Mechanistic Understanding of Nitrogen Behaviour in Floating Treatment Wetlands: Abatement of Ammonia Flux

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Abstract. Nitrogen behaviour in domestic wastewater was investigated to develop a mechanistic understanding of ammonia dynamics in Floating Treatment Wetlands (FTWs) and to improve design and operation. A critical FTW design (full coverage of the floating mat and maximum plant density) was evaluated to optimize treatment performance of a pilot-scale system in removing ammonia under different operational volumes. A system dynamics approach as a framework was employed for robust understanding of the treatment mechanisms and system performance in removing ammonia. The results revealed that ammonia removal was enhanced in FTWs and the magnitude of removal was controlled by the design examined. Findings suggest that a design code of full coverage of water surface with mat material, high plant density, and low water volume can be considered as a critical design for FTW system to remove ammonia from domestic wastewater. This design promoted nitrification as principal ammonia removal process even when plants were present. The contribution of nitrification to overall ammonia removal was estimated to be between 81 and 85%. Plant uptake contributed to 14-19% of the total N loss. Ammonia loss via volatilization was determined to be negligible in examined system. Kinetics parameters for ammonia removal were between 0.14-0.22 day\(^{-1}\) in FTWs compared to 0.01-0.02 day\(^{-1}\) in controls. Understanding the contribution of removal processes of N could be useful to improve treatment system design, and enhance treatment performance.

1. Introduction
Over the past few years, interest has grown in the use of FTWs to help improve water quality by treating both point and non-point source pollution [1, 2]. Treatment systems based on aquatic macrophyte utilise natural microbial processes and are often considered to be more eco-friendly than treatment techniques for nutrient reduction [3]. A key principle employed in FTWs is to increase the surface area and direct contact with water-borne contaminants. This extra surface area can be colonised by microbial biofilms which include organisms capable of processing the contaminant under consideration [3] as well as providing a medium for the establishment of plants which can take up nutrients and provide additional surfaces for microbial colonisation (e.g. roots). Processes such as sorption to suspended solids and subsequent sedimentation and volatilization also operate in parallel [4][5].

The performance of FTWs in removing nitrogenous contaminants has been evaluated in a number of operational settings [6-9]. However, limited information, if any, has been provided on the mechanistic basis of N removal rates reported, particularly for ammonia. This is, in part, because many treatment systems are complex and include a range of different competing and interacting processes. Simple numerical system dynamic models can help to describe and interpret the N behaviour in complex systems and estimate the relative contribution of different removal processes [3].

In this research, the removal of ammoniacal N from batch-operated static chambers receiving treated effluent from a small-scale waste water treatment plant is evaluated using a simple mathematical model.
as a framework for quantifying the contribution of the competing removal processes. The prime objectives of this research are (1) to assess FTW designs in treating ammonia and (2) to understand ammonia removal kinetics under the effect of two operational volumes. A mechanistic understanding of the treatment mechanisms of ammonia is fundamental to improve design and operation in FTW systems.

2. Methods

2.1 Experimental

The study was conducted on a small wastewater treatment system serving a hotel complex near Market Harborough (52°28’40.656”N, 0°55’15.708”W), Leicestershire, UK. A pilot-scale free-surface constructed wetland has been constructed to act as a “polishing” stage (tertiary treatment). This consists of four parallel chambers or cells, two of which have dimensions (2×0.46×0.8 m) and two have dimensions (2×0.70×0.8 m) (Figure 1).

![Experimental set-up](image)

**Figure 1.** Experimental set-up: A- top view of the treatment system, B- FTW planting zone scheme, C- side view of the treatment chamber.

Based on the water depth measurement, initial volumes for the treatment chambers were calculated to be 368±7.6 L and 560±9.4 L for the small and big cells. Four discrete batches (14-day trials) were conducted. In each trial, each cell was filled to its operational volume with pre-treated sewage effluent. Two cells (one with 368 L; one with 560 L operational volume) were fitted with floating mats (FTW\_368L and FTW\_560L). Two cells (one small and one large) had no mat and were considered to act as controls (C\_368L and C\_560L).

FTWs contained maximum plant density (20 individuals of *Juncus effusus* and 20 individuals of *Phragmites australis*, order: Poales, family: Juncaceae and Poaceae).

Water samples (50 mL) were collected from each chamber for NH\(_3\), NO\(_2\), NO\(_3\), and TKN analysis according to established protocols [10] using an automated discrete colorimetric instrument (AQ2: SEAL Analytical, UK). Concentrations of organic N and total N were calculated according to [11]. Ammonia removal was assumed to follow first order kinetics [12, 13]. The losses of ammonia-N via volatilization of unionized ammonia was estimated, assuming full and instantaneous thermodynamic equilibrium between NH\(_3\) and NH\(_4^+\) [1].

At each sampling dissolved oxygen, pH, EC, and water temperature were measured in each chamber at 15 cm from the surface. The water balance of the pilot-scale chambers was evaluated by measuring changes in operational volume as a function of water depth. Plant biomass was collected for each of the vegetated mats at the start and end of experimental time to determine initial and final biomass and TN.
content. Total nitrogen concentration was determined using an elemental analyzer: SERCON ANCA GSL according to [14].

2.2 Model
A system dynamics model (STELLA 1.7, ISEE systems, New Hampshire, UAS) was developed to describe the competing and interacting processes operating in the wetland (see Figure 2). The model was calibrated using data from cell FTW$_{560L}$ (see Table 1).

![Figure 2. Causal-loop diagram for the nitrogen cycle in the experimental systems.](image)

| STELLA symbol | Description | Value/Units | Source |
|---------------|-------------|-------------|--------|
| $\text{ON}_{\text{ini}}$ | Initial Organic-N mass | 1821 mg N | Calculated, FTW$_{560L}$ cell |
| $\text{NH}_x_{\text{ini}}$ | Initial NH$_3$+NH$_4$ mass | 1227 mg N | Calculated, FTW$_{560L}$ cell |
| $\text{NO}_x_{\text{ini}}$ | Initial NO$_2$+NO$_3$ mass | 1313 mg N | Calculated, FTW$_{560L}$ cell |
| Plant uptake | Total-N content in plant | mg N | Measured, FTW$_{560L}$ cell |
| Volatized NH$_3$ | Free ammonia volatilization | mg N | Estimated, FTW$_{560L}$ cell |

| Flow variables | Description | Value/Units | Source |
|----------------|-------------|-------------|--------|
| $J_{\text{amo}}$ | Ammonification rate | mg N day$^{-1}$ | Calculated, FTW$_{560L}$ cell |
| $J_{\text{nit}}$ | Nitrification rate | mg N day$^{-1}$ | Calculated, FTW$_{560L}$ cell |
| $J_{\text{denit}}$ | Denitrification rate | mg N day$^{-1}$ | Calculated, FTW$_{560L}$ cell |
| $J_{\text{up NH}_x}$ | Plant uptake rate of NH$_x$ | mg N day$^{-1}$ | Estimated, FTW$_{560L}$ cell |
| $J_{\text{up NO}_x}$ | Plant uptake rate of NO$_x$ | mg N day$^{-1}$ | Estimated, FTW$_{560L}$ cell |
| $J_{\text{vol}}$ | Volatilization rate | mg N day$^{-1}$ | Whelan, et al. [1] |

Parameters/coefficients:

- [ON]: Organic-N concentration: mg N L$^{-1}$
- [NH$_3$]: NH$_3$+NH$_4$ concentration: mg N L$^{-1}$
- [NO$_x$]: NO$_2$+NO$_3$ concentration: mg N L$^{-1}$
- $k_{\text{amo}}$: Ammonification rate constant: 0.021 day$^{-1}$
- $k_{\text{nit}}$: Nitrification rate constant: 0.149 day$^{-1}$
- $k_{\text{denit}}$: Denitrification rate constant: 0.132 day$^{-1}$
- $k_{\text{up NH}_x}$: Uptake rate constant for NH$_x$: 0.009 day$^{-1}$
- $k_{\text{up NO}_x}$: Uptake rate constant for NO$_x$: 0.009 day$^{-1}$
- $k_{\text{vol}}$: Mass transfer coefficient of NH$_3$: 0.04 day$^{-1}$
- NH$_3$: Concentration of NH$_3$ gas: 0.01 mg N
- V: Operational volume: 560 L

Measured, FTW$_{560L}$ cell
A manual trial and error calibration procedure was performed in which the following four parameters were adjusted: $k_{up}$, $k_{amo}$, $k_{nit}$ and $k_{denit}$, in order to minimize the root, mean square error (RMSE) between the simulated and measured values. Validation was performed by comparing predicted concentrations of NH$_x$ and NO$_x$ with the measured data. The coefficient of determination ($R^2$), Slope of the linear regression and root mean squared error (RMSE) were employed to compare actual and modeled data-sets.

3. Results and Discussion

3.1 Experimental data

3.1.1 Water balance. Water budget of FTW increased by 1.5% at the end of batch 1, 3 and 4, while the controls exhibited increase by 3% for the same periods. Nevertheless, water volume was decreased by 3% in FTWs and controls at the end of batch 2 (see Table 2). The differences in the water budget between treatments could be resulted from the effect of evapotranspiration in the planted cells compared to unplanted, although water loss in the FTWs could be restricted in some extent by full coverage surface area of the floating systems, which relatively restrict water evaporation. However, water gain or loss in the examined systems have not indicated significant differences in the water budget.

| Batches   | Water depth (cm) | Initial water volume (L) | Final water volume (L) |
|-----------|------------------|--------------------------|------------------------|
|           | FTW              | Control                  | FTW                    | Control             |
| Batch 1   | 38.03            | 41.28                    | 548.39                 | 598.61              |
| Batch 2   | 37.93            | 39.18                    | 562.39                 | 585.23              |
| Batch 3   | 38.02            | 40.24                    | 544.87                 | 574.37              |
| Batch 4   | 37.77            | 39.57                    | 550.97                 | 574.76              |

It can be concluded that the dilution effects and concentration effects of the precipitation and evaporation have not substantial impacts on the nitrogen concentrations in the treatments. Therefore, the effect of water volume changes on the N mass balance was, neglected.

3.1.2 Nitrogen removal. The concentrations of organic-N (ON), ammonia-N (NH$_x$) and oxidised-N (NO$_x$) in the starting material (effluent from the WWTP) in across the four experimental batches are summarised in Table 3.

| Batches   | N variables | FTW$_{50L}$ | C$_{50L}$ | FTW$_{650L}$ | C$_{650L}$ |
|-----------|-------------|-------------|-----------|--------------|------------|
| Batch 1   | ON          | 3.17±0.38$^a$ | 2.93±0.53$^a$ | 2.85±0.21$^a$ | 3.41±0.13$^a$ |
|           | NH$_x$      | 2.20±0.06$^a$ | 2.52±0.04$^b$ | 2.41±0.05$^a$ | 2.27±0.06$^b$ |
|           | NO$_x$      | 2.32±0.27$^a$ | 2.58±0.07$^a$ | 2.48±0.31$^a$ | 1.84±0.33$^a$ |
| Batch 2   | ON          | 4.15±0.22$^a$ | 3.74±0.62$^a$ | 3.97±0.19$^a$ | 4.54±0.75$^a$ |
|           | NH$_x$      | 1.84±0.11$^a$ | 1.87±0.05$^b$ | 2.35±0.10$^a$ | 1.85±0.13$^b$ |
|           | NO$_x$      | 2.07±0.34$^a$ | 2.15±0.21$^a$ | 2.25±0.06$^a$ | 2.21±0.39$^a$ |
| Batch 3   | ON          | 3.78±0.54$^a$ | 3.90±0.30$^a$ | 3.31±0.31$^a$ | 3.36±1.54$^a$ |
|           | NH$_x$      | 1.52±0.03$^a$ | 1.57±0.04$^b$ | 1.61±0.02$^a$ | 1.94±0.01$^b$ |
|           | NO$_x$      | 2.24±0.60$^a$ | 2.25±0.44$^a$ | 2.05±0.07$^a$ | 2.72±0.36$^a$ |
| Batch 4   | ON          | 3.26±1.41$^a$ | 3.12±1.25$^a$ | 2.86±0.50$^a$ | 3.76±0.82$^a$ |
|           | NH$_x$      | 2.35±0.04$^a$ | 2.13±0.02$^b$ | 2.38±0.02$^a$ | 2.29±0.03$^b$ |
|           | NO$_x$      | 2.62±0.42$^a$ | 2.51±0.47$^a$ | 2.58±0.14$^a$ | 3.06±0.32$^a$ |
There was a general decrease in ON concentration over time in all treatments (ANOVA, $F_{4, 80} = 5.02; P < 0.05$), although there appeared to be some occasional increases (see Figure 3). At each sampling, there was a high degree of variability in ON concentrations between batches for the same treatment. First order rate constants and corresponding removal half-life from the tested cells were statistically the same indicating insignificant variations of the removal kinetics of ON in treatments (see Table 4). The relatively limited loss of ON in all the treatments could reflect a reduction in ammonification due to low dissolved oxygen (DO) levels (<<2 mg L$^{-1}$). Organic matter decomposition (and associated ammonification) can proceed under low partial pressures of DO and even under anaerobic conditions but at reduced rates [3, 15]. Furthermore, there is always some generation of new ON in wetland systems as well as losses due to primary production (plants and or algae) and subsequent senescence, which reduces the net loss rate [16]. Comparison of the first-order modeled and measured ON-concentrations shows that 66 and 42 % of the variances in the FTW$_{368L}$ and FTW$_{560L}$ was explained by the model, but 58 and 43 % of the C$_{368L}$ and C$_{560L}$ data (see Figure 3 and Table 4).

NH$_4^+$ concentration decreased in all treatments, but the rate of decrease was much lower in the controls compared with the FTW cells in all experimental batches (Figure 3). Based on the calculated correlation coefficient ($R^2$), comparison of the modelled and measured NH$_4^+$ concentrations during study periods shows that 0.99 percent of the variances in the FTW$_{368L}$ and FTW$_{560L}$ can be explained by the model. While 72 and 68 percent of the controls data only be described by the model (Figure 3, Table 4). First order rate constants (shown in Table 4, along with equivalent half-lives) were much higher for the FTW treatments compared with those for the controls, suggesting that the mats provide effective enhancement of NH$_4^+$ removal. This could have been due to a combination of ammonia volatilization, plant uptake, and additional nitrification. Ammonia loss via NH$_3$ volatilization in the system was also studied. The average rate constants of NH$_3$ loss over four experimental batches were $5 \times 10^{-4}$ and $6 \times 10^{-2}$ day$^{-1}$ in the FTW and control systems. The average concentration of NH$_3$ were 0.01 and 0.03 mg N L$^{-1}$ in the FTW and control groups. The low rate of volatilization in all treatments could be due to the dominant low pH values (7.2) throughout the study, which pushed the equilibrium of the ammoniacal nitrogen towards NH$_4^+$ rather than NH$_3$ generation. Overall the enhancement of ammonia removal in the presence of FTWs reported here exceeds that reported by Chang, et al. [7] who observed a 51% improvement in NH$_4^+$ removal in a stormwater retention pond fitted with floating island. This may be because Chang et al. monitored stormwater which will have limited retention time compared with the batch arrangement employed in our work. Winston, et al. [17] are also report a significant enhancement of treatment efficiency for NH$_4^+$ in a stormwater retention pond when fitted as FTWs.

Changes in NO$_2^-$ concentrations are shown in Figure 3. On average NO$_2^-$ concentrations decreased by 0.77±0.02 mg-N L$^{-1}$ in the FTW treatments and 0.59±0.01 mg-N L$^{-1}$ in the controls. These losses represent net removal efficiencies for NO$_2^-$ of approximately 98% for the FTW treatments and 87% for the controls, respectively. The rate constants for NO$_2^-$ loss were 0.36 and 0.27 day$^{-1}$ for the FTW$_{368L}$ and FTW$_{560L}$ cells, respectively and 0.17 day$^{-1}$ for the controls. Corresponding half-lives are shown in Table 4, along with the $r^2$ values for the fits, which suggest that the first order model is reasonable for representing net NO$_2^-$ dynamics. The fact that concentrations of NO$_2^-$ were relatively high at the start of each experimental batch period suggests that the main wastewater treatment plant installed at the hotel complex is not effective at completely converting NH$_4^+$ to NO$_3^-$.

In all four batches, there was a general decrease in NO$_3^-$ concentrations – but most markedly in the first two batches for all treatments and most notably for FTW treatments (Figure 3). The loss of NO$_3^-$ from the experimental chambers could be due to uptake by plants and or algae and immobilization by the microbial biomass [18-20]. Losses could also be due to the process of denitrification. The first order reaction rate constants shown in Table 4 represent a combination of these processes. The rate constant for the FTW$_{368L}$ treatment was slightly higher than that for the respective control. However, for the FTW$_{560L}$ chamber, the rate constant was slightly less than that in its control. This relatively small difference between the FTW treatments and the controls, together with the fact that all four chambers demonstrated high loss rates for NO$_3^-$, suggests that the major loss process in these systems was denitrification.
Figure 3. ON, NH$_x$, NO$_2^-$, NO$_3^-$ and TN behavior in the treatment system with (FTW$_{368L}$ and FTW$_{560L}$) and without (C$_{368L}$ and C$_{560L}$) mats during four experimental periods (mean ± standard deviation).

In each batch period, the wastewater in chambers was static. Since primary-treated domestic wastewater applied in this study is expected to contain reasonably high concentrations of organic matter, a high rate of oxygen consumption is likely, resulting in anaerobic conditions which facilitate denitrification. Lower DO concentration (1.26±0.25 mg L$^{-1}$) observed in tested cells during experimental periods could support such an explanation. Denitrifiers may have developed on the FTW material itself, but are more likely to be present in biofilms on the side walls and the bed substrate, where DO concentrations are likely to have been lower [21]. Plant exudates also introduce dissolved organic carbon (rhizodeposits) to the water column which can act as electron donors [22].
The average total losses of TN were higher for the FTW treatments compared with those for the controls (see Table 4). First order rate constants (along with equivalent half-lives) were relatively higher for the FTW treatments compared with those for the controls, suggesting that the mats provide an effective improvement of TN removal. The extent of the TN removal within treatment systems was almost a result of the reduction of the total inorganic N-forms (TIN) rather than organic-N which demonstrated lower removal rates. This could have been attributed to a combination of N removal pathways including microbial transformations, plant uptake, and physiochemical processes. Data from first order fits showed that 94 and 92% of the measured data in FTW368L and FTW560L were represented by the first order model, while 81 and 85% of the overall TN dynamics in C368L and C560L were described (see Figure 3 and Table 4).

### Table 4. Average values (± standard deviation) of ON, NH₃, NO₂⁻, NO₃⁻ and TN removal (mg N L⁻¹), first order nitrification rate constants ($k_{nitr}$, day⁻¹), half-lives ($T_{1/2}$, day), and removal efficiencies ($RE$, %) over the four batches.

| Parameter | Treatment | Extents (mg N L⁻¹) | $k_{nitr}$ (day⁻¹) | $T_{1/2}$ (day) | RE (%) | R² |
|-----------|-----------|--------------------|-------------------|----------------|--------|----|
| ON        | FTW₃₆₈L   | 1.22±0.37ᵃ         | 0.03±0.01ᵃ        | 21.35±3.36ᵃ   | 32.96±9.09ᵃ | 0.66 |
|           | C₃₆₈ L   | 1.28±0.49ᵃ         | 0.04±0.01ᵃ        | 31.85±18.68ᵃ | 40.15±16.43ᵃ | 0.58 |
|           | FTW₅₆₀L   | 0.87±0.37ᵃ         | 0.02±0.01ᵃ        | 37.56±9.03ᵃ  | 24.92±9.56ᵃ | 0.42 |
|           | C₅₆₀ L   | 0.56±0.40ᵃ         | 0.02±0.01ᵃ        | 48.14±23.92ᵃ | 16.70±11.79ᵃ | 0.43 |
| NH₃       | FTW₃₆₈L   | 1.86±0.18ᵃ         | 0.22±0.01ᵃ        | 3.08±0.19ᵃ    | 94.42±1.18ᵃ | 0.99 |
|           | C₃₆₈ L   | 0.40±0.13ᵇ         | 0.01±0.01ᵇ        | 61.75±23.18ᵇ  | 18.96±7.04ᵇ | 0.72 |
|           | FTW₅₆₀L   | 1.89±0.17ᵃ         | 0.14±0.01ᵃ        | 4.64±0.10ᵃ    | 86.28±0.95ᵃ | 0.99 |
|           | C₅₆₀ L   | 0.55±0.12ᵇ         | 0.02±0.01ᵇ        | 49.67±14.23ᵇ  | 26.73±5.78ᵇ | 0.68 |
| NO₂⁻      | FTW₃₆₈L   | 0.75±0.26ᵃ         | 0.36±0.05ᵃ        | 2.04±0.29ᵃ    | 98.74±0.65ᵇ | 0.99 |
|           | C₃₆₈ L   | 0.58±0.25ᵃ         | 0.17±0.02ᵇ        | 4.45±0.93ᵇ    | 85.91±6.68ᵇ | 0.90 |
|           | FTW₅₆₀L   | 0.78±0.25ᵃ         | 0.27±0.03ᵇ        | 2.66±0.36ᵇ    | 97.25±1.21ᵇ | 0.99 |
|           | C₅₆₀ L   | 0.60±0.24ᵇ         | 0.17±0.02ᵇ        | 4.31±0.90ᵇ    | 88.82±5.81ᵇ | 0.98 |
| NO₃⁻      | FTW₃₆₈L   | 1.45±0.15ᵃ         | 0.20±0.01ᵃ        | 3.44±0.11ᵃ    | 92.99±1.10ᵃ | 0.95 |
|           | C₃₆₈ L   | 1.26±0.44ᵃ         | 0.15±0.06ᵃ        | 9.77±5.22ᵃ    | 64.76±22.41ᵃ | 0.53 |
|           | FTW₅₆₀L   | 1.15±0.12ᵃ         | 0.11±0.01ᵃ        | 6.59±0.65ᵃ    | 74.66±4.42ᵃ | 0.95 |
|           | C₅₆₀ L   | 0.88±0.37ᵃ         | 0.13±0.06ᵃ        | 16.93±8.55ᵃ   | 52.99±24.28ᵃ | 0.65 |
| TN        | FTW₃₆₈L   | 5.29±0.22ᵃ         | 0.08±0.01ᵃ        | 8.18±0.59ᵃ    | 67.12±3.01ᵃ | 0.94 |
|           | C₃₆₈ L   | 3.28±0.76ᵇ         | 0.05±0.10ᵇ        | 22.32±11.19ᵃ  | 44.10±4.00ᵇ | 0.81 |
|           | FTW₅₆₀L   | 4.62±0.42ᵇ         | 0.06±0.01ᵇ        | 11.33±0.99ᵃ   | 59.10±3.62ᵇ | 0.92 |
|           | C₅₆₀ L   | 2.60±0.43ᵇ         | 0.03±0.01ᵇ        | 23.20±4.45ᵃ   | 31.84±6.47ᵇ | 0.85 |

Upper letters denote Tukey HSD test for multiple comparisons of means. Treatments with the same letter are not significantly different from each other (α = 0.05).

#### 3.1.3 Nitrogen mass balance

The daily average TN mass removal rates from the FTW₃₆₈L, FTW₅₆₀L and corresponded controls in each 14-day batch were 151±6, 132±12, 94±22 and 75±13 mg N m⁻² day⁻¹, respectively. Thus, on average, TN-mass removal in FTW chambers were 67 and 59% of the total-N mass inflow to the treatment system, whereas, controls achieved 41.84 and 31.84% of the total-N mass
within the same time frame. Estimated performance of the floating mat was by 37.95% and 43.59% of the whole FTWL 368L and FTW 560L performance, with a net daily removal rate of 57 mg N m$^{-2}$ day$^{-1}$ for both treatments. Therefore, water body processes were estimated to be responsible for 62% and 56% of the total performance of FTW 368L and FTW 560L, cells, with a mass removal rate of 93.9 and 74 mg N m$^{-2}$ day$^{-1}$, respectively.

Microbial transformation onto a floating system, including root zone, has characterized 18.9% and 29% of the total microbial performance in the FTW 368L and FTW 560L systems. Overall, Microbial transformations contribute to between 80 and 85% of the total-N removal in the FTW treatments. Likewise, plant uptake rates revealed a contribution of 19% and 14% of the overall performance of FTW systems, respectively. Uptake by vegetation accounted for 28.8±8.43 and 18.8±8.56 mg N m$^{-2}$ day$^{-1}$ in FTW 368L and FTW 560L, cells, respectively.

Losses in the control chambers include NH$_3$ volatilization, inorganic-N immobilization by microorganisms, settling out of particulate N and adsorption of NH$_4^+$ to the system liner and gravel bed. Since the average water pH during the experimental phase was 7.2, volatilization was calculated to be negligible. Subsequently, the microbial pathway was estimated to be responsible for 62% (93.8 mg N m$^{-2}$ day$^{-1}$) and 56% (74.4 mg N m$^{-2}$ day$^{-1}$) of the overall N-removal of C 368L and C 560L, cells, respectively.

### 3.1.4 Model performance

Four parameters ($k_{up}$, $k_{amo}$, $k_{nit}$ and $k_{den}$) from cell FTW 560L were optimised within effort of model calibration in order to get best fits between simulated and measured values of ON, NH$_3$ and NOx. Model performance for ON, NH$_3$ and NO$_x$ for the calibration on the FTW 560L treatment is illustrated in Figure 4a. The optimized RMSE values were 0.174, 0.145 and 0.118 mg N L$^{-1}$ for ON, NH$_3$ and NO$_x$, respectively. These values are relatively low, reflecting that the model was able to reproduce the pattern of measured concentrations reasonably well (also illustrated in good visual fits between measured and modeled concentrations). Calibrated values of $k_{amo}$, $k_{nit}$, $k_{den}$, $k_{up}$NO$_x$ and $k_{up}$NO$_2$ were 0.0198, 0.17, 0.26, 0.015 and 0.015 day$^{-1}$, respectively. The model was validated against independent data from other treatments (with no further optimization of parameters, except that $k_{up}$ values were set to zero in controls with no vegetation and $k_{nit}$ was reduced from 0.17 to 0.057 day$^{-1}$ in the controls to represent the absence of mat-associated nitrifiers). Measured and simulated time series for ON, NH$_3$ and NO$_x$ in the other treatments are shown in Figure 4b, c, d. R$^2$, slope, RMSE values for concentrations are shown in Table 5. There was a good agreement between predicted and measured data in the FTW 368L treatment. In general, ON, NH$_3$ and NO$_x$ removal efficiencies for equivalent systems (FTW or control) tended to be slightly higher in those chambers with lower volume than in those with higher volume. In part, this could result from the higher plant uptake rate in the FTW 368L that associated with higher biomass growth (28.78±8.43 mg N m$^{-2}$ day$^{-1}$, 4.30 g dry weight m$^{-2}$ day$^{-1}$) compared to FTW 560L (18.85±8.56 mg N m$^{-2}$ day$^{-1}$, 2.20 g dry weight m$^{-2}$ day$^{-1}$, respectively). Higher measured uptake in the FTW 368L treatment (by a ratio of 1.53) compared to the FTW 560L treatment could explain some of the deviation model predictions from observations for NH$_3$ and NO$_x$. Model performance was poor for NH$_3$ in the controls. This could result from the higher value of $k_{nit}$ that consisted the majority of the nitrification in the system, that hold by floating mat, which is absent in the control systems.

Table 5. Comparison of statistical indexes for different variables (ON, NH$_3$ and NO$_x$, mg L$^{-1}$) in different treatments. Slope (mg N L$^{-1}$); RMSE (mg N L$^{-1}$).

|          | ON      |            | NH$_3$   |            | NO$_x$   |            |
|----------|---------|------------|----------|------------|----------|------------|
|          | R$^2$   | Slope      | RMSE     | R$^2$      | Slope    | RMSE       |
| FTW 368L | 0.77    | 1.54       | 0.39     | 0.99       | 1.21     | 0.39       | 0.99       | 1.20     | 0.26     |
| Control 560L | 0.83  | 1.60       | 0.34     | 0.91       | 0.29     | 0.92       | 0.95       | 1.04     | 0.27     |
| Control 560L | 0.43  | 0.64       | 0.43     | 0.82       | 0.30     | 0.92       | 0.95       | 0.83     | 0.23     |
Figure 4. Changes in measured and predicted values of ON, NH\textsubscript{x} and NO\textsubscript{x} in the validation exercise: (a) FTW\textsubscript{560L}; (b) FTW\textsubscript{368L}, (c\textsubscript{1}) Control\textsubscript{368L}, (C\textsubscript{2}) Control\textsubscript{368L} without mat effect, (d\textsubscript{1}) Control\textsubscript{560L} and (d\textsubscript{2}) Control\textsubscript{560L} without mat effect. Each point represents average concentration over four batches ± SD.

Figure 4\textsubscript{c2}, d\textsubscript{2} shows model performance when $k_{\text{nit}}$ reduced by factor 3 in the control treatments. By reducing calibrated $k_{\text{nit}}$ (0.17) to 0.057, model performance for NH\textsubscript{x} dynamic in the control treatments was enhanced. RMSE values between measured and predicted NH\textsubscript{x} concentration were 0.121 and 0.136 mg NH\textsubscript{x} L\textsuperscript{-1} for FTW\textsubscript{368L} and FTW\textsubscript{368L}, respectively. In another word, reducing the effect of floating mat by factor 3 improved model performance in the controls.
These results have supported the idea that the majority of nitrification is generated on the floating mat. Microbial transformations are mainly fixed film processes in which bacteria are immobilized in a viscoelastic layer of biofilm that is attached on the solid surfaces rather than in the bulk of the water [23][24]. These findings have also boosted our hypothesis underpinning the conversion of rate constants obtained via calibration in treatment FTW_{560L}.

3.1.5 Sensitivity analysis. Figure 5 shows the magnitude of the nitrification, plant uptake, and volatilization processes on the model prediction of NH\textsubscript{x} removal under different \( k_{nit} \), \( k_{up} \) and \( k_{vol} \) values. Of the reaction rate constants investigated, model simulations revealed that NH\textsubscript{x} behaviour was most sensitive toward \( k_{nit} \) which control biochemical reaction within the system, confirming the potential of nitrification as loss process. By increasing \( k_{nit} \), predicted NH\textsubscript{x} concentration were sensitively decreased over time.

Though plant uptake makes clear contributions to NH\textsubscript{x} and NO\textsubscript{x} removal; model outputs were less sensitive to \( k_{up} \) than they were to \( k_{nit} \). Model prediction was least sensitive to \( k_{vol} \) which had a relatively little impact on free NH\textsubscript{3} losses and NH\textsubscript{x} dynamics overall.

![Figure 5](image.png)

**Figure 5.** Predicted NH\textsubscript{x} removal in the FTW_{560L} with systematic changes in (a) \( k_{nit} \), (b) \( k_{up} \) and (c) \( k_{vol} \) for FTW_{560L} treatment.

4 Conclusions
In this research, the benefits of FTWs were evaluated in a pilot-scale batch operated tertiary treatment system for real wastewater. Obtained findings confirms that FTWs can, indeed, enhance ammonia removal significantly in a semi-operational context. Nitrification was shown to be the most important loss process for NH\textsubscript{x}, particularly in the FTWs. This supports our hypothesis that higher nitrification
rates are associated with the increasing the surface of mat materials for more biofilm establishment. The contribution of uptake was relatively low compared to nitrification. A simple model was used as an integrating explanatory framework. This allowed the relative contributions of different removal processes to be quantified.

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