WATER AND AIR QUALITY PERFORMANCE OF A RECIPROCATING
BIOFILTER TREATING DAIRY WASTEWATER

A Master's 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

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March 2011

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ABSTRACT

Water and Air Quality Performance of a Reciprocating

Biofilter Treating Dairy Wastewater

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Agricultural non-point source pollution is the leading water quality problem in surface water and the second leading problem in ground water in the US. Among the contaminants, nutrients (such as nitrogen, phosphorus, potassium) can be transported from agricultural fields when cropland is not managed properly. In California, dairy manure application to cropland has become tightly regulated with the goal of decreasing such nutrient pollution. Dairies unable to balance their manure nutrient supply with cropland application area may benefit from a nitrogen removal technology. One such technology is the reciprocating biofilter, known as the ReCip[®] technology. A pilot-scale ReCip[®] unit was installed at the Cal Poly dairy to evaluate its treatment efficacy, in particular for nitrogen removal, when treating wastewater from flush dairies. This pilot-scale system was the first application of the ReCip[®] technology to dairy wastewater, and recently it was found to be effective for removal of ammonium, total nitrogen, and biochemical oxygen demand (BOD). In the ReCip[®], wastewater is repeatedly pumped back and forth between two gravel-filled basins. This reciprocation creates two treatment environments: an aerobic environment, which promotes reactions such as nitrification and BOD oxidation, and an anoxic/anaerobic environment, which promotes reactions such as denitrification of nitrate into nitrogen gas and methanogenesis. At Cal Poly, the ReCip[®] treated storage lagoon water, and ReCip[®] effluent containing nitrate was returned

to the lagoon, possibly contributing to odor control. Emission of air pollutants is a concern about dairy waste in general (volatile organic compounds, hydrogen sulfide, methane, etc.) and for nitrification-denitrification systems in particular (nitrous oxide).

In the present work, the first detailed air emission study was conducted on ReCip[®].

Emissions of air pollutants were measured with flux chambers during different seasons, and, simultaneously, the water quality within the pore volume of the gravel beds was measured to explore whether pore water quality correlated to air emissions. These air emissions studies were performed within a yearlong study of overall ReCip[®] treatment performance. Water quality constituents measured were pH, alkalinity, temperature, dissolved oxygen (DO), total ammonia nitrogen (TAN), soluble nitrogen, soluble non-purgeable organic carbon, nitrite, and nitrate. During the submerged phase of the reciprocation cycle, pore water DO generally declined from 1-2 mg/L to <0.1 mg/L, while TAN declined and nitrate accumulated, although total nitrogen also declined due to denitrification. The extent of denitrification was correlated to influent BOD loading. The average removals by the ReCip[®] were 93% TAN, 61% CBOD₅, 74% TKN, and 57% TSS. A simple CBOD₅ removal model was developed that described and predicted CBOD₅ removal in the system.

Key air pollutants emitted by the ReCip[®] and their annual mean concentrations were nitrous oxide (0.74 ppm), ammonia (0.15 ppm), and methane (3.85 ppm). The air emission potential of the lagoon water influent was compared to that of the ReCip[®] effluent. The decreases in emission potential were 82% for ammonia, 93% for methane, and 99% for hydrogen sulfide. The average masses emitted (g emitted/kg loaded into

system) by the ReCip[®] were 1.7 g N₂O/kg N, 0.15 g NH₃/kg N, 2.1 g CH₄/kg CBOD₅, 1.0 g ethanol/kg CBOD₅, and 0.004 g H₂S/kg CBOD₅.

ACKNOWLEDGMENTS

My family – I couldn't have done this without all of your love and support. Thank you all. Especially thanks to Pricilla who made many adventurous trips out to the dairy with me and helped me every step along the way.

Dr. Tryg Lundquist – You have been an amazing advisor and helpful friend over the last few years and I am grateful for all of your patience and support.

Dr. Tracy Thatcher – Thank you for teaching me how to write technical documents. It has made the writing process much easier.

Dr. Bruce Golden – Thank you for your help with coordinating dairy and ReCip[®] operations together.

USEPA, Region 9 – Provided funding for the ReCip[®] pilot plant construction via Sustainable Conservation, Inc.

Joe Choperena, Sustainable Conservation, Inc. – Thank you for your outstanding support of this project in all ways.

Dr. Les Behrends – Thanks for inventing this technology and giving us advice when we needed it.

Drs. Frank Mitloehner and Yong Zhao, U.C. Davis – Thank you for all your work in planning and executing the air quality testing.

Tennessee Valley Authority – TVA licensed the technology for use at Cal Poly.

Doug Kuentzel, Cal Poly Facilities – Thank you for helping to coordinate with the personnel we needed for construction.

Craig Stubler, Earth and Soil Science Department – Thank you for analyzing our sludge samples.

Rich Silacci, Cal Poly Herd Manager – Thanks for helping to communicating dairy operations with us so that both of our operations would run smoothly.

Jason – You made working on this project easy. When times got tough, you got tougher. You were the perfect man for the job and it was awesome working with you.

Paul, Kyle, Adam, Neal, and Sean – You guys all got dirty with us out at the dairy. We thank you for the blood and sweat that was spilt on the battleground we call the dairy.

Ian, Ruth, Dan, Mike, Maggie, Ashwini and many other lab mates – You guys made it fun to work in the lab. It was awesome hanging out with you guys.

ENVE Department Staff – Thank you Kay, Ron, and Xi. I found myself constantly going to you for help with any and everything and you were always happy to help.

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1. Introduction

1.1 Nutrient problems in agriculture

Agricultural non-point source pollution has been found to be the leading source of water quality problems in surface water and the second leading source of pollution in ground water in the US (USEPA 2005). Runoff from agriculture will contain excessive nutrients (such as nitrogen, phosphorus, potassium, etc.) if cropland is not managed properly.

These nutrients can cause eutrophication of rivers and lakes. Groundwater is particularly susceptible to nitrogen contamination. Nitrate can cause methemoglobinemia in infants when it leaches into groundwater aquifers.

Dairies in the San Joaquin Valley have steadily become more concentrated with cows over the last three decades, meaning more manure is produced but there is less land to spread it on (Hogle 2008). When the cropland available at a dairy is less than required by the CVRWQCB, the main options are exportation of the nutrients to other farms or decreasing herd size, and, in some cases, neither of these options will be physically or economically possible. A new California regulation limiting the application of manure nitrogen to cropland has led to a search for economical means to remove excess nitrogen from dairy wastewater. This regulation requires nutrient management plans for all dairies, resulting in application of less manure per acre of cropland for many dairies.

1.2 Treating nutrient rich wastewater

Wetlands can be particularly appropriate for wastewater treatment in locations that have minimal operator attention because the routine operational burden is minimal. However,

subsurface wetlands can have low nitrification rates due to low dissolved oxygen concentrations (Behrends et al. 1996, USEPA 1993). A new type of subsurface wetland (or biofilm reactor) has been developed by the Tennessee Valley Authority (TVA) that achieves aeration by alternately draining and filling subsurface-flow constructed wetland basins to draw air into contact with biofilm on rock aggregate. The size of this system to treat a full-scale dairy will be on the order of acres. This system is named ReCip[®], and it has been used to effectively treat a variety of wastewaters—swine, aquaculture, industrial, and domestic wastewater (Rice 2005, Behrends 2006).

More specifically, the ReCip[®] is a fixed-film bioreactor that creates two treatment environments: an aerobic environment to allow ammonium to oxidize into nitrate and an anoxic/anaerobic environment to allow nitrate to be reduced into nitrogen gas. It creates these two environments in the same reactor by reciprocating water back and forth cyclically between two separate wetland basins. A benefit of reciprocation is that the nitrate generated from nitrification can be directly exposed to influent lagoon water, removing BOD in conjunction with denitrification. Denitrification reactions require BOD to be available, using this carbon source as an electron acceptor to reduce nitrate into nitrogen gas. Nitrification does not take place until the BOD is low enough to allow nitrifying bacteria to oxidize ammonia. The growth of nitrifying bacteria is limited at DO concentrations below 1 mg/L (Hochheimer et al. 1991). Heterotrophic bacteria (BOD consumers) can out-compete nitrifying bacteria for DO if there is an excess of BOD available. Hence, there has to be a small concentration of BOD first so that nitrification can take place. After nitrification, there needs to be a large enough concentration of BOD

available so that denitrification can take place. This is why maintaining an optimal CBOD/TAN ratio is important in achieving total nitrogen removal.

1.3 Dairy air quality

Dairy wastewater is conventionally treated or stored in anaerobic lagoons which break down organic matter and release methane and hydrogen sulfide (H_2S). Incomplete organic matter degradation can allow the release of volatile organic compounds (VOCs). Ammonia contributes to malodors when it volatilizes from these lagoons.

Livestock production is the leading contributor of ammonia air emissions in the U.S. (Battye 1994, Arogo 2006). Ammonia is emitted during many livestock operations including emissions from wastewater storage lagoons (Aneja et al. 1999). Emissions of ammonia occur in dairy wastewater storage lagoons from the decomposition of organic matter as well as from volatilization directly from an uncovered lagoon (Arogo et al. 2006). Volatilization of ammonia is a function of the concentration of NH_3 in the wastewater as well as temperature and wind speed. Removing ammonia using biological nitrification-denitrification reduces emissions of ammonia drastically. Another air pollutant emitted by dairies is nitrous oxide (N_2O). It has been noted that nitrous oxide emissions from bioreactors that retain high concentrations of nitrite are typically higher than they are in bioreactors that have low concentrations of nitrite (Ahn et al. 2010). This is because nitrite can be denitrified directly to N_2O gas (Ruiz et al. 2006). Nitrite is an intermediate compound in the nitrification of ammonia to nitrate and can be found at high concentrations in reactors that favor incomplete nitrification-denitrification, which is usually caused by chronically low dissolved oxygen concentrations. Nitrite accumulation

in a nitrification-denitrification bioreactor has been found to increase nitrous oxide emissions, especially when coupled with low organic carbon concentrations (Alinsafi et al. 2008). It is important to identify the operational parameters that would maintain low concentrations of nitrite in any nitrification-denitrification reactor to keep N_2O emissions to a minimum.

1.4 Present work

The pilot-scale ReCip[®] system described here has been evaluated in this study for its treatment performance of dairy wastewater. This system is designed to work in tandem with conventional dairy wastewater storage lagoons, which is how the system at Cal Poly was designed. The specific objectives of this research were to describe the water quality at different locations and depths within the gravel bed of the bioreactor with regards to several water quality constituents: $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, TAN, SN, SNPOC, temperature, DO, pH, and alkalinity. Water samples were collected during air quality monitoring sessions to determine if biological nitrification was the main removal mechanism of ammonia as opposed to ammonia volatilization. It was also desired to determine the impact of varying organic loading rates had on the water quality within the gravel bed. Another purpose of this work was to describe the air quality being emitted by the ReCip[®] and how removing different constituents from the waste stream would impact overall air quality.

The ReCip[®] was designed to work in tandem with conventional lagoons which are already in place. The ReCip[®] allows nitrification reactions to take place, turning ammonia into nitrate. Although much of this nitrate is denitrified into nitrogen gas within the reactor, some nitrate can be discharged into the storage lagoon. This nitrate is

expected to denitrify under the anoxic/anaerobic conditions of the lagoon. Bacteria prefer to reduce nitrate into nitrogen gas rather than reduce sulfate into hydrogen sulfide, which normally occurs in anaerobic storage lagoons. Due to the added nitrate, more nitrogen removal will take place in the lagoon and less hydrogen sulfide will be produced. This should help reduce malodors emitted by the lagoon. Although nitrate is measured in the effluent of the ReCip[®], it is actually removed after it enters the lagoon, so total nitrogen removal measured from the ReCip[®] does not account for all of the nitrogen that is removed from by the entire process(ReCip[®] + lagoon) . Total Kjeldahl Nitrogen (TKN) removal is a good indicator of overall nitrogen removal from the ReCip[®] plus lagoon system, because it measures total nitrogen minus nitrate and nitrite.

2. Methods

2.1 Monitoring Plan

ReCip[®] influent and effluent water samples were analyzed for many constituents, described later. In addition, pore water analysis and air emissions analysis studies were conducted three times during 2010, in June, September, and December. The goals were to (1) estimate air emission rates, with nitrous oxide and ammonia being particular concerns, (2) discern if seasonal temperature affected pollutant emission rates, and (3) discover if there were any correlations of water quality to air emissions (e.g., nitrite accumulation corresponding to nitrous oxide concentrations).

Air pollutants emitted by the ReCip[®] were measured using permanent flux chambers installed at several locations in the gravel beds. Each flux chamber consisted of an 18.9-

L bucket with the bottom cut off. Each bucket was buried up to its lip in the gravel bed. The bucket lids were outfitted with gas ports, as described later. While air quality measurements were being made with a flux chamber, the water column within the gravel bed near the flux chamber was sampled at different depths.

2.2 System Specifications and Mode of Operation

The ReCip[®] system was located at the Cal Poly San Luis Obispo dairy. The system was comprised of two concrete basins. Each basin had dimensions of 11.0 m x 6.1 m x 1.3 m, and each basin had a sump with an area of 0.83 m². Each sump held a timer-operated pump (0.5 HP, Aquatic Ecosystems, Apopka, Florida) that was used to drain the basin.

Figure 1 shows a simplified plan view of the ReCip[®] system. Influent water entered the system at Point A in six pulses evenly-timed throughout the day. Effluent was discharged in pulses by overflowing a V-notch weir at Point C whenever Basin 2 was full.

Figure 1. Simplified plan view of the ReCip[®] system (Kane 2010). (A) Influent lagoon water enters the ReCip[®] via a standpipe; (B) Location of sump pumps; (C) Effluent weir box.

Each basin had five rows of septic tank leach field chambers anchored to the basin floor, which permitted sludge to migrate through the chamber gratings. The chamber rows connected to sludge clean-out ports, although no sludge clean-out has been performed. Standpipes (10-cm diam.) to monitor sludge layer thickness were installed through the roofs of the chambers (**Figure 2**).

Rock aggregate was layered on top of the chambers as a substrate for bacterial biofilms. The lowest layer consisted of 30 cm of greywacke cobblestone (15-25 cm diameter) under 23 cm of crushed granite rock (5-10 cm diameter), with a top layer of 64 cm of crushed granitic rock (2-4 cm diameter). The porosity of rock aggregate was measured to be about 0.40, while the porosity of the tank including other void spaces, such as the

leach field chambers, was calculated (using the amount of water needed to fill the basin) to be 0.49.

Figure 2 shows a cross sectional view of the ReCip[®] basin with the three sampling pipes used to collect pore water samples and a flux chamber. This combination of sampling pipes and flux chamber was installed at each of five locations throughout the basins. The sampling pipes were set at three different depths within the gravel bed: 18, 46, and 81 cm from the maximum water surface level. The larger pipe used for sampling the lowest depth was a 10-cm diameter PVC pipe. The other two sampling pipes were 2.5-cm diameter steel pipes.

Figure 2. Cross sectional view of a portion of the ReCip[®]. The two dotted lines represent the high and low water levels. The trapezoidal shape on the basin floor is a leach field chamber for future sludge clean-out. The sampling pipe that comes through the roof of the chamber was used for sampling the lowest depths of the ReCip[®] as well as measuring sludge buildup. The two vertical lines represent steel pipes used to sample pore water within the gravel bed. The flux chamber is an 18.9-L bucket with the bottom cut off.

Wastewater in the ReCip[®] was reciprocated between the basins on a 2-h cycle. The water was pumped from one basin to the other for 25 minutes, lowering the water level of the first basin from 91 cm to about 15 cm and raising the water level in the second basin from 15 cm to 91 cm. Once the water was reciprocated, pumping stopped for the remainder of the hour, or 35 minutes. After this rest period, the water was reciprocated back to the first basin, with the pumping taking 25 minutes, followed by another 35 minutes of rest. At this point, a 2-h cycle had been completed. This reciprocation pattern was continuous, with the 2-h cycle repeating twelve times per day.

Influent wastewater was pumped from the lagoon to the ReCip[®] using a Flex-i-liner[®] rotary peristaltic pump (Vanton Pump and Equipment Corp., Hillside, New Jersey). Lagoon water was delivered in six pulses throughout the day, each pulse delivering 1.42 m³ (375 gal) over the course of one hour for a total of 8.52 m³/d (2,250 gal/d). Water was discharged back into this lagoon. Due to mechanical failure of the Flex-i-liner[®] pump, a 0.5-HP submersible sump pump (Flotec, Model FPOS3200A) was used towards the end of the study. This pump provided a flow rate of 4 gpm and was timed to be on for 48 minutes out of every two hour cycle, yielding a flow rate of 8.7 m³/day (2,300 gpd).

The ReCip[®] was operated with approximately 38 m³ (10,000 gal) of wastewater in the basins, a volume that was used to calculate the theoretical hydraulic retention time (THRT). The average daily influent flow during 2010 was 8.7 m³/d (2,300 gpd), yielding a 4.4-d THRT. Previous tracer studies revealed the mean hydraulic residence time (MHRT) to be 1.8 d (Kane 2010).

During this study, the dairy had an average of about 330 animal units housed in free-stall barns (defined here as one animal unit = one adult cow or two young cows; 230 adult cows and 200 young cows comprising the 330 animal units). Un-flushed soil exercise pens were also available to the animals. The dairy wastewater went through several pretreatment steps before arriving in the storage lagoon. Water first flowed through the free-stalls, collecting waste from the cows four times per day. This wastewater then flowed through a grate and a sand trap. It was then pumped through an inclined screen where fibrous material was separated for composting. The liquid waste from this screen drained to a settling basin for fine solids removal and then into a storage lagoon. A total of 30 m³/day (8,000 gpd) of tap water was used to flush the milking parlor, and, four times per day, 57 m³ (15,000 gal) of lagoon water was flushed through the free-stall barns. All of these flows entered the storage lagoon that was the wastewater source for the ReCip[®]. The largest input of fresh water into the lagoon was rainfall and storm water during the winter months.

2.3 Experimental Procedure

2.3.1 Air Emission Sampling Procedure

The flux chambers, to be described fully below, were connected to three analyzers. An INNOVA 1412 (California Analytical Instruments, Orange, California) was used to measure NH₃, N₂O, CO₂, methanol, and ethanol. A hydrogen sulfide and sulfur dioxide analyzer (TEI 450i, Thermo Fisher Scientific, Franklin, Massachusetts) was used to measure H₂S and SO₂. A direct methane and non-methane hydrocarbon analyzer (TEI 55C, Thermo Fisher Scientific, Franklin, Massachusetts) was used to measure CH₄.

Five flux chambers were installed in the ReCip[®] adjacent to the following structures: influent standpipe, Basin 2 sump, effluent weir box, and on either side of the central wall opposite to the sumps. Thus, Basin 1 had two air sampling points, and Basin 2 had three sampling points. Although each flux chamber was sampled during the June study, only the influent, effluent, and sump flux chambers were sampled during the subsequent studies because the time of sampling each flux chamber was increased from two hours to twenty four hours.

The flux chambers were buried about 30 cm into the gravel bed to collect samples from within the reactor and prevent ambient air from mixing with the sample air. Each of the flux chambers consisted of an 18.9-L (5-gallon) bucket (28-cm average diameter, 37-cm height) with the bottom cut off. A lid was placed on top of the bucket with two polyvinyl tubes connected with tank adapters through the lid: one to extract air samples and the other to insert flush gas (medical grade air) during the period of each reciprocation cycle when the bottom of the flux chamber was sealed by water. When the water level was at or above the bottom of the bucket, flush gas was used so that the minimum flow rate required for the air quality measurement machines could be met. The water level surpassed the bottom of the bucket about five minutes before the end of the pump in phase, and fell below the bottom of the bucket about five minutes after the start of the pump out phase. While the flush gas was on, a small vent was opened using an automated solenoid valve to allow excess gas to be vented off. The concentration of each constituent was then calculated knowing that 3.2 L/min of pollutant free air was being pumped into the chamber while the water level was above the bottom of the bucket. In

June, each chamber was sampled for 2 h at 30-sec intervals. In September and December, each chamber was sampled for 24 h to discern any diel variation.

For this thesis, the air emission potential of the influent and effluent waters was defined as the mass of a constituent that could be sparged from a small volume of water over 24 h. In the procedure, 7.6 L of wastewater was placed in an 18.9-L bucket. The bucket was sealed with a flux chamber lid, such as was described above. One tube passing through the lid was used to collect air samples while the other was placed on the bottom of the bucket to sparge the water with 5 L/min of medical-grade air. A vent allowed excess air to escape the bucket. This procedure was performed during the September and December studies.

2.3.2 Calculation of Flux

The mass flux of air emissions was calculated during the pump-in phase of the reciprocation cycle, when pore space gas was “exhaled” from the ReCip[®]. This phase began as water began to be pumped into a nearly empty basin. This pumping continued for 25 minutes until the basin was filled. For the present analysis, the flux from the other reciprocation phases (full rest, draining, and empty rest) were assumed to be negligible. The maximum water surface was covered by at least 15 cm of gravel at all times, which protected the water surface from wind.

The flux during the exhale phases was calculated by multiplying the flux chamber gas concentration during exhale by the volume of air pushed out of the basin by the rising water (i.e., “Exhale Volume” in Equation 1). The pollutant concentration used in the

calculation of flux was the average of all data from all three (five during the June study) chambers during their respective exhale phases.

In Equation 1, molar volume (MV) is based on the temperature during sampling, molecular weight (MW) depends on the constituent being considered, and the 24 events per day represent the 24 times that a basin exhales each day.

$$\frac{Conc.(ppm)}{1000000} * \frac{Exhale\ Volume(L)}{MV\left(\frac{L}{mol}\right)} * MW\left(\frac{g}{mol}\right) * 24\left(\frac{events}{day}\right) = Flux\left(\frac{g}{day}\right) \quad (1)$$

2.3.3 Pore Water Sampling Procedure

Pore water samples were collected during the three air sampling sessions in June, September, and December 2010. The samples were collected near the flux chamber being operated. Steel pipes were installed in the gravel bed for the purpose of extracting water quality samples at different depths next to each flux chamber. These steel pipes allowed samples to be extracted at 18, 46, and 81 cm below the water surface. Water samples were extracted using a peristaltic pump and 1-cm diameter polyvinyl tubing. The flow rate of water being pumped through the peristaltic pump was set at 500 mL/min to disturb the pore water field as little as possible while maintaining a high enough flow to collect all of the required measurements in a timely fashion. The tubing was flushed before sampling to remove residual liquid. A 90° PVC elbow was connected at the end of the polyvinyl tubing to act as a small upflow sink for DO and pH electrodes, thereby eliminating the chance that atmospheric oxygen would unduly affect the measurement. Once a stable DO and pH reading were obtained, the probes were removed from the 90° elbow, and 400 mL of sample were collected in a 500-mL plastic sample bottle and stored on ice in a cooler for 1-2 h before sample processing.

Alkalinity and pH were measured because alkalinity is produced during denitrification and is consumed during nitrification, making it an additional indicator of removal mechanism. In addition, maintenance of at least 80 mg/L of residual alkalinity is necessary to prevent decline pH during nitrification (Tchobanoglous et al. 2003).

2.4 Water Quality Analyses

Table 1 lists the water quality analysis methods used to measure each constituent.

Table 1. Water quality analysis methods used in the present study. Method numbers refer to Standard Methods (APHA, 2005).

Parameter	Method
<u>Major Organics</u>	
Total & volatile suspended solids	Fisherbrand Glass Fiber G4 Filters (Methods 2540-B, 2540-D, 2540-E)
Total, carbonaceous, soluble and soluble carbonaceous oxygen demand	5-day, 20°C, Fisherbrand Glass G4 Filters (Method 5210-B)
Total & soluble non-purgeable organic carbon	Total Organic Carbon Analyzer Shimadzu Model: TOC-VCSH
<u>Nutrients</u>	
Nitrate and nitrite	Dionex Ion Chromatograph Model: DX-120 (Method 4110-B). Used Dionex 20-µm filter caps and 0.22-µm Millipore Express PLUS® Membrane Filters.
Total ammonia nitrogen	Orion 9512 Ammonia Selective Electrode (Method 4500-NH ₃ -D)
Total Kjeldahl nitrogen	Macro-Kjeldahl Method (Method 4500-N _{org} -B)
Total & soluble nitrogen	Total Nitrogen Measuring Unit Shimadzu Model: TNM-1.
<u>Other Constituents</u>	
Alkalinity	Acid Titration (Method 2330-B)
Dissolved Oxygen	Membrane potential (Method 4500-O-G)

Quality control samples processed in each sample run included blanks, duplicates, splits, and matrix spikes. All methods included these quality control samples except alkalinity, pH, and dissolved oxygen measurements. If matrix spikes were outside $\pm 15\%$ of the expected value, if duplicates or splits were outside $\pm 10\%$ of expected, or if blank results were more than recommended by Standard Methods, then the data were excluded or, when possible, re-analyzed. Samples were prepared and stored according to APHA (2005) recommendations. SN samples were filtered through 0.45- μm Express Plus[®] membrane filters (Millipore, Billerica, Massachusetts), acidified to $\text{pH} < 2$ with concentrated sulfuric acid, and then refrigerated at 4°C until analyzed. These samples were typically analyzed on the day of sampling but sometimes were stored for several days after sampling. Most samples that were analyzed for NO_3^- -N and NO_2^- -N were analyzed on the evening on the sampling date, but some were frozen until later analysis could be performed. Combined nitrate + nitrite results were reported for frozen samples, not individual nitrate and nitrite concentrations since storage may have led to nitrite oxidation.

2.5 Sludge Analysis

To allow for a nitrogen mass balance throughout the system, the amount of sludge that accumulated within the system, as well as the nitrogen composition of the sludge was measured. Sludge accumulation was measured through standpipes that reached the tank floor and extended several inches above the gravel bed. These 10-cm diameter PVC standpipes stood on thin legs to allow sludge to pass through uninterrupted. Each basin had 15 such standpipes, and each standpipe passed through a 10-cm diameter hole in the roof of a leach field chamber. Sludge levels were measured using a peristaltic pump and

1-cm diameter polyvinyl tubing attached to a calibrated 2.5-cm diameter PVC pipe. This calibrated pipe was slowly lowered (about 0.5 cm/sec) into a standpipe until sludge began to be pumped to the top of the standpipe. This effectively measured the distance from the top of the standpipe to the top of the sludge layer. Sludge depth was then simply calculated as the length of the standpipe minus the measured distance to the top of the sludge layer. Any sludge accumulated in the gravel pore spaces was not sampled. It was assumed that the frequent draining and filling of the basins washed most sludge to the floor of the basin where it could be measured via the method described above.

Although sludge accumulation was monitored in every standpipe, sludge samples were only extracted from two locations: the standpipe nearest where the influent entered the system and the standpipe nearest where the effluent left the system. Approximately 400 mL of sludge was collected from each of these standpipes on a near monthly basis. Sludge samples were collected evenly across the area of the standpipe using a peristaltic pump, and they were stored at -20°C until analyses could be performed.

The sampled sludge was analyzed for total and volatile solids (TS and VS), as well as for carbon and nitrogen content using the Dumas Combustion Method (Vario MAX CNS Macro Elemental Analyzer, Elementar Americas Inc., Mt. 14 Laurel, New Jersey). Total nitrogen in the sludge layer was calculated using the total estimated volume of the sludge in the basin, the solids content of the sludge (TS, mg/L), and the mass percentage of sludge as nitrogen (% N). Sludge volume was calculated by measuring the sludge heights from 15 standpipes spread across each basin. An average basin sludge height was used to calculate the volume of sludge in that basin. If the sludge layer was not detected (i.e. sludge layer too thin to get a consistent sample), it was assumed to have a 0.5 cm

height. This total sludge nitrogen estimate was used in a nitrogen mass balance on the system.

2.6 Regression Modeling

SigmaPlot 12.0 (Systat Software, Inc.) was used to produce linear and non-linear models for descriptive and predictive testing of CBOD₅ removal. The variables used in these models included CBOD₅ influent concentration and effluent temperature. Effluent temperature was used because it represented the temperature within the reactor.

Temperature was included in the non-linear model through an Arrhenius temperature correction factor. Hydraulic residence time was not included as a variable because it was held relatively constant throughout the study, so no influence could be determined.

Because DO concentrations were almost constantly changing in the ReCip[®] basins as water levels rose and fell, DO could not be used conveniently in modeling, although it could have been the limiting factor for both BOD and TAN removal.

Following the general method of Kane (2010), who modeled TAN removal in the ReCip[®], one linear model and one non-linear model were used to describe CBOD₅ removal. The linear model is as follows:

$$\Delta C = \alpha C + \beta \quad (2)$$

where

ΔC = CBOD₅ concentration removed in the reactor (mg/L)

C = Influent CBOD₅ concentration (mg/L)

α, β = fitted parameters

A non-linear model was examined as follows:

$$\Delta C = (\alpha C + \beta) * k_T^{T-20} \quad (3)$$

where

k_T = Arrhenius temperature correction factor

T = Effluent temperature ($^{\circ}\text{C}$)

In Equation 3, a temperature of 20°C is used, which is standard in temperature correction factors.

The models were judged on their ability to both describe and predict the data set. For the prediction testing, the models were fit using only the first half of the data set. These fitted models were then used to predict the second half of the data set. The accuracy and precision of the predictions was evaluated by observation of predicted-vs.-measured plots.

Data used in this modeling study was from the period of February 24, 2010 through December 30, 2010. Although sampling routinely took place on a weekly basis, samples were not collected every week due to extreme storms, pump failure, etc. Also decreasing the data set for modeling was incomplete analysis (i.e., missing influent CBOD_5 and/or effluent CBOD_5 and/or temperature data). Because of incomplete data, only twenty-two data points were included from the 40-week modeling period.

2.6.1 Denitrification Model

Simple linear regression analysis was performed to find a relation between denitrification rate (mg/L-d) and several parameters: nitrification rate (mg/L-d), influent CBOD_5 concentration (mg/L), the ratio of influent CBOD_5 concentration/influent TAN concentration (mg/mg), and effluent temperature ($^{\circ}\text{C}$). The data set was tested to see if it followed a normal distribution using the Shapiro-Wilk normality test. Equation 4 shows

the simple linear regression equation used to find any correlation between the aforementioned data.

$$\Delta N/\theta = \alpha X + \beta \quad (4)$$

Where

$\Delta N/\theta$ = Denitrification rate (mg/L-d)

X = Explanatory variable (nitrification rate, inf. CBOD concentration, etc.)

α, β = fitting parameters

3. Results

Both water quality and air quality results from the ReCip[®] operation are presented. Air pollutants emitted by the ReCip[®] were measured using flux chambers buried in the gravel bed once during each season (June, September, and December 2010). Each flux chamber was measured continuously for 2 hours in the June study and 24 hours in the September and December studies so that average values would be representative of the diel emission rates. While each flux chamber was in use, water samples from the pore space next to the flux chamber were collected at three different depths within the gravel bed. Both of these studies took place within a larger yearlong study on the performance (based on weekly influent/effluent water quality data) of the ReCip[®] technology for treating wastewater from flush dairies.

3.1 Summary of the Yearlong Study

The pore water analysis and air quality studies were conducted within a yearlong study that measured the water quality entering and leaving the ReCip[®]. Significant removal of nitrogen took place throughout the whole year, as seen by the removal of total nitrogen (TN), TKN, TAN, and SN (**Table 2**). The ReCip[®] was able to remove 93% of TAN, 54% of TN, 74% of TKN, 61% of CBOD₅, and 57% TSS. The pH in the lagoon averaged 7.6 and the pH in the effluent averaged 8.2. Although the mean effluent concentration of NO₃⁻-N was 73 mg/L, the ReCip[®] has discharged effluent with very low NO₃⁻-N concentrations (down to 0.1 mg/L). The low NO₃⁻-N concentration of 0.1 mg/L was measured during December, while the lowest concentration of NO₃⁻-N measured before December was 50 mg/L. This shows that the ReCip[®] is capable of complete denitrification. Future research will determine proper operational parameters for complete denitrification to take place.

Table 2. Mean concentrations (mg/L) of influent and effluent water quality constituents from January 1, 2010 through January 1, 2011. SD indicates one standard deviation; *n* is the number of samples.

	<i>n</i>	Influent		Effluent		% Removal
		Mean	SD	Mean	SD	
Temperature (°C)	37	17.3	4.1	17.4	3.6	-
pH	39	7.6	0.2	8.2	0.2	-
DO	29	0.2	0.2	1.6	0.8	-
TSS	39	1493	300.0	641	201.1	57%
VSS	39	1189	228.6	498	156.9	58%
CBOD₅	30	304	162.3	117	65.4	61%
SCBOD₅	20	167	162.5	21	11.9	88%
NPOC	30	707	217.4	246	113.7	65%
SNPOC	26	277	111.1	147	28.0	47%
Alkalinity*	39	2707	563.8	1351	330.0	50%
TKN	16	328	46.2	84	16.0	74%
TAN	39	215	38.8	15	7.0	93%

NO₃⁻ as N	35	1.3	3.0	73	33.8	-
NO₂⁻ as N	35	0.1	0.6	1.3	1.3	-
TN	26	308	58.5	141	39.0	54%
SN	26	219	44.3	120	45.8	45%
ON	16	110	31.2	65	21.7	40%

* Total alkalinity as CaCO₃

3.2 Seasonal Water Quality Variation

Influent water quality varied throughout the year due to lagoon water surface elevation changes, temperature changes, and a lagoon clean-out in the summer. The average loading rate of TAN was 14.2 g/m²-d, which is approximately 14 times higher than is recommended for conventional surface-flow wetlands for animal wastewater (Payne Engineering and CH2M Hill 1997). At the end of spring, the TAN concentration in the lagoon was around 300 mg/L, which was much higher than the annual mean of 215 mg/L. This high TAN concentration in the influent lagoon resulted in a 19.1 g/m²-d loading rate during the first air quality test in June. The ReCip[®] removed more TAN when higher concentrations of TAN were entering the system (**Figure 3**). The R² from **Figure 3** and **Figure 4** are overstated because of artifactual correlation in the x- and y-axes: influent TAN concentration is used in the calculation of both the x- and y-axes values.

Figure 3. Response of effluent TAN removal to TAN loading on the ReCip[®]. The resulting R^2_{adj} of 0.89 is overstated due to artifactual correlation.

Figure 4. Response of effluent CBOD₅ removal to CBOD₅ loading on the ReCip[®]. The resulting R^2_{adj} of 0.84 is overstated due to artifactual correlation.

3.2.1 Carbon – Nitrogen Ratio

To assess the effect of carbon-to-nitrogen (C:N) ratios on treatment, carbonaceous biodegradable oxygen demand (CBOD₅) was used as a surrogate for organic carbon. In this work, the C:N ratio is defined as influent CBOD₅ concentration divided by influent total ammonia (TAN) concentration. In simultaneous nitrification-denitrification systems, CBOD₅ concentrations must be low enough to allow nitrification but also high enough to fuel denitrification. For example, due to changes in lagoon conditions in December 2010, the C:N ratio in the ReCip[®] influent more than doubled. Effluent nitrate was then virtually eliminated in the ReCip[®] effluent (**Table 3**).

Table 3. Comparison of monthly mean influent C:N ratios and effluent nitrate concentrations. November was excluded due to lack of data.

Season	Influent (C:N)	Effluent NO ₃ -N (mg/L)
March	1.06	78.6
April	1.16	105.2
May	0.69	119.3
June	0.90	99.3
July	0.93	78.1
August	1.60	88.7
September	1.54	87.8
October	1.68	81.7
December	3.54	1.9

The lagoon C:N ratio increased suddenly in December because the ReCip[®] influent was changed from the East Lagoon to the West Lagoon at the Cal Poly Dairy. While the West Lagoon was the main source of feed for the ReCip[®] during the yearlong study, it was drained in July 2010 for sludge clean out. During July-November, the East Lagoon collected all of the dairy wastewater, and an alternate pipeline was built to use this lagoon water as feed. In November, the wastewater flow returned to the West Lagoon, which once again became the source of ReCip[®] influent. The West Lagoon had a higher carbon

concentration than before (~600 mg/L vs. ~1200 mg/L NPOC). The increase in carbon concentration was the only noticeable difference in influent lagoon water quality.

Nitrate was prevalent in the reactor throughout most of the year, with effluent concentrations ranging from 0.1 to 126.2 mg/L NO_3^- -N. The highest monthly average effluent nitrate concentration was measured in May when the C:N ratio was lowest at 0.69. When the nitrate concentration was at its lowest at 1.9 mg/L NO_3^- -N, the C:N ratio was at its highest at 3.54. **Figure 5** shows nitrate concentration in the effluent as a function of the C:N ratio being fed to the ReCip[®]. Each point is from monthly mean data (Table 3).

Figure 5. Relationship between ReCip[®] influent C:N ratio and effluent nitrate concentration. Each point represents the mean from one month (November is excluded due to lack of data).

3.3 Nitrogen Mass Balance

To estimate the nitrogen mass denitrified, a mass balance was calculated using data from April 2010 through December 2010. The input mass of nitrogen was the sum of nitrite and nitrate, ammonia, and organic nitrogen (the latter calculated as TKN – TAN). Output and accumulated nitrogen was the sum of nitrite and nitrate, ammonia, organic nitrogen, and settled nitrogenous sludge. Nitrous oxide (0.18% of total N removed) and ammonia gas (0.02% of total N removed) were considered negligible. The sludge accumulation rate was not steady perhaps due to consolidation, migration of solids between basins, and sampling error caused by patchiness in the sludge layer (**Table 4**).

Table 4. Sludge accumulation in the ReCip[®] over time.

Date	Basin 1		Basin 2	
	Height (cm)	Volume (m ³)	Height (cm)	Volume (m ³)
April	5.33	3.57	1.90	1.27
May	9.07	6.07	3.00	2.01
July	10.00	6.69	2.97	1.99
August	10.40	6.96	3.27	2.19
October	9.13	6.11	4.73	3.17
December	9.20	6.16	7.13	4.77

Although the nitrogen loading into the system varied from month to month, the ReCip[®] was capable of consistently removing 50% of the total nitrogen entering the system (**Figure 6**).

Figure 6. Monthly nitrogenous mass balance for May through December 2010. November is missing due to lack of data. During this period, 601 kg of nitrogen entered the system while 292 kg of nitrogen were accounted for leaving the system. The 51% nitrogen removed from the system was presumed to leave as nitrogen gas as a result of denitrification of nitrate.

The highest nitrogen removals occurred in June and December. June had a high removal rate presumably because it had a high average temperature (21°C) and had the highest nitrogen loading into the system. Bacteria are more active during warmer periods than they are during cooler periods. December had a high removal rate because denitrification was approaching 100% nitrate removal. Close to complete denitrification was prevalent during periods when the influent had high concentrations of organic carbon, which is required to drive denitrification. **Figure 7** shows the mass balance from the two temperature extremes, June and December. The black arrows show the amount of nitrogen that was removed from the system, while the dashed arrow shows the amount of

nitrogen that was presumed to be removed from the ReCip[®] and lagoon in conjunction. This removal included the nitrogen removed in the ReCip[®] plus the nitrate left in the water discharged to the lagoon. This nitrate was presumed to quickly denitrify in the lagoon, which was anaerobic. In December the potential nitrogen removal and the actual removal were about the same because the nitrate was denitrified within the reactor.

Figure 7. Mass balance for summer and winter. The black arrow shows the total amount of nitrogen removed from the system presumed as nitrogen gas. The dashed arrow shows the amount of nitrogen that is potentially removed due to denitrification in the anaerobic storage lagoon.

3.4 Air Emission Measurement

Air pollutant emissions were compared seasonally at three different locations throughout the system: one where the influent enters the system (Spot 1), one about half way through the reactor near the central recirculation sump (Spot 3), and one next to the

effluent weir box where water exits the system (Spot 5). Averages among these three locations were used to determine overall mass emission rates from the system. Although variables such as TAN and NO_3^- concentrations in the tank, influent water quality, and temperature were different for each study, nitrogenous emissions were reduced as temperature decreased. This trend was not consistent at each individual flux chamber, but is rather a general observation of system averages (**Table 5**).

During December, the organic carbon concentration in the influent lagoon water was approximately double normal. When this extra carbon was introduced to the system, NO_3^- -N was measured at very low concentrations in the effluent. Denitrification was occurring at a higher rate than during most of the study, and emissions of N_2O gas were the lowest recorded from this bioreactor. As previously stated, N_2O emitted by bioreactors is typically higher in reactors that favor accumulation of nitrite (Ahn et al. 2010). Nitrite concentrations in the September study averaged 4.5 mg/L NO_2^- -N and had higher N_2O emissions than in December, when NO_2^- -N was not detected.

Table 5. Mean concentrations of select constituents being emitted by the ReCip[®] during each air monitoring session. To the right are the average concentrations of TAN and NO_3^- -N in the water column next to the flux chamber as well as the average water temperature.

Date	N_2O (ppm)	CO_2 (ppm)	NH_3 (ppm)	CH_4 (ppm)	TAN (mg/L)	NO_3^- (mg/L)	Avg T (°C)
June	1.17	696	0.32	2.44	12.3	43.6	23.8
September	0.72	840	0.11	3.50	11.8	88.6	21.9
December	0.33	706	0.03	5.62	10.4	3.1	11.8

The concentration of each pollutant varied considerably during a reciprocation cycle.

The highest concentrations were measured in the reactor when the water level was falling or low, while the biofilms were exposed to air. The concentrations were the lowest when the basin was full and all of the biofilm was submerged (**Figure 8**). During the pump in

phase (from Time 0:00 to Time 0:25), there was some variation in the amount of gas being released by the biofilm. This variation was probably due to different amounts of biological activity at different depths in the gravel bed. Presumably, different compositions of biofilm organisms are selected at different depths. While the basin was drained and the biofilm exposed to the atmosphere, biofilms released gases into their surrounding pore space. As the basin filled, the exhaust gases that the biofilms had discharged were pushed upwards and out of the basin. If the biofilms at the top of the reactor were more active than the biofilms at the bottom, then more gas would be emitted earlier in the fill phase. During the static high water level phase, the concentration shown is the concentration measured minus the background CO₂ concentration in the flush gas, which varied between 335 and 350 ppm.

Figure 8. The concentration of CO₂ emissions over the course of a reciprocation cycle. The highest concentrations occurred when the biofilm was exposed and the lowest when the biofilm was submerged. Twelve cycles were constantly measured over a 24 hour period. Each point seen here was averaged from 12 data points at that specific time in the cycle.

3.6.1 Flux

The flux of air pollutants being emitted by the ReCip[®], the influent lagoon, and the effluent water were calculated. **Table 6** shows how the flux of pollutants coming off of the ReCip[®] varied throughout the seasons, as well as the annual average flux.

Table 6. Flux of pollutants emitted from the ReCip[®] during the pump in phase. These are the averages of three different locations within the tank. Notice that total sulfur emissions (CS) were very small.

Month	EtOH (g/d)	N ₂ O (g/d)	CO ₂ (g/d)	NH ₃ (g/d)	CH ₄ (g/d)	CS (g/d)
June	1.2	0.8	822	0.24	0.9	<0.001
September	0.4	1.0	1117	0.05	2.4	<0.001
December	0.2	0.4	959	0.01	2.9	<0.001
Annual	0.6	0.7	966	0.1	2.1	<0.001

The emissions from sparged lagoon water and ReCip[®] effluent water were compared (**Table 7**) to indicate the extent to which the ReCip[®] changed the emission potential of different pollutants. Ammonia, methane, and total sulfur compounds (CS) rates are all greatly reduced. The ReCip[®] effluent did contain more ethanol (EtOH) than the lagoon, but overall ReCip[®] reduced the air emissions potential of the lagoon water.

Table 7. Average emission potential from September and December studies.

Location	EtOH (g/d)	N ₂ O (g/d)	CO ₂ (g/d)	NH ₃ (g/d)	CH ₄ (g/d)	CS (g/d)
Lagoon Emissions	0.17	1.90	3,665	15.20	16.71	1.44
Effluent Emissions	0.49	1.75	1,618	2.87	1.93	0.01

3.5 Pore Water Quality

Samples were taken at 18, 46, and 81 cm below the water surface within the gravel bed next to the flux chamber that was being used at the time. While the basin was being filled, samples could be collected at 46 cm and 81 cm (labeled as ‘Fill’ in **Figure 9**). Samples were collected at all three depths at the start, middle, and end of the full rest phase. These rest phase samples are labeled in **Figure 9** as the time they were collected using the 24-hour clock. TAN was consumed during the rest phase, and NO₃⁻-N was produced. Typically a basin had a high concentration of DO when water entered the basin but the DO concentrations were reduced rapidly during the rest phase. The initial high DO was due to the large wetted surface area that became saturated with atmospheric oxygen while the basin was drained. This DO was transferred to the bulk water when the biofilm became submerged. Heterotrophic and nitrifying bacteria then quickly consume all of the oxygen to oxidize ammonia and carbonaceous compounds, creating an anoxic environment where denitrification could take place.

Figure 9 displays three stacked bar graphs, representing water quality at the three different depths of a water column sampled in September 2010. The top graph is the closest to the water surface while the bottom graph is closest to the basin floor. The lowest level in the water column contains a high concentration of TAN because the influent pump was pumping lagoon water down to that depth at the time of sampling. Influent lagoon water was pumped into a standpipe that had to flow through the bottom of the reactor before being mixed with the rest of the bulk water.

TAN was removed and NO_3 produced as water was pushed upwards in the water column over more biofilm. These biofilms collected TAN while they were submerged, then, when they are exposed to atmospheric oxygen during the drain cycle, TAN was converted into NO_3 . This NO_3 was then held in the biofilm until it could be released into the bulk water when it was submerged again. TAN concentrations were always higher at the lower elevations and slowly got lower with increasing elevation in the water column. Nitrate has the opposite trend. These patterns were probably due to the biofilm at the different depths having different exposure times to atmospheric oxygen. The biofilm higher in the water column was exposed to atmospheric oxygen more every day so it could nitrify more, while biofilms lower in the water column were submerged more often (and more deprived of DO), so they could denitrify more. Nitrification occurred even during the stagnant rest phase because there was enough DO in the bulk water for nitrification to take place. **Figure 10** shows the equivalent water from **Figure 9** after it was reciprocated into the adjacent basin. This water column was measured near the effluent weir box. The large TAN concentrations at the bottom of **Figure 9** were not seen in **Figure 10** because of the mixing provided by reciprocation. **Figure 11** shows a

water column near the influent location in December 2010. The C:N ratio was much higher during this time, which is probably why low concentrations of NO_3^- -N were measured. Even with the low nitrate concentrations, the same trend still existed with higher nitrate concentrations higher in the water column.

Figure 9. Water column samples taken within the gravel bed in September 2010 where the influent enters the system. At this time, the influent lagoon water was being pumped into the bottom of this water column. This is seen by the high levels of TAN and low levels of NO₃-N lower in the water column. Higher in the water column, ammonia started to be nitrified into nitrate, shown by TAN decreasing with elevation and NO₃-N increasing with elevation. The label 'Fill' represents a sample taken while the tank was being filled with water, which is to say that the water level was still rising. The following three points were all samples taken while the tank was at rest. Each of these represents the approximately same packet of water, which shows ammonia being removed over time.

Figure 10. Water column samples near the effluent weir box. This water was from the same cycle as Figure 9, but it had reciprocated into Basin 2. Notice that the same trend still existed with TAN concentrations higher in the lower sections and nitrate concentrations elevated in the higher sections.

Figure 11. Water column profile for sample in December 2010. Following the influent/effluent data, nitrate was being denitrified, shown here by the dramatic decrease in nitrate compared to earlier studies. Nitrite was not detected in any of the samples taken during December.

3.5.1 TAN Removal Rate in Pore Space

The removal rate of TAN in the pore space was calculated over a static water column as concentration over time (mg TAN/L-min). Equation 5 shows how pore space removal was calculated and expanded to compare to influent-effluent removal. Overall TAN removed in this case represents the TAN removed over one Mean Hydraulic Residence Time (MHRT), which was 1.8 days, according to a tracer study (Kane 2010).

$$\frac{TAN\ removed(\frac{mg}{L})}{min} * MHRT\ (days) * 1440\ (\frac{min}{day}) = Overall\ TAN\ removed\ (\frac{mg}{L})$$

(5)

The data used in the calculation of pore space TAN removal was from the water column near the effluent weir. **Table 8** shows the comparison of the TAN removal calculated from influent vs. effluent data and the TAN removal calculated from the pore space removal. Although the ReCip[®] processes are complex and removal rates are different during different times in the cycle, the data in **Table 8** still confirm that influent vs. effluent removal has a relationship with removal measured in the pore space.

Table 8. TAN removal from influent-effluent data and short term TAN removal measured in the pore space. Pore space removal was calculated with Equation 7.

Month	Influent TAN (mg/L)	Effluent TAN (mg/L)	Inf. – Eff. removal (mg/L)	Pore space TAN removal (mg/L)	% difference
June	286	21	265	285	7.3
September	186	11	175	173	1.1
December	145	12	133	122	8.6

3.6 CBOD₅ Removal Model

Two models were produced to determine if they could describe the data set (**Table 9**).

Equations 2 and 3 were both found to describe the data set well. They used influent CBOD₅ concentration and temperature (temperature is for Equation 3 only) as the explanatory variables and CBOD₅ removal as the response variable. The best equation for describing the data set was Equation 3 because it adjusted for temperature and had an additional fitted parameter. The temperature range of this study was from 12°C to 25°C. The ability of the model to predict removal outside of this range is unknown.

Table 9. Descriptive model statistics including coefficient of determination (R^2_{adj}), Arrhenius temperature correction factor (k_T), and fitting parameters (α , β) for the one-year data set. The R^2_{adj} values are from correlation of measured CBOD₅ removal versus calculated CBOD₅ removal.

Equation	Model	R^2_{adj}	α	β	k_T
2	$\Delta C = \alpha C + \beta$	0.87	0.861	-73.37	-
3	$\Delta C = (\alpha C + \beta) * k_T^{(T-20)}$	0.90	0.868	-68.04	1.03

Predictive testing was done to help validate the models. The R^2_{adj} value for the fitted and predicted versus measured CBOD₅ removals for Eq. 2 was 0.87 as opposed to 0.90 for Eq. 3. This result was found from using the first half of the data set to produce a model used to predict the second half of the data set (**Figure 12**). Equation 3 was recommended for future use because it has a temperature correction factor, which will presumably make it more accurate in other climate regions.

Figure 12. Fitted and predicted values of CBOD₅ removal plotted against measured values of CBOD₅ removal using Equation 3.

Each model had a negative value for the intercept, indicating that a minimum concentration of CBOD₅ is needed before net removal could take place. Dissolved oxygen was not incorporated into this model due to its transience during the submerged phase of each reciprocation cycle. Bulk DO measurements were taken through several cycles during the pore water analysis study, which showed that the water goes from aerobic to anoxic during every fill/drain cycle.

3.7 Denitrification Correlation

A model of denitrification rate was developed, but it could not describe the data (**Table 10**). Nitrification rate had a low p-value statistic but did not pass the Shapiro-Wilk normality test, meaning that the effect of nitrification rate on denitrification rate could be detected, but the analysis could be improved by transforming the data. Because the R^2_{adj}

was poor, further analysis was not conducted in this study. A correlation between nitrification rate and denitrification rate was explored because the rate and extent of denitrification was tied to nitrification as the source of nitrate. A carbon-nitrogen ratio was also explored because it is known that the right amount of carbon and nitrogen must be present to nitrify and denitrify in the same reactor.

Table 10. Linear correlation tests performed to relate denitrification rate to several other water quality characteristics. These did not show any strong correlation. The nitrification rate and temperature correlations failed the Shapiro-Wilk normality test.

	Denitrification Rate (mg/L-d)	Nitrification Rate (mg/L-d)	CBOD inf (mg/L)	CBOD/TAN (mg/mg)	Temp. (°C)
Mean	28.5	44.5	303.7	1.5	18.2
Std dev	7.9	8.8	162.3	0.8	3.5
<i>n</i>	34	35	30	30	29
R^2_{adj}	—	0.442	0.195	0.032	0.192

Denitrification rates varied substantially without any obvious pattern throughout the year. Although the denitrification rate was not much higher in December than it was throughout the year, near complete denitrification occurred, shown by low nitrate concentrations in the effluent. These low effluent nitrate concentrations were probably caused by a slightly higher than normal denitrification rate and lower TN concentrations in the influent.

4. Conclusions

Nitrogen and carbon removal were prevalent in the reactor throughout the yearlong study. Nitrogen (TN) removal averaged 54% and carbon (NPOC) removal averaged 65% over the study. Solids were removed via settling within the reactor and characterized by sludge accumulation measurements. Air emissions were measured during three separate events during three different seasons. It was found that the ReCip[®] significantly reduced

the emissions potential of ammonia, hydrogen sulfide, and methane compared to lagoon water. The amount of nitrogen and carbon within the gravel bed were not good indicators of pollutant emission rates. Water temperature was the only characteristic that appeared to have an impact on air pollutant emission rates: emission rates were lower when temperature was lower.

Two CBOD₅ models were developed and compared for their effectiveness at describing the data set. A non-linear model was selected that incorporated effluent temperature and influent CBOD₅ concentration as explanatory variables and CBOD₅ removal as the response variable. This model might be useful to describe CBOD₅ removal in larger ReCip[®] systems.

Reciprocation provided sufficient aeration to allow for consistent removal of TAN and CBOD₅ throughout the study. Sludge accumulated at a moderate rate and will continue to be measured to better assess the lifetime of the ReCip[®] technology when treating dairy wastewater.

4.1 Future Research

The next experiment should change operational parameters of the ReCip[®] to measure how the water quality in the effluent would change. Parameters to adjust include influent organic loading rate (through flow rate or THRT adjustment) and reciprocation rate. Since denitrification was not as prevalent as nitrification, rest periods should be expanded. This should reduce the amount of energy used as well as increase the amount of time the reactor is anoxic. The minimum amount of energy that produces the same amount of nitrification should be found through experimentation.

Operating the ReCip[®] under irregular cycles may promote further denitrification.

Reciprocation could cease while influent water is entering the system, allowing for NO₃ to contact the carbon rich wastewater under anaerobic conditions. After the influent has been added, reciprocation could resume as normal. Reciprocation rate and hydraulic residence time have not been altered during the current study, but should be in future research.

A study should be conducted to determine how fast NO₃⁻-N is denitrified in the lagoon.

If the ReCip[®] is to be used on sites that do not have lagoons that are lined, discharging NO₃ into these lagoons could pose a problem if it does not denitrify rapidly. This study could use bench-top experiments with wastewater from the storage lagoon.

Studies are under way to test different types of media in smaller pilot scale bioreactors called the “Mini ReCips.” Four small bioreactors are going to be constructed at the dairy to compare different types of media and their effect on treatment performance.

Another question is how long does it take for ReCip[®] performance to resume after a prolonged shut down? Such shut downs could occur at dairies where nitrogen removal is needed only seasonally.

5. References

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6. Appendices

Appendix A: Detailed Methods (mostly per Kane 2010)

Suspended Solids

Total suspended solids (TSS) and volatile suspended solids (VSS) analysis were conducted according to APHA Method 2540 D and E, respectively. Prewashed and ashed 1.2 μm G4 glass fiber filters (Fisher Scientific) were used for analysis. Duplicates, splits, and a TSS standard were used for quality control.

Biochemical Oxygen Demand

Total, soluble, carbonaceous, and soluble carbonaceous 5-day biochemical oxygen demand testing was conducted according to APHA Method 5210 B. Dilution water was

prepared with Hach BOD Nutrient Buffer Pillows. For CBOD₅, Hach Nitrification Inhibitor Formula 2533 was used. Standards were prepared using Hach BOD Standard Solution for Dilution Method, and blanks were analyzed with each batch of samples.

Total Ammoniacal Nitrogen

Total ammoniacal nitrogen analysis was conducted per APHA Method 4500-NH₃ D (Orion 9512 Ammonia-selective electrode). Four point calibration curves were employed, Using 1, 10, 100, and 1000 mg/L NH₃ as suggested by Standard Methods. Matrix spikes and splits were analyzed for quality control.

Ion Chromatograph

Nitrite and nitrate (NO₂⁻/NO₃⁻) were analyzed using a Dionex DX 120 Ion Chromatograph with the following setup (all parts manufactured by Dionex):

- IONPAC AS22 Analytical Column
- IONPAC AG22 Guard Column
- DS4-1 Detection Stabilizer
- SRS 300 Self-Regenerating Suppressor
- AS40 Autosampler

Eluent was prepared with Grade 1 deionized (DI) water and contained 4.5 mM and 1.4 mM of sodium carbonate and sodium bicarbonate, respectively. The eluent was degassed for 30 minutes using ultra-high purity helium. The ion chromatograph was supplied with ultra-high purity helium at a pressure of 60 psi, with an internal pressure reading between 2000 and 2500 psi. Eluent flow rate was maintained at 1.20 mL/min and allowed to run for at least one hour prior to any analysis of samples. Four point calibration curves ranging from 0.20 – 20.30 mg/L NO₂⁻-N and 0.16 – 16.48 mg/L NO₃⁻-N were prepared

for each batch of samples using Dionex Seven Anion Standard II. Samples were filtered through 0.22- μ m Millipore Express PLUS® membrane filters, diluted by a factor of five, and placed into 5 mL Dionex poly vials and capped with Dionex 20 μ m filter caps. A matrix spike using the standard and sample splits were analyzed in addition to periodic standard splits to account for any peak timing drift in the chromatography. DI water rinses of the injection needle were performed after each sample and DI blanks were analyzed prior to and after each sample set to ensure no background noise existed prior to sample analysis.

Organic Carbon

Non-purgeable organic carbon and soluble non-purgeable organic carbon (SNPOC) were analyzed using a Shimadzu TOC-V CSH Total Organic Carbon Analyzer. The machine sparged each sample to remove inorganic carbon and volatile organic carbon. The sample was then combusted and the resulting CO₂ was detected through a gas analyzer. Five point calibration curves ranging from 50 – 500 mg/L were constructed prior to each run and samples were diluted by a factor of ten. For SNPOC, samples were filtered through 0.45- μ m Millipore Express PLUS® membrane filters. Blanks, standard splits, matrix spikes, and sample splits were analyzed for quality control.

Total Nitrogen

Total nitrogen (TN) and total soluble nitrogen (SN) was analyzed using the Shimadzu TOC-V CSH Total Organic Carbon Analyzer with a supplemental Shimadzu TNM-1 Total Nitrogen Measuring Unit. Like NPOC analysis, each sample was combusted in the TOC analyzer. However for TN/DN analysis the resulting gas from combustion was analyzed by the supplemental TNM unit, where nitrogen monoxide was detected. Five

point calibration curves ranging from 25 – 200 mg/L were constructed prior to each run and samples were diluted by a factor of ten. For SN, samples were filtered through 0.45- μ m Millipore Express PLUS[®] membrane filters. Blanks, standard splits, matrix spikes, and sample splits were analyzed for quality control.

Alkalinity

Alkalinity of samples was determined per APHA Method 2320 B (Titration Method) using 0.5 N H₂SO₄.

Temperature and Dissolved Oxygen

Temperature and dissolved oxygen of samples were measured on site immediately after sampling to ensure accuracy.

Flow Rate

Flow rate of the influent pump was measured each week during sampling to monitor the hydraulic residence time of the system. A five gallon bucket and a stopwatch were used to determine the flow rate (gpm) of the influent.

Appendix B: Supplemental Data

Table 11. Air pollutant concentrations coming off of the ReCip[®] at different locations and during the three different testing periods.

Spot 1 (Near Influent)							
Month	EtOH (ppm)	N ₂ O (ppm)	CO ₂ (ppm)	NH ₃ (ppm)	H ₂ S(ppb)	SO ₂ (ppb)	CH ₄ (ppm)
June	0.713	0.832	573	0.382	3.203	ND	2.203
September	0.161	1.225	1121	ND	ND	3.329	5.773
December	0.10	0.31	565	0.04	0.26	0.44	3.36
Spot 3 (Near Sump, halfway through reactor)							
Month	EtOH (ppm)	N ₂ O (ppm)	CO ₂ (ppm)	NH ₃ (ppm)	H ₂ S(ppb)	SO ₂ (ppb)	CH ₄ (ppm)
June	0.754	0.755	611	0.317	ND	20.688	2.485
September	0.448	0.338	671	0.375	ND	1.346	1.839
December	0.12	0.39	888	0.02	ND	ND	10.52
Spot 5 (Near Effluent)							
Month	EtOH (ppm)	N ₂ O (ppm)	CO ₂ (ppm)	NH ₃ (ppm)	H ₂ S(ppb)	SO ₂ (ppb)	CH ₄ (ppm)
June	1.410	2.845	1116	0.616	2.291	ND	3.191
September	0.112	0.595	729	ND	ND	2.146	2.886
December	0.15	0.28	663	0.02	ND	0.42	2.98

Figure 13. TSS measured in the influent and effluent over the yearlong study.

Figure 14. TAN measured in the influent and effluent over the yearlong study.

Figure 15. TN measured in the influent and effluent over the yearlong study.

Appendix C: Photos

Figure 16. Under drain of ReCip® designed to aid in sludge removal. Each 4" PVC standpipe was installed to monitor sludge accumulation.

Figure 17. Empty ReCip® tanks.

Figure 18. Upflow configuration of pore water sampling. Shown here are the DO probe, pH probe, and the ORP probe

Figure 19. Flux chamber made of a buried 5 gallon pail and a sealed bucket lid with two polyvinyl tubes installed through the top.

Figure 20. Standpipes were installed through 4" holes in bio-diffuser tops with a hole saw. Notice the legs that the stand pipe stands on which allows easy and uninterrupted passage of sludge.

Figure 21. Standpipes were installed through 4" holes in bio-diffuser tops with a hole saw. Notice the legs that the stand pipe stands on which allows easy and uninterrupted passage of sludge.

Figure 22. Photo of the middle layer of the ReCip[®]. This photo shows what it looks like before the final layer of rock was installed. Notice the black perforated pipe which aids in distributing flow evenly across the system. This pipe makes a square figure-8.

Figure 23. Completed ReCip[®]. There is a blower under the green housing that connects to the manifold for future research. It was not used during this study.