

Nitrogen Mass Balance in a High Rate Algal Pond

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Table of Contents

Introduction	1
Wastewater.....	1
Wastewater Treatment.....	2
Nitrogen in Wastewater.....	3
Nitrogen Cycle.....	4
Volatilization	5
Objectives	6
Methods.....	6
Pond Setup.....	6
Pond Maintenance.....	7
Data Collection.....	7
Suspended Solids	7
Nitrate/Nitrite Nitrogen Concentration.....	8
Ammonia Nitrogen Concentrations.....	9
Mass Balance	9
Theoretical Ammonia Volatilization.....	10
Results.....	10
Discussion.....	14
Conclusion.....	15
References	16
Appendix	17
Example Mass Balance Calculation	17

Table of Figures

Figure 1. Nitrogen transformations in a HRAP receiving municipal wastewater.	3
Figure 2. Nitrogen Cycle (Harrison, 2003).....	4
Figure 3. Volatilization (Hwa et al, 2010).....	5
Figure 4 . HRAP (unpublished photograph, July 28, 2010)	6
Figure 5. Total Suspended Solids and Volatile Suspended Solids	11
Figure 6. Measured Nitrogen concentrations in NH_x and NO_x	12
Figure 7. Total Measured Nitrogen Concentrations	12
Figure 8. Comparison of the state of Nitrogen entering the pond to the state of the nitrogen leaving the pond	13
Figure 9. Nitrogen exiting the ponds compared with Nitrogen entering the ponds	13

Introduction

Wastewater

Untreated wastewater is approximately 99.9 percent water and contains only 0.1 percent impurities by mass (Nathanson, 2008). Biochemical oxygen demand (BOD) is a measure of the demand that the microbes in the sewage have for oxygen. A high BOD measurement corresponds to a high amount of organic matter and therefore strong wastewater (Nathanson, 2008). Another constituent that shows the strength of the wastewater is the total suspended solids (TSS) (Nathanson, 2008). From the TSS measurement one can obtain the amount of volatile suspended solids (VSS), which is a measure of the concentration of particulate organic solids in the wastewater.

Typical wastewater has a BOD of approximately 200 mg/L and a TSS of about 240 mg/L (Nathanson 2008). These values are much too high to be discharged into the environment. If the wastewater were discharged straight into the environment it would cause damage to wildlife, especially to fish and other animals. Bacteria and other pathogens in the wastewater can also pollute drinking water and cause beach closures while compounds of chlorine can be toxic to fish species (Environment Canada, 2010). An overabundance of nutrients, the most common being nitrogen (including ammonia) and phosphorus, lead to a harmfully large increase in the growth of algae and aquatic plants (called eutrophication). When the organic matter of these aquatic plants decays, a reduction in the available oxygen can be caused that is toxic to aquatic organisms. Nitrogen in the form of ammonia can be toxic to fish and exerts a high oxygen demand when consumed by nitrifying bacteria (described further below), on the water that the effluent is received into as ammonia is converted to nitrate. High nitrate- and nitrite-nitrogen levels also can lead to eutrophication.

Wastewater Treatment

The role of the wastewater treatment is to destroy harmful pathogenic organisms and to remove the majority of organic matter from the influent, thus lowering the BOD and amount of TSS. The removal of plant nutrients, such as nitrogen and phosphorus, is often required. The treatment of wastewater is most commonly done in more populated areas by a sewage treatment plant. A common way of treating the wastewater is through the use of an activated sludge sewage treatment plant, which consists of a primary settling tank, an activated sludge aeration tank, a secondary settling tank, and possibly a tertiary process. The by-product of the activated sludge process is excess sludge that is then disposed. A second type of wastewater treatment that is common in rural areas is a septic tank which retains septic sludge and scum and allows the remaining effluent to drain into soil. (Nathanson, 2008)

Another wastewater treatment method that is being experimented with is using algae in a high-rate algal pond (HRAP) to treat wastewater. In an activated sludge treatment plant, oxygen is introduced into the system through mechanical means by pumping oxygen through the wastewater. In HRAPs this is accomplished by the algae which produce oxygen through photosynthesis (Oswald, 1993). The oxygen immediately becomes available to the bacteria to oxidize most of the BOD remaining in the pond (Oswald, 1993). The remaining BOD is generally lower than the discharge standards (Oswald, 1993). One way that these HRAPs are used is in an Advanced Integrated Pond system where the capital costs can be up to one-tenth of the cost of a conventional plant (Department of Energy, 1993).

Nitrogen in Wastewater

As mentioned previously, nitrogen removal is an important aspect to wastewater treatment.

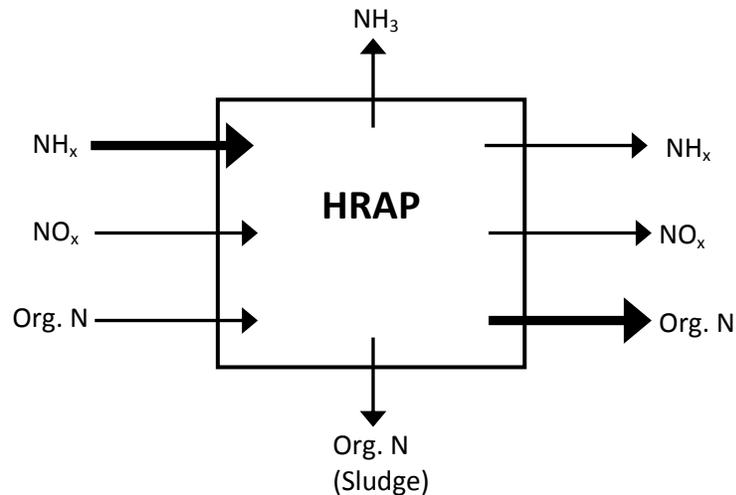


Figure 1. Nitrogen transformations in a HRAP receiving municipal wastewater. The arrows entering the HRAP represent the influent municipal wastewater and the outgoing arrows represent the treated wastewater. NO_x represents the total nitrogen from nitrates and nitrites. NH_x is the total nitrogen from ammonia and ammonium.

The preceding diagram shows the types of nitrogen that will be considered in the nitrogen removal process. The main types of Nitrogen that enter the algal pond are organic nitrogen, nitrates+nitrites (NO_x), and nitrogen from ammonia+ammonium (NH_x). The majority of the nitrogen is removed by the algae and exits the HRAP as organic nitrogen, and is represented by a bolded arrow. The majority of the nitrogen entering the HRAP enters as NH_x and is also represented by a bolded arrow. The method by which the nitrogen is taken up into the algae is called algal assimilation. Two other ways that nitrogen could leave the system are through nitrification and denitrification in pond sediments and through the volatilization of ammonia into the atmosphere. According to previous reports, the majority of the nitrogen was removed through ammonia volatilization, nitrification, and algal assimilation (Zhou et al, 2006).

Nitrogen Cycle

In order to understand the process that takes place in the HRAP, it is helpful to have a simple understanding of the nitrogen cycle.

Nitrogen is an element that can exist in both organic and inorganic forms and microorganisms can play major roles in the major nitrogen

transformations. Besides microbial

transformations there can also be human sources that introduce nitrogen into the system. The first part of the nitrogen cycle is nitrogen fixation, which is the transformation of N_2 to NH_4^+ (ammonium). There is also nitrogen uptake, which is the transformation of ammonium into organic nitrogen (nitrogen mineralization is the reverse of this process). Nitrification is the conversion of ammonium to NO_3^- (this reaction can only take place in oxygen-rich environments such as a HRAP). Lastly, denitrification takes place where there is no oxygen and is the conversion of NO_3^- to N_2 , thus starting the cycle back at nitrogen fixation.

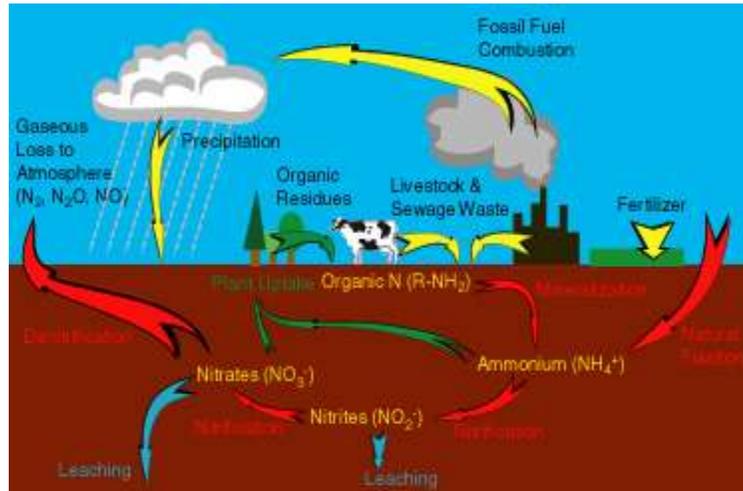


Figure 2. Nitrogen Cycle (Harrison, 2003). Red - Microbial Transformations; Yellow - Human Sources

Volatilization

Ammonia volatilization is the process in which organic nitrogen is taken up into the atmosphere. The following depicts the basic process that takes place:

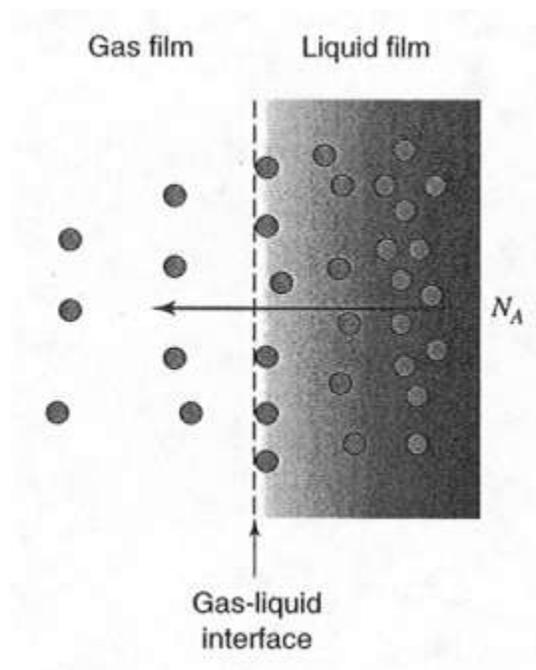


Figure 3. Volatilization (Hwa et al, 2010). N_A is the rate of volatilization. At the gas-liquid interface a percentage of the particles dissolved in the liquid pass the gas-liquid interface and are released as particles dissolved in gas. The concentration of particles in liquid is much higher than the concentration of particles in the gas.

In this figure N_A represents the rate at which ammonia would be volatilizing into the atmosphere. This process is highly dependent on temperature, pH, and the amount of mixing taking place at the surface of the water. The amount of ammonia that is volatilized into the atmosphere increases as temperature, pH, and agitation of the surface increase. A theoretical ammonia volatilization rate can be calculated using a mass transfer equation; this will be detailed further in the Methods section. Although ammonia volatilization is said to be the least of the major factors affecting nitrogen removal, it still is a sizeable enough mode of removal to impact the total amount of nitrogen removed (Zhou et al, 2006).

Objectives

The objective of the study described herein was to perform a mass balance with regards to nitrogen in a series of four HRAPs in order to determine the fate of the nitrogen in the four-pond system. The sources of all incoming nitrogen will be compared to the mode that the nitrogen exits the system. The total percentage of nitrogen lost via ammonia volatilization will be calculated via the mass balance.

Methods

Pond Setup

As part of a large scale project four small scale HRAPs were constructed on the property of the San Luis Obispo water treatment plant using algae to treat wastewater. Each of these ponds were constructed in a race track design and were designed for a water depth of approximately 0.3 m (1 ft), a surface area of approximately 3.1 m² (33 ft²) and could hold approximately 950 L (250 gal). Four paddlewheels were connected in series and run from an electric motor to ensure the same level of mixing in each pond. The municipal wastewater influent was pumped in at a constant rate to achieve a retention



Figure 4. HRAP (unpublished photograph, July 28, 2010). The PVC pipe that collected the effluent is shown at the bottom of the picture, and the in-line paddlewheels are at the top of the picture. The four ponds were constructed next to each other and were labeled Pond 1, 2, 3, and 4 respectively.

time of 3 days, and the effluent was drained via a PVC pipe that kept the water level constant at 0.3 m. The effluent was then collected in a sump and then pumped out of the secondary containment enclosure.

Pond Maintenance

The ponds were checked daily to ensure that all the moving parts were functional. The influent flow rate was measured to ensure a constant retention time and the pumping rate could be adjusted to compensate for slowly decreasing flow rates due to degradation in the tubes. The temperature and pH were measured daily and the dissolved oxygen (DO) concentration was measured if DO levels were reasonable since the DO concentration would increase rapidly once the sun rose and temperatures increased. Other various duties were also performed as needed (usually in the case of malfunctions in the pumps, or paddle-wheel motors). The ponds were maintained initially by Paul Ward, a graduate student at Cal Poly. During the latter half Adam Eberwein, an undergraduate student at Cal Poly, helped on weekdays and Sundays while I helped on Fridays and Saturdays. Brant Haflich, also an undergraduate student at Cal Poly, and Paul Ward helped with major pond maintenance with assistance from Adam Eberwein.

Data Collection

Data were taken from a 4-month period during the summer of 2010 starting the beginning of May and ending on the first of September. Samples were taken at approximately one-week intervals over this time period with a total of 19 data points. Samples were collected from each of the ponds individually, as well as from the influent. Each of the samples were tested to find the concentration of nitrogen from ammonia, nitrates and nitrites, and suspended solids (organic nitrogen). In September, the pond conditions were changed and therefore only data before September was considered.

Suspended Solids

To obtain the total suspended solids, a predetermined amount of the sample is filtered through a very fine filter in the following manner (unpublished TSSVSS Procedure, 2010). The filter must first be prepared in order to obtain accurate TSS and VSS results. To prepare the filter it is first cleaned by

pumping deionized water through the filter, this is repeated for multiple filters. The filters are then put in a furnace and once they are removed they are weighed to determine their tare weight. Once the filter is prepared the sample is filtered through via an air pump to ensure that the entire sample passes through the filter. The sample that passed through the filter is collected and is poured through the filter a second time to ensure all of the solids were trapped by the filter. The filter is then placed in a 105°C (220°F) oven for 1-2 hours, and then weighed. The change in mass is equivalent to the total suspended solids (TSS). The filter is then placed in a 550°C (1020°F) oven for 15 minutes to burn off all organic matter, and weighed. The mass that burned off is equivalent to the volatile suspended solids (VSS). Testing for TSS and VSS was done by Adam Eberwein, Paul Ward, and Brant Haflich.

Nitrate/Nitrite Nitrogen Concentration

The concentration of nitrogen found in nitrates and nitrites was found by testing the samples in a Dionex DX 120 Ion Chromatograph (IC) along with the following: G9-HC IonPac Guard Column, AS9-HC 4mm IonPac IC column, DS4-1 Detection Stabilizer, and an AS40 Automated Sampler (unpublished IC Instructions, 2010). Ion Chromatography works because different ions have different selectivities and will release from resin filled columns at different time periods. The baseline for the peaks is the conductivity of the carrier fluid that the sample to be tested is injected into. The IC uses an electrical conductivity detector that creates a chromatograph, which is a plot of the electrical conductivity versus time. The area under the curve of the peaks on the chromatograph represents the concentration of that particular ion. For the purposes of this test the concentration of nitrate and nitrite ions were found and the final value reported was the concentration of nitrogen from nitrates and nitrites. The IC test was run using the preceding method (unpublished IC instructions, 2010) by Brant Haflich and Paul Ward

Ammonia Nitrogen Concentrations

The concentration of nitrogen found in ammonia was found using ammonia-selective electrode method. An Orion 95-12 Ammonia-selective electrode was used for the duration of this test (Fulton, 2009). This method, according to Standard Methods for the Examination of Water and Wastewater (SMEWW, 1999), uses a gas-permeable membrane that separates the sample solution from an internal ammonium chloride solution. For the test to be accurate all of the dissolved ammonia must become aqueous; this can be accomplished by raising the pH above 11 with a strong base. A pH meter was used to monitor the pH throughout the testing to ensure that the pH was always greater than 11. The aqueous ammonia diffuses through the membrane and changes the internal solution's pH. A potential difference is then measured with a pH meter that has an expanded millivolt scale. This potential difference is calibrated to give the amount of nitrogen from ammonia in the solution. When samples had to be stored for longer than 24 hours the pH was lowered below 2 with a concentrated H₂SO₄ solution. To ensure the accuracy of the machine, certain samples were spiked to contain a known amount of ammonia of 1.5 to 2 times the original concentration. This was then measured and was considered acceptable if it fell within 15% of the original. In addition, duplicate tests were also run of some of the samples to ensure accuracy. Ammonia testing was run by Kevin McCourt, a Cal Poly undergraduate student, and myself.

Mass Balance

The average measured values for organic nitrogen, ammonia-nitrogen, and nitrate- and nitrite-nitrogen were averaged over the course of the 4-month period that samples were selected. A mass balance was run based on the nitrogen content with the following assumptions: All of the influent nitrogen came from organic nitrogen, ammonia-nitrogen, or nitrate- and nitrite-nitrogen; there was zero sedimentation therefore there was no algal sludge buildup; all nitrogen leaving the ponds exited through organic, ammonia, or nitrate- and nitrite-nitrogen, or ammonia volatilization; the amount of organic nitrogen

was 10% of the VSS; the mass balance was assumed to be steady state; and lastly, all ponds were at a 3-day retention time. The mass of N missing from the effluent was assumed to have volatilized. A sample calculation can be viewed in the Appendix.

Theoretical Ammonia Volatilization

The equation used to theoretically calculate the amount of NH₃ that is volatilized into the atmosphere is (Valero et al, 2007):

$$\lambda_{NH_3} = K_l([NH_3]_{pond} - [NH_3]_{air})V/A$$

where λ_{NH_3} is equal to the ammonia volatilization rate (g N/m²-day); K_l is the convective mass transfer coefficient in the liquid phase (day⁻¹); V is the pond volume (m³); A is the pond surface area (m²); and $[NH_3]_{pond}$ is the concentration of ammonia in the pond (g N/m³). In this equation the concentration of NH₃ in the air is assumed to be zero.

Results

The following average values given are on a per pond basis. The amount of total and volatile suspended solids was approximately three times greater in the ponds than the influent with the influent TSS equal to 69.9 mg/L and VSS equal to 63.4 mg/L. The average TSS for the ponds was 218 mg/L, and the average concentration of VSS was 193 mg/L (Figure 5). The average rate of organic nitrogen entering a pond was 2,008 mg/day and 6,070 mg/day leaving the pond through the effluent.

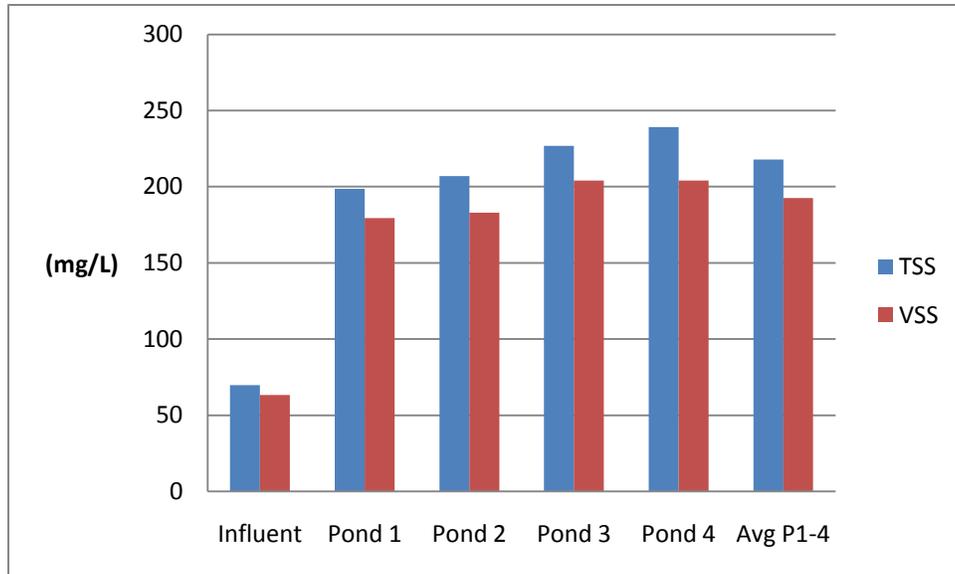


Figure 5. Total Suspended Solids and Volatile Suspended Solids

The amount of measured ammonia was vastly decreased by the HRAPs with the concentration in the ponds equal to approximately 13% of the influent concentration. The ammonia-nitrogen concentration in the influent was 39.7 mg/L compared to 5.1 mg/L in the ponds. The rate of ammonia-nitrogen entering a pond was 12,560 mg/day and the rate leaving the pond was 1,604 mg/day. There were only trace amounts of nitrates and nitrites in the influent (0.03 mg/L) therefore all of the nitrate- and nitrite-nitrogen came through nitrification. The total amount of nitrogen from nitrates and nitrites was 7.4 mg/L in the ponds (Figure 6). The rate of nitrogen from nitrates and nitrites entering the pond was 8.7 mg/day and the rate leaving the pond was 2,227 mg/day.

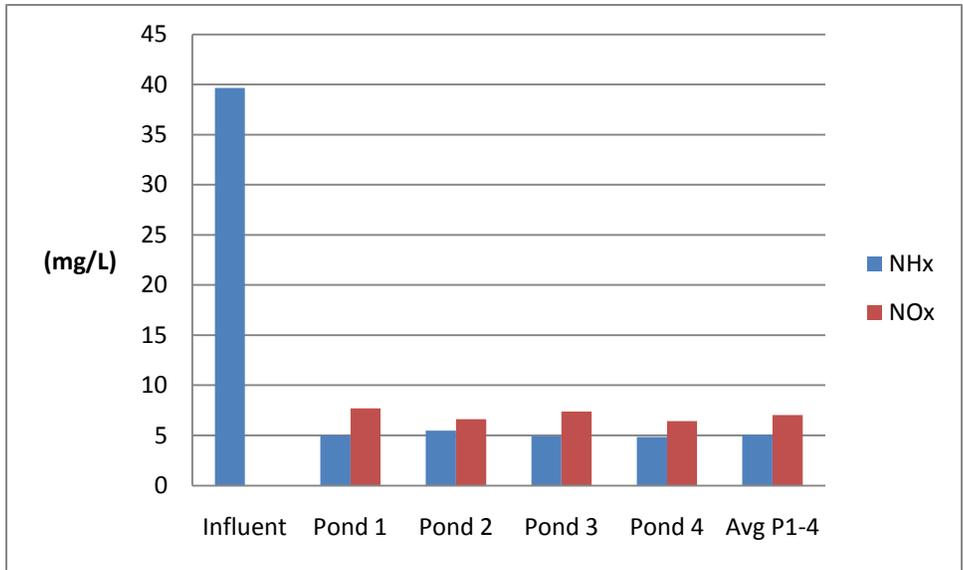


Figure 6. Measured Nitrogen concentrations in NH_x and NO_x

The amount of organic nitrogen was calculated from the VSS data, and then combined with the ammonia and nitrate and nitrite data to show the measured concentration of nitrogen in the influent and in the pond (Figure 7). The total measured nitrogen content in the influent is 46.0 mg/L and the measured nitrogen content in the ponds was 31.4 mg/L. This equates to 14,576 g of nitrogen entering the pond per day and 9,930 mg/day leaving through the effluent.

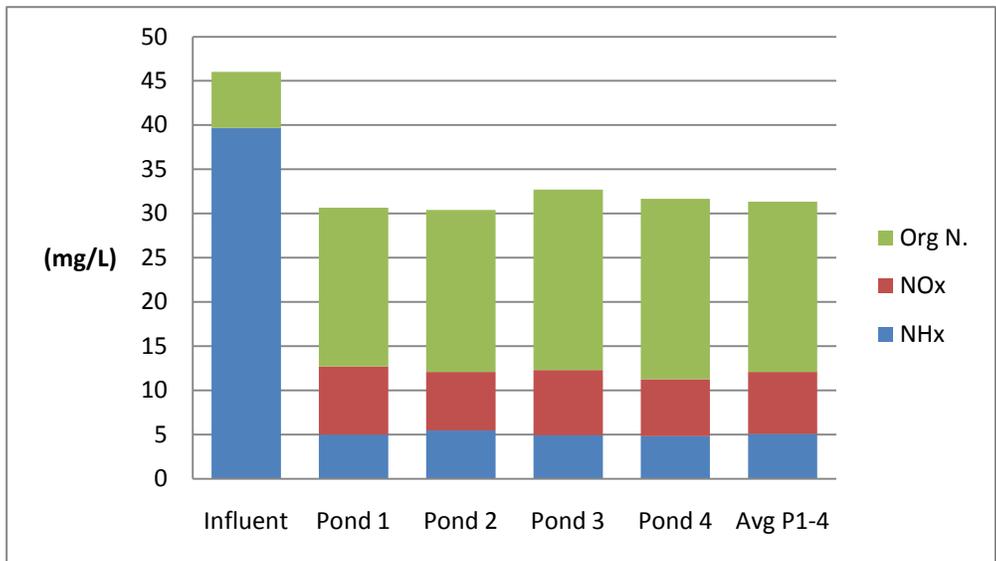


Figure 7. Total Measured Nitrogen Concentrations. Includes nitrogen from organic matter, NO_x, and NH₃

The remaining nitrogen that was not contained in the ponds was assumed to be volatilized. The following graph shows a percent based comparison of the location of nitrogen in each pond (Figure 8).

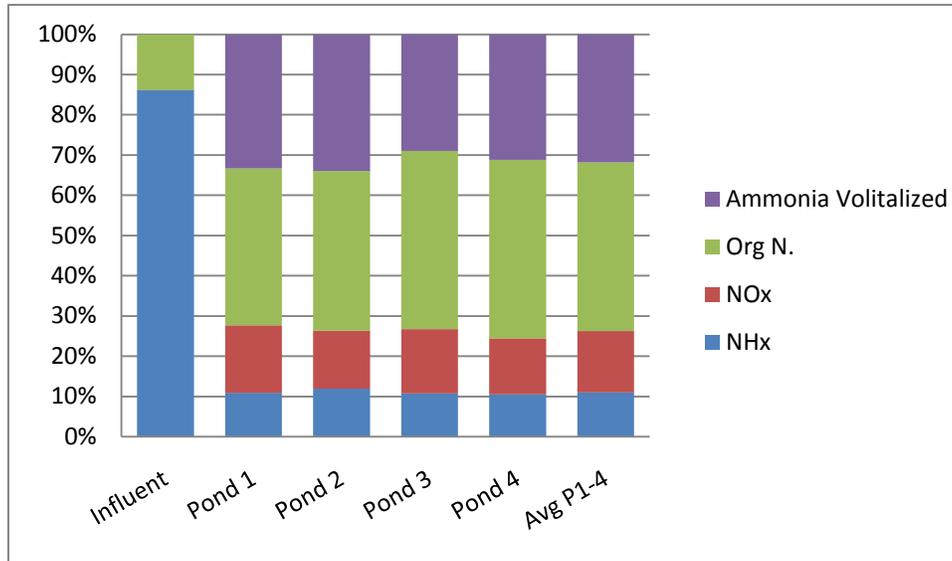


Figure 8. Comparison of the state of Nitrogen entering the pond to the state of the nitrogen leaving the pond

The following charts show the percentage of nitrogen entering and exiting the ponds and the final percentage of ammonia that is volatilized (Figure 9). The resulting ammonia that was volatilized was equal to 32% of the total nitrogen, or 4,645 mg/day of nitrogen released into the atmosphere.

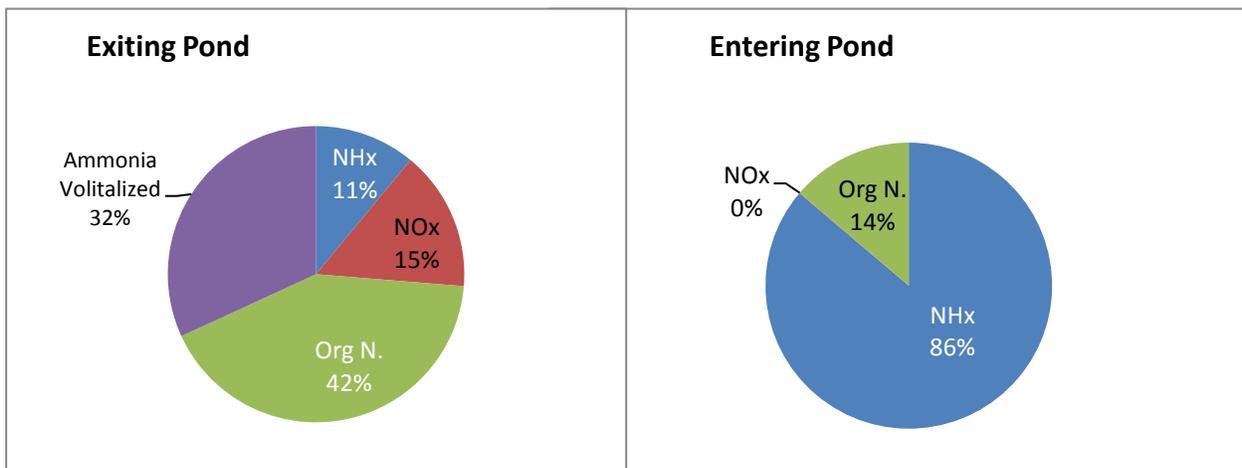


Figure 9. Nitrogen exiting the ponds compared with Nitrogen entering the ponds

Discussion

The HRAPs were highly effective in removing dissolved nitrogen from the wastewater. The amount of ammonia, nitrates, and nitrites were vastly less in the effluent than in the influent (Figure 6). These data seem to be consistent with the data from the summer of 2009 (Lundquist et al, 2010) where concentrations of ammonia dropped from 37 mg/L to 5 mg/L. Ammonia concentrations in the ponds for the summer of 2010 were 13% of the incoming concentration showing a good effectiveness in ammonia-nitrogen removal. The U.S. Environmental Protection Agency has stated that 2 mg/L is the upper limit for chronic exposure to ammonia in water (Dubrovsky et al, 1998). This is also the average monthly limit for discharge into the San Joaquin River for the city of Stockton according to the California Environmental Protection Agency (Cal/EPA, 2008). According to this standard the ammonia concentration is still too high; however, in many counties the regulations are less stringent or the regulatory agency does not have a limit on ammonia levels.

Nitrogen from nitrates and nitrites accounted for 15% of nitrogen leaving the pond (Figure 9). This nitrate and nitrite nitrogen was all assumed to be produced due to nitrification. Organic nitrogen from algal assimilation accounted for 42% of the total nitrogen in the system. The large amount of organic nitrogen in the system shows that algal assimilation was the primary mode of nitrogen transformation and nitrification was only a secondary mode of transformation. According to Zhou et al (2006), organic nitrogen sedimentation should be the primary method of nitrogen removal. If the algae in the effluent were to be removed from the system (possibly from filtration or sedimentation) then this would be the primary mode of nitrogen removal.

According to the nitrogen mass balance, a significant amount of the nitrogen was removed through ammonia volatilization. Approximately 33% of the total nitrogen was removed which is a very large

percentage compared to the study done by Zhou et al (2006). Ammonia volatilization is highly dependent on temperature, pH, and mixing rate of the pond, therefore results could vary widely based on different conditions.

Conclusion

The mass balance was assumed to have performed effectively since it gave results similar to years past (Lundquist et al, 2010); therefore the ammonia volatilization rate that was obtained is assumed to be a fair approximation of the actual rate. Overall, the HRAP is effective at the removal of ammonia-nitrogen (especially through algal assimilation) and has a high rate of ammonia volatilization. Ammonia-nitrogen decreased from 86% of the total nitrogen to only 11% of the nitrogen leaving the system. Organic nitrogen accounts for 42% of the total nitrogen leaving the system compared with 14% entering the system. Nitrogen from nitrates and nitrites accounted for 0% of total nitrogen entering the system yet accounted for 15% of the nitrogen leaving the system due to nitrification. Lastly, ammonia volatilization accounted for a removal of 32% of the total amount of nitrogen.

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Appendix

Example Mass Balance Calculation:

Below is averaged data collected for the influent (entering HRAP) and for the ponds (exiting HRAP) in mg/L of Nitrogen (all data is on a per pond basis):

	NH_x	NO_x	Org N.	Total
Entering HRAP	39.7	0.0	6.3	46.0
Exiting HRAP	5.1	7.0	19.3	31.4

The nitrogen in organic form was calculated based on the assumption that it was equal to 10% of the VSS in mg/L therefore (for the influent):

$$Org\ N. = 0.10(VSS) = 0.10\left(63\frac{mg}{L}\right) = 6.3\frac{mg}{L}$$

To find the total amount of nitrogen leaving or entering the pond the concentration was multiplied by the flow rate based on a 3-day retention time, for example:

$$Flow\ Rate = \frac{Volume}{Time} = \frac{950L}{3\ day} = 316.7\ L/day$$

$$Total\ N\ Entering\ HRAP = \left(46.0\frac{mg}{L}\right)\left(316.7\frac{L}{day}\right) = 14,576\frac{mg}{day}$$

This same calculation is done to the whole table (all values in mg/day):

	NH_x	NO_x	Org N.	TOTAL
Entering HRAP	12,559	9	2,008	14,576
Exiting HRAP	1,604	2,227	6,099	9,931

In order to obtain the amount of nitrogen from volatilized ammonia, the total entering the HRAPs was subtracted from the total exiting the HRAPs based on the assumption of no sludge buildup:

$$Ammonia\ Vol. = 14,576\frac{mg}{day} - 9,931\frac{mg}{day} = 4,645\frac{mg}{day}$$

Therefore the final mass balance table in mg/day is as follows:

	NH_x	NO_x	Org N.	Ammonia Volatilized	TOTAL
Entering HRAP	12,559	9	2,008	n/a	14,576
Exiting HRAP	1,604	2,227	6,099	4,645	14,576

