C:N ratios ranging from 8.7 to 12.4 have been determined for mixed food waste (Kayhanian and Tchobanoglous, 1992; Day et al., 1998), with some high protein components (meat and bone meal) having especially low values (4) and others (potatoes and carrots) having higher values (30) (Eklind and Kirchmann, 2000a). Higher C:N ratios have been observed in yard or landscape waste, with values of 14.5 to 27.7 for yard waste, and 31 to 32 for leaves (Kayhanian and Tchobanoglous, 1992; Day et al., 1998; Eklind and Kirchmann, 2000a; Ono et al., 2003).

In order to successfully treat a low C:N substrate with HSAD (where dilution with water is not an option) a cosubstrate can be added to reach the desired C:N ratio (Kayhanian, 1999). One substrate that can be used to increase the C:N ratio of food waste for AD is paper: in one study the C:N ratio of a mixture of 75% office paper and 25% newspaper was found to be 143:1 (Kayhanian and Tchobanoglous, 1992). In another study computer paper was digested with kitchen food waste, resulting in increased biogas production and decreased total ammonia nitrogen (TAN) concentration (Vermuelen et al., 1993). Which paper to use as a cosubstrate is very important:

newspaper is minimally processed, has high lignin content and is not amenable to AD (Barlaz, 1996). Office paper, however, goes through extensive processing and retains very little lignin, and as a result is highly degradable (Barlaz, 1996). The lignin content of computer or office paper may be as low as 6.5% of TS or 0.4% of VS, and during biodegradability studies up to 90.1% of office paper VS was mineralized (Kayhanian and Tchobanoglous, 1992; Vermuelen et al., 1993). Agricultural residues can also be used as a cosubstrate for AD; in research on codigestion of swine manure with corn stalks, oat straw, or wheat straw, Wu et al. found that the combination of swine manure with corn stalks, at a C:N ratio of 20:1, resulted in a 16-fold increase in methane production (Wu et al., 2010).

2.3. Anaerobic digestion process

2.3.1. Overview

The AD process relies on a number of different groups of microbes, each mediating one step, in a series converting complex organic material into methane and carbon dioxide (Speece, 1996). The first step is depolymerization or hydrolysis, in which particles and complex organic molecules are broken down into simple organic compounds (Chynoweth and Pullammanappallil, 1996; Speece, 1996). Particulate substrates composed of proteins, carbohydrates, and lipids are reduced to amino acids, sugars, alcohols, and fatty acids that can be taken up by microbes (Gujer and Zehnder, 1983; Chynoweth and Pullammanappallil, 1996). This process is driven by extracellular enzymes produced by a distinct population of hydrolytic bacteria (Chynoweth and

Pullammanappallil, 1996). The amount of material that can be depolymerized dictates in large part the final amount of methane that can be produced from the substrate (Chynoweth and Pullammanappallil, 1996).

In the next step, acidogenesis (sometimes called fermentation), some of these hydrolysis products are converted directly to acetate, hydrogen, or methane, while others are converted to longer chain fatty acids (Gujer and Zehnder, 1983; Speece, 1996). Finally, in methanogenesis these fermentation products are converted to methane and carbon dioxide (Speece, 1996). Successful AD requires these steps to proceed at similar rates, with end products from each step being used by the next step as they are generated. If an imbalance does arise, it may take some time to correct. While AD is typically limited by hydrolysis, at high loading rates the limiting step can be methanogenesis, as volatile fatty acids (VFA) can build up faster than methanogens can stabilize them (Speece, 1983; Shin et al., 2000). This is especially true for wastes that are high in carbohydrates and sugars, which are highly digestible (Speece, 1983). In turn, acidogenesis depends on microbial utilization of hydrogen (Chynoweth and Pullammanappallil, 1996). This interspecies hydrogen transfer can serve to balance the rates of acidogenesis and methanogenesis: if methanogenesis slows, hydrogen accumulation slows acidogenesis, preventing the adverse effects of VFA accumulation and allowing methanogens to reduce VFA concentrations (Chynoweth and Pullammanappallil, 1996). In some circumstances the accumulation of organic acids can reduce pH and result in slowed methanogenesis (Chynoweth and Pullammanappallil, 1996). If large quantities of higher order organic acids are formed, they cannot be

metabolized until a suitable microbial population is developed – which may be a time consuming process due to the slow growth of propionate-utilizing microbes (Chynoweth and Pullammanappallil, 1996).

2.3.2. Requirements for successful operation

AD has been successful under a wide array of conditions. Although it progresses at temperatures between 4 and 100°C, digestion proceeds most reliably at mesophilic (35°C) and thermophilic (55°C) temperatures (Speece, 1983). Anaerobic degradation of wastewater at psychrophilic temperatures (around 15°C) has also been demonstrated (Bodík et al., 2000; McHugh et al., 2004). Research in AD of FW and MSW under a range of different moisture levels and reactor configurations has indicated that the best VS destructions and methane production results are achieved at thermophilic temperatures (Oleszkiewicz and Poggi-Varaldo, 1997; Converti et al., 1999; Kayhanian, 1999; Hartmann and Ahring, 2006). Results of one study indicated that thermophilic digestion was slightly less stable at short mass retention times than mesophilic digestion (Oleszkiewicz and Poggi-Varaldo, 1997).

Historically, low-solids AD has been used for biomass reduction after the aerobic step in wastewater treatment, but in recent years an increasing number of projects have demonstrated successful digestion of solid waste at higher total solids (TS) concentrations (Chynoweth and Pullammanappallil, 1996; Hartmann and Ahring, 2006). Although there is some variation in the solids cutoffs and terminology, HSAD is the most commonly used term (others are dry fermentation and dry anaerobic digestion), and it is

typically classified as digestion at solids content higher than 20% (Sharma et al., 1999; Bidlingmaier et al., 2004; Hartmann and Ahring, 2006). An upper limit for solids content in AD is 40% (De Baere, 2004). High-solids digestion can include TS as low as 15% (Shin et al., 2000; De Baere, 2004), or exclude any TS content lower than 25% (Luning et al., 2003). AD at high solids eliminates the need for process water addition, effluent dewatering, and effluent water treatment (Lissens et al., 2001; Bidlingmaier et al., 2004; Hartmann and Ahring, 2006). Under high solids operating conditions reactor heating requirements and size are likely to be lower, reducing both capital and operating costs (Bidlingmaier et al., 2004; Hartmann and Ahring, 2006). Phase separation in low-solids digestion can result in equipment fouling (Lissens et al., 2001; Luning et al., 2003; De Baere, 2004). When floating or deposited materials are removed to protect equipment, VS are lost that could have been digested (Lissens et al., 2001; Luning et al., 2003; De Baere, 2004). However, the low moisture content in HSAD may result in incomplete mixing, resulting in less contact between microbes and substrates, and decreased biogas and methane production rates (Chynoweth and Pullammanappallil, 1996). In general, material handling may be more challenging in HSAD, because of high reactor solids contents (Lissens et al., 2001). Additionally, although HSAD potentially allows for higher loading rates than low-solids digestion (possibly up to 10 kgVS/m³-day), effluent may require additional treatment for complete stabilization (Bidlingmaier et al., 2004; Hartmann and Ahring, 2006).

The optimal pH for AD is between 6.5 and 8.2; outside this range the process can slow or even stop (McCarty, 1964b; Speece, 1983). Bicarbonate buffering capacity is

extremely important in order to maintain stable pH in the desired range (Chynoweth and Pullammanappallil, 1996; Rittmann and McCarty, 2001). Alkalinity in excess of 2,500 to 5,000 mg/L as CaCO₃ is required to protect against a pH drop in the event of VFA accumulation (McCarty, 1964b). It may be necessary to add alkalinity to the digestion process to ensure adequate buffering if the substrate itself does not provide sufficient alkalinity. Alkalinity is affected by the release of ammonium from the degradation of organic material during the treatment process (Chynoweth and Pullammanappallil, 1996; Rittmann and McCarty, 2001). The release of nitrogen from organics allows the formation of un-ionized ammonia, which is then protonated, forming ammonium, releasing hydroxide, and increasing the alkalinity of the system (Angelidaki and Ahring, 1994; Kayhanian, 1999; Bujoczek et al., 2000; Rittmann and McCarty, 2001).

One concern, especially during HSAD when influent is more concentrated, is the presence of inhibitory or even toxic compounds. If a reactor is overloaded or inhibited by a toxic agent, organic acids will accumulate, consume the available alkalinity, and eventually reduce pH (Chynoweth and Pullammanappallil, 1996). VFA concentrations above 10,000 mg/L will inhibit digestion (Chynoweth and Pullammanappallil, 1996). Additionally, because of the slow growth rate of anaerobic microorganisms, even after an inhibitory agent is removed, reactor recovery may be slow (Speece, 1983; Chynoweth and Pullammanappallil, 1996). HSAD of food waste may be especially susceptible to inhibition due to ammonia, because of potentially high protein content of the substrate and the increased concentration (compared to low-solids AD) within the reactor. The temperature dependence of the ammonia equilibrium means that concentrations of free

ammonia (the more toxic species) will be higher at thermophilic temperatures than mesophilic temperatures for the same TAN concentration (Kayhanian, 1999). Both free ammonia and ammonium can cause inhibition or toxicity. Free ammonia can cause inhibition in concentrations between 45 and 150 mg/L (McCarty and McKinney, 1961; Kayhanian, 1999). Ammonium can cause inhibition at concentrations as low as 1670 mg/L, and toxicity at concentrations of 6000 mg/L (Lay et al., 1998). Nitrogen in the substrate is converted to ammonium, which increases the pH and forms more free ammonia, increasing the effects of inhibition. Acclimation of microbes to high ammonia concentrations has been reported by a number of researchers (Lay et al., 1998; Bujoczek et al., 2000). Microbes have acclimated to TAN concentrations of 2300 mg/L and ammonium concentrations of 3 to 3.5 g NH₄-N/kg reactor (Kayhanian, 1994; Oleszkiewicz and Poggi-Varaldo, 1997).

For healthy cell growth, sufficient macro- and micronutrients must be supplied by the substrate or added to the digester. Macronutrients include nitrogen, phosphorus, and sulfur, and micronutrients can include at least iron, cobalt, nickel, and zinc, and sometimes copper, manganese, molybdenum, selenium, tungsten, and boron (Speece, 1983; Rittmann and McCarty, 2001). Although these micronutrients may be present in the substrate, they must be bioavailable in order for the microbes to utilize them – it may be advisable to supplement with a known bioavailable form (Speece, 1983).

Regular monitoring of AD is necessary to allow intervention in the event of process disruption or instability. Parameters that have been used to indicate reactor stress include biogas composition, biogas production, pH, volatile solids destruction, and

volatile fatty acid concentration (Ahring et al., 1995). Biogas methane content is often used as an early indicator of reactor upset (Ahring et al., 1995). However, VFA concentration generally increases more quickly (within 1-2 days of perturbation), varies more, and is of longer duration than changes in methane production (Angelidaki and Ahring, 1994; Ahring et al., 1995; Björnsson et al., 2000). On occasion a high methane percentage may be sustained despite extended reactor overloading (Angelidaki and Ahring, 1994; Ahring et al., 1995; Björnsson et al., 2000). In addition, concentrations of individual VFAs can provide more specific information about reactor health. Increases in HPr have been observed during reactor perturbations, as have increases in I-HBu, HBu, and other higher order VFAs (of 4 to 6 carbons) (Ahring et al., 1995; Björnsson et al., 2000).

2.3.3. Treatment goals

Hartmann et al. (2006) reviewed a large number of AD studies, determining that in general increasing the organic loading rate (OLR) resulted in a decline in biogas yield. Overall, including the cost of residual waste treatment and the value of the biogas produced, it was advantageous to maintain a lower OLR, to allow for maximum biogas production and minimum digestate treatment (Hartmann and Ahring, 2006). Other research also indicates that increasing treatment time can increase waste stabilization, although the improvement may be limited: in one study of aerobic waste treatment, four weeks of treatment produced a 56% decrease in anaerobic biogas potential, while 12 weeks of treatment resulted in a 79% decrease in anaerobic biogas potential, which

indicates that gains in treatment are not necessarily proportionate to treatment time (Scaglia et al., 2010). Goals of maximizing biogas production and waste stabilization and minimizing residual waste need to be balanced with increased treatment costs for larger reactors. When treatment times are shortened, it is important to consider that in HSAD, unlike in LSAD, microbes cannot be retained in the system when effluent is removed; and as a result, when OLR is increased solids retention time is decreased, and adequate time for microbial reproduction needs to be maintained.

When AD is used as an alternative to landfilling, the main goal may be waste reduction, possibly including energy production and reduction in methane emissions as secondary goals. In this case, low OLR operation may be desirable, in order to maximize VS destruction and biogas production. Since waste stabilization is not a primary goal in this scenario, a second processing step to cure or polish the effluent would be undesirable. Adding an aerobic polishing step costs energy and requires additional processing: the loss of energy from curing outweighs the other benefits of combining the technologies (Hartmann and Ahring, 2006). Additionally, because AD takes place at 5 to 40% dry solids, while composting requires about 50% dry solids, either dewatering or the addition of a bulking agent is required (De Baere, 2004). However, when an additional treatment goal is the creation of a useful soil amendment, complete waste stabilization is required. In order to reduce oxygen demand and vector attraction potential, it may be necessary to incorporate a brief (7-14 days) aerobic “polishing” step (Kayhanian and Tchobanoglous, 1993b; 1993a).

2.4. Anaerobic digestion followed by curing for humus and energy production

Kayhanian and Tchobanoglous (1993a; 1993b) studied a thermophilic system fed simulated OFMSW. The combined retention time of the anaerobic and aerobic phases was 30 days. The solids content of the anaerobic phase was 25-30%; during the aerobic phase the solids content increased to 65%. The combined anaerobic and aerobic treatment resulted in a destruction of 6.5 to 7 g biodegradable VS/kg of reactor mass-day. Influent VS content (94% of TS initially) dropped to 70% of TS by the end of the combined anaerobic and aerobic treatment, for 26% VS destruction during treatment. The aerobic phase of treatment qualitatively reduced odors produced during the anaerobic phase. However, there was some phytotoxicity remaining after treatment. When seed germination tests were conducted with humus leachate in dilutions ranging from 10% to 50%, leachate concentrations of greater than 25% resulted in germination of less than 60% of seeds, indicating unacceptable phytotoxicity.

Another study focused on low-solids digestion followed by composting. Vegetable and fruit waste was digested thermophilically at 9% solids, followed by an increase to 25% solids through the addition of peat for a brief composting step. This process was termed anaerobic composting and the loading rate was 2 g VS/L reactor volume-day, with 2-6 weeks of AD and 1-2 weeks of composting. Biogas production from this process was 3.6 L/L reactor volume-day. The researchers observed an increase in ammonium during the study, with a corresponding increase in VFAs. In order to assess the possibility of codigestion of fruit and vegetable waste with a high-carbon substrate, computer paper was added to the digestion process. This allowed an increase in loading

to 12.6 g VS/L reactor volume-day and an increase in reactor solids content to 20%.

There was a corresponding decrease in reactor TAN (Vermuelen et al., 1993).

Vallini (1993) studied post digestion composting as a method of reducing effluent water content, increasing stability, and removing phytotoxicity. Thermophilic and mesophilic digestion were compared (both at 20% solids). Digestate was composted with fresh OFMSW for several weeks. The addition of post digestion composting removed any need to dewater effluent and eliminated phytotoxicity within two weeks or three weeks, for thermophilic and mesophilic digestion, respectively.

The term composting is often used to describe a polishing step after AD (Vallini et al., 1993; Vermuelen et al., 1993; Hartmann and Ahring, 2006). However, when the two processes are combined, the AD step replaces the active stage of composting, which is characterized by high microbial activity and high temperatures (60 or 70°C), during which the majority of easily biodegradable material is consumed (Finstein and Morris, 1975; Sullivan and Miller, 2001). When the effluent from AD is treated aerobically, the process resembles the final stage of composting in which microbial activity is low and temperatures generally remain below 40°C (called curing) (Sullivan and Miller, 2001).

When curing is used after AD the majority of the biodegradation has already taken place, however, it is still important to provide favorable conditions for continued aerobic biodegradation. For composting, those conditions include adequate moisture content, sufficient aeration, and appropriate C:N ratio and pH for microbial growth. The composting of high-solids anaerobic digestate, where solids may range from 20-40% (Sharma et al., 1999; Bidlingmaier et al., 2004; De Baere, 2004; Hartmann and Ahring,

2006) requires the addition of a bulking agent to supply structural support and provide sufficient air space for the circulation of oxygen (de Bertoldi et al., 1983; Eftoda and McCartney, 2004). Requirements of oxygen content range from pore space oxygen of at least 5% (Eftoda and McCartney, 2004) to 18% oxygen in the circulating air (de Bertoldi et al., 1983). A study on wood chips as the bulking agent in composting of biosolids determined ideal bulking agent ratios of 1:2.5 or 1:2.8 (biosolids:wood chips), by volume (Eftoda and McCartney, 2004). Moisture content should be maintained between 40 and 60% (Rynk et al., 1992). A pH between 5.5 and 8 is appropriate for composting, with C:N ratio between 25:1 and 40:1. In general, material from a successful AD process is likely to have the right conditions for composting once the solids content is adjusted and bulking agents are added (Finstein and Morris, 1975; de Bertoldi et al., 1983). Carbon loss occurs early in composting, during the main digestion events, and extensive change in C:N ratio is unlikely during curing (Brewer and Sullivan, 2003).

Although laboratory-scale composting experiments, by necessity, are carried out under very different conditions than full-scale operations, it is possible for a well-constructed laboratory-scale study to provide useful results (Day et al., 1998). Day compared laboratory-scale and full-scale composting to determine to what degree laboratory-scale experiments would be useful in predicting full-scale composting behavior (Day et al., 1998). The material composted was 12.5% yard waste, 10% construction waste, 25% food residues, 25% barnyard bedding material, and 25% oversized recycled material (Day et al., 1998). The study used 6-L insulated vessels which were incubated in a 35°C room during composting (Day et al., 1998). The

laboratory-scale system demonstrated a temperature profile similar to what might be seen in a full-scale composting operation; during the first 12 days of the study the material self-heated to 68°C and then cooled again to about 45°C, which is characteristic of the active stage of composting (Day et al., 1998). Although the changes due to composting were smaller in the lab-scale system than the full-scale system, the lab-scale system provided useful information (Day et al., 1998).

2.5. Determination of compost maturity

Compost maturity (the fitness of compost for an intended use) can be determined through direct assessments of stability such as self-heating (Brinton et al., 1995; Sullivan and Miller, 2001), carbon dioxide evolution, and oxygen consumption (Iannotti et al., 1994). These methods measure the amount of microbial activity within the compost. In addition, attempts have been made to identify universal stability indices that allow for convenient on-site testing with minimal equipment (Iannotti et al., 1994; Brewer and Sullivan, 2003; Changa et al., 2003). When stability indices rely on correlations between microbial activity and chemical or physical characteristics of compost (such as pH, C:N ratio, cation exchange capacity, humic acid:fulvic acid ratio, total organic carbon, and water soluble nitrogen) they are highly substrate-dependent (Jimenez and Garcia, 1989; Eggen and Vethe, 2001; Sullivan and Miller, 2001). Direct tests of microbial activity generally give reliable results across a range of feedstocks (Eggen and Vethe, 2001).

The absence of phytotoxicity and odors indicates compost stability. Compounds known to cause phytotoxicity include VFAs (DeVleeschauwer et al., 1981) and ammonia

(Leege and Thompson, 1997). Odorous substances, such as VFAs and volatile sulfur compounds (VSCs), are formed under anaerobic conditions and may occur when anaerobic zones develop during the composting process as a result of high microbial activity depleting compost oxygen levels.

Considerable self-heating is common during composting of undigested matter (Finstein and Morris, 1975). During active composting, temperatures can rise high enough (between 60°C and 70°C) to limit microbial activity (Finstein and Morris, 1975). In contrast, the final stages of composting are characterized by moderate self-heating with temperatures close to the ambient temperature (Woods End Research, 2004). Compost self-heating is accompanied by oxygen consumption as microbes degrade biological material. Oxygen uptake rates of active compost can exceed 5.0 mg O₂/g TS-h (Leege and Thompson, 1997). Compost oxygen uptake rates below 0.4 mg O₂/g TS-h indicate “very stable” compost that is ready to use (Leege and Thompson, 1997; Compost Guidelines Task Group, 2005).

One problem with many methods of assessing compost maturity is that they require expensive equipment or extensive training to administer. In contrast, the Solvita test, developed by Woods End Laboratories, uses colorimetric gel paddles, which are inserted into a compost sample, exposed to headspace gases for 4 hours, and visually compared to color standards. Paddles are available for both CO₂ and NH₃ testing. Individual NH₃ and CO₂ levels are determined and then can be combined to determine the Solvita maturity index (SMI). An SMI of 6 signifies compost in the curing stage,

which is classified as mature, while an SMI of 8 indicates “finished compost” (Woods End Research, 2004).

During active composting, high microbial respiration can consume the available oxygen, resulting in anoxic zones and the formation of VFAs due to anaerobic activity (Brinton, 1997). As a result, the presence of VFAs indicates immature compost with high oxygen requirements (Brinton, 1997). When aerobic curing follows AD, the presence of VFAs may be due to transfer from the AD process. VFAs can cause phytotoxicity in high enough concentrations; in one study, acetic acid concentrations of 300 ppm inhibited the germination of cress seeds, whereas concentrations of 2000 ppm prevented germination completely (DeVleeschauwer et al., 1981). Another study associated VFA concentrations as low as 500 ppm with compost immaturity (Brinton, 1997). Another phytotoxic compound that may be present in immature compost is ammonia. Nitrification generally decreases ammonia concentrations during composting, as observed during composting of source-separated organic household wastes (Eklind and Kirchmann, 2000b). Excess ammonia is indicated by Solvita ammonia results between levels one and three (indicating 25,000 to 2,500 ppm of ammonia) (Woods End Research, 2004). These concentrations indicate low compost C:N ratio and possible phytotoxicity (Woods End Research, 2004).

Odorous compounds are problematic because many are formed under anaerobic conditions, indicating oxygen shortages and unstable compost. Additionally, the potential for odor formation can interfere with siting projects and the usability of the final product. Both microbial processes and abiotic mechanisms contribute to the formation of

VSCs. These processes can be both anaerobic and aerobic. Some processes that could contribute to VSC production and degradation during curing of anaerobic digestate are shown in Figure 2.1.

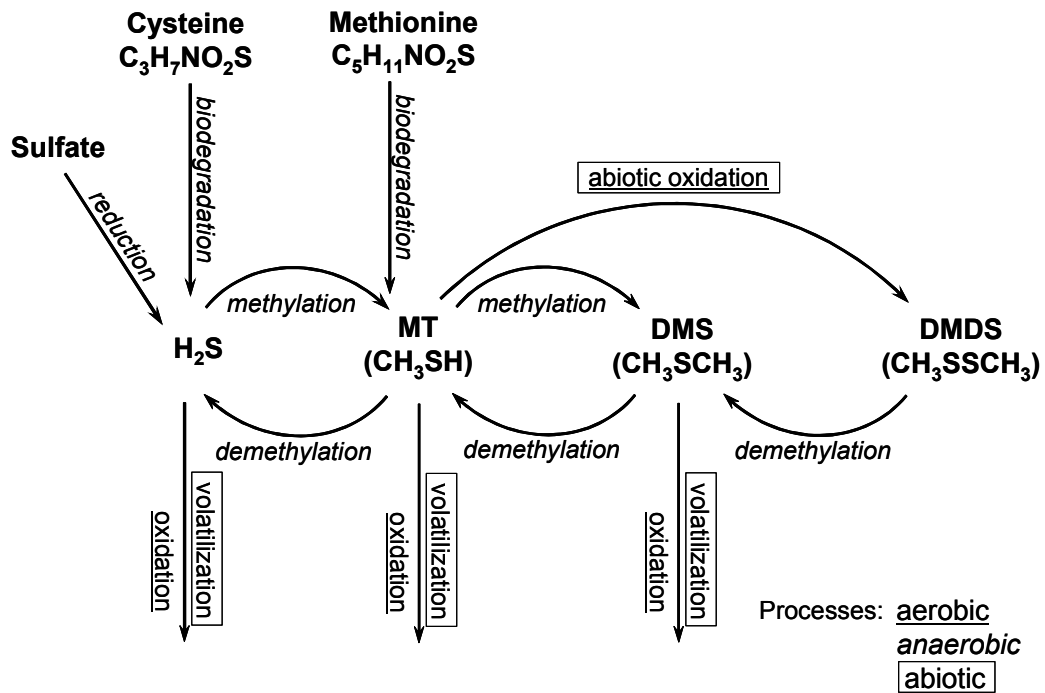
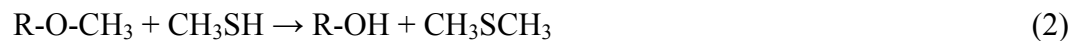


Figure 2.1. Production and degradation of H₂S and volatile sulfur compounds. Adapted from Higgins, Chen et al. 2006, with information from (Forsberg, 1980; Kiene et al., 1986; Zehnder, 1988; Finster et al., 1990; Finster et al., 1992; Visscher and Taylor, 1993; Lomans et al., 1999; Lomans et al., 2002).

Under anaerobic conditions, sulfate can be reduced to H₂S by sulfur-reducing bacteria. H₂S and methanethiol (MT) production from anaerobic degradation of the sulfur-containing amino acids cysteine and methionine, respectively, has been demonstrated (Hayward et al., 1977; Forsberg, 1980; Higgins et al., 2006). Feedstock C:N ratio may be significant here: if high protein feedstocks like meat and bones are present there will be more VSC precursors present (Eklind and Kirchmann, 2000a). Microbes methylate H₂S

and MT under anaerobic conditions, producing MT and dimethyl sulfide (DMS), respectively (Lomans et al., 2002; Higgins et al., 2006). Generally, DMS is the final product, with MT formed only as an intermediate (Bak et al., 1992). The formation of MT and DMS through methylation of H₂S is shown in reactions 1 and 2 (Bak et al., 1992; Higgins et al., 2006).

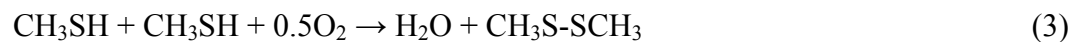


The formation of H₂S, MT, and DMS by these processes would be expected both during AD and during curing if microbial activity was high and anaerobic zones were formed.

Degradation byproducts of lignocellulose can contribute the methyl donors required in Reactions 1 and 2 (Lomans et al., 1997; Lomans et al., 2002). As discussed previously, lignin is biodegraded aerobically by fungi (Tuomela et al., 2000; Komilis and Ham, 2003), so production of VSCs by methylation of H₂S and MT might be expected when high respiration events occur during composting, since these methyl donors would be available. However, during AD, biodegradation of lignocellulose proceeds much more slowly, if at all (Benner et al., 1984; Tuomela et al., 2000; Komilis and Ham, 2003). Formation of significant concentrations of MT and DMS during AD of biosolids indicates that formation can occur in the absence of large quantities of lignocellulose (Higgins et al., 2006). Research has indicated that microbial extracellular polymeric substances can degrade humic compounds which can also supply the methyl donors

required (Frølund et al., 1996). Formation of these compounds during AD of MSW or food waste would be expected to proceed by the dominant mechanisms observed in freshwater sediments and anaerobically digested biosolids: cysteine and methionine degradation, sulfate reduction, and H₂S and MT methylation (Lomans et al., 2002; Higgins et al., 2006).

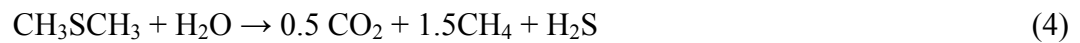
Dimethyl disulfide (DMDS) is formed abiotically under aerobic conditions through the oxidation of MT and will not form under strictly anaerobic conditions (Hayward et al., 1977; Higgins et al., 2006). The formation of DMDS through oxidation of MT is shown in reaction 3 (Higgins et al., 2006).



Because DMDS formation requires the oxidation of MT it would not be expected during AD. Conditions favorable for DMDS formation might occur during composting, if anaerobic zones and the formation of MT preceded turning or other aeration, which would provide aerobic conditions and allow DMDS formation.

MT and DMS concentrations are generally relatively low, because they are simultaneously formed and degraded (Lomans et al., 2001). Inhibition of methanogenesis interrupts conversion of MT and DMS to H₂S (Lomans et al., 1999; Lomans et al., 2002; Higgins et al., 2006). As a result, methylotrophic methanogenesis has been suggested as a mechanism of DMS degradation to H₂S with MT as an intermediate, mediated by sulfate-reducing bacteria and methanogens (Finster et al.,

1992; Lomans et al., 1999; Lomans et al., 2002; Higgins et al., 2006). Reaction 4 illustrates the conversion of DMS to H₂S by this process (Kiene et al., 1986; Finster et al., 1992; Higgins et al., 2006).



In sulfate-poor environments (during AD, under reducing conditions), the activity of sulfate-reducing bacteria would be minimal and the majority of VSC degradation would take place through methylotrophic methanogenesis.

Successful AD of MSW followed by aerobic treatment is well documented in full-scale operation at European plants. Additionally, composting of food waste is common in the US and elsewhere. However, no study has demonstrated the feasibility of AD followed by curing as a zero-waste process for the treatment of university cafeteria food waste.

2.6. References

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CHAPTER 3: Manuscript 1

High-solids anaerobic digestion of university food waste

The following paper is in preparation.

High-solids anaerobic digestion of university food waste

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Abstract

A pilot-scale study was completed to determine the feasibility of high-solids anaerobic digestion (HSAD) of a mixture of food and landscape wastes at Bucknell University. Reactor performance was monitored at two organic loading rates through routine analysis of biogas production, biogas composition, reactor total and volatile solids, total and soluble chemical oxygen demand, volatile fatty acid content, pH, and bicarbonate alkalinity. In addition, total chemical oxygen demand, total and volatile solids, and biodegradability (from batch digestion) were determined for the food and landscape waste collected during the study. Fats, oil and grease and total Kjeldahl nitrogen were determined for some food waste samples. HSAD appeared stable at low loadings (2 g COD/L reactor volume-day), but likely developed inhibitory ammonia concentrations at high loadings (15 g COD/L reactor volume-day). At low loadings methane yields were 232 L CH₄/kg COD fed and 229 L CH₄/kg VS fed, and at high loadings methane yields were 211 L CH₄/kg COD fed and 272 L CH₄/kg VS fed. Based on the characterization and biodegradability studies, Bucknell University dining hall food waste appears to be a good candidate for HSAD at low organic loading rates; however, the development of

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ammonia inhibition at high loading rates suggests that it has a low C:N ratio. The low biodegradability of Bucknell University landscape waste makes it an unsuitable candidate for codigestion to increase the C:N ratio. Codigestion of food waste with a substrate high in bioavailable carbon may increase the C:N ratio sufficiently to allow HSAD at loading rates of 15 g COD/L reactor volume-day.

3.1. Introduction

Biodegradation of municipal solid waste (MSW) under anaerobic conditions converts organic waste into methane, a valuable energy source. Anaerobic digestion (AD) of municipal solid waste has been employed in Western Europe since the 1980s, where 200 facilities have a total capacity of 6 million metric tons (MMT) per year (De Baere and Mattheeuws, 2010). The United States Environmental Protection Agency has estimated that 2009 production of MSW in the US was 221 MMT, of which 120 MMT was landfilled (U.S. EPA, 2010). Approximately 61.4 MMT (27.8%) of the MSW generated was kitchen waste and yard trimmings, also known as green waste, of which 18.9 MMT (31%) was composted (U.S. EPA, 2010).

In the US, substitution of AD for green waste composting processes could result in nationwide net energy production (100-150 kWh/ton) instead of consumption (30-35 kWh/ton) (Hartmann and Ahring, 2006). During one full-scale study, methane yield from AD of green waste was $0.4 \text{ m}^3 \text{ CH}_4/\text{kg VS fed}$ (Bolzonella et al., 2006). Additionally, AD of the organic fraction of MSW (OFMSW) that is currently landfilled in the US could result in significant renewable energy production, as well as reduction of

CO₂ emissions (DiStefano and Belenky, 2009). However, given the relatively low costs associated with landfilling MSW in the US, widespread AD of MSW will only be feasible if the entire AD process is cost-competitive with landfilling (Chynoweth and Pullammanappallil, 1996).

Waste sorting is essential in order to maximize methane production from MSW or green waste. A full-scale study of anaerobic digestion compared source-sorted (SS) OFMSW with mechanically sorted (MS) OFMSW: digestion of SS-OFMSW produced 4.3 kWh for each kWh consumed, while digestion of MS-OFMSW produced only 1.4 kWh per kWh consumed (Bolzonella et al., 2006). Although a substrate with a high chemical oxygen demand (COD) may seem to be a good candidate for AD, waste biodegradability affects COD bioavailability. In addition, substrate C:N ratio affects the success of digestion. Kayhanian and Hardy (1994) studied the effect of C:N ratio on AD and determined an optimal range of 25 to 30. The goal is to supply enough nitrogen to meet microbial growth needs without supplying so much that excess ammonia is formed, potentially causing inhibition or even toxicity (McCarty, 1964c; Kayhanian and Hardy, 1994).

Regular monitoring of AD is essential for reliable methane production and stable operation. Parameters that can be used as indicators of reactor stress include biogas production, biogas composition, pH, volatile solids (VS) destruction, and volatile fatty acid (VFA) concentration (Ahring et al., 1995). Often, the clearest indicator of a perturbation is VFA accumulation (Angelidaki and Ahring, 1994; Ahring et al., 1995). There may be a simultaneous decrease in biogas production or methane percentage;

however, these changes are often small and of short duration, and sometimes a high methane percentage may be sustained despite extended reactor overloading (Angelidaki and Ahring, 1994; Ahring et al., 1995; Björnsson et al., 2000). The danger of VFA accumulation during reactor upset lies largely in the potential of pH decrease, as the optimal pH range for AD is between 6.6 and 7.6 (McCarty, 1964b). The presence of sufficient alkalinity to buffer minor pH changes is essential, but a sustained perturbation may produce enough VFAs to reduce reactor pH.

Previous HSAD research has demonstrated the benefits of HSAD followed by a brief aerobic composting step (often described as polishing or curing), which serves to increase solids content, continue waste stabilization, and reduce odors formed during the anaerobic stage. A pilot-scale study on HSAD followed by aerobic composting was conducted by Kayhanian and Tchobanoglous (1993a; 1993b). During the study a feedstock of simulated OFMSW was digested at thermophilic temperatures at total solids (TS) of 23-30%. The process loading rate was determined in biodegradable volatile solids (BVS), with 6.5 to 7 g BVS fed/kg reactor mass-day, and a mass retention time of 30 days. The aerobic composting stage served largely to dry the humus produced from anaerobic digestion and to eliminate residual odors from HSAD.

One lab-scale study focused on thermophilic AD of vegetable and fruit waste at 9% TS, followed by composting with an increase to 25% TS through the addition of peat. The process (termed anaerobic composting) was loaded at 5.2 g VS/L reactor volume-day, with 2-6 weeks of AD and 1-2 weeks of composting. The biogas production was 3.6 L/L reactor volume-day. During the study there was an increase in ammonium and VFA

concentration. The researchers also studied the biodegradability of paper and the possibility of codigestion of fruit and vegetable waste with computer paper. Paper addition to the AD process allowed a loading rate increase to 12.6 g VS/L reactor volume-day, an increase in reactor solids to 20%, and a decrease in reactor total ammonia nitrogen (TAN) (Vermuelen et al., 1993).

Bolzonella et al. (2006) studied two full-scale HSAD systems using the DRANCO process, in which one reactor was fed a combination of gray waste, MS-OFMSW, and sewage sludge, and one was fed SS-OFMSW. Reactors were fed based on waste total volatile solids (TVS) content (VS proportion of waste as-is). Although the reactor digesting SS-OFMSW demonstrated a higher biogas yield ($0.4 \text{ m}^3 \text{ CH}_4/\text{kg VS}$ fed), each reactor was operated successfully for one year at loading rates of 3 to 8 kg TVS/ m^3 reactor-day (MS-OFMSW) and 4 to 6 kg TVS/ m^3 reactor-day (SS-OFMSW). Methane content in each reactor was high throughout operation (about 55%), and VS removals were 35-40% for MS-OFMSW and 40-45% for SS-OFMSW.

Reactor size plays a role in treatment cost as well as process stability. Although a larger reactor may cost more to construct, increasing SRT can result in decreased net cell growth and greater waste stabilization, as well as increased methane production. However, during aerobic treatment of MSW, increasing treatment time does not necessarily result in proportional increases in waste stabilization. One study of anaerobic biogas potential of aerobically treated MSW showed that 4 weeks of treatment reduced anaerobic biogas potential by 56%, but 12 weeks of treatment resulted only in an additional 23% of anaerobic biogas potential reduction (Scaglia et al., 2010).

During this study the suitability of Bucknell University cafeteria food and landscape waste for high-solids anaerobic digestion was assessed through characterization and biodegradability studies, in order to determine the feasibility of a potential full-scale system. Knowledge about the consistency of substrates for AD is essential in planning systems, and no long-term characterization of this substrate exists. A study of high-solids (20%) anaerobic digestion followed by aerobic curing was conducted at a loading rate of 2 g COD/L reactor volume-day (for the digestion process). Although previous research has assessed the feasibility of HSAD followed by curing, quantitative data on the reduction of odor causing compounds during curing is lacking. The loading rate was increased to 15 g COD/L reactor volume-day to compare the process performance and duration at high loadings, but inhibition was observed at this loading rate. The potential cause and degree of inhibition was assessed through respirometry.

3.2. Material and Methods

3.2.1. Reactor operation

A stainless steel vessel with a horizontally-oriented helical mixer served as the anaerobic digester. The working volume was 280 liters during low OLR operation and 260 liters during high OLR operation. Seed organisms were obtained from a full-scale upflow anaerobic sludge blanket reactor treating brewery wastewater. Mixing was supplied by a 5-hp motor equipped with a reducing gear, controlled by a timer to enable 5 minutes of mixing at 15-minute intervals. Temperature was maintained at 35 °C by

circulating hot water through the water-jacketed reactor. Manual daily wasting and feeding were accomplished via knife/gate valves in the reactor top and bottom. Biogas production was initially measured using a precision wet tip gas meter (Laboratory Gas Meters, Nashville, TN). It was replaced with a wet-test gas meter (Precision Scientific Petroleum Instruments, Model 63126), on day 192 of operation, to accommodate increased biogas production.

Feed stock COD was used to determine the reactor organic loading rate. During reactor startup and testing (days 1 through 141 of operation) the reactor was operated at loading rates of 0.5 g COD/L reactor volume-day (days 1 through 21), 2 to 3 g COD/L reactor volume-day (days 22 through 110), 5 g COD/L reactor volume-day (days 111 through 126), and 7 g COD/L reactor volume-day (days 127 through 141). The OLR was reduced to 2 g COD/L reactor volume-day for the low OLR study, and then held steady for 90 days prior to sampling for an examination of digestate curing. After the low OLR digestion and curing studies, the OLR was increased stepwise to 15 g COD/L reactor volume-day, with stops at OLRs of 5, 7, 10, and 12.5 g COD/L reactor volume-day for acclimation periods of 13, 24, 36, and 8 days, respectively. Time allowed for reactor acclimation was based on indicators of stable digestion (section 3.2.3). The reactor was operated at an OLR of 15 g COD/L reactor volume-day for a total of 54 days when it became clear that the reactor was unstable, at which point feeding was decreased to an OLR of 10 g COD/L reactor volume-day for 6 days and then discontinued.

Food waste and landscape waste from Bucknell University were combined to maintain both a consistent OLR, and reactor solids content at 20%. During operation,

biomass was wasted from the reactor only for sampling and to maintain the working volume. As a result, at the OLR of 2 g COD/L reactor volume-day, the reactor solids retention time (SRT) was on the order of 175 days. Although the reactor could not be operated for three SRTs in order to ensure steady-state conditions, stable operation was identified by consistent methane production and stable soluble COD (SCOD) and VFA content in the digestate. During the high OLR operation, the reactor SRT was on the order of 25 days.

3.2.2. Food and landscape waste characterization

Chemical oxygen demand, solids, total Kjeldahl nitrogen, and fats, oil, and grease

Bucknell University cafeteria food waste was sampled 38 times and landscape waste was sampled 35 times during the 13-month study (from October 2006 until November 2007). Food waste was pulped in the cafeteria before collection and landscape waste was shredded in a lawn chipper/shredder after collection. COD, TS, and VS were analyzed in triplicate for each batch of food or landscape waste. For COD analyses, a 12.5-g sample of food waste or landscape waste was homogenized with water (500 mL total volume) at 22,000 rpm in a laboratory blender (Waring Products, model 7010S). For all samples, COD was measured according to the closed reflux colorimetric method (APHA, 1995). Dilutions (20x) were prepared for both food waste and landscape waste COD. TS and VS analyses were conducted on each batch of food and landscape waste in accordance with Standard Methods (APHA, 1995).

Total Kjeldahl nitrogen (TKN) analysis of food waste was performed from March 30, 2007 through November 2, 2007 (food waste batches 11 through 38). TKN analysis was completed according to Hach et al. (1985), with the following modifications: 20 mL of the homogenized waste and water mixture was used, and 3 mL of concentrated sulfuric acid and 10 mL of 50% hydrogen peroxide were used (Hach et al., 1985).

A sample from each batch of food waste collected between March 23, 2007 and May 5, 2007 (food waste batches 10 through 18) was sent to Wilson Testing Laboratories (Shamokin, PA) for fats, oil, and grease (FOG) analysis. EPA Method 1664A was used to determine the FOG content using Soxhlet Extraction (U.S. EPA, 1989).

Waste study

The volume of biodegradable waste produced every year by Bucknell University Dining Services was assessed. Interviews were conducted with Dining Services staff to determine preliminary information about total waste volume. A waste audit was conducted on May 1st and May 2nd, 2007 (a Tuesday and a Wednesday, respectively) of waste produced in The Bison and Bostwick Dining Hall, respectively. Each facility's garbage was collected during the morning, sorted by biodegradability, and biodegradable waste was weighed. These results were scaled up to project annual waste production based on the quantity of meals served during the collection period and the number of meals served during the year.

Biodegradability study

The biodegradability studies were conducted using a Challenge Technologies AER-200 respirometer. Seed material from the pilot-scale reactor was used to prepare four treatments: control (unfed), food waste (fed 5 g FW COD/L), landscape waste (fed 10 g LW COD/L), and food and landscape waste (fed 5 g FW COD/L and 5 g LW COD/L). Six replicates, each with about 0.5 kg digestate, were prepared for each treatment and incubated in a water bath (35 °C), while biogas production was recorded. Biogas composition of one replicate from each treatment was tested daily to determine the methane content. Each test was continued until the rate of biogas production decreased to about 1 mL/hr. On the final day of the study, biogas composition was determined for each replicate in the test (24 total). It was assumed that the final biogas composition accurately reflected the methane proportion throughout the test, and this was used to determine the total methane produced.

For each trial, biodegradability for the FW and LW used was determined as follows: the methane produced in each treatment was adjusted for endogenous decay by subtracting the methane produced in the control. The experimental COD unit methane was divided by the theoretical maximum COD unit methane production of 395 mL CH₄/g COD degraded (McCarty, 1964a), based on complete mineralization of COD



In addition, the COD unit methane of each food and landscape waste batch (digested alone) was used to calculate the expected COD unit methane when FW and LW were combined:

$$\frac{\left(\text{FW Fed (g FW)} \times \text{FW COD} \left(\frac{\text{g COD}}{\text{g FW}} \right) \times \text{FW Unit Methane} \left(\frac{\text{mL CH}_4}{\text{g COD}} \right) \right) + \left(\text{LW Fed (g LW)} \times \text{LW COD} \left(\frac{\text{g COD}}{\text{g LW}} \right) \times \text{LW Unit Methane} \left(\frac{\text{mL CH}_4}{\text{g COD}} \right) \right)}{\text{FW COD (g)} + \text{LW COD (g)}} \quad (2)$$

$$= \text{Combined waste expected unit methane} \left(\frac{\text{mL CH}_4}{\text{g COD}} \right).$$

The expected combined waste COD unit methane was compared to the actual combined waste COD unit methane to determine whether there was any advantage to combining FW and LW for digestion.

3.2.3. Methane, pH, alkalinity, volatile fatty acids, chemical oxygen demand, total Kjeldahl nitrogen

In order to monitor reactor conditions total methane in L/day was determined daily, as described by DiStefano and Ambulkar (2006), modified as follows: percent methane of the biogas was determined with a Hewlett Packard 6890 series gas chromatograph equipped with a thermal conductivity detector and a Supelco 60/80

Carbosieve column (2.5 m by 6 mm). Biogas methane percentage was multiplied by daily biogas production in order to determine daily methane production.

Digester effluent (about 20% solids) was collected three times per week for pH and VFA analysis. A liquid extraction procedure was developed to determine the VFA content of the high-solid (approximately 20%) digestate. Approximately 25 g of digestate was diluted with 150 mL of reverse osmosis water and mixed at 250 rpm for 10 min. Mixing rates between 100 and 500 rpm were tested to identify the lowest speed that maximized VFA extraction, to reduce volatilization during sample preparation. This method was developed from a procedure used at Bucknell University to determine the bound fraction of cake solids by M. Higgins and Y.-C. Chen.

After mixing, the pH of the diluted effluent was determined with a digital pH meter (Accumet model AR50). Total alkalinity was determined by titration to a pH of 4.3 with 1 N HCl. VFA alkalinity (expressed as CaCO_3) was determined from the pKa and concentration (from gas chromatography) of each acid detected. VFA alkalinity was subtracted from total alkalinity to yield bicarbonate alkalinity (BA). For VFA determination, approximately 6 mL of the diluted digestate sample was centrifuged at 20,000 g for 10 min. The centrate was filtered through a 1 μm glass-fiber filter, and then a 0.45 μm syringe filter. One mL of filtrate was transferred to a 1.5 mL vial, and 20 μL of 5000 mg/L valeric acid (HVa) was added as an internal standard to produce 100 mg/L HVa. The sample was acidified with 20 μL of 75% phosphoric acid to pH 3, and 1 μL was injected on a Hewlett Packard (6890 series) gas chromatograph equipped with an automatic sampler (Agilent technologies, 6890 series injector). A Nukol 30-m capillary

column with an inner diameter of 0.53 mm and a film thickness of 0.45 μm was used. Nitrogen was used as the carrier gas (30 mL/min) and the flame ionization detector and inlet temperatures were 200 °C. The oven temperature was held at 105 °C for the first 4 min, followed by a 5 °C/min ramp to 145 °C and a 10 °C/min ramp to 190 °C, and held at 190 °C for 5.5 min. This method resulted in a detection limit on the order of 10 mg/L for each acid (100 ppm, or 0.01 mg VFA/g). VFA standard (10 mM, Supelco) was added to reactor samples in order to assess the proportionate VFA recovery by the extraction procedure. Recovery was highest for acetic and propionic acid (greater than 97%) and decreased with increasing weight to 81% for heptanoic acid.

Reactor SCOD was determined using 0.45 μm filtrate from the VFA extraction procedure. TKN, TCOD, and solids tests were performed using the methods described in Section 3.2.2. Because reactor solids content was high (about 20%), reactor monitoring parameters were determined in unit of mass/mass. In order to compare with other research, parameters were converted to mass/liquid units as needed using the digestate density, which was determined each testing day by water displacement.

3.2.4. Ammonia analysis and respirometry

Samples from the reactor and ammonia respirometry tests were tested for $\text{NH}_4^+\text{-N}$ using a Dionex cation chromatography system. Samples were prepared using the same procedure as VFA sample preparation (centrifugation and filtering). Quality control samples (Environmental Resource Associates, Arvada, CO) were analyzed regularly and compared to acceptable ion quantification ranges (Environmental Resource Associates).

A Dionex IonPac CS14 Analytical (4 x 250 mm) column was used, with a 10.0 mM methanesulfonic acid eluent flowing at 1.0 mL per minute. A sample loop of 10 μ L and a conductivity detector were used for sample quantification and identification.

A 7-point standard curve was constructed for NH_4^+ -N, which was non-linear. The non-linear working range for undiluted NH_3 -N samples was 0.10-16 mg/L. Dionex technical support confirmed that a non-linear standard curve is typical when using ion chromatography to quantify ammonia. A parametric fit was employed to generate the standard curves. As NH_4^+ -N concentrations increased, the sensitivity of the instrument decreased. Samples were diluted to within the working range, which was selected to ensure adequate sensitivity over the entire range.

Respirometry was performed on samples from the pilot-scale reactor to investigate the possibility of ammonia inhibition. The procedure described in section 3.2.2 for food and landscape waste biodegradability studies was used, with the following modifications: samples were incubated in 500 mL bottles (Wheaton), and each bottle was fed with 5 g COD from glucose, in order to stimulate biogas production. Approximately 25 g of digestate was diluted with basal medium to produce a 500 mL volume with a low ammonia concentration. Five treatments of five replicates each with TAN concentrations of 7928, 4772, 1612, 825, and 306 mg N/L were prepared using NH_4Cl . After NH_4Cl addition, a first trial was conducted in which an attempt to maintain a pH of 8 with a one-time addition of KOH to each replicate was unsuccessful. In order to maintain steady pH K_2HCO_2 was used to return pH to 8 and provide buffering capacity during a second trial. At the conclusion of the second trial, samples were withdrawn from one replicate of each

treatment for SCOD, VFA, and ammonia analysis. SCOD and VFA analysis was performed according to the procedures described in section 3.2.2.

3.2.5. Statistical analyses

All statistical analyses were completed using Microsoft Excel 2002. Waste composition tests (COD, TS, VS, and TKN) were performed in triplicate. A single FOG test was performed for each batch of food waste tested. A single test for reactor methane content was performed daily. Tests of reactor TS and VS were performed in triplicate three times weekly; single tests of other reactor parameters (VFA, pH, alkalinity, SCOD, TCOD) were performed three times weekly. Five respirometry trials assessing the biodegradability of Bucknell University food and landscape waste were conducted, each consisting of six replicates for each of four treatments. Means, standard deviations, coefficients of variability, coefficients of determination, and linear regressions were calculated via Microsoft Excel, as appropriate. The anaerobic digester was fed actual food and landscape wastes; therefore, natural variability in waste characteristics was expected. Calibration curves were prepared for VFA, TKN, and COD analyses, and linear regressions were determined using Microsoft Excel. For VFAs, dilutions were prepared in concentrations ranging from 0.1 mM to 10 mM from a 10 mM standard containing VFAs from acetic acid to heptanoic acid (Supelco, Bellefonte, PA). For TKN, a calibration curve was prepared by digesting Nicotinic Acid p-Toluenesulfonate in concentrations ranging from 5.12 mg/L to 99.99 mg/L. For COD, a calibration curve was prepared by digesting potassium hydrogen phthalate in concentrations ranging from 200

to 1400 mg/L. Standards for VFA, TKN, and COD resulted in linear regressions with coefficients of determination in excess of 0.999. To quantify methane content in samples, the peak area response from direct injection of pure methane (National Specialty Gases) was obtained. Pure methane samples were injected in quadruplicate, and the average peak area response was compared to digester gas samples. The coefficient of variation (standard deviation divided by the mean) for the quadruplicate samples was 1.5%.

3.3. Results

3.3.1. Food and landscape waste characterization

Chemical oxygen demand, total solids, volatile solids, total Kjeldahl nitrogen, and fats, oil and grease

Bucknell University food and landscape waste were characterized extensively in order to determine their suitability for anaerobic digestion. Waste assessment results are presented in Figure 3.1.

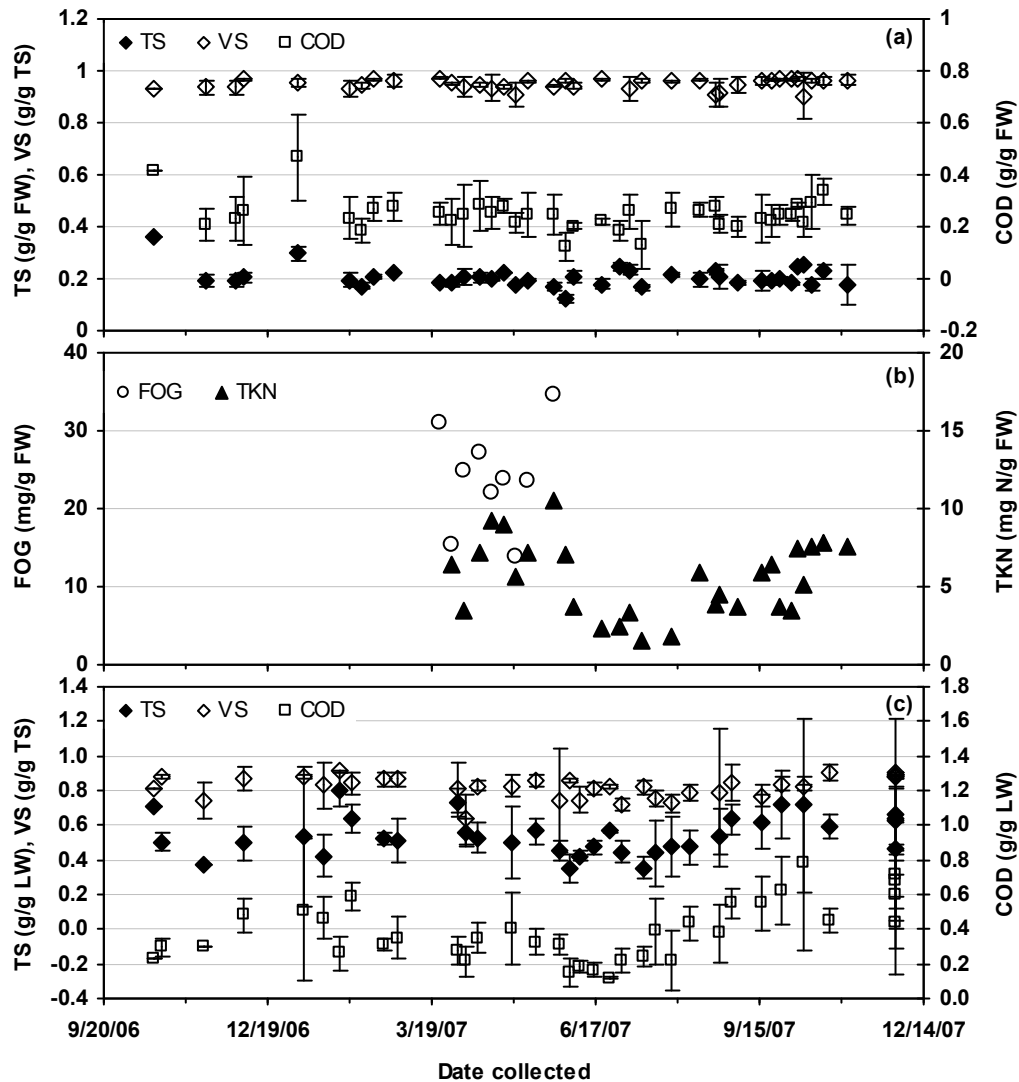


Figure 3.1. Characteristics of Bucknell University dining hall food and landscape waste: (a) TS, VS, and COD of FW, (b) FOG and TKN of FW, and (c) TS, VS, and COD of LW. Error bars represent 95% confidence intervals. FOG and TKN were tested only once for each sample.

In general, food waste TS and VS results were stable (Figure 3.1a). FW COD increased slightly between September and December of 2007, suggesting that there may be seasonal variation; however, this increase was small compared to the variation in FW COD between individual batches.

FOG and TKN testing of FW samples was started in March 2007 (Figure 3.1b). FOG testing was completed by a commercial laboratory to determine the variation in FW FOG, which ranged between about 15 and 35 mg/g FW. TKN decreased during April and May of 2007, was about 1.5 mg/g FW during the summer (June, July, and August, 2007) and increased again (from about 3.5 to 8 mg/g FW) during the fall (September, October, and December, 2007).

TS, VS, and COD varied more between LW samples than between FW samples (Figure 3.1c). There was some seasonal variation in LW TS results, with a slight decrease in TS during the spring, lower values during the summer (about 0.40 g TS/g LW), and an increase in TS during the fall (to about 0.70 g TS/g LW). LW COD triplicate results (the COD of each sample was tested three times) differed more (indicated by larger error ranges) than FW COD triplicate results. Additionally, LW COD appeared to be lower during the spring and summer, with an increase during the fall (although statistical significance was not evaluated). There was no seasonal variation in LW VS.

Results from each batch of food and landscape waste collected and tested were used to determine annual means and 95% confidence intervals (CI) for the characteristics of Bucknell University dining hall food waste and landscape waste (Table 3.1).

Table 3.1. Bucknell University dining hall food waste and landscape waste characterization.

	COD (g/g waste)		TS (g/g waste)		VS (g/g waste)		VS (g/g TS)		TKN (mg/g FW)	FOG (mg/g FW)
	FW	LW	FW	LW	FW	LW	FW	LW	FW	FW
Mean	0.24	0.39	0.21	0.54	0.20	0.44	0.94	0.82	5.49	24.01
95% CI	0.02	0.06	0.01	0.04	0.01	0.04	0.01	0.02	2.39	6.66
Obs. (N)	38	35	38	35	37	34	38	35	28	9

FW TS was significantly lower than LW TS. On a dry weight basis (g VS/g TS), FW VS was higher than LW VS. VS was also calculated on an as-is basis in order to make comparisons with COD. FW COD was higher than FW VS, while LW COD was lower than LW VS. For all parameters, LW measurements varied more from batch to batch, as demonstrated by larger confidence intervals. In addition, COD, TS, and VS were tested in triplicate, and in general LW triplicate results differed more than FW triplicate results. TKN consistently represented less than 1% of FW total weight, while FOG represented 2-3% of FW total weight.

Amount produced per year

On May 1, 2007 (in the Bison, on a Tuesday) and May 2, 2007 (in Bostwick Cafeteria, on a Wednesday) a waste survey was conducted in order to determine the amount of biodegradable waste produced. Due to time constraints, waste at each facility could only be sampled on one day. It was assumed that the waste generated on the sampling day was representative of typical waste production, and that the amount of waste produced per meal served in Bostwick cafeteria (based on the quantity of meals

served during the collection period) was a constant. Then the annual quantity of meals served was used to estimate annual waste production:

$$\frac{\text{amount of waste collected}}{\text{meals served during collection}} \times \frac{\text{meals served}}{\text{year}} = \text{annual waste production} . \quad (3)$$

This calculation was repeated for the Bison, using sales during the collection period and total annual sales in place of meals served and total annual meals served. Waste from the Bostwick kitchen, the Bostwick dining room, the Bison kitchen, and the Bison dining room was used to estimate the annual production of biodegradable waste at each facility (Table 3.2).

Table 3.2. Annual generation of biodegradable organic waste at Bucknell dining facilities.

Facility	Biodegradable Waste (metric tons/year)
Bostwick kitchen	50
Bostwick dining room	20
Bison kitchen	20
Bison dining room	10

The majority of biodegradable waste is generated in the kitchen at Bostwick cafeteria, where all the food preparation takes place. Collection of biodegradable waste in Bostwick and the Bison could yield between 50 and 100 metric tons/year of biodegradable material.

Waste biodegradability

Biodegradability of Bucknell University dining hall food and landscape waste was determined by respirometry. Five trials were conducted comparing unfed microbes with microbes fed FW (5 g COD/L), LW (10 g COD/L), and a combination of FW and LW (10 g COD/L, composed of a 1:1 ratio of FW COD and LW COD). Each trial tested different batches of food and landscape waste. Results from one trial were excluded because of anomalous biogas production rates. Mean rates of biogas production, methane content, and mean cumulative biogas production during biodegradability Trial 3 are presented in Figure 3.2. Trial 3 was chosen because it provides a good demonstration of the variation in initial biogas production among the different treatments. Results from the other three successful trials are presented in the appendix. Aggregated data from all four trials is presented in Figure 3.3 and Table 3.3.

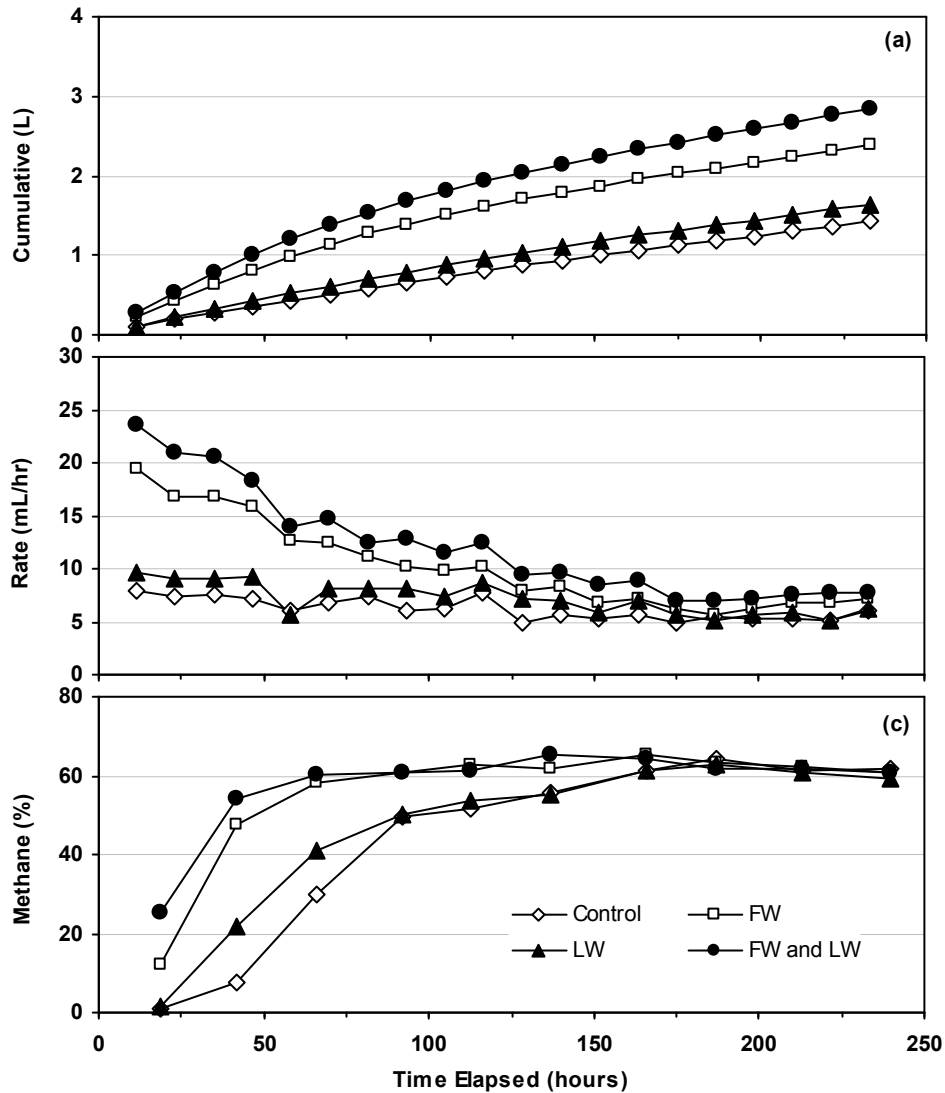


Figure 3.2. Example of data collected during one biodegradability trial. Mean cumulative biogas production (a) and rate of biogas production (b) were determined for an unfed control treatment, a treatment fed LW, a treatment fed FW, and a treatment fed both FW and LW. Methane content of biogas (c) was also determined on a daily basis during the study.

During the course of the 250-hour trial, the biogas production rate decreased from initial highs of about 28 mL/hour (FW and LW), about 21 mL/hour (FW), and about 12 mL/hour (LW) to a stable rate comparable to the biogas production rate of the control (about 1 mL/hr). During the trial the methane content of each treatment increased to a

steady 60%, although the increase in methane was faster for the two treatments fed FW and slower for the control and the LW treatment (Figure 3.2c). The combined FW and LW (Figure 3.2d) had the highest initial rate of biogas production, followed by the FW treatment, LW treatment, and control treatment. The final biogas methane content and the total biogas produced during the trial were used to determine the total methane production in each treatment, as shown in Figure 3.3. Endogenous methane production (measured by the control) was subtracted from total methane produced in each treatment to determine methane production that was due to substrate fed; this was used to determine COD and VS unit methane, which are also presented in Figure 3.3.

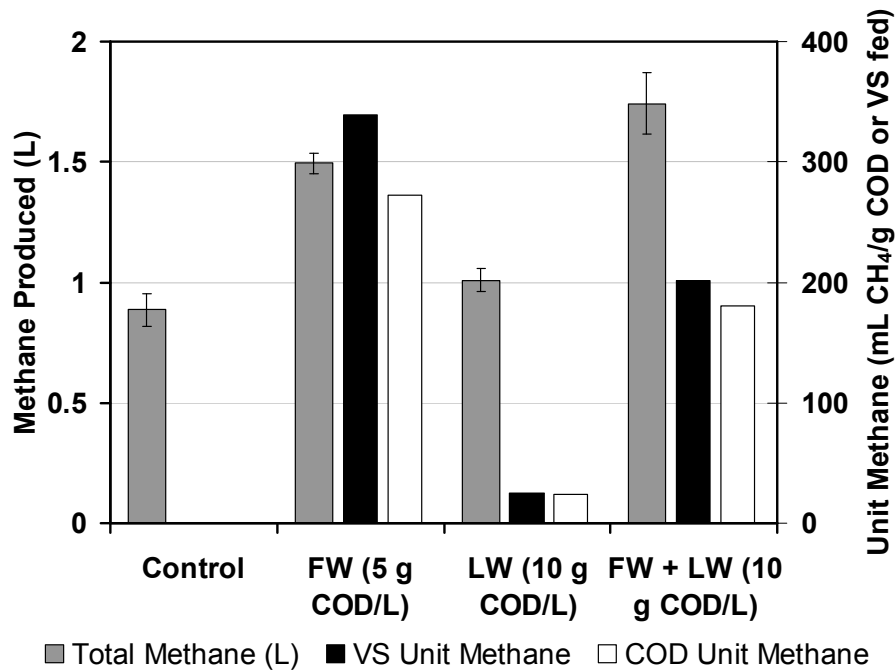


Figure 3.3. Example of results collected during one biodegradability trial. Error bars represent a 95% confidence interval of the mean methane production (based on six replicates in each treatment).

The COD biodegradability was determined (described in Section 3.2.2) for each fed treatment for each of the four successful trials. These results were combined to determine the mean biodegradability of Bucknell University dining hall food and landscape waste as a whole, presented in Table 3.3.

Table 3.3. Biodegradability of wastes based on respirometry (mean results from all successful trials)

	FW	LW	FW and LW
Unit methane (mL CH₄/g COD)	288	29	179
95% CI	22	37	12
Mean biodegradability	0.73	0.07	0.45
95% CI	0.06	0.09	0.03
Observations (N)	4	4	4

In addition, the combined waste expected COD unit methane was compared to the actual combined waste COD unit methane (determined experimentally, for each biodegradability trial), presented in Table 3.4.

Table 3.4. Expected and actual COD biodegradability for combined FW and LW from respirometry.

	Expected		Actual	
	Unit Methane (mL CH₄/g substrate COD)	Biodeg.	Unit Methane (mL CH₄/g substrate COD)	Biodeg.
Trial 1	135	0.34	167	0.42
Trial 2	167	0.42	180	0.46
Trial 3	141	0.36	181	0.46
Trial 5	177	0.45	186	0.47
Mean	155	0.39	179	0.45

In each successful trial there was an improvement in biodegradability when FW and LW were combined. The difference in actual COD unit methane and expected COD unit

methane was statistically significant (results were compared using a paired t-test; $T = 3.18$, $p = 0.04$).

3.3.2. Reactor operation

Low OLR reactor operation

Reactor parameters were monitored regularly throughout low OLR reactor operation in order to assess digestion stability (Figure 3.4). During the first few weeks of low OLR operation the reactor was still processing some accumulated COD from previous operation at an OLR of 7 g COD/L reactor volume-day. Biogas production and methane content were monitored daily. Bicarbonate alkalinity, pH, SCOD, and VFA composition were monitored three times weekly. The reactor was operated at an OLR of 2 g COD/L reactor volume-day for 90 days, but steady operation (after the reactor had stabilized at the low OLR) was 73 days. Mean parameters during low OLR operation were calculated based on stable reactor performance between days 160 and 231.

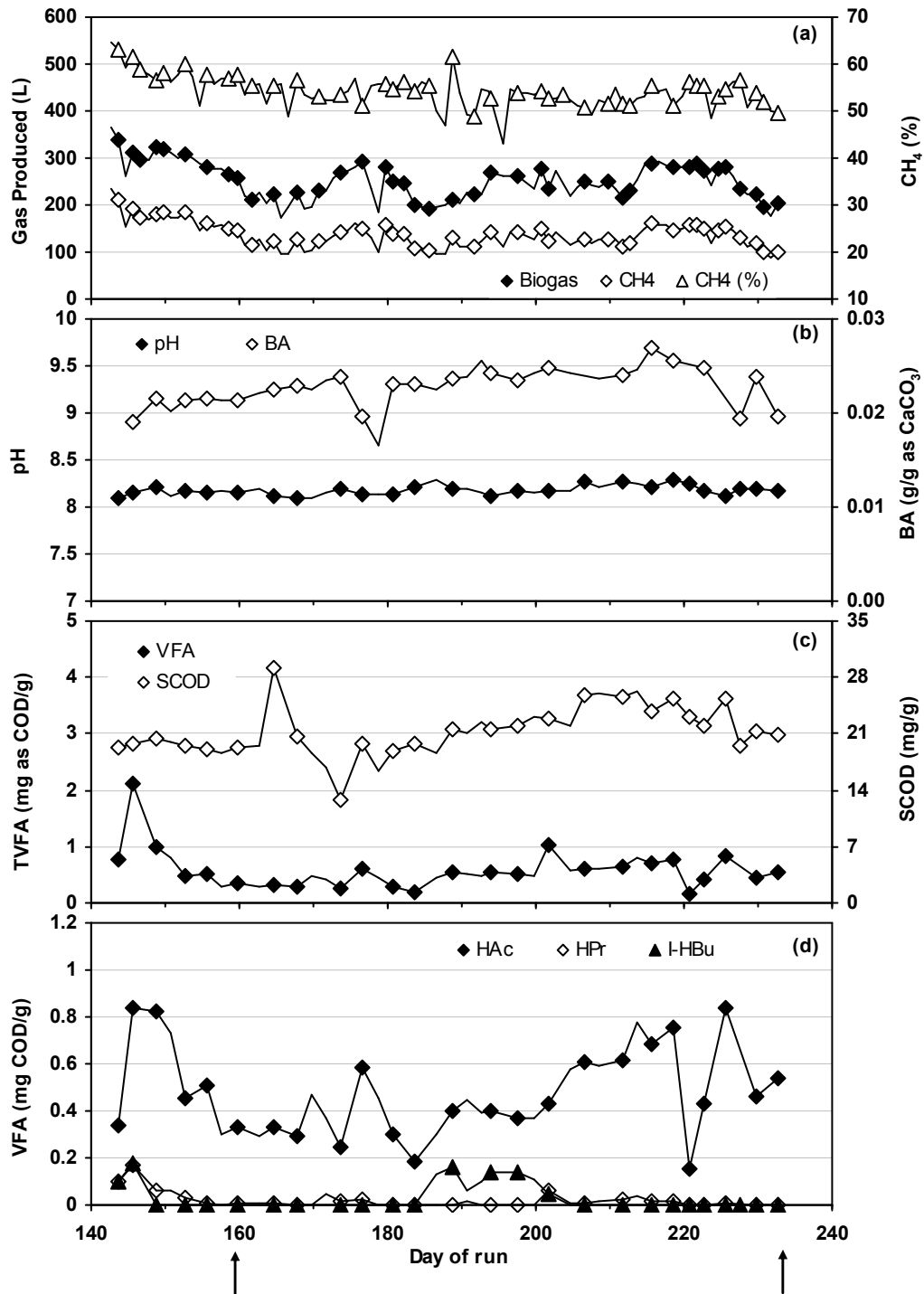


Figure 3.4. Reactor parameters during low OLR reactor operation: (a) biogas production, methane production, and methane content, (b) pH and BA, (c) TVFA and SCOD, and (d) individual VFAs detected (HAc, HPr, and I-HBu). Arrows indicate beginning and end of stable low OLR operation.

The methane proportion was steady during low OLR reactor operation (Figure 3.4a). For a short period of time before the low OLR trial, the reactor was operated at an OLR of 7 g COD/L reactor volume-day. Biogas production was slightly elevated while accumulated substrate from this period was processed. By day 160 of operation, biogas and methane production had stabilized. During the period of stable operation at an OLR of 2 g COD/L reactor volume-day (days 160–231) the mean methane content was 53% with a standard deviation of 3%. The mean biogas production was 240 L/day with a standard deviation of 32 L, and the mean methane production was 128 L/day with a standard deviation of 19 L. The unit methane production during this time was 232 L CH₄/kg COD fed and 229 L CH₄/kg VS fed. Unit methane production was calculated by dividing mean methane production by either mean COD fed or mean VS fed during low OLR operation.

During low OLR operation pH was stable with a mean of 8.2 (Figure 3.4b). The alkalinity increased slowly, from about 0.020 g CaCO₃/g digestate (20 g CaCO₃/L), to about 0.025 g CaCO₃/g digestate (25 g CaCO₃/L). Total and volatile solids were monitored throughout low OLR reactor operation in order to maintain reactor solids at 20%. During low OLR reactor operation, mean TS was 0.19 g solids/g digestate with a standard deviation of 0.02. Mean VS was 0.78 g VS/g TS with a standard deviation of 0.03. Although the reactor was not operated for three SRTs in order to achieve steady state conditions, the low OLR study took place after 140 days of feeding the combined food and landscape waste at OLRs of 2 g COD/L reactor volume-day and above. Stable

performance was identified by steady biogas and methane production, steady pH, and low VFA content.

Concentrations of individual VFAs were used to determine total VFA content (Figure 3.4c and d). As with biogas production, VFA and SCOD were slightly elevated due to previous reactor operation at an OLR of 7 g COD/L reactor volume-day. Once the excess VFA and SCOD were digested, VFA and SCOD were stable during low OLR operation. Mean SCOD was 22 mg COD/g digestate with a standard deviation of 3.4; mean VFA was 0.51 mg COD/g digestate with a standard deviation of 0.2. The majority of the VFA detected during low OLR operation was acetic acid (HAc), with occasional accumulation of propionic (HPr) and isobutyric (I-HBu) acids (Figure 3.4d). Biodegradable OLR (BOLR) during this time period was calculated from the biodegradable FW and LW COD fed (based on biodegradability studies, Table 3.3). Mean BOLR was 0.8 g COD/L reactor volume-day with a standard deviation of 0.1.

Transition from low OLR to high OLR

During the transition from low to high OLR operation, incremental increases were implemented to enable acclimation at intermediate-level OLRs. OLRs used were 5, 7, 10, and 12.5 before the final increase to 15 g COD/L reactor volume-day. The reactor was held at each OLR until gas production and other indicators (VFA, pH, alkalinity) confirmed that the reactor was stable. OLR increases were made as follows: OLR = 5 g COD/L reactor volume-day (days 233-245), OLR = 7 g COD/L reactor volume-day (days 246-269), OLR = 10 g COD/L reactor volume-day (days 270-305), OLR = 12.5 g COD/L

reactor volume-day (days 306-313). The only increase that resulted in evidence of reactor distress was to 7 g COD/L reactor volume-day, after which there was an increase in HAc, HPr, and isovaleric acid (I-HVa). This increase was temporary and was resolved by holding the OLR at 7 g COD/L reactor volume-day for 3 weeks to allow additional acclimation before increasing the OLR again.

High OLR reactor operation

Reactor monitoring continued during high OLR reactor operation (Figure 3.5). The monitored parameters and schedule were the same, with the exception of TCOD testing, which was added three times weekly. The OLR was increased to 15 g COD/L reactor volume-day on day 314 (Figure 3.5a). The reactor was operated at an OLR of 15 g COD/L reactor volume-day for 47 days. However, shortly after the OLR increase the reactor temperature control failed and OLR was decreased to 3 g COD/L reactor volume-day while it was repaired. Once temperature control was restored, feeding at 15 g COD/L reactor volume-day was resumed. Total operation was 43 days. Methane content was high with a mean value of 64% and a standard deviation of 2% during high OLR operation. COD unit methane was 211 L CH₄/kg COD fed and 272 L CH₄/ kg VS fed.

Both pH and alkalinity decreased during high OLR reactor operation (Figure 3.5b). The pH decreased from 8.06 to 7.7 by the end of the high OLR operation period. Alkalinity also decreased, from 0.18 g CaCO₃/g digestate (18 g CaCO₃/L) to 0.10 g CaCO₃/g digestate (10 g CaCO₃/L), although there were brief decreases to values as low as 0.07 g CaCO₃/g digestate (7 g CaCO₃/L).

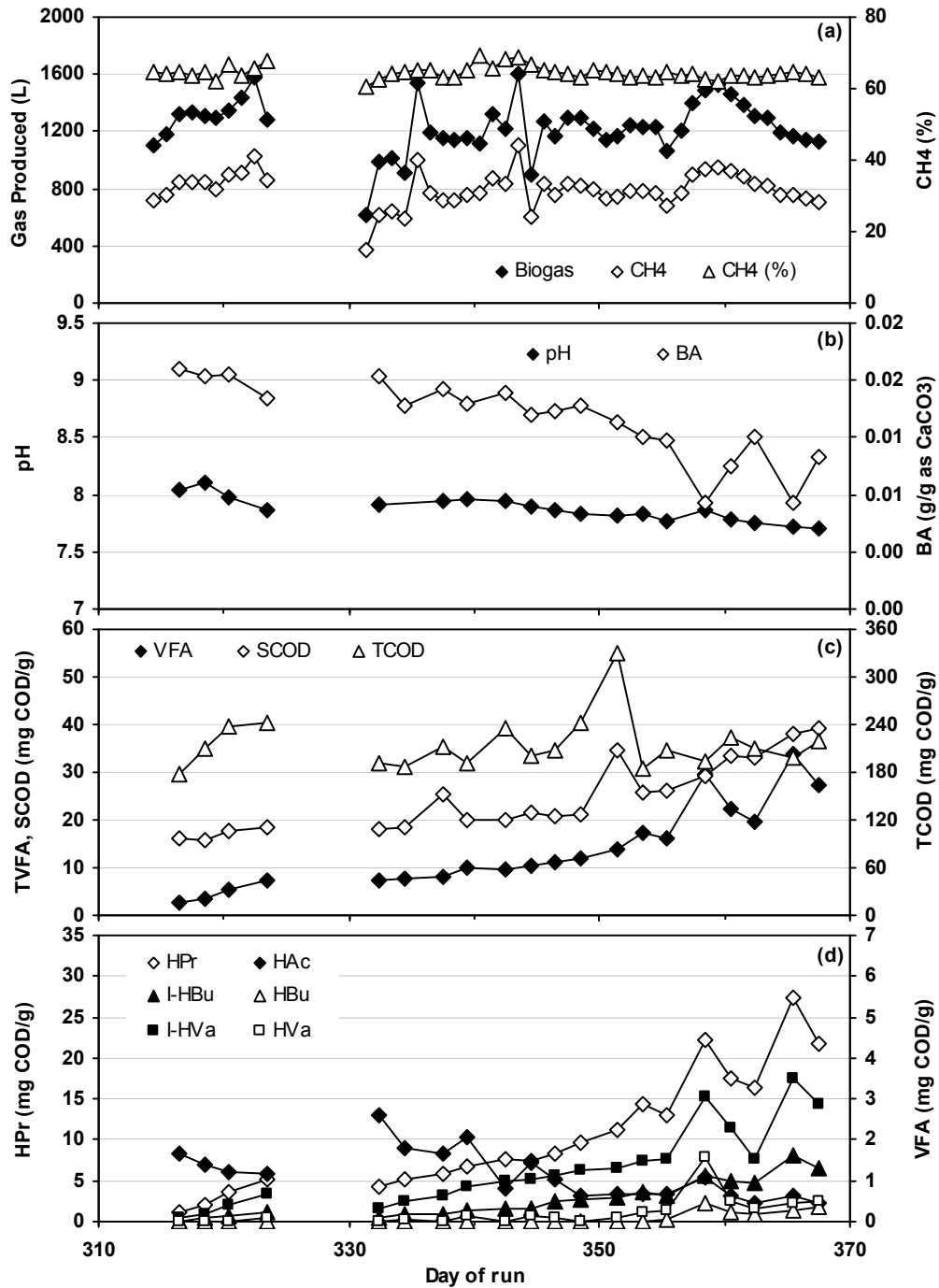


Figure 3.5. Reactor parameters during high OLR reactor operation: (a) biogas production, methane production, and methane content, (b) pH and BA, (c) TVFA, SCOD, and TCOD, and (d) individual VFAs detected (HAc, HPr, I-HBu, HBu, I-HVa, and HVa). The six-day gap in the data between days 324 and 330 indicates the loss of temperature control.

Measurement of reactor TCOD was instituted during high OLR operation, and remained steady with a mean of 220 mg COD/g digestate and a standard deviation of 30, although there was a brief increase to 330 mg COD/g digestate (Figure 3.5c). SCOD increased from 12 mg COD/g digestate to 39 mg COD/g digestate during high OLR operation (Figure 3.5c). A steady increase in total VFA (TVFA) was also observed during this time period (Figure 3.5c). TVFA began to increase as soon as the OLR was increased to 15 g COD/L reactor volume-day, and continued to increase until the experiment was discontinued, reaching a value of 27 mg COD/g digestate. There were transient increases in TVFA, to 30 and 34 mg COD/g digestate. Although there were fluctuations in the difference between SCOD and VFA, generally it remained on the order of 10-13 g COD.

The increase in TVFA was largely due to increasing HPr; HAc remained low throughout high OLR operation (Figure 3.5d). HPr increased from 0.63 mg COD/g digestate to 22 mg COD/g digestate. On day 358 HPr increased to 22 mg COD/g digestate, followed by a decrease, and on day 365 HPr increased to 27 mg COD/g digestate, again followed by a decrease. The same increasing trend was seen in I-HBu, I-HVa, and HVa, although amounts of these acids were much smaller. I-HBu, I-HVa, and HVa also increased sharply and decreased quickly on days 358 and 365. There was no significant production of VFAs of order higher than HVa during high OLR reactor operation. BOLR was 7.8 g COD/L reactor volume-day during this phase of operation., with a standard deviation of 0.4

Recovery from overloading

Due to the increase in TVFA, the reactor OLR was decreased to 10 g COD/L reactor volume-day on day 368 of operation. There was no decrease in TVFA concentrations, and feeding was suspended on day 376. Although feeding had been stopped, TVFA remained at approximately 30 mg as COD/g digestate until day 386. After day 386 TVFA began to decrease and by day 409 TVFA had decreased to 3.13 mg as COD/g digestate (data not shown). A similar decrease was observed in SCOD. After day 376, biogas production decreased quickly to between 120 and 200 L/day. Methane production was extremely variable after feeding was discontinued, ranging between 50 and 70% for the remainder of reactor operation. Between day 386 and day 407 there was a steady and rapid decrease in HPr, which was accompanied by a very slight increase in biogas production, from about 160 L/d to as high as 206 L/d. Methane production was also stimulated by the degradation of HPr, increasing briefly from about 90 L/d to as high as 146 L/day. This reduction in VFA content was accompanied by increases in both pH and bicarbonate alkalinity.

3.3.3. The possibility of ammonia inhibition - respirometry

The ammonia content of the reactor was tested on day 392. At a pH of 8.2 the free ammonia nitrogen (FAN) concentration was 550 mg/L digestate and the NH_4^+ -N concentration was 6460 mg/L digestate. In order to confirm that ammonia buildup was causing the TVFA accumulation, a respirometer study was conducted (Figure 3.6). Digestate from the pilot-scale reactor was diluted with basal medium to reduce ammonia

concentrations, and five treatments were prepared to test the effects of different TAN concentrations on the microbes. Temperature was controlled at 35°C and pH was maintained at 8. NH₄Cl was added to each treatment to produce TAN concentrations ranging from 7928 mg/L to 306 mg/L. This range was chosen in order to expose microbes in the different treatments to TAN ranging from the levels detected within the reactor to levels below concentrations where inhibition has been detected in other research. Because of the sensitivity of the ammonia equilibrium to pH changes, a small decrease in pH (from about 8 to values ranging from 7.7 to 7.9) resulted in a decrease in FAN by the end of the trial (Table 3.5). It was expected that in the low TAN concentration treatments (11 mg/L and 30 mg/L), microbes would recover from TAN inhibition (within the reactor) and produce methane, while in the high TAN concentration treatments (52 mg/L, 126 mg/L, and 212 mg/L), the microbes' recovery from TAN inhibition within the reactor would be adversely affected by the presence of TAN within the respirometer.

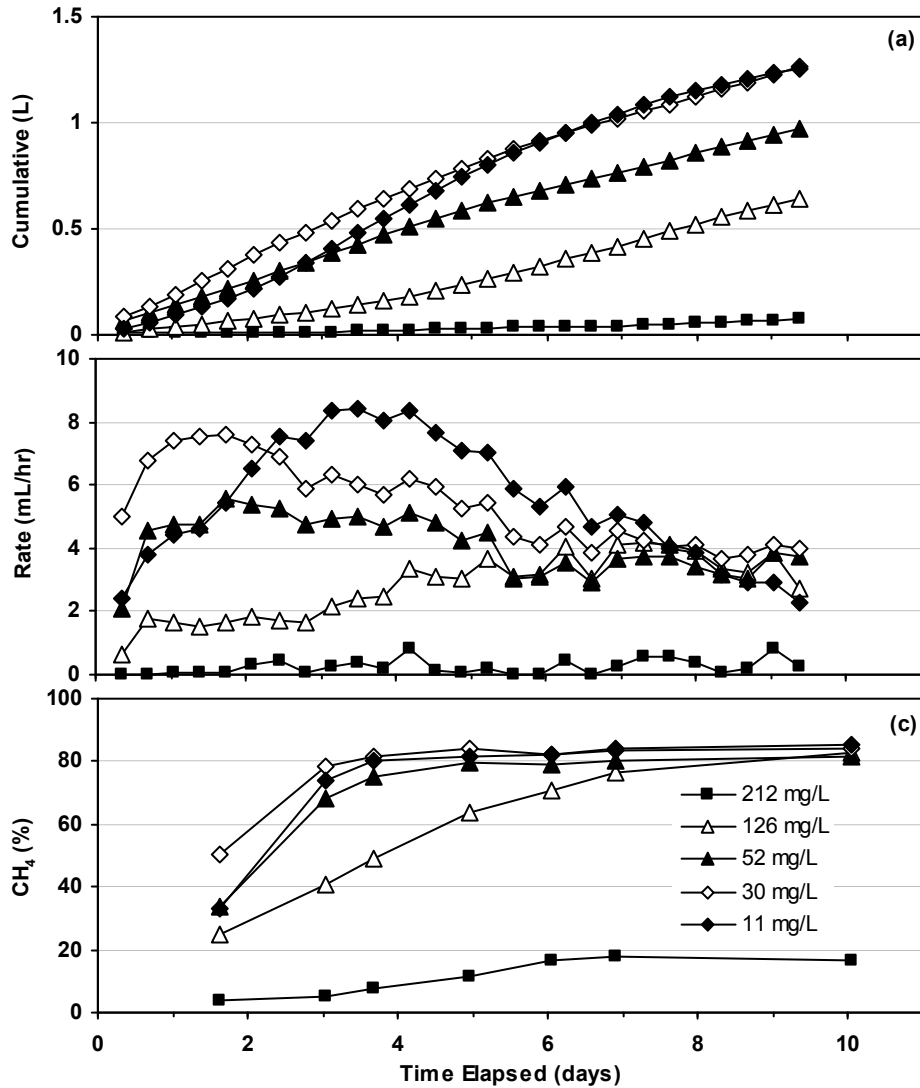


Figure 3.6. A respirometer study was conducted to assess FAN inhibition. Cumulative biogas production (a) and biogas production rate (b) were measured for five treatments with final FAN concentrations of 212 mg/L, 126 mg/L, 52 mg/L, 30 mg/L, and 11 mg/L. Methane content of biogas (c) was determined daily.

Gas production throughout the trial was very low for the treatment with the highest TAN concentration (Figure 3.6a). Methane content did not surpass 10% until the fifth day of the trial and only reached 40% by the end of the trial (Figure 3.6c). In contrast, biogas and methane production were much higher in the two lowest TAN treatments. Mean unit

methane production was 217.5 mL/g COD fed in both the 11 mg/L treatment and the 30 mg/L treatment and methane content quickly exceeded 80%.

SCOD, pH, and VFA were tested at the beginning and end of the trial for one replicate from each treatment (Table 3.5). Initial SCOD results for the 212 mg/L treatment were out of range and as a result SCOD could not be calculated.

Table 3.5. SCOD and VFA changes during ammonia respirometry trial. Mean initial TAN is given \pm standard deviation. Unit CH₄ per g COD fed is given \pm 95% CI.

Final FAN (mg NH₃/L)	212	126	52	30	11
Mean initial TAN (mg NH₃-N/L)	7928 \pm 3	4772 \pm 2	1612 \pm 2	825 \pm 2	306 \pm 2
Final NH₄⁺-N (mg NH₄⁺/L)	8042	4796	1707	836	221
# replicates	4	5	5	5	5
SCOD destroyed (%)	NA	70	82	92	92
VFA destroyed (%)	38	64	70	93	93
Unit CH₄ (mL CH₄/g COD fed)	2.2 \pm 1.5	108.8 \pm 12.3	166.5 \pm 15.7	217.5 \pm 13.6	217.5 \pm 8.7

During the trial, there was significant destruction of both VFAs and SCOD. These changes were largest in the two lowest ammonia treatments, 11 mg/L and 30 mg/L, with greater than 90% destruction of SCOD and VFAs during Trial 2. The lowest VFA destruction (38%) was observed in the highest ammonia treatment, with 212 mg/L.

The composition of individual VFAs at the end of the trial also reveals some information about the effects of ammonia during the respirometer trials (Figure 3.7).

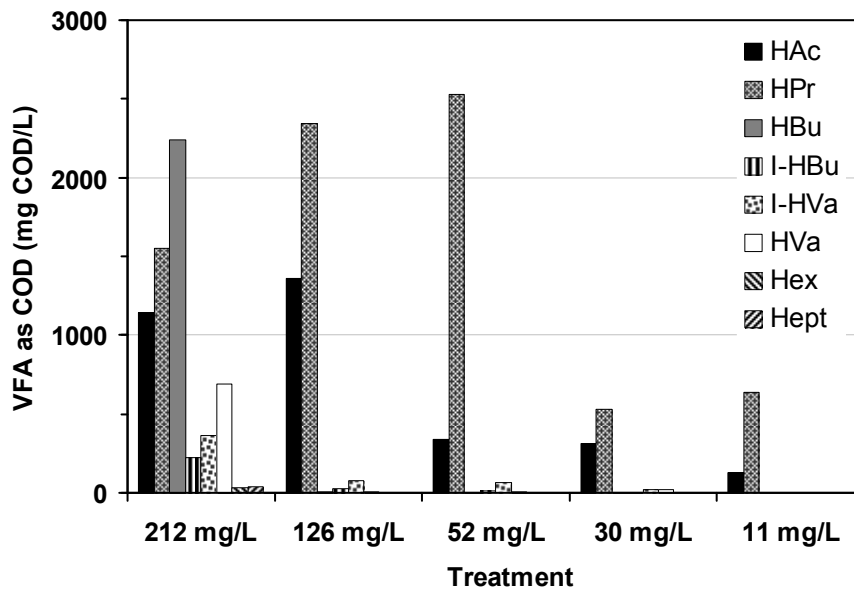


Figure 3.7. Individual VFA composition during respirometer ammonia trial.

VFAs from HAC through hexanoic (Hex) and heptanoic (Hept) were observed in the 212 mg/L treatment. Quantities of higher-order VFAs decreased with decreasing TAN, and VFAs larger than butyric acid were not detected in the 11 mg/L treatment. Total VFA concentrations were significantly lower in the 11 mg/L and 30 mg/L treatment than in the higher TAN treatments.

3.4. Discussion

3.4.1. Food and landscape waste characterization

Landscape waste COD and VS varied more than food waste COD and VS from batch to batch. In addition, the triplicate samples tested for LW TS, VS, and COD had larger confidence intervals than those tested for FW TS, VS, and COD, indicating higher variability within each batch. LW was acquired from outside compost piles, exposed to

temperature variations and rainfall. LW was size reduced using a lawn chipper/shredder, which resulted in more variation in size than FW size reduction, which took place in the dining facility itself with a pulper. As a result the FW was more easily homogenized, resulting in more even moisture distribution and more consistent characterization results, while the landscape waste was more heterogeneous. Bucknell dining hall FW TS was consistent with other studies, where TS has ranged from 12.38% (for Korean food waste) to 27.8% (for simulated household food waste) and 30.9% (for commercial SS-MSW) (Eklind and Kirchmann, 2000a; Kim et al., 2006; Zhang et al., 2007). Other research on restaurant, cafeteria, and simulated food waste, found VS ranging from 79.4 to 89.6% of TS, slightly lower than Bucknell University dining hall food waste (Shin and Jeong, 1996; Day et al., 1998; Eklind and Kirchmann, 2000a; Kim et al., 2006; Zhang et al., 2007). Fewer studies have characterized TS and VS of yard waste; however, in one study yard trimmings arriving at a composting facility had VS of 40.9% of TS (Day et al., 1998), much lower than VS of Bucknell University LW, which was primarily dried leaves. Because COD was determined on an as-is basis (in g COD/g waste), total VS (g/g waste) (TVS) was calculated in order to compare the use of COD and VS for waste characterization. FW TVS was slightly lower than FW COD, while LW TVS was slightly higher than LW COD. Both VS and COD can be used to assess the anticipated biodegradability of a waste for anaerobic digestion. The inconsistency in COD and VS proportions for Bucknell University FW and LW suggests that COD and VS are not consistently related to each other and should not be used interchangeably as an approximation of waste biodegradability.

There was a slight increase in FW COD during the fall of 2007. There was also a seasonal variation in FW TKN, with lower values during the summer followed by an increase during the fall. Both parameters increased during the fall, as students returned to campus and the availability of fresh produce increased. Seasonal variation was also observed in LW COD, which was lower from February through the end of June, and increased in the later summer and fall. During the winter and early summer, minimal additions were made to the compost piles and COD would decrease due to normal degradation within the windrows. In the late summer and fall additions to the piles would be made, both of fallen leaves and pruned branches, contributing new COD to the compost piles.

Batch digestion of FW has resulted in FW methane production of 300.7 mL CH₄/g TS (Wang et al., 1997) and 435 mL CH₄/g VS (Zhang et al., 2007). The FW biodegradability studies conducted in this research are in good agreement, with mean methane production of 354 ± 23 mL CH₄/g TS and 372 ± 21 mL CH₄/g VS (means presented with 95% CI). Methane production from Bucknell University LW was much lower than from FW, with only 22 ± 10 mL CH₄/g TS and 26 ± 11 mL CH₄/g VS (means presented with 95% CI). One of the main factors affecting the biodegradability of a food or landscape waste substrate is the lignin content. Chandler et al. (1980) found an inverse relationship between lignin content and the biodegradable VS of a substrate and used it to estimate biodegradability based on VS lignin content. Kayhanian and Tchobanoglous (1992) used this relationship to estimate the biodegradability of food waste (81.9%) and yard waste (71.5%). Yard or landscape waste is consistently found to have higher lignin

content than food waste. Testing of lignin and cellulose content of different wastes has found lignin content for food waste and simulated food waste ranging from 0.9 to 12.03% (Verrier et al., 1987; Eklind and Kirchmann, 2000a; Komilis and Ham, 2003). In contrast, lignin content in leaves and yard waste range from 16.5 to 33.88% (Eklind and Kirchmann, 2000a; Komilis and Ham, 2003). One study also confirmed that lignin was refractory in anaerobic environments (Komilis and Ham, 2003). The lignocellulosic matrix that forms the structure of plants makes the easily degradable cellulose and hemicellulose inaccessible for anaerobic degradation, resulting in low biodegradabilities for these substrates.

Anaerobic cells are estimated to have a composition of $C_5H_7O_2NP_{0.06}S_{0.1}$ (Speece, 1996). Since the rate of new cell formation is highly substrate dependent, the required COD:N or C:N ratio for successful digestion varies. A theoretical COD:N ratio of 50:1 may be necessary for digestion of a high-carbohydrate substrate (Speece, 1996). In contrast, the COD:N ratio for Bucknell University food waste was 44 (based on the characterization study), with a biodegradable COD:N ratio of 32, significantly lower than the theoretical requirement. A C:N ratio between 25 and 30 is best for AD (Kayhanian and Hardy, 1994). Mixed food wastes have C:N ratios ranging from 8.7 to 12.4 (Kayhanian and Tchobanoglous, 1992; Day et al., 1998), with especially low values for meat meal and bone meal (4) and higher values for vegetables like potatoes and carrots (30) (Eklind and Kirchmann, 2000a). Yard or landscape waste often has higher C:N ratios, with values of 14.5 to 27.7 for yard waste, and 31 to 32 for leaves (Kayhanian and Tchobanoglous, 1992; Day et al., 1998; Eklind and Kirchmann, 2000a; Ono et al., 2003).

The amendment of FW with LW might be expected to improve the substrate C:N ratio and result in improved digestion. During the biodegradability trials, combining FW and LW did result in slightly increased methane production. Given the improvements in biodegradability observed during batch digestion trials, as well as promising results from other research on the codigestion of FW with other, higher carbon substrates, additional research is indicated on the possibilities of FW codigestion with another substrate higher in bioavailable carbon. The addition of LW did allow an increase in reactor solids content to 20%, despite the low solids content of FW, which was the main substrate. One potential advantage of increasing in-reactor solids content is that digestate solids content will be closer to what is needed for composting (about 50%); however, increased reactor solids will require more energy for mixing. The campus LW could also be used as a bulking agent after digestion to increase solids content without affecting in-reactor mixing requirements.

Some research has been conducted on potential cosubstrates that can be used to increase both reactor solids content and C:N ratio. Agricultural residues have been used successfully to increase the substrate C:N ratio and improve biogas production during digestion of swine manure. Wu et al. (2010) studied the codigestion of corn stalks, oat straw, and wheat straw with swine manure, and had the most success with a combination of swine manure and corn stalks, combined to produce a C:N ratio of 20:1, which resulted in increased biogas methane concentration to 68% and an 11.4-fold increase in daily biogas production. The codigestion of kitchen waste with computer paper allowed increased loading and reduced reactor ammonium content (Vermuelen et al., 1993).

Codigestion of food waste, yard waste, and waste paper to increase the substrate C:N ratio was effective at reducing in-digester TAN concentrations (Kayhanian, 1999). The C:N ratio of a mixture of 75% office paper and 25% newspaper is 143:1 (Kayhanian and Tchobanoglous, 1992). Although many types of paper retain high lignin content and have low biodegradabilities, highly-processed and bleached computer or office paper has a very low lignin content (6.5% of TS, 0.4% of VS) and is highly degradable, with up to 90.1% of VS converted to biogas during biodegradability studies (Kayhanian and Tchobanoglous, 1992; Vermuelen et al., 1993). Either of these substrates (agricultural residues or office paper) would be a good candidate for additional studies on codigestion of high-carbon substrates with cafeteria food waste at high OLR.

3.4.2. Low OLR reactor operation

At the low OLR, the reactor parameters monitored were characteristic of stable digestion. SCOD and TVFA remained low, and TVFA was composed almost exclusively of HAc, indicating balanced digestion (Ahring et al., 1995; Björnsson et al., 2000). Reactor pH during this time was high, and BA steadily increased during low OLR reactor operation. The formation of ammonium during anaerobic digestion increases bicarbonate alkalinity and may have been responsible for this trend (Angelidaki and Ahring, 1994; Kayhanian, 1999).

Biogas and methane production both increased significantly during high OLR operation. Methane production was 6.4 times higher during high OLR operation than low OLR operation, which was consistent with the BOLR, which increased by a factor of

six. Biogas methane content increased during this time, from a mean of $53 \pm 3\%$ during low OLR operation to a mean of $64 \pm 2\%$ during high OLR operation (uncertainties represented by standard deviation). However, there was a decrease in COD unit methane which was $232 \text{ L CH}_4/\text{kg COD}$ during low OLR operation and $211 \text{ L CH}_4/\text{kg COD}$ during high OLR operation. In contrast, there was an increase in VS unit methane, from $229 \text{ L CH}_4/\text{kg VS-day}$ during low OLR operation to $272 \text{ L CH}_4/\text{kg VS-day}$ during high OLR operation. The decrease in COD unit methane while there was an increase in VS unit methane can be attributed to an increase in LW COD during high OLR operation, (September and early October, 2007), during which time LW VS remained stable. As a result of the increase in LW COD, LW mass fed was decreased in order to maintain stable feedings of LW COD. The result was a decrease in LW VS fed, and an increase in VS unit methane.

3.4.3. High OLR reactor operation and ammonia inhibition

During the transition from low to high OLR there were temporary increases in VFA, which dissipated when OLR was held steady. The reactor VFA increase began within 5 days of operation at the OLR of $15 \text{ g COD/L reactor volume-day}$, and continued throughout high OLR operation. Biodegradable solid wastes may consist of cellulose, hemicellulose, protein, starch, lignin, and fatty acids (Chynoweth and Pullammanappallil, 1996). Throughout low OLR operation there was some non-VFA SCOD present, however the difference between SCOD and TVFA was consistent, indicating that much of the increase in SCOD during high OLR operation was due to increasing TVFA. On

some occasions there were changes in SCOD that were not observed in VFA. The volume of digestate required in these tests was small, so, although care was taken in sampling, the heterogeneity and the high solids of the digestate made uniform sampling difficult.

The VFA accumulation during high OLR reactor operation was characteristic of reactor upset or instability. The dominance of HPr in TVFA composition is typical of reactor upset (Björnsson et al., 2000). Additionally, the increase in both I-HBu and butyric acid (HBu), as well as other higher order (c4-c6) VFAs, indicates reactor upset (Ahring et al., 1995; Björnsson et al., 2000). Although biogas methane content is often used as the earliest indicator of reactor upset, VFA increases can be seen within 1-2 days of perturbation in reactor operation, and they generally deviate more and are of longer duration than changes in methane production rate and yield (Ahring et al., 1995). The consistent high biogas methane content despite increasing VFAs does not necessarily conflict with the presence of inhibition; biogas methane content can remain high during long-term carbohydrate overloading, even through serious pH drops (Björnsson et al., 2000). Although VFA content was initially low, it did eventually reach levels that have resulted in inhibition in low-solids digestion (TVFA of 10,000 mg/L or concentrations of individual acids between 7,000 mg/L and 17,000 mg/L) (Ahring et al., 1995; Chynoweth and Pullammanappallil, 1996). At the time when the VFA increase started, VFA concentration was low and as a result the initial VFA accumulation can be attributed to the effect of some other inhibitory agent, and is therefore a result of reactor upset rather

than its cause. The high VFA concentration consumed bicarbonate alkalinity, resulting in decreases in both BA and pH.

Reports of what constitutes an inhibitory concentration of FAN or NH_4^+ -N cover an extremely wide range (Table 3.6).

Table 3.6. Inhibitory and toxic concentrations of FAN, NH_4^+ -N, and TAN.

Species	Concentration	Reference
FAN (inhibition)	45 mg/L (thermophilic, pH = 7.2)	Kayhanian, 1999
NH_4^+-N (inhibition)	150 mg/L 1670 – 3710 mg/L (pH 6.5 – 8.5)	McCarty and McKinney, 1961 Lay, 1998
NH_4^+-N (toxicity)	6000 mg/L (pH 6.5 – 8.5)	Lay, 1998
TAN (inhibition)	1000 mg/L (thermophilic, pH = 7.2)	Kayhanian, 1999
	1500 – 3000 mg/L 1.5 g/L – 15 g/L	McCarty, 1964c Chen, 2008
TAN (toxicity)	3000 mg/L	McCarty, 1964c

TAN is often reported without any mention of pH, making it difficult to determine which species is responsible for inhibition. FAN is generally assumed to be the more toxic species because of its ability to penetrate cell membranes (De Baere et al., 1984). At a pH of 8.2 and an OLR of 15 g COD/L reactor volume-day during the reactor upset the FAN concentration was 550 mg/L digestate and the NH_4^+ -N content was 6460 mg/L digestate. These concentrations are certainly on the order of magnitude considered in the literature to be inhibitory. Therefore, it is likely that the poor reactor performance was caused by inhibition due to FAN or NH_4^+ -N.

During the respirometer trial, two treatments were prepared with both FAN and NH_4^+ -N below any reported inhibitory concentrations (11 mg/L and 30 mg/L). COD unit methane was the highest in both of these treatments (although both were much lower than COD unit methane observed in the reactor during high OLR operation). Treatments were prepared with increasing concentrations of TAN (52 mg/L, 126 mg/L, and 212 mg/L), and the result with each TAN increase was decreased biogas and methane production consistent with increasing inhibition. An examination of the individual VFA composition reveals that higher TAN treatments had increased amounts of VFA intermediates, consistent with disrupted digestion (Ahring et al., 1995; Björnsson et al., 2000). The two lowest ammonia treatments had only negligible amounts of HBU and relatively low amounts of HAc and HPr, although HPr was still present in higher concentrations than HAc, indicating some residual instability (Ahring et al., 1995; Björnsson et al., 2000)

The wide range of inhibitory concentrations in the literature makes distinguishing between FAN and NH_4^+ -N as a factor in inhibition difficult. Methane production in the reactor continued despite extremely high FAN and NH_4^+ -N concentration; however, when comparable FAN and NH_4^+ -N concentrations were used in the respirometer trial, biogas and methane content were negligible. Acclimation to ammonia concentrations thought to be inhibitory has been reported (Lay et al., 1998; Bujoczek et al., 2000). Kayhanian demonstrated acclimation to TAN concentrations of 2300 mg/L (Kayhanian, 1994). Other research indicates successful anaerobic digestion at concentrations of 3 to 3.5 g NH_4 -N/kg reactor (Oleszkiewicz and Poggi-Varaldo, 1997). However, the treatment with 212 mg/L (the highest TAN concentration) had a TAN concentration

similar to TAN within the reactor, but demonstrated almost complete inhibition of biogas production, even though the respirometer trial used microbes that had been in the reactor and exposed to in-reactor TAN concentrations. The respirometer trial was prepared with a 20x dilution of the reactor digestate, after which the TAN was adjusted using NH_4Cl . One potential explanation for the intolerance of the microbes in the high ammonia treatment to TAN concentrations similar to those in the reactor is the decrease of antagonists that were present within the reactor. Sodium, calcium, and magnesium have all demonstrated antagonism against the inhibitory effects of TAN when present with high TAN concentrations (McCarty and McKinney, 1961). Possibly the presence of one or more of these antagonists in the reactor moderated the effects of high TAN, and when the concentration of antagonist was reduced by dilution for the respirometer trial, the inhibitory effects of high TAN became clear. The basal medium used to dilute the reactor contents for the respirometer trial contained both sodium and magnesium. However, because the concentrations of these salts inside the reactor are not known, the differences in the concentrations of antagonistic salts between the reactor and the respirometer cannot be compared. Given the wide range of factors that affect the degree of inhibition due to FAN and $\text{NH}_4^+\text{-N}$, it is impossible to determine whether the inhibition observed was due to FAN, $\text{NH}_4^+\text{-N}$, or both.

After reactor feeding was discontinued, TAN continued to increase (due to continued degradation of previously fed solids). Increasing TAN content also resulted in increased pH, with the result that TAN increased and $\text{NH}_4^+\text{-N}$ decreased slightly. Despite increasing ammonia concentrations, reactor SCOD and VFA began a steady decrease

which continued through the end of the study, by which time ammonia content was extremely high (FAN of 859 mg/L and a TAN of 5884 mg/L). Continued digestion of SCOD and VFA present in the reactor despite extremely high FAN and NH_4^+ -N concentrations strongly suggests that either acclimation or antagonism to the toxic effects of ammonia was taking place, in which case, recovery from the inhibition (with digestate dilution to reduce ammonia concentrations) would be a possibility.

3.5. Conclusion

Bucknell University could collect up to 100 metric tons of food waste for anaerobic digestion each year. This waste is a high-quality substrate amenable to anaerobic digestion, with a biodegradable COD that is 73% of total COD. Digestion of this waste on campus could produce as much as 30,400 m³ of methane for heating or hot water generation (based on the batch biodegradability studies). HSAD of cafeteria food waste at an OLR of 2 g COD/L reactor volume-day was successfully demonstrated; however, the low C:N ratio of dining hall food waste resulted in inhibitory ammonia concentrations at high loading rates. Landscape waste was combined with food waste for digestion in an effort to increase both the substrate C:N ratio and the solids content of the reactor. The addition of landscape waste allowed reactor operation at 20% solids and improved methane production from FW. However, the leaves used as a cosubstrate had extremely low biodegradability and the added biodegradable carbon was not enough to ameliorate the effects of low C:N ratio of the food waste. Based on the results of other

research, further investigation on the codigestion of food waste with highly biodegradable paper or agricultural residues is recommended.

3.6. References

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CHAPTER 4:Manuscript 2

Characterization of the curing process from high-solids anaerobic digestion

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Characterization of the curing process from high-solids anaerobic digestion

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Abstract

A laboratory-scale study was completed to simulate aerobic curing of solid-phase residue (digestate) from an anaerobic reactor fed a mixture of food and landscape wastes. The degree of organic stabilization was determined through routine analysis of oxygen uptake rates, percent O₂, temperature, volatile solids, and Solvita Maturity Index; measurements of ammonia and volatile fatty acid (VFA) concentrations served as indicators of phytotoxicity. Results suggest that stabilization of organics and elimination of phytotoxic compounds from anaerobic digestate preceded significant reduction of each volatile sulfur compound (VSC) detected (hydrogen sulfide, methanethiol, and dimethyl sulfide). Within 10–15 days of curing, stabilization of organics was achieved and phytotoxic compounds were eliminated, whereas reduction of VSCs to low levels required 15–20 days of curing. Based on these results, incomplete curing and anaerobic microenvironments within a curing facility may increase odor potential via formation of

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VSCs, whereas sufficiently cured digestate will resist VSC formation, despite the onset of anaerobic conditions.

Keywords: curing; anaerobic digestion; phytotoxicity; volatile sulfur compounds; compost stability

4.1. Introduction

Anaerobic digestion (AD) of municipal solid waste (MSW) has been employed in Western Europe since the 1980s, where 124 facilities have a total capacity of 3.9 million metric tons per year (De Baere, 2006). Biodegradation of MSW under anaerobic conditions converts organic waste into methane, a valuable energy source. Anaerobic digestion represents 28% of the biological treatment of MSW in Europe, wherein 56% of the facilities employ high-solids treatment (solids greater than 15%) (De Baere, 2006).

The US Environmental Protection Agency has estimated that 2007 production of MSW in the United States was 231 million metric tons (US EPA, 2008). Approximately 25% of this material was kitchen waste and yard trimmings, also known as green waste (US EPA, 2008). Although a large proportion of green waste was aerobically composted, 125 million metric tons of mixed MSW were landfilled (US EPA, 2008).

In the US, substitution of AD for green waste composting processes would result in net energy production (100–150 kW h/ton) instead of consumption (30–35 kW h/ton) (Hartmann and Ahring, 2006). Furthermore, AD could be employed for the organic fraction of mixed MSW that is currently landfilled in the US, with significant production of renewable energy and reduction of CO₂ emissions (DiStefano and Belenky, 2009).

However, given the relatively low costs associated with landfilling MSW in the US, it is clear that widespread adoption of AD will only occur if the entire AD process is cost-competitive with landfilling.

In addition to digester capital and operating costs, processing of solid-phase residue from the digester represents additional initial and annual costs. AD facilities in Western Europe typically include dewatering and “curing” of residue (digestate) from the digestion process. Curing is a passive aerobic treatment process intended to minimize residual odor and phytotoxicity. Previous investigations have demonstrated the technical feasibility of AD of MSW in the US, initially in the 1970s and more recently (Pfeffer, 1974; DiStefano et al., 2004). Local experience indicates that successful management of digestate remains a significant issue in the US. Therefore, the work described herein was undertaken to investigate the curing process with the intention of initiating a quantified characterization that eventually may provide a basis for economically sizing a curing facility and reducing total capital and operating costs of an AD facility.

To reduce the operating costs of AD, the final product must be biologically stable and economically viable. Indicators of stable material include reduced microbial activity and the absence of phytotoxicity and odor. Compounds known to cause phytotoxicity include volatile fatty acids, which are intermediates formed during anaerobic decomposition (Devleeschauwer et al., 1981) and ammonia (Leege and Thompson, 1997). Odorous substances, such as VSCs, are formed under anaerobic conditions and may occur when anaerobic zones develop during the curing process.

Methods for determining compost stability include direct assessments of microbial activity such as self heating (Brinton et al., 1995), carbon dioxide evolution, and oxygen consumption (Iannotti et al., 1994). Comparisons of compost stability methods have been completed for different substrates in attempts to identify universal stability indices (Iannotti et al., 1994; Brewer and Sullivan, 2003; Changa et al., 2003). Stability indices that rely on correlations between microbial activity and chemical or physical characteristics of compost (such as carbon to nitrogen ratio or cation exchange capacity) are highly substrate-dependent, whereas microbial activity tests generally give reliable results across a range of feedstocks (Eggen and Vethe, 2001).

Whereas most work on phytotoxicity and biological stability is focused on aerobic composting facilities, limited reports on curing of AD residue exist. Kayhanian and Tchobanoglous (1993a, b) studied a thermophilic system with combined anaerobic and aerobic digestion of the simulated organic fraction of MSW. The combined system retention time was 30 days and the digestate solids content was increased from 25-30% to 65% during curing. The combined AD and curing process reduced VS from 94% (feedstock) to 70% (humus), for a total destruction of 26% of feedstock VS (Kayhanian and Tchobanoglous, 1993b). Curing reduced odors that were produced during the anaerobic phase (qualitatively); however, the digestate retained some phytotoxicity after treatment. Seed germination tests using leachate concentrations (from digestate) of 25% and higher displayed less than 60% germination, indicating unacceptable phytotoxicity (Kayhanian and Tchobanoglous, 1993a).

In another study, mesophilic and thermophilic AD of MSW were compared to determine whether digestion temperature affected the duration of curing needed to eliminate phytotoxicity. Curing following thermophilic digestion eliminated phytotoxicity in two weeks, whereas three weeks of curing were required after mesophilic digestion (Vallini et al., 1993).

4.2. Methods

4.2.1. Anaerobic digester

A 280-L stainless steel vessel with a horizontally-oriented helical mixer served as the anaerobic digester. Seed organisms were obtained from an upflow anaerobic sludge blanket reactor treating brewery wastewater. Mixing was controlled by a timer to enable 5 min of mixing at 15-min intervals. Temperature was maintained at 35 °C by circulating hot water through the water-jacketed reactor. Manual daily wasting and feeding were accomplished via knife/gate valves in the reactor top and bottom. A wet-test gas meter (Precision Scientific Petroleum Instruments, Model 63126) was used to measure gas production.

Feedstock chemical oxygen demand (COD) was used to determine the reactor organic loading rate (OLR), which was incrementally increased from 0.5 to 2 g COD/L-day, and then held steady for 90 days prior to sampling for an examination of digestate curing. Food waste and landscape waste from Bucknell University were combined to maintain both a consistent OLR, and reactor solids content at 20%. During operation, biomass was wasted from the reactor to maintain the 280-L working volume. As a result,

at the OLR of 2 g COD/L-day, the reactor solids retention time was on the order of 175 days and steady-state operation was identified by consistent methane production, soluble COD (SCOD), and VFA content in the digestate.

4.2.2. Curing reactor

A 48-L insulated container served as the curing reactor. Digestate was removed from the reactor 16 h after a previous feeding and combined with dried wood chips to achieve 50% solids, at a volume ratio of approximately 1:3 (digestate:woodchips). The mixture was homogenized by hand and then placed in the curing reactor in a 35 °C room in order to simulate autothermal conditions that would occur in a full-scale curing pile. Temperature was monitored with a probe located in the horizontal center of the reactor, about 2.5 cm from the bottom. Percent oxygen in the curing reactor was measured at six locations using an oxygen analyzer (Engineered Systems and Designs, Model 600) which was equipped with a sampling probe. Gas was drawn into a sampling chamber (Woods End Laboratory) where percent oxygen was analyzed. The sampling locations were in the center of the container (2.5 cm, 7.5 cm, and 12.5 cm below the surface) and 2.5 cm from the edge of the container at identical depths.

Total solids (TS), volatile solids (VS), VFAs, oxygen uptake rate (OUR), VSCs, and Solvita Maturity Index (SMI) were measured on alternate days during the curing study. To obtain a representative sample, curing reactor contents were thoroughly mixed and samples were removed for testing. For the Solvita, VFA, and VSC tests, the sample was screened to exclude large particles (0.95 cm sieve) before analysis. After the sample

was obtained, 1-3 L of water were added to the remaining mixture to maintain the solids content at approximately 50% and the entire contents were returned to the curing reactor (whereas water addition to a full-scale pile is typically unnecessary, the laboratory-scale curing reactor described herein lacked sufficient mass to maintain a stable water content). TS and VFA content were measured immediately after sampling.

4.2.3. Volatile sulfur compounds, oxygen uptake rates, and Solvita tests

VSC samples were stored and tested according to a method provided by Higgins et al. (2006), modified as follows: 20 g of sieved mixture was added to each serum bottle, 125-mL serum bottles were employed, and bottles were incubated at 35 °C. The initial VSC analysis was performed 4 h after samples were placed in serum bottles. Subsequent headspace samples were collected each alternate day for the duration of the curing trial. For each sample, bottles were prepared in triplicate.

VSC concentrations were also determined according to the method provided by Higgins et al. (2006), modified as follows: 6890 N series gas chromatograph equipped with a flame photometric detector and a 60-m Restek capillary column (diameter of 530 μm and film thickness of 7 μm) were employed. The inlet temperature was 230 °C and the detector temperature was 245 °C. The oven was held at an initial temperature of 40 °C for 1.8 min, followed by a 40 °C/min ramp to 220 °C, with a hold at 220 °C of 1 min, for a total run time of 9 min. Nitrogen was used as the carrier gas, with a column flow of 14 mL/min.

Oxygen uptake rates were determined using an AER-200 respirometer from Challenge Technologies. Approximately 50 g (each) of digestate/wood chips mixture was added to perforated compost vessels, which were placed in enclosed tubes and incubated in a water bath to maintain temperature at 35 °C. Once each tube initiated oxygen consumption, the first 4 h of consistent data were used to determine the oxygen uptake rate.

Carbon dioxide production and ammonia levels were estimated using Solvita compost test kits (Woods End Laboratory). Solvita is a colorimetric method wherein gel paddles are inserted into a sieved (0.95 cm), enclosed sample. After 4 h of exposure to headspace gases, gel paddle colors are compared to a color chart to determine CO₂ and NH₃ levels. The individual CO₂ and NH₃ levels are used to identify the Solvita Maturity Index, which may range from a value of 1, indicating “raw compost” to 8, or “finished compost” (Woods End Laboratory, 2004).

4.2.4. Methane, pH, alkalinity, and VFAs

In order to monitor reactor conditions, gas production and total methane were determined on a regular basis, as described by DiStefano and Ambulkar (2006), modified as follows: percent methane of the biogas was determined with a Hewlett Packard 6890 series gas chromatograph equipped with a thermal conductivity detector and a Supelco 60/80 Carbosieve column (2.5 m by 6 mm).

Digester effluent was collected three times per week for pH and VFA analysis. A liquid extraction procedure was developed to determine the VFA content of the high-

solid (approximately 20%) digestate. Approximately 25 g of sample was diluted with 150 mL of reverse osmosis water and mixed at 250 rpm for 10 min. Tests were conducted at mixing rates between 100 and 500 rpm to identify the speed above which no additional VFA extraction was observed, to reduce volatilization.

After mixing, the sample pH was determined with a digital pH meter (Accumet model AR50). After the digestate pH was measured, total alkalinity was determined by titration to a pH of 4.3; VFA alkalinity (expressed as CaCO_3) was subtracted to yield bicarbonate alkalinity. For VFA determination approximately 6 mL of the diluted digestate sample was centrifuged at 20,000g for 10 min. The centrate was filtered through a 1 μm glass-fiber filter, and then, through a 0.45 μm syringe filter. One milliliter of centrate was transferred to a 1.5 mL vial and 20 μL of 5000 mg/L valeric acid (HVa) was added as an internal standard to achieve 100 mg/L HVa. The sample was acidified with 20 μL of 75% phosphoric acid to pH 3 and 1 μL was injected on a Hewlett Packard (6890 series) gas chromatograph equipped with an automatic sampler (Agilent Technologies, 6890 series injector). A Nukol 30-m capillary column with an inner diameter of 0.53 mm and a film thickness of 0.45 μm was used. Nitrogen was used as the carrier gas (30 mL/min) and the flame ionization detector and inlet temperatures were 200 °C. The oven temperature was 105 °C for the first 4 min, followed by a 5 °C/min ramp to 145 °C and a 10 °C/min ramp to 190 °C, held for 5.5 min. This method resulted in a detection limit on the order of 10 mg/L for each acid (or 100 ppm). VFA standard (10 mM, Supelco) was added to digestate samples in order to assess the proportional VFA recovery by the extraction procedure. Results indicated that greater than 90% of

VFA standard added to the water and digestate solution was recovered during centrifugation, filtering, and testing.

4.2.5. COD, solids, and TKN

Samples from each food and landscape waste batch were analyzed for COD, TS, VS, and Total Kjeldahl Nitrogen (TKN). COD and solids analysis were completed in triplicate. For COD analysis, a 12.5 g sample of food waste was homogenized with water (500 mL total volume) at 23,000 rpm in a laboratory blender. Reactor SCOD was determined on filtrate from the VFA extraction procedure. For all samples, COD was measured according to the closed reflux colorimetric method (APHA, 1995). TS and VS analysis were also conducted in accordance with Standard Methods (APHA, 1995). The TS results were used to determine the amount of water to add in order to maintain the moisture content in the curing reactor at 50%, as described previously.

TKN analysis was completed according to Hach et al. (1985), with the following modifications: the test was conducted on a 20-mL sample of the homogenized food waste and water mixture and 3 mL of concentrated sulfuric acid and 10 mL of 50% hydrogen peroxide were used.

4.2.6. Statistical analyses

All statistical analyses were completed using Microsoft Excel 2002. VFA, VS, OUR, and VSC tests were performed in triplicate. Routine measurements of percent oxygen, temperature, pH, and Solvita NH₃ and CO₂ were performed once on each testing

day. The curing procedure itself was completed twice. Means, standard deviations, coefficients of variability, coefficients of determination, and linear regressions were calculated via Microsoft Excel as appropriate. The two curing trials were not compared statistically. The anaerobic digester was fed actual food and landscape wastes; because prepared synthetic wastes were not used, natural variability in waste characteristics was expected, as discussed in section 3.1. Despite variable waste characteristics, similarities were noted between the two curing trials based on trends in individual parameters.

Calibration curves were prepared for VFA and TKN analyses, and linear regressions were determined using Microsoft Excel. For VFAs, dilutions were prepared in concentrations ranging from 0.1 mM to 10 mM from a 10 mM standard containing VFAs from acetic acid to heptanoic acid (Supelco). For TKN, a calibration curve was prepared by digesting Nicotinic Acid p-Toluenesulfonate in concentrations ranging from 5.12 mg/L to 99.88 mg/L. From routine measurements of standards, the resulting linear regressions for VFA and TKN standards each achieved a coefficient of determination in excess of 0.999. To quantify methane content in samples, the peak area response from direct injection of pure methane (National Specialty Gases) was first obtained. Pure methane samples were injected in quadruplicate and the average peak area response was compared to digester gas samples. The coefficient of variation (standard deviation divided by the mean) was 1.5%.

4.3. Results

The entire curing study was repeated in order to examine reproducibility of results; therefore, data from both experiments are presented herein and are referred to as “Trial 1” and “Trial 2”.

4.3.1. High-solids anaerobic digestion

Food waste (FW) and landscape waste (LW) were routinely sampled and analyzed during the reactor study in order to characterize each batch of waste and determine reactor feeding amounts. As shown in Table 4.1, COD, VS, and TS were measured in food and landscape waste, whereas TKN analysis was completed on food waste only.

Table 4.1. Food waste (FW) and landscape waste (LW) characteristics.

	COD		TS		VS		TKN
	(g/g waste)		(g/g waste)		(g/g TS)		(mg/g waste)
	FW	LW	FW	LW	FW	LW	FW
Mean	0.26	0.40	0.21	0.54	0.94	0.82	5.5
Std. Dev.	0.11	0.20	0.04	0.11	0.03	0.11	2.4
Observations	38	35	38	35	38	35	28

Food and landscape waste characteristics exhibited some variability during the study.

Food waste was collected from the university cafeteria on a weekly basis, and characteristics depended on the meals being served that day. Landscape waste was collected from university compost piles, and characteristics depended on recent rainfall,

the age of the landscape waste, and the nature of the landscape waste itself. Leaves were typically used, but occasionally grass clippings or other material were collected.

During reactor operation, parameters were monitored to demonstrate stable reactor operation. A summary of reactor operating parameters is presented in Table 4.2.

Table 4.2. Reactor parameters during curing study (values are on a wet solids basis unless noted).

	pH	Bicarb. Alk. (mg as CaCO ₃ /g)	SCOD (mg COD/g)	VFA (mg as COD/g)	CH₄ (mL/g VS fed)	CH₄ (mL/g COD fed)	CH₄ (%)
Mean	8.2	23.3	21.7	0.52	238	237	53
Std. Dev.	0.05	2.10	3.4	0.19	48	38	3
# Obs,	31	26	31	29	71	71	73

As shown, pH of the reactor contents remained relatively high with a mean value of 8.2. This was most likely due to conversion of proteins in the food waste to bicarbonate and ammonia, which provided significant buffering capacity. Also, the low OLR promoted extremely low levels of VFAs and preserved alkalinity. The SCOD of the reactor contents indicated the presence of a large quantity of non-VFA COD (VFAs typically represented only 3% of the SCOD). The variation in unit methane production (VS and COD basis) was due to the variation in the feed characteristics. Reactor gas remained largely in excess of 50% methane. Typical VS content of combined food waste and landscape waste fed to the reactor was 0.90 g VS/g TS.

4.3.2. Indicators of digestate stability

As shown in Fig. 3.1a, oxygen levels in the curing reactor were monitored during both trials in order to infer the degree of microbial activity and level of aeration.

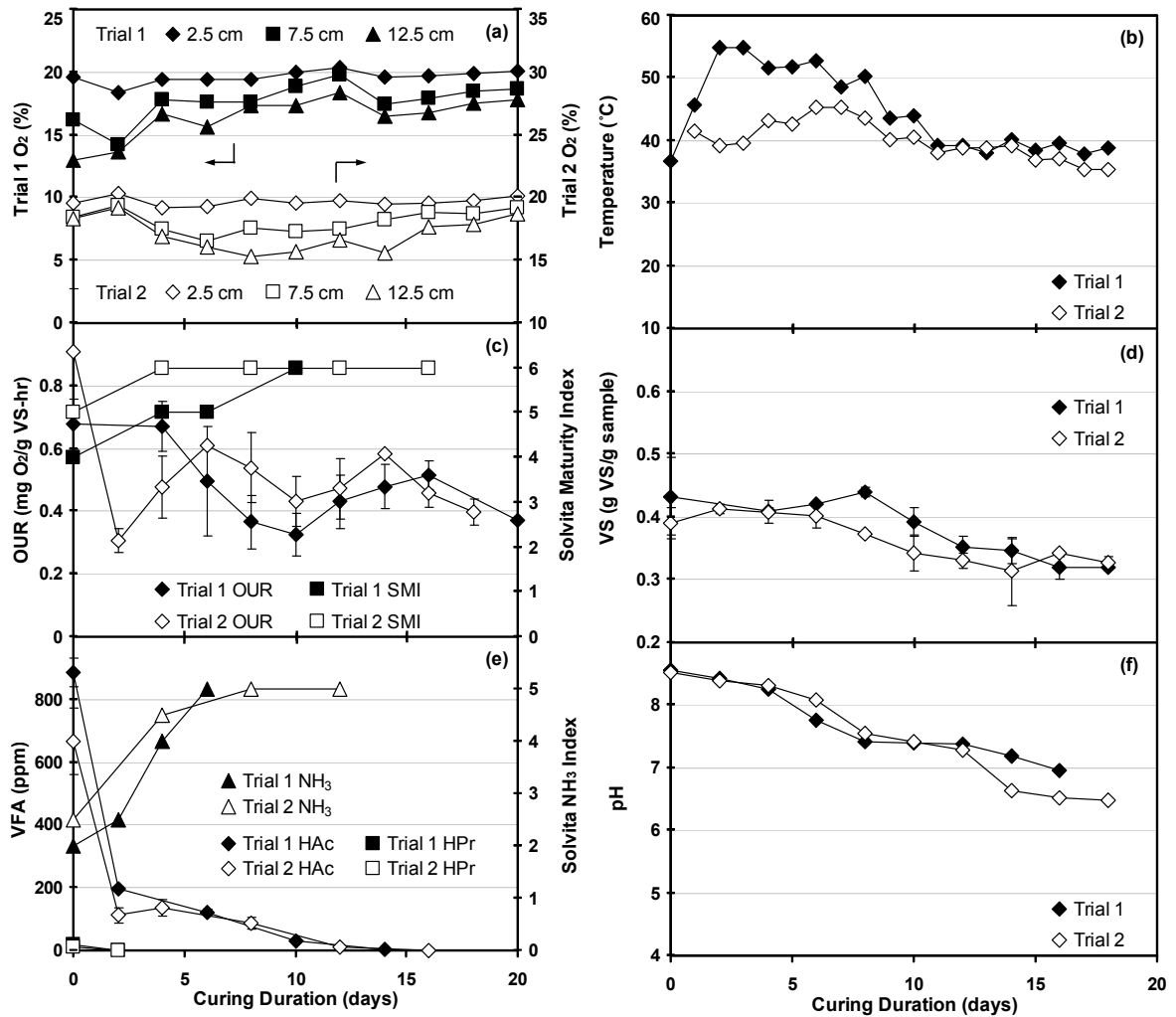


Figure 4.1. Data collected from the curing reactor (a) oxygen levels, (b) maximum daily temperature, (c) oxygen uptake rate and Solvita maturity index, (d) volatile solids, (e) acetic and propionic acid concentrations and Solvita NH₃ index, and (f) pH (error bars represent one standard deviation from the mean).

For both trials, oxygen levels remained mostly in excess of 15%, indicating that air was well distributed and there was sufficient air supply to sustain microbial activity. During Trial 1, the lowest oxygen levels occurred on Day 2 in the center of the curing reactor: 18.4% (at 2.5 cm), 14.2% (at 7.5 cm), and 13.6% (at 12.5 cm). Thereafter, oxygen content increased to the 16-20% range. Similar values were measured along the side of the curing vessel (data not shown), although percent oxygen levels were slightly higher. During Trial 2, the most significant oxygen consumption occurred between days 8 and 14. Whereas oxygen levels remained in the range of 19-20% at 2.5 cm, levels decreased to 16.5% (at 7.5 cm) and 15% (at 12.5 cm). Again, oxygen levels at the side of the curing reactor followed similar patterns, with slightly higher oxygen percentages. The sides of the vessel may have provided access for air to reach the lower levels of material, resulting in slightly higher oxygen levels.

Temperature was monitored constantly during each trial using a maximum-minimum thermometer with a probe. The probe was inserted into the center of the digestate/wood chips mixture and the maximum temperature achieved during each 24-h period was recorded, as shown in Fig. 3.1b. As described previously, because it lacked sufficient mass to retain heat from exothermic aerobic decomposition, the curing reactor was placed in a constant-temperature room at 35 °C. During Trial 1, temperature increased approximately 20 °C (to 54.9 °C) over the initial 3 days before a slow decrease to levels between 39 °C and 40 °C. In contrast, the Trial 2 curing mixture maintained a lower temperature (about 40 °C) during the first 4 days of curing and demonstrated a more moderate temperature increase to 45.4 °C on days 6 and 7, and then slowly

decreased to 35 °C by the end of the trial. The temperature data suggest (in conjunction with the percent oxygen results) that microbial activity was higher in Trial 1 than Trial 2.

SMI and OURs (through respirometry) were determined to further characterize microbial activity during curing, as shown in Fig. 3.1c. Both the SMI and the OUR results indicated increasing organic stability as curing progressed. During Trial 1, the OUR decreased from 0.68 mg O₂/g VS-h to 0.37 mg O₂/g VS-h, whereas Trial 2 OUR decreased from about 0.91 mg O₂/g VS-h to 0.40 mg O₂/g VS-h. Although OUR values were relatively low throughout the curing process, OURs decreased 54% during Trial 1 and 44% during Trial 2. Decreasing oxygen uptake rates indicated oxidation of biodegradable organics by the curing process; however, the low initial OURs demonstrate that the majority of biodegradable material was removed during anaerobic digestion.

SMI, shown in Fig. 3.1c, was determined from the Solvita ammonia and CO₂ test results. The Solvita ammonia test has been adopted by the US Composting Council for ammonia testing of composts (Changa et al., 2003). In addition, comparisons of Solvita CO₂ and NH₃ results to other CO₂ uptake and NH₃ testing methods have demonstrated good agreement (Brewer and Sullivan, 2003; Changa et al., 2003; Wang et al., 2004). Ranging from 1 (least mature) to 8 (mature), the SMI typically is employed to determine the condition of compost. In Trial 1, the initial SMI was 4 (indicating active compost), and progressed to a value of 6 (on Day 10), which was indicative of compost undergoing curing. In Trial 2, the SMI started at a value of 5, advanced to a value of 6 by Day 4, and remained stable for the duration of the trial. The changes in the SMI displayed herein were primarily due to increases in the Solvita NH₃ result during the curing process. Both

OUR and Solvita results indicated that the digestate in both trials was in the curing stage, but might not be considered equivalent to finished compost. Compost with an SMI of 6 is suggested for uses such as hothouse beds, greenhouses, orchards, pastures, hay crops, turf, and general gardening (Woods End Laboratory, 2004).

Volatile solids results for each trial are plotted in Fig. 3.1d, and a decrease in volatile solids during both Trial 1 and Trial 2 is evident. During Trial 1, VS decreased steadily from 43% to 32% and during Trial 2, VS decreased from 39% to 33%. Clearly, the majority of the easily digestible VS content in the food waste and landscape waste was degraded during anaerobic digestion. The main component of VS remaining after the curing phase was likely lignocellulose contributed by the landscape waste and bulking agent used in the curing reactor. During the combined digestion and curing process, VS destruction was 13% (Trial 1) and 22% (Trial 2). Again, because actual food and landscape wastes were employed (instead of synthetic, prepared wastes), variability in VS destruction is attributed to variable waste characteristics during the two trials.

4.3.3. Phytotoxicity

VFAs and ammonia (via the Solvita NH_3 test) were monitored to examine the effect of curing duration on phytotoxicity. Fig. 3.1e shows that ammonia and volatile acids were removed quickly during the curing process. A Solvita ammonia result of 5 indicates that the ammonia concentration is less than 100 ppm; this was achieved after 6 and 8 days of curing during Trials 1 and 2, respectively. During each trial, only acetic (HAc) and propionic (HPr) acids were detected; no doubt, residual levels of these acids

were transferred to the curing reactor in digestate from the anaerobic digester. HPr was undetectable after 2 days and HAc was not detected after 16 days of curing. In both trials, there was a rapid decrease in HAc between Day 0 and Day 2, from 900 ppm to 200 ppm (Trial 1) and from 700 ppm to 100 ppm (Trial 2). Clearly, the curing process facilitated removal of VFAs from anaerobic digestion. No additional VFAs were produced during curing, as the process was well-supplied with oxygen.

During both trials, pH was measured on alternate days; results are shown in Fig. 3.1f. The initial pH for both trials was approximately 8.5. During the curing process, the pH decreased to the 7–6.5 range. This decrease in pH contributed to the reduction in free ammonia in the Solvita test (shown in Fig. 3.1e). Once the pH was reduced below 7.5, although ammonium might have been present in the curing material, no free ammonia would have been released in gaseous emissions from the curing material.

4.3.4. Volatile sulfur compounds

VSCs are significant contributors to nuisance odors detected during composting (Derikx et al., 1990). Whereas other volatile organic compounds may compose the majority of emissions from composting, the low odor thresholds of VSCs result in highly significant contributions to odor problems (Derikx et al., 1990). During both curing trials, H₂S, methanethiol (MT), and dimethylsulfide (DMS) were monitored. Figs. 4.2-4.4 represent the H₂S, MT, and DMS data from curing Trial 1, respectively. Results from Trial 2 were similar (data not shown).

VSC concentrations are shown versus both curing duration (“Days Cured”) and incubation duration (“Days Incubated”). As described previously, VSC data was obtained from gaseous samples of headspace from enclosed serum bottles, which contained digestate. Therefore, “Days Cured” represents the number of days in the curing reactor before a sample was placed in a serum bottle. Likewise, “Days Incubated” indicates the number of days a sample remained in a serum bottle as headspace samples were routinely taken. H₂S (shown in Fig. 4.2) was not produced in large quantities until several days of incubation had elapsed.

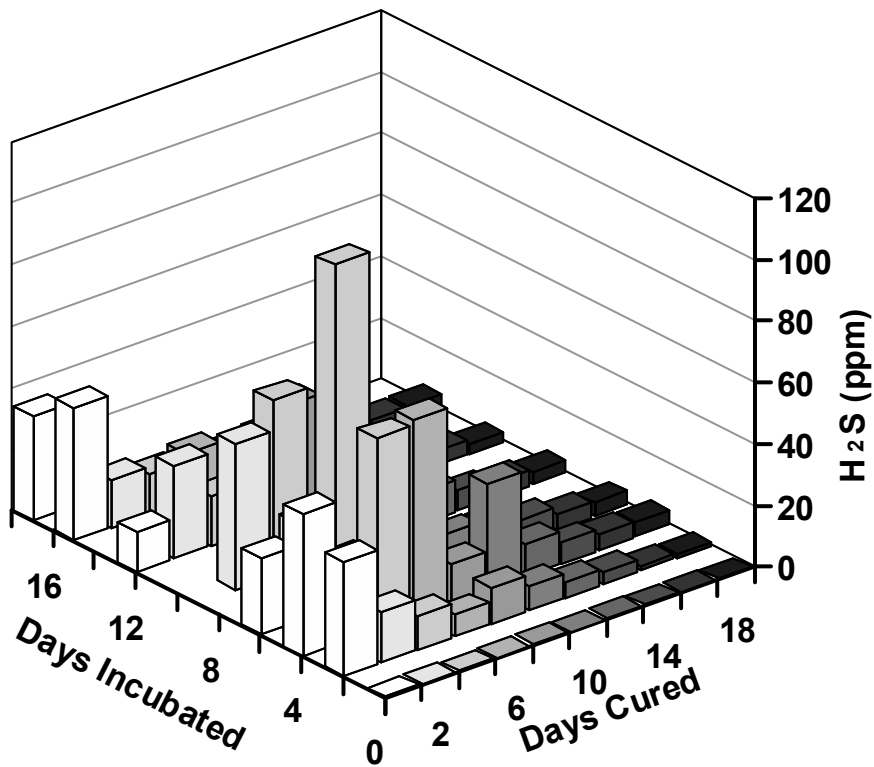


Figure 4.2. Hydrogen sulfide data from curing Trial 1.

Peak H₂S production (112 ppm) occurred in samples that had undergone 4 days of curing and then incubation for 6 days. Additional curing of 10 and 12 days reduced H₂S to

relatively low levels, regardless of the duration of subsequent incubation. After 14 days of curing, H₂S had been reduced to levels of 4 or 5 ppm, with continuing decreases during the remaining days of curing.

From Fig. 4.3, low levels of MT were detected from the beginning of curing, and MT was produced quickly once samples were incubated.

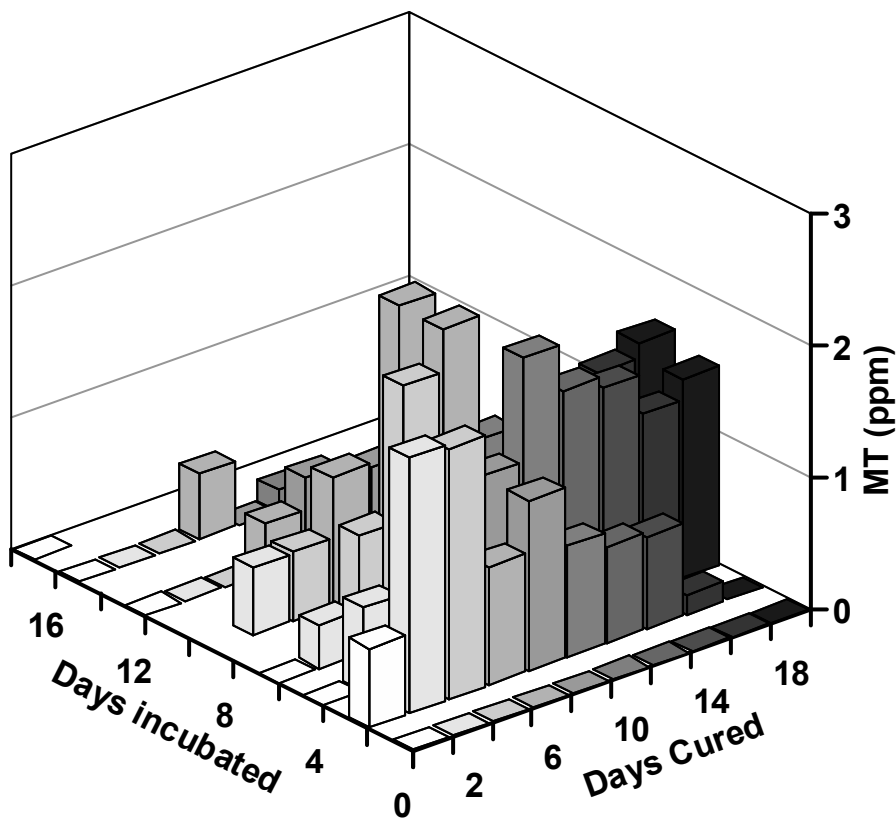


Figure 4.3. Methanethiol data from curing Trial 1.

Generally, maximum levels of MT were reached after several days of incubation. Note, from Fig. 4.3, that MT levels were significantly lower than H₂S levels. For material that was cured up to 2 days, MT peaked after 2 days of incubation, whereas curing durations greater than 2 days delayed the MT peak until 4 to 6 days of incubation. Continued

curing for 18 days reduced but did not eliminate the production of MT, as concentrations on the order of 1-1.5 ppm continued to occur on incubation days 4 and 6 through the end of the curing trial. Whereas incubation stimulated production of MT, continued incubation resulted in a subsequent decrease in MT levels.

Fig. 4.4 shows that a maximum DMS concentration of 11 ppm occurred in samples that had been cured for 4 days and then incubated for 2 days.

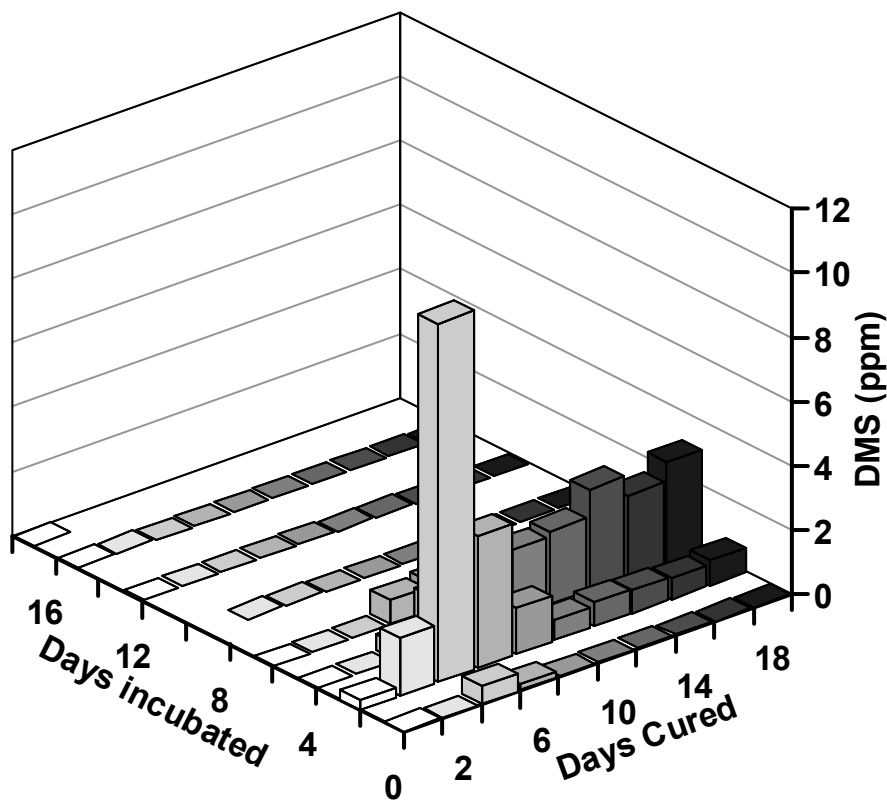


Figure 4.4. Dimethyl sulfide from curing Trial 1.

Prolonged incubation quickly reduced DMS below 1 ppm. Additional curing both reduced total concentration of DMS and shifted DMS production to later in the incubation period. For example, 10 days of curing achieved a DMS peak (2-3 ppm) after

4 days of incubation, which was quickly reduced to zero after several days of incubation. DMS was therefore a transient VSC that exhibited net production during the initial days of incubation and subsequent net loss as incubation continued.

4.4. Discussion

The increase in organic stability and decrease in phytotoxic compounds demonstrated that a curing duration of 10-15 days was sufficient to stabilize digestate from the AD process. The temperature increases during both trials indicated much lower activity than would be expected during composting of undigested matter, which can achieve self-limiting temperatures between 60 °C and 70 °C (Finstein and Morris, 1975). This indicates that the digestate resembled material in the final stage of composting, which is characterized by a moderate temperature increase followed by a decrease to ambient temperatures (Woods End Laboratory, 2004). In addition to moderate temperature increases, oxygen levels within the curing reactor remained in excess of 13%, indicating that oxygen consumption occurred, but not enough to exhaust oxygen and create anaerobic zones. The very low oxygen uptake rates during curing provide additional evidence that microbial activity was limited. The US Composting Council recommends that OURs below 0.4 mg O₂/g TS-h are indicative of “very stable” compost (Leege and Thompson, 1997). For comparison, final OURs reported herein are 0.19 mg O₂/g TS-h (Trial 1) and 0.31 mg O₂/g TS-h (Trial 2); thus, the curing process successfully achieved the “very stable” classification. Similarly, the Canadian Council of Ministers on the Environment recommends OURs no greater than 0.4 mg O₂/g VS-h before use of

compost (Compost Guidelines Task Group, 2005). The final OUR results of 0.37 and 0.40 mg O₂/g VS-h for Trial 1 and Trial 2, respectively, are in agreement with this criterion. Given that the US Composting Council notes that OURs of unstabilized material typically exceed 5.0 mg O₂/g TS-h (Leege and Thompson, 1997), and that initial OURs reported herein ranged from 0.68 to 0.91 mg O₂/g VS-h, anaerobic digestion accomplished a large amount of stabilization. The OUR-based stability criterion was easily fulfilled by the curing process.

The SMI results also demonstrate the stability of the cured digestate. The initial results were 4 (Trial 1) and 5 (Trial 2), and values of 6 were reached by Day 4 and Day 10 in Trial 2 and Trial 1, respectively. An SMI of 6 signifies compost in the curing stage, which is classified as mature (Woods End Laboratory, 2004).

Regarding phytotoxic compounds, volatile acid concentrations as low as 500 ppm have been associated with compost immaturity (Brinton, 1997). VFAs are typically formed during events of high respiration which result in development of anoxic zones, and are indicative of immature composts (Brinton, 1997). VFAs (acetic acid) inhibited the germination of cress seeds in concentrations as low as 300 ppm, and prevented it entirely at concentrations of 2000 ppm (Devleeschauwer et al., 1981). Results indicate that VFA phytotoxicity was eliminated in that HAc and HPr were reduced to less than 100 ppm within 10 days of curing. Ammonia levels ranging from one to three (25,000-2,500 ppm of gas) on the Solvita ammonia test can indicate excess nitrogen or low C:N ratio, and possible phytotoxicity (Woods End Laboratory, 2005). The Solvita ammonia test indicated rapid removal of ammonia by the curing process. Rapid removal of VFAs

and ammonia suggests that cured digestate would not demonstrate phytotoxic behavior after 6-10 days.

The decrease in ammonia and pH during curing was likely due to nitrification, as reported by Eklind and Kirchman during composting of source-separated organic household wastes (Eklind and Kirchmann, 2000).

This analysis suggests that, based on traditional indicators of organic stability and phytotoxicity, adequate curing of digestate was achieved within 10 days. However, analysis of volatile sulfur compounds suggests that additional curing time would be required to mitigate the odor potential of digestate.

A variety of microbial (anaerobic and aerobic) and abiotic mechanisms are responsible for VSC production and degradation. Some processes that could contribute to VSC production and degradation during curing of digestate are shown in Fig. 4.5.

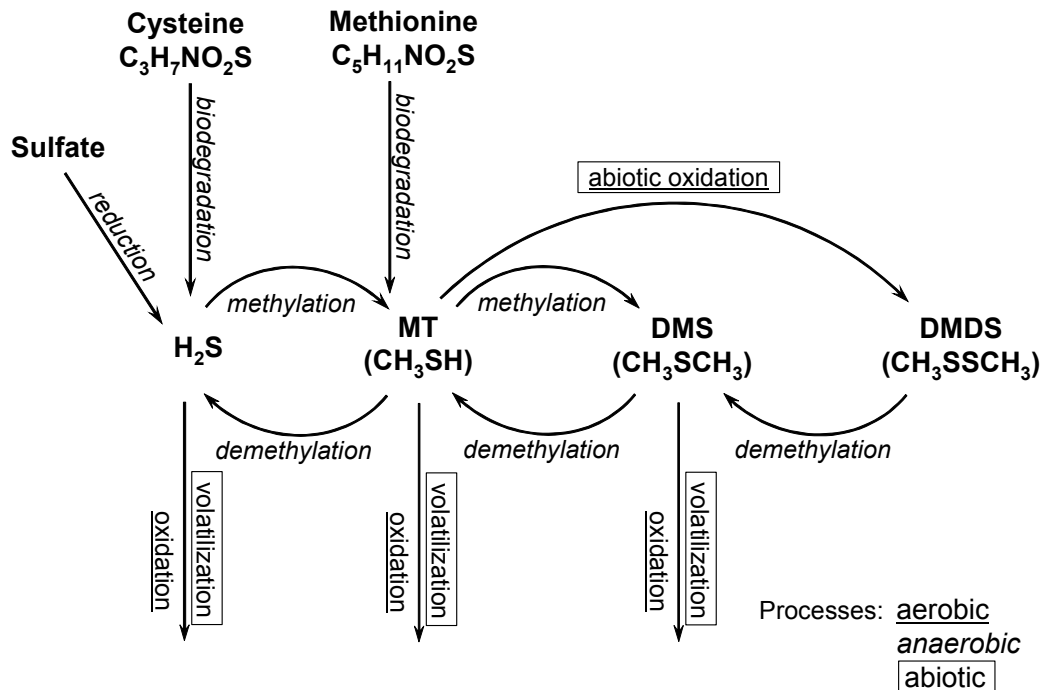
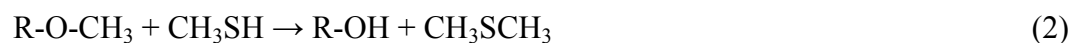


Figure 4.5. Production and degradation of H₂S and volatile organic sulfur compounds. Adapted from Higgins et al. (2006), with information from Forsberg (1980), Kiene et al. (1986), Finster et al. (1992), Visscher and Taylor (1993) and Lomans et al. (1999, 2002).

Under anaerobic conditions in the digester, sulfate may be reduced to H₂S by sulfur-reducing bacteria. H₂S production from anaerobic degradation of the sulfur-containing amino acid cysteine has been demonstrated; likewise, MT is similarly produced from methionine (Hayward et al., 1977; Forsberg, 1980; Higgins et al., 2006). Furthermore, methylation of H₂S and MT under anaerobic conditions is known to produce MT and DMS, respectively (Lomans et al., 2002; Higgins et al., 2006). Reactions (1) and (2) illustrate the formation of MT and DMS through methylation of H₂S (Bak et al., 1992; Higgins et al., 2006). MT is typically formed as an intermediate and the final product is DMS (Bak et al., 1992).



Although digester gas was not analyzed for VSCs, it is expected that H₂S formation and subsequent production of MT and DMS occurred in the digester. Methylation of H₂S and MT could also proceed, via Reactions (1) and (2), in a full-scale curing facility with anaerobic zones. The serum bottle results described herein confirm that, under aerobic conditions (i.e., in the curing reactor and shortly after serum bottles were prepared), VSCs were not produced. Serum bottle volumes and OURs, as determined during the curing study, were used to calculate the duration of aerobic conditions in the serum bottles. Anaerobic conditions would develop within 5-16 h, based on initial and final OURs, respectively. Once oxygen was consumed, prolonged incubation of the serum bottles maintained anaerobic conditions. Therefore, it is suggested that, initially, serum bottle results represent the aerobic curing process, for headspace samples collected shortly after bottle preparation. Thereafter, serum bottle incubation data represent the onset and prolonged existence of anaerobic conditions, which could exist as anaerobic microenvironments within a full-scale curing pile.

The methyl donors in Reactions (1) and (2) are methoxylated aromatic compounds, which are degradation byproducts of lignocellulose (Lomans et al., 2002). The complex structure of lignocellulose results in slow aerobic and extremely slow anaerobic degradation (Tuomela et al., 2000). The relatively short curing duration described herein may have only liberated small amounts of lignin from the lignocellulose

matrix; therefore, production of methoxylated aromatics during curing is unlikely. However, significant concentrations of MT and DMS are known to form in anaerobically digested biosolids (Higgins et al., 2006). Therefore, it is expected that VSC formation during serum bottle incubation can be explained by the dominant mechanisms in both freshwater sediments and anaerobically digested biosolids: cysteine and methionine degradation, sulfate reduction, and very limited H₂S and MT methylation (Lomans et al., 2002; Higgins et al., 2006).

Because they are formed and degraded by simultaneous processes, MT and DMS are typically maintained at low steady-state concentrations (Lomans et al., 2001). Since inhibition of methanogenesis interrupts conversion of MT and DMS to H₂S (Lomans et al., 1999, 2002; Higgins et al., 2006), methylotrophic methanogenesis has been suggested as a mechanism of MT and DMS degradation (Lomans et al., 1999, 2002; Higgins et al., 2006). In sulfate-rich freshwater sediment slurries, sulfate-reducing bacteria and methanogens are putative participants in a syntrophic relationship resulting in the degradation of MT and DMS (Lomans et al., 1999, 2002). Once anaerobic conditions prevailed during incubation of serum bottles, it is expected that reducing conditions and sulfide production resulted in a sulfate-poor environment, which minimized the activity of sulfate-reducing bacteria. Low levels of MT and DMS during incubation indicate that active demethylation was taking place. Because of the sensitivity of methanogens to inhibition, oxygen exposure during curing could have delayed methanogenic degradation of DMS and MT during incubation of serum bottles; resulting in the temporary peaks of MT and DMS during incubation.

Since the curing process was well-aerated, no VSCs were formed while aerobic conditions prevailed (during curing or during the initial hours in the serum bottles). Additionally, no VSC odors were observed while handling the material in the curing reactor.

Curing was shown to decrease H₂S, MT, and DMS, likely due to removal of the VSC precursors (oxidized sulfur and amino acids). Curing would promote biodegradation of cysteine and methionine and volatilization would reduce sulfur availability. During incubation (when anaerobic conditions predominated), removal of H₂S could be attributed to assimilation of sulfur for microbial growth.

Dimethyl disulfide (DMDS) was not detected during this investigation. Although the DMDS precursor MT was likely present during anaerobic digestion, VSCs transferred to the curing reactor with digestate would be likely to volatilize or oxidize quickly as a result of the frequent mixing and well-oxygenated conditions during curing. This would prevent abiotic oxidation of MT. Given that DMDS does not form under strictly anaerobic conditions (Hayward et al., 1977; Higgins et al., 2006), the absence of DMDS during prolonged (anaerobic) incubation of serum bottles was not surprising.

Results indicated that VSC reduction was the critical factor in determining curing duration. With sufficient curing duration to reduce the potential for VSC formation, the curing time was also sufficient to achieve stabilization of organics and eliminate phytotoxic compounds. Excellent agreement between the two trials conducted supported these conclusions. The incubation results indicated that, if anaerobic zones occur in a full-scale pile, VSC formation would be likely. However, it is possible that if VSCs were

produced during full-scale curing at levels reported herein, the dilution of volatilized VSCs with ambient air might render them undetectable. Cured digestate at the level of maturity reported herein is considered appropriate for use on orchards, pastures, as topsoil and for general gardening (Woods End Laboratory, 2004), or in agriculture, gardening, horticulture and nurseries (Compost Guidelines Task Group, 2005).

4.5. Conclusions

Routine analysis of samples from a laboratory-scale curing reactor suggests that stabilization of organics and elimination of phytotoxic compounds from anaerobic digestate preceded significant reduction of volatile sulfur compounds. Within 10-15 days of curing, stabilization of organics was achieved and phytotoxic levels of VFAs and ammonia were eliminated, whereas reduction of VSCs to low levels required 15-20 days of curing. Results suggest that incomplete curing and anaerobic conditions promote the formation of VSCs, whereas curing of sufficient duration will resist VSC formation, despite the onset of anaerobic conditions. Given that a full-scale curing process may be more prone to the development of anaerobic zones, results presented herein should be considered on a relative basis rather than as an absolute predictor of full-scale curing duration.

Acknowledgements

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APPENDIX: Data from all respirometer biodegradability studies

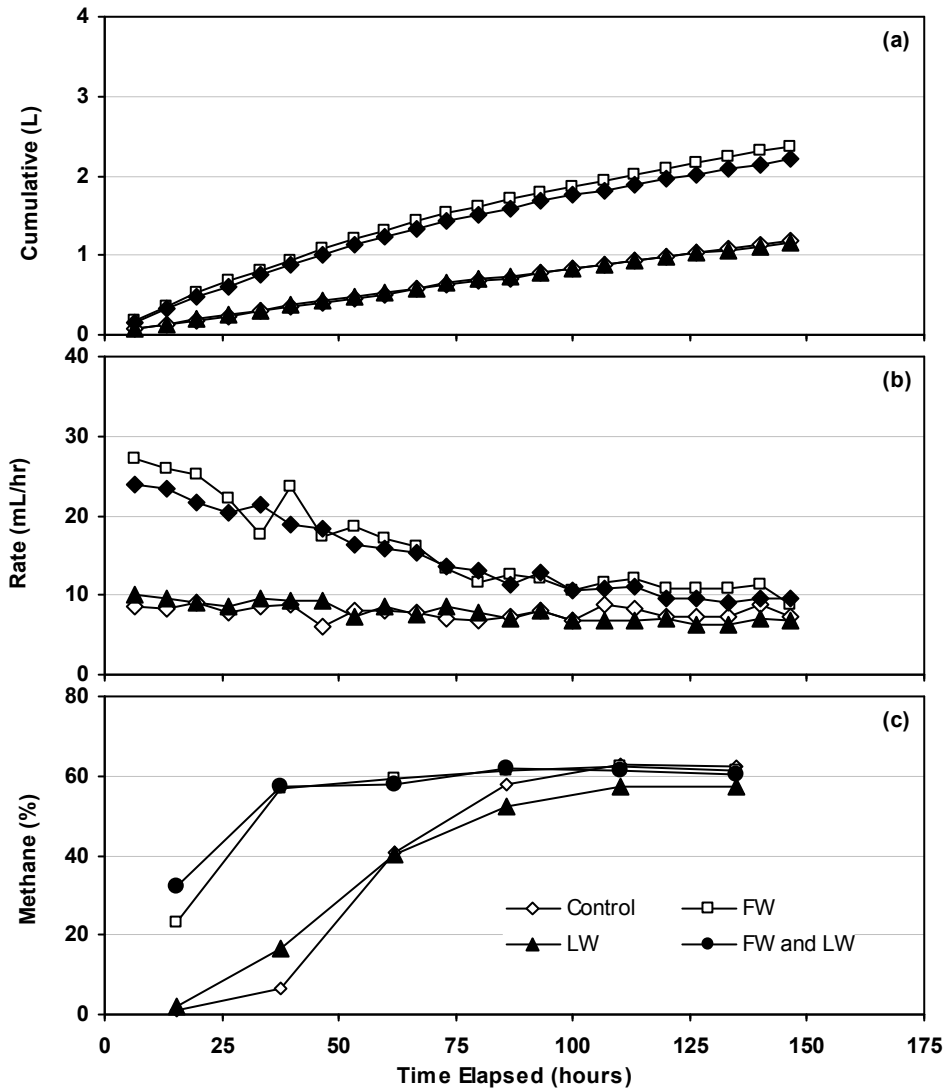


Figure A1. Biodegradability Trial 1. Cumulative biogas production (a) and rate of biogas production (b) were determined for an unfed control treatment, a treatment fed LW, a treatment fed FW, and a treatment fed both FW and LW. Methane content of biogas (c) was determined daily during the study.

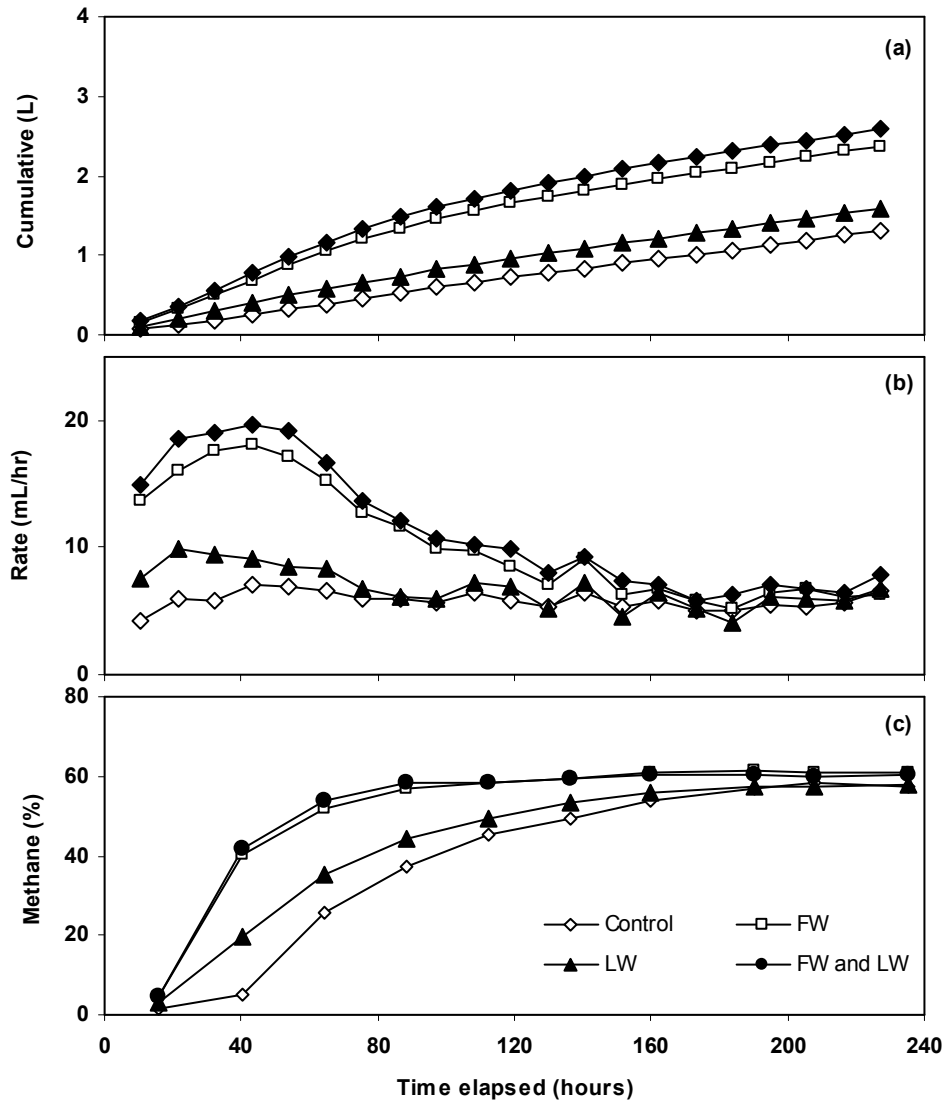


Figure A2. Biodegradability Trial 2. Cumulative biogas production (a) and rate of biogas production (b) were determined for an unfed control treatment, a treatment fed LW, a treatment fed FW, and a treatment fed both FW and LW. Methane content of biogas (c) was determined daily during the study.

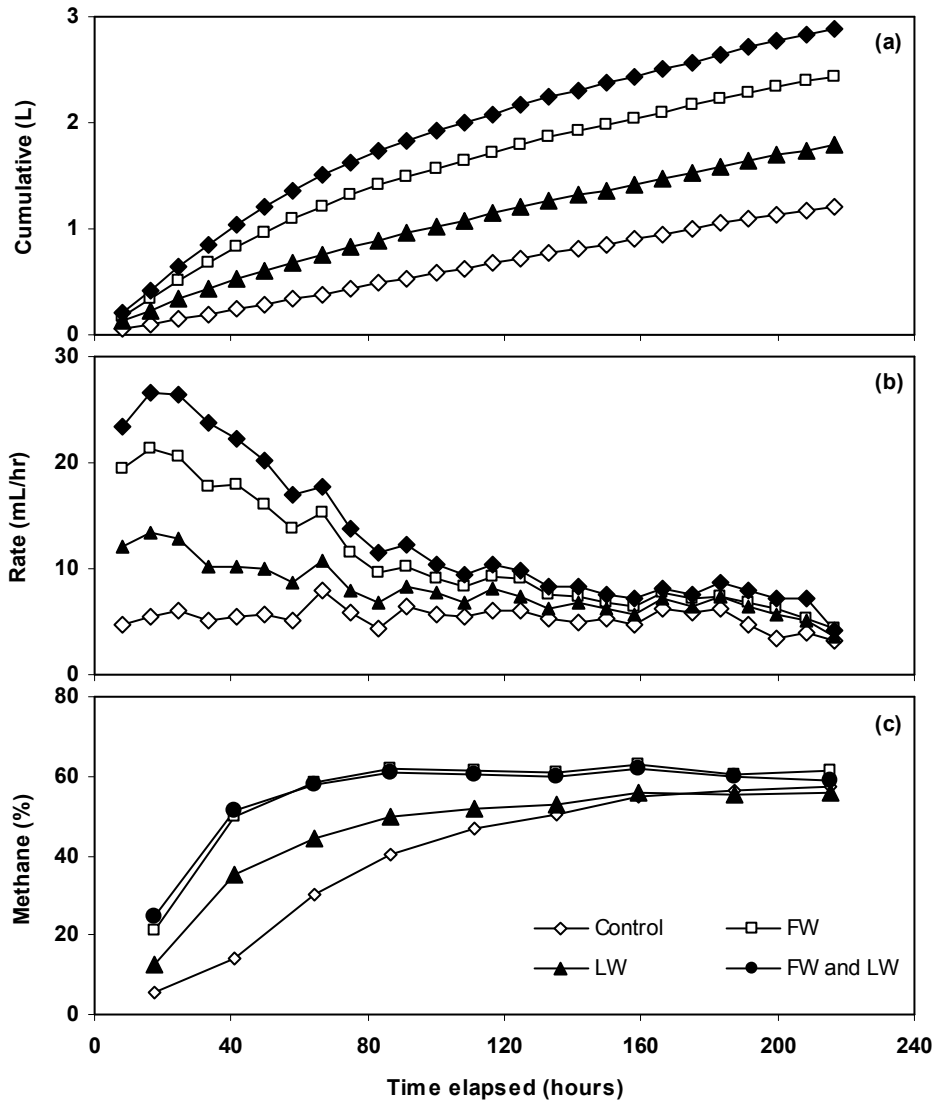


Figure A3. Biodegradability Trial 5. Cumulative biogas production (a) and rate of biogas production (b) were determined for an unfed control treatment, a treatment fed LW, a treatment fed FW, and a treatment fed both FW and LW. Methane content of biogas (c) was determined daily during the study.