

DETERMINING THE SPATIAL VARIABILITY OF NITRATE REMOVAL IN A WOODCHIP BIOREACTOR THROUGH HIGH FREQUENCY MONITORING AT MULTIPLE LOCATIONS

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Abstract

Woodchip bioreactors have been shown to be effective in removing nitrate from artificial drainage. However, performance assessments were usually based only on nitrate concentrations measured at the inlet and outlet. Optical nitrate sensors provide an opportunity for cost-effective monitoring of nitrate at multiple locations and at high frequency. Information on the changes in nitrate along the length of the bioreactor provides a deeper understanding of how bioreactors work and can reveal opportunities for improving their performance. A pilot-scale woodchip bioreactor was constructed on a dairy farm in Waikato and monitored in 2018 and 2019. Dissolved oxygen (DO) and nitrate concentrations were monitored with optical sensors at the inlet and outlet and at 19 locations within the bioreactor. DO was measured manually, whereas nitrate was measured at high frequency (every 1 to 2 hours) with a multiplexer sampling system. In this paper, we present the results for four quarter sections of the bioreactor (0-25, 25-50, 50-75 and 75-100% of the bioreactor length). In the 2018 and 2019 seasons, inlet drainage water was oxic (DO = 2.6-8.0 mg/L), but DO concentrations decreased to reducing conditions (< 2 mg/L) within the first quarter of the bioreactor. This indicates that the conditions in at least three quarters of the bioreactor were conducive for denitrification to occur. Measured nitrate removal varied along the length of the bioreactor. In 2018, the lowest median nitrate removal efficiency (RE) was observed in the first quarter and could be attributed to the partially oxic condition in this section of the bioreactor. The highest median removal rate (RR) and removal efficiency (RE) were observed in the second quarter, presumably due to relatively high (i.e. non-limiting) inflowing nitrate concentrations encountering reducing conditions in this section. Low median RRs were observed in the third and fourth quarter, which could be due to nitrate-limited conditions. The 2018 results revealed that the second half of the bioreactor had some spare removal capacity due to the low nitrate-N concentrations (<10 mg/L) in the inflow water when the intensive sampling was undertaken. This information is useful for determining a suitable bioreactor size for other sites with similar nitrate concentrations. In 2019, with higher nitrate inlet concentrations, the REs and RRs were comparable throughout the length of the bioreactor. Large variations in RE in the first quarter could be attributed to intermittent flow through the bioreactor. These insights into the internal functioning of the bioreactor underline the value of multi-site and high-frequency monitoring.

Introduction

Woodchip bioreactors have been shown to be effective in removing nitrate from artificial drainage. Nitrate removal of between 12 and 76% of the nitrate load has been reported (Christianson *et al.* 2012; Hassanpour *et al.* 2017; Jaynes *et al.* 2008). However, most assessments of bioreactor performance were based only on nitrate concentrations measured at the same time in the inlet and outlet, essentially treating bioreactors as a “black box” and not considering possible variation in nitrate loading to the bioreactors occurring with time (Christianson *et al.* 2012; Hassanpour *et al.* 2017; Husk *et al.* 2017). Therefore, there is a lack of information on what is happening within a bioreactor. In particular, there is a need for more data on how nitrate removal varies within the bioreactor and the factors affecting the variability. Optical nitrate sensors provide an opportunity for cost-effective monitoring of nitrate at multiple locations and at high frequency (Birgand *et al.* 2016; Etheridge *et al.* 2014; Liu *et al.* 2020; Maxwell *et al.* 2018). Information on the changes in nitrate along the length of a bioreactor provides a deeper understanding of how bioreactors work and can reveal opportunities for improving their performance. Thus, the main objectives of this research were to; measure the nitrate concentrations within a woodchip bioreactor at high frequency and at multiple locations; assess the variability in the nitrate removal within a bioreactor; and identify opportunities for enhancing nitrate removal.

Materials and Methods

We monitored the nitrate concentrations in a woodchip bioreactor constructed in 2017 on a dairy farm near Tātuanui in the Hauraki Plains, Waikato, New Zealand (Figure 1). The lined bioreactor, which is trapezoidal in shape, has an effective volume of 56 m³ and intercepts drainage water from an artificial subsurface drain with a drainage area of approximately 0.65 ha. More information on the bioreactor and its performance have been published previously (Rivas *et al.* 2019; Rivas *et al.* 2020).



Figure 1 Schematic of the Tātuanui woodchip bioreactor showing the main components of the bioreactor and the monitoring wells from which water was drawn for high-frequency measurements of nitrate. Flow direction is from right to left.

Nitrate concentrations were monitored using a multiplexer sampling system by pumping water from the inlet, outlet, and 19 wells installed in the bioreactor to the optical nitrate sensor (Figure 2). In 2018, high-frequency monitoring was conducted in the later part of the drainage season,

for a one month period between 8 August and 8 September 2018. Nitrate concentrations were measured approximately hourly at each location with two scan spectrophotometers, one spectrophotometer for each half of the bioreactor. In 2019, high-frequency monitoring was conducted during the entire drainage season. With only one spectrophotometer used (TriOs Opus), nitrate concentrations were measured on a two-hourly cycle. Nitrate concentrations measured by the spectrophotometers in both years were post-calibrated using lab-analysed samples collected after absorbance readings were made. Samples were analysed in the laboratory for nitrate using the cadmium reduction flow injection method following APHA 4500-NO₃⁻ I. High R² values of >0.87 and >0.99 were observed between laboratory and sensor nitrate concentrations in 2018 and 2019, respectively.



Figure 2 Photo of the completed installation of the woodchip bioreactor showing the main components: (1) inlet control structure with auto sampler and stilling well, (2) outlet control structure with auto sampler and stilling well, (3) multiplex sampling system and optical sensor, rain gauge, solar panel, and control panels for the instruments, and (4) monitoring wells. Flow direction is from left to right.

As anaerobic conditions are a key requirement for microbially-mediated denitrification to occur, we also monitored the spatial variability in dissolved oxygen concentrations within the bioreactor. Dissolved oxygen concentrations were measured with a YSI ProODO optical sensor by lowering the sensor into the control structures or sampling wells as required.

While nitrate concentrations were monitored at the two control structures and 19 monitoring wells inside the bioreactor, this paper presents only the results from the control structures and the three fully-screened wells located along the centre line. The changes in nitrate concentrations and thus removal are analysed in quarter sections corresponding to the locations of the centre line wells as shown in Figure 3.

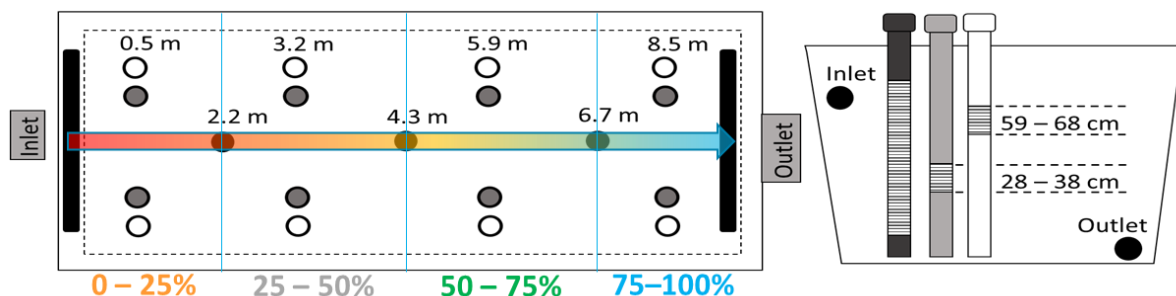


Figure 3 Plan and section diagram of the bioreactor showing the locations and depth of screen, respectively, of the monitoring wells. The arrow across the bioreactor shows the flow direction. Modified from (Maxwell 2019).

Nitrate removal rate, which is defined as the amount of nitrate removed per unit volume of the bioreactor per unit time, has commonly been calculated by pairing the nitrate concentrations measured at approximately the same time at both ends of the bioreactor to determine the amount of N removed (Bock *et al.* 2018; Cameron and Schipper 2010; Christianson *et al.* 2013). However, it is acknowledged that there is some time lag between the entry and exit of a parcel of water. This time lag can create significant errors in the calculations, particularly when nitrate concentrations or flows are variable. To address this, we estimated the time it took for a parcel of water from entering to exiting the bioreactor (or a section of the bioreactor) by using flow rate and bioreactor pore volume (assuming piston flow mechanisms apply). As such, we were able to hydraulically track and relate the nitrate concentration at the exit end of the bioreactor (or a section) to the nitrate concentration measured in this parcel when it entered the bioreactor (or section).

To assess the variability in nitrate removal through the bioreactor, we calculated removal efficiency and removal rate. Nitrate removal efficiency is the mass of nitrate removed expressed as a percentage of the mass that entered the bioreactor (or a section). It is computed by the difference between the inflow and outflow nitrate concentrations divided by the inlet concentration and assuming the flow is the same at the two sites. Nitrate removal rates determine the mass of nitrate (g N) removed per unit of bioreactor volume (m^{-3}) per time unit (day^{-1}). This was determined from the difference in nitrate concentrations for the section investigated, multiplied by the average flow rate for the parcel, to obtain the mass of nitrate and divided by the appropriate bioreactor volume and the time difference between the entry and exit times. In this study, we compared the range of nitrate removal rates in the four sections along the length of the bioreactor to determine the spatial variability of removal rates within the bioreactor. We hypothesised that information on the spatial variability within the bioreactor would improve processes understanding as well as revealing opportunities for enhancing nitrate removal through better design principles.

Results and Discussion

Variability in dissolved oxygen concentrations

In 2018, DO concentrations measured at the inlet revealed aerobic drainage water (Figure 4a). Concentrations had a decreasing trend over the season from approx. 6.6 mg/L in late May 2018 to 2.6 mg/L in mid-September 2018. After passing through the bioreactor, DO concentrations were <0.5 mg/L at the outlet throughout the season, indicating reduced conditions were consistently being achieved within the bioreactor. Results from measurements from monitoring wells along the length of the bioreactor indicate that reduced conditions were achieved within the first 25% of the length of the bioreactor, with concentrations decreased to approx. 1 mg/L within the first 10% of the bioreactor length (Figure 4b). These results show that the majority of the bioreactor had oxygen conditions conducive for denitrification to occur.

Similar results were obtained in 2019 wherein aerobic drainage water was observed at the inlet but reduced water at the outlet (Figure 5a). DO concentrations varied between 4.5 and 8.0 mg/L at the inlet, whereas DO concentrations at the outlet were less than 1 mg/L, except during the early part of the season with DO concentration was just below 2 mg/L, but still considered reduced. Similar to 2018, DO concentrations also decreased to reducing conditions within the first 25% of the bioreactor (Figure 5b).

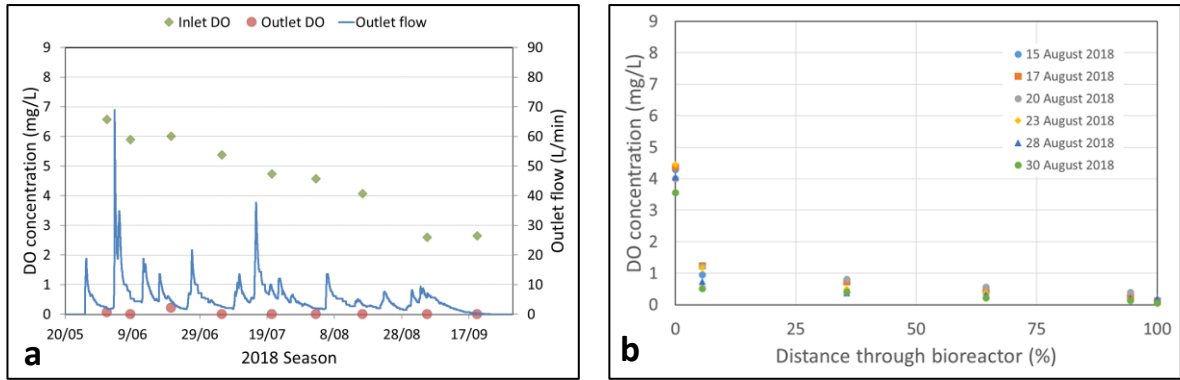


Figure 4 Dissolved oxygen concentrations at the Tatuaniu bioreactor in 2018. The left graph (a) shows the DO trend at the inlet and outlet throughout the season, the right graph (b) shows the DO trend along the length of the bioreactor at several measurement dates conducted in the later part of the season (8 Aug – 7 Sep).

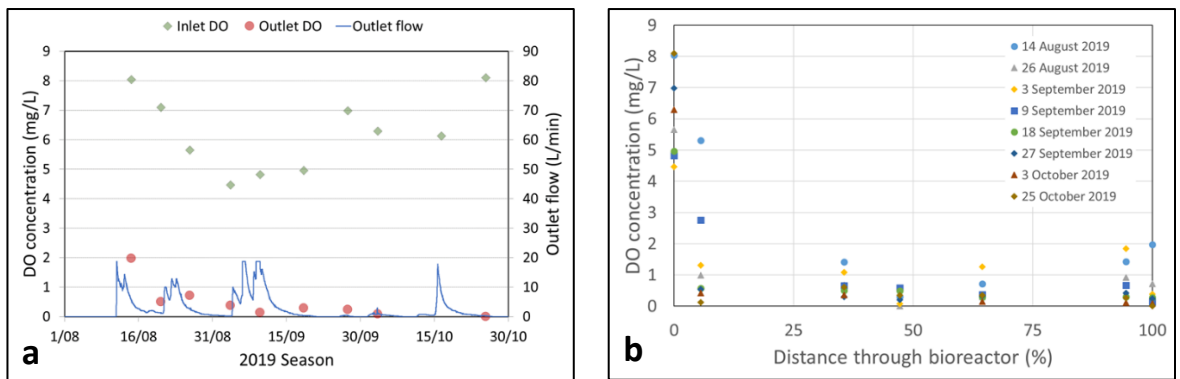


Figure 5 Dissolved oxygen concentrations at the Tatuaniu bioreactor in 2019. The left graph (a) shows the DO trend at the inlet and outlet throughout the season, the right graph (b) shows the DO trend along the length of the bioreactor at several measurement dates.

Nitrate concentrations along the length of the bioreactor

As expected, nitrate-N concentrations at the outlet were consistently lower than concentrations at the inlet, indicating nitrate removal in the bioreactor during the 2018 and 2019 seasons (Figure 6). Maximum nitrate-N concentrations at the inlet were approx. 24 mg/L in 2018 and up to 32 mg/L in 2019. A decreasing trend in inlet nitrate-N concentrations is apparent in both years, indicating the gradual depletion of the nitrate pool stored in the soil profile during the drainage season. However, short-duration nitrate peaks were observed throughout the season, reflecting the flushing out of nitrate from the soil zone during high-flow events.

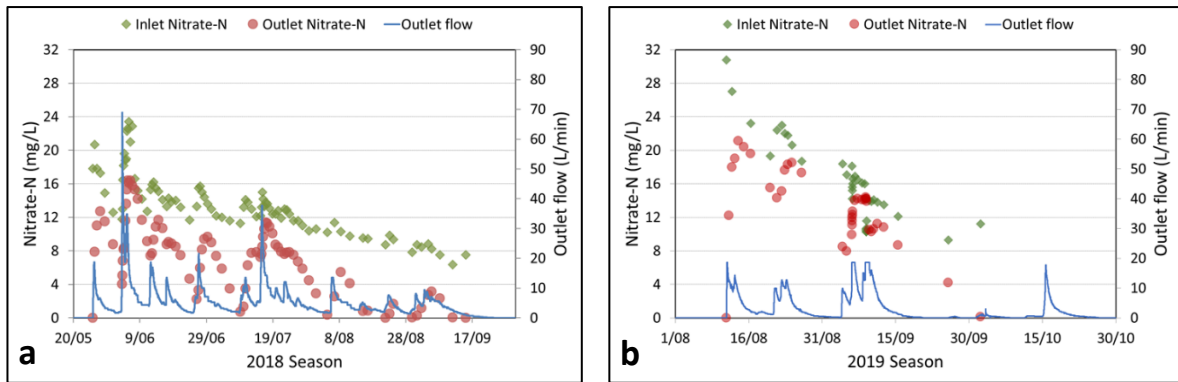


Figure 6 Nitrate-N concentrations at the inlet and outlet at the Tatuani bioreactor in (a) 2018 and (b) 2019.

Hourly measurements of nitrate at the inlet, outlet and the three centre line wells during 8 Aug – 8 Sep 2018 showed the change in concentrations over the length of the bioreactor (Figure 7). A substantial decrease in nitrate-N concentrations from the inlet through the centre line wells to the outlet was evident. The peak concentrations in nitrate-N occurring at different times for the different time series shown reflects the travel time required from one sampling location to the next. Taking this travel time into account allows the nitrate-N concentration peaks to be matched (Figure 8). Two-hourly measurements in 2019 show the same time-lag characteristics (Figures 9 and 10).

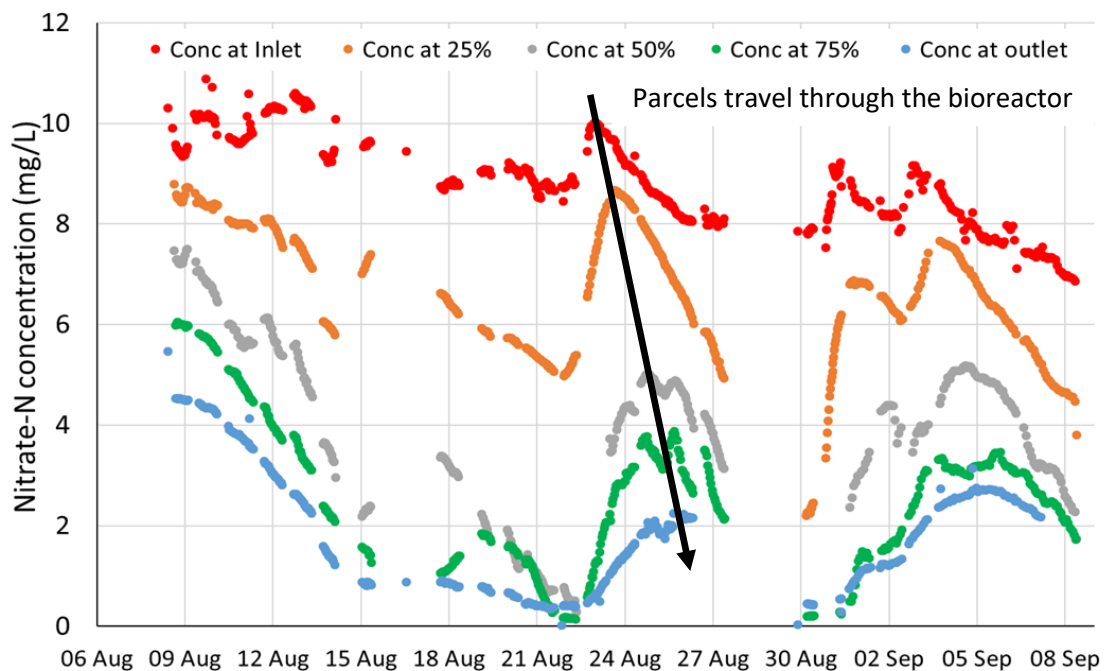


Figure 7 Nitrate-N concentrations at the inlet and outlet plus three centre line wells at the Tatuani bioreactor measured in real-time at high frequency in 2018.

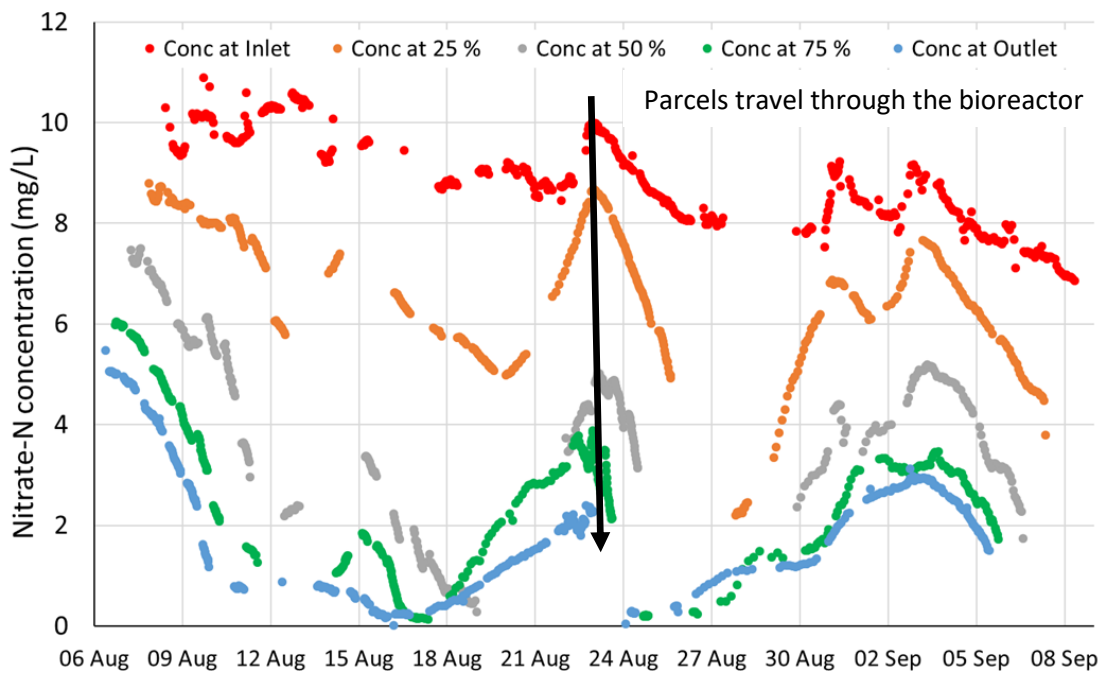


Figure 8 Nitrate-N concentrations at the inlet and outlet plus three centre line wells at the Tatanui bioreactor measured in 2018 and adjusted to match the time of a parcel of water when it entered and exited each section of the bioreactor.

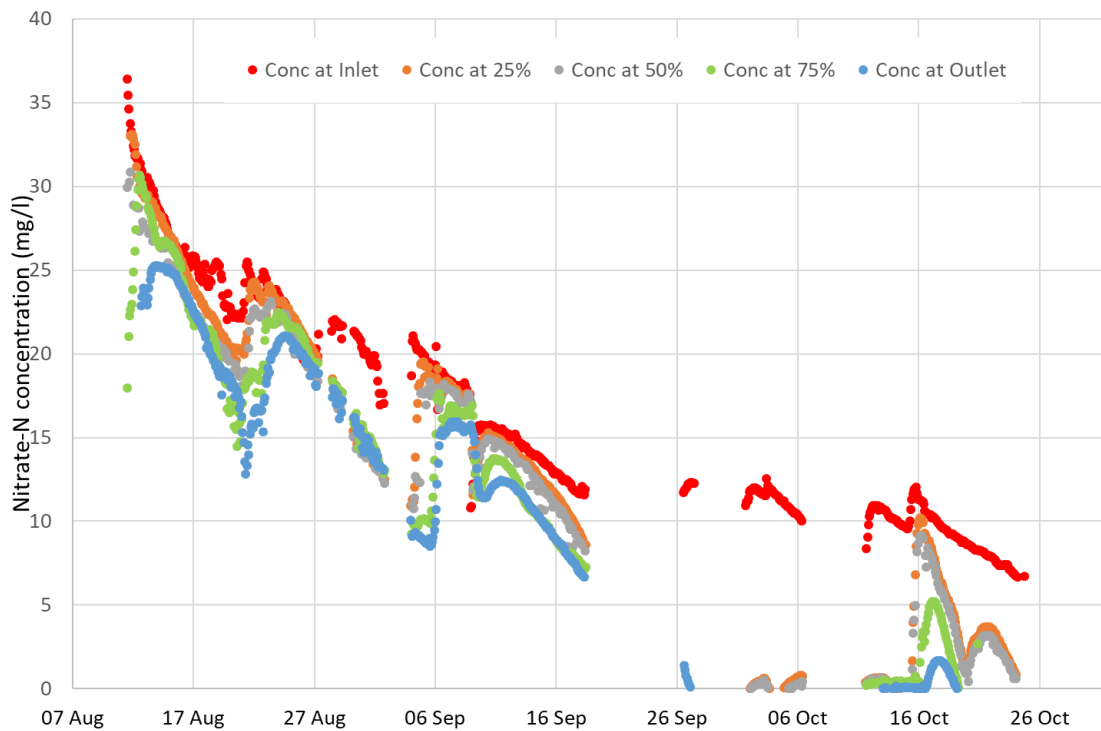


Figure 9 Nitrate-N concentrations at the inlet and outlet plus three centre line wells at the Tatanui bioreactor measured in real-time at high frequency in 2019.

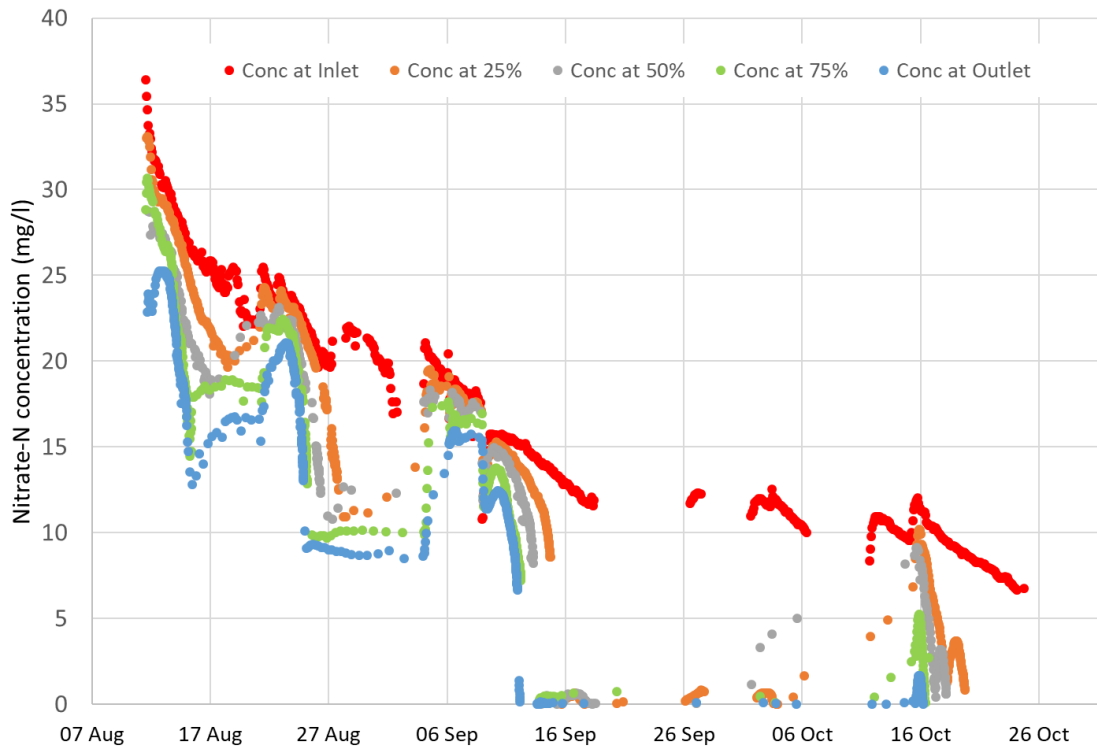


Figure 10 Nitrate concentrations at the inlet and outlet plus three centre line wells at the Tatuani bioreactor measured in 2019 and adjusted to match the time of a parcel of water when it entered and exited each section of the bioreactor.

Variability in nitrate removal along the length of the bioreactor

During 2018, nitrate removal efficiency (RE) and removal rate (RR) varied among the four quarters of the bioreactor (Figure 11). Mean RE and RR were lowest in the first quarter which could be attributed to the partially oxic condition in this quarter. On the other hand, high mean RE was observed in the second and third quarter which could be attributed to the anaerobic conditions and still relatively high nitrate-N concentrations, resulting in no nitrate-N limitation in these quarters. Mean RR was also highest in the second quarter due to the higher nitrate-N concentrations (Figure 11b). Several studies have reported the positive relationship between nitrate concentration and RR (Griessmeier *et al.* 2019; Nordström and Herbert 2019). The lowest median RR were measured in the third and fourth quarters which could be attributed to the nitrate-limiting conditions due to the low nitrate-N concentration in the water entering the bioreactor later in the season (generally < 5 mg/L). This indicates that during the high-frequency monitoring period in 2018, when the nitrate-N concentrations in the drainage water were generally < 10 mg/L, the bioreactor had some spare removal capacity in the second half of the bioreactor. This result could be useful to inform the size of future bioreactors with low nitrate-N concentrations in the drainage water to be treated (< 10 mg/L).

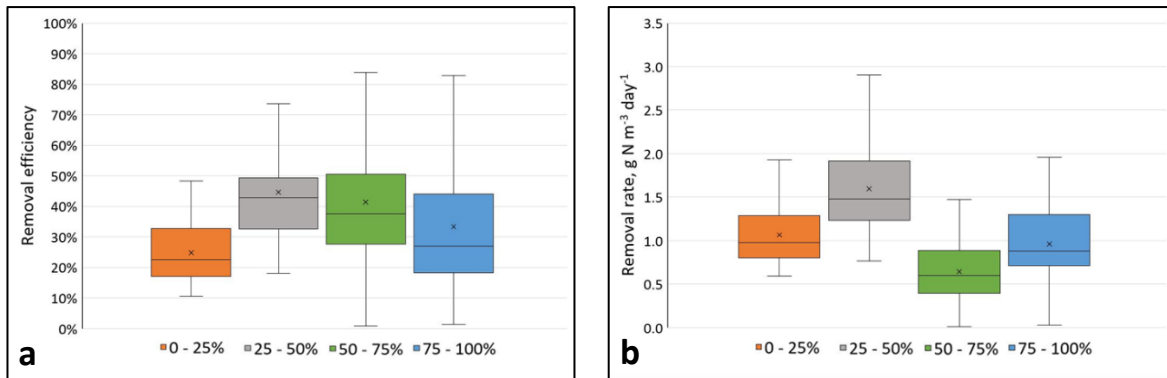


Figure 11 Nitrate removal efficiency and removal rate at the different sections of the bioreactor during 2018.

In 2019, the median REs and RRs across all four sections of the bioreactor were similar (Figure 12). High variation in the RE in the first quarter could be due to the intermittent flow through the bioreactor during the 2019 season (Figure 12a). When flow was interrupted, the nitrate-bearing water entering the bioreactor spent a disproportionate amount of time in the first section, therefore allowing more nitrate to be reduced in this section. This results in higher median RE in the first section compared to conditions when flow is continuous. While higher and more variable RR were observed in the fourth quarter (Figure 12b), this could be due to uncertainty in the estimated effective volume in this section (volume of dead zone above bottom outlet varying with flow rate).

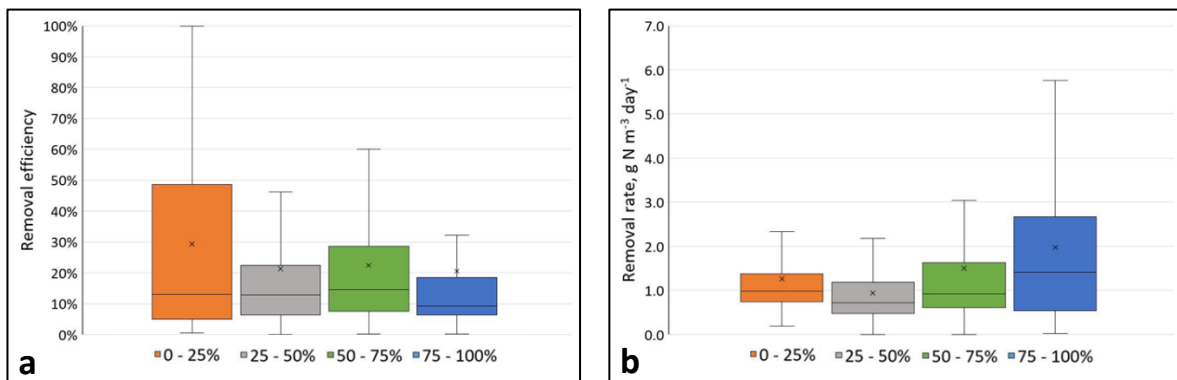


Figure 12 Nitrate removal efficiency and removal rate at the different sections of the bioreactor during 2019.

Conclusions

The monitoring of DO concentrations in the wells along the length of the bioreactor revealed that reduced conditions were achieved within the first quarter of the bioreactor. This indicates that the majority of the bioreactor is conducive for denitrification to occur. The high frequency measurements of nitrate at multiple locations within the bioreactor showed that nitrate removal varied along the length of the bioreactor. Lower nitrate removal in terms of RE and RR was observed in the first quarter of the bioreactor due to the still partly oxic conditions there. Intermittent flow, on the other hand, resulted in highly variable RE values particularly in the first section. Low RR were also observed in the third and last quarters of the bioreactor, indicating nitrate-limiting conditions when nitrate-N concentrations in the drainage water entering the bioreactor were <10 mg/L. This indicated spare removal capacity in this portion

of the bioreactor in 2018. These findings would not have been uncovered by just treating the bioreactor as a “black box” and are useful information for determining suitable bioreactor volumes in similar conditions.

Acknowledgements

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