DAIRY MANURE FLUSHWATER TREATMENT BY PACKED-BED ANAEROBIC
DIGESTERS

A Thesis
presented to
the Faculty of California Polytechnic State University,
San Luis Obispo

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Civil and Environmental Engineering

by
Neal Cary Adler
June 2013

© 2013

Neal Cary Adler

ALL RIGHTS RESERVED

COMMITTEE MEMBERSHIP

TITLE: DAIRY MANURE FLUSHWATER TREATMENT BY
PACKED-BED ANAEROBIC DIGESTERS

AUTHOR: Neal Cary Adler

DATE SUBMITTED: June, 2013

COMMITTEE CHAIR: Dr. Tryg Lundquist, Associate Professor
Civil & Environmental Engineering Department

COMMITTEE MEMBER: Dr. Yarrow Nelson, Professor
Civil & Environmental Engineering Department

COMMITTEE MEMBER: Dr. Sean Hurley, Assistant Professor
Agribusiness Department

ABSTRACT

DAIRY MANURE FLUSHWATER TREATMENT BY PACKED-BED ANAEROBIC DIGESTERS

Neal Cary Adler

Wastewater treatment performance of three pilot-scale packed-bed anaerobic digesters with walnut shell medium was researched for treating dairy freestall barn flushwater. Reciprocation mixing was evaluated as a means to lessen channelization in the media bed and to improve biogas production and organic matter removal at ambient temperatures. Reciprocation has been used in biological nitrogen removal systems to introduce air into the system to repeatedly oxygenate nitrifying biofilm along with mixing (Behrends et al. 2003), but the anaerobic systems benefit from mixing. Two tanks were used in each system, where one was full and one was empty at any given time. Water was repeatedly pumped from one tank to the other and back again (reciprocation). A key research objective was to determine the minimum reciprocation frequency (between 0-10 per day) while still maintaining moderate methane production and treatment performance. Broken walnut shells with a specific surface area of $360 \text{ m}^2/\text{m}^3$ were used as the packed media. Digester influent, which was pretreated to remove large solids, had the following characteristics: total solids (TS) of 5.5 g/L, volatile solids (VS) of 2.8 g/L, 5-day carbonaceous biochemical oxygen demand (cBOD₅) of 800 mg/L, and chemical oxygen demand (COD) of 4340 mg/L. Average digesting liquid temperatures ranged from 14.1 to 23.6 °C. At 6-day theoretical hydraulic residence times (V/Q where V is L_{liquid} , which

is volume of liquid occupying the digester pores, and Q is total daily influent flow) and 1 reciprocation per day, methane production was $0.060 \pm 0.10 \text{ L}_{\text{CH}_4}/\text{L}_{\text{liquid}}\text{-day}$ and at 10 reciprocations methane production $0.058 \pm 0.14 \text{ L}_{\text{CH}_4}/\text{L}_{\text{liquid}}\text{-day}$ (mean $\pm$ standard deviation of measurements over time). COD percent removals were both 51% at 6-day V/Q . Since multiple reciprocations did not appear to make a difference in methane production and treatment performance, fewer reciprocations were used in subsequent experiments. Higher flow rates were also used in subsequent experiments to accelerate sludge clogging and channelization in the walnut-shell bed and thereby allow detection of any advantage provided by reciprocation compared to an upflow reactor. At 0 and 1 reciprocations per day and 0.35 and 0.50-day V/Q s, respectively, methane production was 0.24 ± 0.08 and $0.23 \pm 0.08 \text{ L}_{\text{CH}_4}/\text{L}_{\text{liquid}}\text{-day}$ and COD percent removal was 17 and 22%. Over the study period of 226 days, walnut shell porosities decreased due to sludge accumulation from 0.68 and 0.64 (start-up or clean-bed) to 0.31 and 0.24 in the 1 and 0 reciprocation per day reactors. Sludge accumulation and channelization did not appear to be affected by reciprocation mixing on the scale of this study.

Keywords: packed-bed anaerobic digestion, walnut shell, reciprocation, channelization, dairy manure flushwater, COD removal, fixed-film, anaerobic filter

ACKNOWLEDGMENTS

I would like to thank:

My parents for encouraging me to pursue the master's program

Dr. Yarrow Nelson, Dr. Sean Hurley, Dr. Doug Williams, and Dr. John Benemann for
providing succinct and insightful guidance

Sean Thomson for being an instrumental and dedicated partner throughout this project

David Wendt from Nutrinut Inc., Visalia, CA for a generous donation of walnut shells

Nilay Patel from SKAPS Geonet, Commerce, GA for a generous donation of plastic
geonet for the underdrains

Cal Poly Dairy Management and Agricultural Operations: Boomer, Rich, and Kevin, for
providing us with space to research anaerobic digesters

Kyle, Jim, Seppi, Ian, Ruth, Nate G., Jason, Lortious, Janna, Nate O., Max, Andrew,
Adam, and Danny for their efforts out at the dairy and in the lab, and all of the students
who helped with water quality testing

Amy and Kay for their unwavering administrative support

Dr. Tryg Lundquist for providing me with practical guidance and for challenging me

Table of Contents

1	Introduction.....	1
2	Background.....	3
2.1	Study Objectives	7
3	Methods.....	9
3.1	Dairy Wastewater Process Configuration	9
3.2	Digester System Description.....	12
3.3	Reciprocation System.....	19
3.4	Starvation Experiment.....	21
3.5	Water Quality and Biogas Analyses	21
3.6	Water Sampling Methods.....	23
3.7	Tracer Study Methods	24
3.8	Temperature Monitoring	25
3.9	Treatment Performance and Water Quality Modeling.....	26
4	Results and Discussion	29
4.1	Flushwater Characteristics	29
4.1.1	Hourly Flushwater Variability	33
4.2	Comparisons among COD, cBOD ₅ , and VS	35
4.3	Effects of Reciprocation.....	37
4.3.1	Methane Production	37

4.3.1.1	Empty Tank Starvation Experiment	40
4.3.2	Treatment Performance.....	41
4.4	Hydraulic Characteristics	42
4.5	Water Quality Modeling.....	50
5	Conclusions.....	55
5.1	Characteristics of the Cal Poly Influent Dairy Manure Flushwater	55
5.2	Effect of Reciprocation Mixing	56
5.3	Characterize Reactor Hydraulics.....	58
5.4	CODR Model and First-Order COD Removal Parameter Value	59
5.5	Limitations of the Study	60
5.6	Future Research.....	61
6	References.....	62
7	Appendices.....	66
Appendix A	Detailed Methods	67
A.1.	Chemical Oxygen Demand (COD)	67
A.2.	Total and Volatile Solids (TS & VS)	67
A.3.	Total and Volatile Suspended Solids (TSS & VSS)	68
A.4.	Alkalinity & pH.....	68
A.5.	Total Ammonia Nitrogen (TAN)	69
A.6.	Tracer Study Procedure.....	69

Appendix B	Estimating C:N.....	74
Appendix C	Comparing Composite to Grab Samples.....	75
Appendix D	Linearly Interpolating between Porosity Measurements	76
Appendix E	Cal Poly Dairy Flushwater Treatment System Performance	78
Appendix F	Flushwater Theoretical Hydraulic Residence Time in Cal Poly West Storage Lagoon	85
Appendix G	Example Reciprocation and Influent Pump Schedule	86
Appendix H	Walnut Shell Sieved and Unsieved Dry Bulk Density	87

List of Tables

Table 3.1. Experimental plan for studying effects of reciprocation frequency.....	20
Table 3.2. Water quality and biogas analysis methods used in the present study and frequency.....	22
Table 4.1. Influent water quality summary.	31
Table 4.2. Average methane production from digesters with 0-10 reciprocations per day in low and high-flow studies.....	39
Table 4.3. Percent chemical oxygen demand removal (CODR) and carbonaceous biochemical oxygen demand removal (cBODR) for 0-10 reciprocations per day at low and high flows.	42
Table 4.4. Low- and medium-flow tracer study results and digester operating conditions on July 28, 2012.	46
Table 4.5. High-flow tracer study results and digester operating conditions on December 3, 2012.	47
Table 4.6. Average first-order COD removal reaction rate constants, k_{20} , calculated using (Eq. 3-6).....	54
Table E.1. Dairy Manure Flushwater Characteristics at Cal Poly Dairy.	83
Table E.2. Dairy Manure Flushwater Characteristics at Cal Poly Dairy.	84

List of Figures

Figure 3.1. Process diagram of the freestall barn flushwater system at the Cal Poly Dairy.	10
Figure 3.2. Plan view of flushwater process diagram.	11
Figure 3.3. Plan view of flushwater treatment area.	11
Figure 3.4. Diagram of packed-bed reciprocating anaerobic digester system.	14
Figure 3.5. Packed-bed anaerobic digesters at Cal Poly Dairy.	15
Figure 3.6. Effluent and gas manifold for packed-bed anaerobic digesters.	16
Figure 3.7. Plan view of the underdrain in each digester tank prior to walnut addition.	17
Figure 3.8. Surface of clean walnut shell media bed.	18
Figure 3.9. Influent pump screen box.	19
Figure 3.10. Autosampler for composite influent samples.	24
Figure 4.1. Influent cBOD ₅ concentration over a 12-hour period during May 3-4, 2012.	34
Figure 4.2. Influent solids concentrations over a 12-hour period during May 3-4, 2012.	34
Figure 4.3. Total and volatile solids grabbed from the influent weir box on August 31, 2011.	35
Figure 4.4. Total COD compared to cBOD ₅ for digester influent and effluent.	36
Figure 4.5. Total COD compared to VS for digester influent and effluent.	37
Figure 4.6. Starvation experiment.	41
Figure 4.7. July low-flow tracer study with 1 reciprocation per day.	47

Figure 4.8. July medium-flow tracer study with 1 reciprocation per day.	48
Figure 4.9. December high-flow tracer study with 1 reciprocation per day.	48
Figure 4.10. December high-flow tracer study with no reciprocation.	49
Figure 4.11. Sludge accumulation in walnut shells (left) and car tires (right).	50
Figure 4.12. Influent flow rates of the three packed-bed anaerobic digesters.	51
Figure 4.13. Influent and effluent COD concentrations for the three packed-bed anaerobic digesters.	51
Figure 4.14. Percent total COD removed (not temperature adjusted) over various OLRs.	52
Figure 4.15. Temperature corrected CODR ₂₀ compared to OLR.	53
Figure 4.16. First-order reaction rate constants, k_{20} , calculated using (Eq. 3-6) for COD removal from different V/Qs.	54
Figure A.1. Calibration curves made using DI water and Digester 3 effluent for diluting standards.	71
Figure E.1. Cal Poly Dairy manure flushwater treatment train.	79
Figure E.2. Sample Site 1: Flush Tank Effluent.	80
Figure E.3. Sample Site 2: Sand Trap Effluent.	81
Figure E.4. Sample Site 3: Screen Influent.	81
Figure E.5. Sample Site 4 and 5: Fine Solids Trap Influent and Effluent.	82

1 Introduction

Anaerobic processes are well-known for treating organic waste slurries and high-strength wastewaters while producing biogas rich in methane and carbon dioxide (McCarty 1964; Wilkie 2000). Anaerobic digestion reduces organic solids concentrations and odor potential, while retaining fertilizer nutrients (e.g., N, P, and K) in the effluent solids for subsequent land application (Wilkie 2000). Additionally, anaerobic treatment of animal farm wastewater can help inactivate a wide variety of pathogens, which can protect animal health at farms that clean barns with recirculated wastewater (Wilkie 2000).

California is the top milk producing state in the US (CDFA 2011). Contained anaerobic digestion of dairy manure is considered a major potential source of renewable biogas power and a means to mitigate manure emissions (Wilkie 2005). In California in 2010, dairy and beef cattle farms contributed 4.2% of gross GHG CO₂-equivalent emissions including 1.6% attributed to uncovered dairy manure anaerobic lagoons alone (Cal EPA 2013).

The development of dairy manure anaerobic digesters aligns with the goals of the California Energy Commission (CEC) and California Environmental Protection Agency (Cal EPA) to mature California's renewable energy portfolio and decrease greenhouse gas (GHG) emissions. In 2006, Assembly Bill 32 was enacted to reduce California's greenhouse gas emissions to 1990 levels by 2020 (Cal EPA 2006). Senate Bill X1-2, with similar goals as Assembly Bill 32, was signed by Governor Brown in 2011 with the intent to increase California's electricity generation from renewable energies to 33% by 2020 (CEC 2011).

While California dairies produced the equivalent of 3.9 million dry tons of manure in 2007 (CBC 2007), only 1% of that biomass was anaerobically digested for biogas capture (CEC 2012). Wide-scale implementation of anaerobic digesters on dairy farms has been stymied in California by air quality regulations and unattractive returns on investment (Germain & Katofsky 2006). Of the 1.77 million milking cows and heifers in California (CDFA 2011), 75% are housed dairies in the Sacramento and San Joaquin Valley regions. Those areas have been classified by the US EPA as “severe and extreme nonattainment” areas for ozone standards (Austin 2010). Ozone is attributed to a host of respiratory problems, especially in children (USEPA 2012), and since NO_x is an ozone precursor, the air pollution control districts have deemed it necessary to mandate strict regulations. The San Joaquin Air Pollution Control District and Sacramento Municipal Air Quality Management District have mandated that internal combustion engines and boilers emit less than 9 parts per million of NO_x (Austin 2010), which, for biogas, is difficult and costly with current technology (Krich et al. 2005).

To overcome these barriers, the CEC’s Bioenergy Action Plan encourages the research and deployment of new and emerging technologies that produce biogas from dairy manure (CEC 2012). Packed-bed anaerobic digestion is one promising technology that can decrease the capital cost hurdles for flushwater dairies. This technology is discussed further in the Background, below.

2 Background

The majority of dairy manure management systems in California use freestall barn flush systems (Beene et al. 2006; SJFAP 2005), where water is flushed through the barns to convey manure through rudimentary treatment processes and then into anaerobic storage lagoons.

Dairy manure is excreted at 10 to 12% solids, but after flushing, the manure is diluted to less than 2% solids (SJFAP 2005). After freestall flushwater exits the barns, a portion of coarse solids are typically removed by a settling basin and/or a sloped screen. Finally, flushwater flows into an anaerobic storage lagoon for long retention periods (> 30 days) where remaining particulate matter settles and undergoes some anaerobic treatment. This treatment entails microbial degradation of complex organic compounds into methane and carbon dioxide. The result of this process leaves a supernatant that can be recycled to flush freestalls and ultimately to irrigate and fertilize crops (Martin 2008).

Most anaerobic storage lagoons are uncovered, and methane and carbon dioxide emissions are released into the atmosphere. The few dairies that have anaerobic digesters cover their anaerobic lagoons with a plastic membrane and divert captured methane and carbon dioxide to an internal combustion engine to produce electricity. Seven covered lagoon digesters are operating at California dairies as of September 2012 (AgSTAR 2012). The main alternative to covered lagoon digesters is above-ground tank digesters, but these are not usually used for treating flushwater due to the large costly tanks need to treat the relatively dilute flushwater.

For dilute waste streams with volatile solids of less than one percent, anaerobic attached growth processes are considered preferable (McCarty 1964). For example, the most suitable technology for dairy manure flushwater treatment may be packed-bed anaerobic digesters (also referred to as fixed-film digesters or anaerobic filters), due to their smaller size and smaller subsequent capital costs (Liao & Lo 1985; Wilkie 2005). Packed-bed anaerobic digestion uses physical media for attached growth of bacteria, which allows for pumping dilute substrates at high flow rates without washing out slow-growing methane-producing bacteria. For this reason, biofilm systems are tolerant of hydraulic and organic overloading (Henze & Harremoës, 1983). Theoretical hydraulic residence times can be lower than three days (Wilkie 2003) while sustaining comparable performance to covered lagoons (Powers et al. 1997). This translates to smaller reactors, decreased land requirements, and possibly lower capital costs compared to conventional covered lagoons.

Conventional upflow and downflow packed-bed anaerobic digesters are commonly operated with effluent-to-influent recirculation for good mixing and to provide multiple opportunities for wastewater to contact biofilm (Lomas et al. 2000). Earlier studies suggest that recirculation flow rates of > four times that of influent can mimic the hydraulic conditions of completely-mixed anaerobic digesters (Samson 1990), but these high recirculation rates increase parasitic pump power consumption.

Two or three packed-bed anaerobic digesters are operating in the US (AgSTAR 2012). One of these digesters, a 380 m³ pilot system in Florida, uses vertical 75-mm diameter corrugated drainage pipes for support media (Wilkie 2000). These pipes are bundled together inside the reactor and permit waste water to flow unobstructed through the

reactor. Excess biofilm and sludge can slough off from the pipe walls and collect in the underdrain. While 75-mm vertical pipes are unlikely to clog with biomass, they are expensive and have a low specific surface area. Another pilot digester at Threemile Canyon Farms in Oregon uses waste car tires for attached growth treatment of higher solids dairy flushwater (26 g/L total solids) (Green 2009). Car tires provide nooks for sludge to accumulate and to produce biogas, and they provide wide channels which are unlikely to clog quickly. Other packed-medias used in anaerobic benchtop or pilot studies include assorted plastic media, gravel, clay tiles, and even oyster shells (Henze & Harremoës 1983). However, for more dilute wastes, media with higher specific surface area than tires would provide more surfaces for biofilm growth which may decrease start-up time and improve overall treatment performance. The third system apparently does not have any publicly available information.

The present thesis project developed and piloted a new packed-bed anaerobic treatment/digestion process meant to overcome the high cost of conventional bed media and provide more efficient mixing than the effluent recirculation of conventional packed-bed digesters. The design was novel for anaerobic treatment in two main ways: Broken walnut shells were used as the biofilm media, and mixing was accomplished by “reciprocation” pumping the digester liquid repeatedly between two sealed tanks of media, with no air exposure.

Broken walnut shells were explored as a packed media because they provide a high specific surface area, are inexpensive, and are easy to install in tanks. Walnut shells have been used as a low-cost disposable biofilm attachment media in biological air scrubbing research (Asadi et al. 2009; Zare 2012) and as a medium to promote coalescence of oil in

produced water treatment (Ahmedna et al. 2004; Srinivasan & Viraraghavan 2008), but apparently, broken walnut shells have not been used previously as a biofilm medium in wastewater treatment. However, ground walnut shells are used to wet blast paint and rust from the insides of vehicle engines and/or transmissions (Eco-Shell 2004). While

In reciprocation mixing, at least two tanks are used, where one is full and one is empty at any given time. Water is repeatedly pumped (reciprocated) between the two tanks.

Typically, fixed film digesters are run in an upflow configuration, but require frequent recirculation of effluent to influent for improved contact between organic matter and attached bacteria. With the higher specific surface area and lower pore sizes of walnut shells compared to the other media previously mentioned, constant upward flow may channelize through accumulated sludge causing flow short circuiting and poor performance (Brown et al. 1980). Reciprocation mixing may reduce channelization, because water is frequently pumped upwards and drawn downwards, potentially redistributing the sludge. Reciprocation mixing has been used in aerobic systems for mixing, but more importantly to draw air into the reactor to oxygenate nitrifying biofilm (Behrends et al. 2003, Kane 2010, Henemann 2010, Fooks in preparation), but anaerobic systems only benefit from mixing.

The current thesis project tested, at pilot-scale, the new packed-bed digester design described above (and in detail in the Methods chapter). The Study Objectives are outlined in the following section.

2.1 Study Objectives

The packed-bed digestion study began with many basic questions relating to the anaerobic digestion of dairy freestall barn flushwater with reciprocation mixing and walnut shell media. These questions include:

1. Does reciprocation mixing improve methane production, treatment performance, or reduce sludge accumulation and channelization compared to an upflow reactor?
2. Are walnut shells appropriate media for packed-bed anaerobic digestion of dairy manure flushwater?
3. Does COD percent removal linearly correlate with organic loading rate?
4. Is temperature the other main factor affecting the linear correlation of COD percent removal and organic loading rate?

These questions were addressed through the following study objectives:

1. Quantify water quality characteristics of influent dairy manure flushwater at Cal Poly Dairy
2. Study reciprocation mixing at 0-10 reciprocations per day for effects on
 - A. Methane production
 - B. Organic matter percent removal in terms of chemical oxygen demand (COD) and carbonaceous biochemical oxygen demand (cBOD₅)
 - C. Difference in sludge accumulation and sludge channelization in walnut shell bed
3. Quantify degree of short circuiting and channelizing in walnut shell bed at different flow rates and sludge accumulation

4. Develop COD percent removal correlation based on organic loading rate and determine first-order COD removal parameters
5. Evaluate walnut shells for packed-media digestion based on degree of short-circuiting and sludge accumulation

The fulfillment of these objectives is discussed in the Conclusions section. In the next chapter, the Cal Poly Dairy, packed-bed digester configuration, and the methods of research are described. Further topics will be discussed in the companion thesis (Thomson, in progress), which include an economic analysis of packed bed digesters compared to covered lagoons, methane production and loading rate correlations,

3 Methods

Three packed-bed anaerobic digesters were built and studied for 226 days at the Cal Poly San Luis Obispo Dairy (lat. 35°18'25N, long. 120°40'30W). The procedures for operation, experimentation, and data analysis are described in this section.

3.1 Dairy Wastewater Process Configuration

During this study, the Cal Poly Dairy housed an average of 211 milking cows in freestall barns and dry lots. Of the adult cows, 101 were Holsteins and 110 were Jerseys. The Cal Poly Dairy also housed an average of 89 heifers and 109 calves less than 12 months old. The equivalent number of animal units (AUs) at the dairy was estimated to be 414 AUs, where one AU = 453.6 kg (1000 lbs) of live animal weight (NRCS 2008). Only the fraction of manure that is excreted in the freestalls is cleaned by flushwater. The portion that is excreted in the dry lots or pastures was not treated in this study.

The freestalls were typically flushed twice per day, manually triggered in the early morning and afternoon. The flushwater was manure lagoon water stored in a tank at the upstream end of the freestall barns. This recycled flow was supplemented with clean water used in cleaning the milking parlor and nursing barn. An estimated 340 m³/d passes through the manure treatment system, of which 95 m³/d was freshwater used to flush the milking parlor and nursing barn (R. Silacci, pers. com.). Flushwater flowed out of the freestall lanes and then passed through (1) a ~3-m³ sand trap, (2) an agitation/pumping pit, (3) a sloped screen with wedge wire with 1-mm gaps, (4) a ~5-m³ secondary settling basin, (5) a 3.4-m³ concrete weir box that overflowed or was pumped into (6) the west storage lagoon (**Figure 3.1; Figure 3.2; Figure 3.3**). The west lagoon has a surface area of 8100 m² and a depth of ≤ 2.3 m, and has an estimated flushwater

theoretical hydraulic residence time of ≤ 42 days (**Appendix F**). The water from each flush took roughly an hour to entirely reach the lagoon. An east lagoon was not used by the dairy during this project.

Figure 3.1. Process diagram of the freestall barn flushwater system at the Cal Poly Dairy. Freestall barn flushwater passed through two settling basins and a sloped screen prior to discharge into an anaerobic lagoon. In the pilot digester system, pumps delivered pretreated flushwater into three pilot packed-bed anaerobic digesters. Not pictured are the milking parlor and nursing barn, which are flushed with freshwater. Also not shown is the agitator/pumping pit prior to the screen. Flushwater also passed through window screen of with 1.5-mm openings which protected the digester influent pumps.

Figure 3.2. Plan view of flushwater process diagram. Green lines are storage lagoon effluent and orange lines are flushwater with fresh manure from freestall barns or milking parlor.

Figure 3.3. Plan view of flushwater treatment area. After recirculated lagoon water flushed through the freestall barns, it settled in a sand trap, mixed in an agitation pit, passed through a 1.0-mm mesh sloped screen, settled again in a secondary settling basin, and outflowed into the storage lagoon. See **Figure E.2 - Figure E.5** for more pictures of the flushwater system.

3.2 Digester System Description

Three identical reciprocating digester systems were installed adjacent to the full-scale flushwater treatment system at the Cal Poly Dairy. The novelty and potential utility of the reciprocating design is described in the Background chapter.

Each digester comprised two 1140-liter vertical storage tanks (HDPE, Chemtainer 3581, inner diameter 87 cm, total height 206 cm), which received reciprocating flows of digester liquid. Only one tank (Feed Tank) received influent and discharged effluent. The other tank remained empty until a reciprocation cycle began (**Figure 3.4**).

Both tanks were fitted with external standpipes (schedule 40 PVC, 15.4-cm inner diameter) large enough to fit sump pumps which reciprocate liquid from one tank to the other. The sump pumps used for reciprocation and for influent were 80-W (Little Giant #566612) direct-drive pumps. All pumps were timer-operated, and the digester systems received influent in their standpipes in ten pulses evenly spread throughout the day (see **Appendix G** for example pump schedule). In response to influent flow, effluent was discharged in pulses by overflowing through a 5.1-cm diameter PVC bulkhead and water trap. Each tank was insulated with 5.0-cm thick reflective foam boards to minimize digester temperature fluctuations.

The tanks were gas-sealed by replacing the manufacturer's coarsely threaded lid and ring assembly with HDPE discs that were plastic-welded directly to the tank. The discs were 3.2-mm thick and 47 cm in diameter. In each system, the Feed and Reservoir Tanks' gas ports were connected with a 3.8-cm diameter flexible PVC tube. During reciprocation,

this connection enabled biogas to transfer back into the draining tank as it was pushed out of the filling tank.

Each tank had an underdrain with a septic tank leach field chamber and random-packed 100-mm long pieces of 50-mm diameter PVC pipe on either side (**Figure 3.7**). A geonet with 9.5-mm openings was used to support and separate the walnut shell media from the underdrain.

Figure 3.4. Diagram of packed-bed reciprocating anaerobic digester system. Each system had two tanks: a Feed Tank and a Reservoir Tank. At any given time one tank was filled with liquid. Influent entered and left through the Feed Tank. The Reservoir Tank filled and emptied during the reciprocation cycle. See **Figure 3.6** for the effluent pipe configuration and biogas manifold. The water levels in the sumps were higher than in the tanks because the tank headspaces were under pressure, as controlled by the water depth of the tipping gas meter.

Figure 3.5. Packed-bed anaerobic digesters at Cal Poly Dairy. Effluent discharge into the secondary settling basin. Effluent and biogas manifold are detailed below (**Figure 3.6**).

Figure 3.6. Effluent and gas manifold for packed-bed anaerobic digesters. Effluent (orange) flowed through a water trap to prevent biogas from escaping and discharged into the secondary settling basin. Biogas (green) from the Reservoir Tank (far left) and Feed Tank (left) were combined and flowed to the gas meter. During reciprocation, displaced biogas flowed from the filling tank to the draining tank. A flexible pressure buffer reservoir (car tire inner tube) was installed in the biogas manifold which fills and depresses during influent-effluent cycles. A monometer was also installed into the biogas manifold to monitor pressure. Between 0-140 mm water pressure in biogas was typical.

Figure 3.7. Plan view of the underdrain in each digester tank prior to walnut addition. Along the center was the black septic tank leach field chamber and to its sides were randomly packed 100-mm sections of 50-mm PVC pipe. On top of the underdrain a layer of geonet with openings of 9.5 mm was laid to prevent walnut shell migration into the underdrain.

Above the underdrain, each tank was filled 132 cm high with broken walnut shells for bacterial biofilm growth and sludge retention. English walnut shells (*Juglans regia* sp.) were donated from Nutrinut Inc. in Visalia, Calif. The shells were manually sieved to remove pieces that pass through a 13-mm square screen in order to have larger pore spaces and reduce the clogging rate in the digesters. From a sieve analysis, the discarded fraction of walnut shells constituted 30% of the original shell mass. However, the dry bulk density only changed from 0.238 to 0.245 kg/L after sieving (**Appendix H**). The specific surface area of sieved shells was measured as 360 m²/m³ by wrapping shells with aluminum foil of a known weight per area and weighing the wrappings after (Marsh 1970). After adding sieved shells to each tank (**Figure 3.8**), the walnut shell depth was 1.3 m.

Figure 3.8. Surface of clean walnut shell media bed. The 75-mm pipe in center is a core sampling tube used to monitor walnut shells before and after digestion (discussed in Thomson, in progress).

The digester influent pumps were submerged in the weir box (**Figure 3.1; Figure 3.3**).

Removing coarse solids prior to pumping flushwater into packed-bed digesters reduces clogging issues and impairment of biofilm activity (Wilkie 2000), so the pumps were inside a pump screen box wrapped with two layers plastic window screen with 1.5-mm openings. Accumulated sludge was removed from the pump box while it was submerged by opening a wooden trap door daily. For about five minutes each week, the pump screen box was pulled out of the weir box for rinsing to remove accumulated sludge in between window screen layers (**Figure 3.9**).

Figure 3.9. Influent pump screen box. Three sump pumps were housed in this pump screen box. The box is wrapped with two layers of window screen of 1.5 mm square openings. The box features a wooden trap door that was opened daily to remove accumulated sludge while still submerged. The pump screen box is unsubmerged in this picture for weekly rinsing to remove accumulated sludge in between window screen layers. The tank in this picture is referred to as the weir box.

3.3 Reciprocation System

Reciprocation was used in this study to mix the substrate wastewater, renewing contact between the water and the biofilms, and in an attempt to prevent the channelization of sludge in the walnut shell bed. Liquid was reciprocated from one tank into the other and then back again after a seven-minute resting period. The entire cycle is referred to as a reciprocation, where a single reciprocation refers to the transfer out of and back into the Feed Tank, which typically takes 137 minutes. The sump pumps were plugged into programmable timers which facilitated the changing of reciprocation frequency between 0-10 per day. The reciprocation pump flow rate was not changed over any experiments.

Two experiments were performed on various reciprocation rates (**Table 3.1**). During the first reciprocation experiment during June-July, 2012, the digesters were operated at 1, 5, and 10 reciprocations per day. In the second experiment, during November-December, 2012, the digesters were operated at 1 and 0 reciprocations per day.

Table 3.1. Experimental plan for studying effects of reciprocation frequency. The primary goals of these brief studies were to determine the optimal reciprocation frequency for methane production and treatment performance.

Date Range	Nominal $V/Q^{\dagger}$ (days)	Reciprocation Frequency (d^{-1})		
		Digester 1	Digester 2	Digester 3
June 25 – July 16, 2012	6	5	10	1
Nov. 2 – Dec. 10, 2012	0.25, 0.50, 0.35*	1	1	0

*Digester 3 V/Q was 0.35 days. While the flow rates for Digester 2 and 3 were equal, the Digester 3 liquid volume decreased after removing the Reservoir Tank from the system to run in upflow configuration.

$^{\dagger}V$ is L_{liquid} and Q is total daily influent flow.

To set up Digester 3 (D3) for upflow configuration, the Reservoir Tank was disconnected from the system at its biogas manifold, and the reciprocation pumps from both D3 tanks were removed. Any biogas produced by the residual sludge in the Reservoir Tank during this time was vented and not recorded by the gas meter. The biogas production by the Reservoir Tank was likely minimal based on a starvation experiment to be described below and in the Results and Discussion chapter.

The remaining liquid volume in the D3 upflow system was 882 liters, while the D2 reciprocating system liquid volume was 1090 liters. The reduction in volume in the upflow system is due to the 265 liters of non-pumpable liquid in the underdrain of the

disconnected Reservoir Tank. The reduction in liquid volume in the upflow system also meant that either influent flow rates or V/Q could be set equal to the reciprocating system, but not both. Influent flow rate was chosen to be kept equal in these two systems instead of V/Q because each system then could potentially treat the same mass of influent organic matter daily.

3.4 Starvation Experiment

To quantify the fraction of methane generated from residual sludge in the walnut shells and underdrains compared to total methane production, all systems were starved from September 5 – 13, 2012 in two brief experiments. The first experiment, from September 5, 1:10 PM – September 10, 10:32 AM, liquid was kept in the Reservoir Tank and the gas meters measured gas from Feed Tank only, while the Reservoir Tank's biogas pipe was disconnected from the system and was vented to the atmosphere after bubbling through water. The first day of biogas production during starvation of the Feed Tank was ignored, because the biofilm was likely still converting fresh organic matter from the last time it was wetted with liquid. In the second experiment, liquid was pumped back into the Feed Tank, and the gas meters were connected to the Reservoir Tank, while Feed Tank was vented to atmosphere after bubbling through water.

3.5 Water Quality and Biogas Analyses

Most water quality analyses were performed weekly, while biogas production and temperatures were monitored continuously using electronic data loggers (**Table 3.2**).

Table 3.2. Water quality and biogas analysis methods used in the present study and frequency. Method numbers refer to *Standard Methods for Examination of Water and Wastewater* (APHA, 2006). Further detailed methods are in **Appendix A**.

Constituent	Frequency Measured	Materials and Analysis Method
Alkalinity & pH	3-7 times per week	Acid Titration (APHA 2320 B)
Total Ammonia Nitrogen	Weekly	Orion 9512 Ammonia Selective Electrode, (APHA 4500-NH ₃ D)
Carbonaceous Biochemical Oxygen Demand	Weekly	5-day, 20 °C (APHA 5210 B)
Chemical Oxygen Demand	Weekly	CHEMetrics 0-1500 ppm USEPA Approved Vials, two hour digestion at 150 °C (CHEMetrics method; APHA 5220 D)
Solids (TS, TSS, VS, & VSS)	Weekly	Fisherbrand Glass Fiber G4 Filters for TSS/VSS, (APHA 2540 B, D, E)
Water and Gas Temperature	Continuously	Temperature sensors and electronic Onset brand data logger
Biogas Production	Continuously	Tipping meters and electronic Onset data logger
Biogas Composition	Weekly	SRI 8610 gas chromatograph with TCD and 1.8-m packed inner and outer column

Alkalinity, pH, and total ammonia nitrogen (TAN) were measured throughout the study to monitor digester health, while oxygen demand, solids, biogas production and composition were monitored to evaluate performance. No alkalinity addition was needed during any of the experiments.

Volumetric biogas production was measured using tipping gas meters linked to electronic data loggers. Tipping chamber volume was measured by slowly injecting air into the chamber with a 140-mL syringe. Higher gas flow rates decreased recovery by the tipping

meters, so each tipping meter was calibrated with a dry calibration meter (DryCal[®] DC-2) in the lab over a range of different flow rates that fully bracket the operating flow rates. To further test the accuracy of calibrated tipping meters in the field, a tipping meter was linked in series with a wet test meter (Precision Scientific) to simultaneously measure digester biogas production over two days. The wet test meter measured 8.7% more biogas volume than the tipping meter, so a correction factor of 8.7% was applied to all biogas production results.

3.6 Water Sampling Methods

Water samples were taken each week to assess treatment performance in each of the three digesters. Influent water quality varied throughout the day, so 24-hour influent composite samples were taken using a Hach Sigma 900 Max autosampler (**Figure 3.10**). Grab samples were taken from the effluent of each digester on Fridays during the 8:32 AM effluent pulse. Another composite sample was taken from the effluent from a random digester each week for comparison between composite and grab effluent samples, but grab samples are used for analysis in this thesis (see **Appendix C** for comparison of grab to composite). The samplers collected ten 195-mL samples in synchronization with programmed influent pumping periods, with the last one being the 8:32 AM influent/effluent on Friday. Ice was put in the autosampler each week to keep the samples at an average of 7 °C.

Figure 3.10. Autosampler for composite influent samples. Each week, the autosampler collected ten samples from inside the digester influent pump screen box in synchronization with influent pump cycles.

3.7 Tracer Study Methods

Tracer studies were conducted to characterize hydraulic conditions at different theoretical hydraulic residence times (V/Q_s), reciprocation frequencies, and porosities. The hydraulic conditions are described in terms of mean hydraulic residence time (MHRT) and the degree of short circuiting, quantified as MHRT-to- V/Q ratios. These conditions can have a strong effect on treatment performance and, in turn, methane production. Moreover, it was expected that as sludge accumulated over time in the walnut shells, the extent of short circuiting would increase.

Rhodamine WT dye was used as the tracer because it is fluorescent in a spectrum different than common materials found in wastewaters (USGS 1986). The dye was poured into the feed tank influent standpipe, and effluent fluorescence samples were taken by manually grabbing samples initially and then later by using a 24-bottle autosampler. Samples were transported to the laboratory and stabilized at room temperature (~21 °C) for up to three hours, prior to measuring fluorescence using a benchtop fluorometer (Turner Designs Model 7200, Trilogy Module Model 42). Dye concentration standards were used to convert laboratory fluorometer readings to concentrations. The standards were prepared following procedures outlined in Turner Designs (1995) including that baseline fluorescence be accounted for by using digester effluent as the dilution water used in preparation of the standards. Detailed preparation for the tracer study is described in **Appendix A**.

3.8 Temperature Monitoring

Internal digester temperature was monitored using temperature sensors (Onset Computer Corporation, Model TMC50-HD), one of which was threaded through the effluent port (**Figure 3.4**) just below the water surface into the center of the tank, and another was placed in the influent pump box, next to the pump intakes. The probes were composed of thermistors encapsulated in stainless steel (grade 316) to prevent corrosion from hydrogen sulfide.

A data logger (Onset Computer Corporation, HOBO U12 4-External Channel) recorded temperatures from the four probes in two-minute intervals. Probes recorded water temperature when the Feed Tank was full, or they recorded biogas temperature when the Feed Tank water level was below the effluent port. The headspace had larger

temperature variations throughout each day than the water. The headspace variation was observed earlier in the study, when the systems were reciprocating 10 times per day. However, during the portion of the study with one or no reciprocations per day, the temperature probes were submerged in water for 21.8 or 24 hours per day, respectively. , To adjust biogas production measurements to 20 °C using the ideal gas law, measurements from the temperature probe were all assumed to be from the headspace. This yielded negligible error because the average of maximum and minimum daily headspace temperatures were within 0.4 °C of average daily probe readings.

Daily mean ambient temperatures were downloaded from California Irrigation Management Information System (CIMIS). Weather station #52 was the closest to the Cal Poly Dairy (lat. 35°18'22"N, long. 120°39'37"W; 1.3 km east from the digesters).

3.9 Treatment Performance and Water Quality Modeling

Calculations for evaluating treatment performance are outlined in this section. Organic loading rate (OLR) is the application rate of organic matter normalized by digester volume. OLR was calculated as:

$$OLR = \left(\frac{COD_{fed} Q}{V} \right) \times \left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) \quad (\text{Eq. 3-1})$$

where

OLR = organic loading rate, g_{COD fed}/L_{liquid}-day

COD_{fed} = chemical oxygen demand concentration of influent, mg/L

Q = influent flow rate, L/day

V = liquid volume in the pore spaces of the reactor, L

COD removal was calculated as follows:

$$CODR = \left(1 - \frac{COD_{eff}}{COD_{fed}} \right) \times 100\% \quad (\text{Eq. 3-2})$$

where

$CODR$ = percent chemical oxygen demand removed, %

COD_{eff} = chemical oxygen demand concentration of effluent, mg/L

A first-order steady-state plug flow reactor (PFR) equation for effluent COD is below.

PFR was not the most appropriate model for this type of reactor, but for the scope of this study it was helpful to use a simpler model. The first-order completely mixed flow reactor (CMFR) equation was also evaluated but it failed to decrease variability of results.

$$COD_{eff} = COD_{fed} e^{-k_T(V/Q)} \quad (\text{Eq. 3-3})$$

where

k_T = rate constant for temperature, T , in d^{-1}

This equation can be modified to include temperature using an Arrhenius-type temperature adjustment equation (**Eq. 3-4**) (Eq. 3.81 in Sawyer et al., 2003)

$$k_T = k_{20} A^{T-20\text{ }^{\circ}\text{C}} \quad (\text{Eq. 3-4})$$

where

A = Arrhenius-like constant for temperature correction

T = system liquid temperature, C

and rearranging (**Eq. 3-3**) for k_T (**Eq. 3-5**)

$$k_T = - \frac{\ln \left(\frac{COD_{eff}}{COD_{fed}} \right) Q}{V} \quad (\text{Eq. 3-5})$$

setting equal to (Eq. 3-4) and rearranging for k_{20}

$$k_{20} = \frac{-\ln\left(\frac{COD_{eff}}{COD_{fed}}\right) Q}{V A^{(T-20^{\circ}C)}} \quad (\text{Eq. 3-6})$$

An equation for CODR adjusted to 20 °C ($CODR_{20}$) can be found by combining (Eq. 3-2) with (Eq. 3-5):

$$CODR_{20} = (1 - e^{-k_{20}V/Q}) \times 100\% \quad (\text{Eq. 3-7})$$

where

$CODR_{20}$ = chemical oxygen demand removed, temperature adjusted to 20 °C, %

V/Q is used for design in this thesis, as opposed to solids retention time (SRT). In completely mixed anaerobic digesters, V/Q is almost the same as SRT, which is another operating condition that is directly proportional to the degree of organic matter conversion (Henze & Harremoës 1983). However, in packed-bed anaerobic digesters, SRT can be much longer than V/Q because biofilm grows and sludge accumulates on the media (Henze & Harremoës 1983). Since different media types will have different sludge accumulation rates, SRT will grow with time at different rates among different packed-media systems. For this reason, V/Q is more commonly used for packed media systems to predict treatment performance (Henze & Harremoës 1983) so SRT was not determined.

4 Results and Discussion

The results of this study are described in five main sections as follows:

1. Flushwater characteristics compared with other dairies
2. Comparison of organic matter concentration ratios in influent and effluent of the digesters
3. The effects of reciprocations
4. Reactor hydraulic properties
5. Treatment efficiencies at different loading rates and first-order COD removal rates

4.1 Flushwater Characteristics

At the Cal Poly Dairy, after passing through a sloped screen and settling tank, average total solids (TS) and volatile solids (VS) flushwater concentrations were 5.5 ± 1.8 and 2.8 ± 1.0 g/L (mean $\pm$ standard deviation of samples collected over time; **Table 4.1**), whereas TS and VS at the University of Florida Dairy (UFD; 359 milking cows) were lower at 3.6 ± 0.4 and 2.2 ± 0.3 g/L, respectively (Wilkie et al. 2004). However, at a full-scale covered lagoon at the Castelanelli Brothers Dairy (1500 milking cows, 4060 AUs including dry cows and heifers), TS and VS were 12 and 6.2 g/L, respectively, which are more than double that of observed at the Cal Poly Dairy flushwater in this study (Martin 2008).

Differing solids concentrations among dairies are likely related to the number of cows living in freestalls and total area of freestalls that are flushed. To estimate flushwater usage for different dairies, dairy cattle headcounts were converted into animal units

(AUs) using average weights for calves, heifers, and adult cows (NRCS 2008). One AU is equivalent to 1000 lbs (453.6 kg) of live animal weight. For total flushwater (recirculation water from lagoon + freshwater water for flushing milking parlor), the Cal Poly Dairy uses $0.82 \text{ m}^3/\text{AU-d}$, and the UFD uses $1.08 \text{ m}^3/\text{AU-d}$ (Wilkie et al. 2004), whereas the full-scale Castelanelli Brothers Dairy uses $0.60 \text{ m}^3/\text{AU-d}$ (Martin, 2008). Castelanelli may store milking cows more densely in the freestall barns than at Cal Poly and UFD.

Cal Poly Dairy flushwater also contained between 2.61 – 6.46 mg/L-N of nitrate. Nitrate could be converted from ammonia via nitrification in the storage lagoon due to the aerator, and also due to aeration during flushing. Lower nitrate concentrations are desirable for anaerobic digestion substrates because nitrate is a better electron acceptor than sulfate, and so with higher influent nitrate concentrations methane yields may decrease proportionally (Banihani et al. 2009).

Table 4.1. Influent water quality summary. All constituents, aside from settleable solids and temperature, were measured from 24-hour composite samples.

Influent Constituent*	Units	Average or Range	Standard Deviation
TS	g/L	5.5	1.8
VS	g/L	2.8	1.0
NVS	g/L	2.7	0.9
TSS	g/L	3.1	1.3
VSS	g/L	1.8	0.9
24h Settleable Solids [†]	mL/L	9.5 - 80	N/A
cBOD ₅	mg/L	800	190
COD	mg/L	4340	1520
cBOD ₅ /COD ^{††}	-	0.114	---
Alkalinity	mg/L-CaCO ₃	1610	630
pH	-	7.79	0.29
Temperature	°C	20.0	3.2
TAN	mg/L-N	144	61
Nitrate	mg/L-n	2.61 - 6.46	N/A

*TS = Total Solids; VS = Volatile Solids; NVS = Non-Volatile Solids (or Fixed Solids); TSS = Total Suspended Solids; VSS = Volatile Suspended Solids; cBOD₅ = 5-day carbonaceous Biochemical Oxygen Demand; COD = Total Chemical Oxygen Demand; TAN = Total Ammonia Nitrogen

[†]Two samples for settleable solids were collected from the weir box from which digester influent was pumped: one during a flush (80 mL/L), and one between flushes when the water was stagnant and solids had settled (9.5 mL/L).

^{††}cBOD₅/COD ratio was estimated from plotting influent COD with cBOD₅ and finding the slope of the linear correlation (**Figure 4.4**).

Digester influent was estimated to have a C:N ratio of 5.6:1 (**Appendix B**), much lower than the ratio of 25:1 suggested for maximum gas production (Gerardi, 2003). The Cal Poly influent VS/TS ratio was 51%, which more closely matched Castelanelli (52%). UFD's VS/TS ratio was 61%. The cBOD₅/COD ratio at Cal Poly Dairy was 0.114 (slope of influent linear correlation in **Figure 4.4**). This ratio was much lower than easily treatable wastewater because it was more comparable to secondary effluent at a municipal wastewater treatment plant, which is difficult to further treat using bacteria

(Metcalf & Eddy, 2003). Moreover, the cBOD_5/COD was expected to be low because flushwater from the freestall barns was composed of a small amount of fresh manure with a large amount of recirculated lagoon effluent (see **Figure 3.1** for dairy unit process diagram), which had already been treated and stabilized for ≤ 42 days (**Appendix F**) in a storage lagoon.

Cal Poly Dairy alkalinity was 1610 ± 630 mg/L as CaCO_3 , which was slightly higher than at UFD (1270 ± 160 mg/L- CaCO_3 ; Wilkie et al. 2004). No alkalinity supplementation was provided at the Cal Poly or UFD anaerobic digesters. Alkalinity was not observed at Castelanelli Dairy (Martin 2008). The optimum alkalinity range is 1500 – 3000 mg/L- CaCO_3 for anaerobic digestion (Gerardi 2003). However, this range was established for high solids municipal wastewater sludge, and not for more dilute substrates, like dairy freestall barn flushwater. For instance, during operation of the digesters at the Cal Poly Dairy, influent alkalinity dropped as low as 500 mg/L as CaCO_3 , but COD percent removal did not change noticeably nor did effluent pH decrease below 7.0.

Influent total ammonia nitrogen (TAN) was 144 ± 61 mg/L-N at the Cal Poly Dairy (**Table 4.1**) and 840 ± 100 mg/L-N at Castelanelli Brothers Dairy. UFD did not report total ammonia nitrogen. TAN is the sum of ammonium ions (NH_4^+) and uncharged ammonia (NH_3). Ammonium ions are beneficial because they are the preferred nitrogen source for anaerobic bacteria (Gerardi 2003). However, uncharged ammonia can be toxic (Gerardi 2003). Increases in pH directly transform ionic ammonium into uncharged ammonia, so the toxicity of TAN is not only dependant on concentration, but on pH. For reference, at pH 7, the ratio of $\text{NH}_3:\text{NH}_4^+$ is about 1:200, and at pH 9.3, it is about 1:1. The average influent pH was 7.8 ± 0.3 at the Cal Poly Dairy, which is higher than the

ideal methanogen pH range of 6.8 – 7.2 (Gerardi 2003). At pH 7.8 and 7.9, respectively, most of the TAN at the Cal Poly and Castelanelli dairies was in the form of beneficial ammonium, but regardless of pH, their TAN concentrations are well below the inhibitory threshold of 1500 mg/L-N at $\text{pH} \geq 7$ (Gerardi 2003).

4.1.1 Hourly Flushwater Variability

Influent water quality not only varied over the course of the experiment, but varied hourly. Increases in concentrations were observed during the two daily barn flushes (**Figure 4.1, Figure 4.2**). This variability was assessed by collecting five influent samples over 12 hours. Sampling was synchronized with the digester influent pumping schedule, using an autosampler. Although the exact times of flush events are not known for this day, typical times for Cal Poly Dairy operators to trigger the flush cycle are highlighted in brown. Influent cBOD_5 and solids concentrations are lower between flush cycles (brown), and this type of variation was captured by the use of autosamplers during the routine sampling.

Figure 4.1. Influent cBOD₅ concentration over a 12-hour period during May 3-4, 2012. Samples were taken from the weir box (see **Figure 3.1**). The sag in cBOD₅ is attributed to settling of fresh manure in weir box between barn flushes.

Figure 4.2. Influent solids concentrations over a 12-hour period during May 3-4, 2012. Samples were taken from the weir box (**Figure 3.1**). The sag in concentration is attributed to settling of fresh manure in the weir box between flush cycles.

To better illustrate the rate of solids concentration decrease after a flush, influent TS and VS analyses were performed on samples manually taken over 90 minutes from the weir box (see **Figure 3.1** for flushwater process diagram), with minute-zero equaling the time that the flush ceased. Ten minutes after the flush cycle stopped, TS and VS dropped 11% and 12%, respectively (**Figure 4.3**). The digester influent system was programmed to

pump pulses of influent at ten evenly spaced times throughout the day, and so both unsettled and settled flushwater entered the digesters over the course of each day. This daily variation was captured in the 24-hour composite influent samples that were routinely collected to generate the data shown in this thesis.

Figure 4.3. Total and volatile solids grabbed from the influent weir box on August 31, 2011. Starting samples were taken when the flush stopped, and the rapid declines in concentration seen in the 5- and 10-minute samples indicate the settling of freshly flushed manure in the stagnant weir box. If the digester influent pumps turned on during the flush or up to ten minutes after, then the concentration of organic matter entering the digesters was higher than typical pump cycles. However, as stated previously, this variation was captured by routine composite sampling.

4.2 Comparisons among COD, cBOD₅, and VS

This thesis mostly uses COD percent removal for judging treatment performance, but cBOD₅ and VS are also useful measures of organic matter. To develop useful conversion ratios, COD was correlated with cBOD₅ (**Figure 4.4**) and VS (**Figure 4.5**). Influent and effluent ratios are separated into two correlations. Data from the whole study are used. Compared to COD, cBOD₅ and VS would be expected to contain a higher proportion of biodegradable organics, so that the effluent correlations would be expected to have

smaller slopes than influent concentrations. However, influent and effluent correlations for both graphs are close to parallel.

Figure 4.4. Total COD compared to cBOD₅ for digester influent and effluent. One influent data point (green triangle) was excluded from the correlation because it was a consequence of a change in dairy operation.

Figure 4.5. Total COD compared to VS for digester influent and effluent. One influent data point (green triangle) was excluded from the correlation because it was a consequence of a change in dairy operation.

4.3 Effects of Reciprocation

Two reciprocation experiments were conducted to find the minimum mixing-energy input from reciprocation while still maintaining moderate methane production and treatment performance. The first experiment investigated the effects of reciprocation at a low influent flow rate: a three-week study in June-July with 1, 5, and 10 reciprocations per day. The second experiment covered high flows with 1 and 0 reciprocations per day during a five-week study in November- December (see **Table 3.1** for detailed experimental plan). Methane production and then treatment performance from both experiments are discussed below.

4.3.1 Methane Production

Methane production (in $L_{CH_4}/L_{liquid}\text{-day}$, where L_{liquid} is volume of liquid occupying the digester pores) did not appear to differ among digesters operating at 1, 5, and 10

reciprocations per day (**Table 4.2**). This experiment was conducted between June 25 and July 15, 2012, and each digester was operated at a nominal theoretical hydraulic residence time (V/Q where V is L_{liquid} and Q is total daily influent flow) of 6 days. Mean liquid temperatures inside Digester 1 (D1), Digester 2 (D2), and Digester 3 (D3) were 21.4, 20.8, and 20.2 °C, respectively. Since this experiment was conducted soon after start-up, sludge and biofilm accumulation in the walnut shells were probably not as mature as in the later experiment. Estimated walnut-shell-bed porosities shortly after the conclusion of the experiment (July 15, 2012) for D1, D2, and D3 were 0.64, 0.68, and 0.64 (**Appendix D**, where Porosity = pore volume/total volume), respectively, while the estimated startup clean-bed porosity was 0.70.

Since multiple reciprocations did not appear to make a difference in methane production and treatment performance, fewer reciprocations were used in subsequent experiments.

In the second reciprocation experiment, with higher flow rates (November 1 through December 6, 2012), no differences in methane production were observed between D2 and D3 operating at 1 and 0 reciprocations per day, respectively (**Table 4.2**). Their hydraulic loading rates were 2390 and 2590 L/day, with resulting V/Q s of 0.50 and 0.35 days, respectively. While D1 operated at 0.25-day V/Q and 1 reciprocation per day, its methane production was inexplicably lower than D2 or D3. This high-flow experiment was meant to accelerate clogging and channelization in the walnut-shell bed and thereby allow detection of any advantage provided by reciprocation in preventing these problems. However, no differences in clogging or channelization were observed between the reciprocating and non-reciprocating system. Biogas production during this period had greater standard deviations from the mean (**Table 4.2**) than in June-July. This was

apparently due to temperature swings (D2 range = 16.0-19.9 °C where D1 and D3 temperatures were almost identical) and decreasing porosity due to sludge accumulation (D1, D2 and D3 Feed Tank porosities were measured as 0.28, 0.28, and 0.24 on December 10, 2012). Despite the variability, methane production rates did not appear to be different.

Table 4.2. Average methane production from digesters with 0-10 reciprocations per day in low and high-flow studies. Reciprocations did not appear to change methane production. Larger standard deviations in methane production in November-December than in June-July were attributed to decreasing temperatures and sludge accumulation in November-December. The daily mean temperature range from June 25 – July 15, 2012 was 14.3 – 18.8 °C and 8.8 – 23.7 °C from November 2 – December 9, 2012. SD is standard deviation of daily measurements over time.

Date Range	Reciprocations per day	Reactor	V/Q (days)	Temp. (°C)	OLR		Methane Production	Methane Yield
					OLR _{COD} (g _{COD} fed/ L _{liquid-day})	OLR _{cBOD} (g _{cBOD5} fed/ L _{liquid-day})	(L _{CH4} /L _{liquid-day} ± SD)	(L _{CH4} /g _{VS} fed ± SD)
June 25 – July 15, 2012	1	D3	6.1	20.2	0.88	0.13	0.060 ± 0.010	0.12 ± 0.016
	5	D1	6.2	21.4	0.87	0.13	0.066 ± 0.011	0.11 ± 0.025
	10	D2	6.3	20.8	0.86	0.13	0.058 ± 0.014	0.11 ± 0.015
Nov. 2 – Dec. 9, 2012	1	D1	0.25	16.0	18	3.6	0.18 ± 0.072	0.015 ± 0.005
	1	D2	0.50	16.0	8.9	1.8	0.23 ± 0.078	0.038 ± 0.010
	0	D3	0.35	16.0	13	2.6	0.24 ± 0.083	0.028 ± 0.009

While methane production was the primary biogas metric used in these experiments, methane yield was also calculated. Methane yield best describes the degree of conversion of fed organic matter into biogas, and it is generally expected that as V/Q decreases, yield decreases. While methane production in D2 and D3 was similar for the high-flow reciprocation experiment (**Table 4.2**), the methane yield was higher with reciprocation than without reciprocation (calculations shown in Thomson, in progress). D3 (no reciprocations) was only operating with one tank, so its liquid volume was 882

liters, however the influent flow rates were kept similar between D2 and D3. The higher yield in the reciprocating digester may have been due to gas produced in the Reservoir Tank where the walnut-shell bed was wetted once per day by digester liquid. Another effect could have been gas from the residual sludge in the second tank, discussed below.

4.3.1.1 Empty Tank Starvation Experiment

During the starvation experiment from September 5 - 13, 2012, residual sludge in the walnut shells and underdrains contributed between 16 - 24% in the Feed Tanks and 4.9 - 16% in Reservoir Tanks to daily methane production (**Figure 4.6**). Average daily methane production was estimated from August 18 – 24, 2012. Walnut shell porosities were measured on September 13 in D1, D2, and D3 were 0.61, 0.67, and 0.59, so 17, 26, and 14% of walnut shell pore spaces were occupied by sludge, respectively. As sludge accumulates, it would be expected that the proportion of daily biogas generated by sludge would increase.

Figure 4.6. Starvation experiment. Residual sludge in the walnut shells and underdrain contributed between 16 - 24% in the Feed Tanks and 4.9 - 16% in Reservoir Tanks to daily methane production. Average methane production from August 18 – 24, 2012 is shown for comparison.

4.3.2 Treatment Performance

The second indicator for observing the effects of reciprocation was treatment efficiency.

Chemical oxygen demand (COD) and carbonaceous biochemical oxygen demand ($cBOD_5$) were the main water quality constituents monitored in this study.

For the reciprocation experiment in June-July, COD percent removal (CODR) did not appear to differ among the three reciprocation rates (**Table 4.3**). CODR ranged from 51% to 48%. The $cBOD_5$ percent removal ($cBODR$) also did not appear to differ, with removals of 59% and 63% at 1 and 10 reciprocations per day, respectively. Although the $cBODR$ was 48% at 5 reciprocations per day, only one data point is available due to analytical quality control problems.

In the high-flow experiment with 1 and 0 reciprocations per day, both CODR and $cBODR$ were lower, apparently due to increased flow rates and/or lower temperatures

(Table 4.3). However, the 1 reciprocation per day digester appeared to have better removals than the 0 reciprocations per day digester. This difference was greatest with cBODR (63%), which was expected because a higher fraction of the cBOD₅ is biodegradable, compared with the total COD which incorporates a higher fraction of nonbiodegradable matter.

Table 4.3. Percent chemical oxygen demand removal (CODR) and carbonaceous biochemical oxygen demand removal (cBODR) for 0-10 reciprocations per day at low and high flows. The “n” is number of weekly CODR and cBODR measurements in the average. CODR and cBODR were calculated using (Eq. 3-2).

Reciprocations per day	Date Range	Reactor	V/Q (days)	Temp. (°C)	OLR _{COD}	OLR _{cBOD}	Removal Efficiency	
					(g _{COD fed} / L _{liquid-day})	(g _{cBOD5 fed} / L _{liquid-day})	CODR (%, n)	cBODR (%, n)
1	June 25 - July 15, 2012	D3	6.1	20.2	0.88	0.13	51, 3	59, 2
5		D1	6.2	21.4	0.87	0.13	48, 3	48, 1
10		D2	6.3	20.8	0.86	0.13	51, 3	63, 2
1	Nov. 2 - Dec. 7, 2012	D1	0.25	16.0	18	3.6	14, 6	18, 6
1		D2	0.50	16.0	8.9	1.8	22, 6	39, 6
0		D3	0.35	16.0	13	2.6	17, 6	24, 6

4.4 Hydraulic Characteristics

Biogas production and treatment efficiency may also be affected by hydraulic properties such as short circuiting. In the context of bacterial treatment reactors, short circuiting refers to a portion of influent bypassing the reactor much quicker than intended. By performing tracer studies, the degree of short circuiting can be observed and compared to operating conditions that affect short circuiting such as difference between influent and system temperature, degree of sludge accumulation in shells, and reciprocation.

Degree of short circuiting is characterized by the MHRT-to-V/Q ratio, where MHRT stands for mean hydraulic residence time, which is a more realistic estimate for residence time than V/Q (MWH 2005). MHRT values were based on estimation of time for 50% of mass of dye to exit the system (Kane, 2010). For a perfect tracer in an ideal plug flow reactor, MHRT is equal to V/Q (MWH 2005). Lower MHRT-to-V/Q ratios indicate higher degrees of short circuiting.

Four tracer studies were performed, two in July and two in December. In July, high short circuiting was observed with the 6-day V/Q digester, but low short circuiting was observed with the 1-day V/Q digester (**Table 4.4; Table 4.5**). In December, high short circuiting was observed in both reactors operating at 0.50- and 0.35-day V/Qs. In December, the reciprocating digester had a higher degree of short-circuiting than the non-reciprocating digester.

While some tracer studies can account for more than 95% of the mass of tracer dye applied (MWH 2005), percent dye recovered ranged from 27.4% to 67.5%, likely due to adsorption into biofilm and sludge (**Table 4.4; Table 4.5**). Mass of dye recovered is calculated as the integral of the effluent tracer dye concentration curve with respect to time, so it is important to keep monitoring the systems until the effluent dye concentration decreases to background levels. However, in the tracer studies from July, the dye concentration did not return to background levels before sampling was discontinued (due to time constraints), and so the data were extrapolated using an exponential decay fitted to the tails of each tracer curve (Time/MHRT = 0 for extrapolation equations where Time/MHRT = 0 on graph). The July tracer studies were performed while the walnut shell media was closer to clean-bed, with average shell

porosity of 0.68 and 0.64 for both D2 and D3, respectively (**Appendix D**). The shell layer during the December studies could then be described as dirty-bed, with Feed Tank shell porosities of 0.28 and 0.24 for D2 and D3, respectively.

To understand how the digesters distribute influent compared to the theoretical scenario, the ideal continuously stirred tank reactor (CSTR) washout function ($C = M/V e^{-t/(V/Q)}$) is shown for comparison (**Figure 4.7 - Figure 4.10**). Tracer dye in a CSTR would instantly and perfectly distribute throughout the reactor. Effluent concentration would follow an exponential decay function. All of the actual tracer curves shown below exhibit a short lag phase before the influent tracer dye reaches the effluent port, then a sharp increase in dye leaving the reactor, followed by a sharp decline. While expected, this is nevertheless indicative of a high degree of influent flow short circuiting the reactor. In the future, a CSTR-in-series equation may exhibit a theoretical tracer curve closer to actual reactor tracer curves.

Between reciprocation cycles, the digesters behave like steady-state plug-flow reactors, but during a reciprocation cycle, the digesters behave closer to a CSTR. All tracer studies, except D3 in December, were reciprocating once per day, between 6:15 AM and 8:32 AM. However, influent entered each reactor in ten evenly spaced pulses through each day. Tracer dye was injected with the next influent pulse after the reciprocation cycle ceased. Throughout the study, this influent pulse consistently started within five minutes of the end of a reciprocation. For D2 in December ($V/Q = 0.5$ days), > 99% of the recovered dye outflowed from the reactor before the first reciprocation (**Figure 4.7, Figure 4.8**) which indicates that a many influent pulses do not benefit from the redistribution effects of reciprocation under those conditions. For D2 and D3 in July

($V/Q = 6.15$ and 1.21 days, respectively), 43% and 47% of recovered dye outflowed from the reactors before the first reciprocation, indicating that with 1 reciprocation per day under clean-bed conditions and higher V/Q , all influent pulses benefit from the redistribution effects of reciprocation. Incrementally less short circuiting would be observed if tracer dye had been injected during later influent pulses.

Due to reactor design, reciprocation cycles only pumped 75% (**Figure 3.4**) of system liquid back and forth. Consequently, after tracer injection, only 75% of remaining tracer dye benefited from the redistribution effects of reciprocation. However, subsequent reciprocations helped redistribute the dye throughout the system, as evidenced by lowered effluent dye concentrations (reciprocations marked by vertical lines in **Figure 4.7**, **Figure 4.8**). Adsorption of dye onto biofilm in the shells also may have contributed to the decreases in dye concentration during reciprocations.

Table 4.4. Low- and medium-flow tracer study results and digester operating conditions on July 28, 2012. The mass of dye exiting system, shown below, excludes the extrapolation seen in **Figure 4.7** and **Figure 4.8**.

	Units	July 28 th 2012	July 28 th 2012
		6 day V/Q	1 day V/Q
Digester System	-	Digester 2	Digester 3
Reciprocation Frequency	d ⁻¹	1	1
Input Solution Volume	mL	100	50
Input Solution Concentration	g/L-RWT	2.00	2.00
Actual Mass of Dye Delivered	mg	200	100
Background Concentration	µg/L	6.16	0.76
Dye Exiting System	mg	52.9	67.5
Percent Dye Exiting	%	26.4	67.5
Percent Dye Attenuated	%	73.6	32.5
V/Q	Days	6.15	1.21
MHRT	Days	1.26	1.11
MHRT-to-V/Q ratio	-	0.20-to-1.0	0.92-to-1.0

Table 4.5. High-flow tracer study results and digester operating conditions on December 3, 2012. No extrapolation of the data was necessary.

		Dec. 3, 2012	Dec. 3, 2012
	Units	0.5 day V/Q	0.35 day V/Q
Digester Number	-	Digester 2	Digester 3
Reciprocation Frequency	d ⁻¹	1	0
Input Solution Volume	mL	50	50
Input Solution Concentration	g/L-RWT	2.00	2.00
Actual Mass of Dye Delivered	mg	100	100
Background Concentration	µg/L	3.49	6.54
Dye Exiting System	mg	53.3	55.2
Percent Dye Exiting	%	53.3	55.2
Percent Dye Attenuated	%	46.7	44.8
V/Q	Days	0.50	0.35
MHRT	Days	0.11	0.10
MHRT-to-V/Q ratio	-	0.22-to-1.0	0.29-to-1.0

Figure 4.7. July low-flow tracer study with 1 reciprocation per day. V/Q was 6.15 days, and MHRT was 1.26 days, or 20% of theoretical. Vertical lines represent samples taken after a reciprocation cycle. The dots extending the tracer curve are an extrapolation. See text.

Figure 4.8. July medium-flow tracer study with 1 reciprocation per day. V/Q was 1.21 days, and MHRT was 1.11 days, or 92% of theoretical. Vertical lines represent reciprocations. The dots extending the tracer curve are an extrapolation. See text.

Figure 4.9. December high-flow tracer study with 1 reciprocation per day. V/Q was 0.50 days, and MHRT was 0.11 days, or 22% of theoretical. The vertical line represents a reciprocation. The step-like shape was due to the effluent flowing in pulses, and because all of the tracer dye left the reactor much quicker than in July.

Figure 4.10. December high-flow tracer study with no reciprocation. V/Q was 0.35 days, and MHRT was 0.10 days, or 29% of theoretical. The step-like shape was due to the effluent flowing in pulses, and because all of the tracer dye left the reactor much quicker in December than in July.

Differences in influent and system temperature can affect the degree of short circuiting.

For instance, if influent pulses are warmer (less dense) than system water, influent may quickly rise inside the reactor and leave through the effluent port at the water surface, yielding a lower MHRT. In July's tracer studies, maximum influent minus effluent temperatures during the first 24 hours after tracer injection were 4.6 and 2.8 °C for D2 and D3, respectively. The larger temperature difference during July's D2 tracer study may have been a driving factor in the low MHRT-to- V/Q ratio of 0.20:1, while the D3 ratio was 0.92:1. In December's tracer study, maximum influent-minus-system temperatures during the first 24 hours for D2 and D3 were both 2.0 °C. However, both of their MHRT-to- V/Q ratios indicate high degrees of short circuiting, 0.22:1 and 0.29:1, respectively. In December, perhaps the reduced porosities in the dirty-bed shell layer were a stronger factor in short circuiting than temperature difference.

The high short circuiting and sludge accumulation in the walnut-shell packed-bed anaerobic digesters suggest that the shells were poor packed media for anaerobic

digestion of dairy manure flushwater. The large pore spaces in the car tires used in the pilot anaerobic digester in Oregon (**Figure 4.11**) would likely yield less short circuiting.

Figure 4.11. Sludge accumulation in walnut shells (left) and car tires (right). The walnut shells shown were from D2's Reservoir Tank after 226 days of operation. The high degree of short circuiting and sludge accumulation suggest that walnut shells are a poor packed media for anaerobic digestion of dairy manure flushwater. In a pilot anaerobic digester in Oregon, car tires exhibited less sludge accumulation relative to pore space volume despite having 5-fold higher influent TS concentrations.

4.5 Water Quality Modeling

To aid in future predictions of treatment in packed-bed anaerobic digesters, weekly CODR rates are plotted against OLR, and a linear correlation was created. Total COD removal (CODR) fluctuated over the course of the study in response to changes in influent concentration and loading rates, as well as temperature. The average daily temperature range was 14.1 to 23.6 °C. Digester flow rates ranged between 200 and 4700 L/day (**Figure 4.12**) and V/Q ranged from 6.3 to 0.25 days. Influent COD concentrations ranged from 2300 to 9000 mg/L (**Figure 4.13**). COD was used in this section instead of cBOD₅ because COD results had better quality control.

Figure 4.12. Influent flow rates of the three packed-bed anaerobic digesters. Vertical lines represent experimental changes or dairy operators changing influent strength, as noted in the table below. Occasional spikes or dips in flow rate are attributed to operator error or pump malfunctions, but are included in analysis. The influent pumps were shut down for one week in early September to study the biogas performance under starved conditions.

	Experimental Conditions Between Event Lines (D1, D2, D3)							
V/Q:	6, 6, 6	6, 6, 6	3.5, 6, 1	3.5, 6, 1	----	3.5, 0.5, 0.5	3.5, 0.5, 0.5	0.25, 0.5, 0.35
Reciprocation Frequency:	10,10,10	5, 10, 1	1,1,1	1,1,1	----	1,1,1	1,1,1	1,1,0
Influent Strength:	High	High	High	Low	(Starved)	Low	High	High

Figure 4.13. Influent and effluent COD concentrations for the three packed-bed anaerobic digesters. Vertical lines represent experimental changes or dairy operators changing flushwater strength, as noted in the table above. High influent strength refers to normal dairy operation. Low influent strength refers to flushing the barns with freshwater instead of recirculated lagoon water. The influent concentration spike in October occurred at the same time as dairy operators switched from flushing with freshwater to lagoon effluent. There may have been multiple days of manure accumulation in the lanes while the operators modified the flush system.

To aid in future predictions of treatment in packed-bed anaerobic digesters, weekly CODR rates are plotted against OLR, and a linear correlation is created. Total COD removal (CODR) ranged from 60% to < 20% as organic loading rate (OLR) increased from 0.50 to 20 g_{COD fed}/L_{liquid}-day (**Figure 4.14**). A poor correlation between CODR and loading rate was observed ($R^2 = 0.327$). However, the linear correlation drawn in **Figure 4.14** uses CODR values that were not corrected for temperature. Only water quality data from digesters operating at 1 reciprocation per day were included in this section to exclude any possible effects from different reciprocation frequencies.

Figure 4.14. Percent total COD removed (not temperature adjusted) over various OLRs.

Since average system liquid temperatures ranged from 14.1 °C to 23.6 °C over the course of all experiments, it was feasible that normalizing for temperature could improve the R^2 in the correlation between OLR and CODR. An Arrhenius-like temperature correction expression (**Eq. 3-4**) was incorporated to normalize weekly CODR to 20 °C (CODR₂₀)

using (Eq. 3-7). An Arrhenius-like constant of 1.05 was used for normalization (Kayombo et al. 2005). However, the R^2 decreased from 0.327 to 0.250 after normalizing for temperature (Figure 4.15). While temperature undoubtedly increases CODR, other factors, like MHRT-to-V/Q, appear to have a greater affect.

Figure 4.15. Temperature corrected CODR₂₀ compared to OLR. CODR₂₀ is calculated with (Eq. 3-7) and uses an assumed Arrhenius-like constant of 1.05. This dataset has a lower R^2 than with the non-temperature corrected dataset (Figure 4.14) because other factors appear to affect CODR more strongly than temperature.

Calculated first-order COD removal constants varied with different V/Qs and effluent COD concentrations, despite (Eq. 3-6) normalizing for both (Figure 4.16). Average k_{20} values ranged from 0.11 ± 0.02 to $0.7 \pm 0.5 \text{ d}^{-1}$ with V/Qs ranging from 6.3 to 0.25 days, respectively (Table 4.6). When calculating k_{20} , (Eq. 3-6) normalizes for V/Q, CODR, and temperature, so other factors appear to affect treatment efficiency stronger, which may include MHRT-to-V/Q ratio and porosity.

Figure 4.16. First-order reaction rate constants, k_{20} , calculated using (Eq. 3-6) for COD removal from different V/Qs. Only data from reactors that were reciprocating once per day are included.

Table 4.6. Average first-order COD removal reaction rate constants, k_{20} , calculated using (Eq. 3-6). Weekly COD removal data is corrected to 20 °C using this equation, and the Arrhenius-like constant, A , is estimated to be 1.05 (Kayombo et al. 2005). Only data from reactors reciprocating once per day were included.

V/Q (days)	Reactor(s)	Date Range (2012)	COD _{fed} (mg/L)	CODR (%)	k_{20} (d ⁻¹)	n
6.3	D2, D3	Jun 29 - Aug 31	4370	51	0.11 ± 0.02	10
3.7	D1	Jul 20 - Oct 26	4020	54	0.22 ± 0.11	13
1.2	D3	Jul 20 - Aug 31	3870	37	0.36 ± 0.04	7
0.51	D2, D3	Sep 21 - Dec 7	4270	34	0.9 ± 0.6	18
0.25	D1	Nov 2 - Dec 7	4430	13	0.7 ± 0.5	6

For comparison, Wilkie’s upflow pilot digester in Florida operated at ≤ 3 -day V/Q and achieved 50% COD removal at ≤ 20 °C (Wilkie 2003). Using (Eq. 3-6), Wilkie’s k_{20} was estimated to be ≥ 0.23 d⁻¹, which is similar to this study’s k_{20} of 0.22 d⁻¹ at 3.7-day V/Q (Table 4.6).

5 Conclusions

Three packed-bed anaerobic digester systems were operated for 226 days at the California Polytechnic State University, San Luis Obispo Dairy. Dairy freestall barn flushwater was digested at ambient temperature using reciprocation mixing with the intent to prevent flow channelization through the media, reduce organic matter concentrations in flushwater and subsequently produce biogas. Each digester system was comprised of two 1140-L tanks containing broken walnut shells as biofilm media. However, small pore spaces in the packed media tend to cause channelization and flow short circuiting (Brown et al. 1980), so reciprocation mixing was investigated to mitigate this problem. At any one time, one tank was full of liquid, and the other was empty. Mixing was accomplished by slowly pumping (reciprocating) the liquid repeatedly back and forth between the two tanks. Production and composition of biogas, and water treatment efficiency were monitored over a range of reciprocation frequencies (0-10 per day) and hydraulic residence times (0.25 - 6.3 days). The four main objectives for this study and corresponding results are summarized below.

5.1 Characteristics of the Cal Poly Influent Dairy Manure Flushwater

Sufficient alkalinity is necessary to sustain a neutral pH without alkalinity supplementation, and a high amount of influent ammonia is inhibitory to methane producing bacteria (McCarty 1964). Several water quality constituents were measured to quantify the performance of packed-bed anaerobic digester systems filled with walnut shell media. In this study, the term digester “influent” refers to flushwater that has flowed through a sand trap, a sloped screen, and a secondary settling basin.

During this study the Cal Poly Dairy housed 211 milking cows, or 414 animal units (AUs), in freestall barns flushed with manure lagoon water. The AU conversion factor is explained in Section 4.1. The flushwater total solids (TS) and VS concentrations were 5.5 ± 1.8 g/L and 2.8 ± 1.0 g/L, respectively (mean $\pm$ standard deviation of samples collected over time). The flushwater use per AU was $0.82 \text{ m}^3/\text{AU}$. Influent settleable solids ranged from 9.5 - 80 mL/L. The cBOD_5 and chemical oxygen demand (COD) were 800 and 4340 mg/L, respectively. Total ammonia nitrogen (TAN) at Cal Poly was 144 ± 61 mg/L-N. The average influent pH was 7.8 ± 0.3 , which means most TAN was in the form of ammonium, but regardless of pH, the TAN concentration was well below the inhibitory threshold of 1500 mg/L-N at $\text{pH} > 7$ (Gerardi 2003; McCarty 1964).

Influent alkalinity was 1610 ± 630 mg/L- CaCO_3 , which sometimes fell below the optimum alkalinity range for high-solids municipal wastewater sludge digestion of 1500 – 3000 mg/L- CaCO_3 (Gerardi 2003). However, no alkalinity supplementation was provided over the course of the study. During operation of the digesters at the Cal Poly Dairy, influent alkalinity dropped as low as 500 mg/L as CaCO_3 , but COD removal percent did not change noticeably nor did effluent pH decrease below 7.0. The optimum alkalinity could be different for more dilute substrates, like dairy freestall barn flushwater.

5.2 Effect of Reciprocation Mixing

Reciprocation does not appear to prevent media channelization or improve performance at this scale for broken walnut shell media. An upflow configuration may be more appropriate. However, upflow configuration usually requires effluent-to-influent

recirculation (McCarty & Smith 1986; Wilkie 2000), which may increase energy consumption compared to reciprocation mixing.

In this study, reciprocation mixing was judged based on three criteria: methane production, treatment performance, and channelization. The input variable for this portion of the study was reciprocation frequency, including a control system without reciprocation, which comprised a single upflow tank, also containing a bed of walnut shells.

Criterion A: Methane Production. No differences in methane production could be discerned between 1, 5, and 10 reciprocations per day (0.060 ± 0.011 , 0.066 ± 0.010 , and 0.058 ± 0.014 L_{CH_4}/L_{liquid} -day, respectively where L_{liquid} is volume of liquid occupying the digester pores) at 6-day nominal theoretical residence time (V/Q where V is L_{liquid} and Q is total daily influent flow). Similarly, no differences were observed between 0 and 1 reciprocations per day (0.24 ± 0.08 and 0.23 ± 0.08 L_{CH_4}/L_{liquid} -day at 0.35 and 0.50 day V/Q s, respectively; V/Q s were different because the control system comprised a single tank, which lowered its liquid volume).

Criterion B: Oxygen Demand Removal. No differences in chemical oxygen demand removal (CODR) or carbonaceous biochemical oxygen demand removal (cBODR) were observed between 1, 5, and 10 reciprocations per day at 6-day nominal V/Q . CODR ranged from 48-51%, and cBODR from 48-63%. However at 0.50 day V/Q , the 1 reciprocation per day reactor performed better than the upflow reactor at 0.35 day V/Q . CODR was 22% and 17%, and cBODR was 39% and 24% for the 1 and 0 reciprocations per day reactors, respectively. So at high flow rates, cBODR was treated

63% more efficiently in the reciprocating reactor compared to the upflow reactor. The 1 reciprocation per day system perhaps performed better due to additional particulate entrapment in the media in the second tank. Additionally, treatment performance results presented in this thesis cannot be sustained without periodic cleanout of sludge from media.

In summary, no appreciable performance enhancements were observed with reciprocation mixing under this scale of study.

5.3 Characterize Reactor Hydraulics

Three of four tracer studies indicated high short circuiting occurred in the packed-bed anaerobic digesters. The tracer studies in July on clean-bed digesters yielded MHRT-to-V/Q ratios of 0.20:1 and 0.92:1 for 6-day and 1-day V/Qs, respectively (**Table 4.4**).

Despite these very different V/Qs, each reactor had similar MHRTs (**Figure 4.7; Figure 4.8**). The high short circuiting in the 6-day V/Q reactor could possibly be due to warmer influent rising quickly through cooler tank contents to the surface effluent pipe.

Maximum influent minus effluent temperature in first 24 hours of the tracer test was 4.6 °C for the high short circuiting reactor and 2.8 °C for the low short circuiting reactor.

The high specific surface area and low pore sizes of broken walnut shells may not be suitable for dairy freestall barn flushwater because over half of the void spaces in the shells clogged with sludge after 226 days of study. For the higher flow rate reactors in December, the dirty-bed digesters exhibited high short circuiting, yielding MHRT-to-V/Q ratios of 0.22:1 and 0.29:1 for 1 and 0 reciprocations per day, respectively (**Table 4.5**), which shows that reciprocation did not improve short circuiting or channelization

compared to an upflow configuration. While these ratios are similar to the 0.20:1 MHRT-to-V/Q ratio from the 6-day V/Q reactor in July, the December ratios both had a maximum influent-effluent temperature differences during the first 24 hours of the tracer test of 2.0 °C, half that of high short circuiting reactor in July. From July to December, the shell-beds accumulated a large amount of sludge. Porosities in the two systems studied for short circuiting had dropped from 0.68 and 0.64 to 0.28 and 0.24 for the 0.50 and 0.35-day V/Q systems, respectively. Moreover, 56% and 59% of the shell pore spaces became clogged with sludge in the 0.50 and 0.35-day V/Q systems, respectively, indicating that the reciprocating system did not decrease sludge accumulation rate. The reciprocating (0.50-day) reactor accumulated and channelized sludge similar to the upflow reactor (0.35-day), thus reciprocation does not appear to prevent media channelization at this scale for broken walnut shells. The mild influent minus effluent temperature differences and the high degree of sludge accumulation in the December tracer studies suggest that clogging of the pore spaces was a stronger factor in causing high short circuiting.

5.4 CODR Model and First-Order COD Removal Parameter Value

CODR decreased with increasing loading rate, but the linear regression of these data suggested a poor correlation ($R^2 = 0.327$). Even after normalizing for temperature, the correlation between CODR and OLR was poor. In fact, the R^2 was worse (0.250) with the normalization. While temperature undoubtedly plays a role in anaerobic treatment, other factors appear more influential in the mild climate of San Luis Obispo.

First-order total COD removal rate constant, k_{20} , varied over time with different V/Qs and effluent COD concentrations, despite (Eq. 3-6) normalizing for them in the first-order equation.

$$k_{20} = \frac{-\ln\left(\frac{COD_{eff}}{COD_{fed}}\right) Q}{V A^{(T-20^{\circ}C)}} \quad (\text{Eq. 3-6})$$

where

A =Arrhenius-like constant for temperature correction

COD_{fed} and COD_{eff} = chemical oxygen demand concentration of influent and effluent, respectively, mg/L

T =system liquid temperature, C

After averaging weekly COD results into five categories based on nominal V/Qs, the k_{20} parameter was calculated for each nominal V/Q. The maximum and minimum k_{20} values were $0.9 \pm 0.6 \text{ d}^{-1}$ and 0.11 ± 0.02 for 0.51- and 6-day V/Qs. Since (Eq. 3-5) accounted for influent concentrations, temperature, and V/Q, other factors appear to have a stronger impact. Likely factors include the shell-porosity declining over the course of the study due to sludge accumulation.

5.5 Limitations of the Study

There are a couple limitations to this study. First, about 99% of English walnuts produced in the United States come from California, with almost all production taking place in Sacramento and San Joaquin valleys (AgMRC 2013), so walnut shell media is not as readily available in the Midwest or east coast. A mass balance that could account for accumulation inside the reactor was not performed in this study, so percent COD and cBOD₅ removals are due to both organic matter conversion and sludge settling.

5.6 Future Research

If walnut shells are explored further for anaerobic digestion, then clean-out methods could be explored to remove sludge. Cleaning methods could include biogas sparging or backwashing with lagoon water. Alternatively, if walnut shells were to be excavated, then disposal solutions could be investigated, including using shells and digested sludge as a bulking agent for composting. Future research could also explore upflow packed-bed reactors with different recirculation flow rates and/or different media. Alternative green waste media that are more readily available on other regions of the United States could be investigated. Media that allow accumulated sludge to settle to the bottom of the reactor are advantageous because they could facilitate periodic sludge removal via pumping from the underdrain. Choosing a media with $100 \text{ m}^2/\text{m}^3$ specific surface area or less may help decrease the sludge accumulation rate without inhibiting COD removal or biogas production (Young 1991). Also, the NVS/VS ratio of the influent and sludge in the walnut shells could be compared to estimate how much sludge has been captured and degraded over time. However, biofilm growth would also affect this estimate.

6 References

- Agricultural Marketing Resource Center (AgMRC) (2013). "English Walnuts Profile." Accessed June, 2013. <http://www.agmrc.org/commodities__products/nuts/english-walnuts-profile/>
- AgSTAR. (2012). "Operating Anaerobic Digester Projects." *Anaerobic Digester Database*. Accessed May, 2013. <<http://www.epa.gov/agstar/projects/index.html>>
- Ahmedna, M., Marshall, W. E., Husseiny, A. A., Rao, R. M., & Goktepe, I. (2004). "The use of nutshell carbons in drinking water filters for removal of trace metals." *Water Research*, 38(4), pp 1062-1068. DOI: 10.1016/j.watres.2003.10.047
- American Public Health Association (APHA) (2006). "Standard Methods for the Examination of Water and Wastewater," *American Water Works Association, and Water Environment Federation*.
- Asadi, M., Najafpour, G. D., Hashemiyeh, B. A., & Mohammadi, M. (2009). "Removal of Acetone from Contaminated Air in Biofilter using *Pseudomonas putida*." *American-Eurasian Journal Agriculture & Environmental Science*, 5(5), 712-719.
- Austin, A. (2010). "Methane Migraine." *Biomass Magazine*. Accessed May, 2013. <<http://biomassmagazine.com/articles/3377/methane-migraine>>
- Banihani Q., Sierra-Alvarez R., Field J. A. (2009). "Nitrate and nitrite inhibition of methanogenesis during denitrification in granular biofilms and digested domestic sludges. *Biodegradation*. 20(6) pp 801-812. DOI: 10.1007/s10532-009-9268-9
- Brown, G. J., Cocci, A. A., Landine, R. C., Viraraghavan, T., Lin, T. (1980). "Sludge Accumulation in an Anaerobic Lagoon-Anaerobic Filter System Treating Potato Processing Wastewater." *Proc.*, 35th *Industrial Waste Conference*, pp 610-616.
- Cal EPA (2013). "Greenhouse Gas Inventory Data – 2000 to 2010." *2000-2010 Inventory by economic sector – Full Detail*. Accessed May, 2013. <<http://www.arb.ca.gov/cc/inventory/data/data.htm>>
- California Biomass Collaborative (CBC) (2007). "An Assessment of Biomass Resources in California." *CEC*, Accessed May, 2013. <<http://biomass.ucdavis.edu/files/reports/2008-cbc-resource-assessment.pdf>>
- California Department of Food and Agriculture (CDFA) (2011). "California Dairy Statistics 2011."
- California Energy Commission (CEC) (2011). "Renewable Energy Programs." Accessed May, 2013. <http://www.energy.ca.gov/renewables/renewable_links.html>
- California Environmental Protection Agency (Cal EPA) (2006). "Assembly Bill 32: Global Warming Solutions Act." Accessed May, 2013. <<http://www.arb.ca.gov/cc/ab32/ab32.htm>>

CEC (2012). "Bioenergy Action Plan." *Bioenergy Interagency Working Group*. Accessed May, 2013. <http://www.resources.ca.gov/docs/2012_Bioenergy_Action_Plan.pdf>

Eco-Shell, Inc. (2004). "Blasting." Accessed June, 2013. <<http://www.ecoshell.com/Blasting.htm>>

Germain, R., & Katofsky R. (2006). "Recommendations for a Bioenergy Plan for California." *Bioenergy Interagency Working Group*. Accessed May, 2013. <<http://www.energy.ca.gov/2006publications/CEC-600-2006-004/CEC-600-2006-004-F.PDF>>

Green, T. M. (2009). "TIREPower ANAEROBIC DIGESTER". Accessed May, 2013. <[http://www.pacificbiomass.org/documents/Green%20\(B2\).pdf](http://www.pacificbiomass.org/documents/Green%20(B2).pdf)>

Henze, M., & Harremoës, P. (1983). "Anaerobic treatment of wastewater in fixed film reactors—a literature review." *Water Science & Technology*, 15(8-9), 1-101.

Kane, J. P. (2010). "Water quality performance of a reciprocating biofilm reactor for treatment of dairy wastewater." MS Thesis, Civil and Environmental Engineering Department, California Polytechnic State University, San Luis Obispo.

Kayombo, S., Mbvette, T. S. A., Katima, J. H. Y., Ladegaard, N., & Jørgensen, S. E. (2005). "Waste stabilization ponds and constructed wetlands design manual." *UNEP International Environmental Technology Center*. Accessed June, 2013. <http://www.limpiemoselagua.com.mx/archivos/Libros/38_WASTE%20STABILIZATION%20PONDS%20AND%20CONSTRUCTED%20WETLANDS%20DESIGN%20MANUAL.pdf>

Krich, K., Augenstein, D., Batmale, J. P., Benemann, J., Rutledge, B., & Salour, D. (2005). "Biomethane from Dairy Waste: A Sourcebook for the Production and Use of Renewable natural Gas in California." *Western United Dairymen*. Accessed May, 2013. <http://www.calstart.org/Libraries/Publications/Biomethane_from_Dairy_Waste_Full_Report.sflb.ashx>

Liao, P. H., & Lo, K. V. (1985). "Methane Production Using Whole and Screened Dairy Manure in Conventional and Fixed-Film Reactors." *Biotechnology and Bioengineering* 27(3). 266-272. DOI: 10.1002/bit.260270309

Lomas, J. M., Urbano, C., & Camarero, L. M. (2000). "Influence of recirculation flow in a pilot scale downflow stationary fixed film anaerobic reactor treating piggery slurry." *Biomass and Bioenergy*, 18(5), 421-430. DOI: 10.1016/S0961-9534(00)00007-6

Marsh Jr, J. A. (1970). "Primary productivity of reef-building calcareous red algae." *Ecology*, 255-263.

Martin, J. H. (2008). "An Evaluation of a Covered Anaerobic Lagoon for Flushed Dairy Cattle Manure Stabilization and Biogas Production." *AgSTAR Program*. Accessed April, 2013. <http://www.epa.gov/agstar/documents/flushed_dairy_cattle.pdf>

McCarty, P. L. & Smith, P. D. (1986). "Anaerobic Wastewater Treatment." *Environmental Science & Technology*. 20(12), pp 1200-1206.
DOI: 10.1021/es00154a002

McCarty, P. L. (1964). "Anaerobic waste treatment fundamentals." *Public works*, 95(9), 107-112.

Metcalf & Eddy (2003). "Wastewater Engineering, Treatment and Reuse." New York, McGraw-Hill Companies Inc.

MWH, J. (2005). "Water treatment: Principles and design." New Jersey, John Wiley & Sons, Inc. ISBN 0-471-11018-3

NRCS (2008). "Animal Waste Management: National Engineering Handbook Part 651." *Agricultural Waste Management Field Handbook, Natural Resources Conservation Service, U.S. Department of Agriculture*. Accessed April, 2013.
<<http://directives.sc.egov.usda.gov/OpenNonWebContent.aspx?content=31475.wba>>

Powers, W. J., Wilkie, A. C., Van Horn, H. H., & Nordstedt, R. A. (1997). "Effects of Hydraulic Retention Time on Performance and Effluent Odor of Conventional and Fixed-Film Anaerobic Digesters Fed Manure Wastewaters." *ASAE*. Vol. 40(5) pp.1449-1455.

Samson R., Guiot S. (1990). "Les nouveaux secteurs a fort poten-tiel de developement en digestion anaerobie." *Centre Quebecois de valorisation de la bio-masse*. Quebec, Canada.

San Joaquin Valley Dairy Manure Technology Feasibility Assessment Panel (SJFAP). 2005. "An Assessment of Technologies for Management and Treatment of Dairy Manure in 30 California's San Joaquin Valley." Accessed May, 2013.
<<http://www.arb.ca.gov/ag/caf/dairypnl/dmtfaprprt.pdf>>

Sawyer C.N., P.L McCarty, G.F. Perkin. (2003). "Chemistry for Environmental Engineering and Science, 5th Ed." *McGraw-Hill*, ISBN 0-07-123045-9

Srinivasan, A., & Viraraghavan, T. (2008). "Removal of oil by walnut shell media." *Bioresource technology*, 99(17), 8217-8220. DOI: 10.1016/j.biortech.2008.03.072

Thomson S. (2013). "Methane Production by Packed-Bed Anaerobic Digesters Fed Dairy Barn Flushwater," MS Thesis, Civil and Environmental Engineering Department, California Polytechnic State University, San Luis Obispo.

Turner Designs (1995). "Preparation of Standards for Dye Studies using Rhodamine WT," Revised 1995. Accessed March, 2013.
<<http://www.turnerdesigns.com/t2/doc/apnnotes/998-5111.pdf>>

United States Environmental Protection Agency (USEPA) (2012). "Health Effects: What are the effects of ozone?" Accessed May, 2013. <<http://www.epa.gov/glo/health.html>>

United States Geological Survey (USGS) (1986). "Fluorometric procedures for dye tracing," J.F. Wilson, E.D. Cobb, and F.A. Kilpatrick, *Chapter A12, Book 3, Applications of Hydraulics*, revised 1986.

Wilkie, A. C. (2000). "Fixed Film Anaerobic Digester." Accessed May, 2013. <http://www.epa.gov/agstar/documents/Fixed_Film_Anaerobic_Digester.pdf>

Wilkie, A. C. (2003). "Anaerobic Digestion of Flushed Dairy Manure." *Proc., Anaerobic Digester Technology Applications in Animal Agriculture – A National Summit*, WEF, pp. 350-354.

Wilkie, A. C. (2005). "Anaerobic Digestion: Biology and Benefits." *Dairy Manure Management: Treatment, Handling, and Community Relations*. NRAES-176, pp 63-72. Natural Resource, Agriculture, and Engineering Service, Cornell University, Ithaca, NY, 2005. Accessed May, 2013, <<http://dairy.ifas.ufl.edu/other/files/NRAES-176-March2005-p63-72.pdf>>

Wilkie, A. C., Castro, H. F., Cubinski, K. R., Owens, J. M., & Yan, S. C. (2004). "Fixed-film anaerobic digestion of flushed dairy manure after primary treatment: wastewater production and characterization". *Biosystems engineering*, 89(4), 457-471.

Young, J. C. (1991). "Factors affecting the design and performance of upflow anaerobic filters." *Water Science & Technology*, 24(8), 133-155.

Zare, H., Najafpour, G., Rahimnejad, M., Tardast, A., & Gilani, S. (2012). "Biofiltration of ethyl acetate by *Pseudomonas putida* immobilized on walnut shell." *Bioresource Technology*.

7 Appendices

Appendix A: Detailed Methods, page 67

Appendix B: Estimating C:N, page 74

Appendix C: Comparing Composite to Grab Samples, page 75

Appendix D: Linearly Interpolating between Porosity Measurements, page 76

Appendix E: Cal Poly Dairy Flushwater Treatment System Performance, page 78

Appendix F: Flushwater Theoretical Hydraulic Residence Time in Cal Poly West Storage
Lagoon, page 85

Appendix G: Example Reciprocation and Influent Pump Schedule, page 86

Appendix H: Walnut Shell Sieved and Unsieved Dry Bulk Density, page 87

Appendix A Detailed Methods

Specific COD, TS and VS, TSS and VSS, alkalinity, pH, TAN, and tracer study methods are detailed in this section.

A.1. Chemical Oxygen Demand (COD)

COD was performed with CHEMetrics 0-1500 ppm vials following the CHEMetrics and APHA 5220 D methods. Standard concentrations of 180, 360, 540, and 720 mg/L as COD were diluted from a 6000 mg/L stock solution of potassium hydrogen phthalate to create a calibration curve and R^2 values above 0.97 were typical. The Hach DR700 colorimeter was used for measuring percent transmittance until August 17, 2012. Afterwards the Hach DR890 was used. Weekly results with split recoveries outside of 90 -110% and spike recoveries outside of 85 – 115% were rejected. Samples were diluted between 1:20 -1:10 using 100 mL volumetric flasks in order to keep the resultant concentrations below 720 mg/L, the maximum of the standard concentration range.

A.2. Total and Volatile Solids (TS & VS)

TS and VS samples were dried at 105 °C for 24-72 hours, measured and then incinerated at 550 °C for 15 minutes (APHA 2540 B, E). About 10- 20 mL of well mixed sample (10 inversions) was pipetted into aluminum weighing dishes (08-732-100, Thermo Fisher Scientific). Residues left inside the pipettes were rinsed into their respective sample dishes using a few mL of deionized water. For quality control, splits were performed on each sample and were accepted within 15% difference.

A.3. Total and Volatile Suspended Solids (TSS & VSS)

TSS and VSS was measured by vacuum filtration method (APHA 2540 D, E) using 55-mm diameter G4 filters (Thermo Fisher Scientific). Samples were diluted 5:1 for easier filtering. For quality control, splits were performed on each sample and were accepted within 15% difference

A.4. Alkalinity & pH

Digester influent and effluent alkalinity and pH were measured from three to seven times per week to monitor the health of the digesters. During start-up or subsequent increase of flow rates, alkalinity and pH were monitored daily, but then relaxed to three times a week during steady-state operation.

Alkalinity as CaCO_3 was measured by the acid titration method (APHA 4230D) using a digital meter (Oakton pH 11 series) and electrode pH probe (Sensorex S200C). H_2SO_4 normality of 0.1, 0.2 & 0.5 N were used for the titration, 0.2 being the most common. Typical sample volumes were 30 to 40 mL.

Anaerobic digester water has high dissolved CO_2 content which effervesces when exposed to air, and subsequently increases pH (Sawyer et al., 2003). To combat the subsequent rise in pH, acid was titrated into the sample very quickly until the pH approached 5.5, and then slowly as the pH approached 4.50. It was helpful to increase mixing speed toward the end of the titration to help apply enough mixing energy to the sample-plus-added-acid volume. A high enough mixing speed helps dampen premature pH dips below 4.5 due to slow homogenizing. It is assumed that the error from increased

effervescence due to quicker mixing is smaller than the error from premature pH dips from slow mixing.

A.5. Total Ammonia Nitrogen (TAN)

Ammonia was measured as nitrogen by the selective electrode method (APHA 4500 NH₃-D) at pH >11 with detection meter (Corning 355) and electrode probe (Orion 9512HPBNWP). To ensure sampling accuracy, calibration and spikes were employed by diluting 2500 ppm ammonia standard. Calibration points included 1, 10, 100 & 1000 mg/L as N. For quality control, splits were accepted within 10% error. Spikes were accepted within 15% of the estimated nitrogen concentration.

A.6. Tracer Study Procedure

The following operating procedure is based on USGS (1986) and Turner Designs (1995).

A baseline effluent fluorometer reading prior to dye addition was necessary because the wastewater effluent contained constituents that fluoresced or had turbidity that was interpreted as fluorescence. A calibration curve using the Rhodamine concentrations desired for the study was made to ensure that correct concentrations were read. The range of detectable fluorescence was very low, between 0.02 and 1000 ppb as Rhodamine WT.

The following equation was used to estimate an appropriate mass of dye to pulse into the system:

$$M_{\text{pulse}} = C_{\text{max}} * V / (1 - \%_{\text{attenuated}})$$

where

M_{pulse} = Mass of dye to pulse into the system (μg)

C_{max} = desired peak concentration, 50 $\mu\text{g/L}$ is appropriate ($\mu\text{g/L}$)

V = liquid volume in reactor (L)

$\%_{\text{attenuated}}$ = estimated percent of dye attenuating in reactor

For biofilm systems like the packed-bed anaerobic digester, typically between 40 and 75% of the mass of dye is retained on the media.

A concentrated solution of 238 g/L Rhodamine WT was used in this study. The dye had a specific gravity of 1.19. The usable linear range of dye concentration standards using dairy manure flushwater ranged from 0 to 500 $\mu\text{g/L}$, however 0 to 100 $\mu\text{g/L}$ was typically preferred. The raw tracer solution was actually a 20% solution of Rhodamine WT (RWT) in water. Serial dilutions were made to obtain a 1000 $\mu\text{g/L}$ -RWT solution. A 2 g/L- RWT solution, a 200 mg/L- RWT, and a 1000 $\mu\text{g/L}$ as RWT serial dilution was made. The steps for preparing tracer dye standards are below.

Dye Standard Concentration Preparation

1. A dry 100-mL volumetric flask was tared on a scale. A fresh plastic dropper transfer pipet was used to add drops from the raw tracer solution to the flask until it reached 1.000 grams $\pm$ 0.01. The flask was removed from the scale and filled with deionized (DI) water. While this solution was 10 g/L-tracer, it was also 2 g/L-RWT since the stock tracer solution was a 20% mixture of RWT.
2. Ten-mL of the 2 g/L-RWT solution was transferred into a new 100 mL volumetric flask with a fine-tipped glass 10 mL pipet. This was filled up with DI to finish the 200 mg/L-RWT solution.

3. Five mL from the 200 mg/L-RWT solution was transferred into a 1L volumetric flask to make the 1000 $\mu\text{g/L}$ -RWT solution. The flask was filled with **system** water and this process was repeated with respective system water for another simultaneous tracer study. Effluents from Digester 2 and 3 were used because their solids contents were different enough to cause different interference levels during fluorescence measurements. As a side note, **Figure A.1** illustrates the importance of making the 1000 $\mu\text{g/L}$ -RWT with system water instead of DI water.

Figure A.1. Calibration curves made using DI water and Digester 3 effluent for diluting standards. The high turbidity in Digester 3 effluent interfered with the fluorometer measurements, and so it was important to make tracer dye concentration standards using system water. Fortunately, the system water curve remains linear. A 500 $\mu\text{g/L}$ -RWT solution was made (in addition to 0, 25, 50, 75, and 100 $\mu\text{g/L}$ -RWT) in case the tracer curve peaks above 100 $\mu\text{g/L}$ -RWT and to see if the curve is still linear above 100 $\mu\text{g/L}$ -RWT.

4. Further dilutions were made to construct calibration curve at 25, 50, 75, and 100 $\mu\text{g/L}$ -RWT (and 500 $\mu\text{g/L}$ as a backup in case the peak concentration spiked above 100

$\mu\text{g/L-RWT}$). From the 1000 $\mu\text{g/L-RWT}$ dye concentration solution, 2.5, 5, 7.5, 10, and 50 mL was transferred into respective 100 mL volumetric flasks. These were filled with system water, shaken, and transferred into glass vials. Plastic containers were avoided because Rhodamine WT adsorbs to plastic.

Sample Collection

Baseline measurements of system effluent were taken prior to introduction of the dye tracer slug, because the system water may have had background fluorescence. Several background samples were taken to the lab and were left on the benchtop to reach room temperature. Flat-bottomed 60-mL glass vials were used for sample collection. Once the tracer was introduced into the system, samples were taken every two or three minutes, and measured in the field to estimate when the peak tracer concentration left the reactor. When the concentration rapidly increased, samples were taken more frequently so that the tracer curve would have a higher resolution and calculating MHRT would be more accurate. After the tracer curve peak passed and the concentrations decreased, samples were collected less frequently using an autosampler.

Dye Injection

After the slug of dye was prepared, it was introduced into the reactor during an influent pulse. The 2 g/L-RWT solution was used to prepare the tracer slug. The time of injection was recorded.

During the four tracer studies described in this report, the systems were dosed with influent ten times per day, but reciprocated once per day, at 6:15 AM. Dye was injected

after the reciprocations finished, at 8:32 AM, to observe the influent pulse that theoretically had the least short circuiting.

Fluorometer Operation

To measure tracer dye concentration samples, the benchtop fluorometer (Turner Designs Model 7200) with the appropriate cartridge (Turner Designs module 42) was used in this study. Two-mL cuvettes were used to hold sample to be measured in the fluorometer. Baseline effluent samples were read first, followed by dye concentration standards, using a baseline sample for the zero-concentration. Samples were not shaken prior to measurement. Individual concentration curves were made for each reactor, because each reactor effluent varies in turbidity and/or solids content. Linear correlations of dye standards and fluorescence were plotted for tracer sample analysis. Also, the temperature of samples was recorded. The same calibration curve was used throughout the multiple-day study.

Appendix B Estimating C:N

C:N can be calculated as $C:N = C/TN$. Carbon is estimated as 55% of VS concentration.

The bulk of Total Nitrogen is quantified by Total Kjeldahl Nitrogen (TKN).

Assume:

- 55% of dry VS is Carbon (NRCS 2008)
- Nitrite is negligible

Knowns:

- Influent TKN = 217 mg/L-N (tested once, Nov. 9, 2012; method: Macro-Kjeldahl Method (APHA Method 4500-N_{org} - B)
- Influent Nitrate = 4.54 mg/L-N (average of two measurements in August, 2012; method: Nitrate Electrode (APHA Method 5400-NO₃- D)
- Influent VS = 2.28 g/L on Nov. 9, 2012

Solution:

$$C:N = \frac{C}{TN}$$

$$C:N = \frac{0.55 \cdot VS}{TKN + NO_3^-}$$

$$C:N = \frac{0.55 \cdot 2.25 \text{ g/L}}{\left(217 + 4.5 \frac{\text{mg}}{\text{L}}\right) \left(\frac{1 \text{ g}}{1000 \text{ mg}}\right)}$$

$$C:N = 5.6:1$$

Appendix C Comparing Composite to Grab Samples

Composite effluent samples were taken by an autosampler from a one random digester each week, along with the normal grab sample. The average of the percent differences of the composite sample from the grab sample is reported below. The “n” is number of weekly composite samples in the average for that digester.

Water Quality Constituent	D1 (%, n)	D2 (%, n)	D3 (%, n)
COD	-2.5, 1	-0.6, 9	10.2, 11
cBOD ₅	-3.9, 1	-18.7, 9	0.5, 10
TS	9.8, 1	1.2, 9	1.2, 10
VS	8.5, 1	0.2, 9	0.5, 10
Alkalinity	---- 0	2.6, 3	1.3, 5

Appendix D Linearly Interpolating between Porosity Measurements

The estimated walnut-shell porosity on July 28, 2012, is desired to support tracer study data. The initial startup porosity of the shell bed was estimated at 0.70, as determined in the lab with a representative sample of walnut shells, and actual porosity was measured on September 13, 2012. Assuming that sludge accumulation (and in turn, porosity decrease) is linearly correlated with influent TS loading, then a linear interpolation of TS loaded between startup and September 13 would be the best estimate for porosity at the time of the tracer study. Linear interpolation by time only would not be quite as accurate since the flow rate and organic loading rates were increased 5-fold in July. Actual porosity measurement methods are in Thomson (in progress), and porosity was calculated as $\text{Porosity} = (\text{pore volume} / \text{total volume})$. For reciprocating systems, porosity measurements from both tanks are averaged. TS loaded are estimated by the sum of multiplying daily flow rates with their respective TS concentrations

Assume

- Porosity change is linearly correlated with TS loaded
- Influent TS loaded = $\sum [Q * TS]$, where Q = daily flow rate, and TS = Total Solids concentration of influent

Knowns

- Initial Porosity on startup (April 26, 2012) = 0.70
- D1, D2, and D3 Porosity on September 13, 2012 = 0.61, 0.67, and 0.59
- Total TS loaded between April 26 and September 13 = 172.8, 159.6, and 346.2 kg TS for D1, D2, and D3, respectively.

- Total TS loaded between April 26 and July 28 = 116.2, 126.1, and 181.8 kg TS for D1, D2, and D3, respectively.

Solution

$$\frac{\Delta \text{Porosity}_{\text{Apr-Sept}}}{\Sigma TS_{\text{Apr-Sept}}} = \frac{\Delta \text{Porosity}_{\text{Apr-Jul}}}{\Sigma TS_{\text{Apr-Jul}}}$$

Use Φ symbol for porosity,

$$\frac{\Phi_{\text{Apr}} - \Phi_{\text{Sept}}}{\Sigma TS_{\text{Apr-Sept}}} = \frac{\Phi_{\text{Apr}} - \Phi_{\text{July}}}{\Sigma TS_{\text{Apr-Jul}}}$$

Rearrange for Φ_{July} ,

$$\Phi_{\text{July}} = -1 \left[\frac{\Phi_{\text{Apr}} - \Phi_{\text{Sept}}}{\Sigma TS_{\text{Apr-Sept}}} (\Sigma TS_{\text{Apr-Jul}}) - \Phi_{\text{Apr}} \right]$$

Solving,

$$\Phi_{\text{July}} = -1 \left[\frac{0.70 - 0.59}{346.2 \text{ kg TS}} (181.8 \text{ kg TS}) - 0.70 \right]$$

$$\Phi_{\text{July}} = 0.64 \text{ for D3 on July 28, 2012}$$

$$\Phi_{\text{July}} = 0.68 \text{ for D2 on July 28, 2012}$$

$$\Phi_{\text{July}} = 0.64 \text{ for D1 on July 28, 2012}$$

Appendix E Cal Poly Dairy Flushwater Treatment System

Performance

The flushed manure treatment area at the Cal Poly Dairy was characterized from monthly water quality samples taken from November 2010 through April 2011, to supplement design of the upcoming anaerobic digester pilot system and a separate on-going nitrogen removal pilot project. The Cal Poly Dairy operates a recirculating treatment system using diluted manure from its anaerobic storage lagoon to sweep fresh manure from the cow lanes. The flushwater is screened to separate the fibrous un-digested portion and is settled in an unusual secondary settler to further remove fine solids. Composite samples were taken from five locations in the treatment system to judge the performance of each treatment process and to estimate the organic matter concentration uptake after flushwater passes through the freestall barns.

The freestall barns are flushed twice per day, and the pumps at the flushwater treatment area typically were operated automatically for about an hour in the morning and afternoon. A treatment train flow diagram is outlined in **Figure E.1** and it indicates the five sample points in red numbers.

Figure E.1. Cal Poly Dairy manure flushwater treatment train. Sample site pictures that correspond with the red numbers are displayed in **Figure E.2** through **Figure E.5**.

The five sample points are indicated by red arrows in **Figure E.2** through **Figure E.5**, and are in order of treatment sequence, starting with flush water released from the flush tank and ending with discharge back into the storage lagoon. The Fine Solids Trap is also referred to as a secondary settling basin in this thesis.

Figure E.2. Sample Site 1: Flush Tank Effluent. To initiate a flush cycle, an operator opens the flush valve (bottom) and a high volume of recycled manure water from the storage lagoon sweeps fresh manure from the alleys. This picture was taken after the flush valve was closed. This sample point is practically equivalent to the storage lagoon effluent

Figure E.3. Sample Site 2: Sand Trap Effluent. Large pieces of leftover food are retained by the bar screen (lower right), coarse solids are settled out in the sand trap (center), and further filtering occurs through the weeping wall (left). The resultant Sand Trap Effluent flows into the sump basin (top left) through the PVC pipe opening (far left).

Figure E.4. Sample Site 3: Screen Influent. Flushwater is pumped from the sump basin into a trough on top of the static manure screen separator. Solids are retained on the slanted screen and form a pile underneath for composting.

Figure E.5. Sample Site 4 and 5: Fine Solids Trap Influent and Effluent. After flushwater is screened, it flows through this fine solids trap, which is an unusual treatment process, different than those of most flush dairies. Influent enters from the upper right, and exits on the left. The overall purpose of this unit is to further reduce the cleanout frequency of the storage lagoons and reduce clogging of recirculating pumps and irrigation lines.

Sampling Methods

Over the duration of one flush, composite samples were taken at each site by filling a 500 mL bottle every five minutes and combining in a bucket. Total solids (TS), volatile solids (VS), alkalinity, pH, and total ammonia nitrogen (TAN) were performed soon after the samples were transported back to the lab. Chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), and total phosphorus were performed at a later date on samples acidified to pH less than 2.0 and refrigerated at less than 4 °C (APHA, 1995). Each water quality test follows APHA Standard Methods.

Results and Discussion

Changes in water quality strength are evident as flushwater progresses through the treatment train. After the flush swept up fresh manure, average TS concentrations rose by 2,300 mg/L, or 38%. VS concentrations rose by 1,900 mg/L, or 73%. COD concentrations rose by 2,500 mg/L, or 74% (**Table E.1, Table E.2**). Flushwater increased in strength after passing through the large screen transfer sump basin, in between the sand trap and mechanical screen separator. This is likely due to measured flushes combining with a partially full sump basin that contains higher strength flushwater from earlier in the day. The unique fine solids trap did not significantly change water quality, possibly due to a very quick retention time. However, from personal observations, sludge accumulation in the solids trap likely occurs from the remaining fraction of flushwater that stagnates in the trap at the end of each flush cycle.

Table E.1. Dairy Manure Flushwater Characteristics at Cal Poly Dairy. These are average values from each sample day between November 2010 and April 2011.

Sample Site	TS (mg/L)	VS (mg/L)	pH	Alkalinity (mg/L as CaCO ₃)	COD (mg/L)
1. Flush Tank Effluent	6000	2600	7.8	2180	3400
2. Sand Trap Effluent	8300	4500	7.9	2150	5900
3. Screen Influent	9800	5600	7.9	2390	7300
4. Fine Solids Trap Influent	9000	5100	8.0	2330	7300
5. Fine Solids Trap Effluent	9300	5000	8.0	2320	7200
Number of Observations	5	5	6	6	4

Table E.2. Dairy Manure Flushwater Characteristics at Cal Poly Dairy. These are average values from each sample day between November 2010 and April 2011. Organic Nitrogen was calculated by subtracting TAN from TKN.

Sample Site	TAN (mg/L as N)	TKN (mg/L as N)	Organic N (mg/L as N)	Total Phosphorus (mg/L as P)
1. Flush Tank Effluent	131	254	163	45.2
2. Sand Trap Effluent	164	420	271	63.2
3. Screen Influent	191	383	245	72.0
4. Fine Solids Trap Influent	188	381	233	78.7
5. Fine Solids Trap Effluent	194	381	245	66.5
Number of Observations	6	3	3	1

Conclusion

Recommendations for future testing include total and volatile dissolved solids to better quantify the fraction of solids that anaerobic bacteria can readily metabolize. Settleable solids analysis would assist in sludge accumulation estimates for a packed-bed anaerobic digester.

Appendix F Flushwater Theoretical Hydraulic Residence Time in Cal Poly West Storage Lagoon

To estimate degree of stabilization of fresh manure in west storage lagoon, the theoretical hydraulic residence time (V/Q) was estimated from reported lagoon volumes and estimated daily flushwater flow rates.

Estimated knowns:

Volume of lagoon (V) = 14,300 m³ when full (Cal Poly, unpublished internal report, 2008)

Flushwater Flow Rate (Q) = 340 m³/day (**Appendix E**)

Solution:

$$V/Q = 14,300 \text{ m}^3 / 340 \text{ m}^3/\text{day}$$

$V/Q = 42$ days when lagoon is full, however lagoon depth varies, so

$$\mathbf{V/Q \leq 42 \text{ days}}$$

Appendix G Example Reciprocation and Influent Pump Schedule

Revised: 9/17/12 Time	Reciprocation Pumps				Influent Pumps					
	All systems: 1 reciprocation/day				D1: 3.5 day V/Q 9 pulses @ 5 min ea.		D2: 0.5 day V/Q 10 pulses @ 35 min ea.		D3: 0.5 day V/Q 10 pulses @ 35 min ea.	
	Feed Tank		Reservoir Tank		+ 1 influent @ 4 min.					
	ON	OFF	ON	OFF	ON	OFF	ON	OFF	ON	OFF
1:20 AM					1:20 AM		1:20 AM		1:20 AM	
1:25 AM						1:25 AM				
1:55 AM							1:55 AM		1:55 AM	
3:44 AM					3:44 AM		3:44 AM		3:44 AM	
3:49 AM						3:49 AM				
4:19 AM							4:19 AM		4:19 AM	
5:38 AM							5:38 AM		5:38 AM	
6:08 AM					6:08 AM					
6:13 AM						6:13 AM	6:13 AM		6:13 AM	
6:15 AM			6:15 AM							
7:20 AM			7:20 AM							
7:27 AM	7:27 AM									
8:32 AM		8:32 AM			8:32 AM		8:32 AM		8:32 AM	
8:37 AM						8:37 AM				
9:07 AM							9:07 AM		9:07 AM	
10:56 AM					10:56 AM		10:56 AM		10:56 AM	
11:01 AM						11:01 AM				
12:15 PM							11:31 AM		11:31 AM	
1:20 PM					1:20 PM		1:20 PM		1:20 PM	
1:25 PM						1:25 PM				
1:55 PM							1:55 PM		1:55 PM	
3:44 PM					3:44 PM		3:44 PM		3:44 PM	
3:49 PM						3:49 PM				
4:19 PM							4:19 PM		4:19 PM	
6:08 PM					6:08 PM		6:08 PM		6:08 PM	
6:13 PM						6:13 PM				
6:43 PM							6:43 PM		6:43 PM	
8:32 PM					8:32 PM		8:32 PM		8:32 PM	
8:37 PM						8:37 PM				
9:07 PM							9:07 PM		9:07 PM	
10:56 PM					10:56 PM		10:56 PM		10:56 PM	
11:00 PM						11:00 PM				
11:31 PM							11:31 PM		11:31 PM	

Appendix H Walnut Shell Sieved and Unsieved Dry Bulk Density

Dry bulk density of sieved and unsieved walnut shells was measured by weighing shells in 18.9-L buckets. Walnut shells were taken from the unsieved and sieved piles in random locations, placed in buckets and taken back to the lab for weighing. Shells were sundried, but were not oven dried, and likely contained a small fraction of water. The sieved pile was composed of shells that were retained on a 12.7-mm square sieve. The 18.9-L fill level was verified by taring the bucket on a large scale and filling with 5.0 kg of water and marking its final water level. The buckets were then filled with walnut shells to this level. After measuring weights of walnut shells, bulk density (ρ) was calculated:

$$\rho_{sieved} = \frac{M_{bucket+shells} - M_{bucket}}{V_{bucket}}$$

$$\rho_{sieved} = \frac{0.778 \text{ kg} - 5.284 \text{ kg}}{18.9 \text{ L}}$$

$$\rho_{sieved} = 0.238 \text{ kg/L}$$

$$\rho_{unsieved} = 0.245 \text{ kg/L}$$