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*Original Research Paper*

# Quantification of Ammonium Release from an Aging Free Water Surface Constructed Wetland To Improve Treatment Performance

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One potential cause of declining performance in free water surface (FWS) constructed wetlands (CW) is the accretion of decaying biomass or detritus. Over time (10–20 years), this detritus can form a new substrate above the antecedent wetland soil. As FWS CWs continue to age across the country, we must better understand the influence of this accumulated detritus substrate on nitrogen (N) removal to improve design and inform operators about the importance of management and removal. A laboratory study was conducted to quantify the ammonium ($NH_4$-N) released from accumulated detritus and to develop a kinetic model that would represent this release. Three experimental runs were conducted, each using 9 wetland microcosms equally loaded with detritus (mainly from *Typha spp.*) from a 20+ year-old FWS CW. Each run was conducted with 3 variable initial $NH_4$-N concentrations in the water column (0 mg $L^{-1}$, 5 mg $L^{-1}$, and 10 mg $L^{-1}$). Each initial concentration was triplicated and randomly assigned. The release of $NH_4$-N was inversely proportional to initial water column concentrations and was reasonably represented using first order kinetics (mean $R^2 = 0.77$). Valid parameter values were calibrated for 23 of the 27 experimental units (i.e., wetland microcosms). The porewater $NH_4$-N concentration ($C_{pw}$) and the rate constant ($k_u$) parameter values ranged from 4.7 mg $L^{-1}$ to 21.5 mg $L^{-1}$ and 0.004 m $d^{-1}$ to 0.13 m $d^{-1}$ (1.5 m $yr^{-1}$ to 47.4 m $yr^{-1}$), respectively. The potential areal $NH_4$-N release rates ($J_{UF}$) from the detritus substrate at an overlying water column concentration of 4 mg $L^{-1}$ and 6 mg $L^{-1}$ were 0.21 g-N $m^{-2}$ $d^{-1}$ and 0.14 g-N $m^{-2}$ $d^{-1}$ (70 g-N $m^{-2}$ $yr^{-1}$ and 50 g-N $m^{-2}$ $yr^{-1}$), respectively. At these rates, $NH_4$-N diffusion from the detritus substrate would substantially influence N removal performance in lightly loaded systems (TKN load <120 g-N $m^{-2}$ $yr^{-1}$). These results provided an initial estimate of the magnitude of $NH_4$-N release from accumulated detritus, as well as evidence to support the inclusion of $NH_4$-N flux in initial design models and the importance of regular FWS CW maintenance.

**Keywords** Detritus; Diffusion; Nitrogen; Treatment efficiency; Wetlands



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**Highlight**

Laboratory experiments and modeling indicated ammonium flux from detritus porewater to the overlying water column is significant in aging free water surface constructed wetlands, which reduces treatment efficiency and thus has important design and maintenance ramifications. .

## 1. Introduction

Within free water surface (FWS) constructed wetlands (CW), the accumulation of decaying biomass (i.e., detritus) has the potential to negatively influence treatment performance (Kadlec and Wallace 2009; Martinez and Wise 2003; Thullen et al. 2005; Wang et al. 2006). The accumulation of detritus begins with the stands of macrophyte vegetation that thrive in FWS CWs treating wastewaters with high nutrient levels. This vegetation is necessary for optimal wetland performance because it intercepts suspended solids, assimilates nutrients, contributes a carbon source for denitrification, and provides a surface for biofilm growth (Brix 1997; Kadlec and Wallace 2009; Mitsch and Gosselink 2015; Thullen et al. 2005). At the end of each growing season, the detritus from this vegetation falls back into the FWS CW basin. Because saturated conditions are maintained in these systems, this detritus decays slowly, allowing for a buildup of organic matter, including nutrients, over time (Kadlec et al. 2010; Kadlec and Wallace 2009; Mitsch et al. 2012; Thullen et al. 2005). Detritus accumulation rates have been observed to be between 1 cm $yr^{-1}$–3 cm $yr^{-1}$ in depth in high nutrient environments (Kadlec et al. 2010; Kadlec and Wallace 2009). While some detrital material enhances wetland treatment, accumulation at these rates over 10–20 years may significantly reduce water depths, effective treatment area, basin volume, and hydraulic retention time resulting in decreased treatment efficiency (Kadlec et al. 2010; Kadlec and Wallace 2009; Martinez and Wise 2003; Wang et al. 2006). In addition to its negative influence on internal hydraulics, a thick layer of accumulated detritus has also been identified as a potential internal nitrogen (N) source in wetlands (Reddy et al. 1984; Sartoris et al. 1999; Thullen et al. 2002).

The potential internal nitrogen (N) source is the product of the previously assimilated N within accumulated organic matter (e.g., detritus from years of dense vegetation) and soil diagenetic processes. Over time, ammonium ($NH_4$-N) accumulates within the substrate porewater due to the mineralization of organic N to $NH_4$-N through microbial respiration and the inhibition of nitrification under anaerobic soil conditions often present in FWS CWs (Reddy et al. 1984). The accumulation of $NH_4$-N in the anaerobic zone of the sediment creates a concentration gradient, which drives $NH_4$-N upward through diffusion from the sediment into the overlying water column (Fig. 1). Under oxidized conditions, the $NH_4$-N that diffuses into the aerobic upper layer of the sediment can be nitrified. Therefore, even though there is upward flux of the $NH_4$-N, the majority can be converted to nitrate ($NO_3$-N) prior to entering the water column. This $NO_3$-N can then be denitrified—significantly reducing the internal N source. However, under highly reduced conditions, likely present in aging FWS CWs with thick detritus layers inducing high microbial oxygen ($O_2$) demand, nitrification, if present at all, is greatly reduced at the sediment-water interface. Instead, much of the diagenetic $NH_4$-N is driven into the water column creating a significant internal N source in aging FWS CWs.

While these processes are known, research to quantify the internal N source created by accumulated detritus is scarce. Due to the lack of field and laboratory data from aging wetlands, this process also has not been sufficiently represented in the current FWS CW design models. For example, the P-k-$C^*$ model (Kadlec and Wallace 2009), commonly used to determine N removal performance when designing FWS CWs, accounts for N return from the soil profile using a basic single irreducible N concentration constant, $C^*$, to represent this complex process. The value recommended for $C^*$ in the $NH_4$-N removal process is often a very low concentration (often 0 mg $L^{-1}$), which essentially assumes the internal $NH_4$-N source to be neglgible in the model. Without more laboratory and field data to support a more robust method to account for an internal N source created by accumulated detritus, we are limited in our ability to create an accurate prediction of N removal performance in aging wetlands. The scarcity of research on pollutant return rates is noted in Kadlec and Wallace (2009), where the authors state that although chemical return rates from the wetland substrate are likely significant, there was "at present [2009], no scientific study to provide guidance on modeling this transfer."

We identified two, 20+ year-old FWS CW cells within the treatment train of the Walnut Cove Wastewater Treatment Plant (WWTP) that appeared to show significant signs of poor N treatment performance.

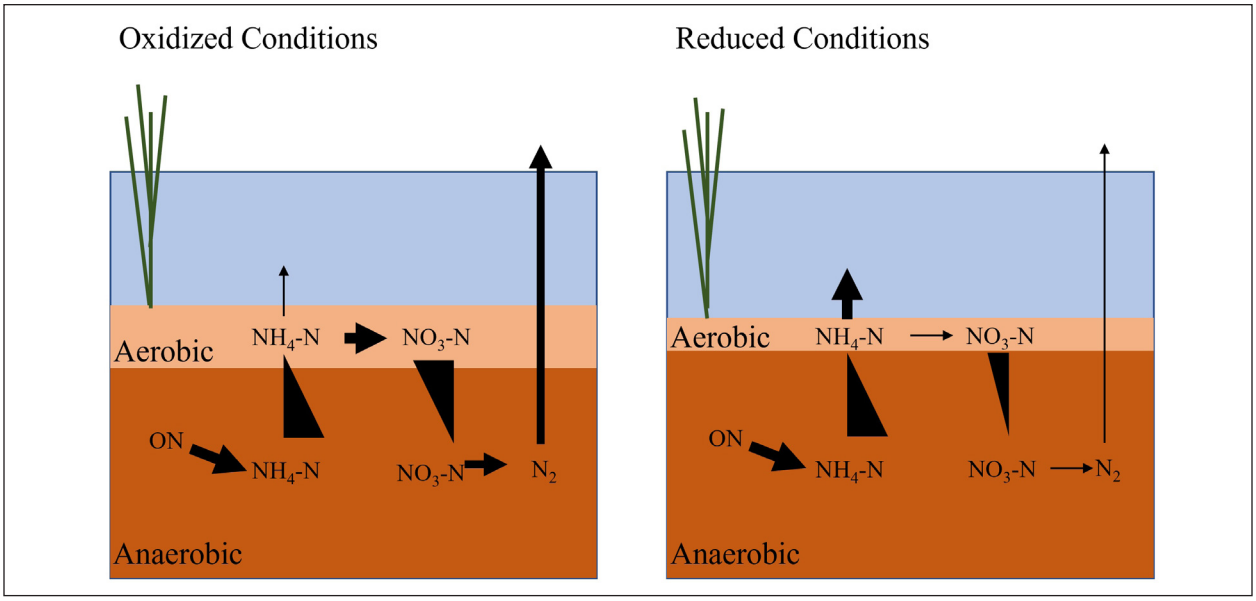


**Fig. 1.** Simplified diagram of internal N processing in highly organic FWS CW soils under oxidized and reduced conditions. The thickness of the arrows indicates magnitude of N movement. Note the thinner aerobic layer in reduced conditions.

A preliminary monitoring study in May 2016 found that the average daily $NH_4$-N concentrations increased from 2.6 mg $L^{-1}$ at the inlet to 6.9 mg $L^{-1}$ at the outlet in one of the wetland cells (Burchell et al. 2016). A longer-term study from September 2018 to March 2019 also indicated poor treatment, since average inlet and outlet $NH_4$-N concentrations for both cells were 8.0 mg $L^{-1}$ and 8.3 mg $L^{-1}$, respectively (Kamrath 2021). Additionally, it was observed that over their lifespan, the wetland cells had accumulated detritus at depths of approximately 30 cm (12 in) and there was a trend of increased $NH_4$-N outlet concentrations in the historic WWTP effluent data (Fig. 2). We hypothesized that the N removal performance had been negatively influenced by an internal N source produced by accumulated detritus, and that during many times of the year, the wetland could be a $NH_4$-N source rather than a sink (Kamrath 2021).

In this study, we aimed to quantify the potential internal N release from accumulated detritus in aging FWS CWs using a laboratory microcosm experiment. This experiment would allow us to quantify and model the upward flux of $NH_4$-N from this detritus to the water column at this site, then use these results to evaluate the potential return of $NH_4$-N from the substrate back to the water column in similar full-scale systems. Results of this study are intended to improve the understanding of how and why N treatment in constructed wetlands might change over time, and what types of maintenance practices may be needed to extend the treatment effectiveness of these systems.

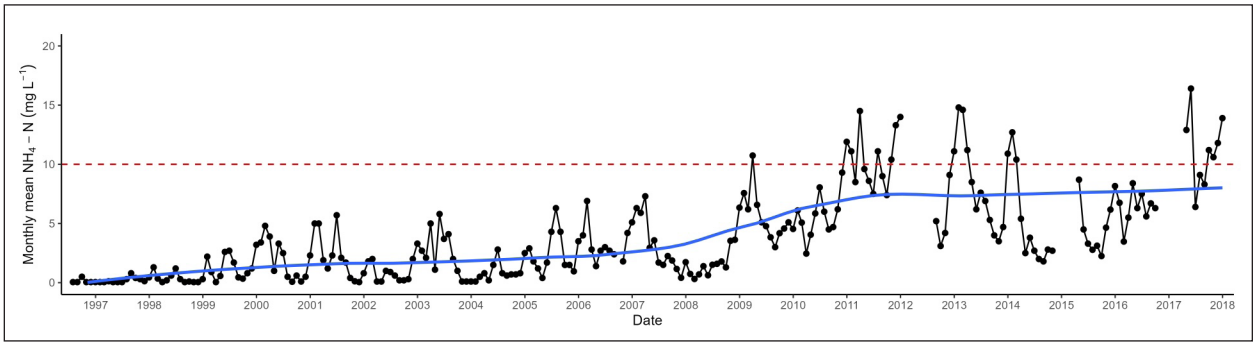


**Fig. 2.** Monthly mean $NH_4$-N concentrations at the outlet downstream of the constructed wetland treatment at the Walnut Cove WWTP. The blue line represents the trend in the data using a local polynomial regression (loess) fitting while the red dashed line represents the permitted $NH_4$-N discharge limit (10 mg $L^{-1}$).

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## 2. Materials and Methods

### 2.1 Site Description

The sampled constructed wetlands are part of the WWTP for the Town of Walnut Cove, North Carolina, United States of America (36° 17'38.5" N, 80° 07'57.3" W). The Walnut Cove WWTP has been described previously in Sardana et al. (2019) and Kamrath (2021); here we provide a short overview of the site. The Walnut Cove WWTP was permitted to discharge a monthly average flow below 2273 $m^3$ $d^{-1}$ (0.5 MGD) and serves an estimated population of 1,800 persons (UNC 2020). The WWTP was modified to its current configuration in 1996. Within the WWTP, 2 aerated lagoons in series received untreated wastewater. The lagoons discharged wastewater to a serpentine pond dominated by *Lemna* (known as a duckweed raceway), which facilitated sedimentation by creating a quiescent environment, removed nutrients via plant uptake, and stabilized pH and temperature by providing widespread shading that prevents algal growth (Zirschky and Reed 1988). This duckweed raceway discharged into the 2 FWS CW cells, which were designed primarily to provide final N polishing through nitrification and denitrification (Wolverton 1992; Wolverton et al. 1983). During on-site monitoring (Kamrath 2021), the influent $NH_4$-N concentrations of the pre-treated wastewater that entered the treatment wetlands ranged from 1 mg $L^{-1}$ to 13 mg $L^{-1}$, while $NO_3$-N concentrations entering the wetlands averaged <1 mg $L^{-1}$. Following the wetlands, the water passed through a disinfection basin before discharge to the adjacent Town Fork Creek. This natural treatment train was designed to maintain pollutant concentrations well below the effluent discharge limits set in the site's NPDES permit ($BOD_5$ = 30 mg $L^{-1}$, TSS = 30 mg $L^{-1}$, and $NH_4$-N = 10 mg $L^{-1}$).

### 2.2 Porewater $NH_4$-N Concentration Profiles in the Field

Dialysis porewater samplers were installed into the detritus substrate of one of the wetland cells in October 2019 and in January 2020 to measure $NH_4$-N concentration in the porewater and above the sediment. The dialysis porewater samplers were constructed of Plexiglas and a dialysis membrane following the description of an in-situ porewater sampler in Hesslein (1976) (Fig. 3). Porewater chemical concentrations with depth can be obtained given the equilibration through a dialysis membrane of water within the porewater sampler with the surrounding water.

The porewater sampler was machined from a piece of Plexiglas (36.83 cm × 10.0 cm × 1.27 cm). Long slots, 5 mm wide and 8 cm long, were cut parallel to the short side of the original piece and all the way through the thickness of the piece. Thirty parallel slots were machined, the center of each slot being spaced by 1 cm from the next resulting in a 30 cm-deep porewater sampler that could be sampled at 1 cm intervals. One end was sharpened to ease penetration into the sediment. Two, cellulose-based dialysis membranes were applied on each side of the sampler, isolating after application in distilled water, the equivalent of 5 ml of water per slot (Brandl and Hanselmann 1991). The membranes were maintained against both sides of the sampler by 2 thinner, concurrently slotted pieces of Plexiglas.

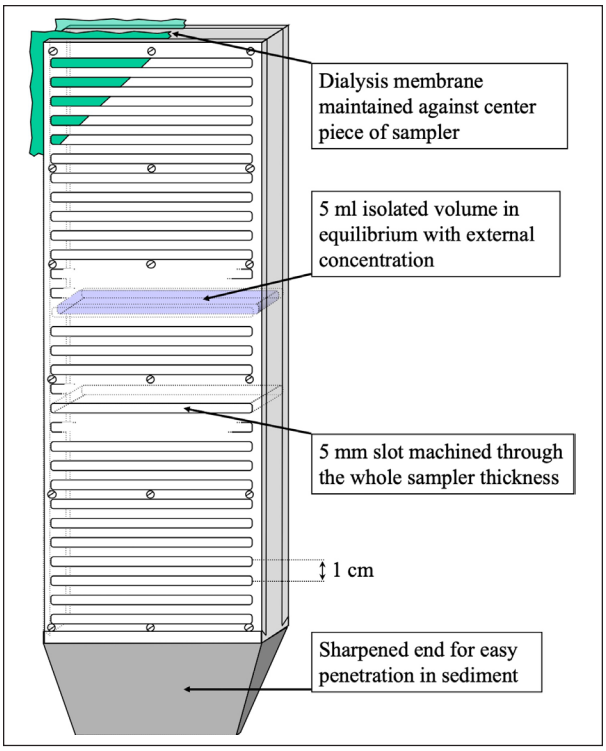


**Fig. 3.** Schematic of the porewater sampler.

The samplers required laboratory preparation before field installation. The acid-washed Plexiglas centerpiece of the sampler was placed into a container filled with distilled water. The membranes were first soaked in distilled water to be softened and then applied under water and maintained against the center piece by attaching the thinner Plexiglas plates on both sides of the center piece using screws. The membranes were applied tightly enough against the centerpiece so that the samplers could be removed from the water without water leaking between slots. The samplers were not taken out of the distilled water container until they were installed in the field. There, the samplers were carefully pushed down vertically into the sediment so that approximately the last 5 slots would remain above the sediment-water

interface. Hesslein (1976) recommended an equilibration time of at least 5 days between the contained water and the surrounding water. The samplers were thus left in the sediment for 1 week until the next trip to the field.

After retrieval, most of the sediment was removed from the samplers and the samplers were cleaned further with distilled water. Each slot was then sampled using hypodermic needles and syringes through the membranes, transferred into glass vials, and kept on ice until analysis. Water quality samples were analyzed immediately using a HACH DR3900 Spectrophotometer (HACH, Loveland, Colorado, United States). Samples were analyzed for $NH_4$-N concentrations (mg $L^{-1}$) using TNTplus 830, 831, and 832 vials and the USEPA compliant method 10205 (Hach 2023a). The method detection limit was 0.015 mg $L^{-1}$.

### 2.3 Laboratory Experimental Design

The experiment was performed within Weaver Laboratory at North Carolina State University. Nine experimental units (i.e., microcosms) consisted of 20 cm x 13 cm x 30 cm plastic containers with internal baffles filled with an aged detritus substrate. The detritus substrate was collected from several different locations within the 24-year-old FWS CW cell treating municipal wastewater in Walnut Cove, North Carolina, United States. Detritus was collected from across the vertical profile of the detritus, which was approximately 30 cm deep, and placed into three, 19-L (5-gal) buckets. Care was taken to obtain only detritus and avoid active vegetation. These buckets were brought back to the lab in Raleigh, North Carolina, United States, where they were left undisturbed for at least 24 h before excess water was poured off and the contents of each bucket were combined in a 66-L (17.4-gal) bucket. The detritus was analyzed for N content prior to use in the experiment (between 4,000 mg-N /kg DW–7,000 mg-N /kg DW [or 0.4 N–0.7% N]—see Supplemental Material). From the bottom to the top, each microcosm was filled with the detritus substrate (3 kg wet weight; ~9 cm depth) followed by 3 L of tap water (~9 cm water column depth) (Fig. S1, Supplemental Material). Care was taken to minimize the disturbance of the detritus substrate when adding water. Advective transport was minimized by using batch design instead of a flow-through design for the wetland microcosms. The microcosms were then covered with black plastic to limit both light exposure and gas exchange with the atmosphere, both of which had the potential to increase confounding N conversions (assimilation and nitrification).

The experiment was conducted 3 times. A new batch of detritus was obtained from the Walnut Cove FWS CW cell for each experimental run. Each run lasted approximately 2 weeks. For each experimental run, the initial water column $NH_4$-N concentration was selected to represent one of 3 target concentrations (0 mg $L^{-1}$, 5 mg $L^{-1}$, and 10 mg $L^{-1}$) (Fig. 4). These initial values spanned the range of likely influent $NH_4$-N concentrations observed entering the Walnut Cove wetlands. The initial $NH_4$-N concentrations were achieved using powdered, standard grade (>99%) ammonium sulfate ($[NH_4]_2SO_4$) (Alpha Chemicals, Missouri, United States) dissolved into a source water reservoir. Each of the initial water column $NH_4$-N concentrations were replicated in triplicate and randomly assigned to the 9 wetland microcosms.

To create the source water reservoir for each treatment, three, 66-L (17.4-gal) buckets were each filled with 10 liters of filtered tap water. Zero g, 0.24 g, and 0.47 g of $(NH_4)_2SO_4$ were added to the water column of the 0 mg $L^{-1}$ treatment bucket, 5 mg $L^{-1}$ treatment bucket, and 10 mg $L^{-1}$ treatment bucket, respectively. After the $(NH_4)_2SO_4$ additions, each bucket was mixed for approximately 1 min. After mixing, each source water reservoir was sampled and analyzed to obtain the initial $NO_3$-N and $NH_4$-N concentrations. Source water $NH_4$-N concentrations were within 1.3 mg $L^{-1}$ of the target concentrations for each experiment (Table 1).

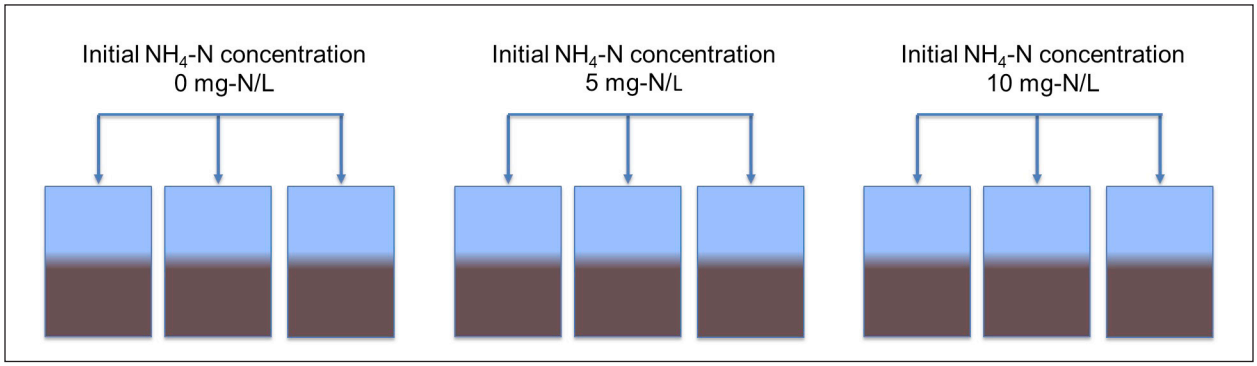


**Fig. 4.** Experimental setup for each run. Nine microcosms were created from a new batch of detritus for each run. In each run, 3 target initial $NH_4$-N concentrations were applied in triplicate.

**Table 1** The initial $NH_4$-N concentrations (mg $L^{-1}$) in the source water relative to the target initial $NH_4$-N concentrations for each experimental run

| Run | Dates | Initial $NH_4$-N concentration for each treatment | | |
|---|---|---|---|---|
| | | 0 mg $L^{-1}$ | 5 mg $L^{-1}$ | 10 mg $L^{-1}$ |
| **1** | 11/12/20 to 11/26/20 | 0.4 | 6.2 | 10.7 |
| **2** | 12/10/20 to 12/21/20 | 0.4 | 5.9 | 11.3 |
| **3** | 1/25/21 to 2/5/21 | 0.8 | 5.5 | 10.2 |

### 2.4 Water Quality Analysis

Water quality samples were collected directly from the water column of each microcosm using a 1000-µL pipette with Fisherbrand SureOne pipette tips (Thermo Fisher Scientific, Waltham, Massachusetts, United States). Initial samples were collected in the first hour after the microcosms were complete. After this initial sampling, samples were collected on days 1, 2, 3, 5, 7, 8, and 18 for the first experimental run and days 1, 3, 5, 7, and 11 for the final 2 runs.

Water quality samples were analyzed immediately after collection using a HACH DR3900 Spectrophotometer (HACH, Loveland, Colorado, United States). Samples were analyzed for $NH_4$-N concentrations (mg $L^{-1}$) using the method described in section 2.2. Samples were also analyzed for nitrate ($NO_3$-N) concentrations (mg $L^{-1}$), as a check for potential nitrification within the microcosms, using TNTplus 835 vials and the USEPA compliant method 10206 (Hach 2023b). The 10206 method had a detection limit of 0.2 mg $L^{-1}$.

The mean $NO_3$-N concentration in all runs for samples taken between Day 0 and Day 7 was 0.3 mg $L^{-1}$ (Kamrath 2021). Although nitrification was possible in the microcosms, the nitrification rate was likely negligible in the first 7 days of each experimental run because dissolved oxygen (DO) consumption measured over the first 7 days did not produce a corresponding increase in $NO_3$-N over that same period (Kamrath 2021). However, increased $NO_3$-N concentrations were observed in samples collected after Day 7 (up to 1.5 mg $L^{-1}$) (Kamrath 2021). Because nitrification removes $NH_4$-N by oxidizing it to $NO_3$-N, $NH_4$-N release rates estimated with data influenced by nitrification would not estimate a true release rate from the substrate, but instead a net $NH_4$-N release rate (i.e., the $NH_4$-N release rate minus the nitrification rate). Therefore, to best estimate $NH_4$-N release rates and remove the potential nitrification influence in this study, samples taken after Day 7 were omitted from analysis. The reduction to a 7-day period was also deemed acceptable because wastewater flowing through the wetland study site had a residence time less than 3 days and the average nominal hydraulic retention time (HRT) in most FWS CWs is approximately 7 days (Gerke et al. 2001; Kadlec and Wallace 2009). However, it must be noted that the assumption of negligible nitrification during the first 7 days cannot be completely proven by the data gathered in this study. If nitrification did occur in the first 7 days, then the $NH_4$-N release rates reported herein should be considered conservative.

After each sample was collected, additional water quality parameters including pH, DO, specific conductivity, and temperature were measured in 6 of 9 microcosms using a YSI Pro field probe (Xylem US, Yellow Springs, Ohio, United States). Water quality parameters (temperature, DO, pH, and specific conductivity) obtained on Day 1 and Day 7 of all 3 experimental runs (n = 18) were compared to evaluate the changes in these parameters during the study period.

Air temperature in the lab was maintained at approximately 20 ˚C. Initial mean (± standard deviation) water temperature was 21.8 ± 1.3 ˚C. Mean water temperatures dropped slightly during each experimental run to 20 ± 0.5 ˚C on Day 7. Initial mean pH values (6.9 ± 0.2) were nearly identical to the final mean pH values (6.9 ± 0.1). Initial mean DO concentrations were 75.5 ± 17% and then dropped to 27.0 ± 17.3% at the end of the studies. Alternatively, mean specific conductivity increased from 263 ± 38.5 µS $cm^{-1}$ on Day 1 to 314 ± 44.9 µS $cm^{-1}$ on Day 7.

### 2.5 N Dynamics Modeling

N removal in treatment wetlands is often represented using the steady-state first-order k-C* model (Kadlec and Wallace 2009). To represent the internal hydraulics of a treatment wetland more accurately, this k-C* can be expanded to include the number of tanks-in-series (TIS) derived from the wetland's residence time distribution (RTD), referred to as the P-k-C* model. From this baseline, first-order areal conversions for organic nitrogen (ON), $NH_4$-N, and $NO_3$-N can be combined to

create a sequential N dynamics model. A mass balance can then be computed for each tank in the model to produce a model that better represents the entire N cycle within a wetland (Gerke et al. 2001; Kadlec 2008; Kadlec and Wallace 2009). In this model, C* is typically set to 0 mg $L^{-1}$ for the $NH_4$-N removal flux. Therefore, $NH_4$-N production within the wetland is limited to the ammonification of water column ON and considers the $NH_4$-N return from the substrate as negligible (Equation 1) (Kadlec 2008).

$$QC_{A,out} = Q_{in}C_{A,in} + (J_A - J_N - J_{AU})A_j \quad (1)$$

where the first term ($Q_{in}C_{A,in}$) is the $NH_4$-N load into the tank (g $d^{-1}$; $Q_{in}$ = inflow rate; $C_A$ = $NH_4$-N concentration), the second term ($J_A = k_aC_{0,j}$) is the $NH_4$-N load added due to ammonification of ON in the water column, the third term ($J_N = k_nC_{A,j}$) is the $NH_4$-N load removed due to nitrification to $NO_3$-N, and the fourth term ($J_{AU}$) is the $NH_4$-N load removed by plant uptake (assimilation or uptake).

Here we suggest adding a first-order release rate to the model to represent the upward flux of $NH_4$-N from an accumulated detritus substrate (Equation 2 and Fig. 5).

$$V\frac{dC_A}{dt} = J_{UF}A = k_uA(C_{pw} - C_A) \quad (2)$$

where $J_{UF}$ is the upward flux (g-N $m^{-2}$ $d^{-1}$), A is the surface area ($m^2$), $k_u$ is the rate constant or upward diffusion velocity constant (m $d^{-1}$), $C_{pw}$ is the $NH_4$-N concentration in the porewater (mg $L^{-1}$), and $C_A$ is the $NH_4$-N concentration in the water column (mg $L^{-1}$). Mechanistically, this model describes the diffusive transport of $NH_4$-N from the substrate porewater to the overlying water column if $C_{pw}$ is greater than $C_A$. As $C_A$ nears $C_{pw}$, diffusive transport upward will slow. This term could easily be added as a fifth term to the previous sequential model (Equation 1). Equation 2 was derived analytically to provide an equation that could be used to predict $C_A$ at time t ($C_A$[t]) (Equations 3–6).

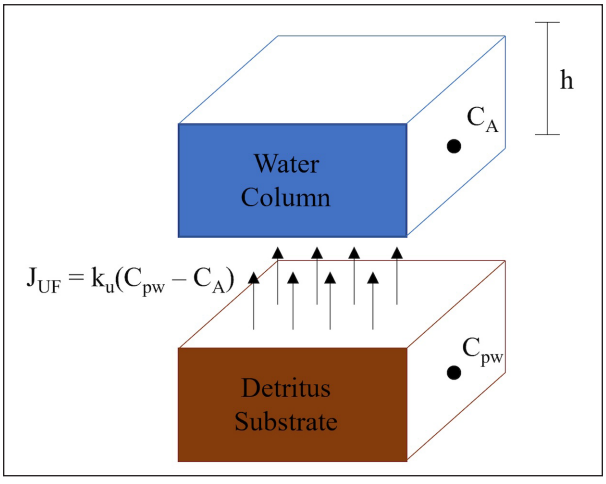


**Fig. 5.** Return of $NH_4$-N produced within the detritus substrate to the overlying water column.

For an overlying water depth, h, we hypothesize that the accumulation of $NH_4$-N in the water column can be approximated by a first order rate and be written as:

$$\frac{dC_A}{dt} = \frac{k_u}{h}(C_{pw} - C_A) \quad (3)$$

This can be further developed:

$$\frac{dC_A}{(C_{pw} - C_A)} = \frac{k_u}{h}dt \quad (4)$$

$$\int_{C_A(0)}^{C_A(t)} \frac{dC_A}{(C_{pw} - C_A)} = \int_0^t \frac{k_u}{h}dt \quad (5)$$

$$C_A(t) = C_{pw} - \left(C_{pw} - C_A(0)\right) * e^{-\frac{k_u}{h}t} \quad (6)$$

where $C_A(0)$ is the initial water column $NH_4$-N concentration (in g $m^{-3}$); $C_A(t)$ is the water column $NH_4$-N concentration at time, t (in g $m^{-3}$); and h is the depth of the water column (in m). The experimental data from the laboratory study were used to calibrate the model parameters ($k_u$ and $C_{pw}$) in Equation 6.

Model parameters ($C_{pw}$ and $k_u$) were calibrated to data from each experimental unit (n = 27). The "optim" function within the R stats package was used to generate the optimum calibration values (Posit team 2022). Optimization was conducted by using the Nelder-Mead method to minimize the root mean squared error (RMSE) between measured $NH_4$-N concentrations ($C_t$) and predicted $NH_4$-N concentrations (Nelder and Mead 1965). The initial $k_u$ value was set to 0.1 m $d^{-1}$ (36 m $yr^{-1}$) (a value within the range of rate coefficients for ON removal in FWS CWs [Kadlec and Wallace 2009]), h was set to 0.09 m (equal to the depth of the water column), $C_{pw}$ was set to 10 g-N $m^{-3}$ (based on the upper range observed from field porewater samplers), and $C_A(0)$ was set to the $NH_4$-N concentration in the source water (Table 1). Model performance was evaluated using the coefficient of determination or Nash-Sutcliffe Efficiency ($R^2$).

### 2.6 Statistical Analysis

A one-way ANOVA was used to evaluate differences between experimental runs (run) (i.e., each batch run with new detritus) for each calibrated parameter values ($C_{pw}$) and ($k_u$). Differences between runs would suggest variability in $NH_4$-N release relative to both detritus composition and season of harvesting. There were 3 replicates of each treatment per experimental run for a total of 27 experimental units. The statistical model in this analysis is described below (Equation 7).

$$Y_{ij} = \mu + \alpha_i + \varepsilon_{ij} \quad (7)$$

where $Y_{ij}$ = parameter value for the $i^{th}$ run, $\mu$ = overall mean, $\alpha_i$ = the fixed effect of the $i^{th}$ run, and $\varepsilon_{ij}$ = experimental error in $j^{th}$ observation on a response variable at the $i^{th}$ run. The null and alternative hypotheses to be used were given as:

$H_0$: $\mu_{run1} = \mu_{run2} = \mu_{run3}$

$H_a$: Not all $\mu$ are equal or, at least one is different from the others

As a follow up to the one-way ANOVA, Tukey's Honestly Significant Difference (Tukey's HSD) tests were run to assess the significance of differences between pairs of group means. All statistical tests were considered significant at an alpha = 0.05.

## 3. Results and Discussion

### 3.1 $NH_4$-N Porewater Profiles

Results from the porewater samplers in the full-scale wetlands showed substrate $NH_4$-N concentrations between 4 mg $L^{-1}$–5 mg $L^{-1}$ in October 2019 and 7 mg $L^{-1}$–12 mg $L^{-1}$ in January 2020 (Fig. 6). In 2019, $NH_4$-N concentrations were clearly lower in the water column above the substrate, which strengthened our hypothesis that this concentration gradient existed and could result in an upward flux to the water column. The samplers were installed deeper within the substrate in January 2020, but the concentration gradient between the water column and the substrate was not as apparent. It is unclear whether the observed variability of the average concentration was due to the temporal variability or reflected spatial heterogeneity. These field values were used to inform initial field observation estimates of porewater concentrations during $NH_4$-N upward flux modeling.

### 3.2 Observed $NH_4$-N Concentrations from Microcosm Experiments

$NH_4$-N concentrations were measured in the overlying water column over the 7-day period in each of the experimental units (Table 2 and Fig. 7). In all but one period (Day 5 – Day 7 in Run 3 at an initial $NH_4$-N concentration of 10 mg $L^{-1}$), mean $NH_4$-N concentrations increased between each measurement for each treatment in each experimental run. The highest increases in water column $NH_4$-N concentrations were observed in the microcosms with lowest initial water column $NH_4$-N concentrations. The microcosms with an initial water column concentration ($C_A$) of 0 mg $L^{-1}$ increased to 8.5 mg $L^{-1}$, 7.8 mg $L^{-1}$, and 5.1 mg $L^{-1}$ by Day 7 during runs 1, 2, and 3, respectively. Meanwhile, the concentrations in microcosms with an initial $C_A$ of 10 mg $L^{-1}$ increased to 14.8 mg $L^{-1}$, 13.3 mg $L^{-1}$, and 11.2 mg $L^{-1}$ by Day 7 during runs 1, 2, and 3, respectively. These results suggested an inverse relationship between initial $NH_4$-N concentration and the amount of $NH_4$-N released from the substrate. Furthermore, the mean $NH_4$-N concentration change in the water column decreased over time. Between Day 1 and Day 3, the $NH_4$-N concentration increased by 1.4 mg $L^{-1}$, on average across all runs and treatments. This change dropped to 0.9 mg $L^{-1}$ between Day 3 and Day 5, and to 0.5 mg $L^{-1}$ between Day 5 and Day 7 (Table 2). Both inverse relationships suggested that not only was the $NH_4$-N release rate lower when the overlying water column had higher $NH_4$-N concentration, but that the release rate decreased as $NH_4$-N concentrations in the overlying water increased over the 7-day period. These relationships were consistent with the hypothesis

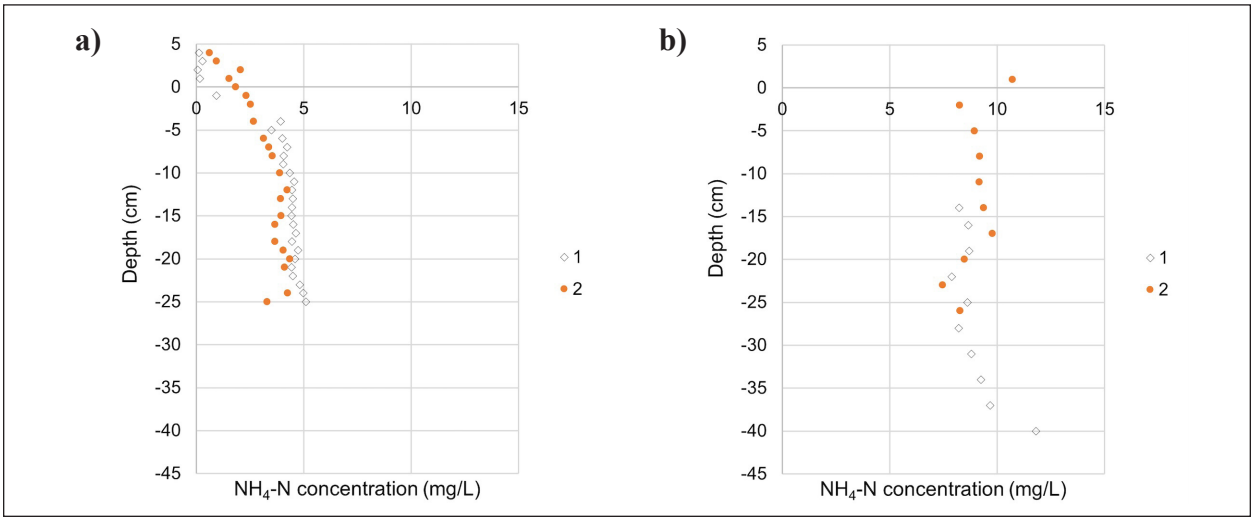


**Fig. 6.** $NH_4$-N concentrations profiles in the wetland substrate muck layer from the 2 porewater samplers installed in a) October 2019 and b) January 2020.

**Table 2** The mean water column $NH_4$-N concentrations (mg $L^{-1}$) on each sampling day for each initial $NH_4$-N concentration during each experimental run. Day 0 represented the $NH_4$-N concentrations approximately 1 h after the microcosms were prepared. The higher Day 0 values of $NH_4$-N concentrations were likely tied to unintended mixing during loading.

| Experimental Run | Initial target $NH_4$-N concentrations | Mean water column $NH_4$-N concentrations (mg $L^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| | | Day 0 | Day 1 | Day 3 | Day 5 | Day 7 |
| **Run 1** | 0 | 3.0 | 3.4 | 5.8 | 7.1 | 8.5 |
| | 5 | 7.1 | 7.8 | 9.7 | 11.1 | 11.9 |
| | 10 | 11.3 | 12 | 13 | 13.5 | 14.8 |
| **Run 2** | 0 | 1.6 | 2.9 | 5.4 | 7.0 | 7.8 |
| | 5 | 6.9 | 7.6 | 8.7 | 10.3 | 10.7 |
| | 10 | 12.1 | 12.0 | 12.4 | 13.0 | 13.3 |
| **Run 3** | 0 | 1.5 | 2.2 | 3.6 | 4.5 | 5.1 |
| | 5 | 5.8 | 6.9 | 8.0 | 8.3 | 8.3 |
| | 10 | 10.1 | 10.4 | 11.7 | 11.8 | 11.2 |

that $NH_4$-N mass transfer rates from the substrate porewater (created as a byproduct of respiration processes) to the overlying water column are driven by the magnitude of the concentration difference between 2 volumes (i.e., diffusion).

### 3.3 Model Calibration

For each of the 3 runs, the $NH_4$-N upward flux in each of the 9 microcosms was calculated using the model represented in Equation 3 with calibrated model parameters (Table 3). For each experimental unit (n = 27), the parameters calibrated were the effective porewater $NH_4$-N concentration ($C_{pw}$) and the upward velocity flux or rate constant ($k_u$). The calibrated $C_{pw}$ values ranged from 4.7 mg $L^{-1}$ to 21.6 mg $L^{-1}$, with an average of 11.2 mg $L^{-1}$ and a median of 11.8 mg $L^{-1}$. The calibrated $k_u$ values ranged from 0.004 m $d^{-1}$ to 3.2 m $d^{-1}$, with an average of 0.3 m $d^{-1}$ and a median of 0.04 m $d^{-1}$. Model efficiencies ($R^2$) ranged from 0.04 to 0.99, with an average of 0.77 and a median of 0.89.

Although the model generally performed well, there were 4 experimental units that were not well represented by the model. Each of the 4 had $k_u$ values greater than 0.5 m $d^{-1}$. The low $R^2$ values associated with these units ($R^2$ <0.5) indicated that each was poorly calibrated to the model. In each case, it appeared that there was a delay in $NH_4$-N release, which resulted in data that were poorly represented by the proposed equation. As a result, this small subset of values was omitted from further analysis.

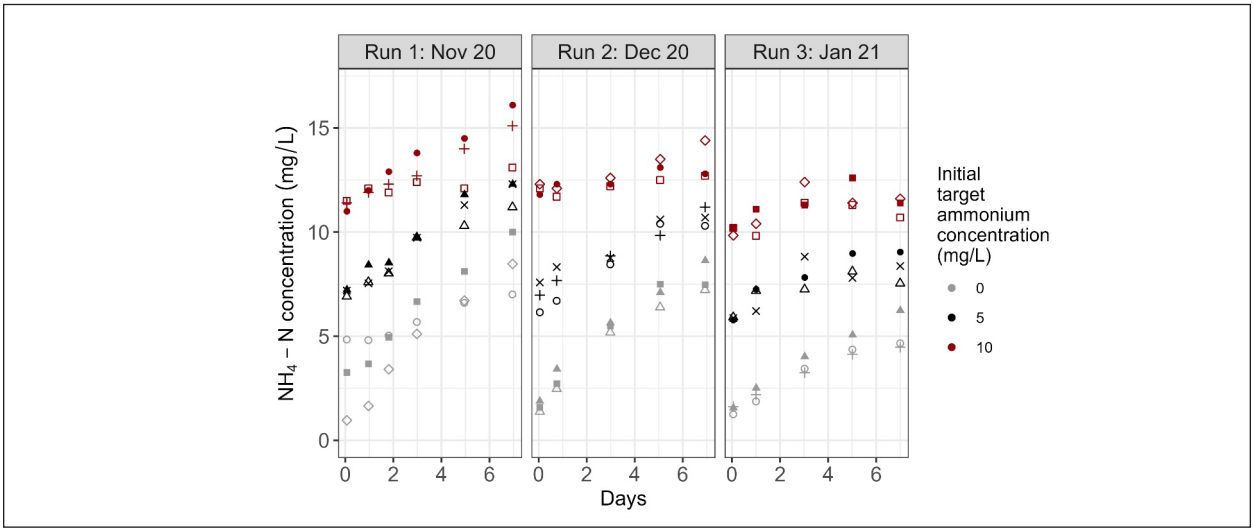


**Fig. 7.** The measured $NH_4$-N water column concentrations over time for each experimental unit. The plots are split by experimental run. The x-axis represents days after each microcosm was loaded. Shapes represent individual experimental units (i.e., wetland microcosms) within each run.

**Table 3** Results of model calibration for each experimental unit. Note: Treatment is described by the target water column initial $NH_4$-N concentrations in the microcosm study. E.U. = experimental unit, $k_u$ = velocity flux or rate constant (m $d^{-1}$), $C_{pw}$ = effective porewater $NH_4$-N concentration (mg $L^{-1}$).

| Run | Treatment | E.U. | $k_u$ | $C_{pw}$ | $R^2$ |
|---|---|---|---|---|---|
| **1** | 10 | 1 | 1.103 | 12.3 | 0.39 |
| **1** | 0 | 2 | 2.691 | 5.8 | 0.18 |
| **1** | 5 | 3 | 0.023 | 12.2 | 0.95 |
| **1** | 10 | 4 | 0.011 | 18.3 | 0.93 |
| **1** | 5 | 5 | 0.013 | 15.9 | 0.96 |
| **1** | 0 | 6 | 0.013 | 12.9 | 0.99 |
| **1** | 0 | 7 | 0.031 | 10.5 | 0.78 |
| **1** | 10 | 8 | 0.017 | 17.7 | 0.98 |
| **1** | 5 | 9 | 0.022 | 13.8 | 0.92 |
| **2** | 10 | 10 | 3.182 | 12.3 | 0.04 |
| **2** | 5 | 11 | 0.019 | 12 | 0.97 |
| **2** | 0 | 12 | 0.036 | 7.5 | 0.97 |
| **2** | 5 | 13 | 0.023 | 11.8 | 0.84 |
| **2** | 5 | 14 | 0.061 | 10.4 | 0.48 |
| **2** | 10 | 15 | 0.005 | 21.5 | 0.68 |
| **2** | 0 | 16 | 0.039 | 8 | 0.95 |
| **2** | 10 | 17 | 0.865 | 12.6 | 0.54 |
| **2** | 0 | 18 | 0.037 | 8.6 | 0.89 |
| **3** | 10 | 19 | 0.038 | 11.1 | 0.47 |
| **3** | 0 | 20 | 0.027 | 5.3 | 0.98 |
| **3** | 5 | 21 | 0.133 | 7.7 | 0.84 |
| **3** | 0 | 22 | 0.034 | 4.7 | 0.9 |
| **3** | 5 | 23 | 0.052 | 8.4 | 0.79 |
| **3** | 10 | 24 | 0.056 | 11.8 | 0.68 |
| **3** | 10 | 25 | 0.059 | 11.9 | 0.67 |
| **3** | 5 | 26 | 0.042 | 9.1 | 0.95 |
| **3** | 0 | 27 | 0.021 | 7.3 | 0.95 |

Using the 23 remaining experimental units, the calibrated $C_{pw}$ values had the same range and average values, but the median value changed to 11.2 mg $L^{-1}$. Meanwhile, the calibrated $k_u$ values ranged from 0.004 m $d^{-1}$ to 0.13 m $d^{-1}$, with an average of 0.03 m $d^{-1}$ and a median of 0.03 m $d^{-1}$. Average and mean model efficiencies ($R^2$) increased to 0.85 and a median of 0.92, respectively. The high mean and median efficiency values suggested that the upward flux of $NH_4$-N from the detritus into the water column was captured using this simple first order model. Therefore, our hypothesis, that $NH_4$-N mass transfer rates from the substrate porewater (created as a byproduct of respiration processes) to the overlying water column are driven by the magnitude of the concentration difference between 2 volumes (i.e., diffusion), was also supported by the modeling exercise.

### 3.4 Variability of Calibrated Porewater and Upward Flux Values

Statistical analysis revealed some differences in the calibrated values of $C_{pw}$ and $k_u$ between experimental runs. A statistically significant difference was found in the calibrated $C_{pw}$ values between experimental runs (F-value = 23.5, $p < 0.012$). A Tukey post-hoc test revealed that the detritus in Run 3 simulated lower $C_{pw}$ values on average (8.6 mg $L^{-1}$) than the detritus in Run 1 (14.5 mg $L^{-1}$) ($p < 0.01$) (Fig. 8). The mean simulated $C_{pw}$ value for Run 2 (11.4 mg $L^{-1}$) was not significantly different than the mean in Run 1 or Run 3. These results indicated that there was a difference in the potential maximum $NH_4$-N concentrations in the porewater between Run 1 and Run 3.

A statistically significant difference was found in the calibrated $NH_4$-N upward velocity flux values between experimental runs (F-value = 3.97, $p < 0.035$). A Tukey post-hoc test revealed that the detritus in Run 3 resulted in a greater $k_u$ value on average (0.051 m $d^{-1}$) than the detritus in Run 1 (0.018 m $d^{-1}$) ($p < 0.05$) (Fig. 9). The mean $k_u$ value for Run 2 (0.031 m $d^{-1}$) was not significantly different than the mean in Run 1 or Run 3. These results indicated that there was a slight but statistically significant difference in the rate of $NH_4$-N release from the substrate, with Run 3 having the greatest release rate constant.

One potential cause for the differences in parameter values was the greater detritus N content in Run 1 (3.6 g-N, or 7270 mg $kg^{-1}$-DW) relative to Run 3 (1.9 g-N, or 3824 mg $kg^{-1}$-DW), which indicated that there were differences in detritus composition. Recall that detritus was harvested just prior to each experimental run. The difference could simply reflect the heterogeneity of the detritus within the wetland, regardless of the sampling date. Alternatively, the difference in detritus composition may have been due to increased microbial activity within the Run 1 detritus due to the time of sampling. Detritus for Run 1 was gathered in November, while detritus for Run 3 was collected in the colder month of January. In terms of the model, this greater detritus N content corresponded with greater $C_{pw}$ values in Run 1 relative to Run 3. The link between greater N content and greater $C_{pw}$ supported the idea that the difference in effective $C_{pw}$ between Run 1 and Run 3 might be an accurate reflection of the differences in the detritus used in each experimental run.

Nitrogen release also depends on the hydraulic conductivity of the substrate. Here, the upward diffusion velocity constant ($k_u$) provided an equivalence to hydraulic conductivity in seepage studies. If the different parameter values were indicative of physical differences

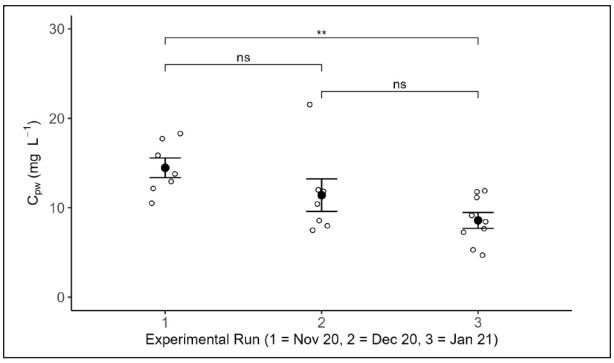


**Fig. 8.** Calibrated porewater values ($C_{pw}$, mg $L^{-1}$) for each experimental run (n = 23). Solid dots represent the mean for each run and error bars represent the standard error. Each run was compared using post-hoc Tukey's HSD. *ns* indicates no significant difference. ** indicates a p-value <0.01.

in the detritus, then the lower vs. higher effective $k_u$ for Run 1 vs. Run 3 would also suggest that detritus from Run 1 was less prone to upward $NH_4$-N diffusion compared to that of Run 3 (i.e., the Run 1 detritus may have been older and more compacted with lower porosity). This could explain why $NH_4$-N would tend to accumulate in the detritus and why the N composition was higher for detritus in Run 1. However, the parameters varied in an opposite manner between runs, which could imply that the differences in parameter values were simply the product of model calibration, which compensated for lower $C_{pw}$ values with greater $k_u$ values or vice versa.

### 3.5 Estimated Internal $NH_4$-N Release from the Treatment Wetlands at the Walnut Cove WWTP

The microcosm experiments coupled with modeling allowed the development of upward flux values that could be used to estimate the internal $NH_4$-N release into the water column within a FWS CW. The range of influent $NH_4$-N concentrations observed entering the FWS CWs at the Walnut Cove WWTP were similar to the 1 mg $L^{-1}$ to 10 mg $L^{-1}$ range of $NH_4$-N concentrations in the effluent of WWTPs with a conventional activated sludge process (Carey and Migliaccio 2009) and, therefore, reasonably representative of a typical FWS CW used for tertiary treatment. Therefore, all calibrated models (n = 23) were used to calculate a range of upward fluxes expected at the Walnut Cove FWS CWs (and likely others) using influent $NH_4$-N concentrations ($C_A$) of 2 mg $L^{-1}$, 4 mg $L^{-1}$, 6 mg $L^{-1}$, 8 mg $L^{-1}$, and 10 mg $L^{-1}$ (Table 4).

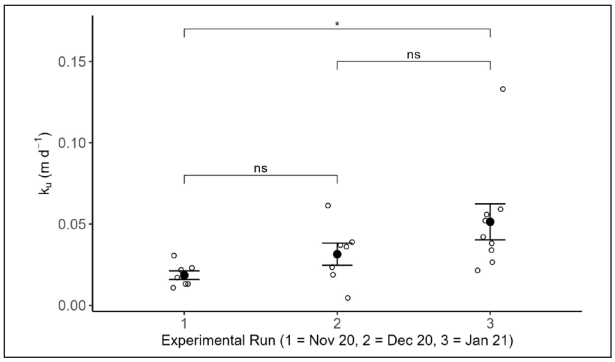


**Fig. 9.** Calibrated upward velocity flux values ($k_u$, m $d^{-1}$) for each experimental run (n=23). Solid dots represent the mean value for each run and error bars represent the standard error. Each run was compared using post-hoc Tukey's HSD. *ns* indicates no significant difference. * indicates a p-value <0.05.

Each of the calculated $J_{UF}$ values were plotted based on water column $NH_4$-N concentration ($C_A$) and experimental run (Fig. 10). The mean $J_{UF}$ values were similar for each run despite the differences in $C_{pw}$ and $k_u$ values across each run discussed earlier. Therefore, the expected internal $NH_4$-N release was relatively constant for each sample of detritus. This finding supported the use of this model to represent $NH_4$-N release across the entirety of the wetland cell.

In terms of magnitude, this study showed that when influent $NH_4$-N concentrations are between 2 mg $L^{-1}$ and 10 mg $L^{-1}$, this aged detritus substrate will likely release between 0.28 g-N $m^{-2}$ $d^{-1}$ and 0.00 g-N $m^{-2}$ $d^{-1}$ (100 g-N $m^{-2}$ $yr^{-1}$ and 0 g-N $m^{-2}$ $yr^{-1}$), respectively (Table 4). As a comparison to another aquatic ecosystem, Beutel (2006) found that ammonia ($NH_3$) release rates from bottom sediments in eutrophic/hypereutrophic lakes were greater than 0.015 g-N $m^{-2}$ $d^{-1}$ in laboratory chamber studies. In a more recent study, Beutel (2021) observed $NH_3$ release from anoxic sediments from the hypereutrophic Lake Henshaw in California ranging from 0.15 g-N $m^{-2}$ $d^{-1}$ to 0.26 g-N $m^{-2}$ $d^{-1}$ (normalized to 20 °C).

Based on the modeled release rates, the Walnut Cove wetland study site, which had two, 7200 $m^2$ wetland cells with an average inlet $NH_4$-N concentration between 4 mg $L^{-1}$ and 6 mg $L^{-1}$, would have an internal $NH_4$-N load between 370 kg $yr^{-1}$ and 550 kg $yr^{-1}$ per wetland cell. This internal $NH_4$-N load was equivalent to between 30% and 45% of the ~1200 kg-N $yr^{-1}$ influent N load to each wetland cell at the study site (Kamrath 2021). For comparison, the P-k-C* model for $NH_4$-N removal would predict a constant return rate of 0.04 g-N $m^{-2}$ $d^{-1}$ (15 g-N $m^{-2}$ $yr^{-1}$), when the irreducible $NH_4$-N concentration and $NH_4$-N removal rate coefficient are set to values of 1 mg $L^{-1}$ and 15 m $yr^{-1}$, respectively (Kadlec and Wallace 2009). This 0.04 g-N $m^{-2}$ $d^{-1}$ return rate would equate to an internal load of only 108 kg-N $yr^{-1}$ in a Walnut Cove wetland cell. While this low rate is likely to be representative of young systems, our results suggest that it will not be appropriate to use that method for predicting outlet

**Table 4** Upward flux ($J_{UF}$) ranges expected in the full-scale wetland using parameters developed from the microcosm experiments. The values are reported in g-N $m^{-2}$ $d^{-1}$ across the expected range of influent $NH_4$-N concentrations to the Walnut Cove wetland cells.

| Experimental Run | Statistical Value | Upward flux ($J_{UF}$), in g-N $m^{-2}$ $d^{-1}$ | | | | |
|---|---|---|---|---|---|---|
| | | Influent 2 mg $L^{-1}$ | Influent 4 mg $L^{-1}$ | Influent 6 mg $L^{-1}$ | Influent 8 mg $L^{-1}$ | Influent 10 mg $L^{-1}$ |
| **Run 1** | Mean | 0.22 | 0.18 | 0.14 | 0.11 | 0.07 |
| | Min, Max | 0.14, 0.27 | 0.12, 0.23 | 0.09, 0.20 | 0.06, 0.16 | 0.01, 0.13 |
| **Run 2** | Mean | 0.24 | 0.18 | 0.12 | 0.05 | 0.00 |
| | Min, Max | 0.10, 0.51 | 0.09, 0.39 | 0.05, 0.27 | -0.02, 0.15 | -0.09, 0.06 |
| **Run 3** | Mean | 0.35 | 0.24 | 0.15 | 0.04 | -0.06 |
| | Min, Max | 0.09, 0.76 | 0.02, 0.49 | -0.04, 0.35 | -0.11, 0.23 | -0.31, 0.11 |
| **Overall** | Mean | 0.28 | 0.21 | 0.14 | 0.06 | 0.00 |

concentrations or loads for aging wetland systems with accumulated detritus.

### 3.6 Influence of Internal N Source on Treatment Performance

The influence of an internal N source from an aged detritus substrate on FWS CW treatment performance is likely to be a function of both influent N loading and influent $NH_4$-N concentrations. Treatment wetlands built to remove N can be classified as lightly or heavily loaded systems using the influent total kjeldahl nitrogen (TKN) loading rate, which represents the sum of the $NH_4$-N and ON species (Kadlec and Wallace 2009). If the influent TKN loading rate is less than 120 g-N $m^{-2}$ $yr^{-1}$, the system can be considered lightly loaded and vice versa. If the aged detritus substrate at this site is a reasonable representation of the detritus substrate at other sites, then lightly loaded systems, with lower inlet $NH_4$-N concentrations, will be most heavily impacted by the $NH_4$-N release from an aged detritus substrate.

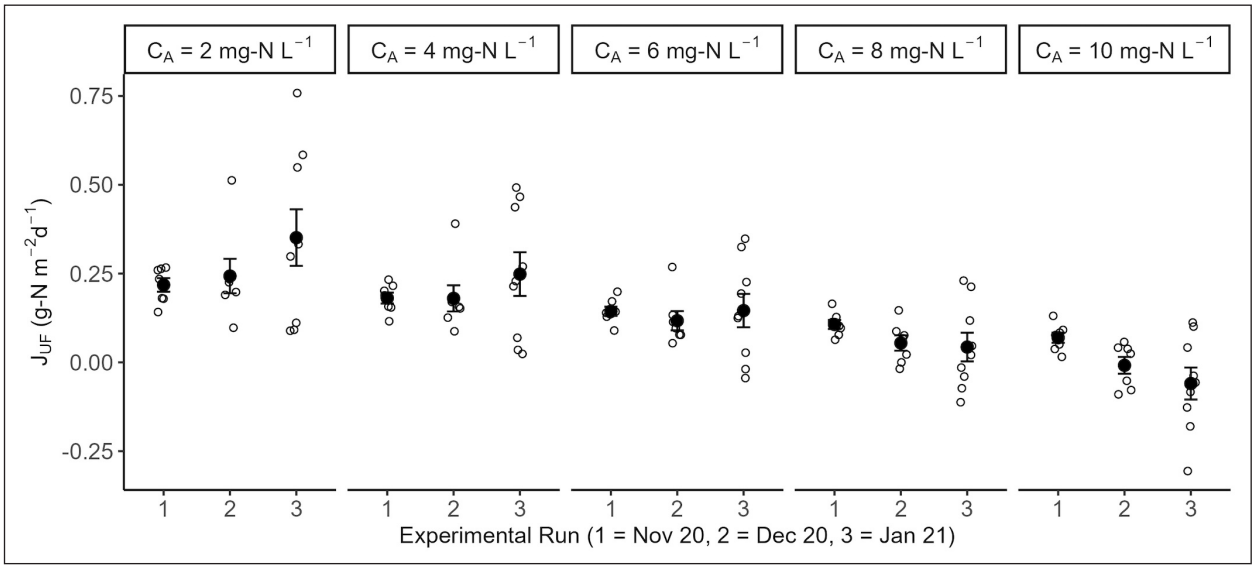


**Fig. 10.** Calculated upward flux ($J_{UF}$) values for each run (1, 2, and 3) and each water column $NH_4$-N concentration (2, 4, 6, 8, and 10 mg $L^{-1}$) (n = 23). The black dot represents the mean $J_{UF}$ value, and the error bars represent the standard error.

Results of this study ($J_{UF}$ ranging from 0 g-N $m^{-2}$ $yr^{-1}$ to 100 g-N $m^{-2}$ $yr^{-1}$) suggested that the apparent N removal efficiency of lightly loaded FWS CWs will markedly decrease over time as detritus substrate builds and releases more $NH_4$-N into the overlying water and offsets treatment, as observed in the Walnut Cove treatment wetlands.

It should be noted that as the detritus begins to fill the basin, the effective surface area of the FWS CW will decrease due to preferential flow paths (Kamrath 2021). With this decrease in the effective surface area, $J_{UF}$ will act over a smaller area of the most active flow. Therefore, even though $J_{UF}$ will likely increase over time (as the detritus substrate builds), the lower effective surface area may mitigate a portion of its impact. For example, the Walnut Cove wetland cells were designed to have a surface area of 7200 $m^2$. This resulted in an estimated internal $NH_4$-N load of 370 kg $yr^{-1}$ to 550 kg $yr^{-1}$ or 30% to 45% of the influent N load. However, the effective surface area of the cell was estimated through tracer studies to be only 3800 $m^2$ (Kamrath 2021). At this effective area, the internal $NH_4$-N load for $C_A$ values of 4 mg $L^{-1}$ and 6 mg $L^{-1}$ would be a smaller 190 kg $yr^{-1}$ to 290 kg $yr^{-1}$, respectively, or 16% to 24% of the influent N load. While still a large percentage of the influent N load, the lower effective surface area may theoretically reduce the potential internal $NH_4$-N load.

For heavily loaded FWS CWs, the influence of internal $NH_4$-N release from an aged detritus substrate will likely have a lesser effect on treatment performance. In these systems, the internal $NH_4$-N release (if porewater concentrations are similar to what we observed in this study) will either be limited by a) high $NH_4$-N concentrations in the water column (>10 mg $L^{-1}$), which will reduce upward flux, or b) in the case of high hydraulic loading rates, even a relatively high internal $NH_4$-N release (i.e., 50 g-N $m^{-2}$ $yr^{-1}$) could be dwarfed by the high influent N load (>>120 g-N $m^{-2}$ $yr^{-1}$). Instead, in these heavily loaded FWS CWs, the hydraulic inefficiencies, such as preferential flow paths, produced by the accumulated detritus substrate perhaps will exert a greater negative influence on wetland treatment performance by reducing residence time within the wetland cells (Martinez and Wise 2003; Wang et al. 2006).

### 3.7 N Dynamics Model Validation

Despite the lack of direct model validation in the field, checks were performed to ensure that the calibrated parameter values were reasonable. The $k_u$ values were compared to the rate constants for $NH_4$-N wetland removal. Because both processes occur within the treatment wetland systems and are a function of the water column $NH_4$-N concentration, the calibrated $k_u$ values should be within an order of magnitude of the $NH_4$-N removal rate constant. In Kadlec and Wallace (2009), the median reported $NH_4$-N removal rate constant was 0.04 m $d^{-1}$ (14.7 m $yr^{-1}$), which was close to the mean $k_u$ value of 0.03 m $d^{-1}$ (11 m $yr^{-1}$) determined in this study. For $C_{pw}$, the calibrated values (11.2 ± 4.0 mg $L^{-1}$) were near the upper end of the porewater $NH_4$-N concentrations observed at the Walnut Cove wetland site (Fig. 4) and the porewater $NH_4$-N concentrations observed using porewater samplers placed in the organic substrate of a drainage canal in North Carolina (Birgand 2000).

To use this method, the other potentially confounding $NH_4$-N processes (see Equation 1) were assumed to be negligible within the wetland microcosms in the first 7 days of each experimental run. Plant uptake or microbial assimilation ($J_{AU}$) was likely negligible because there were no plants in the microcosms, and the microcosms were covered by a black plastic tarp to limit photosynthetic biological activity. Ammonification ($J_A$) was likely negligible since they were loaded with tap water, which had negligible ON concentrations. Finally, the nitrification rate was likely negligible in the first 7 days of each experimental run as discussed earlier.

Another concern was the depth of detritus used in this experiment. Within the microcosms, detritus was added to a depth of 9 cm. While 9 cm was shallower than the actual detritus substrate depth in the wetland cells (30 cm–45 cm), the vertical profile of porewater $NH_4$-N concentrations (obtained via in-situ porewater sampling, see Fig. 6) indicated that the depth to maximum porewater concentration was less than 9 cm. Our first order hypothesis on the upward flux $J_{UF} = k_u(C_{pw}-C_A)$ (Equation 2) gives no particular indication on the diffusion process and the actual shape of the concentration gradient in the sediment. Embedded in the $k_u$ value is the diffusivity and the effective diffusion distance. Thus, the actual depth of the detritus matters little here, although it needed to be deep enough not to limit $NH_4$-N fluxes during the experiments. Additionally, the detritus used in the microcosms was gathered from the entire detritus substrate profile in the field and was representative of the entire vertical profile of the detritus. In the future, the influence of detritus depth on $NH_4$-N release could be assessed by performing another experiment with varying detritus depths, and by monitoring the $NH_4$-N gradients in the sediment. Furthermore, an additional experiment could be conducted using both the detritus sampling method used above and detritus cores that maintain the vertical structure of the detritus. Should there be no difference in the parameter values between the 2 methods, this would indicate that the method used in this experiment adequately represented the field conditions.

### 3.8 Application of Results for Design and Management of Surface Flow Constructed Wetlands

This study was intended to help fill the constructed wetland N return rate knowledge gap expressed by Kadlec and Wallace (2009), and to investigate the poor $NH_4$-N removal observed in the Walnut Cove constructed wetlands. Both the microcosm experiment and the modeling results clearly demonstrate how $NH_4$-N release from accumulated detritus can negatively affect treatment performance.

The current method for representing N dynamics in a treatment wetland are first-order areal conversions (Gerke et al. 2001; Kadlec 2008; Kadlec and Wallace 2009). While this method may be acceptable for the design of new FWS wetlands for wastewater systems, disregarding this internal $NH_4$-N release produces the potential for suboptimal treatment performance predictions (relative to the initial expected performance) as the system ages. To address this issue, we see 2 options for future wetland designers. First, an improved wetland model that accounts for increases in internal N loads would allow wetland designers to appropriately size lightly loaded systems to allow for future increases in internal loading while maintaining expected N removal performance. Second, wetland designers need to focus on designing FWS CW systems that allow for scheduled cleanouts of accumulated detritus every 5–10 years. This could be as simple as allowing for easy access for excavators and recommending a detritus removal methodology (whole cell or partial cell removal on a rotating basis) that would retain a small amount of detritus in the wetland to maintain the microbial and vegetative communities. The removal of accumulated detritus would reduce the internal N source and improve the internal hydraulic performance, in hopes of resetting the effluent concentrations to the original design expectations.

However, while the results clearly demonstrate the significance of $NH_4$-N upward flux from accumulated detritus in FWS CWs, care should be taken in completely extrapolating the results of this study to other sites. While the goodness of fit is high for the first order model, the results shown here indicated that there is likely variability in the calibrated parameter values. As a result, the calibrated parameter values have the potential to be site specific. Therefore, since this study only used detritus from only one FWS CW, the calibrated parameter values presented herein should be used as an initial estimate for $NH_4$-N release in other FWS CWs.

To develop stronger parameter estimates representative of $NH_4$-N release from an aged detritus substrate, data from other sites and from different times of the year are needed. Therefore, to further our efforts to fill this knowledge gap, the next step would be to gather aged detritus from several different FWS CWs (of various ages, accumulated detritus depths, dominant plant types, etc.) to evaluate if differences in detritus composition influence the $NH_4$-N release rates. To further validate the release rates observed in the laboratory, this study could be scaled up to evaluate $NH_4$-N release from detritus-filled wetland mesocosms placed outdoors.

While a larger sample size is needed before the results presented herein can be endorsed for widespread use, these results indicated that the model represents the mechanics of this release well and suggested that it has the potential to effectively predict this release. Overall, this study provided a positive first attempt at modeling this release, provided an estimate of $NH_4$-N release from the accumulated detritus substrate at one study site, and created a foundation to build upon for future analysis of various detritus substrates at different locations derived from different dominant vegetation types.

## 4. Conclusion

Overall, this study showed that $NH_4$-N accumulation in thick detritus layers can be a sizable contributing source to the water column in FWS CWs. The simple kinetic model proposed herein sought to better represent return rates of N in aging treatment wetlands. The results showed that diffusion can transfer a substantial amount of $NH_4$-N from accumulated detritus porewater to the overlying water column, particularly in older FWS CWs. The proposed model adequately represented the mechanics of upward $NH_4$-N release from an accumulated detritus substrate to the overlying water column. Valid parameter values were calibrated for 23 of the 27 wetland microcosms (mean $R^2 = 0.85$). Parameters ranged from 4.7 mg $L^{-1}$ to 21.5 mg $L^{-1}$ for the porewater $NH_4$-N concentration ($C_{pw}$) and 0.004 m $d^{-1}$ to 0.13 m $d^{-1}$ (1.5 m $yr^{-1}$ to 47.4 m $yr^{-1}$) for the upward velocity flux rate constant ($k_u$). Despite this range of parameter values developed from the experimental runs, the range of upward flux ($J_{UF}$) values estimated for the Walnut Cove treatment wetlands was relatively constant for each overlying water column concentration evaluated in the model. At the Walnut Cove wetlands, the areal $NH_4$-N release rates ($J_{UF}$) from the detritus substrate at overlying water column concentrations of 4 mg $L^{-1}$ to 6 mg $L^{-1}$ were estimated to be 0.21 g-N $m^{-2}$ $d^{-1}$ and 0.14 g-N $m^{-2}$ $d^{-1}$ (70 g-N $m^{-2}$ $yr^{-1}$ and 50 g-N $m^{-2}$ $yr^{-1}$) respectively, which could add 30% to 45% more $NH_4$-N to the average influent N load. It is likely that the $NH_4$-N release from the substrate with accumulated detritus will offset to some extent the treatment efficiency of this, and possibly other, lightly loaded systems (TKN load

<120 g-N $m^{-2}$ $yr^{-1}$). The N release from an aged, accumulated detritus observed and modeled in this study provides a starting point for future and perhaps more intense research that can fully quantify the influence of this internal N source on treatment efficiency across a range of FWS CWs, and the methods to control or prevent it to extend the useful life of these systems.

## Supplementary Material

The online version of this article contains a link to supplementary material that includes: **Fig. S1** Microcosms from Run 1 after detritus substrate addition and a microcosm from Run 3 after detritus and source water addition, **Table S1** Nitrogen content of detritus substrate in microcosms prior to experiment initiation.

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## Author Contributions Statement

Conceptualization: BK & MB; methodology: BK & MB; data analysis: BK, MB, & FB; laboratory analyses: BK; writing original draft: BK; review/editing original draft: MB, FB, & TA; resources: MB, FB, & TA; data curation: BK; supervision: MB; project administration: MB; funding acquisition: MB. All authors have read and agreed to the published version of the manuscript.

## Conflict of Interest Statement

The authors have no conflict of interest to report.

## Data Availability Statement

Data will be made accessible upon request to the corresponding author.

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