Reducing Agricultural Nitrate Leaching

Investigating the performance of denitrification bioreactors in New Zealand conditions

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Harry Ratcliffe

MASSEY UNIVERSITY
TE KUNENGA KI PUREHUROA
UNIVERSITY OF NEW ZEALAND

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Supervisors:

Associate Professor Ranvir Singh [PhD, MTech]

Associate Professor in Environmental Hydrology and Soil Science
School of Agriculture and Environment
Massey University, Private Bag 11222, Palmerston North
https://www.massey.ac.nz

Professor David Horne

Professor in Soil Science
School of Agriculture and Environment
Massey University, Private Bag 11222, Palmerston North
https://www.massey.ac.nz

Professor Surinder Saggar [PhD, MSc, BSc Hons]

Senior Scientist Land Use Ecosystems Agriculture Greenhouse Gases
at Manaaki Whenua - Landcare Research
https://www.landcareresearch.co.nz/

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Abstract

Denitrifying woodchip bioreactors are a tool that is used in the agriculture sector to reduce undesired nitrate-nitrogen (NO_3-N) concentrations in subsurface drainage water before entering downstream environments. As well as their ability to reduce the NO_3-N pollutant, denitrifying bioreactors tend to produce other unwanted pollutants such as nitrogen dioxide (N_2O), carbon dioxide (CO_2), and methane (CH_4).

This thesis presents research from 2 pre-installed denitrification bed bioreactors in the Manawatu-Whanganui region of New Zealand. The aim of this research was to measure the performance of these bioreactors in terms of nitrate removal rates and nitrate removal efficiency, as well as measuring any unwanted pollutants produced. Nitrate removal performance was assessed by measuring the nitrate concentrations flowing into the bioreactor and comparing them to the nitrate concentrations flowing out. The difference between these values, per unit time, is the nitrate removal rate (NRR). To recreate different New Zealand seasonal conditions different flow rates were changed, hence, the length of time the dissolved solutes remained in the bioreactors (hydraulic retention time or HRT) also changed. Measurements were undertaken to see if these changes in flow rates had any effect on nitrate removal, N_2O, CO_2, and CH_4 production.

Results indicated that during the spring of 2022, the denitrifying bioreactors removed an average of 2.25 and 3.70 grams of NO_3-N per m^3 of water per day, with an average nitrate removal efficiency (NRE) of 76.3 and 76.5%. Relatively smaller fractions of 1.81 and 0.77% of the NO_3-N removed was converted to N_2O within the bioreactors. Of the N_2O produced, 99.5 and 99.8% was dissolved and leached in the outflow, whilst 0.5 and 0.2% was released as a gas. This supports previous literature from Rivas et al., (2019), stating that bioreactors produce high NO_3-N removal rates with relatively low N_2O emissions, with the main export pathway of N_2O via outflow of water in dissolved form.

Results also indicated that, for both bioreactors, there is strong correlation that as HRT decreased, NRR exponentially increased. As HRT increased, the ratio of N_2O-N produced to NO_3-N removed decreased, with an *R*-squared value of 0.8007 proving significant correlation.

The average CO_2 produced was 6.13 and 0.441 g CO_2-C/m^3/day and the average CH_4 produced was 5.10E-04 and 3.17E-03 g CH_4-C/m^3/day. The concentrations of CO_2 and CH_4 produced by the bioreactor were difficult to compare to average concentrations produced from agricultural land in New Zealand due to varying climate, soil, and pasture species. Varying the HRTs of the 2 bioreactors produced no significant effect on CO_2 or CH_4 production.

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List of abbreviations and acronyms

ACRE: Agricultural Communities Respecting the Environment

CH_4: Methane

CO_2: Carbon dioxide

CH_4-C: Methane carbon

CO_2-C: Carbon dioxide carbon

GHG: Greenhouse Gas

H_2S: Hydrogen sulphide

HRT: Hydraulic retention time

N: Nitrogen

N_2: Dinitrogen

N_2O: Nitrous oxide

N_2O-N: Nitrous oxide-nitrogen

NO_3-: Nitrate

NO_3-N: Nitrate-nitrogen

STDEV: Standard deviation

List of definitions

Alluvial: soil formed from alluvium, which is a deposit of clay, silt, and sand carried by flowing rivers or streams caused by weathering of rocks (Merriam-Webster Inc, 2022).

Artificial drainage: The artificial removal of a surface water and sub-surface water from an area, many agricultural soils need artificial drainage to improve production or to manage water supplies (Skaggs et al., 1994).

Controlled drainage: a water management practice that increases water retention within the soil profile to reduce losses of nitrogen from agricultural subsurface drained fields to surface waters through the recycling of nutrients (Kęsicka et al., 2022).

Denitrification: Part of the natural nitrogen cycle. It is a process where bacteria convert nitrate into atmospheric N_2 gas in the soil (NO_3 -→NO_2→NO→N_2O→N_2) (Harrison, 2010).

Gas flux: "the difference between the amount of gas added to the atmosphere by emissions from 'sources and the amount taken up by 'sinks' which remove gas from the atmosphere" (Copernicus, 2019).

Greenhouse gas (GHG): a gas that absorbs and emits radiant energy within the thermal infrared range, causing the greenhouse effect (Kweku et al., 2018).

Hydraulic Retention Time: The average duration cells and substrates stay inside the bioreactor. Calculated as the ratio of bioreactor volume to flow rate (David et al., 2019).

Nitrate attenuation factor: the ability of a catchment to carry out biological processes that reduce nitrates. Denitrification attenuates NO_3-N from the soil-groundwater continuum. (Elwan et al, 2015).

Nitrate Removal Efficiency (NRE): the percentage of nitrate that is removed from the system (Fan et al., 2022).

Nitrate Removal Rate (NRR): the daily reduction of nitrate concentration (Fan et al., 2022).

Pollution Swapping: The increase in one pollutant because of a measure introduced to reduce a different pollutant (Stevens & Quinton, 2009).

Silt loam: "a soil containing no less than 70 percent silt and clay, and no less than 20 percent sand" (Merriam-Webster Inc, 2022).

Silt: a sediment material in the soil that is smaller than sand and larger than clay (Merriam-Webster Inc, 2022).

1. Introduction

Farming practices with high levels of nitrogen (N) loss to surface water and groundwater are facing increasing global and national scrutiny as it is one of the largest issues of environmental concern. Nitrogen is highly mobile in water, thus applications of effluent and fertilisers with high N concentrations can lead to N leaching through drainage into the soil subsurface ending up in surface waters. Artificial drainage allows excess water to be removed from poorly drained soils, so they can become productive and economically viable. However, it also provides a pathway for nutrients to be passed through the soil into streams without being taken up by the soil, lowering the nitrogen attenuation factor. In New Zealand, out of the potential 5.4 million hectares suitable for artificial drainage, 2.5 million hectares of land is currently artificially drained (Manderson, 2018).

Nutrient enrichment of water (eutrophication) can cause negative impacts such as algal blooms, a decrease in biodiversity, and oxygen deficiency, which all degrade water quality (Rabalais, 2002). The New Zealand government's focus has been on improving water quality through proposed legislation, such as the Essential Freshwater work programme. Through these reasons there has been increased interest in developing edge-of-field practices that manage the quality of critical drainage flows and reduce nutrient loads to receiving waters.

Denitrifying 'woodchip' bioreactors have the potential to reduce the environmental effects of nitrogen losses to water (Hoover et al., 2016). They are an environmental engineering-based concept that makes use of the naturally occurring denitrification process, where microbial bacteria convert nitrate in water to inert, harmless dinitrogen gas (N_2) already abundant in the atmosphere. This works by providing a carbon source from woodchips and low oxygen (anaerobic) conditions which support the microbial respiration process (Schipper et al., 2010).

Denitrifying bioreactors are widely used in the USA and Europe due to having a superior cost-to-benefit ratio (Rivas & Barkle, 2017). Compared to other techniques, bioreactors have low land use, maintenance, and start-up costs. Coupled with their proven effectiveness at reducing nitrate transferred to surface waters, attracts farmers and industry researchers (Rivas & Barkle, 2017).

In New Zealand very few bioreactors are in place as they are still in their trial phase. New Zealand's differing agricultural practices, variations in climate and soil types, and rainfall variability, means that there is no 'one size fits all' design and every bioreactor site must be carefully planned. Therefore, more research needs to be undertaken on their design and performance before they become a widely used technology to treat drainage waters in NZ.

The overall aim of this thesis was to research two woodchip bioreactors by measuring their effectiveness at reducing NO_3- under different drainage flows, whilst seeing if they produced any unwanted pollutants during this process. The overall aim is to

This study examines the operational efficacy of two pre-installed woodchip denitrifying bed bioreactors located in the Manawatu-Whanganui Region of New Zealand. It endeavours to quantify their nitrate removal rates and nitrate removal efficiencies across various hydraulic

retention times, simulating diverse flow conditions. In tandem, this investigation assesses the emission of undesirable greenhouse gases. The overall aim is to develop more of an understanding of how woodchip bioreactors will perform at an optimal level under New Zealand conditions.

2. Review of Literature

2.1. Bioreactor Design

The type of bioreactors studied in the research paper are woodchip denitrifying bed bioreactors. This method is suitable in agricultural settings that have input nitrate fluxes of 2–22 g N m^{-3} day^{-1} (Schnipper et al., 2010) to the reactor. These bioreactors are favoured due to their low cost, low maintenance and the ability to operate over several years without replacement of the substrate (carbon consumption <2% of the total woodchips/year) (Van Driel et al., 2006). The concept of these bioreactors is shown in figure 1 below. The inlet control structure regulates the flow rate of water from artificial drainage into the bioreactor which ensures that the wood chips have sufficient contact time with the water as well as maintaining anoxic conditions for denitrification to occur. The solid carbon source substrate beds are around 1-2 m deep and are lined with an impermeable layer keeps water contained within the woodchips (Schnipper et al., 2010). The outlet control structure regulates the outflow of water which allows retention of water for longer periods of time so that the denitrifying bacteria have enough time to convert nitrate into nitrogen gas. Installing bypass flow diverters can mitigate the risk of high overflows and flooding (Schnipper et al., 2010).

There are currently no woodchip bioreactor regulations in New Zealand, however, in the United States, the design and construction of bioreactors for subsurface drainage treatment follows the USDA-NRCS Conservation Practice Standard 605 (Christianson et al., 2021).

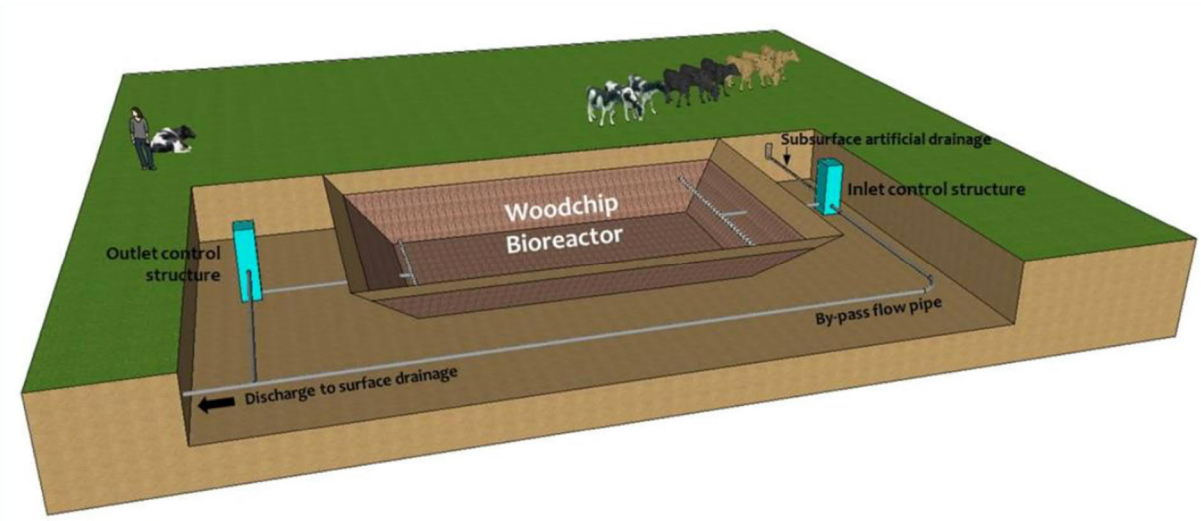

Figure 1. Woodchip bioreactor schematic (Rivas et al., 2019).

2.2. Denitrification chemistry

Denitrifying bioreactors are an edge-of-field technique that takes advantage of the nitrogen cycle by using the natural process of denitrification to treat nitrate contamination of water. The complete denitrification process, shown in the equation 1 below, converts nitrate (NO_3) into dinitrogen gas (N_2).

$$5C + 4NO_3^- + 2H_2O \Rightarrow 2N_2 + 4HCO_3^- + CO_2$$

Equation 1. Chemical equation for complete dentification. (Christianson et al., 2012)

The woodchip filled trench that input water is passed through provides the carbon source (5C) for the reactant in the above equation. The complete denitrification process involves several stages of intermediate gaseous products with different oxidation states and is shown in equation 2. All these intermediaries are greenhouse gases.

$$NO_3^- \xrightarrow{\text{nitrate reductase}} NO_2^- \xrightarrow{\text{nitrite reductase}} NO \xrightarrow{\text{nitric oxide reductase}} N_2O \xrightarrow{\text{nitrous oxide reductase}} N_2$$

Equation 2. Denitrification pathway showing the intermediate N oxide products (electron acceptors). (L. E. Christianson et al., 2012)

The woodchip carbon source acts as the electron donor and the N oxides are electron acceptors (Christianson & Helmers, 2011). It is important to design the bioreactors to have enough woodchips so that there is sufficient energy source to allow complete denitrification of nitrate into benign nitrogen gas (N_2). If incomplete denitrification occurs, nitrous oxides, such as the intermediaries shown in equation 2, are emitted instead. This can lead to unwanted pollution swapping.

2.3. Hydraulic Retention Time

Hydraulic retention time (HRT) is the length of time dissolved solutes remain in the bioreactor. HRT influences bioreactor performance. Higher flow rates (lower HRT) mean that water is held within the woodchip bed for a shorter time, which can limit their nitrate removal performance (Schnipper et al., 2010). Smaller flow rates (higher HRT) mean that water is held in the bed for too long, and the limiting factors are the carbon source or nitrate for the denitrifying microbes (Schnipper et al., 2010). Low HRT during seasonal periods of high drainage events means that more untreated water is diverted through the bypass flow pipe (figure 1). This can also limit the total nitrate removed as lower volumes of water per day are denitrified.

According to a study undertaken by Lepine et al. (2016), longer HRTs demonstrated a higher nitrate removal efficiency, however, shorter HRTs demonstrated a higher nitrate removal rate due to passing more volume of water through the system per day. This indicates the importance of designing HRTs so that nitrate removal rate and removal efficiency are balanced to improve desired water chemistry. The NRCS Conservation Practice Standard recommends designing a flow rate that is at least 15% of the peak estimated flow rate from

the drainage system into the bioreactor (USDA, 2015). In the USA the desired HRT is between 4-8 hours (USDA, 2016).
Woodchip bioreactors in the mid-west of the USA are designed to remove NO_3- from a steady supply of water due to snow melting in the spring (Rivas & Barkle, 2017). However, under New Zealand conditions, due to differing climate, soil drainage systems, and land use (all-year round pastoral grazing), drainage events are more frequent and have much greater variability, and therefore impose a larger range of HRTs. This emphasises the importance of finding out how HRT affects bioreactor performance (Rivas & Barkle, 2017).

Davis et al., (2019), carried out a pilot scale study on bioreactors removing nitrate from agricultural runoff in the Mississippi River Basin. They investigated the production of methane and nitrous oxide in bioreactors of different sizes and hydraulic residence times (HRTs). They found that nitrous oxide and methane were produced in all bioreactors. The highest levels of nitrous oxide were produced in bioreactors with a 2-hour HRT, while the highest levels of methane were produced in bioreactors with an 8- or 16-hour HRT. Overall, bioreactors with a 6- to 8-hour HRT appeared to strike the best balance between removing nitrate and minimizing greenhouse gas emissions.

Rivas et al., (2020), conducted research on a woodchip bioreactor that had a volume of 78 cubic meters. The bioreactor was built on a dairy farm located in the Hauraki Plains region of Waikato, New Zealand. Research methods involved monitoring rainfall, flow, hydrochemistry and dissolved gases in the inflow and outflow. In 2017 the bioreactor exhibited a higher removal efficiency due to longer hydraulic residence time (HRT) of the water in the bioreactor. In the 2018 drainage season, a strong positive relationship between HRT and removal efficiency was also observed (Rivas et al., 2020). HRTs greater than 5 days performed at a high nitrate removal efficiency (≥59%) and allowed complete denitrification of NO_3- to occur (equation 1), but also resulted in the production of CH_4 due to strongly reducing conditions. On the other hand, HRTs shorter than 4 days performed at moderate nitrate removal efficiency (≤43%) and allowed only partial denitrification (equation 2) which constrained the complete reduction of NO_3-, resulting in higher N_2O rates in the outflow (Rivas et al., 2020). Thus, nitrate removals above 50% were not able to be achieved without CH_4 generation (Rivas et al., 2020).

2.4. Pollution Swapping

General research shows that a possible side effect of denitrifying bioreactors is the production of greenhouse gases (GHG) such as nitrogen oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2). This would effectively mean that one problem is potentially swapped with several others with detrimental effects on the environment.

A 2010 study undertaken in Canada using denitrifying bed bioreactors showed that the monthly average removal of nitrate was 0.3-2.5 mg N/L (between 18% and 100% removal rate), however it produced dissolved N_2O and CH_4 fluxes at rates of 6.4 μg N/L and 974 μg C/L respectively (Elgood et al., 2010). One pollutant is being removed, whilst concomitantly producing others above normal background agricultural ranges.

A study carried out by Healy et al. (2015) analysed the contaminants CH_4, CO_2 and N_2O that were produced as well as NO_3- removed on laboratory scale bioreactors. Net NO_3- removal

performed best at shorter HRTs. This study showed a strong positive correlation between bioreactors with the high denitrifying activity and high nitrogen oxide emissions. Pollution swapping occurred with all bioreactors. The longest HRTs produced the most CH_4 and CO_2 emissions, with CH_4 being the greatest mass of GHG produced. This study agrees with Rivas et al., (2020), where pollution swapping was also observed during periods with very long HRTs where CH_4 was produced.

Other studies have produced different results. Bioreactors installed on high intensity farms in the Canterbury plains of New Zealand were measured by Goeller et al (2019). These bioreactors produced masses of carbon dioxide and nitrogen dioxide that were not significantly different to normal masses recorded by surrounding pastures: 185 – 286 mg of CO_2-C per meter squared per hour and 49 – 90 μg of N_2O-N per square meter per hour. These gas fluxes suggest that, in terms of carbon dioxide and methane, bioreactors do not add any negative impacts on the atmosphere.

2.5. NO_3-N removal Performance of Bioreactors

Bioreactors installed on high intensity farms on the Canterbury Plains, located on the East coast of New Zealand's South Island, were measured by Goeller et al (2019). The efficiency of nitrate removal in the woodchip bioreactors range from 10 - 99%. These results were measured from 3 types of bioreactors, one of these types being a single tile drain bioreactor that removed 0.41 kg nitrate-nitrogen (NO_3-N) per day, which was equivalent to roughly 10% of the mean daily tile drain nitrate load.

Schipper et al. (2010) also demonstrated that high rates of nitrate removal (5 to 10 g N/m^3/day) were achievable under New Zealand conditions through denitrification. A study done in New Zealand also showed that denitrifying bioreactor N load removal rates were on average 9.6 g N m^{-3} d^{-1} and an average reduction of 40 % (Christianson et al., 2020).

Rivas et al., (2020), studied a 78 m^3 woodchip bioreactor constructed on a dairy farm in the Hauraki Plains (Waikato, NZ) with an artificial drainage area of 0.65 hectares. The estimated nitrate removal efficiency of the bioreactor was 99% and 48% in 2017 and 2018, respectively. Removal rates of the bioreactor varied from 0.67–1.60 g N m^3/day and were positively correlated with inflow nitrate loads (Rivas et al., 2020).

The performance of 8 woodchip bioreactors was measured during a 2–4 year study in Denmark by Audet et al., (2021). They explained that woodchip bioreactors have the potential to effectively eliminate nitrogen from agricultural drainage water, but they also have the tendency to generate varying levels of the potent greenhouse gas nitrous oxide (N_2O). The degree of nitrogen elimination in eight bioreactors fluctuated between 17% and 73%, (Audet et al., 2021), while the typical N_2O emission factor was 0.6%, which is less than the emission factor recommended by the Intergovernmental Panel on Climate Change (IPCC).

Subsurface drainage denitrifying bioreactors have been shown to reduce 20% to 40% of annual nitrate-N loss in the Midwest, and studies published in the past three years show that bioreactors around the world have an average N load reduction of 40% ±26%, n =27 (Christianson et al., 2021). Reported N removal rates were approximately 7.2 g N/m^3/day ±9.6; n = 27 (Christianson et al., 2021).

2.6. Dissolved oxygen concentration

Dissolved oxygen concentrations play a critical role in influencing the removal rate of nitrates in woodchip bioreactors. These bioreactors primarily operate under anaerobic (low oxygen) conditions to promote denitrification. When dissolved oxygen levels are high, aerobic bacteria thrive and compete with denitrifying bacteria for available oxygen, limiting the denitrification process (Wegscheidl et al., 2021). In contrast, when dissolved oxygen concentrations are low or near zero in an anaerobic environment, denitrifying bacteria can dominate and efficiently convert nitrate to nitrogen gas. New Zealand's diverse and often high-flow drainage systems can introduce varying levels of dissolved oxygen into the bioreactors, therefore, managing dissolved oxygen becomes essential. To maximize nitrate removal in woodchip bioreactors operating in New Zealand conditions, maintaining low dissolved oxygen concentrations within the system is imperative. Low dissolved oxygen levels <2.0 mg/L favours full denitrification (Wegscheidl et al., 2021).

2.7. Temperature

Nitrate removal rate increases with warmer temperatures of water (Addy et al., 2016). A meta-analysis was undertaken by Addy et al. (2016), found that a proportional positive linear relationship existed between nitrate removal and denitrification bed temperature, with a 95% confidence interval. Elevated temperatures provide more energy for microbial metabolism, allowing denitrification to occur at a faster rate. Higher temperatures also increase enzyme activity. Denitrifying bacteria produce enzymes that are essential for the denitrification process. These enzymes function more efficiently at warmer temperatures. As temperature rises, enzyme activity increases, accelerating the conversion of nitrate to nitrogen gas. Therefore, under colder conditions, HRT should be adjusted to allow for an increase in nitrate removal efficiency (Addy et al., 2016).

2.8. Other factors

The pH of the water within woodchip bioreactors can significantly affect the nitrate removal process. Denitrification, the microbial reaction responsible for converting nitrates into harmless nitrogen gas, is pH sensitive. When the pH of the water in the bioreactor is between 5.5 and 8.0, the nitrate removal is at an optimum (Wegscheidl et al., 2021). In cases where the pH is too acidic (below 6.5), denitrification can slow down or become inhibited, reducing nitrate removal rates. Conversely, excessively alkaline conditions (above 8.5) may also impede denitrification (Wegscheidl et al., 2021). In New Zealand, variations in pH levels of drainage waters can be influenced by factors such as soil composition and land use practices. Therefore, monitoring and, if necessary, adjusting the pH within the woodchip bioreactor can be crucial to maintaining an environment conducive to efficient nitrate removal, ensuring these systems effectively mitigate nitrate pollution in local agricultural settings.

3. Research Objectives

The purpose of this thesis is to investigate the nitrate removal rates and efficiencies of 2 pre-installed woodchip denitrifying bed bioreactors in the Manawatu-Whanganui Region of New Zealand. The effect of hydraulic retention time on nitrate removal performance and the greenhouse gases N_2O, CH_4, and CO_2 was also investigated.

3.1. Research Questions

For the 2 bioreactors under investigation, the specific research questions were as follows:

- What are the nitrate removal rates under varying flow rates?
- How do nitrate removal rates vary with Hydraulic Residence Time?
- What percentage of NO_3-N removed is converted to N_2O-N produced?
- What fraction of NO_3-N reduction is converting into N_2O-N air and N_2O dissolved?
- How does the percentage of NO_3-N removed/ N_2O-N produced vary with Hydraulic Residence Time?
- How much CO_2 and CH_4 is being produced?
- How do CO_2 and CH_4 fluxes vary with Hydraulic Residence Time?

4. Farm Information

4.1. Site 1: Waitatapia Station

Waitatapia Station is a 2200 ha farm hosting a variety of farming enterprises such as sheep and beef finishing, crop, vegetable and cereal production, and forestry. The farm is located approximately 10 km west of Bulls in the Rangitikei District.

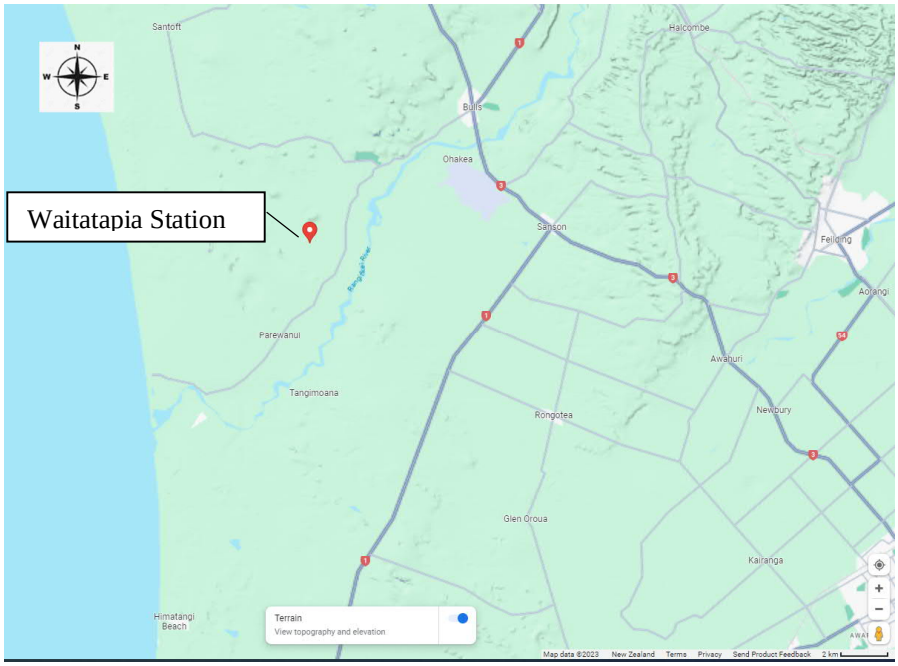

Figure 2. Location of Waitatapia station and surroundings, source: Google Maps.

Soil type

Typic Sandy Recent Soil.
Soil properties:

- Well drained
- Low structure
- Poor water retention
- High permeability
- Low organic matter content
- Susceptible to wind erosion
- Shallow groundwater levels (Manaaki Whenua: Landcare Research, 2023)

Climate

- Average annual rainfall: 1000 - 1,200 mm (NIWA, 2023)
- Average temperature range: 3 - 25 °C (NIWA, 2023)

Management

750 ha of the farm is under centre pivot irrigation. The farm regularly tests the soil for nutrient requirements to ensure the correct level use of fertilizer application. Shallow groundwater conditions require drainage in some parts of the farm for successful pastoral grazing and crop production. Hence, the farm is installed with open surface drains generally 1.2 m deep. Woodchip bioreactors are being trialled as edge-of-field practices to reduce drainage losses from the farm to surface water via these drains.

Waitatapia woodchip bioreactor

Figure 3. Waitatapia denitrification bed prior to soil covering (February 2021), (R. Gray, Massey University).

- The bioreactor is a woodchip denitrifying bed
- Volume of saturated woodchips = 60 m^3
- 0.3m of topsoil covering the woodchips
- Total depth of woodchips = 1.3 m

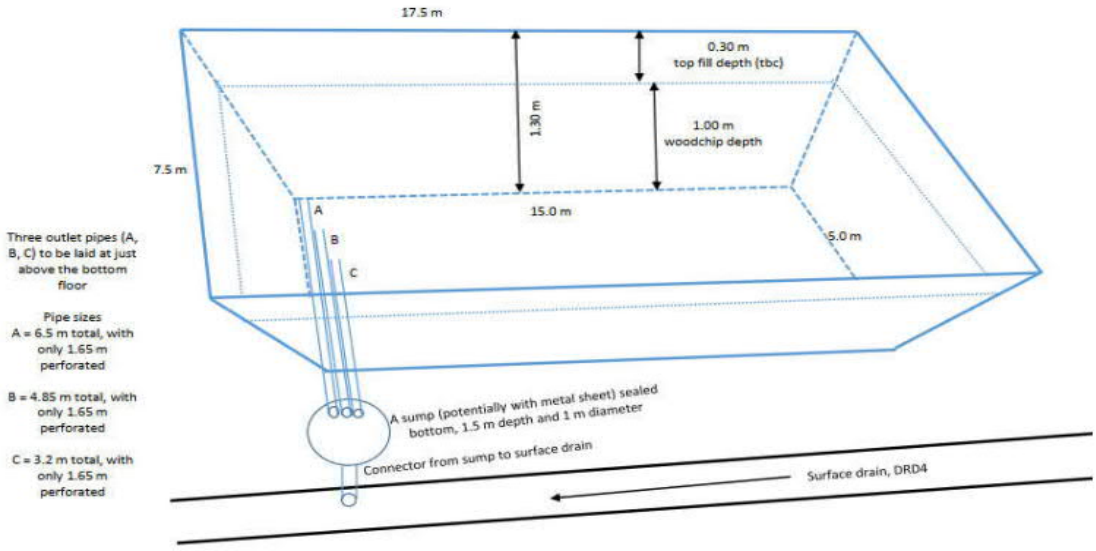

Figure 4. Waitatapia bioreactor dimensions.

The denitrification bed bioreactor is located downstream from irrigated sheep and beef finishing operations on the farm. This end-of-pipe mitigation is designed to reduce the NO_3^- concentration in drainage water before it leaves the farm and is discharged downstream.

Horizons Regional Council in New Zealand are actively involved in managing nutrient levels, including nitrogen, in waterways to protect and improve water quality. To be proactive, farmers need to come up with cost-effective ways to limit nitrogen leaching, so they can be profitable and sustainable.

Figure 5. Waitatapia station paddock, upstream from the bioreactor, source: Allan Barber (Rural News)

Funding

The Ministry of Primary Industries (MPI), Massey University, OB Group, and Waitatapia Farming funded the bioreactor installation. The Agricultural Communities Respecting the Environment (ACRE) group provided local knowledge and support.

4.2. Site 2: Te Maunga Farm

Te Maunga farm is a 429 ha dairy farm located 13km North East of Dannevirke in the Manawatū-Whanganui region.

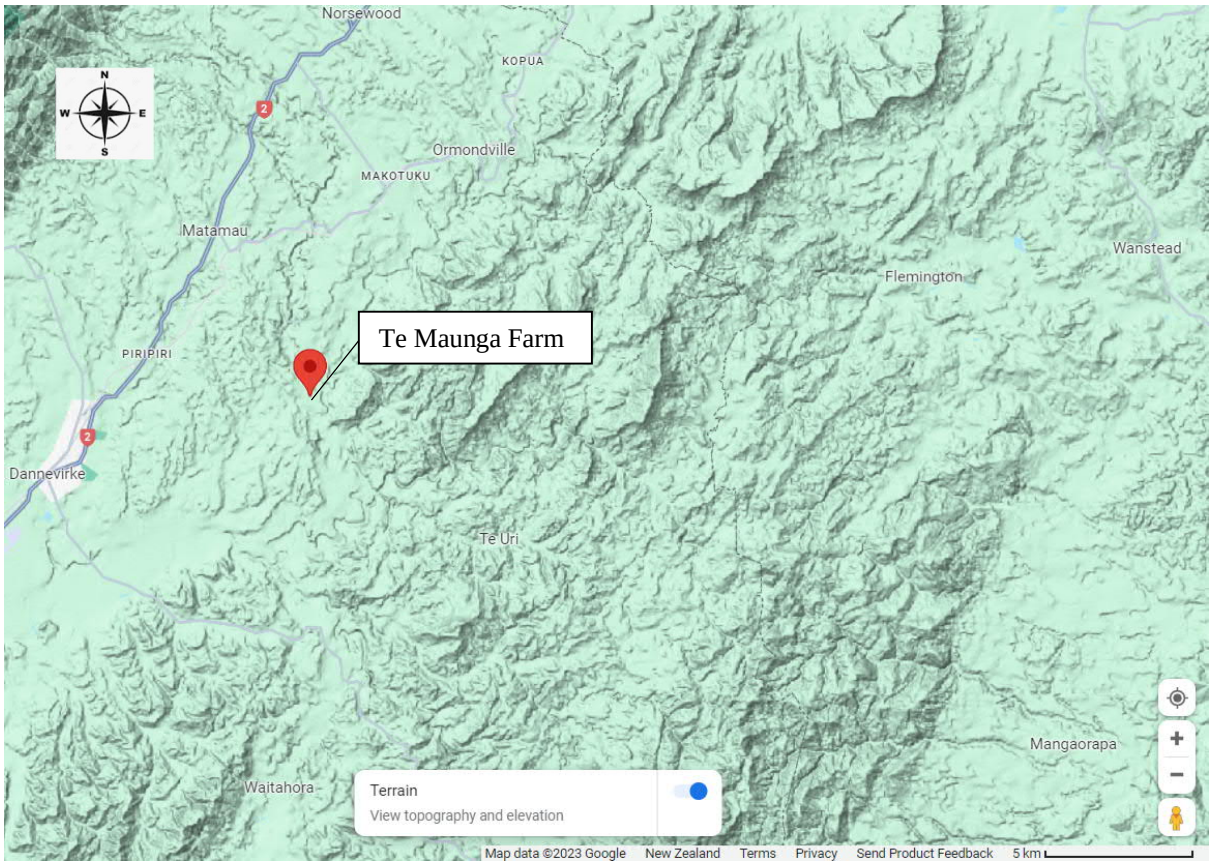

Figure 6. Location of Te Maunga Farm and surroundings, source: Google Maps.

Soil type

Typic Orthic Allophanic Soil.
Soil properties:

- Well drained, except in some area poorly drained (artificial drainage installed)
- Rich in Potassium and lime
- Prone to erosion (Manaaki Whenua: Landcare Research, 2023)

Climate

- Average rainfall: 900 – 1,100 mm (NIWA, 2023)
- Average temperature range 3 - 25 °C (NIWA, 2023)

Management

The farm irrigates 125 ha via centre pivot and Bosch long laterals. The farm grows its own chicory, plantain, and fodder beet and has 35ha of fenced riparian margins, and 29ha of native bush.

Installing artificial drainage can help to improve soil structure and fertility, reduce the risk of crop damage from excess water, and increase crop yields (Guerena & Dufour, 2019). However, excess nitrate transport from artificial drainage has negative impacts on downstream water quality and ecosystem health (Michigan State University, 2023), hence, the use of a woodchip bioreactor has the potential to improve soil water by reducing nitrate levels entering downstream ecosystems.

Te Maunga woodchip bioreactor

Figure 7.Denitrifying bioreactor set up (August 2022), (Photo taken by author).

- The bioreactor type is also a woodchip denitrifying bed.
- Woodchip volume of 180 m^3
- Unlike Waitatapia, water flowing into the bioreactor is directly from drainage and has not been treated before entering the bioreactor.
- No layer of soil covering, woodchips are exposed to the air. This reduces the risk of clogging as adequate air exposure can help prevent clogging in the bioreactor, improving its longevity and performance. Exposed bioreactor, however, may produce higher emissions of greenhouse gases due to the aerobic conditions which can contribute to global warming (Mardini et al., 2020).

Dimensions:

Length: 15m
Width: 11m
Saturated chip depth: 1.1m

The bioreactor intercepts artificial drainage from 60 ha of dairy land. It is an end-of-pipe mitigation designed to reduce the NO_3^- concentration in water before it leaves the farm and is leached into on-farm streams, and eventually the Manawatu River.

The farm has won:

- A supreme award at the Horizons Ballance Farm Environment Awards.
- The DairyNZ Sustainability and Stewardship Award
- The Hill Laboratories Agri-Science Award
- The WaterForce Integrated Management Award.

Installing this bioreactor indicates a conscious effort to reduce nitrogen losses from this farm to the environment.

5. Methods and Materials

5.1. Sampling Locations

The performance of 2 woodchip denitrifying bioreactors at 2 different sites were measured and analysed using the same method to see whether similar trends in performance were occurring.

Figure 8 below illustrates the sampling setup of the bioreactors. Water samples were taken at the inflow site, outflow site. Each bioreactor had 9 gas sampling chamber locations evenly spread out over the woodchip area. The sampling runs 1,2,3, and 4 for the Waitatapia bioreactor were taken on 07/08/22, 08/09/22, 20/09/22, and 10/10/22, respectively. The sample runs for the Te Maunga bioreactor were taken on 09/08/22, 12/09/22, 22/09/22, and the 13/10/22, respectively. No major weather events occurred near these dates.

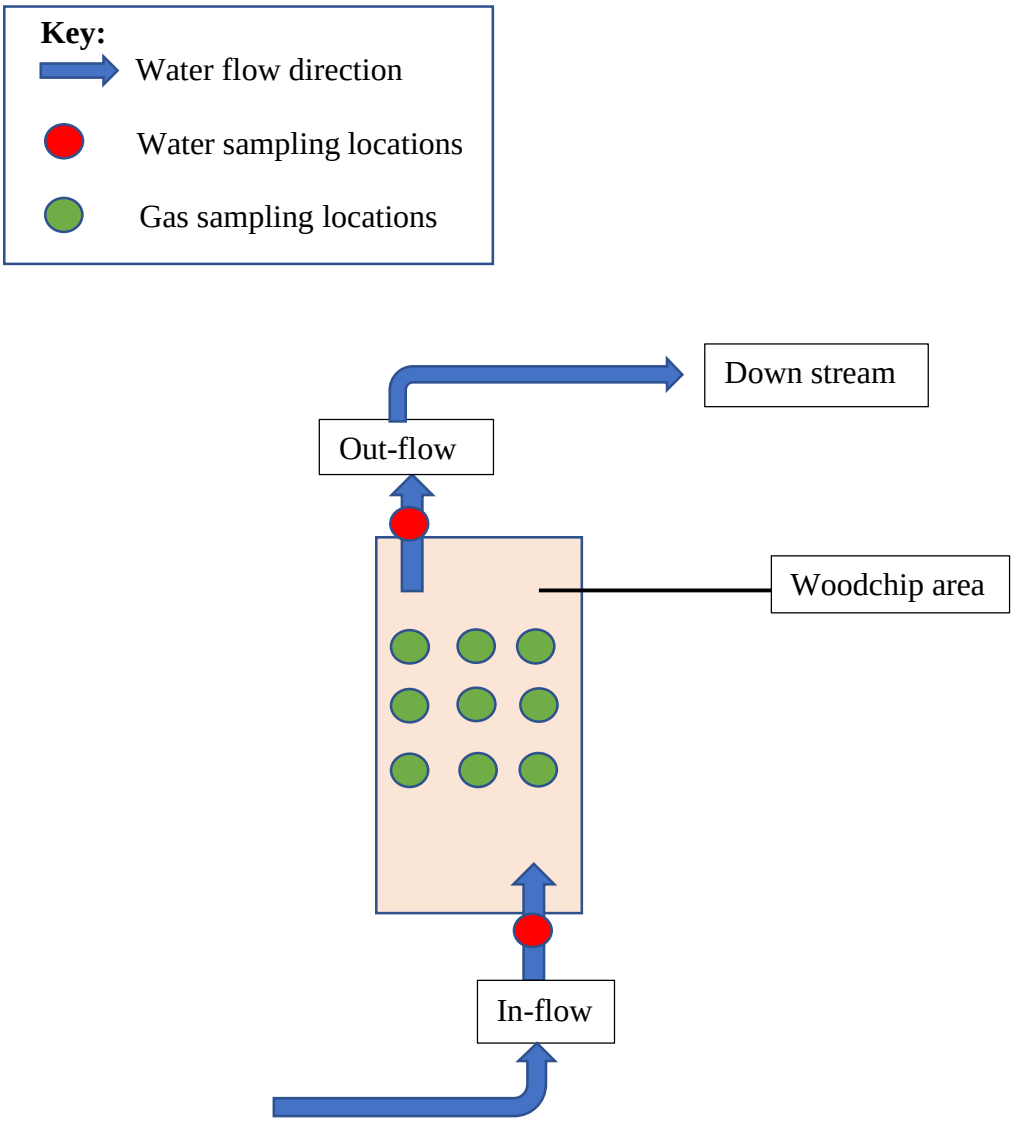

Figure 8. Schematic of bioreactor sampling locations.

5.2. Inflows and outflows

Hydraulic retention times were varied by roughly 5, 12, 16 and 24 hours. To vary the hydraulic retention times the inflow rates were adjusted by controlling the inflow valves. Equation 3 below shows how HRTs were calculated.

$$HRT = \tfrac{1}{2} (L1 + L2)\, w d\Theta / (q \times 3600/1000)$$

Where:
HRT = hydraulic retention time (hours)
L1 = length of top parallel base of bioreactor (m)
L2 = length of bottom parallel base of bioreactor (m)
w = width of bioreactor (m)

d = average depth of flow in bioreactor (m)
Θ = effective media porosity (%)
q = flow rate (L/s)

Equation 3. HRT formula (USDA, 2016).

To get an estimated HRT of 5, 12, 16, and 24 hours, the inflow rates for each sample run were estimated as:

Waitatapia: 0.60, 1.38, 0.43, 0.31 (L/s)
Te Maunga: 4.05, 3.12, 1.49, 0.59 (L/s)

These were adjusted using the inflow valve of the bioreactor at least 3 days before the sampling to ensure equilibrium will be reached by the system before sampling. Outflow readings from the ultrasonic flow meters were assumed to be the same as inflows. For calibrations of the flow meters see Appendix B.1.

5.3. Nitrogen from water samples

Nitrate nitrogen (NO_3-N) samples measured over 4 locations within each reactor (represented by the red dots in figure 8) were repeated 3 times. When travelling to and from the sampling sites to the laboratory, water samples were kept insulated to avoid the effect of temperature on dissolved nitrate levels. NO_3-N levels were measured using a calibrated TRIOS-OPUS nitrate sensor available in the Soil and Water Laboratory at Massey University, following a procedure as flows:


Figure 9. TRIOS-OPUS nitrate sensor.

- Use acetone to clean the lens.
- A 1:2 dilution may be needed if the nitrate concentration is above 100 mg/L.
- Path length of 10mm and a +/- accuracy of 5%, which is routinely checked.

5.4. Gas sampling from water

The nitrous oxide (N_2O) dissolved in water was sampled 3 times from 2 locations; inflow and outflow (represented by the red dots in figure 8).

In the field: 150 ml glass bottles were filled with flowing water from the 4 locations. Rinsed thoroughly, enough for 3 volumes to be passed through the glass bottles. Whilst they were

still underwater, the lids were crimped with watertight rubber seals. This was repeated 3 times per location.

In the lab: the glass bottles were placed upside down on a retort stand, 50 mL of water was extracted from each glass bottle by inserting a freely suspended needle in the rubber ring whilst 50 mL of inert nitrogen was pushed into the glass bottle with a syringe. The glass bottles were then shaken for 2 hours to mix so that the dissolved N_2O (g) is fully released from the solution and enter the gas phase with the unreactive nitrogen. Next step: 25 mL of nitrogen/nitrous oxide mix from the headspace of the glass bottles was extracted and inserted into a 12 mL evacuated vials. These headspace samples were then taken to Manaaki Whenua - Landcare Research to be analysed for N_2O (g).

5.5. Gas from water data processing

To calculate the total dissolved N_2O concentration in the original water samples, the concentrations of N_2O in the headspace samples (ppb) had to be converted into mg/L of dissolved N_2O-N. This was done using a method proposed by Roper et al. (2013). This required calculating the N_2O (mol) in the headspace, calculating the amount of N_2O (mol) dissolved in water, adding the two together and expressing this as a function of the volume of water of the sample (Roper et al., 2013). The molar concentration (mol/L) was then converted to mg/L (see Appendix A.4).

5.6. Gas sampling from chambers

For each bioreactor, 9 gas chambers were evenly installed 5 cm into the ground across the woodchip area, represented by the green dots in figure 8.

Figure 10. Gas chambers. Left: uninstalled and no lid. Right: Gas chamber buried in the ground with the lid on.

Gas samples were collected from the chambers (figure 10) using 2 syringes with 3-way stopcocks (figures 11 and 12). Gases were then mixed inside the chamber and syringes by pumping the syringes 3 times whilst ensuring no collected gases could mix with air. Collected gases were injected using a 0.45 μm syringe-tip into pre-evacuated 12ml vials.

Figure 11. 3-way stopcocks

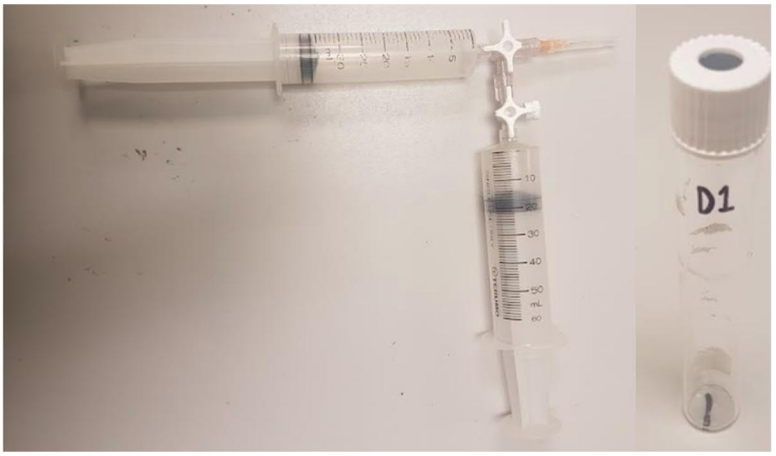

Figure 12. Left: 2 x 60 ml syringes. Right: evacuated vial.

- 3 samples were taken from each chamber at time intervals of 0, 20 and 40 minutes.
- Air samples were taken at t0, t20 and t40 minutes to measure background gases.
- Temperatures inside the chambers were measured once per sample run.
- Manaaki Whenua Landcare - Research analysed the concentrations of N_2O (g), CO_2 (g), and CH_4 (g).

5.7. Gas Chromatography

Manaaki Whenua - Landcare Research analysed the gas samples using a Shimadzu Nexus 2030 gas chromatogram (figure 13) that measured the concentrations in ppm of N_2O (g), CO_2 (g), and CH_4 (g). This technique uses pressurised, inert N_2 gas as a carrier gas that carries the sample to columns that physically separate different gases in the sample. The detector then produces an output graph that is proportional to their concentration (French, 2017).

Figure 13. Shimadzu Nexus 2030 gas chromatogram. (Source: Shimadzu, 2019)

5.8. Data processing gas samples from chambers

The average concentration of N_2O (g), CO_2 (g), and CH_4 (g) per time interval were plotted using Microsoft Excel. In equation 4 below, the slope of the graph represents the change in gas concentration over time (dc/dt), the slope was usually linear ($R^2 > 0.9$).

F = dc/dt * D * ((Mr)/(0.08206*(T+273))

Where:

- **F** is the gas flux (mg/m^2/h)
- **dc/dt** is the slope of the graph (change in the gas concentration over time)
- **D** is average depth of the sampling chamber (m)
- **Mr** is the molar mass of the element (12 or 14)
- **T** is the temperature (°C)

Equation 4. Conversion of gas flux concentrations (Saggar et al., 2004).

The ppm units were converted into mg N_2O-N/m^2/h, mg CO_2-C/m^2/h, mg CH_4-C/m^2/h. Average values per sample run were calculated (see Appendix A.1 A.2, and A.3). The measured fluxes of N_2O-N, CO_2-C and CH_4-C expressed as 'mg /m^2/h' were converted to 'g /m^3/day', by using the surface area and volume of woodchips in the bioreactors (see Appendix D.1).

6. Results

For each bioreactor the data was collected from 4 sampling runs between August 2022 and October 2022. Each subheading in this chapter relates to a defined research objective in the introduction.

6.1. NO_3-N removal

To measure how much nitrate nitrogen is being removed by the bioreactors, the Nitrate Removal Efficiency (NRE) and the Nitrate Removal Rate (NRR) were calculated using equations 5 and 6.

NRE (%) = (NO_3-N in - NO_3-N out) / (NO_3-N in)

NRR (g/m^3/day) = (NO_3-N in - NO_3-N out(mg/L)) * (flow rate (L/s) *60*60*24(seconds in a day))/1000 mg *volume of woodchips (m^3)

Equation 5, Equation 6. Nitrate removal indexes.

Table 1 presents the nitrate removal rates measured at the Waitatapia bioreactor. The average flow rate was 0.682 L/s and the average HRT was 15.1 hours (Table 1). It removed an average of 2.08 mg of N per litre of water passed through it. This resulted into an average NRR of 2.25 g/m^3/day, and the average NRE of 76.3%, which means 76.3% of the nitrate nitrogen entering the bioreactor, on average, was converted into other forms of nitrogen.

Sample run 1 had the highest NO_3-N input (4.07 mg/L). This is due to the sampling date (7th August) being wetter. Higher rainfall leads to an increase in water flow over the land surface. This runoff can carry nitrate pollutants from various sources, such as agricultural fields, into nearby water bodies like rivers, streams, and groundwater. Therefore, having a higher nitrate runoff and leaching potential.

Sample run 2 had the highest NRR with 5.24 g/m^3/day. Sample run 4 had the lowest with 0.70 g/m^3/day. Sample 2 is the highest performer because of the warmest sample day (17 °C). Samples 3 and 4 have low NO_3-N flowing into the bioreactor. This suggests that they are under N-limiting conditions. When there is a low nitrate input into the bioreactor, performance is limited.

Table 1. NO_3-N removal of the Waitatapia bioreactor.

	Sample run 1	Sample run 2	Sample run 3	Sample run 4	Average	STDEV
Flow rate (L/s)	0.602	1.385	0.428	0.314	**0.682**	0.5
HRT (h)	12.6	5.5	17.8	24.3	**15.1**	8
NO_3-N in (mg/L)	4.07	3.51	2.03	1.86	**2.87**	1
NO_3-N out (mg/L)	1.78	0.84	0.25	0.28	**0.79**	0.7
NO_3-N in - NO3-N out (mg/L)	2.29	2.67	1.78	1.58	**2.08**	0.5
NRE (%)	56.3	76.1	87.8	85.1	**76.3**	14
NRR (g/m^3/day)	1.96	5.24	1.08	0.70	**2.25**	2

The Te Maunga bioreactor's average NRR was 3.7 g/m^3/day. The average flow rate was 2.31 L/s and the average HRT was 16.5 hours. It removed an average of 2.94 mg of N per litre of water passed through it. The average NRE was 76.5 %. These are shown in Table 2 below.

Sample 1 had the highest NRR of 7.14 g/m^3/day. This is due to having the largest input of N (4.92 mg/L). In this sample N inputs were not limiting the NRR. Sample 4 had the lowest NRR of 0.39 g/m^3/day and the N inputs of sample 4 was much lower (2.39 mg/L). According to Lepine et al., (2016), low NO_3-N values entering the bioreactor below 3 mg/L become a limiting factor on bioreactor performance.

Table 2. NO_3-N removal of the Te Maunga bioreactor.

	Sample run 1	Sample run 2	Sample run 3	Sample run 4	Average	STDEV
Flow rate (L/s)	4.05	3.12	1.49	0.59	**2.31**	2
HRT (h)	5.6	7.2	15.1	38.3	**16.5**	15
NO_3-N in (mg/L)	4.92	3.64	4.11	2.39	**3.77**	1
NO_3-N out (mg/L)	1.25	0.48	0.55	1.00	**0.82**	0.4
NO3-N in - NO3-N out (mg/L)	3.67	3.16	3.56	1.39	**2.94**	1
NRE (%)	74.7	86.7	86.6	58.0	**76.5**	14
NRR (g/m^3/day)	7.14	4.72	2.55	0.39	**3.70**	3

Figure 14 below shows that as the HRT of each bioreactor increases, NRR exponentially decreases. At lower the HRTs, the flow rate is higher, therefore, if more water is being passed through at a faster rate per day, even at a lower NRE, the total NRR will be greater because more grams of NO_3-N can be removed per m^3 of woodchip per day.

At higher HRTs, the flow rate is lower and the NRR is much lower. This could be due to the drainage water inflow moving too slow and potentially not reaching the full volume of woodchips. This would mean less surface area of woodchips is maximised which would therefore limit microbial activity for denitrification.

The high R^2 values (0.9473 and 0.9872) indicate that the regression model is a good fit for the data and that a large proportion of the variance in the NRR is explained by the change in HRT for both bioreactors.

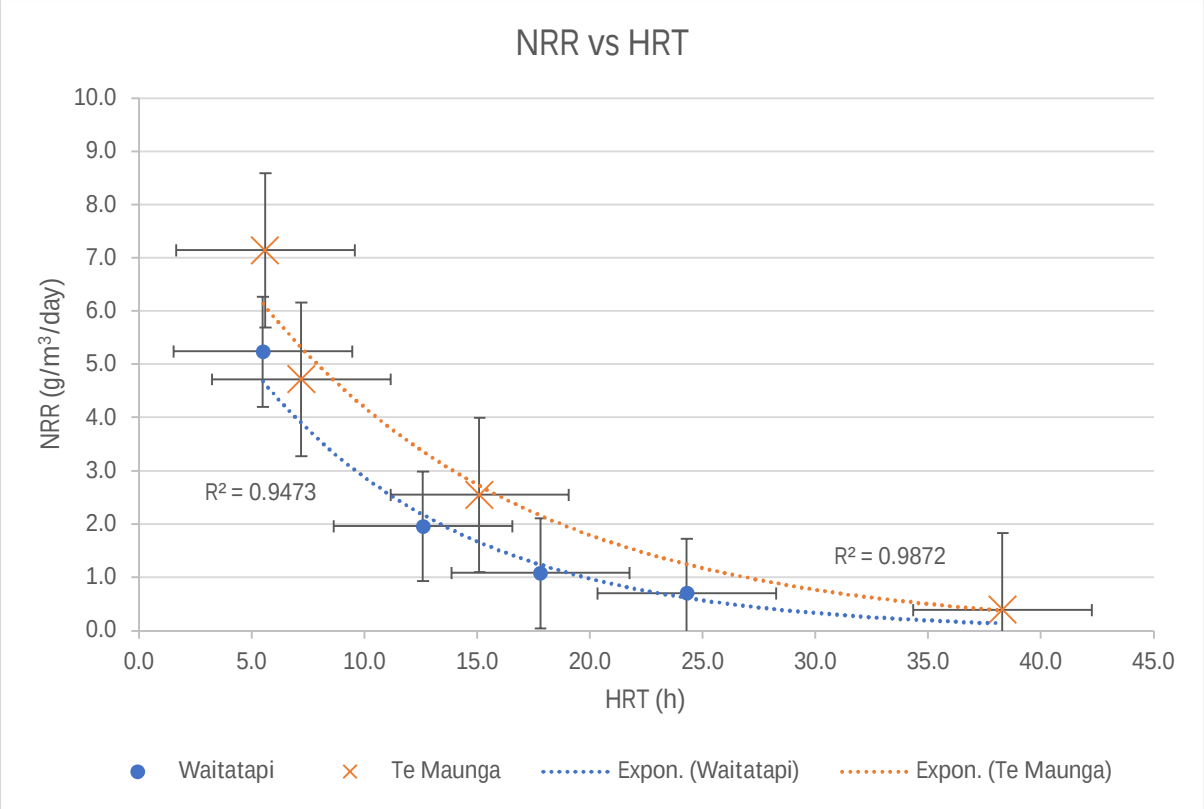

Figure 14. Relationship between Nitrate Removal Rate (NRR) and Hydraulic Retention Time (HRT). Error bars represent the standard error.

Figure 15 below shows a weakly directly proportional relationship between NRE and HRT. The scatter points are too far apart to distinguish a trendline from this graph.

One reason for the high variation is sensitivity to initial concentration. Nitrate removal efficiency is highly sensitive to the initial nitrate concentration of the inflow. When the inflow nitrate concentration varies, the removal efficiency can vary significantly even if the removal rate remains relatively constant.

Another possible reason for the high variation in nitrate removal efficiency may be the variability of temperature of the water entering the bioreactor. Water temperature can fluctuate seasonally and daily. Warmer temperatures typically promote microbial activity and denitrification, while cooler temperatures may slow down these processes.

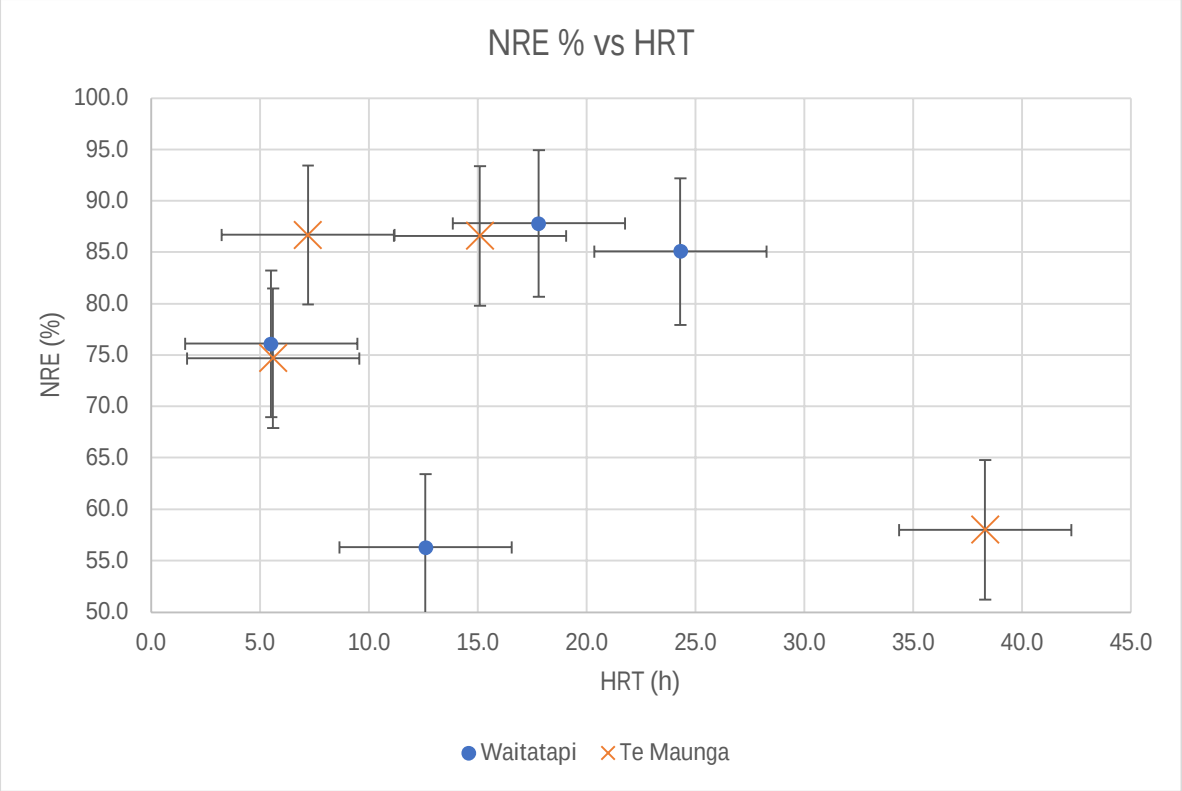

Figure 15 . Relationship between Nitrate removal efficiency (NRE) and Hydraulic Retention Time (HRT). Error bars represent the standard error.

6.2. Nitrogen dioxide (N_2O-N) produced / nitrate-nitrogen (NO_3-N) removed

In woodchip bioreactors, the ratio of N_2O-N/NO_3-N is an important in determining the denitrification performance. The Waitatapia bioreactor results in Table 3 show that the average N_2O-N dissolved in water that is produced by the bioreactor (out – in) is 174.78 mg/h. The sampling runs 1 and 2 both indicated that water travelling out the bioreactor had an increased dissolved N_2O-N by 172 and 535 mg/h respectively when compared to inflow of water. While sampling runs 3 and 4 indicated a decrease in N_2O-N dissolved in water by 6.52 and 1.77 mg/h, respectively.

The average rate of N_2O-N gas released into the atmosphere was estimated as 0.93 mg/h.
The average total rate of N_2O-N produced (dissolved + gas) was estimated as 175 mg/h, compared to the average rate of N_3O-N removed of 5,701 mg/h (Table 3)
The average ratio of N_2O-N produced/NO_3-N removed is quantified at 1.81%. This means that of the total NO_3-N that was reduced form the water inflow, 1.81% was converted into harmful N_2O. With N_2O gas contributing 0.5% and N_2O dissolved contributing 99.5%.

Table 3. Waitatapia N_2O-N levels and percentage ratio of N_2O-N produced to NO_3-N removed.

	Sample 1	Sample 2	Sample 3	Sample 4	Average
Flow rate (L/s)	0.602	1.385	0.428	0.314	0.682
HRT (h)	12.7	5.5	17.8	24.3	15.1
N_2O-N in (mg/h)	10.42	33.26	6.93	2.54	13.29
N_2O-N out (mg/h)	182.69	568.40	0.41	0.77	188.07
Dissolved N_2O-N (out - in)(mg/h)	172.27	535.15	-6.52	-1.77	174.78
N_2O-N air (mg/h)	0.44	1.88	1.51	-0.10	0.93
Total N_2O-N (mg/h)	172.71	537.02	-5.01	-1.87	175.71
Total N_3O-N removed (mg/h)	4963	13313	2743	1786	5701
N_2O-N produced / N_3O-N removed	3.48%	4.03%	-0.18%	-0.10%	1.81%

The Te Maunga bioreactor results in Table 4 show that the average N_2O-N dissolved in water that is produced by the bioreactor (out – in) is 261.2 mg/h. The sample run 1, 2 and 3 indicated that water travelling through the bioreactor was slightly increased in dissolved N_2O-N by 1009.5, 18.5, and 27.4 mg/h respectively. The sample runs 4 indicated a small decrease in N_2O-N dissolved in water by -10.6 mg/h.

The average rate of N_2O-N gas released into the atmosphere was 0.30 mg/h, and the N_2O-N dissolved released was 261.2 mg/h.
The average total rate of N_2O-N produced (dissolved + gas) was 262.5 mg/h.
The average total rate of N_3O-N removed was 19,070 mg/h (Table 4).
The average ratio of N_2O-N produced/NO_3-N removed was estimated at 0.77%. This means that of the total NO_3-N that was reduced form the water inflow, 0.77% was converted into harmful N_2O. With N_2O gas contributing 0.2% and N_2O dissolved contributing 99.8%.

Table 4. Te Maunga N_2O-N levels and percentage ratio of N_2O-N produced to NO_3-N removed.

	Sample 1	Sample 2	Sample 3	Sample 4	Average
Flow rate (L/s)	4.05	3.12	1.49	0.59	2.31
HRT (h)	5.6	7.2	15.1	38.3	16.5
N_2O-N in (mg/h)	59.2	91.7	37.0	14.6	50.6
N_2O-N out (mg/h)	1068.7	110.2	64.4	4.0	311.8
Dissolved N_2O-N (out - in)(mg/h)	1009.5	18.5	27.4	-10.6	261.2
N_2O-N air (mg/h)	0.8	-0.2	0.5	0.1	0.3
Total N_2O-N (mg/h)	1010.4	18.4	27.9	-10.5	261.5
Total N_3O-N removed (mg/h)	33388	29989	9548	3356	19070
N_2O-N produced /NO_3-N removed	3.03%	0.06%	0.29%	-0.31%	0.77%

The ratio of N_2O-N produced to NO_3-N removed per sample run of each bioreactor as a function of HRT is represented in the figure 16 below. The Waitatapia and Te Maunga bioreactors both showed a decrease in N_2O-N/NO_3-N ratio as the HRT increased. In the Waitatapia bioreactor, once the HRT reaches 22 hours the ratio becomes negative which means that there is no N_2O-N being produced.

A likely explanation of this is as HRT increases there is more contact time between microbes NO_3-N, hence, more complete denitrification and less incomplete denitrification occurs. This means that NO_3-N removed increases and N_2O-N produced decreases, resulting in a smaller ratio (Aalto et al., 2020). On the other hand, as HRT decreases, full removal of nitrate becomes less likely due to microorganisms in the woodchips not having enough time to reduce nitrate. This can result in lower NO_3-N removed and more N_2O-N being produced, increasing the ratio (Aalto et al., 2020).

The Waitatapia's R2 value of 0.8007 indicates that there is a high level of correlation between the ratio of N_2O-N/NO_3-N and the HRT within the range of 5 to 25. This degree of correlation between the ratio of N_2O-N/NO_3-N and the HRT in the woodchip bioreactors is likely because the HRT influences the rate and completeness of denitrification, affecting the ratio of N_2O-N/NO_3-N (Aalto et al., 2020).

For calculations of the N_2O-N/NO_3-N ratio see Appendix C.1.

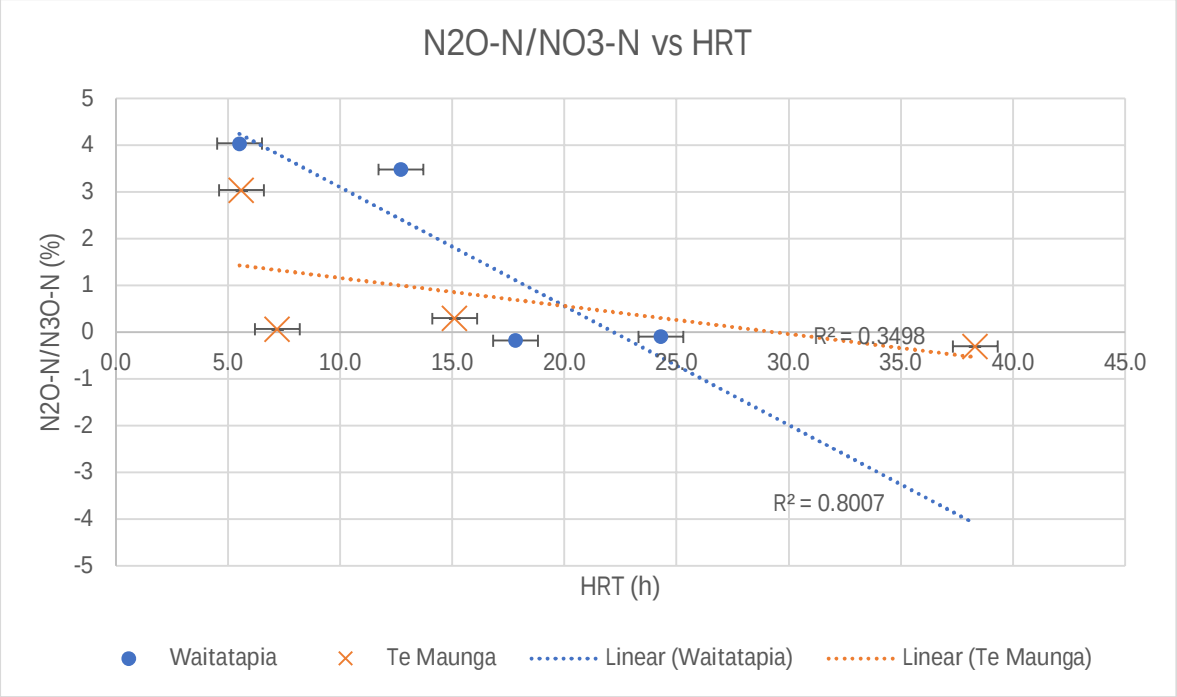

Figure 16. Relationship between N2O-N produced/NO3-N removed and Hydraulic Retention Time (HRT).

6.3. Carbon dioxide (CO_2) and Methane (CH_4) fluxes

Table 5 shows that the Waitatapia bioreactor produced an average CO_2 flux of 6.13 g CO_2-C/m^3/day and an average CH_4 flux of 5.10E-03 g CH_4-C/m^3/day. The largest CO_2 flux was measured in sampling run 2 (6.35 g CO_2-C/m^3/day) which had the highest flow rate and lowest HRT. The largest CH_4 flux was measured in sampling run 4 (7.24E-03 CH_4-C/m^3/day) which had the lowest inflow rate and the highest HRT.

Table 5. Waitatapia CO2 and CH4 fluxes.

	Sample 1	Sample 2	Sample 3	Sample 4	Average	STDEV
Flow rate (L/s)	0.602	1.385	0.428	0.314	**0.682**	0.5
HRT (h)	12.7	5.5	17.8	24.3	**15.1**	8
CO_2 flux (g CO_2-C/m^3/day)	5.86	6.35	5.95	6.34	**6.13**	0.3
CH_4 flux (g CH_4-C/m^3/day)	5.65E-04	6.20E-03	6.38E-03	7.24E-03	**5.10E-03**	0.003

Table 6 shows that the Te Maunga bioreactor produced an average CO_2 flux of 0.441 g CO_2-C/m^3/day and an average CH_4 flux of 3.17E-03 g CH_4-C/m^3/day. The largest CO_2 flux was measured in sampling run 2 (0.678 g CO_2-C/m^3/day) which had a flow rate of 3.12 L/s and an HRT of 7.2 hours. The largest CH_4 flux was measured in sampling run 3 (7.34E-03 g CH_4-C/m^3/day) which had a flow rate of 1.49 L/s and an HRT of 15.1 hours.

Table 6. Te Maunga CO_2 and CH_4 fluxes.

	Sample 1	Sample 2	Sample 3	Sample 4	Average	STDEV
Flow rate (L/s)	4.05	3.12	1.49	0.59	**2.31**	2
HRT (h)	5.6	7.2	15.1	38.3	**16.5**	15
CO_2 flux (g CO_2-C/m^3/day)	0.361	0.678	0.328	0.398	**0.441**	0.2
CH_4 flux (g CH_4-C/m^3/day)	4.16E-04	4.58E-03	7.34E-03	3.33E-04	**3.17E-03**	0.003

The CO_2 fluxes of each bioreactor's sampling runs as a function of HRT are shown in figure 17 below. The graph indicates that the Waitatapia and Te Maunga's CO_2 fluxes are constant for both sites, regardless of HRT. Low R^2 values show the trendline between CO_2 flux and HRT is a weak relationship.

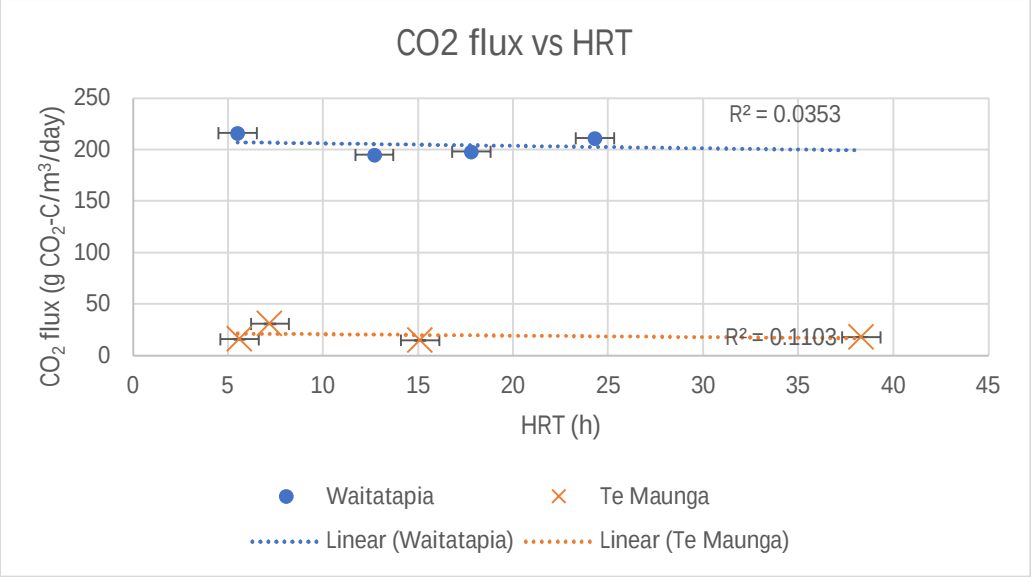

Figure 17. Relationship between CO2 flux and Hydraulic Residence Time (HRT).

The CH_4 flux of each bioreactor's sample runs as a function of HRT is shown in figure 18 below. The widely spread data point on the scatter graph illustrate that there is little if any correlation between the Waitatapia and Te Maunga's CH_4 fluxes and the HRT. This is due to very small concentrations of gas being produced that highly fluctuate with seasonal variation (de Klein et al., 2001).

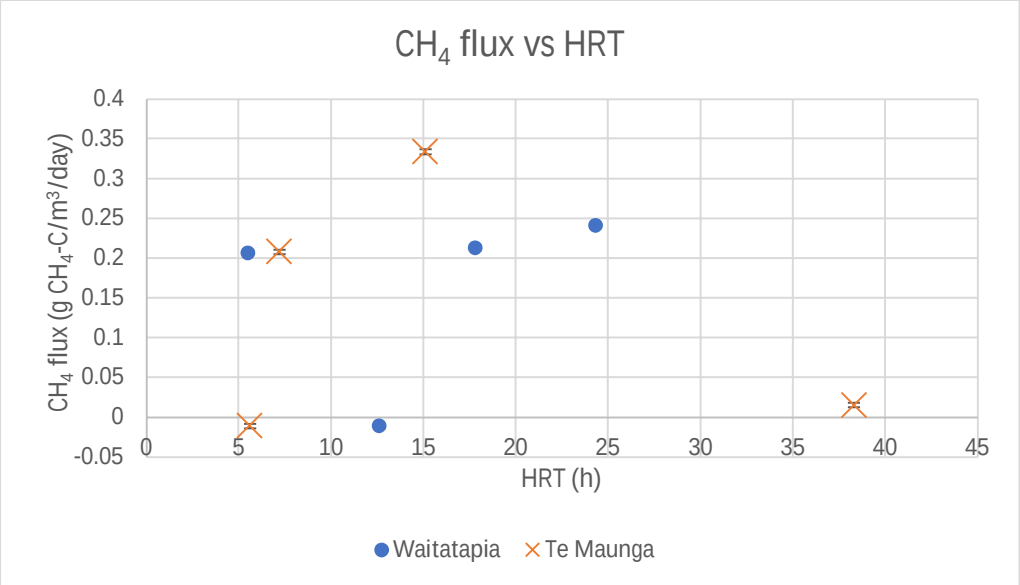

Figure 18. Relationship between CH4 flux and Hydraulic Residence Time (HRT).

7. Results Discussion

7.1. NO_3-N removal

Existing studies in Canada, America and in New Zealand, show that denitrification bioreactors have produced average Nitrate Removal Efficiencies (NREs) of:

- 18 – 100% (Elgood et al., 2010)
- 10 – 99% (Goeller et al., 2019)
- 20 – 40% (27 (Christianson et al., 2021)

and average NRRs of:

- 5 – 10 g N/m^3/day (Schipper et al., 2010).
- 9.6 g N/m^3/day (Christianson et al., 2020).
- 0.67–1.60 g N m^3/day (Rivas et al., 2019).

Tables 1 and 2 show that the performances of both bioreactors in terms of reducing nitrate levels of incoming drainage waters. The Waitatapia bioreactor had an average Nitrate Removal Efficiency (NRE) of 76.3%, and the Te Maunga bioreactor had a similar NRE of 76.5%. These results show that the bioreactors have higher efficiency when compared to Christianson et al and are within the ranges of efficiencies produced by studies from Elgood et al and Goeller et al.

The Waitatapia bioreactor removed, on average, 2.25 g NO_3-N/m^3/day. The Te Maunga performed better as it removed on average 3.7 g NO_3-N/m^3/day. These results are comparable to previous studies. A possible reason for Te Maunga's better performance is that Te Maunga has roughly twice the volume of woodchips than Waitatapia. A carbon source is necessary for the bacteria in denitrification bioreactors to convert nitrate to nitrogen gas. According to Hassanpour et al. (2017), the availability of the organic carbon sources directly affects the nitrate removal rate. They stated that carbon source availability is directly related to microbial activity, and once carbon availability reduces to a certain level it becomes a limiting factor in the bioreactor's performance.

Another factor that explains why Waitatapia has lower nitrate removal is controlled drainage. Controlled drainage helps reduce nitrogen leaching by slowing the movement of water through the soil. Slowing the movement of water through the soil allows for more opportunity for micro-organisms to deplete oxygen in soil water, thus promoting more reducing conditions that are more conducive to nitrate reduction (Ayars et al., 2006). Controlled drainage is a technique that lowers the N concentration before entering the bioreactor. NO_3-N values entering the bioreactor below 3 mg/L becomes a limiting factor on bioreactor performance (Lepine et al., 2016). Nitrate-rich water is necessary for denitrification to occur, as it is the primary form of nitrogen that the bacteria can use. Therefore, Waitatapia's lower nitrogen inputs may be a limiting factor on denitrification performance.

Figure 14 shows the relationship between NRR and HRT. The NRRs of both bioreactors exponentially decreased as HRT increased. This is because NRR is plotted in g/m^3/day and

therefore if more water is being passed through at a faster rate per day, the total NRR will be greater. Lower retention times will remove NO_3-N at a greater efficiency due to the storage of water for longer periods of time allowing more microbial respiratory activity and hence more denitrification occurs (USDA, 2016). Farmers need to be cautious, as longer retention times could cause other pollutants to be produced. For example, if HRTs are too long and the efficiency reaches 100%, all nitrates are removed, thus, promoting the production of unwanted greenhouse gases, such as, nitrous oxides and methane (Woli et al., 2010).

7.2. N_2O-N produced / NO_3-N removed

The results produced from this experiment illustrate that the lowest HRTs produced the highest N_2O emissions for both bioreactors. This is shown in Table 3 and 6 where the lowest HRTs of 5.5 and 5.6 produced the highest total N_2O-N levels of 537 and 1010 mg/h, respectively.

The exact ratio of N_2O-N produced to NO_3-N removed in woodchip bioreactors depends on the efficiency of the system. According to Aalto et al. (2020), N_2O-N produced is much lower than NO_3-N removed, as most of the nitrogen is removed in the form of nitrated-nitrogen. However, under high $NO3^-$ input concentrations and low amounts of bioavailable carbon, circumstances do occur when N_2O-N produced can be relatively higher. This is because the woodchips provide a large surface area for bacteria to colonize and produce nitrous oxide, which is then released into the atmosphere (Aalto et al., 2020).

Tables 5 and 6 illustrate the measurements and process used to obtain the ratio of N_2O-N produced/ NO_3-N removed for each bioreactor. Waitatapia's average N_2O-N produced/ NO_3-N removed is 1.18% with N_2O gas contributing 0.5% and N2O dissolved contributing 99.5%. Te Maunga's average N_2O-N produced/ NO_3-N removed is 0.77%. N_2O gas contributed 0.2% and N_2O dissolved contributed 99.8%. Both bioreactors produced low ratios which means there is low pollution swapping. N_2O is a highly water soluble greenhouse gas that is an intermediate product of the denitrification process (see equation 1). This suggests anaerobic conditions are being achieved to allow for complete denitrification and hence low levels of N_2O pollution swapping. These results agree with previous studies that show that N_2O gas emissions from the surface of bioreactors are generally between 0.002 and 0.89% of the NO_3-N removed (Hartfiel et al., 2022), with the majority of these N_2O emission being dissolved. Although these are small levels of N_2O (g) being emitted, N_2O has 298 times the global warming potential of CO_2, therefore it is important to note the small amounts being produced (Skiba & Rees, 2014).

Figure 16 shows the relationship between N_2O-N produced/ NO_3-N removed and HRT. Waitatapia and Te Maunga both showed a slight increase in N_2O-N/NO_3-N as HRT increased. This is logical because as HRT increased NO_3-N removal rate exponentially decreased (figure 14). According to Hartfiel et al. (2022), lower HRTs are more likely to produce higher emissions of N_2O due to insufficient time for the denitrification process. This would increase the N_2O-N/NO_3-N ratio.

7.3. CO_2 flux

CO_2 gas is a greenhouse gas produced from the decomposition of woodchips, where the organic carbon, needed for the denitrification process to occur, is oxidised (Healy et al., 2012).

Table 5 shows the average CO_2 fluxes of both bioreactors from each sample run. The Waitatapia bioreactor produced an average CO_2 flux of 205 g CO_2-C/m^3/day, whereas the Te Maunga bioreactor produced an average CO_2 flux of 20 g CO_2-C/m^3/day. The difference between the two bioreactors is likely due to Waitatapia having a layer of soil covering the woodchips, whereas Te Maunga has no soil as its woodchips exposed to the air. Soil can produce carbon dioxide gas through various natural processes. One of the primary mechanisms for CO_2 production in soil is microbial respiration. Microorganisms in soil, including bacteria and fungi, break down organic matter as part of their metabolic processes. During this breakdown, they consume organic carbon compounds and release carbon dioxide as a byproduct. This a fundamental component of the carbon cycle. This would explain the therefore Waitatapia's elevated CO_2 levels.

According to Ford-Robertson et al. (1999), pasture in New Zealand is estimated to produce between 1 and 5 tonnes of carbon dioxide per hectare per year and soil produces 50 kg of carbon dioxide per hectare per year. The bioreactor's CO_2 emissions are difficult to compare to NZ's average pasture growing conditions due to the carbon dioxide produced by pastures being widely dependent on the type of soil and climate conditions. This research was carried out in the spring, where pasture growth rates and plant respiration rates are high, hence the CO_2 levels released by pasture will be high.

Figure 16 displays the relationship between CO_2 flux and HRT. A study undertaken by Bock et al., (2018), measured the CO_2 flux rates produced with HRTs of 3, 6 and 12 hours. Their results indicated that CO_2 fluxes were not considered to increase net GHG emissions for all ranges of HRT. This agrees with the results of this thesis as both bioreactors showed that CO_2 levels remained relatively constant for various HRTs. This shows that varying the HRT of the 2 bioreactors, over this trial period, produced no apparent effect on CO_2 flux.

7.4. CH_4 flux

CH_4 is produced by bacteria called methanogens which are in competition with denitrifying bacteria. At high nitrate concentrations the denitrifying bacteria outcompete the methanogens (Liu et al., 2017), however at low nitrate concentrations methanogens are more prevalent, hence the bioreactors produce more methane and is less efficient in nitrate removal.

Waitatapia produced an average CH_4 flux of 0.162 g CH_4-C/m^3/day and Te Maunga produced a similar average CH_4 flux of 0.136 g CH_4-C/m^3/day. Methane production from soil is much less than that of carbon dioxide and is estimated to be between 0.1 and 1.0 kilograms of methane per hectare per year. According to a study by New Zealand's Ministry for Primary Industries, the average annual methane emission rate from pastures without livestock is 0.36 kg per hectare per year. CH_4 emissions produced by the bioreactors are also hard to compare to NZ's average pasture growing conditions due to the methane produced by pasture is widely dependent on soil type, climate conditions, and livestock intensity and breed.

Figure 18 displays the relationship between CH_4 flux and HRT. A study undertaken by Davis et al., (2019), observed that methane was produced at all three hydraulic residence times. The shortest hydraulic residence time resulted in the lowest amount of methane generated. This meant that the CH_4 production during the shortest hydraulic residence time.

Figure 18 agrees with Davis et al., conclusions as there is methane produced at every HRT. However, the graph shows a wide scatter of data points, illustrating that there is no apparent correlation between CH_4 fluxes and HRT during these sampling dates. The results indicate that for these bioreactors, there is no HRT range that would minimise emissions of CO_2 and CH_4. This could be due to the short range of HRTs used in the experiment. Ideally there needs to more data points over a longer trial period to get a better statistical representation.

7.5. Limitations

Seasonal variation in temperature, precipitation and drainage flows can influence bioreactor performance (Hassanpour et al., 2017). This research was carried out over a short timeframe between late winter to mid spring 2022, which means other seasons were not considered. Greater rates of denitrification, hence lower NO_3-N concentration could be seen during higher temperatures in summer. A study undertaken by Hoover et al. (2016), showed that by increasing the temperature of the water in the bioreactor from 10 to 20 °C, the NRR had a stepped increase of 2.2 to 2.9 g/m^3/day. This was caused by an increase in microbial activity and lack of dissolved oxygen.

Woodchip bioreactor designs are generally capable of treating 10-20% of peak drainage flow (Hoover et al., 2016). Bypass flow pipes are a design feature of woodchip bioreactors to prevent overflow and flooding during periods of high rainfall and surface runoff. However, it allows untreated water to bypass the bioreactor. It is important to consider this trade-off between allowing high inflows and low HRTs to result in high NO_3 reduction, whilst also reducing the environmental risk of flooding (Herbstritt, 2014).

7.6. General discussion

During the spring of 2022, results indicate that the denitrification bed bioreactors situated on Waitatapia Station and Te Maunga farms removed an average 2.25 and 3.70 g NO_3-N/m^3/day, with an efficiency of 76.3 and 76.5 % respectively (Tables 1 and 2). This helps support the literature that denitrification bioreactors are a potential end-of-pipe technique that can be used to effectively reduce NO_3 concentrations in water before entering the downstream environment.

Further investigation into the by-products of the denitrification process showed that the Waitatapia Station and Te Maunga bioreactors produced, on average, 0.93 and 0.30 mg/h of N_2O-N gas. The average total rate of N_2O-N produced (dissolved + gas) was estimated as 175 and 261 mg/h (Table 3 and 4). These levels of pollutants emitted are far outweighed by the average total N_3O-N removed from the water (5,701 and 19,070 mg/h). Low levels of methane (CH_4) produced by both Waitatapia Station and Te Maunga bioreactors (were

(5.10E-03 and 3.17E-03 g CH4-C/m3/day). Low levels of carbon dioxide (CO_2) were also produced (6.13 and 0.441 g CO2-C/m3/day).

This practice should be considered as part of a suite of on-farm nitrate mitigation practices. Sustainable practices that can improve overall N removal include controlled drainage, riparian planting, taking stock off paddock during winter grazing periods, N fertiliser management, etc.

Installation of larger bioreactors in multiple water catchments could perhaps increase their positive impact on water quality and assist farmers in reaching N leaching targets below the limits set by the government and regional councils.

8. Research recommendations

This thesis recommends further studies on the effect of varying water temperature, carbon availability, and dissolved oxygen concentrations on denitrification performance. To account for seasonal variability this research could be carried out in a laboratory under consistent conditions with more replicates. Altering an exact range of dissolved oxygen concentrations, carbon inputs, and temperatures entering the bioreactor model would test to see their impact on nitrate removal. Additionally, a recommended study would be to investigate using different types of readily available woodchips in NZ and analysing the effect that these have on denitrifying microbial activity, nitrate removal and pollution swapping.

9. Conclusions

This thesis supports the conclusion that denitrifying bioreactors are a potentially effective mitigation measure to reduce nitrate levels at end-of-pipe water catchment sites in the agriculture industry.

During the spring of 2022:

- The Waitatapia bioreactor removed, on average, 2.25 g NO_3-N/m^3/day, with an average Nitrate Removal Efficiency (NRE) of 76.3%.

- The Te Maunga bioreactor removed, on average, 3.7 g NO_3-N/m^3/day, with an average Nitrate Removal Efficiency of 76.5%.

- Results indicate that for both bioreactors there is strong correlation that as the HRT increases, NRR exponentially decreases, i.e., the longer the water was held in the bioreactors, the lower the flow rate, the less total water was passed per day, and the less total grams of NO_3-N per m^3 of water were removed per day.

- During the study it is estimated that 1.18% of NO_3-N removed was converted into N_2O-N in the Waitatapia bioreactor and 0.77% of NO_3-N removed was converted into N_2O-N in the Te Maunga bioreactor.

- Dissolved N_2O is the main pathway for N_2O leaving the bioreactor, with 99.5% and 99.8% of N_2O produced being in dissolved form and 0.5% and 0.2% in gaseous form for Waitatapia and Te Maunga respectively.

- Decreasing the flow rate of water through the bioreactor increases the HRT. By increasing the HRT, the N_2O-N produced decreases, therefore, the ratio of N_2O-N produced to NO_3-N decreases. In these New Zealand conditions, a higher HRT means that less N_2O-N GHG will be produced (Figure 16) but a lower total nitrate removal rate will be seen (Figure 14).

- The Waitatapia bioreactor produced an average CO_2 flux of 6.13 g CO_2-C/m^3/day and an average CH_4 flux of 5.10E-03 g CH_4-C/m^3/day.

- The Te Maunga bioreactor produced an average CO_2 flux of 0.441 g CO_2-C/m^3/day and an average CH_4 flux of 3.17E-03 g CH_4-C/m^3/day.

- Varying the HRTs of the 2 bioreactors produced no significant effect on CO_2 flux as CO_2 levels remain relatively constant.

- No significant correlation was found between CH_4 fluxes and HRT.

Further research is needed on the effect of seasonal variation so that best bioreactor management practices are defined to maximise NO_3-N removal, whilst also minimising the negative effects of N_2O, CO_2, and CH_4 greenhouse gases production under New Zealand conditions.

Declaration of competing interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

10. Appendices

Appendix A

A.1. N_2O-N (gas) data analysis calculation example

				Chamber air Temp (°C) =			17								
				weather:	OVERCAST					N2O-N			N2O-N	N2O-N	N2O
Plot No	Sample ID	depths (cm)	Average depth (m)	Sampling time (hr)	ppb N2O	ppm N2O	Temp °C	Slope ppm/hr	R^2	Flux linear mg	A	B	Non linear Mosier	Best choice	
1	Chamber 1	14	0.1328	0.00	333.38	0.33338	17	0.161	1.00	0.0252	0.0697	0.16130		0.0252	0.040
		14.4		0.33	382.60	0.3826									
		10.5	14.2	0.67	440.91	0.44091									
2	Chamber 2	13	0.1488	0.00	333.90	0.3339	17	0.114	0.99	0.0199	0.0478	0.11390		0.0199	0.031
		11		0.33	365.18	0.36518									
		19.2	16.3	0.67	409.83	0.40983									
3	Chamber 3	14.8	0.1420	0.00	337.07	0.33707	17	0.067	1.00	0.0111	0.0305	0.06666		0.0111	0.018
		15.9		0.33	361.12	0.36112									
		12	14.1	0.67	381.51	0.38151									
4	Chamber 4	14.6	0.1340	0.00	330.68	0.33068	17	0.253	0.97	0.0399	0.1020	0.25278		0.0399	0.063
		10.9		0.33	389.32	0.38932									
		13.6	14.5	0.67	499.2	0.4992									
5	Chamber 5	15.5	0.1625	0.00	331.94	0.33194	17	0.010	0.88	0.0020	0.0038	0.01037		0.0020	0.003
		14.9		0.33	333.15	0.33315									
		18.9	15.7	0.67	338.85	0.33885									
6	Chamber 6	11.8	0.1605	0.00	341.45	0.34145	17	0.079	1.00	0.0148	0.0338	0.07854		0.0148	0.023
		14.6		0.33	364.94	0.36494									
		20.8	17.0	0.67	393.81	0.39381									
7	Chamber 7	17.4	0.1380	0.00	0	0	17	0.845	0.90	0.1371	0.4626	0.84458		0.1371	0.215
		11		0.33	440.80	0.4408									
		12.9	13.9	0.67	563.05	0.56305									
8	Chamber 8	13	0.1263	0.00	327.92	0.32792	17	0.017	0.70	0.0026	0.0055	0.01719		0.0026	0.004
		12		0.33	327.17	0.32717									
		13	12.5	0.67	339.38	0.33938									
9	Chamber 9	14.4	0.1240	0.00	332.35	0.33235	17	0.366	0.98	0.0534	0.1490	0.36582		0.0534	0.084
		12.3		0.33	420.86	0.42086									
		10.9	12.0	0.67	576.23	0.57623									

	N2O flux (mg N2O-N/m^2/h)
n	9
Average	0.0340
S.D.	0.042169037
S.E.	0.014056346

A.2. CO_2 flux data analysis calculation example

Date	8-Sep-22														
Site description: Wet															
				Chamber air Temp (°C) =		13									
				weather:	WET										
Plot No	Treatment	Sample ID	depths (cm)	Average depth m	incubation time (hrs)	ppm CO2	Temp °C	Slope ppm/hr	R^2	Flux linear mgCO2-C/m^2/h	A	B	Non linear Mosier mg CO2-C/m^2/h	Best choice - CO2-C	Best choice CO2
1		Chamber 1	21	0.21	0.00	404.45	13	772.0647	0.774	83.17675	498.7308	-23.79533		83.17675	304.9814
			21		0.33	902.30									
			21	21.00	0.67	924.14									
2		Chamber 2	21	0.21	0.00	370.11	13	42.44565	0.884	4.572792	15.56395	-1.217261		4.572792	16.7669
			21		0.33	375.17									
			21	21.00	0.67	398.46									
3		Chamber 3	21	0.21	0.00	349.52	13	25.74087	0.911	2.773138	9.671134	-1.284541		2.773138	10.16817
			21		0.33	353.33									
			21	21.00	0.67	366.72									
4		Chamber 4	21	0.21	0.00	356.96	13	412.8949	0.760	44.48235	137.8904	-1.003499		44.48235	163.1019
			21		0.33	357.92									
			21	21.00	0.67	632.26									
5		Chamber 5	21	0.21	0.00	379.51	13	46.62667	0.952	5.023225	23.81356	-3.180894		5.023225	18.41849
			21		0.33	400.97									
			21	21.00	0.67	410.81									
6		Chamber 6	21	0.21	0.00	357.09	13	11.06356	0.987	1.191909	5.273602	-2.456954		1.191909	4.370333
			21		0.33	361.49									
			21	21.00	0.67	364.51									
7		Chamber 7	21	0.21	0.00	390.60	13	13.99762	0.867	1.508004	8.042516	-5.88125		1.508004	5.529349
			21		0.33	398.41									
			21	21.00	0.67	400.01									
8		Chamber 8	21	0.21	0.00	352.84	13	22.71028	0.998	2.446643	9.836059	-1.830325		2.446643	8.971025
			21		0.33	359.74									
			21	21.00	0.67	368.05									
9		Chamber 9	21	0.21	0.00	360.80	13	162.8331	0.760	17.54248	54.38268	-278.3846		17.54248	64.32241
			21		0.33	361.19									
			21	21.00	0.67	469.37									

	CO2 flux (mg CO2-C/m^2/h)
n	9
Average	18.0797
S.D.	28.12122131
S.E.	9.373740436

A.3. CH_4 flux data analysis calculation example

Date	7-Aug-22														
Site description:	Wet														
				Chamber air Temp (°C) =		13									
				weather:	WET										
Plot No	Treatment	Sample ID	depths (cm)	Average depth m	incubation time (hrs)	ppm CH4	Temp °C	Slope ppm/hr	R^2	Flux linear mgCH4-C/m^2/h	A	B	Non linear Mosier mg CH4-C/m^2/h	Best choice - CH4-C	Best choice CH4
1		Chamber 1	14	0.1328	0.00	6.950	13	0	**0.000**	0	0	0		0	0
			14.4		0.33	6.940									
			10.5	14.2	0.67	6.950									
2		Chamber 2	13	0.1488	0.00	6.930	13	1.41	**0.766**	0.107598205	0.475053763	-1.02173913		0.107598205	0.143345118
			11		0.33	6.950									
			19.2	16.3	0.67	7.870									
3		Chamber 3	14.8	0.1420	0.00	6.930	13	0.12	**0.842**	0.008741753	0.042666667	-1.142857143		0.008741753	0.01164599
			15.9		0.33	6.940									
			12	14.1	0.67	7.010									
4		Chamber 4	14.6	0.1340	0.00	6.970	13	-0.03	**0.750**	-0.002062315	-0.01	-1		-0.002062315	-0.002747469
			10.9		0.33	6.970									
			13.6	14.5	0.67	6.950									
5		Chamber 5	15.5	0.1625	0.00	6.970	13	-0.015	**0.250**	-0.001250471	-0.003333333	-0.5		-0.001250471	-0.00166591
			14.9		0.33	6.980									
			18.9	15.7	0.67	6.960									
6		Chamber 6	11.8	0.1605	0.00	6.950	13	0.045	**0.582**	0.003705241	0.039130435	4.285714286	0.014066583	0.014066583	0.018739867
			14.6		0.33	6.987									
			20.8	17.0	0.67	6.980									
7		Chamber 7	17.4	0.1380	0.00	6.920	13	0.045	**0.355**	0.003185815	0.09	1.5	0.007750421	0.003185815	0.004244225
			11		0.33	6.970									
			12.9	13.9	0.67	6.950									
8		Chamber 8	13	0.1263	0.00	6.920	13	0.045	**0.519**	0.002914559	0.045	3	0.009605911	0.009605911	0.012797243
			12		0.33	6.960									
			13	12.5	0.67	6.950									
9		Chamber 9	14.4	0.1240	0.00	7.000	13	-0.06	**0.923**	-0.003816822	-0.032	-4		-0.003816822	-0.005084869
			12.3		0.33	6.970									
			10.9	12.0	0.67	6.960									

	CO2 flux (mg CO2-C/m^2/h)
n	9
Average	0.0151
S.D.	0.035208809
S.E.	0.01173627

A.4. N_2O-N (dissolved) data analysis calculation example

Sample Name	N2O from GC	N_2O ppm from GC	Headspace of vial (l)	volume of liquid in vial	PN_2O(kPa)	Pa in liquid phase (Pa)	henry's gas constant (mol/m3 Pa)	R	T	N_2OHS	N_2OL	N_2O in liquid and gas phase	N_2O(µmoles/l)	N2O-N (mol/L)	N2O-N (g/L)	N2O-N (mg/L)
Inflow 1	2150.55	2.15055	0.04188	0.075	100.7	0.101	0.00024	8.314	292	0.003736	3.91E-06	0.00374	0.049864	4.99E-08	2.89E-06	0.002893
Inflow 2	1497.07	1.49707	0.04464	0.075	100.7	0.101	0.00024	8.314	292	0.002772	2.72E-06	0.002775	0.036997	3.7E-08	2.15E-06	0.002146
Inflow 3	6123.23	6.12323	0.04308	0.075	100.7	0.101	0.00024	8.314	292	0.010942	1.11E-05	0.010953	0.14604	1.46E-07	8.47E-06	0.008472
Outflow 1	258.94	0.25894	0.04072	0.075	100.7	0.101	0.00024	8.314	292	0.000437	4.71E-07	0.000438	0.005838	5.84E-09	3.39E-07	0.000339
Outflow 2	233.11	0.23311	0.04428	0.075	100.7	0.101	0.00024	8.314	292	0.000428	4.24E-07	0.000429	0.005714	5.71E-09	3.32E-07	0.000332
Outflow 3	92.59	0.09259	0.04416	0.075	100.7	0.101	0.00024	8.314	292	0.00017	1.68E-07	0.00017	0.002264	2.26E-09	1.31E-07	0.000131

A.5. Converting gas fluxes from mg/m^2/h to g/m^3 wood chips/day example

	CO_2 flux (mg CO_2-C/m^2/h)
n	9
Average	16.3958
S.D.	18.84615335
S.E.	6.282051117

Bioreactor dimensions	
Length (m)	15
Width (m)	11
Surface area (m^2)	165
Depth of saturated woodchips (m)	1.1
Volume of woodchips (m^3)	181.5
CO_2 flux (g CO_2-C/m^3/h)	0.35772654

Appendix B

B.1. Calibrations of flow meters

19/10/21

OUTFLOW			Actual Sampled	
Actual l/s	Meter	% Conformity	litres	Seconds
0.4299	0.3768	87.64%	1.35	3.14
0.4585	0.3768	82.19%	1.6	3.49
0.4502	0.3768	83.70%	1.4	3.11
0.2828	0.3016	106.66%	1.1	3.89
0.2755	0.3016	109.48%	1	3.63
Average Difference		90.05%		

INFLOW			Actual Sampled	
Actual l/s	Meter	% Conformity	litres	Seconds
1.3333	1.1944	89.58%	2.4	1.8
1.2048	1.1944	99.14%	2	1.66
1.2136	1.1944	98.42%	2.5	2.06
1.3939	1.1944	85.69%	2.3	1.65
1.1944	1.1944	100.00%	2.65	2.05
Average Difference		93.20%	Meter = 4.3 m^3/hr	

Appendix C

Example calculation of N_2O-N/NO_3-N:

Waitatapia sample run 1:

Average total removed NO_3-N: 2.29 mg/L
Average flow rate = 0.602 L/sec
= 2167.2 L/h
2.29 mg/L x 2167.2 L/h = 4,963 mg/h

Average N_2O (air) = 0.0058 mg N_2O-N/m^2/h
mg/m^2/h x Area (m^2) = mg/h
0.0058 x 75 = 0.435 mg/h

Average inflow N_2O-N (dissolved) = 0.0829 µmol/L
0.0829 / 10^6 = 8.29 x 10^{-8} mol/L
mol/L x Mr (N_2O-N) = g/L
(8.29 x 10^{-6}) x 58.013 = 4.81 x 10^{-6} g/L
g/L x 1000 = mg/L
(4.81 x 10^{-6}) x 1000 = 4.81 x 10^{-3} mg/L

Average flow rate = 0.602 L/sec
4.81 x 10^{-3} mg/L x 0.602 L/sec x 3600 = 10.42 mg/h

Repeat the same above for outflow N_2O-N to get 182.69 mg/h

Outflow – inflow: 182.69 – 10.42 = 172.27 mg/h

Total N_2O = N_2O (air) + N_2O (water)
= 0.435 mg/h + 172.27 mg/h
= 172.71 mg/h

% N_2O-N/NO_3-N = (172.71 mg/h) / (4,963 mg/h) x 100
= 3.48%
(Shown in Table 5).

Appendix D

D.1. Converting CO_2 gas fluxes from mg CO_2-C/m^3/h to g CO_2-C/m^3/day:

- Step 1 - multiply the **mg CO_2-C/m^2/h** by **the surface area (m^2)** of the bioreactor**.** The surface area of the bioreactor will be its Length (m) multiplied by its Width (m).
- Step 2 - multiply the Step 1 calculation **mg CO_2-C/h** by 24 to convert into **mg CO_2-C/day**
- Step 3 - divide the Step 2 calculation **mg CO_2-C/day** by 1000 to convert into **g CO_2-C/day**
- Step 4 - divide the Step 3 calculation **g CO_2-C/day** by the volume of woodchips (m^3) to convert into **g CO_2-C/ m^3/day**

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