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EVALUATING THE INFLUENCE OF A DROPLET SPRAYING/MISTING SYSTEM TO ENHANCE AMMONIA VOLATILIZATION FROM A LEACHATE STORAGE POND: A CASE STUDY AT THE THREE RIVERS SOLID WASTE AUTHORITY

Kaitlen Drafts [1], Suzie Boxman [2], Scott Ribes [3], Mike Terry [3], Bryan Staley [4], Joseph Flora [1] and Nicole Berge [1,*]

[1] Department of Civil and Environmental Engineering, University of South Carolina, 300 Main Street , Columbia, South Carolina, United States
[2] Environmental Research and Education Foundation, Raleigh, North Carolina, United States
[3] Three Rivers Solid Waste Authority, 9900 Atomic Road , Jackson, South Carolina 29831, United States
[4] EREF, Raleigh, NC, United States

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ABSTRACT

The Three Rivers Solid Waste Authority (TRSWA) operates a MSW landfill outside Jackson, South Carolina (USA) at which leachate ammonia concentrations are of concern. The landfill operates a droplet spraying/misting system (known as the Lilypad system) in their pond to enhance both leachate evaporation and, possibly, ammonia volatilization. The overall goals of this study were to determine the fate of nitrogen in the pond and to ultimately quantify the role the Lilypad system plays in enhancing ammonia removal. To accomplish the study goals, an empirical model based on collected leachate and mist samples, climatological data, and pond hydraulic data was developed to quantify the extent of ammonia volatilization, nitrification, and denitrification that occurred in the pond over the study period. Results from this work indicate that volatilization, nitrification, and denitrification were occurring in the pond, with volatilization of ammonia-nitrogen accounting for the majority of nitrogen removed from the pond. Results also indicate that the Lilypad system has the capability to significantly enhance the volatilization process.

1. INTRODUCTION

Proper management of municipal solid waste (MSW) landfill leachate is complex and costly. Typically, leachate is either fully or partially treated on-site and/or sent to a publicly owned treatment works (POTW). Full on-site treatment often requires high capital, operating and maintenance costs, as well as a skilled operator. Off-site treatment at a POTW is often the less costly and an easier to operate/manage option but can be uncertain as POTWs often charge fees that can change at the POTW's discretion, or they can refuse to accept leachate if contaminant levels are deemed unacceptable. As a result, many landfills conduct some on-site pre-treatment to reduce specific contaminant concentrations in the leachate.

The Three Rivers Solid Waste Authority (TRSWA) operates a MSW landfill outside Jackson, South Carolina at which leachate ammonia-nitrogen concentrations are of concern, prompting the landfill consider partial on-site treatment. The landfill produces an average of approximately 152,300 L of leachate per day, which is stored in an on-site collection pond before eventual discharging to an off-site POTW. This landfill operates a droplet spraying/misting system (known commercially as the Lilypad system) in order to enhance leachate evaporation and, potentially, promote ammonia volatilization. Volatilization or stripping of ammonia-nitrogen from landfill leachate has been reported previously, and is commonly accomplished in ponds, aerated lagoons, and/or stripping towers (Bakhshoodeh et al., 2020; Costa et al., 2017; dos Santos et al., 2020; Frascari et al., 2004; Leite et al., 2011; Martins et al., 2013). Some volatilization of ammonia-nitrogen occurs naturally, promoted by site climatological conditions (e.g., temperature, wind), leachate properties (e.g., pH), and pond aeration. Leite et al., (2011) reported up to 99.5% ammonia volatilization from a series of shallow stabilization ponds. They attributed this volatilization to large surface areas, high pH levels resulting from photosynthetic processes

* Corresponding author:
Nicole Berge
email: berge@engr.sc.edu

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performed by the algal mass generated, and water temperatures. Purposeful stripping of ammonia-nitrogen has also been performed. Stripping towers have been shown to be quite effective for ammonia-nitrogen removal, with removal percentages ranging between 44% and 99% at retention times ranging from 0.75 hours to 9 days. These systems are costly to build and operate, especially because they generally include some form of pH adjustment, air addition, and/or possibly addition of heat (Campos et al., 2013; Cheung et al., 1997; dos Santos et al., 2020; Ferraz et al., 2013; Marttinen et al., 2002; Renou et al., 2008).

The droplet spraying/misting system employed at the TRSWA landfill is operated without the use of external heat or chemical addition. Instead, the system consists of a series of nozzle heads, or baskets, mounted on poles located on a dock in the middle of the pond. Leachate is pumped through these baskets and subsequently sprayed, as a fine mist, into the air above the pond surface. This approach relies on the increased air-water interface with the small droplets in the mist to promote volatilization. If effective, use of such a system to promote ammonia volatilization would be advantageous, particularly in developing countries (Lavagnolo and Grossule, 2018). However, little work investigating the efficacy of such a system has been reported in the peer reviewed or gray literature. In very few instances, ammonia losses from sprinkler systems spraying wastewater (e.g., animal, human) over land have been reported. Chastain and Montes (2005) reported that up to 26% of ammonia was lost during the spraying of animal manure, which was dependent on air temperature, relative humidity, irrigation pressure, drop diameter, spray velocity, total ammonia-nitrogen content of the irrigated manure, and pH. Saez et al. (2012) reported the volatilization of 15-35% of the ammonia present in secondary-treated wastewater after being sprayed with a center pivot irrigation system and found that removal was correlated with temperature and wind speed.

The results reported by Chastain and Montes (2005) and Saez et al. (2012) suggest that the Lilypad system in operation at the TRSWA site has the potential to promote ammonia volatilization. The overall goal associated with this study was to determine the impact the Lilypad system has on nitrogen removal. The specific objectives of this work were to: (1) evaluate the fate of nitrogen in the pond by quantifying the extent of volatilization, nitrification, and denitrification that occurred in the pond and (2) evaluate and quantify the impact of the Lilypad system on ammonia volatilization.

2. MATERIALS AND METHODS

2.1 Leachate pond description and operation

Leachate from the TRSWA Class 3 landfill is collected via a series of leachate collection pipes located in the landfill cells and is pumped via six sump pumps into an on-site leachate storage pond with a capacity of approximately 10.2 million liters and lined with a High-Density Polyethylene (HDPE) geomembrane. Leachate is stored in this pond until its removal by tanker truck to an off-site POTW. The pond is equipped with a single surface aerator (Aqua-Jet surface mechanical aerator) that continuously aerates the pond and a Typhoon Lilypad evaporation system (New Waste Concepts, Inc.) that utilizes a droplet spraying/misting approach to enhance leachate evaporation and, possibly, ammonia volatilization. The Lilypad system consists of 8 nozzle heads, or baskets, mounted on poles located on a dock in the middle of the pond. Leachate is pumped through these baskets and subsequently sprayed, as a fine mist, into the air above the pond surface. The Lilypad system records pond hydraulic measurements (e.g., inflow, outflow, pond depth) every 15 minutes. Climatological measurements from an on-site weather station (e.g., ambient temperature, relative humidity, precipitation, wind speed) are also recorded every 15 minutes. Figure 1 contains a schemtic of the pond system, illustrating where the Lilypad system and aerator are installed, as well as a picture of the Lilypad system.

2.2 Leachate pond sampling and analysis

A series of pond hydraulic and site climatological measurements and leachate samples were taken to understand the fate of nitrogen in the leachate collection/storage pond. These data were subsequently used to develop a model describing the fate of nitrogen and organics in the pond.

2.2.1 Pond hydraulic measurements and analysis

Specific pond-related hydraulic parameters measured include the pond depth and flow of leachate in and out of the pond. These measurements were taken both manually and from data recorded by the Lilypad system. Pond depths were measured using an ultrasonic level sensor installed in the pond. Data from this sensor were recorded every 15 minutes. The last six 15-minute recorded pond depths of the day were averaged and used with pond geometric information to calculate the daily pond surface area and volume.

Leachate flows into and out of the pond were taken by onsite personnel. Inflow data were taken daily by manually reading the pump meters. For days in which readings were not taken (e.g., weekends or holidays), the flow from the day with the next meter reading was divided evenly over the number of days from the previous reading. Daily average outflows from the pond were determined by taking monthly totals of outflow and dividing them evenly over the days of each month.

2.2.2 Climatological measurements and analysis

Climatological data required to understand the biological and physical processes that occurred in the pond include air temperature and wind speed. These data were collected from multiple sources, including from an on-site weather station and from on-line database tools, including the National Oceanic and Atmospheric Administration (NOAA)'s Climate Data Online tool (https://www.ncdc.noaa.gov/cdo-web/) and the National Air and Space Administration (NASA)'s POWER Data Access Viewer (https://power.larc.nasa.gov/data-access-viewer/). The weather station located at Augusta's Bush Field Airport (33.36°, -81.96°) was selected. The NASA tool allows the user to select a

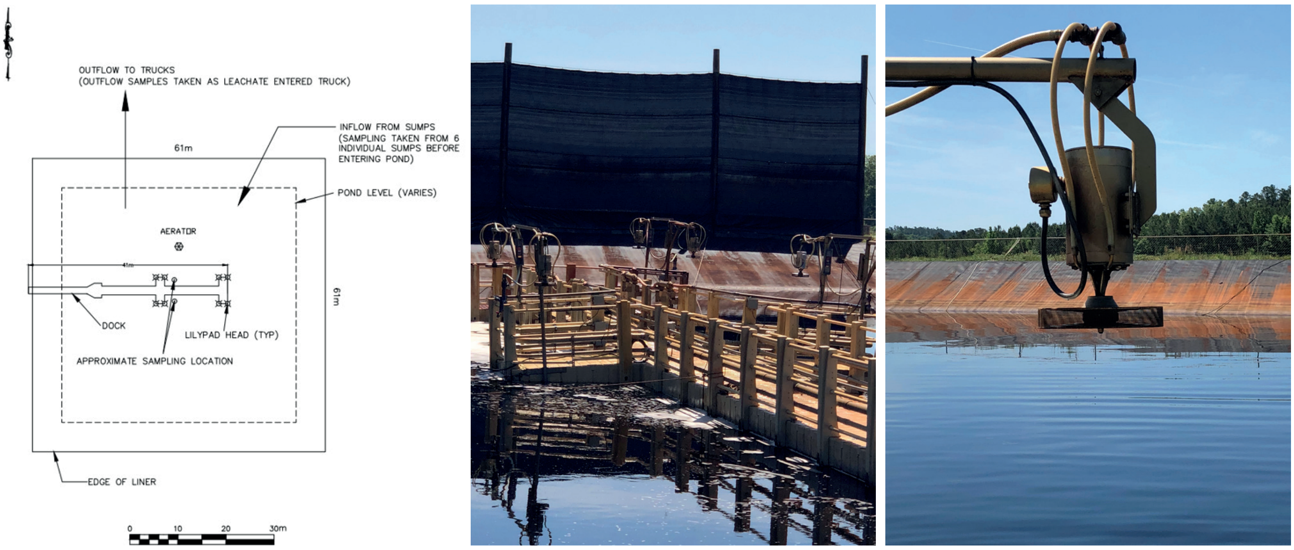

FIGURE 1: Schematic and pictures of the leachate pond and Lilypad system: (a) Schematic of the leachate pond with the sampling locations and (b) Lilypad system installed on the dock, and (c) Lilypad basket.

point on a map, for which data is provided. The landfill site (33.26°, -81.735°) was selected. All data from these sources were averaged and a daily average of each parameter (air temperature and wind speed).

2.2.3 Leachate sampling and analysis

Leachate samples were periodically taken from the leachate collection pond, leachate sumps, pond effluent, and in the mist collected from the Lilypad system, as illustrated in Figure 1. Each quarter, the landfill takes single grab samples from the leachate collection pond. These samples were analyzed for the following parameters (Pace Analytical Services), with specific methods found in parentheses:5-day biochemical oxygen demand (BOD$_5$, SM5210B), total suspended solids (TSS, SM2540D), chemical oxygen demand (COD, SM5220D), total dissolved solids (TDS, SM2540C), alkalinity (SM2320B), total organic carbon (TOC, SM5310B), ammonia-nitrogen (E350.1), total kjeldahl nitrogen (TKN)-nitrogen (E351.2), Nitrate plus nitrite-nitrogen (E353.2), and metals (arsenic, barium, cadmium, chromium, lead, 200.8/200.7). Over the course of this project, seven quarterly sampling periods occurred. Additional leachate sampling events occurred throughout the study period. During these events, grab samples were taken from two different locations in the pond, from each of the sumps, and from the pond effluent. All samples were analyzed for the parameters listed above (CSRA Analytical Laboratory), with the addition of pH (SM4500-H+ B), dissolved oxygen (DO, SM4500-O-G), and chloride (E300.0). These sampling events took place during three sampling campaigns, during which sampling occurred every one to two weeks for a total of four sample events.

2.2.4 Mist sampling

Mist sprayed by the Lilypad system was periodically sampled to determine the amount of ammonia being volatilized during Lilypad system operation. Five mist sampling events occurred: 4/16/19, 9/19/19, 11/7/19, 6/15/20, and 6/16/20. Influent samples were collected near the two pump intakes going to the Lilypad system. Following each intake sample, mist samples were collected in four to eight, 5-gallon plastic pail buckets placed in a pattern at increasing distances from the spray heads on the dock supporting the Lilypad system. All leachate collected in the buckets was aggregated into two or three 1 L bottles for duplicate or triplicate samples, respectively. During these events at least two and up to seven grab samples were taken from the pond throughout the day. The ammonia-nitrogen concentrations in the samples of both the leachate and the mist were measured (Pace Analytical Services).

2.3 Model development

The main objective associated with this modeling effort was to quantitatively determine the fate of nitrogen species in the leachate pond. A model was developed to account for the nitrogen-related transformation processes expected to occur, including ammonia volatilization, nitrification, and denitrification. Although partial nitrification and denitrification, anaerobic ammonium oxidation (ANAMMOX), completely autotrophic nitrogen removal over nitrite (CANON), and single reactor system for high-activity ammonium removal over nitrite (SHARON) have been documented to occur in leachate treatment systems (e.g., Sri Shalini & Joseph, 2012; Wang et al., 2010; Zhang et al., 2019), these processes were not included in this model. All reactions were assumed to occur within the liquid-phase, with no organic nitrogen hydrolysis and/or mineralization accounted for in the model. Organic carbon degradation was also modeled because of its role during denitrification. It was assumed that the pond was well mixed. The concentrations of all constituents leaving the pond were similar to those found in the pond (always less than 25% different for all nitrogen species), indicating this assumption was valid. In addition, the model assumes there is particulate matter that does not serve as either a source or sink for any of the constituents modeled in this study. The low TSS concentrations (always < 400 mg/L) in the leachate pond support this assumption.

2.3.1 Nitrogen transformations and associated relationships

Mass balances on the nitrogen species, including ammonia, total nitrate and nitrite, and TKN, as well as other parameters influenced by the change in nitrogen (e.g., organic carbon) were conducted, as shown in Eqs. (1)-(4).

$$\frac{d[NH_3]}{dt} = \frac{Q_i}{V}[NH_3]_i - \frac{Q_e}{V}[NH_3] - r_{nit} - r_{vol} \tag{1}$$

$$\frac{d[NO_3+NO_2]}{dt} = \frac{Q_i}{V}[NO_3+NO_2]_i - \frac{Q_e}{V}[NO_3+NO_2] + r_{nit} - r_{denit} \tag{2}$$

$$\frac{d[TKN]}{dt} = \frac{Q_i}{V}[TKN]_i - \frac{Q_e}{V}[TKN] - r_{nit} - r_{vol} \tag{3}$$

$$\frac{d[COD]}{dt} = \frac{Q_i}{V}[COD]_i - \frac{Q_e}{V}[COD] - r_{denit}X - r_{org} \tag{4}$$

where [NH$_3$] is the concentration of ammonia in the pond (mg/L-N), Qi is the flowrate entering the pond from the sumps (L/day), V is the pond volume (L), [NH3]i is the concentration of ammonia entering the pond from the leachate sumps (mg/L-N), Qe is the flowrate of leachate exiting the pond (L/day), rnit is the rate of nitrification occurring (mg/L-day), rvol is the rate of ammonia volatilization (mg/L-day), [NO$_3$ + NO$_2$] is the concentration of nitrite and nitrate in the pond (mg/L-N), [NO$_3$ + NO$_2$]i is the concentration of nitrate and nitrite entering the pond from the leachate sumps (mg/L-N), rdenit is the rate of denitrification occurring (mg/L-day), [TKN] is the concentration of TKN in the pond (mg/L-N), [TKN]i is the concentration of TKN entering the pond from the leachate sumps (mg/L-N), [COD] is the concentration of COD in the pond (mg/L), [COD]i is the concentration of COD entering the pond from the leachate sumps (mg/L), X is a fitting parameter that describes the ratio of biodegradable COD removed per mass of NO3 + NO2 removed (mg COD/mg N), and rorg is the rate of organics degradation occurring (mg/L-day).

2.3.2 Ammonia volatilization

The rate of ammonia volatilization (r_{vol}, mg/L-day) is defined in Eq. (5) as a first-order reaction.

$$r_{VOL} = [NH_3]_l K_{OL}\left(\frac{SA}{V}\right) \tag{5}$$

where [NH$_3$]l is the liquid-phase free ammonia concentration (mg/m^3-N), KOL is the ammonia mass transfer coefficient (m/day), SA is the pond surface area (m^2), and V is the pond volume (m^3).

The liquid-phase free ammonia concentration ([NH3]l) is determined using Eq. (6) (Metcalf & Eddy, 2013).

$$[NH_3]_l = \frac{[NH_3]\times 10^{pH}}{\frac{1}{K_a}+10^{pH}} \tag{6}$$

where, [NH3] is the concentration of ammonia in the pond (mg/L-N), pH is the pH of the pond and Ka, is the ionization constant for ammonium (unitless), that depends on temperature. The temperature dependence of Ka is shown in Eq. (7).

$$K_a = \frac{1}{e^{6334/T}} \tag{7}$$

where T is the temperature of the pond (K).

The ammonia mass transfer coefficient (KOL, m/s) describes the transfer of ammonia from the leachate pond to the air. This coefficient was adopted from Arogo et. al (1999) and is described in Eq.(8).

$$K_{OL} = C\,\frac{{D_{A-air}}^{0.58}{\mu_{air}}^{0.31}{U_{air}}^{0.12}{T_L}^{0.77}}{L^{0.88}{\rho_{air}}^{0.31}{T_{air}}^{0.77}} \tag{8}$$

where C is fitting constant (unitless), DA-air is the diffusivity of ammonia in air (m^2/s), μair is the air viscosity (kg/m-s), Uair is the average wind speed (m/s), TL is the pond temperature (°C), L is the length of the water surface of the pond (m), ρair is the air density (kg/m^3), and Tair is the air temperature (°C). The fitting constant, C, was determined by fitting the model to the pond data.

The temperature of the pond was not measured. Instead, it was calculated using an approach developed by Mohseni et al. (1998). Mohseni et al. (1998) developed a non-linear expression to estimate weekly stream temperatures from air temperatures by analyzing graphs comparing air temperature to stream temperature in the Spokane River, Washington. This correlation is shown in Eq. (9). Typical values of the variables in Eq. (9) were then determined for use in any part of the country by fitting Eq. (9) to temperature data from 584 stream gauging stations across the country and air temperature data from 197 weather stations (the closest weather station to each stream temperature station was used) (Mohseni et al., 1998).

$$T_L = \mu + \frac{\alpha-\mu}{1+e^{\gamma(\beta-T_a)}} \tag{9}$$

where μ is a constant representing the estimated minimum liquid temperature (0.8°C), α is a constant representing the estimated maximum liquid temperature (26.2°C), β is a constant representing the air temperature at the inflection point (13.3°C), γ is a constant representing the steepest slope of their function (0.18), and Ta is the temperature of the air (°C).

2.3.3 Nitrification

Because the availability of specific mechanistic information associated with microbial dynamics in the pond were unavailable, the rate of nitrification ($r_{nit,}$ mg/L-day) was modeled as a single step, assuming first-order kinetics, as described in Eq. (10).

$$r_{nit} = [NH_3]k_{nit}{\theta_{nit}}^{T_p-T_{nit}} \tag{10}$$

where [NH$_3$] is the concentration of ammonia-nitrogen in the pond (mg/L-N), knit is the first-order kinetic coefficient (day-1), θnit is a temperature coefficient (unitless), TP is the temperature of the pond (°C), and Tnit is the reference temperature for nitrification (°C).With the exception of the ammonia concentration and the pond temperature, the remaining parameters were determined by fitting the model to the pond data.

2.3.4 Denitrification

The rate of denitrification (r_{denit}, mg/L-day) was also modeled as a single-step process and assuming the process was first-order, as shown in Eq. (11).

$$r_{denit} = [NO_2+NO_3]k_{denit}{\theta_{denit}}^{T_p-T_{denit}} \tag{11}$$

where, [NO$_2$+NO$_3$] is the combined concentration of nitrate and nitrite in the pond (mg/L-N), kdenit is the first-order kinetic coefficient (day-1), θdenit is a temperature coefficient (unitless), TP is the temperature of the pond (°C), and Tdenit is the reference temperature for denitrification (°C). With the exception of the combined nitrate/nitrite concentration and the pond temperature, the remaining parameters were determined by fitting the model to the pond data.

2.3.5 TKN

Changes in leachate TKN are expected when changes in the nitrogen species occur. TKN concentrations were determined by accounting for the mass of ammonia nitrogen removed via either nitrification or volatilization, as shown in Eq. (3).

2.3.6 Organics removal

Organics removal as a result of denitrification and biodegradation were modeled, as described in Eq. (4). Limited BOD data existed, therefore the fate of organics in the leachate collection pond was modeled using the pond COD concentrations. It was assumed that the carbon source for denitrification is the biodegradable soluble COD (bsCOD) in the leachate. Because this fraction is unknown for this pond, the concentration of bsCOD present in the leachate was assumed to be 0.13 of the total COD concentrations which was based on the average BOD/COD ratio for a limited set of data. The rate of COD decline (mg/L-day) was determined based on Eq. (12).

$$r_{org} = [bsCOD_{avail}]k_{org}{\theta_{org}}^{T_p - T_{org}} \tag{12}$$

where, [$bsCOD_{avail}$] is the concentration of biodegradable soluble COD in the leachate available for organics degradation after the removal of it due to denitrification (mg/L), korg is the first-order kinetic coefficient (day-1), θorg is a temperature coefficient (unitless), TP is the temperature of the pond (°C), and Torg is the reference temperature for organics removal (°C). With the exception of the COD concentration and the pond temperature, the remaining parameters were all determined by fitting the model to the pond data.

2.3.7 Model fitting, parameter determination, and model evaluation

All model equations were solved simultaneously using Euler's Method, with a time-step of 1 day. All model fits were compared to the actual pond measurements and the sum of square errors (SSE) for all processes were determined. To determine the parameter values associated with the best fit of the data, the SSE was minimized using the solver function in Microsoft Excel. First, model fits were performed that minimized the SSE for ammonia-nitrogen and nitrate and nitrite-nitrogen. Subsequently, the COD and TKN-N reactions were successively added to this analysis and the SSE minimized. This process was repeated by varying initial variable values to ensure the global minimum SSE was determined. Fitting was also done by minimizing the SSE for ammonia-nitrogen, nitrate and nitrite-nitrogen, COD, and TKN. Due to changes in the system operation, three separate model fits were performed over the study period (Table 1). After determining the values for each model parameter, a common value across all fits was chosen for the temperature-related coefficients (θ and T) because these values should be consistent between all fits.

Mean absolute percentage error (MAPE) and normalized mean absolute error (NMAE) were used to evaluate the performance of the model fits. MAPE is a common measure of prediction accuracy that indicates the average absolute percentage error (Hyndman and Koehler, 2006). The calculation of MAPE (%) is described in Eq. (13).

$$MAPE = \frac{100}{n}\sum_{t=1}^{n}\left|\frac{Y_{pred,i} - Y_{obs,i}}{Y_{obs,i}}\right| \tag{13}$$

where, $Y_{pred,i}$ represents the prediction, $Y_{obs,i}$ represents the observation, and n represents the number of observations.

NMAE (unitless) is often used to compare errors of models with different scales. This metric is the mean absolute error normalized by the mean of the actual data points, as described in Eq. (14).

$$NMAE = \frac{\sum_{t=1}^{n}|Y_{pred,i} - Y_{obs,i}|}{\frac{1}{n}\sum_{i=1}^{n}|Y_{obs,i}|} \tag{14}$$

2.4 Determining the influence of the Lilypad system on volatilization

All collected mist samples were used in combination with the pond samples taken during these sampling events to estimate the fraction of ammonia volatilized by the Lilypad system. The differences in ammonia concentrations measured in the pond and those measured in the mist samples were used to determine the fraction of ammonia volatilized by the Lilypad system. The mass of ammonia-nitrogen removed from the pond per day as a result of the Lilypad system was determined using Eq. (15).

$$m_{NH3} = V_{system} \times v[NH_3]_l \tag{15}$$

where m_{NH3} is the mass of ammonia-nitrogen removed from the pond per day from the Lilypad system (g/day), V_{system} is the volume of leachate passing through the Lilypad system per day (L/day), v is the fraction of ammonia-nitrogen volatilized determined from the mist and pond samples, and [NH_3]l is the concentration of ammonia-nitrogen (g/L-N) found in the pond.

3. RESULTS AND DISCUSSION

3.1 Nitrogen species in the leachate pond over time

The observed concentrations of all nitrogen species measured in the leachate collection pond during the study period suggest that volatilization, nitrification, and denitrification occurred. Evidence of nitrification and/or volatilization is rooted in the changes in ammonia-nitrogen concentrations; ammonia-nitrogen mass entering the pond from the sumps was consistently greater than that exiting the pond (Figure 2), but a corresponding increase in concentration in the pond was not observed (Figure 3) and the concentrations in the pond were always lower than those expected when only considering pond hydraulic data and site climatological conditions (e.g., mixing only, no reactions). Figures 3-5 present the nitrogen species measured in the pond during the study period. Additionally, the trend of TKN concentrations (Figure 5) was mostly consistent with the

TABLE 1: Description of the time periods modeled in this study.

Model Fit Number	Start Date	End Date	Description of the model fit time period
1	11/27/18	4/29/19	This study commenced in 11/18. This fit ended in 04/19 because the Lilypad system was upgraded in May 2019. During the upgrades, the system was not operational, and data were not collected.
2	8/20/19	10/31/19	A set of leachate samples was taken in 08/19 to begin this period. This fit ended in 10/19 because significant changes in leachate composition occurred due to a new landfill cell opening in November 2019. Leachate sampling was not conducted during this event to document changes that may have occurred,
3	01/21/20	8/31/20	A set of leachate samples were taken in 01/20 to begin this period and 08/20 represents the end of the study period.

ammonia-nitrogen trend, supporting such ammonia-nitrogen removal. The presence of nitrite and nitrite-nitrogen in the pond (Figure 4), coupled with increases in these concentrations while virtually no nitrite and nitrite-nitrogen entered the pond through the sumps, provides evidence that ammonia-nitrogen removal is in part due to nitrification. It

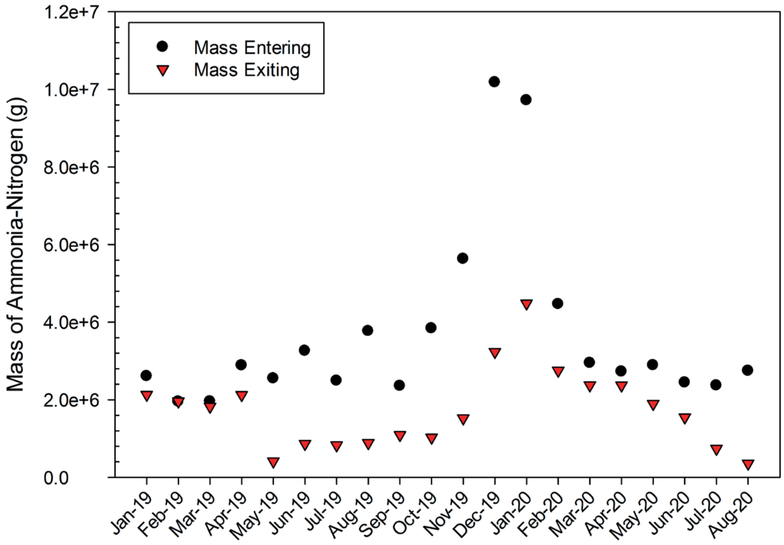

FIGURE 2: Monthly total mass of ammonia-nitrogen entering and exiting the leachate collection pond.

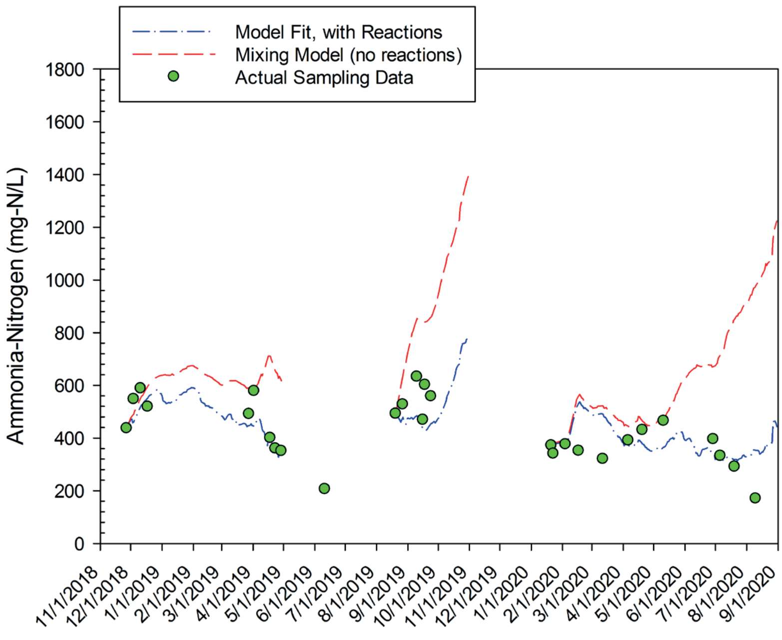

FIGURE 3: Fit of ammonia-nitrogen concentrations with volatilization and nitrification and concentrations computed from a mixing only model (e.g., no reactions occurring).

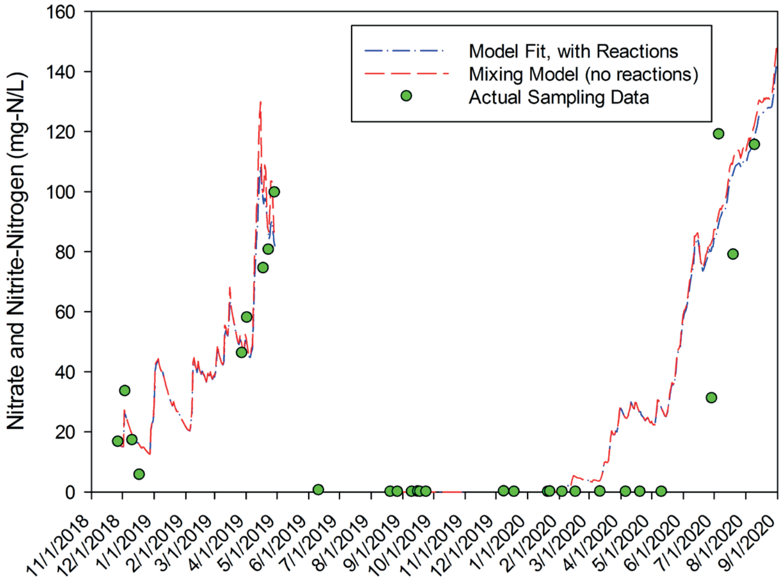

FIGURE 4: Fit of nitrate and nitrite-nitrogen concentrations with denitrification and concentrations computed from a mixing only model (e.g., no reactions occurring).

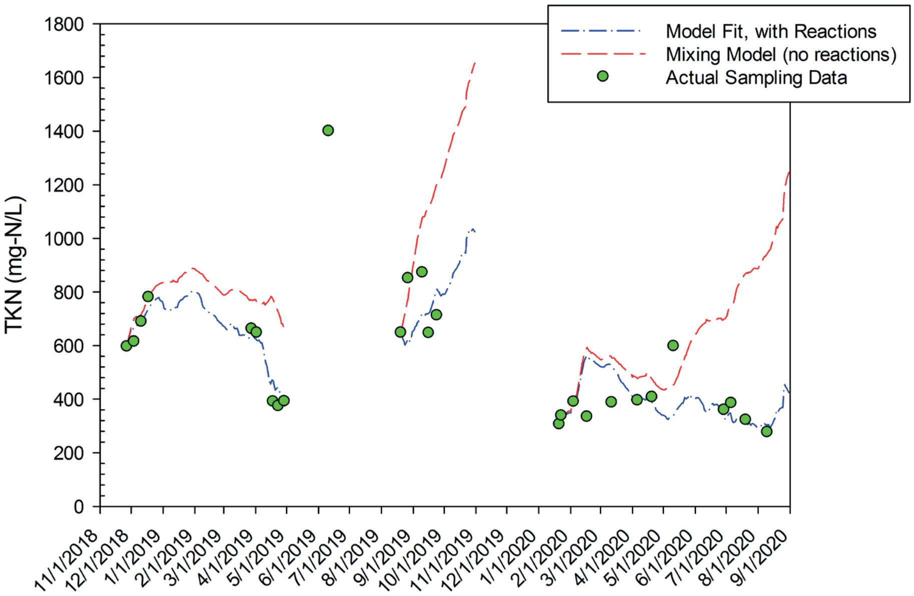

FIGURE 5: Fit of TKN concentrations with reactions and concentrations computed from a mixing only model (e.g., no reactions occurring).

is difficult to discern the presence of volatilization and denitrification by using the leachate data alone. When the observed concentrations of nitrate and nitrite-nitrogen in the pond drop to near-zero (from June 2019 to May 2020), it is possible either that no nitrification is occurring in the pond, or that the effect of nitrification is offset by denitrification during this time. Observations of an ammonia odor while at the site suggest volatilization was occurring.

3.2 Nitrogen fate

All leachate data were fit to the model describing volatilization, nitrification, and denitrification processes (Figures 3-6). The kinetic coefficients determined for each model fit are presented in Table 2. Overall, the model fits appear reasonable, suggesting the model accounts for the major processes occurring in the pond. The MAPE and NMAE associated with each fit are presented in Table 3. The lowest MAPE and NMAE for all parameters were associated with model fit 1, suggesting the data fit the model best during this time period (Table 3). Generally, with the exception of COD, the MAPE and NMAE associated with the fits for all parameters was lowest during fit 1 and highest for fit 3. The MAPE was less than 25% for all fits and all parameters, with the exception of nitrate and nitrite-nitrogen. Accordingly, the NMAEs were also relatively low for the fits associated with all parameters, with the largest NMAEs associated with the nitrate and nitrite-nitrogen data of each fit.

Results from the modeling suggested volatilization,

TABLE 2: Summary of kinetic coefficients determined for each model fit.

Variable	Model Fit #		
	1	2	3
C	1.000	1.000	1.097
k_{nit}	1.824	0.000	0.216
k_{denit}	4.801	0.000	0.332
k_{org}	0.186	0.034	0.184
θ_{nit}	1.5		
θ_{denit}	1.5		
θ_{org}	1.0		
T_{nit}	30		
T_{denit}	30		
T_{org}	30		
X	0.500	0.500	6.000

nitrification, and denitrification occurred during the time period associated with fit 1. These processes were not all found to occur during fit 2. The kinetic coefficients for nitrification and denitrification associated fit 2 were zero, suggesting that no nitrification or denitrification occurred during this time period, which is consistent with the zero or near-zero nitrate and nitrite-nitrogen concentrations observed in the pond during this period (Figure 4). It is important to note that the time period associated with fit 2 was short with few data points, making accurate modelling difficult. Although the MAPEs and NMAEs were low for fit 2, concentrations based on the model fit of some species, such as ammonia-nitrogen, did not follow the trends observed in the actual data.

The model also appeared to reasonably fit the data during time period 3, despite having the largest MAPE and NMAE for all parameters, with the exception of COD, across all fits. Results indicated that volatilization, nitrification, and denitrification all occurred during this time period. However, the model was not able to capture the changing ammonia-nitrogen, TKN, nitrate and nitrite-nitrogen, and COD concentrations from mid-February – March 2020 and July – August 2020. During mid-February 2020 – March 2020, the model indicated little volatilization or nitrification were occurring, and the fitted values of ammonia-nitrogen concentration in the pond were higher than the actually observed values. From the beginning of this fit period until March 2020, significant changes in mass entering and exiting the pond were observed (Figure 2). More ammonia-nitrogen was still entering the pond than exiting it, but the concentration observed in the pond decreased, suggesting greater levels of nitrification/or volatilization occurred. However, the model was not able to capture these increased levels of nitrification and/or volatilization. From June 2020 – August 2020, the model found that volatilization and nitrification were occurring, but at levels lower than observed. During this time period, the difference between ammonia-nitrogen masses entering and exiting the pond steadily increased (Figure 2) while the concentration observed in the pond decreased. Again, the model was not able to account for the increased levels of nitrification and/or volatilization occurring during this period. As a result of the poor fit in February/March and June – August, the MAPE and NMAE values were the largest for fits associated with the nitrate and nitrite-nitrogen data.

For comparative purposes, concentrations over time from a mixing only model (e.g., no reactions occurring) were computed in the case of ammonia-nitrogen and TKN and are also included in Figures 3, 5-6. In the case of nitrite and nitrate-nitrogen, concentrations over time from a mixing only model assuming no denitrification was occurring (e.g., only mixing, but with nitrification) were also computed, with results shown in Figure 4. The difference between the lines representing the model fit and results from the mixing model (e.g., no reactions) indicate the level of removal/transformation that occurred. Overall, these results suggest that significant nitrification and volatilization did occur throughout the study period (Figure 3), while significant amounts of denitrification did not occur (Figure 4) during the majority of the study period. These results are consistent with those observed in aerobic lagoons and stabilization ponds containing leachate. Mehmood et al. (2009) reported that 63% of ammonia-nitrogen was transformed via nitrification from a mature leachate with an average pH of 8.5 treated in an aerated lagoon, with the remaining ammonia-nitrogen lost via volatilization. Martins et al. (2013) reported up to 27% of the ammonia-nitrogen present in leachate (pH > 9.0) being treated in a stabilization pond was volatilized, while nitrification was responsible for only up to approximately 7% of ammonia-nitrogen removal. Several studies have also reported that if conditions were not optimal for volatilization (pH > 9.0, temperatures > 20°C), long hydraulic residence times may promote volatilization (Martins et al., 2013; Mehmood et al., 2009; Shrimali & Singh, 2001). In the present study, the leachate pH ranged from 8.0-8.6, with average hydraulic residence times 33, 76, and 90 days for model fits 1, 2, and 3, respec-

TABLE 3: MAPE and NMAE associated with all fits for all parameters.

	Fit 1		Fit 2		Fit 3	
	MAPE	NMAE	MAPE	NMAE	MAPE	NMAE
NH_3-N	8.3	0.098	14.5	0.155	24.4	0.201
NO_3+NO_2	30.9	0.171	-[1]	-[1]	56.7	0.325
TKN	7.5	0.064	14.3	0.153	16.2	0.176
COD	12.5	0.134	8.9	0.082	23.4	0.192

[1] *these processes were not found to occur within fit 2, therefore no MAPE or NMAE were computed*

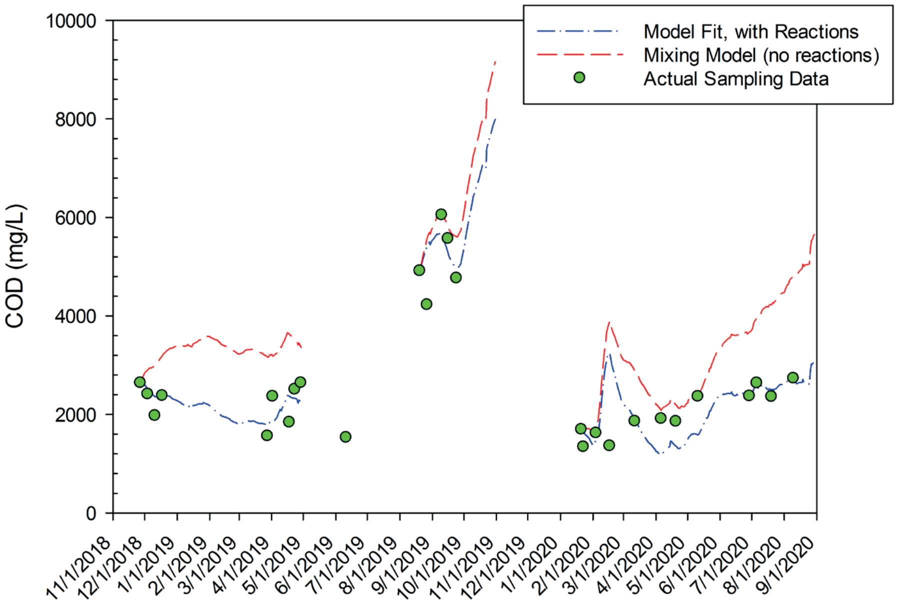

FIGURE 6: Fit of COD concentrations with organics degradation occurring and concentrations computed from a mixing only model (e.g., no reactions occurring).

tively, which are within the typical range of HRTs reported for lagoon and stabilization ponds.

Although significant denitrification did not occur during the study period, appreciable levels did occur during model fits 1 and 3. Simultaneous nitrification and denitrification was expected, particularly at the DO levels observed at this site (average concentration of 2.3 mg/L over the course of the study period). Others have reported the occurrence of these processes occurring simultaneously in landfill leachate treatment processes (Berge et al., 2005, 2006; Chen et al., 2016; Li et al., 2019). Denitrification may have been inhibited by the presence of dissolved oxygen in the pond or possibly by the metals present (e.g., arsenic, cadmium, etc.), limiting the degree of nitrogen removed via this pathway. It should be noted that many of the metals present in the leachate were observed at their highest quantities during fit 2. It is also possible that nitrification was inhibited, to some degree, by the low DO levels and the presence of metals.

3.3 Comparison of nitrogen transformation processes

The cumulative estimated mass of nitrogen removed/transformed via nitrification, volatilization, and denitrification associated with each fit is shown in Figure 7. Volatilization and/or nitrification were found to be the most predominant nitrogen removal processes during this study. Ammonia removal via volatilization accounted for approximately 39%, 100%, and 60% of the total nitrogen transformed during the periods of model fit 1, fit 2, and fit 3, respectively. During the first and third model fits, nitrification was also significant, accounting for 44% and 30% of the total nitrogen transformed, respectively. Denitrification was also determined to occur during model fits 1 and 3, although the levels were significantly lower (< 20%). As discussed previously, no nitrification or denitrification were found to occur during fit 2.

The trends associated with the cumulative nitrogen mass volatilized and nitrified differed slightly during each model fit. Volatilization was the predominant process occurring for the majority of this study, with the exception of April 2019. During this month, nitrification activity increased significantly, ultimately resulting in significantly more ammonia removal than volatilization. It appears that as the temperature of the pond increased, so too did the amount of nitrification and denitrification occurring, as evidenced by the changes in slope in the cumulative lines shown in Figure 7a. Nitrification and denitrification processes are known to increase in warmer months. Such a significant increase was not observed in April 2020 (Figure 7c), possibly because the average daily temperatures in April 2019 were higher than those found in April 2020. It should be noted, however, that as the temperatures in 2020 warmed, an increase in nitrification and denitrification was observed, as shown by the change in slope of the cumulative lines in Figure 7c. It should also be noted that in the summer months, an increase in all three removal pathways was observed, perhaps due to rising air and pond temperatures.

3.4 Sensitivity analysis

Although the kinetic coefficients in Table 2 were determined from the best fit for each model period, there is some uncertainty in the actual parameter values. To evaluate how this uncertainty may influence estimates of total masses of nitrogen transformed/removed, a sensitivity analysis was performed. First, values above and below that associated with each kinetic constant (C, k_{nit}, and k_{denit}) that resulted in a 10% change in the SSE were determined. Next, all combinations of these values for all parameters for each model fit were simulated (8 unique combinations for each model fit) and the total mass of nitrogen volatilized, nitrified, and denitrified was determined. The total

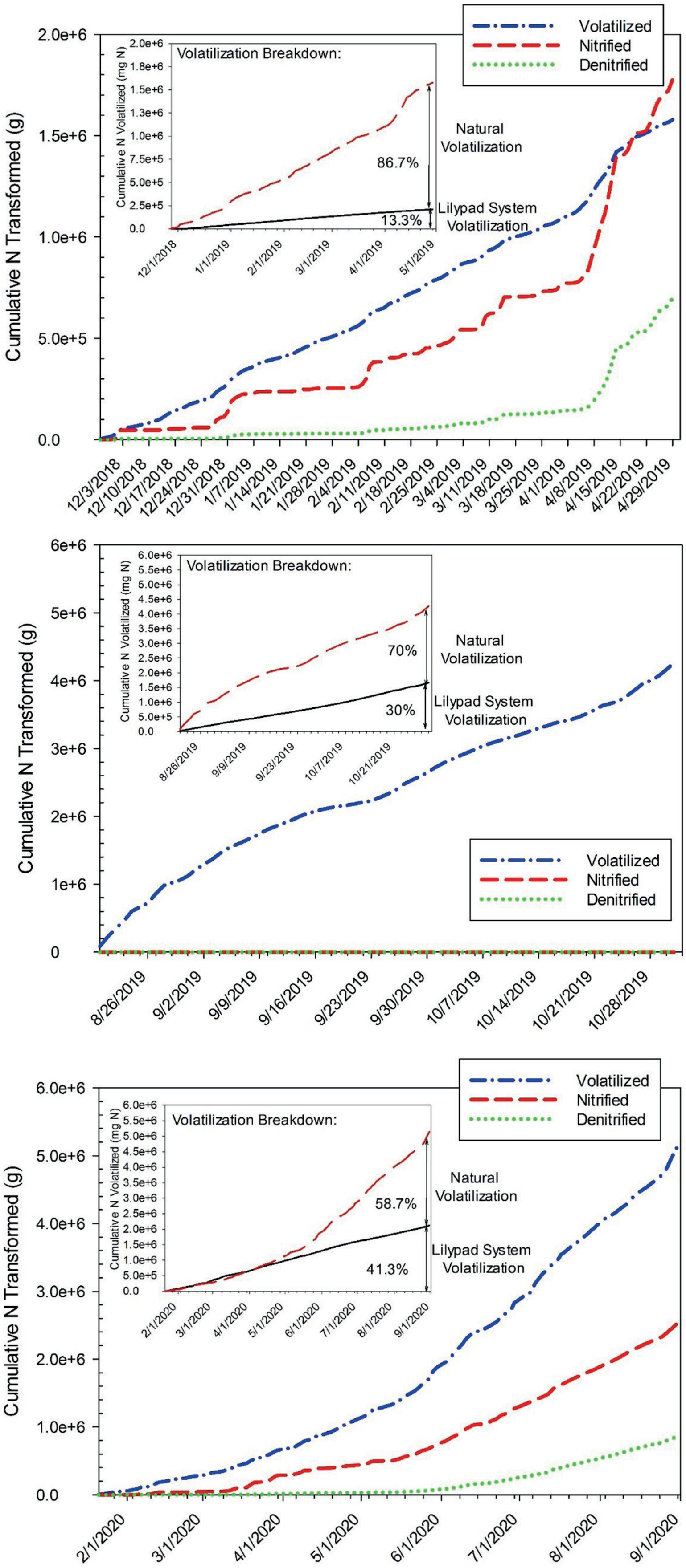

FIGURE 7: Cumulative nitrogen transformed via volatilization, nitrification, and denitrification for the model fit (a) 1, (b) 2, and (c) 3. Smaller graphs represent the cumulative mass of nitrogen volatilized due to both natural phenomena and the Lilypad system.

TABLE 4: Potential Variability of Each Nitrogen Removal/Transformation Process When Compared to the Best Fit for Each Model Period.

Model Fit	Range of mass of nitrogen transformed normalized by the mass determined from the model best fit		
	Volatilization	Nitrification	Denitrification
1: November 2018 – April 2019	0.9 – 2.5	0.2 – 1.9	0 - 14
2: August 2019 – October 2019	0.9 – 1.2	*	0
3: January 2020 – August 2020	– 2.4	0 - 0.2	0 - 5.4

** dividing by zero is not possible, the range of nitrogen mass removed via nitrification during this fit was determined to be 0 – 1,028,998 g N*

mass of nitrogen determined to be transformed from these simulations was normalized by the mass determined from the best fit for each model period to indicate the potential variability associated with these processes. Results from this analysis are shown in Table 4. For all model fits in which denitrification occurred, it was determined to be the most uncertain process. The mass of nitrogen removed via denitrification ranged from 0 – 14 times of that predicted with the best fit. Nitrification during fit 2 was also quite uncertain. During this period, the best fit indicated that no nitrification occurred. However, results from this sensitivity analysis suggests some nitrification during this period was possible. Importantly, conclusions from this analysis remain consistent with those observed with the best fit, suggesting that the predominant nitrogen removal process was either volatilization or nitrification.

3.5 Influence of the Lilypad system

The percent volatilization of ammonia determined from the mist and pond samples are shown in Figure 8. All percentages occurring during each model fit were averaged to obtain an overall percent volatilization for each fit and used in Eq. (14) to determine the mass of ammonia-nitrogen removed from the pond due to the Lilypad system each day. Results from this analysis are shown in Figure 7 and suggest that the total amount of nitrogen being volatilized due to the Lilypad system ranged from 13 (fit 1) – 41% (fit 3, Figure 7). This level of ammonia loss is consistent with that reported by Chastain and Montes (2005) and Saez et al. (2012), who reported that up to 26% and between 15 – 35% ammonia, respectively, was lost during the spraying of animal manure and secondary-treated wastewater. Volatilization due to natural phenomena resulted in the greatest level of ammonia-nitrogen volatilization.

The contribution of the Lilypad system on ammonia volatilization depends on several factors, including the percentage of volatilization occurring, the volume of leachate being passed through the system, site climatological conditions, and the ammonia concentrations in the pond. The lowest contribution of the Lilypad system occurred during fit 1, where the measured average volatilization percentage was much lower than that observed during other time periods (Figure 8). In addition, the volume of leachate passed through the system during this time period was the lowest. The volume of leachate passed through the Lilypad system increased significantly for subsequent fits because at the end of fit 1, the Lilypad system underwent significant upgrades. These upgrades increased the efficiency of the system and the total amount of leachate passing through the system. During the time associated with fits 2 and 3, much larger average daily volumes passed through the system, which ultimately resulted in the Lilypad system playing a more significant role in volatilization during those periods.

Two factors likely inhibited further amounts of enhanced volatilization by the Lilypad system. First, the average pH of the leachate pond over the study period was 8.3. A higher

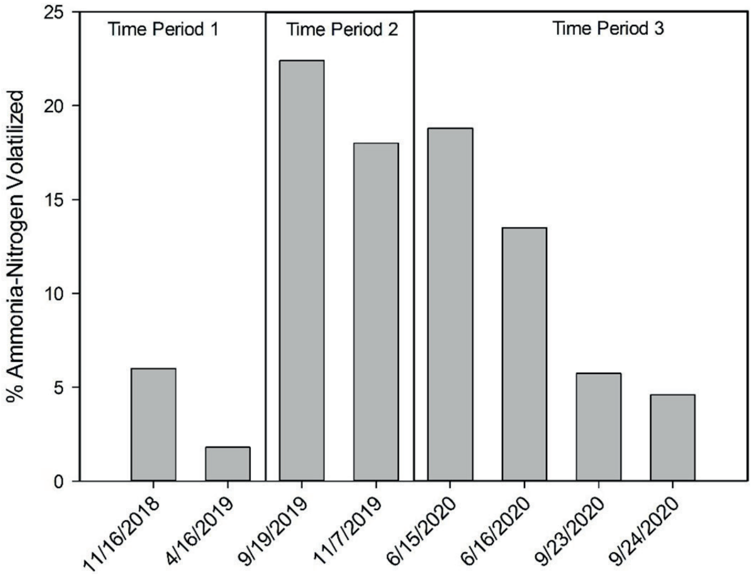

FIGURE 8: Volatilization percentages determined from collected mist and pond samples.

pH in the pond would have resulted in increased volatilization. At a pH of 8.3, only approximately 15% of ammonia-nitrogen is present as volatilizable ammonia-nitrogen, while the remaining 85% is present as ammonium-nitrogen. Increasing the pH to at or above 9.25 has the potential to increase the presence of ammonia and increase volatilization (Metcalf & Eddy, 2013). The second factor influencing the amount of enhanced volatilization is the amount of leachate that passes through the Lilypad system on a daily basis. This volume is small compared to the volume of the pond. On average, only 2.1%, 5.2%, and 4.3% of the daily pond volume was passed through the Lilypad system daily during model fits 1, 2, and 3, respectively. Thus, to increase the amount of volatilization, it is recommended that the volume of leachate passing through the Lilypad system be increased and pH adjustment be considered. It is also important to note that the Lilypad system aerates the leachate, which may have also influenced the nitrification and denitrification processes. This specific contribution, however, could not be quantified.

4. CONCLUSIONS

Results from this work indicate that volatilization, nitrification, and denitrification were occurring in the pond. Volatilization of ammonia-nitrogen accounted for the majority of nitrogen removed from the pond, representing approximately 65% of the total nitrogen transformed. Nitrification and denitrification also occurred and, at times, accounted for a significant fraction of the nitrogen transformed. It appears, with the exception of fit 2, that nitrogen transformed via nitrification and denitrification increased during warmer months. Results from this study also indicate that the Lilypad system has the potential to significantly enhance ammonia-nitrogen volatilization, suggesting the use of a misting/droplet spraying system to enhance ammonia-nitrogen volatilization from leachate is a viable approach. The degree of this enhancement appears to be dependent on the volume of liquid passing through the system. Increasing the levels of ammonia-nitrogen removal from the pond could be accomplished by passing more liquid through the Lilypad system, increasing the operational time of the system, or adding additional baskets. Another option to increase ammonia-nitrogen removal would be to increase the pH of the leachate in the pond prior to it being passed through the Lilypad system, although further study is recommended before implementing pH adjustment at the site. Future studies that focus on investigating the link between Lilypad operational parameters and nitrogen fate are recommended. Using such information to develop a predictive model to develop optimal ammonia removal strategies would be extremely beneficial.

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