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NITRATE REMOVAL EFFICIENCY AND SECONDARY EFFECTS OF A WOODCHIP BIOREACTOR FOR THE TREATMENT OF AGRICULTURAL DRAINAGE

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Abstract

Artificial drainage has been instrumental in the viable use of poorly drained soils for agriculture. However, artificial drains can also provide a pathway for fast and unattenuated nutrient transfers to streams and rivers. To remove nitrate from drainage water, bioreactors have recently been widely adopted as an edge-of-field mitigation measure, particularly in the USA. Bioreactors are fundamentally a lined pit filled with woodchips as a source of carbon, which microorganisms use to transform nitrate through the process of denitrification into gaseous forms of nitrogen, mostly N_2. However, there is a lack of information on the performance of these bioreactors under the very flashy agricultural drainage flow conditions typical for New Zealand. Moreover, to avoid pollution-swapping, any possibly occurring negative side effects need to be investigated. A pilot-scale woodchip bioreactor was constructed on a dairy farm on the Hauraki Plains in Waikato and was monitored for one and half drainage seasons (part of 2017, 2018). The nitrate removal efficiency of the bioreactor, calculated from the difference in nitrate load between the bioreactor inflow and the outflow, was 99% and 48% in 2017 and 2018, respectively. The difference in removal efficiencies can be attributed to the much longer residence times and greater organic carbon (OC) availability in the bioreactor in 2017. While the long residence times in 2017 resulted in nearly complete denitrification with reduced concentrations of the greenhouse gas nitrous oxide in the bioreactor outflow, it also led to very strongly reduced conditions with production of methane (another greenhouse gas) and hydrogen sulphide ("rotten egg smell"). The shorter residence times occurring in 2018 following the modification of the bioreactor inlet manifold rectified this strongly reduced condition; however the nitrate removal efficiency concomitantly decreased. Elevated discharges of OC and dissolved reactive phosphorus (DRP) were evident during the first start-up phase of the bioreactor in 2017. In 2018 significant removal (89%) of DRP was measured over the drainage season, with no initial elevated DRP discharge. Ongoing investigations aim to optimise installation costs and treatment efficiency, while minimising any potential side effects. Specifically, options to improve the poor treatment during high flows will be investigated in the 2019 drainage season (e.g. by adding readily available OC source such as methanol).

Introduction

Artificial drainage has been instrumental in the viable use of poorly drained soils for agriculture. However, artificial drains can also provide a pathway for fast and unattenuated nutrient transfers to streams and rivers (Algoazany *et al.* 2007; Arenas Amado *et al.* 2017; King *et al.* 2015). In an effort to mitigate the impacts of artificial drainage on surface water quality, several measures have been proposed including controlled drainage (Ballantine and Tanner 2013; Tan *et al.* 1999) and denitrifying bioreactors (Addy *et al.* 2016; Christianson *et al.* 2012b; Schipper *et al.* 2010). The latter is a recently developed technology for treating artificial drainage water at the edge of the field (Schipper *et al.* 2010). A bioreactor is fundamentally a lined pit filled with woodchips as a source of carbon, which microorganisms use to transform nitrate through the process of denitrification into gaseous forms of nitrogen, mostly N_2. Bioreactors are being adopted increasingly in cropped lands in the USA (Christianson *et al.* 2012a) as one of the US Department of Agriculture's Conservation Practices (Standard No. 605). However, a different bioreactor design and operation is necessary in New Zealand due to the shallower subsurface drainage systems installed in our pastoral lowland areas with accompanying highly variable flows and nitrate concentrations compared to the deeper and more continuous, snow melt-fed drainage flows common in many of the drainage systems installed in cropped areas in the USA.

Bioreactors have been found to be effective in removing nitrate in drainage water but detrimental side effects (i.e., pollution swapping) have also been reported. Removal of nitrate from artificial drainage by bioreactors has been reported to range from 12 to 76% of nitrate load (Christianson *et al.* 2012b; Hassanpour *et al.* 2017; Jaynes *et al.* 2008). On the other hand, negative side effects observed include, high concentrations of dissolved organic matter and/or phosphorus in the outflow, emission of greenhouse gases such as methane and nitrous oxide, and production of poisonous hydrogen sulphide gas (Healy *et al.* 2015; Herbstritt 2014; Schipper *et al.* 2010; Weigelhofer and Hein 2015). Thus, the main objective of this research was to assess the applicability and performance of denitrifying bioreactor technology in reducing nitrate loads from subsurface drains in New Zealand pastoral lands. We aimed to identify the factors affecting the performance as well as potentially occurring side effects of bioreactors to optimise the cost and efficiency of future installations in New Zealand.

Materials and Methods

We constructed a woodchip bioreactor in early 2017 on a dairy farm near Tatuanui in the Hauraki Plains in the Waikato region, New Zealand. The bioreactor intercepts drainage water from an artificial subsurface drain with a drainage area of approximately 0.65 ha. The bioreactor was lined with Ethylene Propylene Diene Monomer (EPDM) and filled with flat untreated pine (*Pinus radiata)* chip (median width = 8.6 mm). A geotextile membrane was placed on top of the woodchips to prevent the soil (approximately 500 mm thick) placed above the chips from mixing and clogging the woodchips. The effective volume of the bioreactor was approximately 56 m^3 with a drainable porosity, measured during end of season drainage, of about 48%. Figure 1 is a schematic of the bioreactor showing its main components, including the inlet and outlet control structures that regulate and measure the flow through the bioreactor. A photo of the completed bioreactor, Figure 2, shows the potential for grazing of the pasture above the bioreactor in on-farm applications, although in this case the bioreactor area was fenced off to protect the research instruments installed.

Rainfall, flow through the bioreactor and the bypass flow during high flow events, electrical conductivity and temperature at the inlet and outlet were all measured. Flow proportional samples were collected automatically from the inflow and outflow every 10 m^3 of flow through the bioreactor for analyses of nutrients and organic carbon. We also collected additional intermittent water samples manually at the inlet and outlet and analysed for dissolved gases and metals.

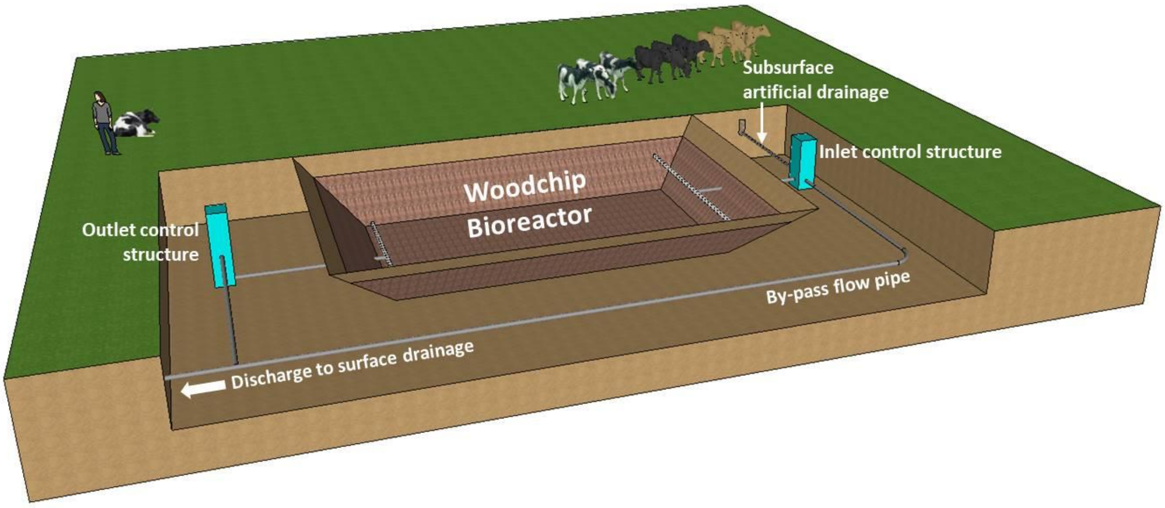

Figure 1 *Schematic of the Tatuanui woodchip bioreactor showing the main components of the bioreactor.*

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) rain gauge, solar panel, and control panels for the instruments.*

Results and Discussion

Nitrate removal efficiency and factors

Figure 3 shows the flow and nitrate concentrations in the bioreactor inflow and outflow for the two monitoring periods in 2017 and 2018. The total flow through the bioreactor was 337 m^3 for the 3.5 months monitoring in 2017, compared to the 952 m^3 for the whole drainage season of four months monitored in 2018 (Table 1). While rainfall totals during the bioreactor operation were similar (444 in 2017 and 415 in 2018) for both monitoring periods, the lower flow volume through the bioreactor in 2017 was due to clogging. The inlet manifold was covered with a filter sock to prevent small wood chips entering it, however, fine silt and microbial growths reduced inlet flows. This clogging could not be remedied, and the header modified, until drainage had ceased at the end of the drainage season in November 2017. The flow volume through the bioreactor in 2018 corresponded to approximately 35% of rainfall falling on the assumed catchment during the drainage period. Nitrate concentrations in the subsurface drainage water, measured at the bioreactor inlet, ranged from 3.0-8.5 mg N L^{-1} in 2017 and from 6.4-23.4 mg N L^{-1} in 2018. The higher nitrate concentrations were not measured in 2017, as the bioreactor was not operational until the end of July 2017, although the 2017 drainage season had started in early April. Despite this late start, a trend of decreasing nitrate concentrations in the subsurface drainage water within the drainage season was still apparent in both years, with R^2 of 0.74 and 0.66 in 2017 and 2018, respectively.

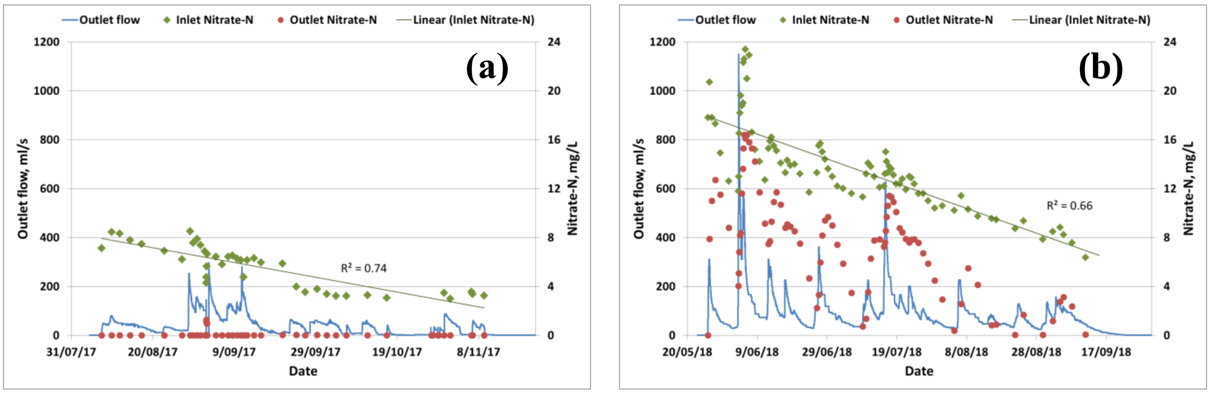

Figure 3 *Flow and nitrate concentrations at the Tatuanui bioreactor in (a) 2017 and (b) 2018*

Table 1 *Flow, nitrate loads, and nitrate removal efficiency at the Tatuanui bioreactor during the two drainage seasons (2017 and 2018).*

Drainage year	**Operation dates**	**Cum. rainfall (mm)**	**Cum. flow (m^3)**	**Cumulative Nitrate load (kg N)**			**Removal Eff. (%)**
				Subsurface drainage delivery	Bioreactor inflow	Bioreactor outflow	
2017	31 Jul – 13 Nov	444	337	2.36	1.95	0.02	99
2018	24 May – 24 Sep	415	952	12.49	12.38	6.47	48

The cumulative loads from the subsurface drain and at the bioreactor inlet and outlet are provided in Table 1. The nitrate removal efficiency of the bioreactor, calculated as the difference between the total inflow and outflow loads divided by inflow load, was 99 and 48% in 2017 and 2018, respectively.

The most obvious factors affecting the removal efficiency of the bioreactor were found to be the residence time of water in the bioreactor and the availability of organic carbon (OC). The higher removal efficiency in 2017 could be partly attributed to the longer residence of water in the bioreactor with an average residence time of 22 days (average flow rate of 3.2 m^3 day^{-1}), compared to the average of just 5 days in 2018 (average flow rate of 7.7 m^3 day^{-1}). The longer average residence time allowed more opportunity for microorganisms to reduce the nitrate in the drainage waters. The effect of residence time on nitrate removal is also apparent within a drainage season. As shown in Figure 4, the difference between inflow and outflow nitrate concentrations is larger when the residence time is longer (examples highlighted in green shading) compared to periods when the residence time is shorter (examples highlighted in yellow shading). The greater removal efficiency in 2017 could also be attributed to more available OC in the bioreactor as indicated by the amount of dissolved organic carbon (DOC) in the outflow. In 2017, approximately 17.9 kg DOC was discharged compared to 9.3 kg DOC in 2018, despite the greater flow through the bioreactor in 2018 (Figure 5). The equivalent average DOC concentrations in the outflow were 53 mg L^{-1} and 10 mg L^{-1} in 2017 and 2018, respectively.

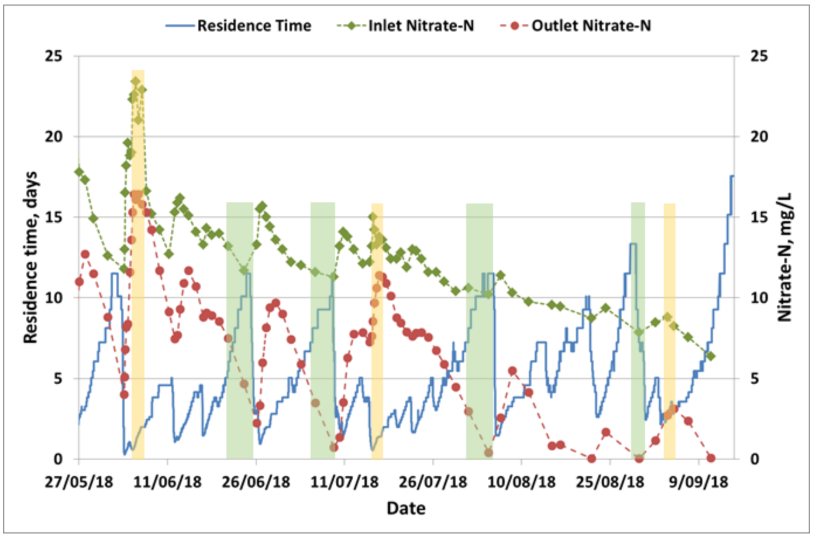

Figure 4 *Residence time of drainage water in the bioreactor and nitrate concentrations at the inlet and outlet. Shaded in green are examples of periods of longer residence time; shaded in yellow are examples of periods of shorter residence time.*

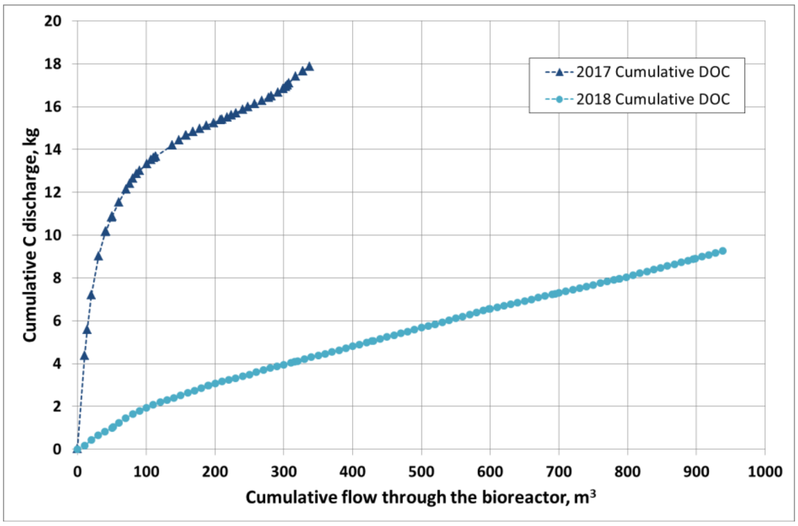

Figure 5 *Plot of cumulative dissolved organic carbon (DOC) discharged from the bioreactor against cumulative flow through the bioreactor in 2017 and 2018.*

Secondary effects

Release of dissolved organic carbon

One of the side effects of the Tatuanui bioreactor was the high release of DOC during the early stage of the operation, i.e. the first 100 m^3 of flow which is roughly equivalent to 3.5 times the pore volume of the bioreactor (Figure 5). Enhanced DOC release was also observed at the start of the second drainage season in 2018, but to a much lesser degree. Thus, it is recommended that the initial discharges of 3-4 pore volumes of the bioreactor, particularly in the first start-up phase, be applied on land rather than discharged into a surface drain.

Nitrous oxide concentrations

Release of nitrous oxide (N_2O), a greenhouse gas, from the bioreactor is possible if the denitrification process in the bioreactor is incomplete, and resulting in N_2O being the terminal product instead of the benign N_2 gas. Figure 6 shows the dissolved N_2O concentrations in the subsurface drainage water (measured at the inlet control box) and bioreactor outlet for the two drainage seasons.

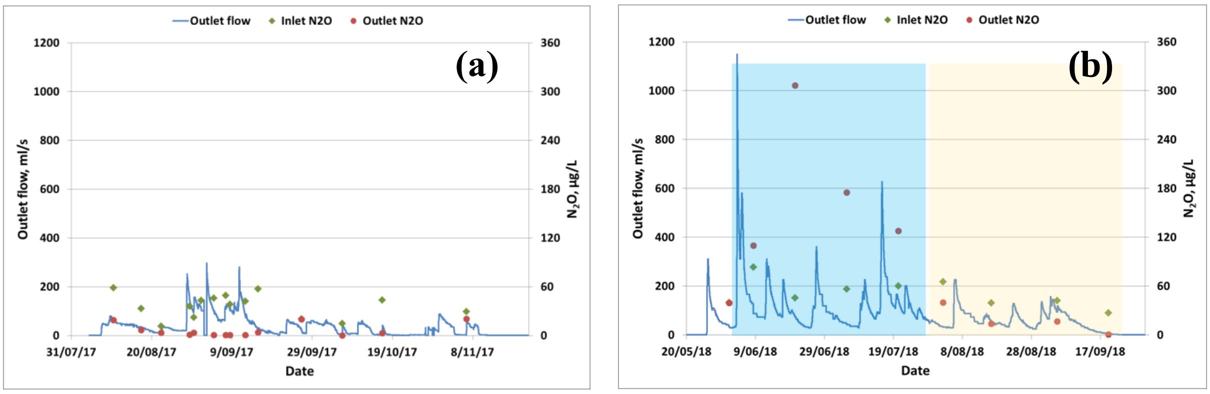

Figure 6 *Flow and nitrous oxide concentrations at the Tatuanui bioreactor in (a) 2017 and (b) 2018. Highlighted in blue shading in (b) is the period with higher flow, inflow nitrate concentrations, and outflow nitrous oxide concentrations; highlighted in yellow shading in (b) is the period with lower flow, inflow nitrate concentrations, and outflow nitrous oxide concentrations.*

In 2017, it is apparent from the N_2O concentrations in the bioreactor outflow being much lower than concentrations in the subsurface drainage water that denitrification proceeded nearly completely to N_2. N_2O concentrations in the drainage water were up to approximately 60 µg N_2O L^{-1}, which is substantially higher than the dissolved N_2O concentration of 0.35 µg N_2O L^{-1} at equilibrium with the atmosphere at 20 °C (Jurado *et al.* 2017). With higher flow rates and subsequent shorter residence times observed in 2018, incomplete denitrification process may be experienced. This incomplete denitrification was apparent in the first half of the drainage season (highlighted in blue shading in Fig. 6) in which dissolved N_2O concentrations in the outflow (40-307 µg N_2O L^{-1}) were greater than in the subsurface drainage water (40-83 µg N_2O L^{-1}). The higher nitrate concentrations in the subsurface drainage during this early part of the drainage season (Figure 3) may also have contributed to the incomplete nitrate reduction process, as more available carbon and/or a longer residence time would have been required for complete reduction of this enhanced nitrate load. However, much lower outflow N_2O concentrations were observed in the latter half of the season, when lower flow rates and lower nitrate concentrations occurred (highlighted in yellow shading in Fig. 6).

Methane (CH_4) and hydrogen sulphide (H_2S) production

The longer residence time of drainage water in the bioreactor in 2017 resulted in highly reduced conditions in the bioreactor, and consequently the production of CH_4 and H_2S. The production of CH_4 was apparent from its substantially increased concentrations in the outflow (640-4500 µg L^{-1}) compared to the inflow (<1-85 µg L^{-1}). H_2S production was evident from the rotten egg smell observed at the site at times when flow rates were very low. While H_2S was not directly measured, it can be assumed to occur from the reduction in sulphate concentrations. Sulphate concentrations were substantially higher in the inflow (80-140 mg L^{-1}) compared to the outflow (9-91 mg L^{-1}) in 2017, indicating sulphate reduction and resulting in H_2S production. In contrast, the shorter hydraulic residence times observed in 2018 resulted in significantly reduced CH_4 production with much lower observed concentrations in the outflow (15-307 µg L^{-1}) compared to 2017. Moreover, insignificant H_2S production was apparent from comparable sulphate concentrations in the inflow (34-150 mg L^{-1}) and in the outflow (69-130 mg L^{-1}).

Phosphorus release and/or removal

Contrasting observations of dissolved reactive phosphorus (DRP) release and removal were observed at the Tatuanui bioreactor. In 2017, it is apparent that DRP concentrations at the outlet (<0.01-7.94 mg L^{-1}) were much greater than the concentrations at the inlet (<0.01-0.09 mg L^{-1}) (Figure 7). The high DRP concentrations discharged at the outlet were more evident in the early part of the bioreactor operation, with comparable concentrations in inflow and outflow occurring after around 100 m^3 of flow through the bioreactor. This release of high concentrations of phosphorus at the early stage of operation of a woodchip bioreactor was also observed in other studies (Fenton *et al.* 2016; Healy *et al.* 2015). In contrast, much lower DRP concentrations were observed at the outlet (<0.01-0.04 mg L^{-1}) compared to the inlet (0.02-1.33 mg L^{-1}) in 2018, indicating removal of DRP in the bioreactor. Approximately 0.095 kg DRP entered the bioreactor and only 0.010 kg DRP exited from the bioreactor, representing approximately 89% removal. This observed DRP removal was unexpected as limited data in the literature seemed to highlight the release of DRP (Fenton *et al.* 2016; Healy *et al.* 2015; Herbstritt 2014; Weigelhofer and Hein 2015) especially at the early stage of bioreactor operations, and several studies proposed modifications of woodchip bioreactors (e.g., adding P adsorbent materials) for phosphorus removal (Bock *et al.* 2016; Christianson *et al.* 2017; Gottschall *et al.* 2016; Zoski *et al.* 2013), apparently assuming that woodchips bioreactors did not have P removal capacity. Continued monitoring of DRP concentrations over multiple seasons would be essential to confirm the longer term DRP removal capacity observed at the Tatuanui woodchip bioreactor during its second year of operation.

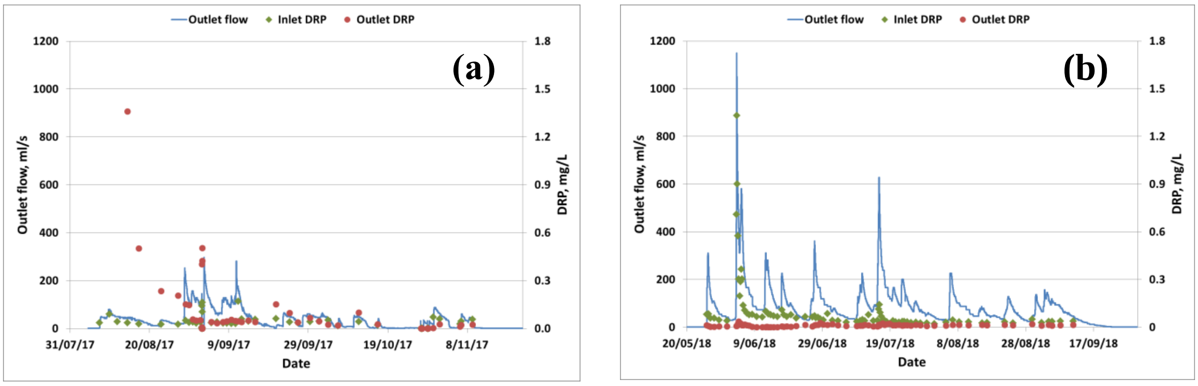

Figure 7 *Flow and dissolved reactive phosphorus (DRP) concentrations at the Tatuanui bioreactor in (a) 2017 and (b) 2018*

Conclusions

The preliminary analysis of a suite of parameters confirmed the efficiency of a woodchip bioreactor to remove nitrate from subsurface drainage waters at a NZ field site with dynamic flow rates and nitrate concentrations. The main factors identified were residence times and carbon availability, and both are positively correlated with nitrate removal efficiency. This was clearly illustrated in the higher removal efficiency of 99% in 2017 compared to 48% in 2018, with longer residence times and greater carbon availability observed in 2017. Longer residence time also favoured nearly complete denitrification to dinitrogen gas, as evidenced by the low nitrous oxide concentrations measured in the outflow in 2017 and in the latter half of the 2018 drainage season. However, some pollution swapping was observed when residence times were very long and promoting strongly reduced conditions, which resulted in the production of hydrogen sulphide and even methane. Thus, it is not a viable strategy to increase overall nitrate removal efficiency solely by increasing the residence time in the bioreactor (by increasing its size or by manipulating the flow through it). However, making more carbon available to the microbial community during periods with high nitrate loads (high flow and/or high nitrate concentrations) may help achieve the maximum nitrate removal that is feasible without incurring substantial negative side effects. This may well be accomplished by adding readily available carbon (e.g., methanol) (Hartz *et al.* 2017) during periods of high flow and/or high nitrate concentrations in the inflow. As an unexpected co-benefit of the denitrifying bioreactor, substantial removal (89%) of dissolved reactive phosphorus was observed in the 2018 drainage season. Especially given that such a result has not previously been reported in the literature, continued monitoring is required to confirm the persistence of this desirable property of a woodchip bioreactor.

Acknowledgements

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