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Influence of medium specific retention on nitrification in unsaturated treatment wetlands☆

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ABSTRACT

Hydraulic loading rate (HLR) and the size distribution of the treatment medium have been shown to influence treatment efficacy in vertical flow treatment wetlands (VFTW). The effect of operational parameters like dose volume (DV) has received comparatively little attention. Using conversion of ammonium to nitrate as a measure of performance, this study defines the ratio of DV to the retention volume (RV), controlled primarily by the specific retention (S_r) of the medium, $\Psi = DV/RV$, as a parameter unifying the effects of HLR, DV and S_r on VFTW performance. Experiments were conducted in unplanted mesocosms using two media with unique size distributions and S_r (sand, $d_{50} = 0.4$ mm, $S_r = 0.19$ and gravel, $d_{50} = 5$ mm, $S_r = 0.09$), two DV values and four HLR values. More nitrate was produced in sand than gravel at any HLR. In both sand and gravel, nitrification efficiency increased as HLR decreased and, for a given HLR, lower DV. Use of the parameter Ψ minimized the interacting effects of media size, HLR and DV. When Ψ was identical ($\Psi = 0.17$), both sand and gravel achieved nearly identical nitrate concentrations despite the sand receiving twice the HLR. Similarly, nitrate concentration increased as the value of Ψ decreased for a given HLR regardless of medium size. Thus Ψ might be used to optimize HLR to the size of the medium and optimize DV for a given HLR. The parameter has potential to be applied in other porous medium based treatment systems.

1. Introduction

Hydraulic loading rate (HLR, a volume of water per unit area per day) and the interrelated mass loading of a particular pollutant (mass per unit area per day), have long been recognized as important design considerations in unsaturated vertical flow treatment wetlands (VFTW) [1,2]. HLR and mass loading are typically applied as a series of pulsed doses of wastewater distributed over time, such as one dose per hour. At a constant HLR, a system can be operated with either large, infrequent doses or smaller, more frequent doses. Dosing frequencies can be highly variable, ranging from as low as 4 to upwards of 48 doses per day [3–5]. Design literature for sand filters already recognizes the importance of varying dose volume (DV) for media characteristics, requiring more frequent, smaller doses for coarse-grained recirculating sand filters and larger, less frequent doses for single-pass filters constructed with finer media [3]. For example, Healy et al. demonstrated that the hydraulic and organic loading rates, along with dosing frequency significantly affect the performance of sand filters [6]. Sabbah et al. observed that reducing the number of daily doses from 10 to 3, at the same HLR, resulted in a significant 20–30 % reduction in ammonium removal efficiency in intermittent sand filters [7]. Only a few papers have focused on optimization of dosing schedule for a given HLR in VFTWs [8,9]. Molle et al. observed that the management of DV and dosing frequency in VFTW is crucial for ensuring effective treatment performance, as smaller batches with more frequent cycles enhance oxygenation, while larger volumes with longer intervals reduce contact time with the biomass, potentially leading to poorer pollutant removal [10].

HLR, mass loading, and other typical VFTW design parameters such as hydraulic retention time (HRT) do not adequately describe dose-scale hydraulic behavior in unsaturated systems. Although medium properties such as particle size and porosity influence the retention characteristics of the bed, they alone do not capture the dynamic behavior of pulse-loaded operation. Calculating an effective HRT in unsaturated VFTW is inherently challenging due to the unsaturated media and the pulse-loaded operation. Unlike saturated systems, where water uniformly fills pore spaces, unsaturated VFTW operates with pores largely filled with air, and water rapidly drains between doses. This makes it difficult to determine both how much water remains in contact with the medium

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and for how long after each dose. In fact, in such systems, the residence time distribution (RTD) of flow through the media, typically derived from the outflow hydrograph, is often used in place of HRT, although it may not directly represent the fate of the specific water applied during a single dose [11]. Common methods to estimate RTD in unsaturated VFTW include tracer tests or analyzing outflow hydrographs of applied doses of wastewater, which can provide parameters such as median (t_{50}) time water stays in the system [11,12]. This approach recognizes that in pulse-fed, unsaturated systems, traditional HRT calculations (based on total porosity) are inappropriate. Porosity reflects total void space but does not differentiate between retained and non-retained water. HLR is a system-level loading parameter that ignores media-retention volume (RV). These limitations highlight the need for a parameter that captures how much of a given dose is likely to be retained, offering a more accurate operational-scale metric and enabling better prediction and comparison of system performance across media types and dosing strategies.

This study aims to fill this knowledge gap by introducing a parameter, the Dose Volume Fraction ($\Psi = DV/RV$), to standardize DV across a range of HLR and media sizes. The RV of a VFTW bed is the product of the total volume of the porous medium and its specific retention (S_r). S_r refers to the fraction of water that remains in a porous medium after gravitational drainage and is expressed as the ratio of retained water volume to the total medium volume. It is influenced by particle size, surface texture, and pore structure. S_r is often considered analogous to field capacity in soil science and can be measured directly through saturation–drainage methods [13–15] or can be estimated empirically from grain-size properties using regression models [16].

Under ideal plug flow conditions, any value of Ψ less than one would maximize the contact time between water and the unsaturated porous medium because the entire dose could be retained. Inevitable flow short-circuiting and mixing of individual DV between doses suggests the optimal Ψ value would be considerably less than one. Conversely, the retention of a specific contaminant within a VFTW might be longer than the retention of water if the contaminant reacts with the medium and/or the biofilm [17], and maximizing the retention time of a pollutant should be a major goal of any set of design criteria. By extending the retention time of an individual dose in the filter medium without reducing HLR, by optimizing a DV to a specific media size, more efficient removal in wetland systems may be achieved as a maximum mass of pollutants would have more time to interact with the media biofilm.

To test the applicability of Ψ as potential design parameter we investigated the effect of including Ψ on NH_4-N removal and NO_X-N production across two media sizes (sand and gravel) commonly used in VFTWs. While the scope of this study is limited to these two media, they were selected to represent distinct S_r and thus RV values. A matrix of four different HLR and two different DV were applied to both media to examine whether including Ψ as a parameter would allow for better optimization of the dose volume to HLR and media properties. In addition, tracking NH_4-N removal is likely a conservative estimate of the influence of the Ψ on other pollutants because sorption increases the residence time of NH_4-N relative to water [17–20].

2. Methodology

2.1. Experimental setting of mesocosms

Eight unplanted vertical flow mesocosms were operated to compare the effects of DV and S_r on NH_4-N removal via nitrification. The unplanted mesocosms allowed isolation of physio-chemical processes without the influence of plants. Mesocosms were constructed from polyvinyl chloride (PVC) pipe with a height of 61 ± 1 cm and inner diameter of 20 cm and had a 4 mm drain hole approximately 1 cm above the bottom. Four mesocosms were filled with either air-dried sand (d_{50} = 0.4 mm C_u = 4.3) or air-dried gravel (d_{50} = 5 mm, C_u = 2.4) to a total depth of 50 cm. Both media were sourced from the same alluvial deposit of similar geologic origin thus likely similar surface chemistry and base sorption capacity. Although we did not specifically test surface chemistry, this shared origin reduces the likelihood that surface chemistry differences significantly influenced nitrification, allowing us to focus on physical retention characteristics. The finer medium consisted of washed natural sand from the deposit, while the gravel was crushed from larger gravel particles. The sand-filled mesocosms had approximately 5 cm of gravel on the bottom to enhance drainage. Mesocosms were weighed with and without air-dried medium, after filling to the medium surface with tap water and after gravity draining for 4 h to determine the porosity, S_r and RV as shown in Table 1. Porosity was measured by the weight difference between airdried and saturated mesocosms. S_r and RV were measured using a saturation–drainage method [15]. RV is the weight difference between the gravity-drained and air-dried mesocosms, and S_r is RV divided by the total volume.

2.2. Synthetic wastewater composition and dosing system

A synthetic wastewater with a influent of 120 ± 1 mg l^{-1} NH_4-N, made from NH_4-N chloride salt, and containing micronutrients delivered by a liquid fertilizer (0.13 % Boron, 0.125 % Copper, 4.6 % Iron, 1.25 % Manganese, 0.015 % Molybdenum, 0.6 % Zinc) and 10 mg l^{-1} phosphorus using a liquid NPK (0-32-25) were applied to the surface of mesocosms via one standard drip irrigation emitter per mesocosm (Raindrip Corp). Dosing was controlled using an automated delivery system that allowed a specified volume to be distributed at variable dose frequencies (λ) recorded as the number of evenly spaced doses per day. To ensure consistency between replicates and over time, emitters were calibrated whenever the DV was changed, and an emitter was replaced if it varied by >10 % from the specified DV (250 and 500 ml).

2.3. Experimental design and operating conditions

The experiment was conducted at a constant temperature of 24 °C after a 17-month startup period serving as a pre-conditioning phase, during which mesocosms received synthetic wastewater without any experimental manipulation. The purpose of this phase was to allow for microbial community stabilization [21] and saturation of NH_4-N sorption sites prior to data collection [22]. Although microbial community dynamics were not directly monitored, the long duration and consistent loading exceed recommended maturation times and support the assumption of biofilm maturity at the onset of the experimental phase [23]. All experimental data presented in this study were collected after this pre-loading phase. Two DVs (250 and 500 ml) were delivered at four different frequencies (λ) (every 4, 2 or 1 h) to develop a matrix of HLR, NH_4-N loading rates, DVs, λ and Ψ values as shown in Table 2.

2.4. Sampling procedure and water quality preservation

Feeding conditions for the experiments in Table 2 were maintained for one week before sampling. During sampling, the entire discharge volume generated from a single DV application was collected from each column in pre-washed plastic bottles. For example, when mesocosms were dosed every 4 h (λ = 6 doses d^{-1}) at 250 ml (HLR = 4.8 cm d^{-1}), the 250 ml discharge volume over 4 h was collected. This sampling protocol allowed analysis of the water quality over the entire DV pulse for each DV-HLR combination. From the collected discharge in the plastic bottles, a 50 ml subsample was collected, immediately filtered using 0.22 μm syringe filter, and placed in a cooler filled with ice for

Table 1
Porosity and retention volume characteristics of filter media used in mesocosms.

	Porosity	Specific retention-S_r	Retention volume-RV (l)
Sand	0.34	0.19	3.0
Gravel	0.48	0.09	1.5

Table 2
Matrix of experimental conditions for feeding sand and gravel mesocosms.

HLR (cm d^{-1})	NH_4-N load (g m^{-2} d^{-1})	DV (cm $dose^{-1}$)	λ (dose d^{-1})	Ψ sand	Ψ gravel
4.8	5.7	0.8	6	0.08	0.17
9.5	11.5	0.8	12	0.08	0.17
		1.6	6	0.17	0.34
19.1	22.9	0.8	24	0.08	0.17
		1.6	12	0.17	0.34
38.2	45.8	1.6	24	0.17	0.34

preservation and transportation to the lab for water quality analysis. All water quality analyses were completed within 24 h.

2.5. Water quality analysis

Water samples were analyzed for NH_4-N, nitrate and nitrite concentrations. NH_4-N analyses were conducted using the 2-phenyl phenol colorimetric method [24]. NO_X-N (nitrate and nitrite) analysis was performed using ion chromatography (Metrohm, USA).

2.6. Statistical analysis

Statistical analyses were conducted using RStudio (version 4.3.2) and Origin Pro (OriginLab). Multiple linear regression models assessed the effects of HLR, DV, RV, and medium type (sand vs. gravel) on relative NO_X-N production. Interaction terms were included in the models to examine how HLR, DV, and RV interact to affect relative NO_X-N production. Subgroup analyses evaluated HLR's influence within each medium size and the effect of DV at different HLR levels. To compare NO_X-N production between sand and gravel under identical Ψ values (Ψ = 0.17), Welch Two Sample *t*-tests were performed. Model assumptions were checked with Shapiro-Wilk tests for normality and Breusch-Pagan tests for homoscedasticity [25]. In addition, multicollinearity among predictors was evaluated using Variance Inflation Factors (VIF), with all values below 1.5, indicating low multicollinearity. Linearity and independence of observations were supported by the experimental design and confirmed through residual diagnostic plots.

2.7. Residence time distribution analysis

RTD tests were conducted a month before the nitrification study, while mesocosms were operating under a 500 ml DV and 12 doses d^{-1} loading regime. Effluent was collected in 2-liter bottles suspended from load cell sensors (Load Cell 100 N, PS-2200) connected to an Explorer GLX datalogger (PASCO Scientific). The sensors had an accuracy of ±1 N, enabling high-sensitivity, real-time measurement of effluent water weight. PASCO Capstone software was used to pre-visualize the hydrographs and extract time-series data. The median effluent time (t_{50}), defined as the time at which 50 % of the applied DV exited the system, was calculated from these hydrographs as a proxy for RTD within the mesocosms, although the outflow may not correspond exactly to the water applied in a single dose. The RTD testing, including sensor setup, calibration, data logging, and hydrograph analysis, was completed over a two-week period.

3. Results and discussion

3.1. Effluent nitrogen composition

Measured effluent concentrations of NH_4-N and NO_X-N from each evaluated combination of HLR and DV for both sand and gravel are shown in Table 3. In all tests, total nitrogen removal was <0.5 %, thus any reduction in NH_4-N corresponds to an increase in NO_X-N, verifying that sorption was not a meaningful removal mechanism and nitrification was the dominant nitrogen transformation in the system. This was expected because the influent contained no organic carbon to support denitrification and the mesocosms had been receiving high concentrations of NH_4-N for 17 months, thus sorption sites were likely filled prior to the experiment. Nitrate dominated oxidized forms of nitrogen. Nitrite averaged 0.4 % over all samples and never exceeded 1 % of the total NO_2-N plus NO_3-N. Therefore, the sum of nitrate and nitrite (NO_X-N) is called simply nitrate in the results.

3.2. Influencing factors for ammonium removal and nitrate production

The average fraction of the total applied NH_4-N converted to NO_X-N for each combination of media size, Ψ and HLR is shown in Fig. 1. Overall, nitrate production was significantly better ($p < 0.001$) in sand 54 % than gravel 31 %. Increasing the HLR had a significant negative influence on nitrate production overall ($p < 0.01$) and in both sand and gravel individually ($p < 0.001$ and $p < 0.05$, respectively). Nitrate concentrations increased from 21 % to 75 % of applied TN in sand and from 6 % to 67 % of TN in gravel as HLR decreased from 38.2 to 4.8 cm d^{-1}. Despite these significant trends, consideration of HLR or media size alone does not fully explain NH_4-N removal efficiency in our study. Nitrate production was higher when smaller DV, as reflected in lower Ψ values, were applied at the same HLR to the same medium. In gravel and when HLR = 9.5 cm d^{-1}, significantly more ($p < 0.05$) nitrate was produced for Ψ = 0.17 than Ψ = 0.34. In sand and when HLR =19.6 cm d^{-1}, the difference between Ψ = 0.08 and Ψ = 0.17 was significant ($p < 0.05$). These trends suggest that consideration of Ψ better defines the relationship between NH_4-N removal efficiency and HLR for specific media sizes.

To better explore the influence of Ψ on NH_4-N removal in VFTW,

Table 3
Effluent NH_4-N and NO_X-N concentrations (average ± SD) measured across different HLR and DV for both sand and gravel media. Influent NH_4-N averaged 120 mg l^{-1}.

HLR (cm d^{-1})	DV (cm $dose^{-1}$)	Sand		Gravel	
		NH4-N (mg l^{-1})	NO_X-N (mg l^{-1})	NH4-N (mg l^{-1})	NO_X-N (mg l^{-1})
4.8	0.8	29.7 ± 1.8	90 ± 1.9	39.7 ± 6.1	80 ± 5.8
9.5	0.8	36.0 ± 2	84 ± 1.7	69.8 ± 2	50 ± 1.8
	1.6	38.8 ± 4.4	81 ± 4.4	89.4 ± 2.9	31 ± 3
19.1	0.8	63.2 ± 1.5	57 ± 1.6	92.4 ± 0.9	28 ± 0.9
	1.6	69.9 ± 1.4	50 ± 1.3	90.6 ± 0.4	29 ± 0.4
38.2	1.6	94.8 ± 2.5	25 ± 2.9	113.2 ± 0.1	7 ± 0.2

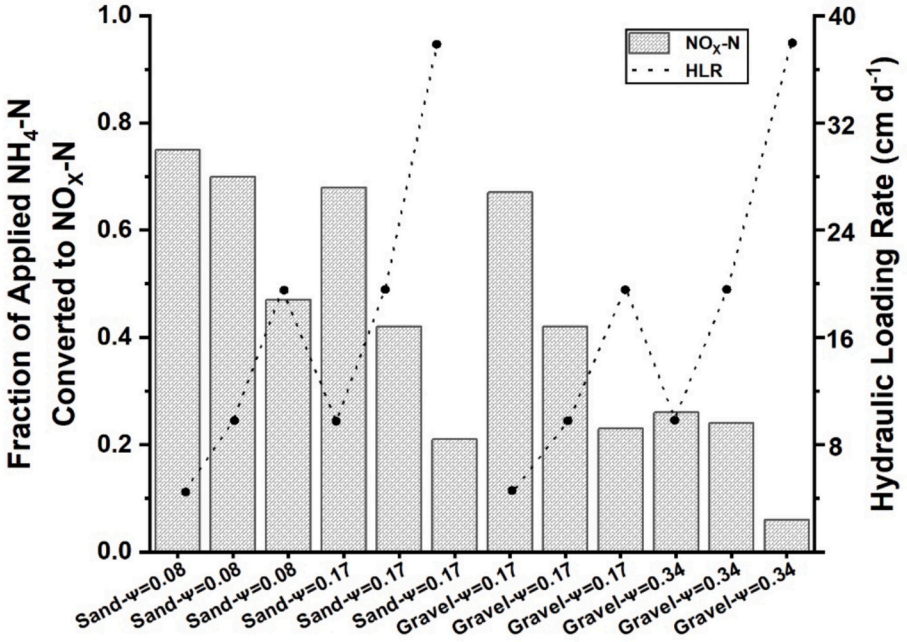

Fig. 1. Average nitrification efficiency for sand and gravel media at different dose volume fractions (Ψ) and hydraulic loading rates. The bars represent normalized fractions of influent NH_4-N converted to NO_X-N on the left y-axis. The points indicate the corresponding HLR on the right y-axis.

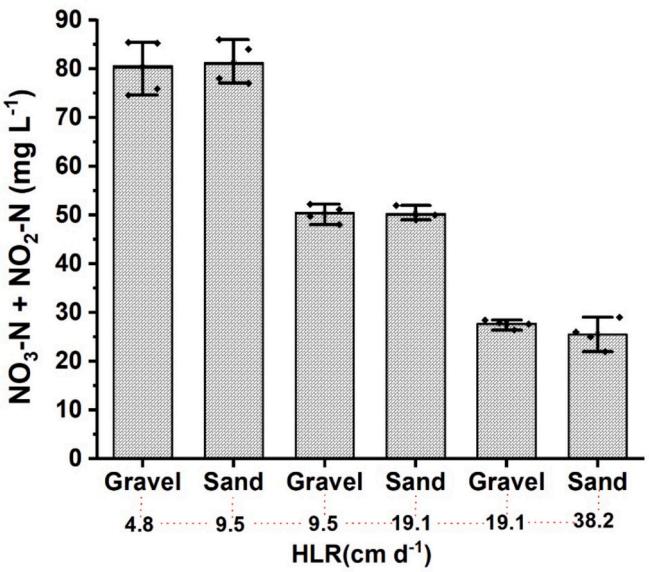

Fig. 2. Effluent NO_X-N concentrations in sand and gravel media at different HLRs for Ψ = 0.17. Sand and gravel have statistically equivalent NO_X-N production when HLR on sand is twice that of gravel corresponding to sand having twice the RV when Ψ is equal to both media. Error bars represent 95 % confidence intervals.

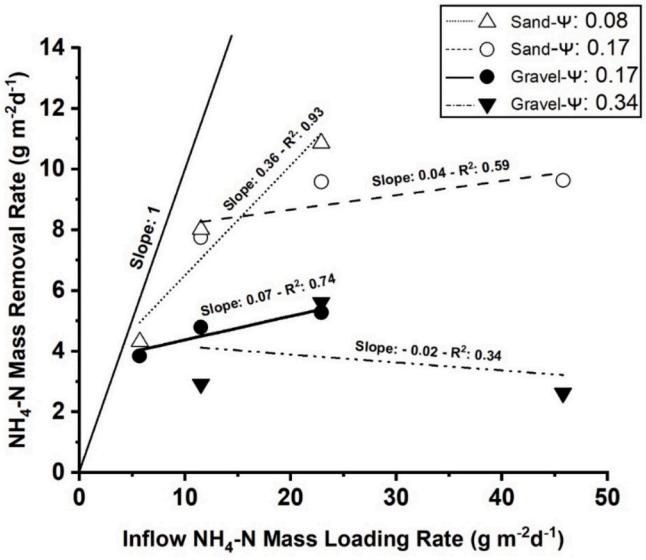

Fig. 3. NH_4-N mass removal rate as a function of influent NH_4-N mass loading rate for sand and gravel and different Ψ values. Incorporating Ψ improves the correlation compared to mass loading alone ($R^2 = 0.042$, $p > 0.05$ without Ψ).

Fig. 2 shows that the interacting effects of medium type and HLR on nitrification shown in Fig. 1 are minimized when Ψ is identical. For Ψ = 0.17, a doubling of the HLR (in gravel, 4.8 to 9.5 to 19.1 cm d^{-1} versus sand, 9.5 to 19.1 to 38.2 cm d^{-1}) results in nearly identical drops in nitrate production in both media. Additionally, NO_X-N production is statistically similar ($p < 0.05$) when the HLR to sand is twice that of gravel which compares favorably to the fact that sand has nearly double the RV.

A mass plot comparing NH_4-N removal to its areal mass loading is shown in Fig. 3. Overall, mass loading is a poor predictor of mass removal as there is virtually no correlation ($R^2 = 0.04$, $p > 0.05$) when differences in media size and Ψ are ignored (trend not shown). Correlations improve dramatically when regressions are run for unique combinations of media size and Ψ, ranging from $R^2 = 0.93$ for Ψ = 0.08 in sand to $R^2 = 0.34$ for Ψ = 0.34 in gravel, as shown in Fig. 3. Additionally, correlation slopes decrease (poorer performance) as Ψ increases from 0.08 to 0.17 to 0.34, suggesting smaller DV relative to RV improves the relationship between mass load and mass removal. This is further supported by the improvement in correlation ($R^2 = 0.49$, $p < 0.001$) in a multiple linear regression model including Ψ (trend not shown).

The dose frequency, λ, is defined by HLR/DV. A plot of NH_4-N mass removal versus λ is shown in Fig. 4. As with HLR and mass loading,

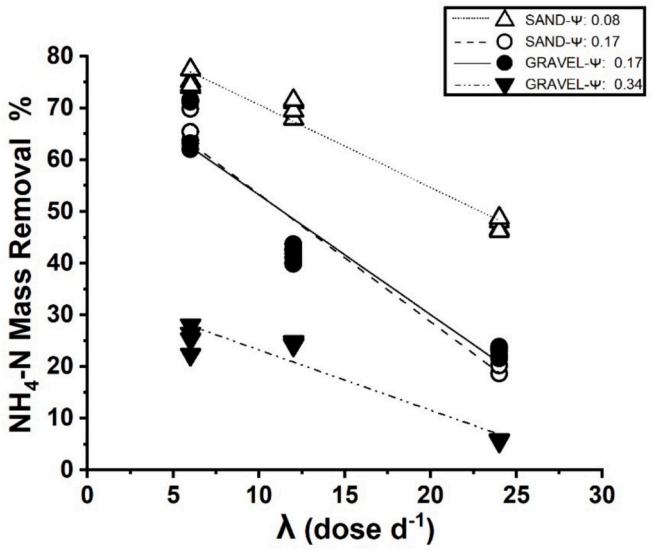

Fig. 4. NH_4-N mass removal percent plotted against dose frequency (λ = HLR/DV) for different Ψ values. For any given λ, mass removal increased as Ψ decreased from 0.34 to 0.17 to 0.08. When Ψ was identical (Ψ = 0.17), differences due to media size were minimal, suggesting Ψ effectively normalizes NH_4-N mass removal percent across media.

consideration of the parameter Ψ refines the relationship and minimizes the variation due to media size. The difference between sand and gravel is virtually indistinguishable when Ψ = 0.17 and mass removal increases for any λ as Ψ decreases from 0.34 to 0.17 to 0.08.

3.3. Comparison to other studies

Ammonium removal in our study is consistent with other studies [26–30] considering the effect of either HLR and/or media size (Table 4). For example, NH_4-N removal efficiency in our sand media mesocosms (21–75 %) was comparable to the range reported by Chen et al. (33–77 %). Likewise, gravel mesocosms in our system achieved up to 67 % removal, significantly exceeding the 35 % reported by Carballeira et al. despite higher (sometimes dramatically higher) values for influent concentration, HLR and mass loading in our study. Importantly, our results show that when Ψ is identical, the effect of HLR is consistent across media size (Fig. 2). Also including the parameter Ψ increased the correlation between NH_4-N mass load and mass removal (Fig. 3) and correlation between NH_4-N mass removal and dose frequency (Fig. 4). Thus, the parameter Ψ, which was not considered in the other studies, might further explain the variation of removal efficiencies in those studies, emphasizing the potential utility of Ψ as a design variable in VFTW and other unsaturated porous media systems.

3.4. Media RTD

The cumulative hydrographs for both sand and gravel for a DV of 500 ml (the dose was applied over a 4 min interval) are shown in Fig. 5. As expected, water is discharged from the gravel medium more quickly than the sand medium. The median time for 50 % of the DV to be collected (t_{50}) was only 11 min in gravel but 26 min in sand. Similarly, the time for 90 % of the DV to be collected (t_{90}) was 68 min for gravel and 113 min for sand. Interestingly, the ratio of sand/gravel for t_{50} and t_{90} (2.3 and 1.7 respectively) is similar to the ratio of sand/gravel RV = 2.1 suggesting that differences between media in the RTD of a given dose size may be related to or explained by the media's retention volume. At lower dose volumes, decreasing Ψ, RTD likely increases as the downward progression of a larger fraction of the applied water is retarded, moving through water films and capillaries instead of through the macro pore spaces. The increase of RTD for smaller dose volumes was observed by Cota et al. within a single media potentially illustrating this phenomenon [11]. Because the parameter Ψ is a ratio of volumes, it can be more readily applied as a design criterion. Thus, Ψ might be a suitable surrogate for the complete RTD during design. These results suggest that Ψ and RTD can serve complementary roles: Ψ provides a practical volume-based parameter for system design, while RTD, though harder to determine before operation, offers insight into actual flow behavior as the system matures.

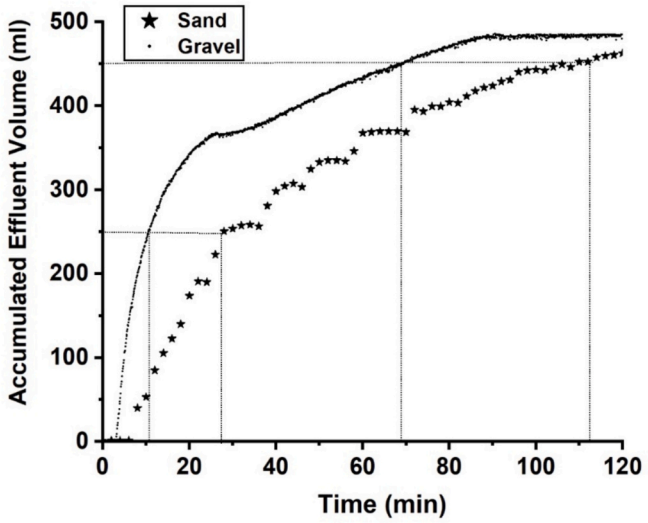

Fig. 5. Effluent cumulative hydrographs for sand and gravel operated under identical dosing conditions (500 ml dose volume, 12 doses d^{-1}). The time required for 50 % of the dose to pass (t_{50}) was 26 min for sand and 11 min for gravel. The time required for 90 % of the dose to pass (t_{90}) was 113 min for sand and 68 min for gravel, indicating longer water retention in the finer medium.

Table 4
Summary of ammonium removal efficiencies under different HLRs and media types in VFTWs, including results from this study for both sand and gravel media.

Study (author, year)	Media size (diameter)	Hydraulic loading rate (cm d^{-1})	NH_4-N mass load (g m^{-2} d^{-1})	Influent NH_4-N concentration (mg l^{-1})	NH_4-N removal (%)	Ψ
This study	Sand (0.4 mm)	4.8–38.2	5.7–46	120	21–75	0.08, 0.17
Chen et al. (2024)	Sand (0.2–1 mm)	48, 64	6.3–10	13–16	33–77	?
Carballeira et al. (2021)	Sand (1–3 mm)	10.2	6.3	62	55	?
This study	Gravel (5 mm)	4.8–38.2	5.7–46	120	6–67	0.17, 0.34
Carballeira et al. (2021)	Gravel (2–6 mm)	10.5	6.5	62	35	?
Weerakoon et al. (2016)	Gravel (10–20 mm)	3.5–30	0.6–6.9	16.2	58–97	?
Saeed et al. (2016)	Gravel (5–10 mm)	68	45.3	66.6	47	?

3.5. Ψ as a potential design parameter

The influence of HLR, mass load and λ on ammonium removal and nitrate production is shown in Figs. 2, 3 and 4, respectively. In all cases, considering the influence of Ψ strengthened the relationship between these variables and minimized differences between media size for the same value of Ψ. However, the media size within a VFTW bed, which controls S_r, and the bed volume can only be adjusted during design. Because RV is the product of S_r and bed volume, it too is fixed design criterion. Mass load of a pollutant is linked to the HLR because concentrations typically vary minimally for a specific application. HLR (or mass load) is often the primary design criterion in VFTW systems and while it is possible to lower the design HLR by adding additional VFTW beds, this is not trivial. Thus, DV and the inversely proportional λ are the only operationally controllable variables which can be adjusted post-construction.

It should be possible to define an optimal DV, or λ, for a given HLR based on the parameter Ψ. However, for a given HLR, λ can be decreased (increasing percent removal of NH_4-N, Fig. 4) only by increasing the DV thus increasing Ψ. Conversely, if the DV exceeds the RV of the medium (Ψ <1), the volume of the dose exceeding the RV will pass through the system very quickly. This excess volume would not be able to take advantage of the rest period between doses that infrequent dosing provides. Thus, a theoretical maximum Ψ value to optimize the available retention time (defined by DV/HLR) should be 1.0 (DV = RV). In this scenario, the entire DV would be retained within the medium's retention capacity subjected to the same reaction processes at the lowest possible value of λ and thus the maximum possible retention time (1/λ). Inevitable short-circuiting within the medium and hydraulic mixing would require an optimum value of Ψ <1.0, as some water short circuits through macro-pore spaces. Conversely, if a specific pollutant is held within the media longer than water through adsorption, an optimum Ψ could be larger than considering hydraulics alone. In our study, the highest NH_4-N removal percent at a given loading rate was observed at the lowest value of Ψ (Ψ = 0.08), suggesting that dose volumes should be quite small relative to the retention volume. However, this value may be biased by inclusion of relatively large HLR and NH_4-N mass loading values in our study. NH_4-N removal and nitrate production was nearly as good when Ψ = 0.17 in both sand and gravel at the lower values of HLR (9.6 cm d^{-1} in sand and 4.8 cm d^{-1} in gravel, Fig. 1) emphasizing the interrelationships between HLR, DV and λ.

Calculation of the RV of the medium, which is required to determine Ψ, requires knowing the S_r of the medium. Under controlled conditions, standardized testing methods are commonly used to determine porosity and specific retention (S_r), typically involving measurements of a medium sample's weight and volume under air-dried, saturated, and free-drained conditions [15]. Unfortunately, dry weight, and thus the S_r of a given medium is difficult to measure under field conditions. To compare expected NH_4-N removal efficiency of different media sizes, or to optimize the relationship between HRT and DV for a specific medium, S_r of the medium is best determined before the system is constructed. Plant and biofilm growth within the medium likely alters the S_r as the system matures. Our experiments were conducted on unplanted mesocosms of identical maturation age, likely minimizing these temporal effects. Nevertheless, we did not quantify changes in S_r over time and future investigations should explore how S_r is influenced by biofilm development and organic matter accumulation. Additionally, we compared only two media sizes and only one overlapping value of Ψ. More experimentation on the influence of this parameter is obviously warranted, but our initial findings suggest that it may prove useful to compare the effect of different media and to better optimize a DV for a given HLR. Future research should explore the applicability of Ψ across a broader range of contaminants in addition to media sizes and types, including materials like biochar and zeolite, to assess its robustness in systems with different retention characteristics and adsorption properties. We also encourage other VFTW researchers to report, in addition to HLR, the dose volume used in studies so that their work could be used to evaluate Ψ.

4. Conclusions

This study introduces the dose volume fraction (Ψ = DV/RV) as a pivotal design parameter in VFTW, offering a scalable approach to optimize the relationship between DV and HRT for a given media size. By standardizing DV relative to medium RV, Ψ effectively harmonizes the efficiency of processes such as nitrification across different media, making it a unifying metric that ensures similar percent removals regardless of medium type. In this study, nitrification was higher in sand than in gravel for any given HLR and increasing the HLR decreased nitrification in both sand and gravel media. However, by adjusting the DV to the RV of the medium to achieve an identical Ψ, differences between media were effectively neutralized and the relationship between HLR and nitrification were similar in both media. The analysis also highlights the importance of the interaction between DV and HLR. At higher HLRs, DV had a greater influence on nitrification in sand, while in gravel, the effect was more pronounced at lower HLRs. This interaction suggests that the optimal DV for achieving maximum treatment efficiency is context-dependent, varying with medium type and HLR. Overall, Ψ improved the correlation between ammonium percent removal and commonly used VFTW design criteria, such as HLR and pollutant mass loading, by accounting for the inherent ability of each medium to retain water and thereby optimize the time available for critical reactions to occur. The results suggest that future design approaches could incorporate Ψ as a key parameter, potentially enabling more tailored and effective systems for wastewater treatment. Future research may extend these insights by examining Ψ's applicability to a wider range of pollutants and media structures, thereby supporting broader application in wetland-based treatment systems.

CRediT authorship contribution statement

Mohammad-Hosein Mozaffari: Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Christopher R. Allen:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Formal analysis, Conceptualization. **Ellen G. Lauchnor:** Writing – review & editing, Supervision, Funding acquisition, Formal analysis, Conceptualization. **Otto R. Stein:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Formal analysis, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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