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Enhanced Nitrate Removal with Methanol Dosing in Woodchip Bioreactors: Laboratory and Field Evidence

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Abstract

Woodchip denitrifying bioreactors are well-established ecotechnologies for removing nitrate from wastewater such as agricultural tile drainage. However, nitrate removal in bioreactors is dependent on the supply of carbon from woodchips, which diminishes with time owing to woodchip decomposition. The purpose of this project was to assess the effect of methanol dosage on nitrate removal in woodchip bioreactors and estimate the negative consequences on bioreactors and downstream receiving waters.

In the first study, methanol was dosed into a pilot-scale bioreactor installed in an agricultural catchment in Waikato, New Zealand, during the drainage seasons of 2020 and 2021. Regardless of the input flow or nitrate loads, the bioreactor received a constant flow of 8% methanol solution. Methanol dosing increased volumetric nitrate removal rates significantly, increasing from 1 g N m^{-3} d^{-1} in 2018 to 8 g N m^{-3} d^{-1} in 2020 and 5 g N m^{-3} d^{-1} in 2021. The project's second phase established a long-term mesocosm experiment to evaluate the impact of methanol dosing in bioreactors under hydrology-controlled conditions. The results showed that methanol dosing increased nitrate removal rates from 7 to 28 g N m^{-3} d^{-1}. The optimal C: N ratio of 0.7 was identified based on the experimental results, which increased nitrate removal while

minimizing sulfate reduction, a potential adverse effect of methanol dosing. The project's third phase aimed to quantify the hydraulic evolution of bioreactors under various carbon dosing treatments. Across drainage seasons, methanol dosing reduced field bioreactor conductivity by about 3000 m d $^{-1}$. For the mesocosm bioreactors, conservative tracer tests revealed that methanol-dosed bioreactors had a 30% shorter actual hydraulic retention time (AHRT) than controls. The findings of the study suggest methanol dosing improves improving nitrate removal in bioreactors while minimizing adverse effects on bioreactors and downstream receiving waters.

1 Introduction

Nitrate pollution from intensive agricultural land use is a major environmental concern that can adversely affect water quality and human health (Basu et al., 2022; Shortle et al., 2021). Excess nitrate levels in water bodies can cause eutrophication, harmful algal blooms, and oxygen depletion, all of which can be disastrous for aquatic ecosystems and the organisms that rely on them (Basu et al., 2022; Withers et al., 2014). Agricultural activities such as fertilizer application and livestock production are significant contributors to nitrate pollution, and effective treatment options are required to address this issue (Basu et al., 2022).

Woodchip bioreactors, detainment bunds, constructed wetlands, and riparian buffers are examples of well-known technologies that can be used to remove diffuse pollution caused by agriculture, such as nitrate and phosphorus losses (Jaynes and Isenhart, 2019; Levine et al., 2021; Mayer et al., 2007; Schipper et al., 2010b; Tanner et al., 2012). Bioreactors are particularly low-cost treatment systems that support microbial denitrification by using woodchips as a carbon source. The idea is that microbes use nitrate as an electron source to break down the carbon in the woodchips, converting nitrate to harmless nitrogen gas (Rambags et al., 2019; Schipper et al., 2010a; Schipper et al., 2010b).

However, bioreactor performance might decline with time due to decreasing carbon availability from woodchips (Addy et al., 2016). This long-term low nitrate removal rate may limit the long-term establishment of bioreactors and render them less efficient than alternative treatment options such as constructed wetlands. Carbon dosing, which provides an additional energy source for microbial denitrification, is one potential approach for improving bioreactor performance (Jansen et al., 2019; Roser et al., 2018). Methanol, in particular, is a low-cost carbon source that has been shown by Hartz et al. (2017) as an effective approach to enhancing nitrate removal rates. Methanol, on the other hand, may raise concerns about potential adverse effects on both bioreactors and downstream receiving waters. Methanol may promote increased carbon losses and sulfate reduction, which may result in the production of hydrogen sulfide, a toxic gas that can harm aquatic organisms (Aalto et al., 2022; Hartfiel et al., 2022). Methanol dosing can also have a negative impact on hydraulic performance as it might promote microbial growth, which reduces the capacity of bioreactors to accept hydraulic loads (Christianson et al., 2016).

To address these concerns and optimize the performance of bioreactors, this Ph.D. study aimed to assess the potential of methanol dosing to enhance nitrate removal while minimizing adverse environmental impacts. The research was conducted in three phases(Moghaddam et al., 2023a; Moghaddam et al., 2023b; Moghaddam et al., 2022), including a pilot-scale bioreactor in an agricultural catchment, a long-term mesocosm experiment, and an assessment of the hydraulic performance of bioreactors following carbon dosing. Here we summarize findings from these studies to explore the overall benefits of dosing of bioreactors.

2 Material and methods

The experiments were conducted in replicate mesocosm bioreactors running under hydrologically controlled conditions and a pilot scale bioreactor installed on a dairy paddock in Waikato, New Zealand.

2.1 The Pilot scale bioreactor

A pilot-scale bioreactor in Tatuanui, Waikato, New Zealand, that had been operating without external carbon dosing from 2017 to 2019 (Rivas et al., 2020), was dosed with a constant flow of methanol (8 percent (v/v)) at 10 mL min^{-1} in 2020 and 5 mL min^{-1} in 2021. The added methanol was added based on a C: N ratio of 1.4, to remove untreated nitrate loads during the 2019 drainage season. This trial was conducted to assess the effects of carbon dosing in field settings and to measure potential adverse impacts, such as added carbon losses, sulfate reduction, and changes in hydraulic performance.

The study employed a TriOS Opus multispectral nitrate sensor (Oldenburg, Germany) to continuously monitor nitrate concentrations along the bioreactor (inlet, well1, well2, well3, outlet) using a high-frequency, multipoint sampling technique, as outlined in Moghaddam et al. (2023b).

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

The volumetric nitrate removal rates were calculated using equation (1), which takes into account the nitrate-N concentration (N_i) of each water parcel passing through the bioreactor (inlet, well1, well2, well3, outlet), the hydraulic retention time (HRT) of the parcel, and the average drainable porosity of the bioreactor (ϕ).

2.2 Mesocosm experiment

The mesocosm experiment utilized twelve bioreactors, each containing 26 liters of saturated Monterey pine (*Pinus radiata*) woodchips. The purpose of the experiment was to investigate the effects of carbon dosing under controlled conditions and for modelling purposes. The bioreactors were fed through gravity and downflow, and received continuous doses of methanol, nitrate, and sulfate to create three experimental treatments. These treatments were: the "BN treatment" for nitrate-fed bioreactors, the "BM treatment" for methanol-fed bioreactors, and the "BNM treatment" for bioreactors fed with both methanol and nitrate. Sulfate, which was present in the tap water, was administered to all treatments. The dosed concentrations were 80 mg N L^{-1} for nitrate, 60 mg CH_3OH–C L^{-1} for methanol, and 8 mg SO_4^{2-}-S L^{-1} for sulfate. Every two weeks, samples from the bioreactors were taken to analyze various parameters, such as nitrate concentrations. This data was used to calculate the nitrate removal rates, which were determined using the following equation.

$$RR = \frac{(C_{inlet} - C_{Outlet}) \times Q}{V_{saturated}} \quad (2)$$

3 Results

3.1 The Pilot scale methanol dosing experiment

The concentrations of nitrate in the inlet water varied between 20 and 35 mg N L^{-1} during the 2020 season and 20–40 mg N L^{-1} during the 2021 season (Figure 1). In the 2020 season, when a higher methanol dosing rate was applied, the greatest reduction in nitrate concentrations was observed in the first compartment of the bioreactor (Figure 1). The nitrate concentration decreased at a slower rate in the subsequent compartments. In the 2021 season, when the methanol dosing rate was halved, a significant reduction in nitrate concentration was observed between the inlet and the first well, while the nitrate levels in the downstream wells of the bioreactor remained relatively unchanged (Figure 1).

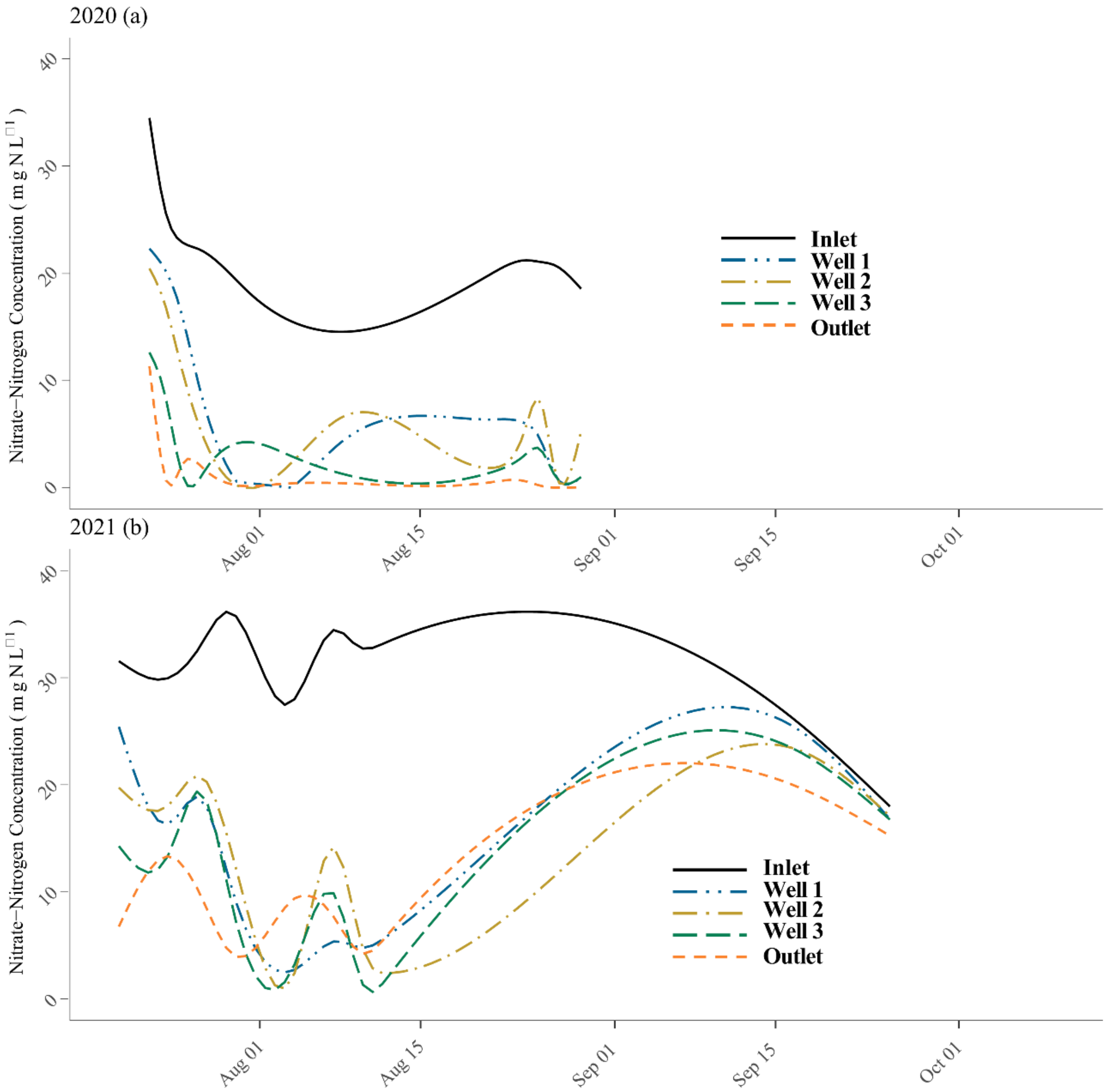

Figure 1: Nitrate concentrations at the inlet, outlet, as well as sampling wells over the drainage seasons of (a) 2020 and (b) 2021 for the pilot scale bioreactor

At the very beginning of the 2020 season, the nitrate concentration in the outlet water was approximately one-third of that in the inlet water (around 10 mg N L^{-1}). However, with continued methanol dosing, the outlet nitrate concentrations dropped to less than 1 mg N L^{-1} by the end of the drainage season (September 9, 2020).

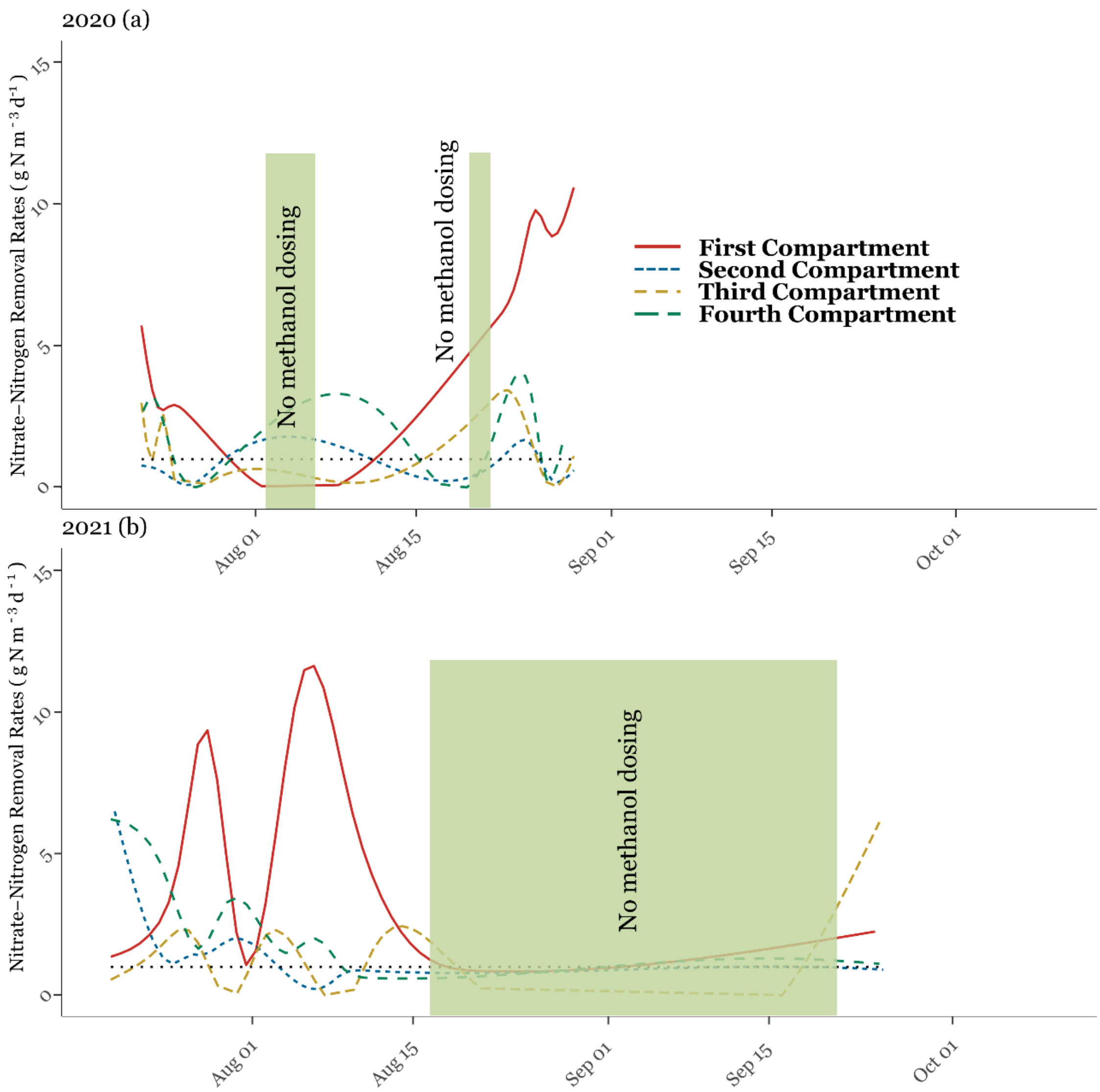

Figure 2: The bioreactor's nitrate removal rate from different compartments in (a) 2020 and (b) 2021. The black dashed-dotted line depicts mean nitrate removal rates without methanol dosing over the 2018 drainage seasons (Rivas et al., 2020).

In 2020 and 2021, during the dosing of methanol in the bioreactor, there was a significant increase in nitrate removal rates compared to the average seasonal removal rate in 2018 (1 g N m^{-3} d^{-1}), when the bioreactor was not dosed (Figure 2). The first compartment showed the highest removal rates, while the subsequent three downstream compartments had rates similar to those observed in 2018 without dosing (Figure 2).

3.2 Mesocosm scale methanol dosing experiment

When compared to the BN bioreactors, the BNM bioreactors showed a significantly higher nitrate removal rate (Figure 3). Initially, the average outlet nitrate concentration in the BN bioreactors was 7 mg N L^{-1}, while the inlet nitrate concentration was around 20 mg N L^{-1}

(Figure 3). During the second month of operation, the nitrate removal rates in the BN treatment bioreactors decreased as the outlet nitrate concentrations approached the inlet nitrate concentrations. During the first two months, the BN treatment bioreactors removed 10.4 g N m^{-3} d^{-1}. Following that, the nitrate removal rates fell to 5.9 g N m^{-3} d^{-1}, a level that was maintained until the trial's conclusion (Figure 3).

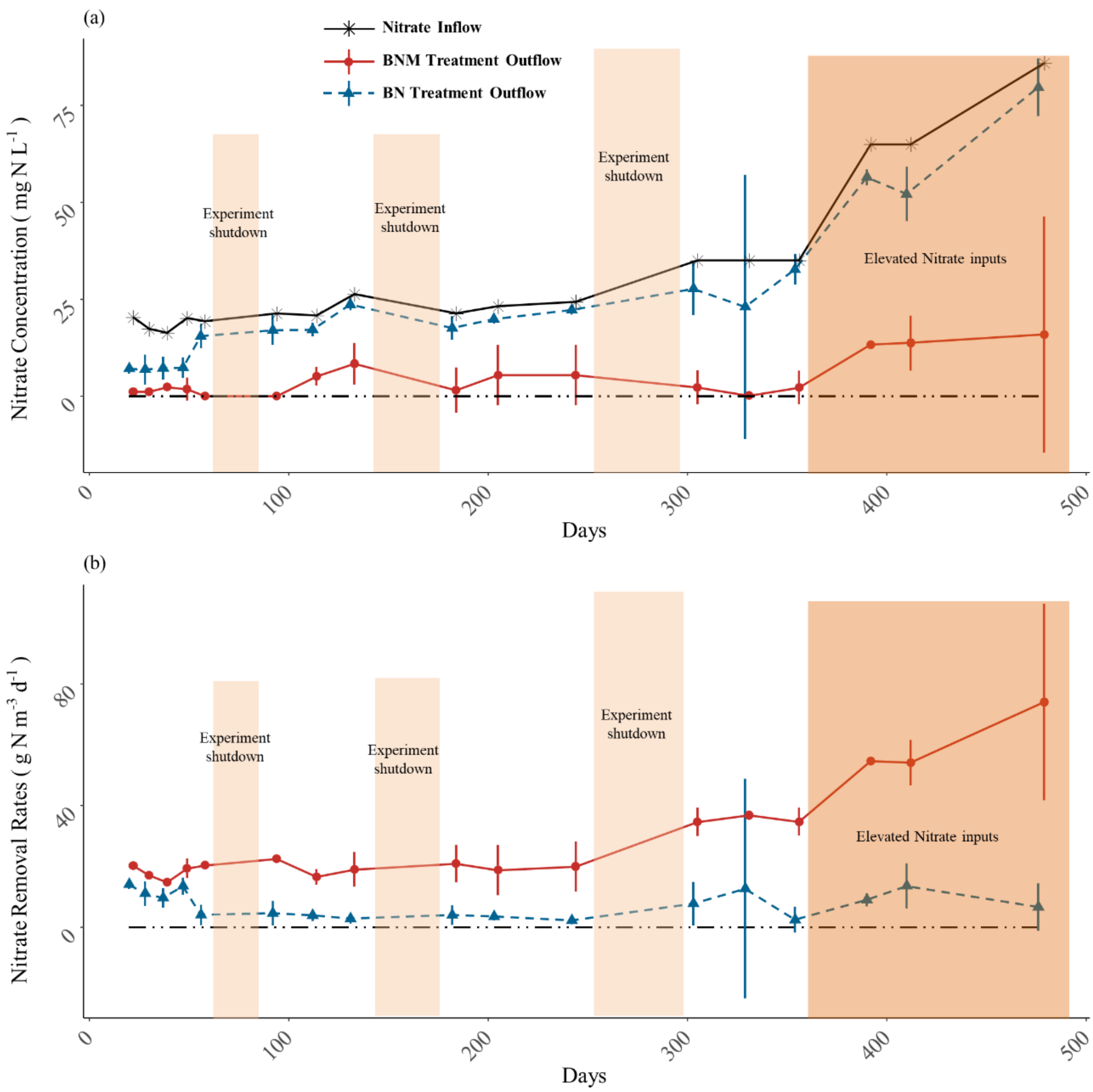

Figure 3: Nitrate concentrations in the inflow and outflow of BN and BNM bioreactors (a) as well as removal rates (b). The error bars represent a 95% confidence interval around the mean.

The BNM bioreactors showed nitrate concentrations in the outlet that were generally within the limiting range, with nitrate removal rates of 27 g N m^{-3} d^{-1}. When the inputs of nitrate and methanol to the bioreactors were doubled, the nitrate removal rates increased to 54 g N m^{-3}

d^{-1}. However, this led to an increase in the output nitrate concentration, which rose to around 13 mg N L^{-1}.

3.3 Hydraulic effects of methanol dosing

In 2018, the hydraulic conductivity of the field bioreactor was significantly higher at 4601 m d^{-1} when it was not carbon-dosed. However, in 2021, which marked the second year of carbon dosing, the hydraulic conductivity reduced to 1600 m d^{-1}.

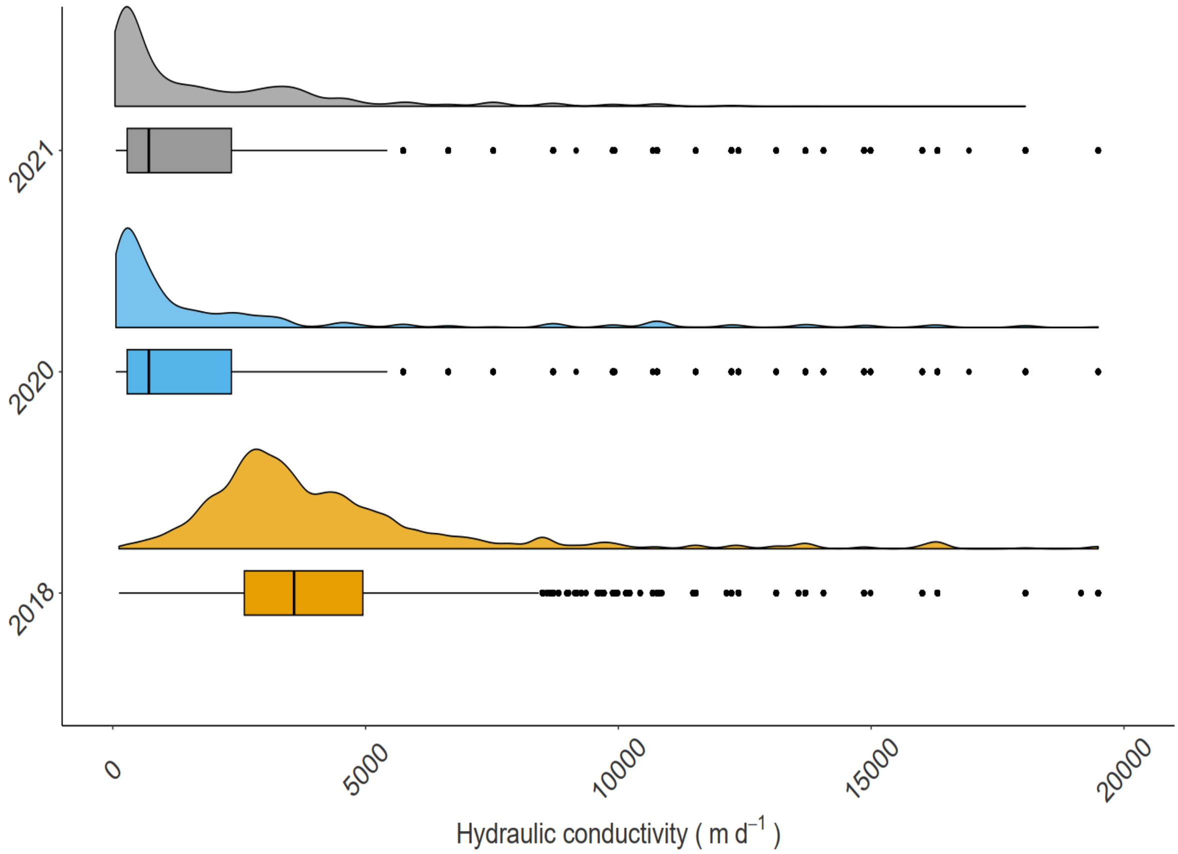

Figure 4: Hydraulic conductivity of the field bioreactor with different methanol dosing treatments over different drainage seasons.

Furthermore, results from the tracer test conducted on the mesocosm bioreactors revealed that the BN bioreactors exhibited the longest average hydraulic retention time (AHRT) of 13.2 hours, whereas those treated with BNM had the shortest AHRT of 10 hours.

Conclusion

This study aimed to investigate the long-term effects of methanol dosing on nitrate removal in bioreactors, utilizing mesocosm experiments and field-scale bioreactors. The goal was to determine the feasibility of this approach for enhancing the performance of bioreactors in removing nitrate from agricultural runoff. The pilot-scale bioreactor experiment showed that dosing methanol in 2020 and 2021 resulted in a significant increase in seasonal nitrate removal rates, with rates of 8.6 g N m^{-3} d^{-1} in 2020 and 5.1 g N m^{-3} d^{-1} in 2021, compared to the average seasonal removal rate of 1 g N m^{-3} d^{-1} in 2018 (Rivas et al., 2020) without external carbon dosing. By the end of the 2020 drainage season, the outlet nitrate concentration dropped to less than 1 mg N L^{-1}. However, the lower dosing rate in 2021 led to an increase in the outlet nitrate concentration, ranging between 0 to 20 mg N L^{-1}. The study also found that the hydraulic conductivity of the bioreactor was significantly higher in 2018, at 4601 m d^{-1} when it was not carbon-dosed. However, conductivity was reduced to 1600 m d^{-1} in 2021, the second year of carbon dosing.

In the mesocosm experiment, BNM bioreactors (with methanol dosing) demonstrated a significantly higher nitrate removal rate compared to BN bioreactors (without methanol dosing). In the first two months, BN treatment bioreactors had a nitrate removal rate of 10.4 g N m^{-3} d^{-1}, which declined to 5.9 g N m^{-3} d^{-1} and was maintained until the trial's end. BNM bioreactors, however, maintained nitrate concentrations in the outlet generally within the limiting range, with nitrate removal rates of 27 g N m^{-3} d^{-1}. When nitrate and methanol inputs to the bioreactors were doubled, nitrate removal rates increased to 54 g N m^{-3} d^{-1}, but this resulted in a higher output nitrate concentration of approximately 13 mg N L^{-1}.

In summary, this study showed that using methanol dosing is a promising method to enhance nitrate removal rates in woodchip bioreactors, while also having minimal negative impacts on both the bioreactors themselves and the water bodies downstream.

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