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Carbon dosing enhances nitrate removal effectiveness in denitrifying bioreactors: A field trial in New Zealand

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Abstract

Denitrifying woodchip bioreactors are simple ecotechnologies that could help preserve the water quality by reducing nitrate loads from both point and non-point pollution sources. These systems consist of lined pits filled with a solid carbon source (e.g., woodchips) that convert nitrate to harmless dinitrogen gas by a microbial process known as denitrification. However, due to a lack of sufficient carbon supply from the woodchips, the efficiency of the bioreactor might be overwhelmed by large nitrate input pulses, especially in bioreactors containing aged woodchips. The current research aimed to develop a simple and effective carbon dosing approach that would increase nitrate removal rates while minimizing excess losses of carbon from the system. During the 2020 and 2021 drainage seasons, a bioreactor in Waikato, New Zealand, was dosed with constant rates of methanol (serving as a supplementary carbon source). The performance of the bioreactor was compared between the two seasons as well as with data from 2018 – a season in which no methanol dosing was performed. Under extremely variable flow conditions, methanol dosing considerably increased nitrate removal rates from 0.1-1.60 g N m^{-3} day^{-1} in the 2018 drainage season (undosed) to 10 g N m^{-3} day^{-1} in 2020 and 16 g N m^{-3} day^{-1} in 2021. The results also revealed a considerable drop in methanol concentrations along the length of the bioreactor (removal rates ranging from 24 to 218 g C m^{-3} day^{-1}), indicating a methanol removal efficiency of greater than 99 percent. Overall, methanol dosage increased nitrate removal rates in the bioreactor, and methanol concentrations at the outlet were substantially below thresholds of concern, even when nitrate was limited as a

terminal electron acceptor. Therefore, while improving nitrate removal rates dramatically, constant rate methanol dosing did not result in significant methanol loss from the system.

Introduction

Nitrogen losses to the environment, notably nitrate loss to natural water bodies such as lakes and rivers, are one of the most serious environmental consequences of intensive farming (Mosier, Syers, and Freney 2013; Stark and Richards 2008). Several mitigation measures have been proposed to reduce this nitrate loss from agriculture, especially land with subsurface drainage, including denitrifying bioreactors and constructed wetlands (Stark and Richards 2008). Denitrifying bioreactors have received recent interest as they are simple and cost-effective passive systems that can be installed on the edge of fields to treat high-nitrogen drainage waters (Addy et al. 2016; Christianson et al. 2020; Christianson and Schipper 2016). The efficacy of nitrate removal in bioreactors is influenced by several environmental factors, including carbon supply from woodchips and temperature (Addy et al. 2016; Schipper et al. 2010). Carbon availability, in particular, has been determined to be the key limiting factor in nitrate removal rates in bioreactors containing older woodchips (Addy et al., 2016).

The use of liquid organic carbon sources, such as methanol and acetate, has recently been investigated as an external carbon source for bioreactors in which nitrate removal rates had declined (Roser et al. 2018; Hartz et al. 2017). However, there is a lack of understanding of field-scale bioreactor design and scaling with additional carbon sources under variable operating conditions and inputs. Additionally, the fate of added methanol in bioreactors deployed in agricultural catchments with extremely transient nitrate inputs is not well quantified. Significant methanol losses from the bioreactors would raise the biochemical oxygen demand (BOD) in the receiving waters and might be harmful to aquatic organisms (Kaviraj, Bhunia, and Saha 2004). The goal of this study was to determine if methanol dosage could increase nitrate removal in a field-scale bioreactor and if excess methanol could be removed in the bioreactor under varying concentrations of nitrate inputs.

Methodology

Our methanol dosing trial was conducted across two drainage seasons on a field-scale bioreactor deployed on a dairy farm in Waikato, New Zealand. The bioreactor had been in operation for three drainage seasons. Without dosing, nitrate removal rates in this bioreactor varied from 0.67 to 1.60 g N m^{-3} d^{-1} (Rivas et al., 2020).

Bioreactor design

The bioreactor was located on a dairy farm in Morrinsville, New Zealand. Nitrate-contaminated water from the pasture was transported to the bioreactor by tile drainage via the inlet structure and distributor. The bioreactor was trapezoidal with a volume of 54 m^3 filled with *pinus radiata* woodchips (9 m long x 5 m wide x 1.2 m deep).

Dosing strategy

When the bioreactor was draining (i.e. flow existed at the outlet structure), a peristaltic pump was programmed to provide methanol at a constant rate of 10 mL min^{-1} in 2020 and 5 mL min^{-1} in 2021 to the bioreactor inlet distributor. The 2020 dosing rate was determined based on the nitrate load that went untreated in the bioreactor during the 2019 drainage season in the absence of carbon dosing. In 2021, we reduced the dosing rate by half to reduce the secondary effects of excess carbon in the bioreactor (e.g., sulfate reduction and carbon loss to the receiving water) also lowering the quantity of methanol used.

Nitrate concentrations and removal rates

A TriOS Opus multispectral nitrate sensor (TriOS, Oldenburg, Germany) was used to continuously measure nitrate concentrations in situ using a high-frequency, multipoint sampling technique (Rivas et al., 2020). The volumetric nitrate removal rates were calculated using:

$$N_{rr} = \frac{(N_{i+1} - N_i) \times \phi}{HRT} \quad (1)$$

N_i is the nitrate-N concentration of each parcel of water (mg N L^{-1}) passing along the length of the bioreactor (inlet, well1, well2, well3, outlet), HRT is the hydraulic retention time of the parcel (days) and ϕ is the average drainable porosity of the bioreactor.

Methanol concentrations and removal rates

A gas chromatograph equipped with DB-WAX (30 m × 0.25 mm × 0.5 m, Agilent) column with a flame ionization detector (FID) was used to determine methanol concentrations. Methanol volumetric removal rates (M_{rr}) were determined using methanol concentrations from water grab samples, the daily average of outflow rates on the sampling day, and the saturated volume of the bioreactor where methanol concentrations were stable afterward without significant changes.

$$M_{rr} = \frac{\left(M_{inlet} - M_{limiting}\right) \times Q_{average}}{V_{limited}} \quad (2)$$

Results

Nitrate concentrations

The major decrease in nitrate concentrations occurred in the first compartment (first quarter of the saturated volume of the bioreactor) during both drainage seasons of 2020 and 2021 (with methanol dosing), with a smaller decline in downstream wells (Figure 1). Except for a few days of lag time at the start of the season in 2020, nitrate outlet concentrations were constantly zero until the end of the season, whereas in 2021, outlet nitrate concentrations varied from 4 to 22 mg N L^{-1} throughout the season.

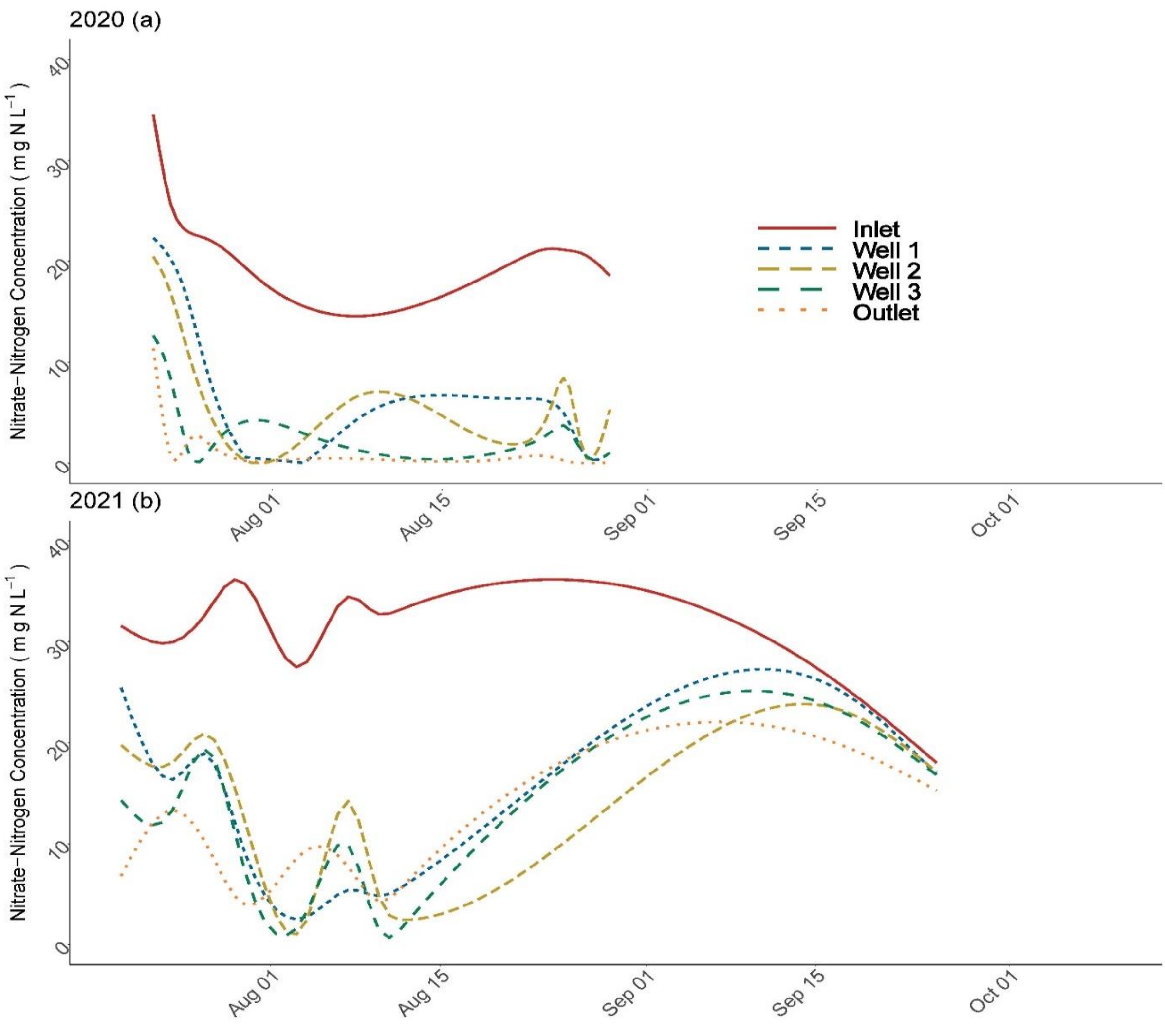

Figure 1: Nitrate concentrations profile along the bioreactor at the inlet, outlet, and sampling wells during the drainage seasons of 2020 (a) and 2021 (b)

Nitrate removal performance

Compared to 2018, when the bioreactor was not dosed with methanol, nitrate removal rates improved dramatically in 2020 and 2021 with methanol dosing (Rivas et al. 2020).

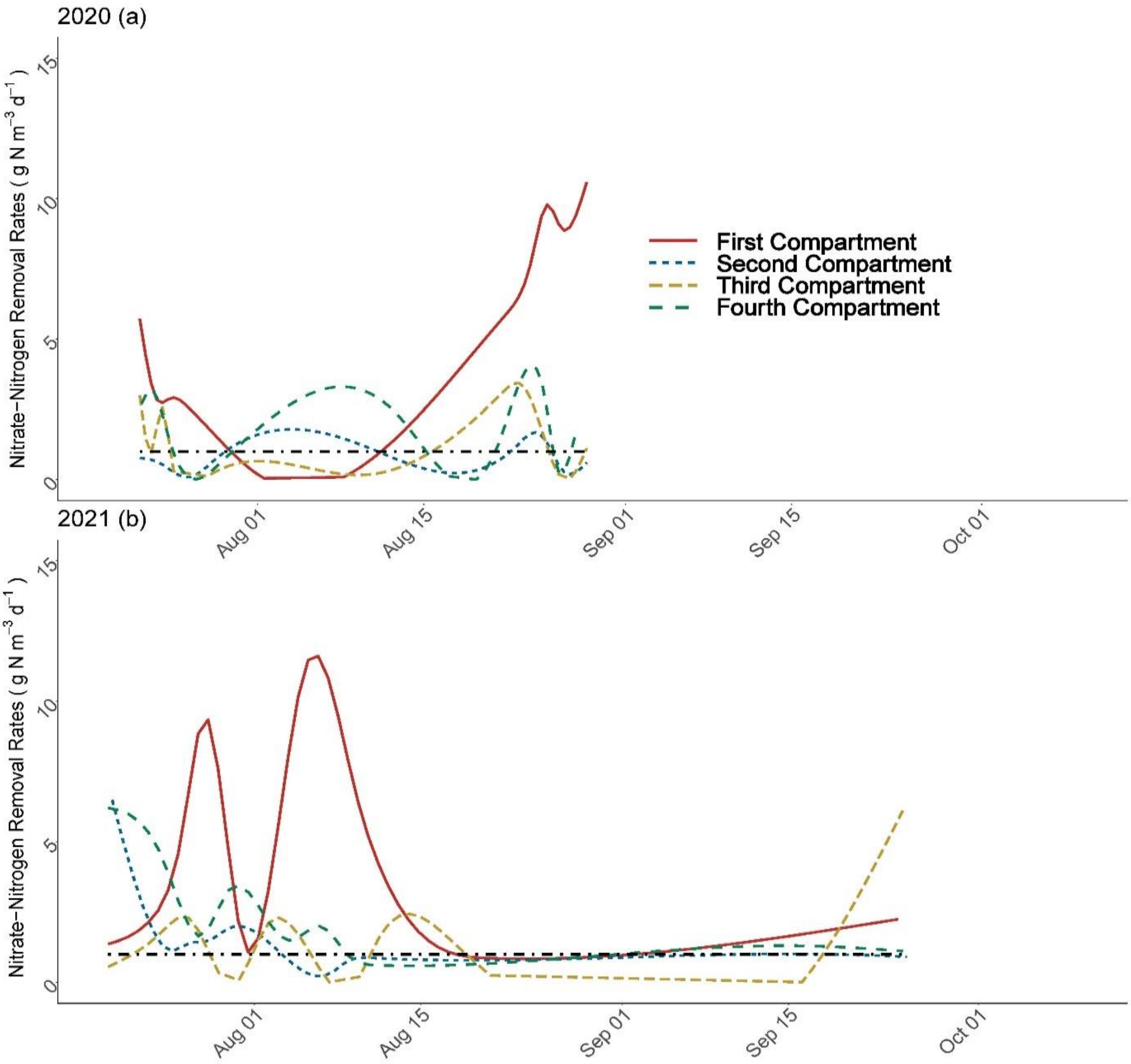

Figure 2: Performance nitrate removal rates in different compartments in (a) 2020 and (b) 2021, the two seasons when the bioreactor was dosed with methanol. The black dash-dotted line shows mean nitrate removal rates without methanol dosing throughout the 2018 drainage season (Rivas et al., 2020).

With methanol dosing, the first compartment had the highest nitrate removal rates in both seasons, whereas the downstream compartments had removal rates comparable to control removal rates without dosing (the black dash-dotted line, figure 2).

Methanol removal

Methanol removal was highest in the bioreactor's first compartment throughout both drainage seasons, with methanol concentrations remaining relatively constant in the downstream compartments (Figure 3). The average methanol removal rates were 109 g CH_3OH-C m^{-3} day^{-1} (95% CI of 216 g CH_3OH-C m^{-3} day^{-1} to 0 g CH_3OH-C m^{-3} day^{-1}) in 2020 removal efficiency of 99% and 106 g CH_3OH-C m^{-3} day^{-1} (95% CI of 218 g CH_3OH-C m^{-3} day^{-1} to 0 g CH_3OH-C m^{-3} day^{-1}) with a removal efficiency of 100% in 2021.

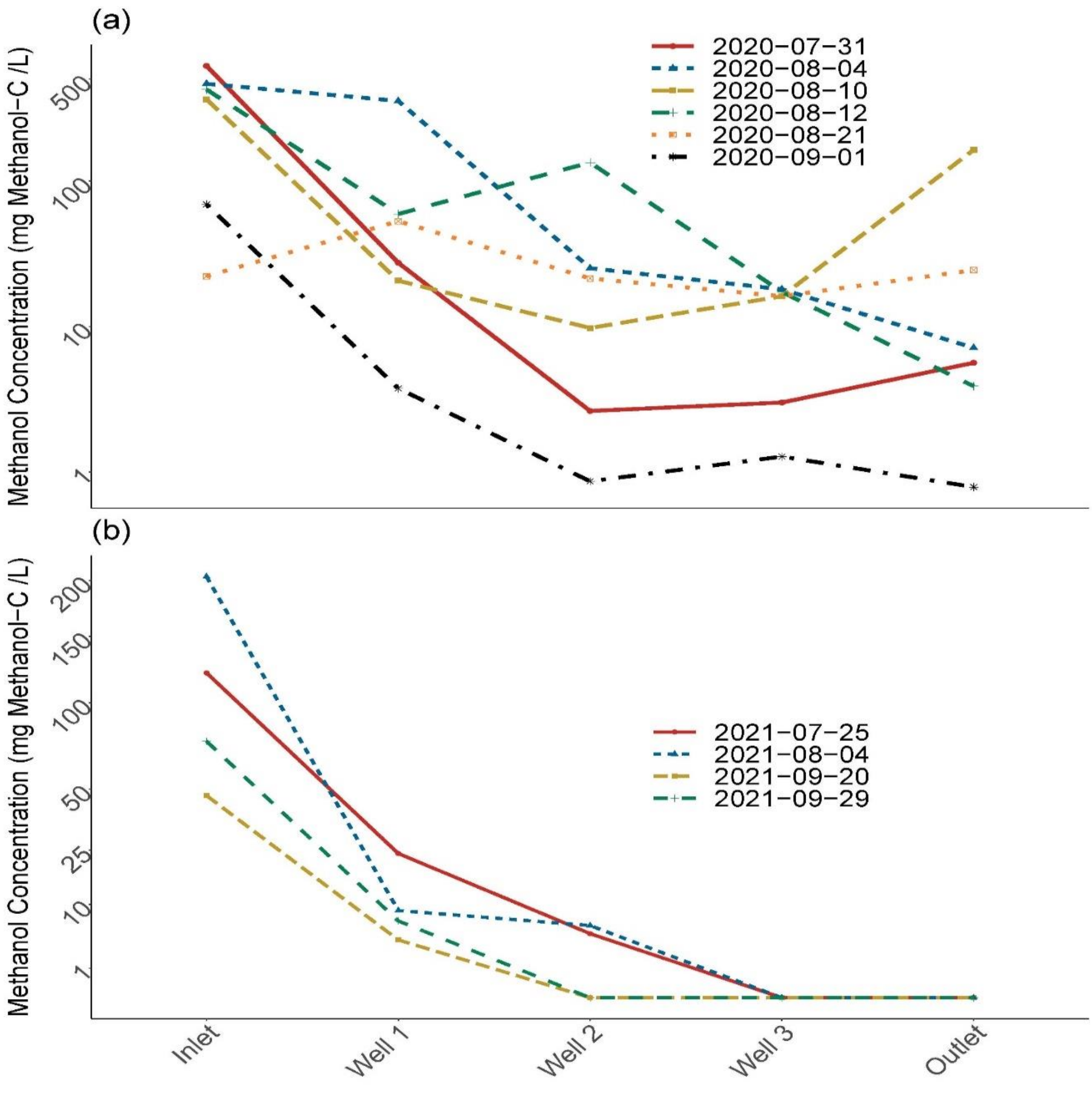

Figure 3 Methanol grab samples concentrations along the bioreactor in two seasons collected on different sampling days

Conclusion

Our research demonstrated that continuous methanol dosing considerably increased nitrate removal rates in a field-scale bioreactor treating tile drainage water. Adding methanol at two constant rates in two consecutive drainage seasons resulted in significantly greater nitrate removal rates in the bioreactor in both drainage seasons compared to the season without dosing. Despite producing comparable nitrate removal rates to the higher dosing rate, the increased nitrate input to the bioreactor with the halved dosage rate resulted in significant nitrate loss from the bioreactor. This carbon dosing approach worked effectively and was safe in terms of methanol loss to receiving surface waters since excess methanol was cleaned up in different nitrate inputs.

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