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HIGH-FREQUENCY SPATIOTEMPORAL DATA IMPROVES ESTIMATES OF NITRATE REMOVAL PERFORMANCE AND UNDERSTANDING OF PROCESSES IN WOODCHIP BIOREACTORS

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Abstract

The use of woodchip bioreactors for reducing nitrate loads from agricultural systems to receiving freshwater has gained popularity in many countries due to its simplicity, low cost and efficiency. However, performance assessments have to date relied on low-frequency sampling (e.g., weekly) at inlet and outlet only. Given that high-frequency data have enabled substantial knowledge gains in many environmental studies, we investigated whether such data also would prove beneficial in the context of bioreactors. We monitored nitrate concentrations at multiple locations in a pilot-scale woodchip bioreactor installed on a dairy farm in the Waikato region. We used an optical nitrate sensor to measure nitrate in porewater samples from the inlet and outlet and monitoring wells within the bioreactor at one- to two-hourly intervals using a multiplex sampling system. We developed a complementary new method for calculating nitrate removal rates (RR) that accounts for the variable lag time between entry and exit of the parcel of incoming water. We compared results using this improved method with results using the conventional practice of calculating instantaneous removal rates using low-frequency, concurrent measurements of inlet and outlet concentrations that cannot consider the lag time of the parcel within the bioreactor. Our results show that RRs calculated using high-frequency data (2-hr interval) and the new method were significantly higher than the instantaneous RRs calculated using low-frequency data (e.g., 6-, 12-, 24-hr interval). Conversely, there were no significant differences observed among instantaneous RRs at different lower frequency sampling intervals. Moreover, based on sampling data from monitoring wells strategically placed to investigate the quarter sections of the bioreactor, the average RRs among these sections were found to be significantly different; with the section having the highest or lowest average RR differing between 2018 and 2019 seasons. For example, the final quarter section of the bioreactor had the lowest average RR in 2018 but had the highest average RR in 2019, which could be partly attributed to the extensive N limiting conditions that occurred in this section in 2018, conditions which were not prevalent in 2019. These results show high-frequency monitoring helps in obtaining more accurate representation of bioreactor performance and better understanding of processes occurring in woodchip bioreactors, enabling better and more efficient design of such mitigation techniques.

Introduction

The use of woodchip bioreactors for reducing nitrate loads from agricultural systems to receiving freshwater has gained popularity in many countries due to its simplicity, low cost and efficiency. However, assessments of the nitrate removal performance of bioreactors have to date relied on low-frequency sampling (e.g., weekly) at inlet and outlet only (Rivas *et al.* 2020b; Schipper *et al.* 2010a). These assessments essentially treat bioreactors as 'black boxes' and therefore no information can be gained on the variability of performance within the bioreactors and the influencing factors (Christianson *et al.* 2012; Hassanpour *et al.* 2017; Husk *et al.* 2017). Moreover, such performance assessments usually do not account for the lag time of the travel of a parcel of water from entry to exit and relied on concurrent measurements of nitrate concentrations at entry and exit (Bock *et al.* 2018; Cameron and Schipper 2010; Christianson *et al.* 2013). This lack of accounting for the lag time and low-frequency data has significant implications on the accuracy of performance measures (e.g., removal rates), particularly in drainage systems with highly dynamic flows. A number of hydrological studies have showed the importance of high-frequency data for improved estimates of nitrate loads (Liu *et al.* 2020). The availability of optical nitrate sensors provides the opportunity to carry out monitoring of the performance of the bioreactor at multiple locations and at high frequency. Therefore, we investigated whether such high-frequency data also would prove beneficial in the context of bioreactors. In this study, we introduced a novel method for accounting for the variable lag time and we aimed to determine the variability of nitrate removal performance within the bioreactor and to compare estimates of nitrate removal efficiencies and rates using high- and low-frequency data.

Materials and Methods

For two drainage seasons, we conducted high-resolution spatiotemporal monitoring of nitrate concentrations in a woodchip bioreactor constructed on a dairy farm near Tatuanui in the Waikato region, New Zealand. With a saturated volume of 56 m^3, the lined bioreactor intercepts drainage water from an artificial drain with a drainage area of approximately 0.65 ha. Several publications have reported more information on the bioreactor characteristics and performance (Maxwell *et al.* 2020; Rivas *et al.* 2020a; Rivas *et al.* 2019; Rivas *et al.* 2020b).

We employed a multiplexer sampling system to draw water from the inlet, outlet, and 19 monitoring wells in the bioreactor and pump the water through an optical nitrate sensor. In the 2018 drainage season, we used two separate sampling and nitrate measurement systems for each half of the bioreactor to measure nitrate at approximately hourly interval during the latter part of the drainage season, i.e., for a one month period between 8 August and 8 September 2018. In the 2019 season, only one system was used with high-frequency measurements of every two hours carried out during 9 August to 26 October. Maxwell *et al.* (2020) provide the detailed description of the 2018 investigation including the post-calibration of optical nitrate measurements with laboratory measured nitrate concentrations. Similarly, Rivas *et al.* (2020a) described the experimentation in the 2019 season including the post-calibration. This paper, however, focuses on the results for the nitrate measurements along the centreline of the bioreactor comprising measurements at the inlet, two wells in the bioreactor (C1 and C3), and the outlet (Figure 1). These measurements enabled us to analyse the bioreactor performance in quarter sections and of the whole bioreactor. Information on pore water sample collection and laboratory analysis have been provided in previous publications (Maxwell *et al.* 2020; Rivas *et al.* 2020a; Rivas *et al.* 2019; Rivas *et al.* 2020b).

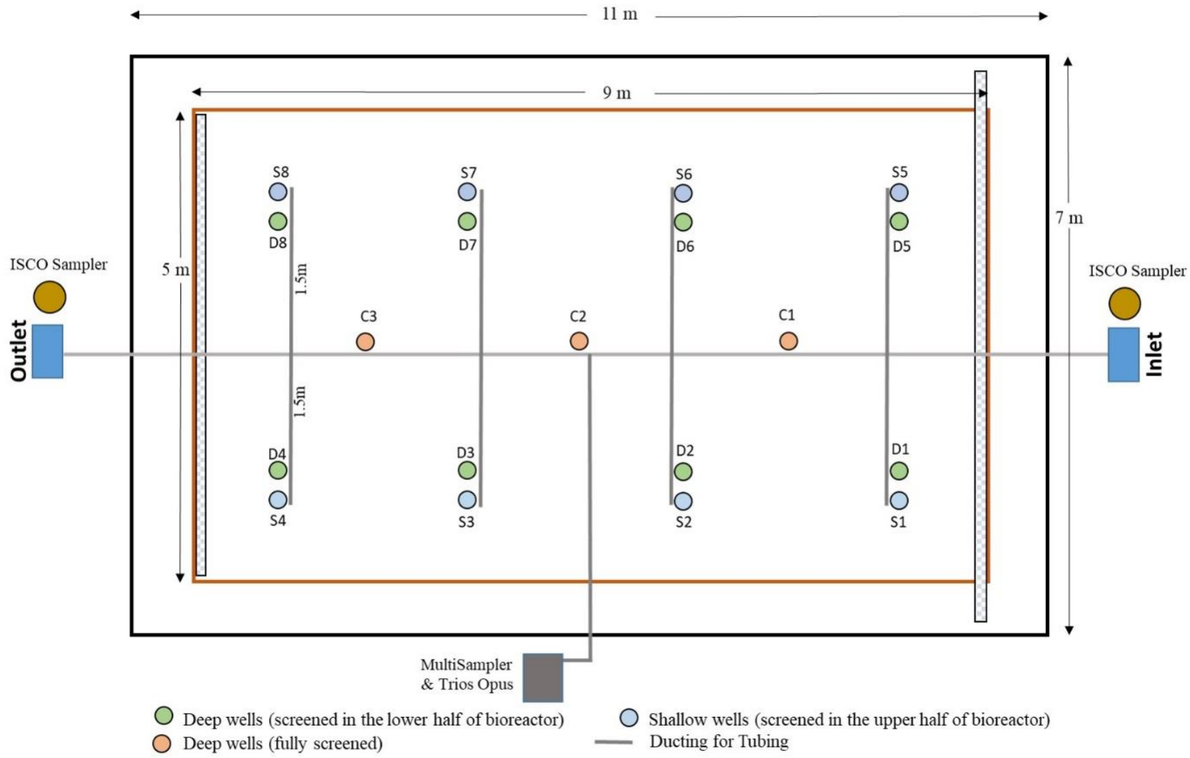

Figure 1 *Schematic of the Tatuanui bioreactor and monitoring wells.*

We assessed the nitrate removal performance of the bioreactor in terms of removal efficiency and removal rate at quarter sections and for the whole bioreactor. Removal efficiency refers to the proportion of nitrate that was removed from what entered a section of the bioreactor or at the inlet (for the whole bioreactor analysis). Removal rate refers to the amount of nitrate that was removed per unit volume of the bioreactor per unit time (i.e., units in g N m^{-3} day^{-1}). In this study, we calculated the amount of nitrate removed by tracking drainage water parcels between entry and exit. These drainage parcels correspond to the water volume in between nitrate measurements (approx. hourly in 2018 and two-hourly in 2019). We tracked water parcels starting from the outlet where flow was measured. We were able to track flow parcels by developing a method that accounts for the lag time based on using effective pore volume, not the drainable pore volume used in usual practice, to determine the hydraulic retention time (HRT). This effective volume was determined from the product of hydraulic efficiency * drainable pore volume. Hydraulic efficiency, e_h, was calculated as e_h = time between nitrate peaks / theoretical HRT, where theoretical HRT is drainable pore volume divided by flow. We used the 2019 nitrate time series data to determine the time between nitrate peaks. This novel method using effective pore volume was inspired by the method developed by Persson *et al.* (1999) using the ratio of 'time to peak' in tracers to theoretical HRT to understand wetlands flow dynamics and the use of concentration break points for determining HRT by Pluer *et al.* (2019).

Results and Discussion

Effective pore volume and hydraulic inefficiencies

Our results show the deviation of effective pore volumes from the drainable pore volumes particularly in the first (Q1) and last quarter sections (Q4) of the bioreactor. The hydraulic efficiency at Q1 was 1.41 (±0.14), whereas in Q4 it varied with flow (e_h = 0.07203*Q + 0.15734, where Q is flow in L min^{-1}; $R^2 \approx 1.00$). With effective pore volume being the product of e_h and drainable pore volume, the greater effective pore volume in Q1 compared to the drainable pore volume could indicate that some water may have flowed back first away from the exit before proceeding given that the distribution header was perforated throughout its circumference. In Q4, the flow-e_h relationship shows that effective pore volume is low when flow is low, indicating that at lower flows, greater portions of the bioreactor became inactive, or dead zones. This explains the very low nitrate concentrations in the shallow wells near the outlet (S4 and S8) observed during low flows (Maxwell *et al.* 2020). In the middle section covering the second and third quarter sections of the bioreactor (Q2+Q3), the hydraulic efficiency was 0.97 (±0.09), indicating plug flow conditions may be valid in this section of the bioreactor.

Matched parcels and nitrate concentrations

With lag time accounted for, the time series of matched nitrate concentrations from inlet to outlet are shown in Figs. 2 (2018) and 3 (2019). There is a clear decreasing trend in nitrate concentrations entering the bioreactor as shown by the inlet concentrations. In both seasons, greatest reduction in nitrate concentrations occurred between wells C1 and C3, due to the larger bioreactor volumes between these two wells.

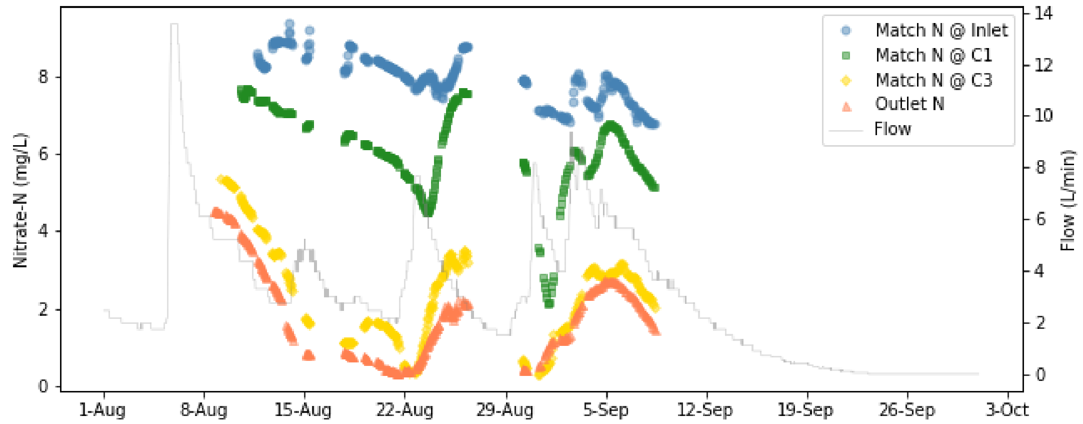

Figure 2 *Nitrate concentrations at the inlet and outlet plus two centre line wells at the Tatuanui bioreactor measured in 2018 and adjusted to match the time of a parcel of water when it entered and exited each section of the bioreactor.*

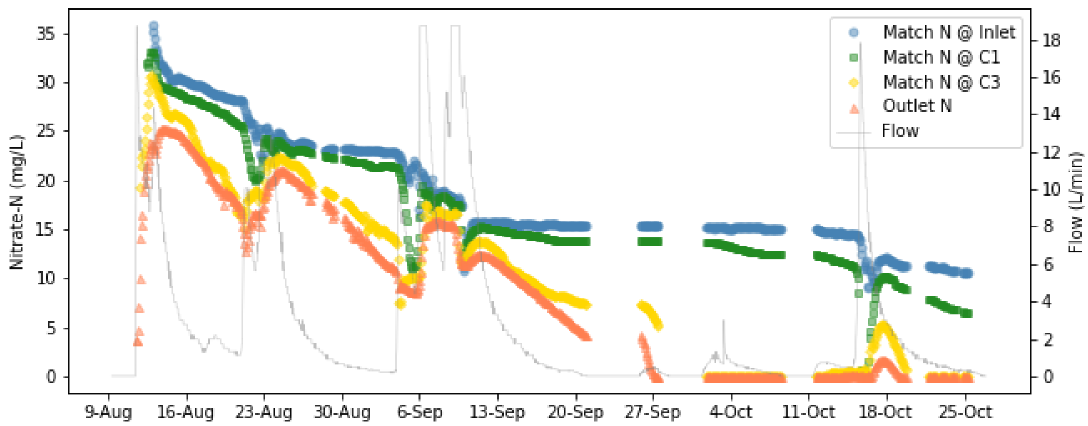

__Figure 3__ Nitrate concentrations at the inlet and outlet plus two centre line wells at the Tatuanui bioreactor measured in 2019 and adjusted to match the time of a parcel of water when it entered and exited each section of the bioreactor.

Variability in nitrate removal performance along the length of the bioreactor

2018 season

In the 2018 season, removal efficiency (RE, %) was found to be highest in the Q2+Q3 section with an average of 65.1 (±14.0), compared to 24.4 (±11.3) and 30.9 (±18.5) in Q1 and Q4, respectively (Fig. 4a). The average RE between inlet and outlet was 80.3 (±10.8), which is higher than the section REs as this overall RE comprises the whole bioreactor. This overall RE falls within the range of reported bioreactor efficiencies (12 to 99%) (Christianson *et al.* 2012; Hassanpour *et al.* 2017; Jaynes *et al.* 2008). The significantly higher RE ($p < 0.01$) in the middle section could be attributed to the larger bioreactor volume, which is approx. twice the other sections. When normalised to the respective effective pore volumes of sections, RE was found to increase from Q1 to Q4, indicating increasing efficiency along the length of the bioreactor. This could be partly explained by the decreasing nitrate concentrations, and corresponding loads, along the length of the bioreactor.

The spatial variability in removal rates (RR) among the sections was similar to RE (Fig. 4b). Significantly higher RR ($p<0.01$) was observed in the Q2+Q3 section with an average RR of 1.00 (±0.13) g N m^{-3} day^{-1}, compared to the similar average RRs of 0.67 (±0.13) and 0.67 (±0.37) g N m^{-3} day^{-1} in the Q1 and Q4 sections, respectively. However, since RR is based on a per unit volume of the bioreactor, the larger volume of the middle section does not explain this higher RR. The significantly lower RR in Q1 compared to Q2+Q3 is attributed to the partially oxic conditions in this section (Rivas *et al.* 2020a), indicating conditions less conducive for denitrification to occur. On the other end, the similarly lower RR in Q4 could be due to the nitrate-limiting conditions in this section. The average nitrate concentrations in parcels entering Q4 was only approx. 2.5 mg N L^{-1}. The overall average RR between inlet and outlet was 0.83 (±0.12) g N m^{-3} day^{-1} and falls in the lower range of reported RR (0.01 to 22 g N m^{-3} day^{-1}) in the literature (Addy *et al.* 2016; Griessmeier *et al.* 2019; Manca *et al.* 2021; Schipper *et al.* 2010b).

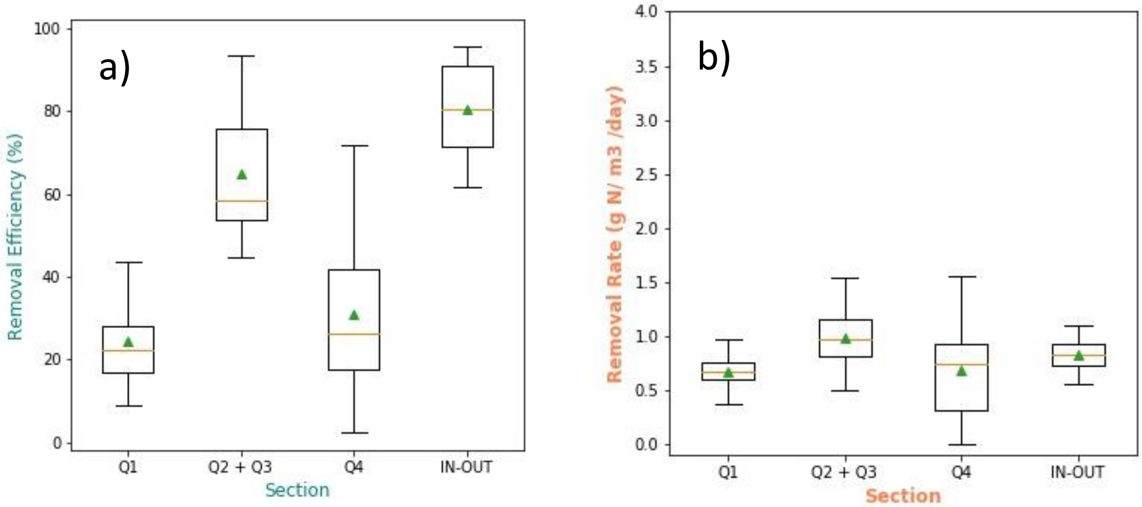

__Figure 4__ Nitrate removal efficiency (a) and removal rate (b) at the different sections of the bioreactor during the latter part of 2018 season.

2019 season

With respect to RE, a similar trend was observed in the 2019 season with higher average RE in the middle section (Q1+Q3) (Fig. 5a). But again, if RE is normalised to the bioreactor effective pore volume per section, RE was found to increase along the length of the bioreactor. The overall RE between inlet and outlet was 38.5 (±22.7) %.

In terms of RR, significantly higher ($p<0.01$) average RR of 1.26 (±1.30) g N m^{-3} day^{-1} was observed in Q4, compared to sections Q1 and Q2+Q3. This higher RR at the end section of the bioreactor is attributed to higher DOC (data not shown) and non-limiting nitrate concentrations. The average RR between inlet and outlet was 0.92 (±0.49) g N m^{-3} day^{-1}.

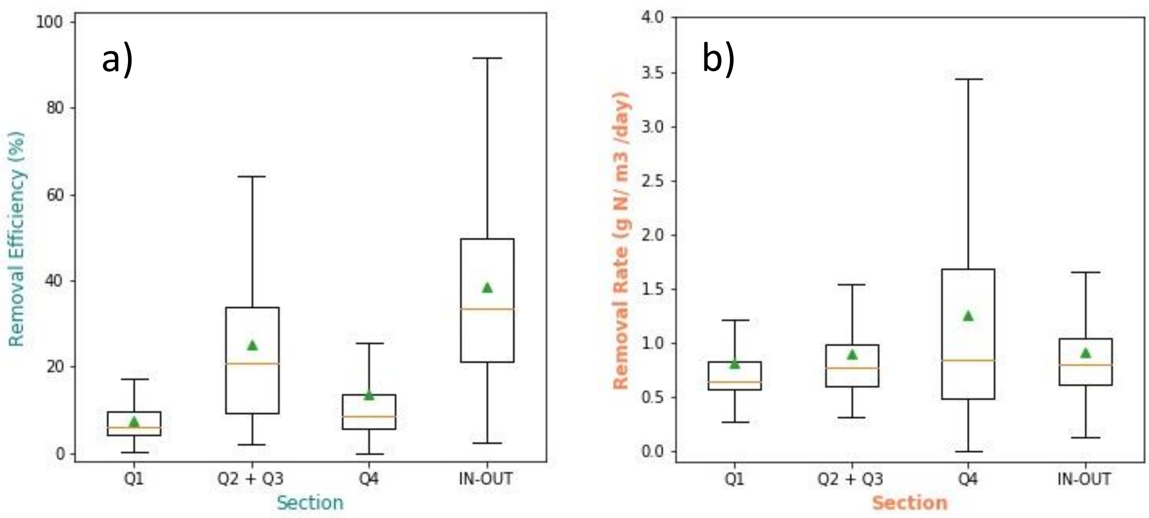

***Figure 5** Nitrate removal efficiency (a) and removal rate (b) at the different sections of the bioreactor during the 2019 season.*

Nitrate removal performance in two seasons

Comparing RE between the monitored periods in the two seasons, higher RE was observed in 2018. This is attributed to lower average nitrate concentrations entering the bioreactor of approx. 8 mg L^{-1}, compared to 19 mg L^{-1} in 2019. These lower concentrations and corresponding lower loads meant that the fixed removal capacity of the bioreactor is not exceeded as often in 2018, as it is in 2019; therefore, greater percentage removal of nitrate occurred in the partial 2018 season. The lower average RR in 2018 compared to the 2019 season could be attributed to the lower nitrate load and, consequently nitrate limiting conditions. This nitrate limiting condition was not prevalent in the 2019 season. In particular, the average nitrate concentrations entering Q4 in 2019 was approx. 15 mg L^{-1}, approx. six times the average concentrations entering Q4 in 2018. This result demonstrates that even with a lower average RR, the RE was substantially higher in 2018, 80.3 cf. 38.5 in 2019, and therefore shows why RE is not a good measure of the functioning of a bioreactor between seasons.

In general, the average RRs between inlet and outlet determined in both seasons fell in the lower part of the range of RR reported in the literature. Several factors could affect RR including, nitrate load, substrate (woodchips), denitrifier abundance and composition, and temperature. While identifying these factors is outside the scope of the paper, Warneke *et al.* (2011) found lower RR in bioreactors using soft wood, such as pine used in this study compared to other sources of carbon such as maize cobs, saw dust, eucalyptus woodchips, etc. Given the positive relationship observed between RR and total nitrite reductase genes per unit of dry substrate (Warneke *et al.* 2011), they attributed the low RR to the lesser amount of nitrite reductase genes found in bioreactor barrels with pine wood. Nitrite reductases are enzymes responsible for nitrite reduction, an intermediate reaction in the denitrification process.

Comparison of estimates of nitrate removal performance using high-frequency and low-frequency sampling

The cumulative RE in the 2019 season computed using high-frequency data between inlet and outlet was 26.7%. On the other hand, the cumulative RE using low-frequency data, based on samples collected automatically from the inlet and outlet every 10 m^3 of flow through the bioreactor, was 17.6% (data not shown). This meant that the cumulative RE using high-frequency data was over 50% higher than the estimate using low-frequency data. This difference could be attributed to the greater number of data points (482) from high-frequency monitoring compared to less data points (43) with low-frequency monitoring, indicating greater accuracy.

We also compared estimates of RR using high-frequency (2-hourly interval) data that accounts for the lag time using the method introduced in this study against using low-frequency (6-, 12-, 24-hourly intervals) data without accounting for the lag time. In the latter, we paired concurrent samplings at the inlet and outlet to determine the amount of nitrate removed. Our results show that the average RR using the high-frequency data and accounting for the lag time was significantly higher ($p<0.01$), with an average RR of 0.92 (±0.49) g N m^{-3} day^{-1} (Fig. 6a). The average RRs using the 6-, 12-, and 24-hourly interval were 0.62 (±0.83), 0.60 (±0.83), and 0.63 (±0.84) g N m^{-3} day^{-1}, respectively. No significant difference was found between the RRs computed using concurrent and low-frequency data.

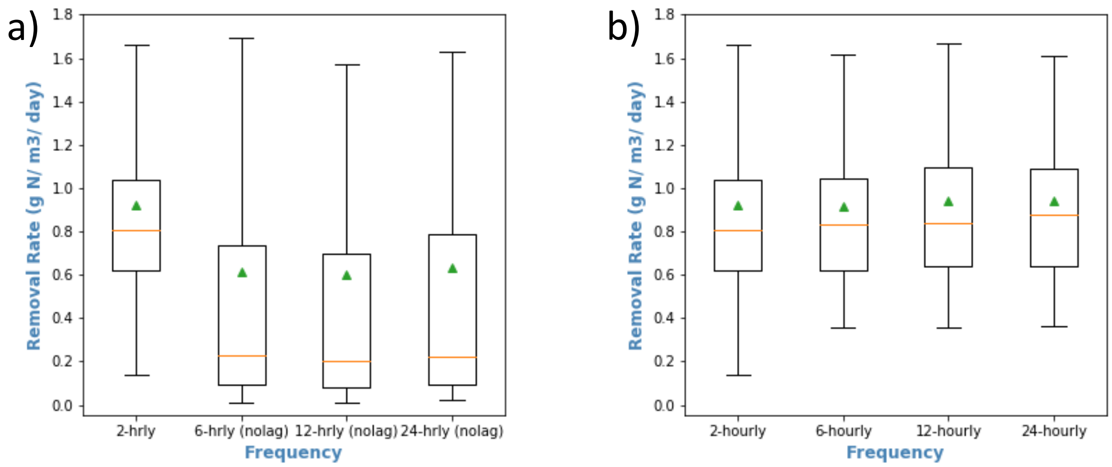

***Figure 6** Comparison of RR computed at different frequencies during the* 2019 *season. a) 2-hourly interval accounts for the lag time, whereas other frequencies did not account for the lag time (nolag); b) all accounted for the lag time. Green triangles and the orange line in the box are the mean and median, respectively.*

On the other hand, if lag time is accounted for even with low-frequency data, we observed no differences in average RRs between inlet and outlet. The average RRs using the 2-, 6-, 12-, and 24-hourly interval data were 0.92 (±0.49), 0.92 (±0.47), 0.94 (±0.43), and 0.94 (±0.42) g N m^{-3} day^{-1}, respectively. However, it should be noted that we could not account the lag time accurately without the high-frequency data of two-hourly intervals. These results underline the importance of high-frequency data to obtain accurate estimates of the nitrate removal performance of woodchip bioreactors.

Conclusions

This study demonstrated the benefits of using high-frequency monitoring data to gain more understanding of the hydraulic and denitrification processes occurring within a bioreactor. The presence of a dead volume in the last quarter section of the bioreactor during low flows was observed and quantified. Moreover, the variability in nitrate removal performance along the length of the bioreactor underlined the effects of dynamic nitrate loading and abundance or lack of electron donors. Comparison of estimates of removal performance showed significantly higher removal efficiency and rates using high-frequency data than using low-frequency data. These results show high-frequency monitoring helps in obtaining more accurate quantification of bioreactor performance and better understanding of processes occurring in woodchip bioreactors, enabling better and more efficient design of such mitigation techniques.

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