The use of functionalised biochar to enhance phosphorus removal in woodchip bioreactors.

The integration of mātauranga Māori to enhance the cultural aspects of woodchip bioreactors.

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Abstract

Nutrient pollution, resulting from excessive releases of nitrogen (N) and phosphorus (P) into waterways, poses a significant threat to aquatic ecosystems worldwide. Elevated nutrient levels can result in eutrophication, which can have detrimental effects on the health of waterbodies and their biota. Woodchip bioreactors are effective, edge-of-field technologies that can help mitigate nutrient pollution by lowering nutrient concentrations in agricultural drainage systems known to carry leached N and P into waterways. However, one limitation to their design is their ineffectiveness at removing P. The inclusion of functionalised biochar is one potential solution to enhance P removal in woodchip bioreactors. There is a growing need to mitigate nutrient pollution in New Zealand that does not depend on a western-centric perspective only. Integration of mātauranga Māori and western science into the design and operations of a woodchip bioreactor is one approach to incorporate both knowledge systems to the goal of mitigating nutrient pollution. In this dissertation, a column experiment was used to compare the P removal efficiencies of two treatments of functionalised biochar, and one treatment of woodchips when subjected to stream water spiked with P. Subsequently, a single phosphate extraction was done to determine the phosphate absorption capacities of each treatment. The results showed that the two functionalised biochar treatments had the highest efficacy in reducing P concentrations in the P-spiked stream water compared to the woodchip-only treatment. Both treatments also showed higher P absorption, evidenced from the Fe-P/Feox ratio, within the phosphate extraction experiment. A wānanga was organised at Matahuru Marae, Lake Waikare, to share mātauranga Māori on how to culturally enhance woodchip bioreactors from a Te Ao Māori perspective. Participants recommended that native woodchips be incorporated into woodchip bioreactors because of their inherent association to the land and people. Overall, the results implied that functionalised biochar is an effective solution to enhance P removal in woodchip bioreactors due to their biophysical properties to absorb and retain P. Secondly, incorporating native woodchips into woodchip bioreactors systems potentially offers a sustainable and culturally respected alternative to conventional wood chips, aligning with Māori values and tikanga

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Table of Content

List of Figures

List of Tables

Māori translations

Hapū	Subtribe
Hauroa	Well-being
Iwi	Tribe
Kaitiakitanga	Guardianship/protection/stewardship.
Karakia	Prayer
Koha	Gift
Mahinga kai areas	Places of traditional food gathering.
Mana	Power
Mana whenua	People of the land
Mātauranga Māori	Traditional Māori knowledge.
Mauri	Life force
Mokopuna	Grandchildren
Papatūānuku	Earth mother
Pōwhiri	Welcoming
Puna	Natural spring sites
Pūrākau	Traditional Māori narratives.
Rangatahi	Individuals who are of adolescent youth.
Ranginui	Sky father
Te Ao Mārama	Relationship between the spiritual and natural world.
Te Ao Māori	Māori worldview and perspectives.
Tikanga	Māori traditional practises.
Tūpuna	Ancestor(s)
Waiata	Song
Wairua	Spiritual essence
Wānanga	Platform to share knowledge.
Whaikōrero	Formal speech
Whakapapa	Genealogy
Whenua	Land

Chapter 1
Introduction

The United Nations (UN) forecasted that due to increased fertility rates and falling death rates owing to longer life expectancy, the world's population will increase from 7.8 billion in 2022 to 9.3 billion by 2050, with an annual growth rate of 1.08% before peaking at 10.4 billion by 2100 (Roser et al., 2013). As the population rises, it is inevitable that this will have an impact on the planet's capacity to produce enough food. The Food and Agriculture Organization of the United Nations (FAO) suggested that by the year 2050 there will be a need for an additional 60% of more food to satisfy increased demands (Food and Agriculture Organization of the United Nations [FAO], 2018). To satisfy these needs, the world will turn to the agriculture sector to meet increasing global food demands (Shaw, 2008).

The agricultural sector is widely recognized as being the cornerstone of global food production, producing around 80% of the world's food. Agriculture also contributes 4% to 25% of a country's global gross domestic product (GDP) supplying two to four times as much employment and income than any other primary industry worldwide (Hobbs, 2007). Agriculture occupies around 38% of the total land area in the world, with croplands occupying 11%, and pasture lands occupying 27%. This equates to a total of 5 billion hectares of agricultural land used (Ramankutty, 2018). Farming is one of the key businesses that comprises the agricultural industry. Farming occupies the bulk of privately held agricultural land which is home to almost 460 million farms globally. Farming produces most of the world's agricultural goods, including food but also fabrics, biofuels, and raw materials (Ritchie & Roser, 2021). To sustain higher demands for food supply, it is projected that farmers would need to increase their food production by intensifying their practices per unit of input per hectare. This means increasing land, labour, and fertiliser usage to produce greater yields. Among all these anticipated increases, nutrient fertilisers pose one major threat to the health of the environment and the planet (Mallin, 2009; Ritchie & Roser, 2021).

Nutrient fertilisers are utilised to provide crops with vital nutrients for promoting accelerated growth and increased yields (Fixen et al., 2015). The application of nutrient fertilisers has rapidly increased since 1965, from 46.31 million metric tonnes to more than 200 million metric tonnes of nutrient fertilisers used in 2022. It is anticipated that 105 million tonnes more are to be required in 2050 as the need for more food continues to increase (Statista, n.d.). Nitrogen

(N) and phosphorus (P) are the two minerals found in nutrient fertilisers. They are necessary for successful growth and development of plants and crops. However, losses of excessive amounts of these two plant nutrients from agricultural land can have serious environmental problems, one of which is nutrient pollution in waterways (Rovira & Pardo, 2006; Fixen et al., 2015).

Nutrient pollution is the process through which nutrients, frequently N and P, enter bodies of water causing eutrophication (Rovira & Pardo, 2006). Eutrophication promotes the dense growth of plant and algae growth in bodies of water. This can have serious repercussions towards the environment, such as decreased water quality, the formation of toxic algal blooms and the creation of hypoxic "dead" zones (Glibert et al., 2005). Smith et al. (2016) demonstrated the significance of limiting N and P input to prevent eutrophication in Lake Rotorua. The degradation of water quality in the lake has been observed since the late 1800s, attributed by changes in land-use and clearing of vegetation. Alum dosing was introduced into Lake Rotoura in the early 2000's to provide reductions in total nutrients and chlorophyll-*a*. An assessment conducted in 2006 predicted that alum dosing would decrease total phosphorus (TP) from 60 mg m^{-3} to 15 mg m^{-3}, decrease total nitrogen (TN) ranging from 400-600 mg m^{-3} to 250 mg m^{-3}, and lower chlorophyll-*a* (Chl-*a*) levels from 20 mg m^{-3} to 10 mg m^{-3} over a 9-year period. However, despite these outcomes, it was concluded that this method would not be sustainable for long term mitigation, since continuous additions of alum would potentially pose a threat to freshwater life (Smith et al., 2016).

One relatively recent technology being used to mitigate nutrient pollution is denitrifying woodchip bioreactors. Denitrifying woodchip bioreactors are simple and effective edge-of-field mitigation systems designed for agricultural tile drainage, with the purpose of reducing high concentrations of nitrate in farm effluent water (Schipper et al., 2010). Published studies have shown the efficacy of denitrifying woodchip bioreactors in the field. One study by Christianson et al. (2012) demonstrated the efficacy of four field-scale denitrifying woodchip bioreactors used to lower nitrogen concentrations in agricultural drainage in Iowa, United States. The four bioreactors had different initial nitrate-nitrogen influent concentrations, with one bioreactor exhibiting low concentrations ranging from 1.23 mg NO_3^--N L^{-1} to 8.54 mg NO_3^--N L^{-1}, while the remaining three bioreactors had higher concentrations, ranging from 7.70 mg NO_3^--N L^{-1} to 15.18 mg NO_3^--N L^{-1}. The study reported a range of annual rates for nitrate removal for all bioreactors, which varied from 0.38 to 7.76 g m^{-3} d^{-1}. The nitrate load reductions were also found to vary between 12% to 76% (mean: 45%) for flow through the bioreactor and

12% to 57% (mean: 32%) for total flow, including bypass flow. These results corresponded to a range of 0.5 to 15.5 kg N ha^{-1} removed (Christianson et al., 2012). A second study by Christianson et al. (2021) compared the efficacy of woodchip bioreactors in the Midwestern United States to the rest of the world. Findings indicated that Midwestern woodchip bioreactors demonstrated an annual rate of nitrate-nitrogen removal between 20% and 40%, like bioreactors around the world. When compared to New Zealand, Denitrification beds demonstrated higher daily rates of nitrate removal ranging from 5 to 10 g N m^{-3} d^{-1} (Christianson et al., 2021) Although denitrifying woodchip bioreactors are sufficient at removing significant quantities of N, they are less effective at removing P.

According to Sanchez Bustamante-Bailon et al. (2021), improving phosphorus removal in denitrifying woodchip bioreactors is crucial due to the co-occurrence of nitrogen and phosphorus in farm runoff (Sanchez Bustamante-Bailon., 2021) Husk et al. (2018) supports this assertion by stating that even a low concentration of P can trigger eutrophication in the presence of nitrogen (Husk et al., 2018). Previous research has placed significant emphasis on the use of mix-media substrates as a potential solution for enhancing P removal in woodchip bioreactors (Husk et al., 2018). The mix-media substrate used in this dissertation was functionalized biochar. Biochar is a carbon-rich material produced by the pyrolysis of biomass, such as agricultural waste, woodchips, or organic residue. Due to its unique absorption characteristics, it is often regarded as a viable absorbent of N and P nutrients (Weidner et al., 2022). Functionalized biochar refers to biochar that has been enhanced in terms of their physio-chemical characteristics and absorption efficacy by chemical, physical or biological activation, (Hamid et al, 2022). This is one way in which P removal in woodchip bioreactors might be enhanced.

Solutions aimed at reducing nutrient pollution have predominantly been derived from a western scientific perspective and methodology. Although this perspective is prevalent in the sciences, it is not the only perspective from which solutions can be derived from. Bala & Gheverghese (2007) assert that there is an urgent need to progress beyond the strict adherence of western-dominated science and seek solutions from other knowledge-based systems, such as indigenous knowledge (Bala and Gheverghese Joseph, 2007). In New Zealand, indigenous knowledge comes in the form of traditional Māori knowledge known as mātauranga Māori. Mātauranga Māori is the indigenous understandings of the natural world from a Māori perspective (Hikuroa, 2017). Mātauranga Māori can help in providing solutions to environmental problems because its knowledge is based on place-based values derived from the deep connection Māori

have to the land and water (Wilkinson et al., 2020). Mātauranga Māori follows that of tikanga used throughout history by Māori tūpuna and eventually passed down from generation to generation. Solutions founded on mātauranga Māori must therefore respect tikanga to protect both the environment and Māori culture (Hikuroa, 2017). Integration of western science and mātauranga Māori is therefore essential, as it can generate new or improved approaches to protecting and sustaining New Zealand's unique environment for future generations.

1.1. Aim

This dissertation focused on two aims. The first aim was to investigate how P removal can be improved within woodchip bioreactors by determining the P removal efficiencies of woodchips-only and mix-media biochar's to lower P concentrations from farm river water using laboratory columns experiment and phosphate extraction.

The second aim was to integrate woodchip bioreactor science and mātauranga Māori to enhance the cultural aspects of woodchip bioreactors from a Te Ao Māori perspective.

1.2. Layout

Following on from this introduction; chapter 2 introduces the literature reviews for both woodchip bioreactors and mātauranga Māori; chapter 3 presents the methodologies employed; chapter 4 presents the results; chapter 5 provides a detailed discussion of these results and chapter 6 presents the conclusion of this dissertation.

Chapter 2
Literature Review

Woodchip bioreactors have gained global recognition as a viable and sustainable mitigation technology to improve water quality of wastewater in agricultural tile drainage systems. Increased usage of nutrient fertilizers has the potential to amplify nutrient leaching of N and P into these tile drainage systems. This can result in increased risks of nutrient pollution, ultimately culminating in the occurrence of toxic eutrophication. The main objective of woodchip bioreactors is to mitigate nutrient pollution, specifically through the removal of N from agricultural wastewater before it is discharged into nearby waterbodies, such as streams, rivers, and lakes (Schipper et al., 2010; Glibert et al., 2005). However, while woodchip bioreactors demonstrate high efficiency in removing N, their inability to effectively remove P has been a subject of concern. Research has explored the use of functionalised biochar as a potential enhancement for P removal in woodchip bioreactors. The use of a column experiment and sequential extraction can assess the efficacy of functionalised biochar in absorbing and removing P from nutrient contaminated water. This is to determine wither its use can enhance the P removal capabilities of woodchip bioreactors.

Mātauranga Māori refers to the knowledge, wisdom, and understandings of Māori in New Zealand. It encompasses a holistic worldview that integrates environmental, social, and spiritual elements, deeply rooted in a symbiotic relationship between the people and the land. In the face of environmental challenges, mātauranga Māori can be integrated with western perspectives and methodologies by providing indigenous insight and place-based knowledge. This integration can lead to a more holistic and comprehensive understanding of environmental issues and foster more effective strategies for sustainable management (Hikuroa, 2017; Wilkinson et al., 2020). The incorporation of mātauranga Māori into woodchip bioreactors has the potential to enhance their cultural aspects to ensure that they align with traditional values and respect tikanga. A wānanga is one platform that offers an opportunity for Māori to share knowledge. It therefore has the capabilities to acquire insight and recommendations into ways of enhancing the cultural aspect of woodchip bioreactors from a Te Ao Māori perspective.

This literature review chapter is composed of two sections: (i) The introduction of denitrifying woodchip bioreactors, the bio-physical aspects of P removal and the experimental methods

used to assess P removal, and (ii) the incorporation of mātauranga Māori, including an understanding of Māori knowledge, traditional values, and the Te Ao Māori worldview.

2.0. Denitrifying woodchip bioreactors

2.0.1. Background information

Denitrifying woodchip bioreactors are engineered, edge-of-field technologies designed for treating agricultural wastewater containing excess nitrate (NO_3^-) levels within subsurface (tile) drainage systems (Shipper et al., 2010). Tile drainage systems are used to manage excess water in agricultural fields with poor drainage. They collect surplus water from the soil and discharge it into nearby ditches or natural waterbodies, such as streams, rivers, and lakes (Studyt & Dierickx, 2006). Denitrifying woodchip bioreactors are integrated within these subsurface systems to treat NO_3^- levels in effluent drainage water. A microbial process known as denitrification is facilitated within the bioreactor that effectively removes NO_3^- from the effluent water before it is discharged into waterways. Woodchips serve as the carbon source that provides denitrifying bacteria with the energy needed to carry out this process (Shipper et al., 2010).

Blowes et al. (1994) in Canada and Schipper and Vojvodi-Vukovi (1998) in New Zealand are credited as the early proponents of introducing the denitrifying woodchip bioreactor concept to the published literature. Their work has since established this method as one globally recognized approach for addressing nutrient pollution. The innovation introduced by these researchers has facilitated the subsequent advancement of woodchip bioreactors, particularly in the United States (Hassanpour et al., 2017). This paved the way for subsequent studies, such as Greenan et al. (2009) and Hover et al. (2016), to focus on improving various parameters of woodchip bioreactors. For instance, Greenan et al. (2009) demonstrated that increasing water flow in bioreactors effectively decreased nitrate-nitrogen concentrations (Green et al., 2009). Hover et al. (2016) revealed that older woodchips better retain organic carbon compared to fresh woodchips. Additionally, they found that longer hydraulic retention times (HRT's), higher amounts of NO_3^-, and elevated temperatures can also lead to higher nitrate reduction rates (Hover et al., 2016).

Schipper et al. (2010) classifies the design of woodchip bioreactors into three distinct categories: Denitrification walls, denitrification beds and denitrification layers. Denitrification walls refer to excavated trenches situated below the water table and contain woodchips

arranged in a perpendicular position relative to the inflow water. Denitrification walls are typically utilised to treat ground water containing high nitrate levels. Denitrification beds refer to a large container filled with woodchips that are designed to treat effluent water pumped from tile drainage systems (Schipper et al., 2010; University of Waikato, 2013). Denitrification layers refer to horizontal layers of woodchips commonly placed under septic tanks or effluent-irrigated topsoil. Denitrification layers remove nitrate from effluent that seeps below these areas before it is leached into waterways (Schipper et al., 2010). Among these three types of woodchip bioreactors, the most common in practise are denitrification beds.

Figure 1 below shows the water treatment process that typically occurs within woodchip bioreactors. Effluent water from tile drainage systems enters the bioreactor through an inflow control structure positioned at the uppermost part of the bioreactor. During periods of high-water flow, excess water can be redirected into nearby waterways via a by-pass line. Effluent water that has entered the bioreactor is brought into contact with a bed of woodchips. During this contact, denitrifying bacteria found on the woodchips perform denitrification, where they convert nitrate (NO_3^-) into nitrogen gas (N_2). This gaseous nitrogen exits the bioreactor and is released into the atmosphere. The process of denitrification leads to a substantial decrease in the concentration of NO_3^- in the effluent water. After undergoing complete treatment, effluent water exits via an outflow structure at the bottom of the bioreactor. This water is then discharged into waterways with lower N concentrations, reducing the risk of nutrient pollution (Christianson et al 2018 woodchip bioreactor factsheet, n.d.).

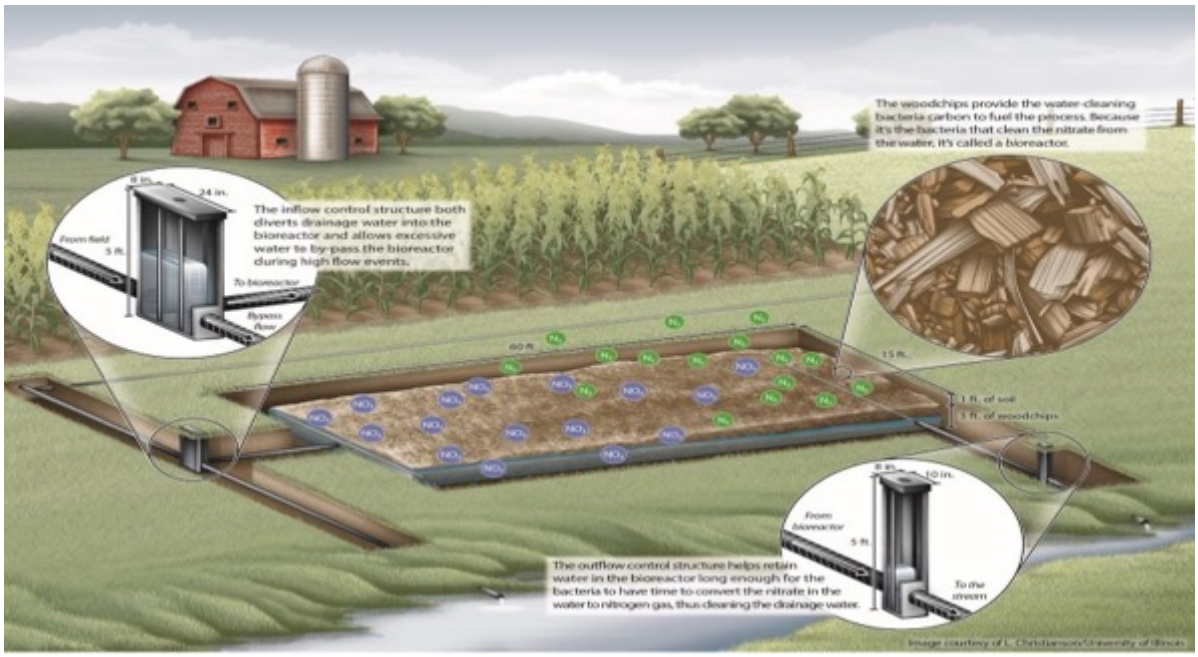


Figure 1. Water treatment process that occurs within woodchip bioreactors, including control structures, by-pass line, and woodchip chamber (From AgBMPs, n.d).

2.0.2. Nitrogen removal

Denitrification is the principal mechanism responsible for nitrogen removal in woodchip bioreactors. Denitrification is a natural microbial process that plays an imperative role in the nitrogen cycle, converting NO_3^- and nitrites (NO_2^-) into N_2 and nitrous oxide (N_2O). Denitrification primarily takes place in anaerobic environments where oxygen levels are low or absent (Science Learning Hub, n.d.). Redox reactions, which involve the transfer of electrons between molecules, plays a fundamental role. When oxygen is absent, denitrifying bacteria resort to using NO_3^- and NO_2^- as an electron acceptor to facilitate bacterial respiration and generate energy. Subsequent reduction reactions produce N_2 and N_2O, which is recycled back into the atmosphere (Bernhard, 2010).

2.0.3 Phosphorus removal

Sanchez Bustamante-Bailon et al. (2022) asserts that woodchip bioreactors have shown some promise in the removal of P due to the ability of woodchips to function as a physical filter, effectively capturing sediment and particle P. However, the study posits that enhancing P removal in bioreactors would be more advantageous in efficiently mitigating nutrient pollution in waterways. Westholm (2006) conducted research that examined the efficacy of different substrates in the removal of P from wastewater. Among the substrates investigated, industrial by-products, such as industrial slag material, showed promise as one effective P absorbent (Westholm, 2006). Sellner et al. (2019) demonstrated the effectiveness of using industrial by-products to enhance P removal by comparing their phosphate removal capacities to natural minerals. The results found that industrial by-products exhibited superior phosphate absorption, attributed to the strong chemical bonding between phosphate and metals. The incorporation of steel filters alongside woodchip bioreactors was suggested to boost P removal (Sellner et al., 2019), which was proved to be highly effective in a study by Christianson et al. (2017).

2.1. Methods of phosphorus removal

While there are several methods for P removal, the two predominate approaches are chemical and biological P removal. The use of these two methods is common in addressing issues of eutrophication in freshwater ecosystems, attributed to the discharge of urban and domestic wastewater (Morse et al., 1998). This section will elaborate on these two P removal methods.

2.1.1. Chemical phosphorus removal

Chemical phosphorus removal is a method used to remove inorganic phosphates from wastewater. The method involves adding chemical coagulants, such as ferric chloride (Fe(III)) or aluminium sulphate ($Al_2(SO_4)_3$) salts, to the wastewater to initiate a serious of chemical reactions. As these coagulants mix with the water, they neutralize negative charges on suspended P particles, causing them to aggregate into flocs. Within these flocs, P present in the wastewater reacts with metal ions from the coagulants, resulting in the formation of insoluble P precipitates. These precipitates are not soluble in the water and can be easily separated from the wastewater through sedimentation or filtration (Bunce et al., 2018).

Chemical phosphorus has several advantages as a wastewater treatment method, besides from addressing eutrophication. It is a treatment that has a reputation of showing high degrees of effectiveness and is a relative straightforward process to implement. However, the disadvantages of using this treatment are its potential of high costs, which can vary depending on the quantity of chemicals used, and the possibility of producing large quantities of non-biodegradable precipitates (Wang et al., 2005).

2.1.2. Biological phosphorus removal

Biological P removal is a method that harnesses the capabilities of certain bacteria and microorganisms that can accumulate and store P within their cells as intracellular polyphosphates. In this method, wastewater is treated in an activated sludge process within controlled conditions, including alternating between anaerobic and aerobic stages. In this process, microorganisms take up soluble P present in the wastewater. As a result, a significant amount of P is accumulated within their biomass. This biomass, known as phosphorus-rich activated sludge, can then be removed from the wastewater (Bunce et al., 2018).

Biological P removal has several advantages. The treatment offers enhanced efficacy in the elimination of organic P, reduces cost by using fewer chemical reagents and allows its by-products to be recycled back to the environment. The disadvantage of this method includes it complexity and limited applicability to only large-scale wastewater treatments (Stratful et al., 1999.

2.2. Mechanisms of phosphorus removal

In addition to the methods of P removal, it is also important to understand the fundamental mechanisms involved. Phosphorus removal in wastewater treatment relies on several key mechanisms to effectively reduce P concentrations in effluent water. There are various mechanisms of P removal exists, with chemical precipitation, biological uptake, and chemical absorption being the primary ones (Bunce et al., 2018). This section will elaborate on these various mechanisms of P removal.

2.2.1. Chemical precipitation

Chemical precipitation is the mechanism involved in chemical P removal. Upon introducing chemical coagulants to the wastewater, they dissociate and release metal ions, such as Al^{3+} and Fe^{3+}. These metal ions then undergo hydrolysis, leading to the formation of metal hydroxide species, such as $Al(OH)_3$ and $Fe(OH)_3$. These metal hydroxide species exhibit a positive charge and possess a high surface charge. In wastewater, metal hydroxides will bind to the surfaces of negatively charged colloidal particles, such as suspended particles or organic matter. Colloidal particles naturally repel each other due to their negative charge but the positively charged metal hydroxides neutralize this negative charge. The reduced electrostatic repulsion facilitates the proximity of colloidal particles, leading to their aggregation around the metal hydroxide species. Flocculation arises because of this progressive aggregation of colloidal particles, leading to an increase in size and mass. When the cluster becomes heavy, it descends to the bottom of the tank, where it accumulates as a sludge layer. This sludge layer is then subjected to dewatering and then disposed of. The treated wastewater is removed from the sludge fill tank and discharged (Yeoman et al., 1988).

2.2.2. Biological uptake

Biological uptake is the mechanism involved in biological P removal. The process involves a series of biochemical reactions performed by phosphorus-accumulating organisms (PAO's).

During the anaerobic stage of biological uptake, PAO's undergo decomposition of polyphosphates already stored in their cellular structure to provide energy in the absence of oxygen. As a result, this leads to the discharge of phosphate ions into the wastewater. Simultaneously, during this decomposition process, the PAO's begin to consume and store organic carbon in the form of polyphosphates, thus replenishing their intracellular reserves. During the aerobic stage, the PAO's continue to decompose the accumulated polyphosphates

and phosphate ions, thus leading to a reduction in P concentrations within the wastewater (Kerrn-Jespersen & Henze, 1993).

2.2.3. Absorption

Chemical absorption is a process by which P molecules adhere to the solid surface of adsorbent materials, such as iron oxides. When wastewater containing P flows through these materials, bonding can occur between the P molecules and functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and amine (-NH2), present on the surface of the absorbents. These functional groups can attract P ions through electrostatic attraction and ion exchange. In the case of iron oxide-based absorbents, high P removal is attributed to their high affinity for phosphate ions. This strong affinity prevents the desorption of P back into the wastewater, ensuring efficient removal (Bunce et al., 2018).

2.3. Experimental methods to test phosphorus removal

Various experimental methods have been explored for the removal of P. These experimental methods include batch test experiments, field-scale experiments, column experiments and sequential extraction. This section will elaborate on these experimental methods.

2.3.1. Batch test experiments

Batch test experiments are used across various scientific fields to investigate specific processes, reactions, and behaviours under controlled conditions. For instance, in the environmental sciences, batch test experiments can serve as a tool for understanding the behaviours of contaminates within soil or water samples. Within the experiment, a small quantity of samples is mixed inside a batch container. Different factors can then be introduced, such as varying concentrations of substances or changes in environmental parameters. The data is collected and analysed to understand how these different factors affect the contents inside the batch container (Galarneau & Gehr, 1997).

A study by Mohammed & Rashid (2012) utilized a batch test experiment to investigate P removal in wastewater using oven-dried alum sludge. The batch experiment collected data pertaining to the absorption of P onto the dried alum sludge. This enabled the researchers to investigate the absorption characteristics of the alum sludge in terms of P under different experimental conditions, such as varying pH levels and P concentrations (Mohammed & Rashid, 2012).

2.3.2. Field-scale experiments

Field-scale experiments are large-scale experiments conducted in real-world environments. They are typically used to investigate natural processes, such as waterflow patterns or soil erosion and are subjected to environmental conditions. Field scale experiments are used across many scientific disciplines and can provide a more realistic analysis and understanding of the interactions between different variables, spatial heterogeneity, and temporal dynamics (Kravchenko et al., 2017).

A study by Penn et al. (2020) utilized a field-scale experiment to address P losses from soils characterised by having high P concentrations. The study used large field-scale structures containing steel slags for the purpose of treating tile drainage water originating from these high P soil areas. The study revealed that steel slags did not provide long-term P removal, as there showed signs of inhibited P removal overtime. This finding suggested that steel slags were not viable for long-term removal of P unless they are either replaced every 4-6 months or chemically modified to sustain their P removal stabilities (Penn et al. (2020).

2.3.3. Column experiments

Column experiments provide a more realistic representation of certain environmental processes than batch experiments. The experimental setup involves the use of cylindrical columns packed with a representative material, such as a porous substrate medium. The arrangement is designed to replicate a particular environmental state or situation, such as reactions in porous media or nutrient transportation. The columns are subjected to a controlled fluid flow containing substances, such as pollutants or nutrients, to test on the material inside the columns. The interactions between the substances and material within the columns aim to replicate the same circumstances that are likely to occur in the natural environment (Banzhaf & Hebig, 2016).

In a study conducted by Jensen et al. (2022), a column experiment was used to evaluate the efficacy of calcium containing materials and non-calcium containing materials in removing P from tap water spiked with P for a duration of two years. The column setup consisted of 15 columns, each containing two or more replicates of either the calcium or non-calcium materials, except for a single column that only contained one material. P-spiked water was directed into the columns via an inflow pipe, which allowed water to flow through the materials, and the effluent water was collected for analysis. The results indicated that calcium containing materials exhibited efficient P removal through the two-year study. Conversely, the other

material showed a decline in P removal effectiveness after around 80-90 weeks of the study. The conducted column experiment effectively demonstrated the efficacy of calcium containing materials in P removal (Jensen et al., 2022).

2.3.4. Sequential extraction

Sequential extraction is a laboratory method used to fractionate and separate different forms of a chemical element, typically metals or metalloids, in a sample based on their chemical association with the sample matrix. The purpose of sequential extraction is to understand the distribution and speciation of elements in distinct samples. In the context of environmental research, sequential extraction is commonly used to study the speciation and behaviour of elements like heavy metals in soils. The process of sequential extractions involves subjecting the sample to a series of chemical treatments, with each step targeting a specific group of chemical associations to produce fractions. The fractions obtained from the sequential extraction can then be analysed (Rodger et al., 2015).

2.4 Mātauranga Māori

Mātauranga Māori refers to a comprehensive and holistic indigenous knowledge system that has been cultivated and passed down by Māori tupuna over many generations. Mātauranga Māori comprises of a diverse range of Māori knowledge domains, such as oral traditions, environmental knowledge, spirituality, traditional healing, celestial navigation, language, history, and art. At its core, mātauranga Māori places significant emphasis on the concept of interconnection, highlighting the deep, inherent connections that exist between individuals, the environment, and the spiritual realm. (Mercier, 2018). Mātauranga Māori is founded upon traditional principles that are associated with Te Ao Mārama. Within Māori cosmology, Te Ao Mārama encompasses a holistic understanding of the relationship between the spiritual realm and the natural world. It asserts that the natural world is not seen as distinct from humans, but rather recognised as interconnected via traditional values such as whakapapa, which in Māori culture traces all living things back to the primal parents Ranginui and Papatūānuku. The interconnectedness and spiritual emphasis of Te Ao Mārama is one fundamental concept that significantly contributes to both Māori culture and understanding of the Māori worldview (Kia Eke Panuku, n.d.).

Mātauranga Māori recognizes the significance of the environment and its resources in sustaining life. Māori tupuna developed comprehensive knowledge of the natural world,

including ecosystems, vegetation and animals through observation and study (Mercier, 2018) Oral traditions, such as pūrākau, waiata or whaikōrero, were used to ensure that this acquired knowledge would be passed down from one generation to the next, thereby ensuring their continued relevance in the modern era (Hikuroa, 2017).

2.5. Traditional values

Māori traditional values hold great importance in understanding mātauranga Māori because they provide the fundamental principles and beliefs that shape this indigenous knowledge system. For traditional values that hold importance in mātauranga Māori are whakapapa, tikanga, wairua and hauora. Incorporating mātauranga Māori into environmental projects necessitates the implementation of these values to ensure preservation and acknowledgement of indigenous knowledge and cultural practises. Doing this will ensure further efficient collaborations between mātauranga Māori and western science (Mercier, 2018; Stewart, 2022). This section will elaborate on these traditional Māori values.

2.5.1. Whakapapa

Whakapapa encompasses the genealogy and ancestral connections of Māori. It is an intrinsic system of knowledge that allows an individual to trace their lineage back to their ancestors, their whenua, the natural world, and even the spiritual world. It establishes a deep sense of belonging and interconnectedness within Māori communities, reinforcing the notion that all living things are linked through whakapapa and share a common heritage. In mātauranga Māori, whakapapa is regarded as one of the foundations upon which all aspects of life are built upon. Understanding one's whakapapa provides insights into one inherent rights and responsibilities as a member of a particular iwi or hapū, and as a kaitaki of the land and environment (Roberts, 2013)

2.5.2. Tikanga

Tikanga refers to the customs, protocols, values, and practises that govern Māori behaviour, interactions, and decision-making, Tikanga plays an integral role in mātauranga Māori because it guides how knowledge is acquired, transmitted, and used within Māori communities. At its core, tikanga is rooted in the principles of respect, reciprocity, and interconnectedness. Respecting these principles are a crucial aspect of Māori culture to provide harmony, interconnectedness and sustain Māori cultural identity. While tikanga is based on ancient customs, it is not static but adaptive and evolves over time. It incorporates contemporary

realities and can adapt to changing circumstances. This adaptability ensures the continuity and relevance of Māori customs and practises in modern contexts (Smith et al., 2016).

2.5.3. Wairua

Wairua refers to the spiritual essence or life force that exists within all living beings and the natural world. Wairua holds great significance within mātaurnaga Māori because it represents the spiritual belief that everything is interconnected. Māori believe that all elements of the environment, such as the land, rivers, animals, and other elements, have their own mauri. Wairua acknowledge the mauri these environmental elements, being deeply intertwined with the environment, as they are essential for the existence of mankind. Understanding the importance of wairua in mātauranga Māori is important because it is a concept that emphasizes the spiritual connectiveness when working on the environment (Kennedy et al., 2015).

2.5.4. Hauora

Hauora refers to a holistic state of well-being that encompasses not just physical health, but also mental, emotional, and spiritual well-being. Hauroa encompasses not just the well-being of humans, but also extends to include the well-being of the environment. Hauroa acknowledges the interconnectedness that each of these different aspects of well-being can influence and affect the other. In mātauranga Māori, hauroa is an important concept because it emphasizes the importance of balance and overall wellness for all areas of life (National Library of New Zealand, n.d.).

2.6. Incorporating mātauranga Māori and western science

The integration of mātauranga Māori and western science represents a potentially powerful approach to addressing environmental issues in New Zealand. Mātauranga Māor is deeply rooted in the interconnectedness of nature, acknowledging the spiritual and physical relationships between people and the environment. Western science relies on empirical data, systematic observation, and experimentation to gain knowledge about the world. By combining these two knowledge systems, it is possible to develop a more holistic and culturally inclusive approach to environmental problem-solving, decision-making and research, that in turn can help mitigate environmental issues, such as nutrient pollution (Mercier, 2018).

Several studies within the published literature have shown the successful integration of mātauranga Māori and western science. For instance, a study by Ogilvie et al. (2018) examined

the potential improvement of commercial scampi (Metanephrops challenger) fishing in New Zealand via the integration of Māori knowledge and western science. Through the collaboration of these of these two distinct knowledge systems, a programme was developed with the objective of transitioning away from harmful underwater trawling techniques and towards alternative methods that prioritised the well-being of scampi fish in their natural habitat. These alternative methods included pot fishing, the utilisation of specialised lures and the establishment of sustainable aquacultures dedicated to scampi preservation. The study presented evidence of the effective integration of mātauranga Māori and western science, highlighting the importance of further integration in New Zealand's fisheries sector (Ogilvie et al., 2018). Another study by Moller, (2009) investigated the population dynamics of Tītī (sooty shearwater) bird species (*Ardenna grisea*). It was revealed that current tracking methods were unsuitable for the well-being of female tītī and her off-spring. Due to this, mātauranga Māori was incorporated to monitor the bird species whist minimising disruption effectively and ethically to nesting female (Moller, 2009). This study also demonstrated the effectiveness of integration of mātaurnaga Māori and western science.

The above studies demonstrated the efficacy of integrating mātauranga Māori and western science in a collaborative way that both enhanced methodologies for tītī bird conservation (Moller, 2009), and addressed solutions to environmental scampi fishing (Ogilvie et al., 2018). Due to these studies, there is potential that by incorporating mātauranga Māori into the western methodologies of a woodchip bioreactors can have similar enhancements that can aid in the mitigation of nutrient pollution.

Chapter 3
Methods

This study compared two types of functionalised biochar with a controlled treatment consisting solely of woodchips as substrates to remove P. A column experiment was conducted to determine phosphate ($PO^{-}4$) removal of different treatments from phosphate-dosed stream water. At the end of the experiment, a phosphate extraction was used to quantify the extent of phosphate absorption and fractions in substrates from each treatment. Nitrate concentrations were also analysed during the column experiment and fractions. The objective of these experiments was to investigate whether the utilisation of functionalized biochar could lead to an improvement in the removal of P in woodchip bioreactors.

Additionally, a wānanga was held at Matahuru Marae where the mātauranga of Lake Waikare and the surrounding whenua was shared from Matahuru Marae members (mana whenua), along with information about woodchip bioreactors. Upon conclusion, members were invited to share their insights on strategies for enhancing the cultural aspects of woodchip bioreactors. The objective of the wānanga was to learn and understand the stories of the lake, the land, and its connection to the people to foster a clear understanding and appreciation of the members perspectives. This, in turn, would assist in formulating approaches to enhance the effectiveness of woodchip bioreactors from a Te Ao Māori perspective.

This method chapter comprises of two sections: (i) The methodology employed for the columns experiment, laboratory analysis and phosphate extraction, and (ii) the organisation of the wānanga to obtain place-based mātauranga Māori.

Utilizing functionalised biochar to enhance phosphorus removal in woodchip bioreactors.

3.0. Material and methods

This section will focus on the materials and methods used during the column experiment. This includes the methodology of the collection of river water, aeration of the intermediate bulk container (IBC), the establishment of the 12V pump setup, measuring flow rate, and the configuration of the 12V battery and timer.

3.0.1. Stream water collection

On November 17th, 2022, water samples were obtained from Tainui Farms. Stream water (1000 L) was collected using a Lowara submersible water pump manually lowered into the stream. Stream water was stored in a trailer-mounted IBC. Once IBC was filled, the pump was removed from the stream and stored in the rear section of the trailer. The IBC was transported to the NIWA Rurakura laboratory, where the water was transferred into a second IBC via a AQUAPRO MK-3 fountain pump. A large, light-reflective tarp was placed over the second IBC and secured with concrete slabs and ratchet tie down straps to ensure no sunlight could enter the container, thereby mitigating for the potential growth of algae.

3.0.2. IBC aeration

On November 21st, 2022, the IBC underwent aeration for a duration of 5 minutes, which was then repeated at the start of each week. The purpose of aeration was to replicate the same environmental conditions of that of the stream inflow and mix air into the water. A HAILEA air compressor was fixed to the tip of a garden hose and secured by hose clamps (11-13 mm). The opposite end of the hose was fixed to a steel rod using a zip tie (Figure 2). The steel rod was lowered into the IBC and the air compressor was turned on to initiate aeration. After 5 minutes, the air compressor was turned off and the steel rod was removed. The IBC was then re-covered with the tarp and secured,

Figure 2. HAILEA air compressor attached to one end of a garden hose using a hose clamp (11-13 mm). The opposite end of the garden hose affixed to a steel rod using a zip tie.

3.0.3. Pump set-up

The delivery of stream water to the columns (described below, section 4.2) was through a TOPMAQ ATV 12V pump motor from a Farmate 60-litre polythene container (Figure 3). Prior to set-up, a Lowara submersible water pump transported stream water from the second IBC outside the lab into the Farmate 60-litre container inside the lab. Upon activation of the 12 V pump, stream water inside the 60-litre container was first channelled into a Solo 150 psi pressure regulator set to 20 psi to regulate the flow of stream water into the columns (Figure 3 Red). Afterwards, stream water was channelled into Netafim PCJ pressure compensating non-leak irrigation drippers situated atop each column to deliver stream water into each individual column (Figure 3 Blue). Surplus water returned to the 60-litre container via a return hose. All tubing were secured using hose clamps (11-13 mm). The lid was left off the 60-litre container to allow aeration.

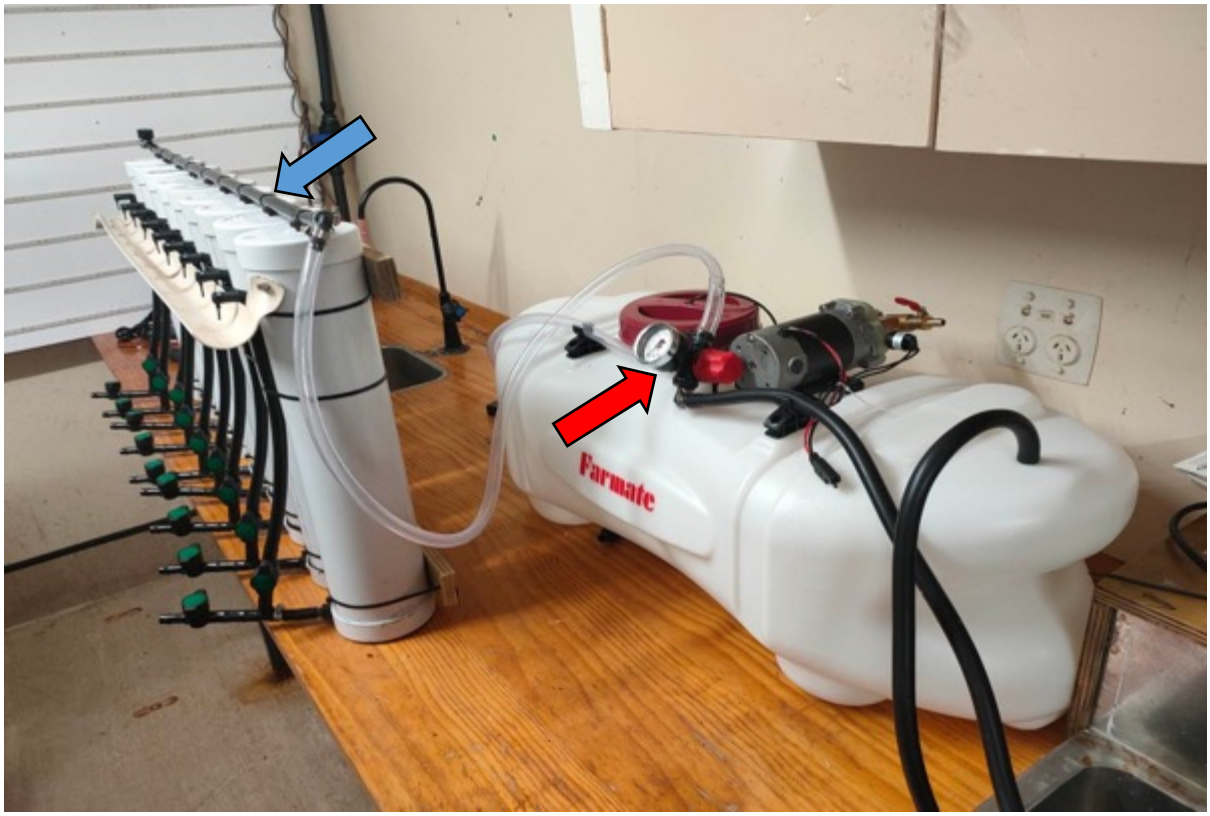


Figure 3. TOPMAQ ATV 12V pump motor and 60-litre Farmate polythene container. **Figure 3 Red.** Solo 150 psi pressure regulator (red arrow). **Figure 3 Blue.** Netafim PCJ pressure compensating non-leak irrigation drippers on top of columns (blue arrow).

3.0.4. Measuring flow rate

Flow rate was measured from each irrigation dripper to determine dispensation of water (20 mL) into each column for every pumping event. The irrigation drippers were raised above the columns and measuring cups (100 mL) were placed underneath each dripper for 1 minute of pumping to determine flow rate (Figure 4). Volume of liquid measured, and flow rate calculated as volume divided by pumping time. Flow rate was measured once every week. Drippers behaved well and gave reasonable flow rate throughout experiment.

Figure 4. Stream water collecting in measuring cups (100 mL) placed underneath dripper for 1 minute to measure flow rate.

3.0.5. Battery and timer setup

The TOPMAQ ATV 12V pump motor was powered by a 12V battery. A Banngood timer used operated the 12V pump motor on timed trails. These trials consisted of a 1-minute pumping period followed by a 15-minute interval of inactivity, which intended in running without interruptions. Configuration of the battery and timer setup is as followed: Two metallic sheets with apertures at their centre were fixed to the positive and negative terminals of the 12V battery. The positive terminal was connected to the timer's common (COM) and VN inputs using an alligator jumper clip (40 mm). Another alligator jumper clip (40 mm) connected the negative terminal to the timer’s ground (GND) input. Copper wire was exposed by severing one end of an alligator jumper clip before being inserted into the normally open (NO) input of the timer. The opposite end was connected to the 12V pump's positive wiring. A final alligator clip connected the pumps negative wiring to an exposed piece of copper wire on the cable that linked the battery's negative terminal to the GND input on the timer. A circuit diagram of this illustrated in Figure 5.

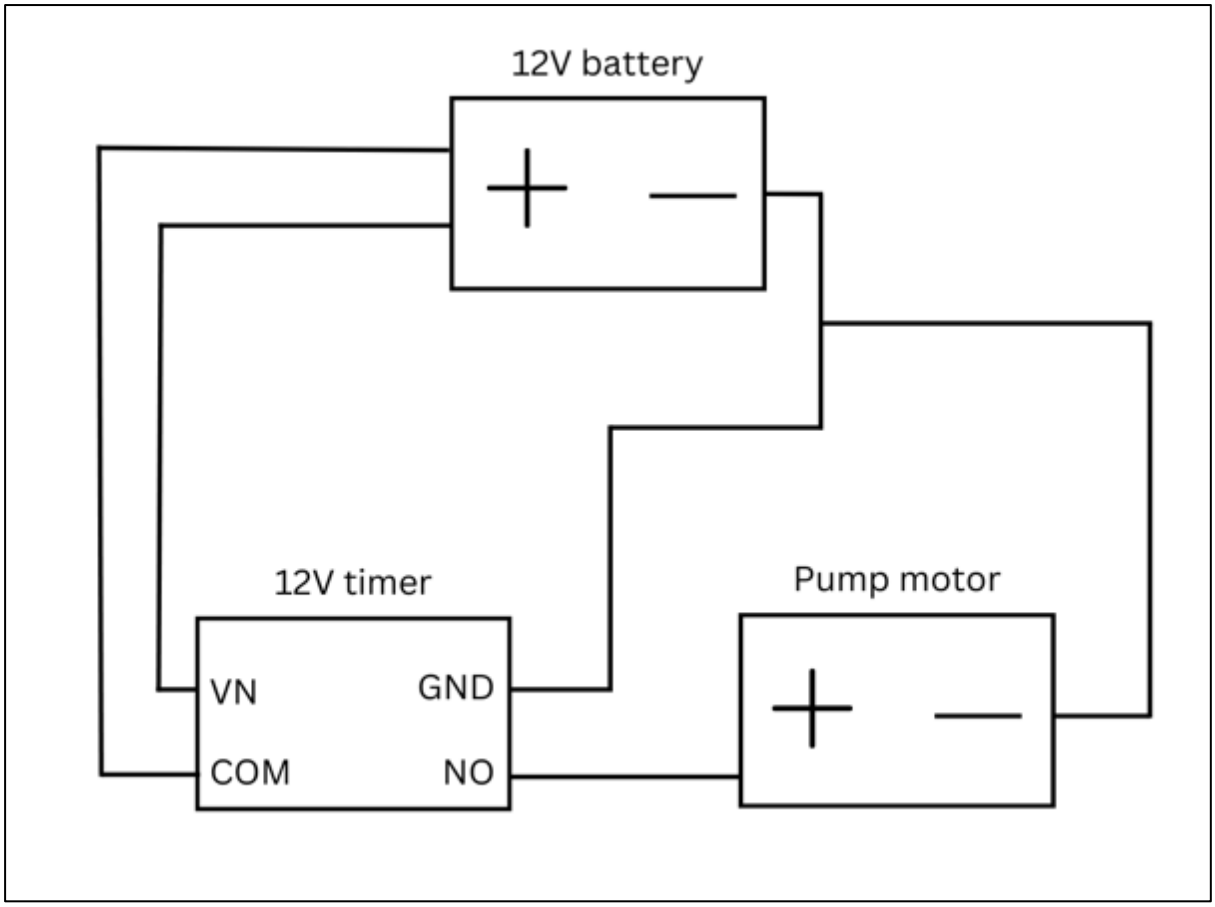


Figure 5. Circuit diagram illustrating the setup of the battery and timer.

Between the 31st of January to the 8th of March, the 12V battery underwent fortnightly periods of temporary deactivation to allow for re-charging via a 12V DC battery charger. This resulted in periodic changes in pumping rates. These periods consisted of one or two days, during which water was either supplied or not supplied to the columns. Between the 8th of March to the 5th of April, the pumping set-up was changed to where the battery was consistently re-charging whilst suppling water into the columns.

3.1. Columns experiment

This section focuses on the techniques employed within the columns experiment. This includes the methodology of the column set-up, substrate treatments, column sampling techniques, and phosphate dose spiking procedures.

3.1.1. Columns set-up

Columns were constructed with PVC piping with a height of 500 mm and a diameter of 100 mm. Columns were designed with a 70 mm spacing at the top to facilitate inflow and a 30 mm spacing at the bottom to accommodate outflow (Figure 6). Small holes on top of each column allowed inflow water to pass from the drippers into the upper part of the column. Water moved down the column, passing through the substrate. Water flowed to the base of the column where it was retrievable via a sample tap for lab analysis. To maintain a continuous flow of inflow water through the column, water exited the column from an outlet riser into a gutter line. This gutter line stretched along the columns where water could be discharged into a sink (Torres-Rojas et al, 2023).

Figure 6. Colum experiment setup.

3.1.2. Substrates

Three substrate treatments were tested in the column experiment to evaluate their efficiencies in removing phosphate from phosphate-dosed stream water. Treatments included: (i) Woodchips-only (W), (ii) woodchips and functionalized iron biochar (W+Fe), and (iii) woodchips and functionalized iron and manganese biochar (W+Fe+Mn). Each substrate treatment was replicated three times and randomly assigned to an individual column. A total of 9 columns were utilised. Each column was allocated a letter (A-I) and number (1-9) in a left-to-right sequence to differentiate the substrate treatments in each column. Woodchips were sourced locally and consisted of untreated pinewood (*Pinus radiata*). Biochar was derived from pinewood charcoal that underwent pyrolysis at 700^{o}C within a gas-fired drum located at Massey University in Palmerston North, New Zealand (Torres-Rojas et al., 2023). The functionalization process of Fe-biochar was carried out by soaking pine wood shavings in a 1 M iron (III) (Fe^{3+}) chloride-saturated sodium chloride solution, followed by drying in a microwave, iron fixation by treating the pine wood shaving with a 5 M ammonium hydride solution and rinsing of wood shavings with de-ionised water (DI) to remove salt and any absorbed iron (Ramasahayam et al., 2012). The functionalization process of Mn-biochar was carried out by adding biochar with dissolved $KMnO_4$ in DI water and stirred with ethanol. Resulting Mn-biochar was then rinsed and dried overnight (Subramanian et al., 2008).

Prior to packing into columns, woodchips were dried at 40^{o}C and sieved to obtain woodchips ranging from 4.25 mm to 8 mm in size. Woodchips were flushed of dissolved carbon (C) and P for 24 hours in a container (50 L) filled with deionised water (DI) and then drained. The dry bulk density of each substrate treatment intended to be compacted into the columns was determined by filling a bucket (3 L) with each substrate in increments of 400 mL and lightly compressing the material. This was repeated 3 times. A stainless-steel mesh secured on top of each substrate inside the columns ensured that the volume stayed consistent and prevented the expansion of woodchips during the experiment (Torres-Rojas et al., 2023).

Treatment W+Fe was prepared by mixing 10,000 g of woodchips with 1,000 g of Fe functionalized biochar in a mixing drum. The mixture was transferred into a subsampler compartmentalised into six sections. Visual inspection on each compartment made sure that an even quantity of Fe-biochar and woodchips was present in every subsample. Three subsamples with uniform distributions of both substrates were packed into allocated columns. The remaining subsamples were utilised in the W+Fe+Mn treatment (Torres-Rojas et al., 2023).

Treatment W+Fe+Mn was prepared by mixing 80 g of Mn-biochar into 1600 g of W+Fe substrate, with a weight ratio of 1:20. The mixture was packed into allocated columns (Torres-Rojas et al., 2023).

3.1.3. Column leachate sampling

Column leachate sampling occurred from the 31st of January to the 5th of April 2023. Daily column sampling was performed during the week, with occasional sampling in the weekends. Upon sampling, the outlet riser tap was closed to prevent water flowing into the gutter line and the Bannggod timer was temporarily turned off to prevent the motor from running while sampling. An initial 15 mL of column water was collected from the sample tap and discarded to ensure each sample accurately represented the water passing through the substrate treatment. Column water (40 mL) was then collected into a 50 mL sampling tube labelled corresponding to the sampled column. This procedure was repeated for each column until 9 samples were collected. Sampling tubes were stored in a freezer inside a freezer proof plastic bag and labelled with the date until lab analysis could be conducted. The outlet riser tap was re-opened and Bannggod timer was turned back on following completion of sampling.

3.1.4. Phosphate dose spiking

An initial phosphate concentration of 0.10 mg L^{-1} from the inflow showed that the Tainui stream water had lower than expected phosphate concentrations. To determine whether there were differences in phosphorus removal across all three treatments, 3.97 g of di-potassium hydrogen phosphate trihydrate ($K_2HO_4P*3H_2O$) was mixed with stream water in a bucket and added to the Farmate 60-litre container to increase the phosphate concentration to 9 mg L^{-1} PO^{-}_4-P L^{-1}. This was carried out once every three days when the 60-litre container ran close to empty, including weekend.

3.2. Lab analysis

This section focuses on the measurement of phosphate and nitrate concentrations using colorimetric analysis. This includes a description of vacuum filtration, weekly preparations of standard concentrations, standard curves, and testing of phosphate and nitrate in column samples.

3.2.1. Vacuum filtration

All column leachate samples underwent vacuum filtration. Four vacuum filtration columns were used. A container (100 mL) was placed inside each filtration column at the bottom to collect the filtered leachate sample and the filter plate was overlaid with filter paper (Whatman 47 mm diameter glass microfiber filter paper). Deionized water (DI) was used to moisten the filter paper before the vacuum filtration pump was turned on. The vacuum valve was turned vertically to allow suction to occur, by which each leachate sample was poured into the filtration columns in alphabetical order. Each leachate sampling tube (50 ml) was rinsed with hot water to eliminate any residue left inside. After filtration, the vacuum valve was repositioned horizontally, and the vacuum filtration pump turned off. The filtrated leachate samples were transferred back into their designated sampling tubes and placed into an alphabetically organized test tube rack for subsequent phosphate and nitrate analysis.

3.2.2. Standard concentrations

Standards were made for the determination of phosphate and nitrate concentrations utilising stock solutions of 50 mg L^{-1} phosphate (PO^{-}_{4}-P) solution and 100 mg L^{-1} nitrate-N (NO^{-}_{3}-N) solution. Solutions were taken out of the refrigerator and placed into a tray of warm water to allow them to reach room temperature before being dispensed into separate glass beakers (50 mL).

A series of phosphate (PO^{-}_{4}-P) standards were prepared with concentrations of 0.5 mg L^{-1}, 1 mg L^{-1}, 2 mg L^{-1}, 4 mg L^{-1}, 6 mg L^{-1} and 8 mg L^{-1} in volumetric flasks. Volumes of PO^{-}_{4}-P solution for making each standard were: 0.5 mL of solution used to make a 0.5 mg L^{-1} standard, 1 mL of solution used to make a 1 mg L^{-1} standard, 2 mL of solution used to make a 2 mg L^{-1} standard, 4 mL of solution used to make a 4 mg L^{-1} standard, 6 mL of solution used to make a 6 mg L^{-1} standard, and 8 mL of solution used to make a 8 mg L^{-1} standard. Phosphate standard absorbance testing followed in accordance with the methodology employed for phosphate concentration (see section 3.2.4).

Similarly, a series of nitrate standards were prepared with concentrations of 0.2 mg L^{-1}, 0.5 mg L^{-1}, 1 mg L^{-1}, 2 mg L^{-1}, 4 mg L^{-1}, 6 mg L^{-1}, and 8 mg L^{-1} in volumetric flasks (50 mL). Each nitrate standard was made by adding a volume of stock solution of NO^{-}_{3}-N to DI water until the solution reached the designated mark on the volumetric flask. Volumes of NO^{-}_{3}-N solution for making each standard were: 0.1 mL of solution used to make a 0.2 mg L^{-1} standard, 0.25

mL of solution used to make a 0.5 mg L^{-1} standard, 0.5 mL of solution used to make a 1 mg L^{-1} standard, 1 mL of solution used to make a 2 mg L^{-1} standard, 2 mL of solution used to make a 4 mg L^{-1} standard, 3 mL of solution used to make a 6 mg L^{-1} standard, and 4 mL used to make a 8 mg L^{-1} standard. Volumetric flasks were sealed with a stopper and inverted three times to mix the solution. NO^{-}_{3}-N standard absorbance testing followed in accordance with the methodology employed for nitrate concentration (3.4.5).

3.2.3. Standard curves

Concentrations of phosphate (Figure 7) and nitrate (Figure 8) were determined through the utilisation of a standard curve. Standard curves were produced weekly. R^2 values of standard curves ranged from 0.91 to 0.99, however, the majority were greater than 0.98.

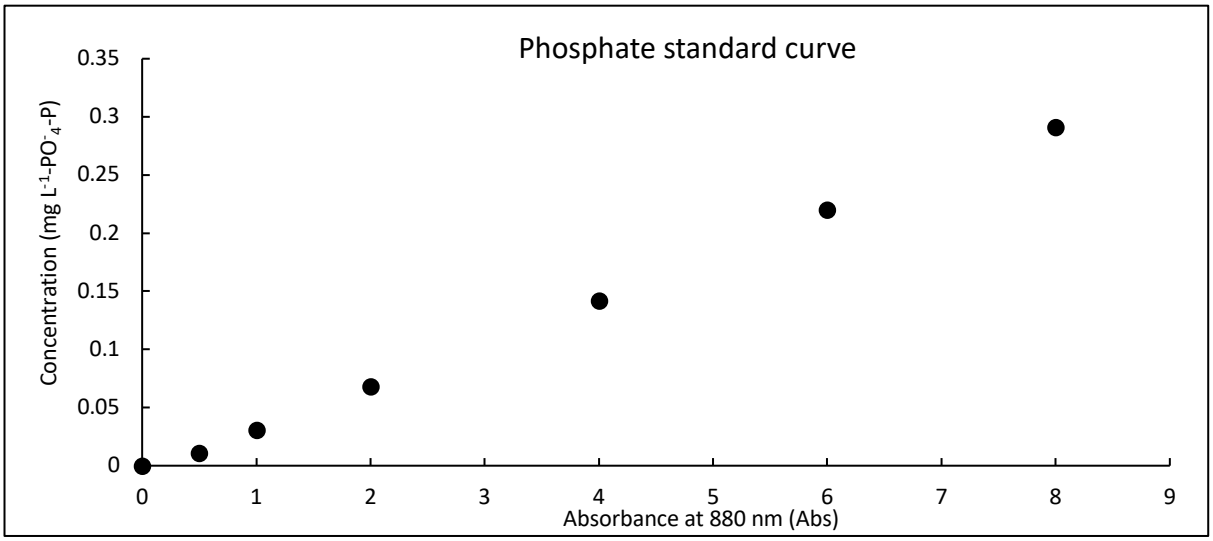


Figure 7. Weekly phosphate standard curve.

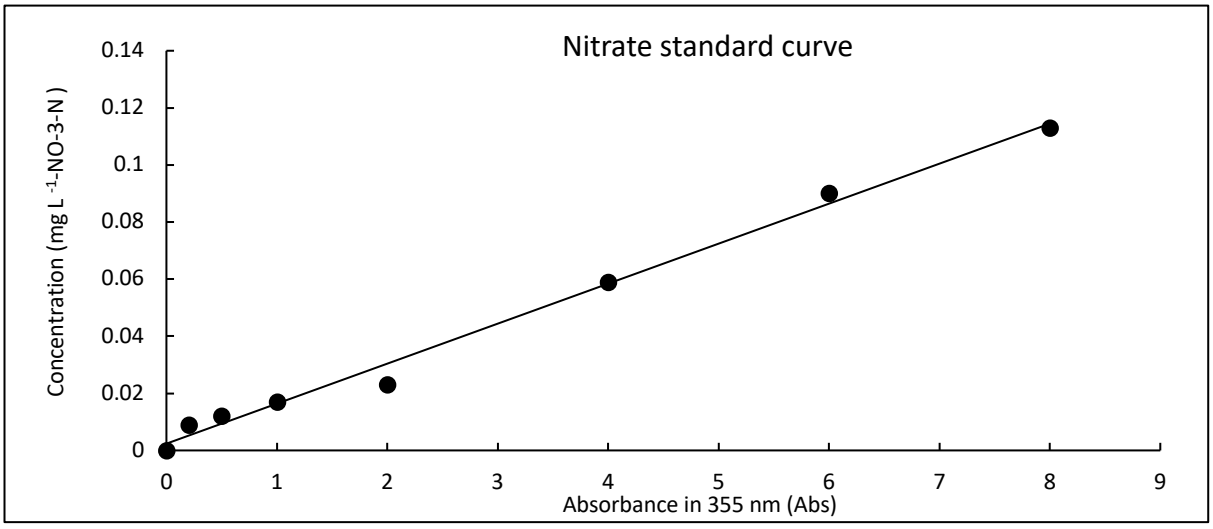


Figure 8. Weekly nitrate standard curve.

3.2.4. Phosphate concentration

Phosphate concentration was measured using the HACH spectrophotometer, set to a 880 nm wavelength. Prior to testing, the pipettes were calibrated. A reagent solution consisting of 50 mL of sulphuric acid 5N (H_2SO_4), 5 mL of potassium antimonyl tartrate ($K(SbO)C_4H_4O_6$ – $1/2H_2O$), 15 mL of ammonium molybdate ($(NH_4)_6Mo_7O_{24}$ – $4H_2O$) and 30 mL of ascorbic acid 0.1M was prepared in a glass beaker (100 mL) to be used for phosphate determination. Leachate sample (1 mL) was transferred into a second sample tube (100 mL) containing DI water (11.5 mL) and reagent solution (2 mL). A separate sample tube containing DI water (12.5 mL) and reagent solution (2 mL) was allocated as the blank and used to zero the spectrophotometer. Samples rested for 10-minutes to undergo mixing with reagent solution. During this time, a phosphoantimonylmolybdenum blue colour was observed within the solution of each second sample tubes because of reaction between phosphate within the leachate samples and the reagent solution. The chromatic intensity indicated the presence of high amounts of phosphate ions (Drummond & Maher, 1995). Samples were transferred into sample cells (10 mL), surfaces wiped with a tissue to remove any fingerprints, and inserted into the spectrophotometer. Absorbance (abs) was recorded for each sample and phosphate concentration (mg L^{-1} PO^{-}_4-P) was determined using the standard curve. At completion of phosphate testing, samples were disposed into the sink, sample cells were rinsed with hot water and stored. Removal of phosphate was calculated as percentage decreases from inflow concentration and as also rates of milligram (mg) P removal by the volume of substrate (m^3) per day (d).

3.2.5. Nitrate concentration

Nitrate concentration was measured using the HACH spectrophotometer, set to a 355 nm wavelength. Each individual sample was transferred alphabetically into 10 mL sample cells, to which a sachet of NitraVar5 nitrate powder was added. Sample cells were shaken vigorously for 60-seconds to dissolve powder into the samples, followed by a 5-minute rest period to allow samples to mix. During this time, samples underwent cadmium reduction where nitrates reacted with cadmium chloride, forming a light-yellow colour (Huffman & Barbarick, 1981). A separate sample cell (10 mL) filled with DI water was used as the blank to zero the spectrophotometer. The surface of the sample cells was wiped with a tissue and inserted into the spectrophotometer. Absorbance was recorded for each sample and nitrate concentration (mg L^{-1}-NO^{-}_3-N) was determined using the standard curve. Following completion, solutions

within the sample cells were disposed of in the sink and sample cells were rinsed with hot water and stored.

3.3. Phosphate extraction

Due to time constraints, sequential extraction was not performed. Instead, a single extraction of phosphate was performed for each substrate treatment.

This section focuses on the methodology of the phosphate extraction at the completion of column experiment. This includes collecting substrate from the columns and preparing extraction solution for iron and dissolve reactive phosphorus (DRP) analysis.

3.3.1. Substrate collection

At the end of the column experiment (5th April 2023), all columns were drained of water and weighed. Each individual column was divided into 3 sections (top, middle and bottom) using a ruler and the sections were marked on the surface of column with a marker. Wet substrate (100 g) was collected from the centre of each section and transferred into allocated bags labelled according to their section and column. A total of 27 wet substrate samples were collected. Next, a further 20 g of wet substrate was collected from each section and weighed to obtain wet sample weight in grams. The wet substrate (20 g) was then transferred into a heat-resistant tray and labelled according to its section and column. The trays were dried in a CONTHERM 270 M oven for 48 hours to produce dry samples. Dry samples were re-weighed to obtain dry sample weight in grams. All remaining substrate was evenly distributed onto baking trays and dried in the oven for 48 hours. Columns were then re-weighed. This was done to measure the substrate capacity of each column, with the aim of using this metric as a predictor for substrate amounts necessary in future experiments involving larger columns or woodchip bioreactors.

3.3.2. Preparation of oxalate extractant

Substrate (2.5 g) from each allocated bag was transferred into sample tubes (30 mL) filled with 30 mL of oxalate extract solution (0.175 M ammonium oxalate ($(NH_4)_2C_2O_4$) + 0.1 M oxalic acid ($C_2H_2O_4$)) at a pH of 3. Sample tubes were vigorously shaken for 1-hour inside a Thermolyne Bigger Bill Orbital Shaker to allow mixing of the oxalate extractant with the substrate. The sample tubes underwent centrifugation for 30-minutes to settle any substrate suspended within the oxalate extractant to the bottom of the sample tube (Schwertmann, 1964).

The oxalate extractant (20 mL) was transferred into sample containers (20 mL) and sent to Flinder Cook Limited, Auckland to undergo iron analysis. Iron analysis was done by atomic absorption spectroscopy (AAS) and used to calculate Fe/dry ratio in the phosphate extraction experiment (see section 4.0.2). Iron analysis data can be observed in Table 6A in appendix. A further 10 mL of oxalate extractant was transferred into test tubes (10 mL) to undergo DRP analysis in the lab. DRP analysis followed the methodology of phosphate concentration (see section 3.4.3.).

3.4. Organising a wānanga

This section focuses on the methodology for preparing the wānanga. This includes initial proposal to participate in a wānanga with academic mentors, collaboration in organising wānanga with Matahuru Marae. Arrangements before the wānanga and preparation of research presentation for the wānanga.

3.4.1. Proposal to participate in a wānanga

An initial meeting was conducted among myself, my academic supervisor Louis Schipper, and Associate Dean of Māori Te Taka Keegan, to discuss the arrangements for organising a wānanga. Te Taka provided guidance on the appropriate course of action, advising to establish communications with Matahuru Marae board members to propose a wānanga at Matahuru Marae and identify feasible dates for its commencement. Furthermore, it was discussed that a presentation of the dissertation be made, along with questions to ask participants at the end of the wānanga to encourage sharing of mātauranga. A final recommendation was to create a research poster (Figure 9) to serve as a visual illustration of the dissertation research to participants. This would be effective at introducing the dissertation to the participants prior to the wānanga.

3.4.2. Collaboration with Matahuru Marae

Communications were established with Matahuru Marae board members through email and text. On November 29th, 2022, a meeting was held with a representative of the Matahuru Marae Board to deliberate on the proposal of arranging a wānanga at Matahuru Marae. Subsequent discussions included the intent of engaging with Matahuru whanau by asking them to share their mātauranga on Lake Waikare, the whenua, and to give their perspective on ways to cultural enhance woodchip bioreactors. The proposal was accepted and information about the upcoming wānanga and suitable dates were conveyed with the Matahuru whanau by the representative. Further correspondence with the Matahuru Marae Board was done via text and email.

3.4.3. Preparing for the wānanga

An ethics approval from the University of Waikato was completed to obtain approval for the wānanga (Figure 1A in appendix). As part of the approval process, a participant information sheet and consent form (Figure 2A in appendix) were created and emailed to the Matahuru Marae Board for distribution. Individual brainstorming and multiple meetings with Te Taka generated 27 questions to ask participants. The research poster (Figure 9) was created using the Canva platform and emailed to the Matahuru Marae Board for distribution. Arrangement of my support team who accompanied me to the wānanga consisted of my whanau, including my spouse, as well as Louis Schipper. A koha of $150 was gifted to Matahuru Marae on the day of the wānanga and the waiata "Waikato te awa" was learnt to sing during the pōwhiri onto Matahuru Marae. Wānanga commenced on December 10th, 2022.

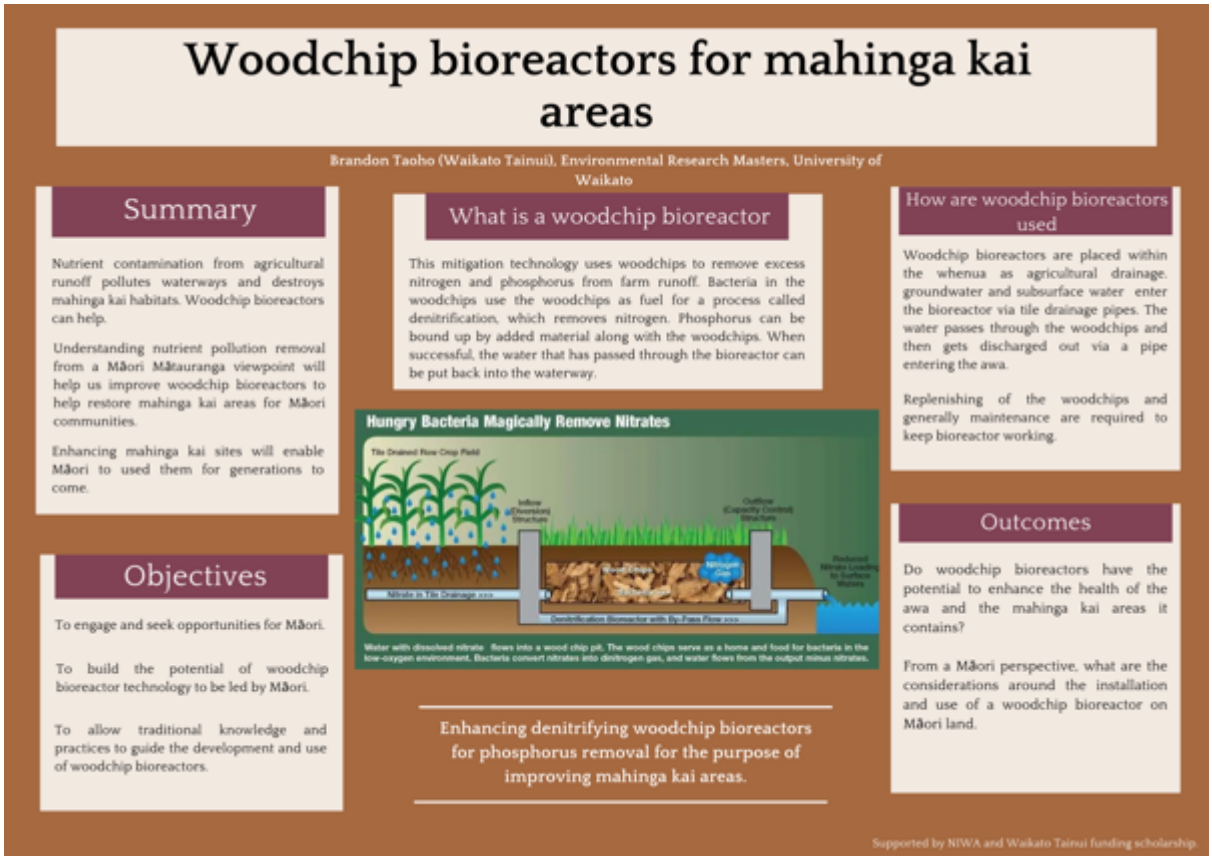


Figure 9. Master's research poster sent to participants before the wānanga.

3.4.4. Preparation of presentation

A presentation of this dissertation was created again using Canava. The presentation's content was divided into three sections (Figure 3A in appendix).

The first section introduced woodchip bioreactors, outlining their effectiveness in mitigating eutrophication, their design, and advantages, how they operate and their use in both New Zealand and overseas.

The second section introduced the methods used in the dissertation, outlining the aim of enhancing phosphorus removal in woodchip bioreactors, a description of the columns experiment, a description of the sequential extraction method and hypothesised outcomes.

The third section introduced the integration of mātauranga Māori in the dissertation. Here, the significance of matauranga Māori was described, why matauranga Māori is important, the integration of matauranga Māori with western science and the potential advantages this could yield for freshwater mahinga kai areas. The final slide provided a summary of the objectives of the wānanga and the rationale for the involvement of the participants. Interview questions were asked at the end of the wānanga. List of questions are shown in Table 1 below.

Table 1: Questions asked to participants at the end of the wānanga.

Q.1: Have you ever participated in a research wānanga before?
Q.2: Have you ever been asked to share knowledge and tikanga with researchers?
Q.3: What has been your experience with other researchers?
Q.4: How do you feel about research being conducted on your whenua?
Q.5: What is the age bracket of the audience?
Q.6: How many live in the area?
Q.7: How long have you or your whanau lived in the area for?
Q.8: Can you tell me any stories about this area?
Q.9: What were the things you did as a kid growing up in the area?
Q.10: Do you or your whanau own land in the area?
Q.11: What do you think of the health of Lake Waikare?
Q.12: Do you believe the mana and mauri of the lake is diminished?
Q.13: What mātauranga can you tell me about the lake?
Q.14: Is there any Tikanga surrounding the lake?
Q.15: Are there mahinga kai areas around the lake?

Q.16: Do you believe the health of the lake and its mahinga kai areas can be improved?

Q.17: What are your thoughts on nutrient pollution?

Q.18: Is there any cultural tikanga that deals with nutrient pollution?

Q.19: Have you been involved with any projects dealing in reducing nutrient pollution?

Q.20: What do you think about woodchip bioreactors?

Q.21: Is there any mātauranga or tikanga that works similar to what a woodchip bioreactor?

Q.22: Do you think woodchip bioreactors are culturally acceptable?

Q.23: Do you think woodchip bioreactors can benefit mahinga kai areas?

Q.24: Do you think woodchip bioreactors can be a form of kaitiakitanga?

Q.25: Is where the woodchips are sourced important?

Q.26: Have you enjoyed your participation in the wānanga today?

Q.27: Any further questions?

Chapter 4

Results

This chapter presents an overview of the results from the column experiment, phosphate extraction, and wānanga.

This chapter comprises two sections: (i) the results of the phosphate concentrations measured from all the column samples and the results of the phosphate extraction, in addition, nitrate concentrations will briefly be presented towards the end of section (i), and (ii) the outcomes from the questions deliberated on at the end of the wānanga.

4.0. Phosphate concentration and phosphate extraction

4.0.1. Phosphate concentration

Phosphate removal was demonstrated by the reduction in average concentrations across all treatments compared to the inflow concentrations (9 mg L^{-1}-PO^{-}_{4}). There was clear indication of phosphate removal across all treatments (Figure 10). The degree of phosphate removal was significant from the influent across all three treatments. The woodchip-only treatment exhibited lower efficiencies in phosphate removal compared to the two functionalised biochar treatments. Daily phosphate removal within the woodchip-only treatment ranged from 0.005 to 2.21 mg P m^{-3} d^{-1} (mg P removed by the volume of substrate (m^{-3}) per day (d^{-1}) (Table 1A in appendix), with an average phosphate removal percentage of 13% (Table 2A in appendix). Functionalised biochar exhibited superior phosphate removal capabilities. Daily phosphate removal within the W+Fe treatment ranged from 2.18 to 5.72 mg P m^{-3} d^{-1} (Table 1A in appendix), with an average phosphate removal percentage of 84% (Table 2A in appendix). Daily phosphate removal within the W+Fe+Mn treatment ranged from 1.43 to 5.71 mg P m^{-3} d^{-1} (Table 1A in appendix), giving an average phosphate removal percentage of 85% (Table 2A in appendix). The data from which the daily phosphate removal and average phosphate removal percentage was calculated from can is shown in Table 3A in appendix.

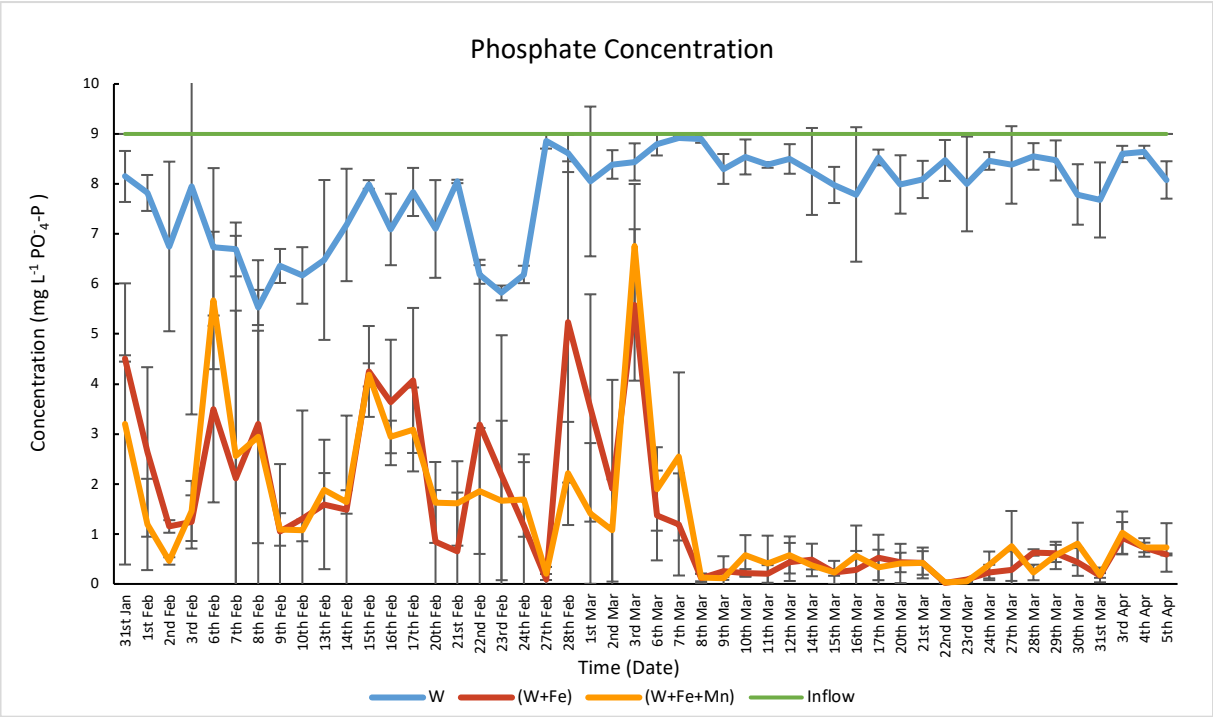


Figure 10. Daily mean phosphate concentrations for each treatment, along with their 95% error bars for each sampling occasion.

From the 31st January to 7th March, all treatments exhibited intermittent fluctuations in mean phosphate concentrations, with high variations between replicates. This was attributed to the periodic deactivation of the 12V battery for one to two days to be re-charged. On March 8th, changes were made to the pumping set-up where the battery became consistently charged while maintaining pumping stream water into the columns. This resulted in more consistent levels of mean phosphate concentrations, which persisted through to the end of the column experiment.

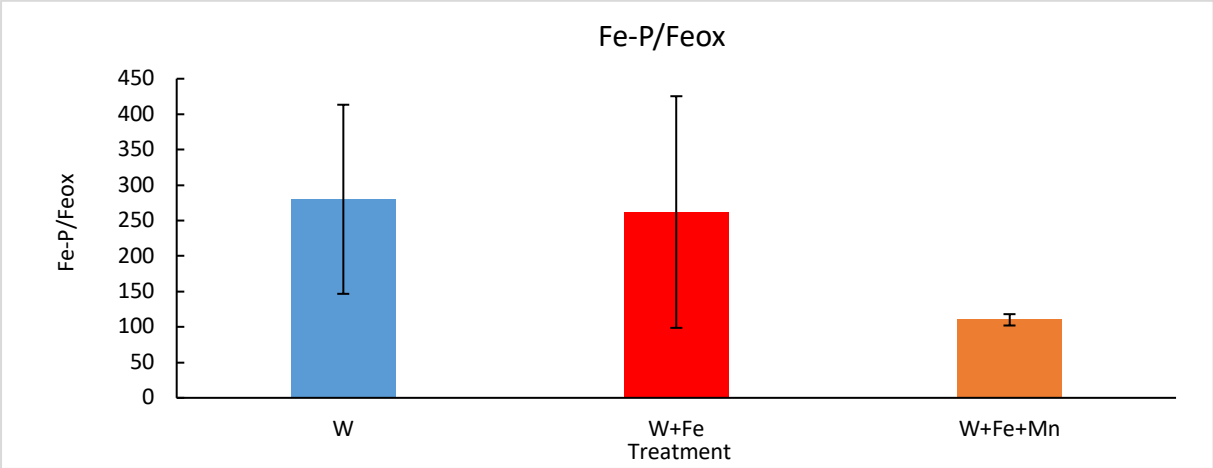
95% error bars were used to compare the variability in mean phosphate concentrations across all treatments. Despite some error bars in the woodchip-only treatment overlapping with the inflow concentration, generally, error bars did not include the inflow concentration, indicating that woodchips were absorbing phosphate for much of the experiment.

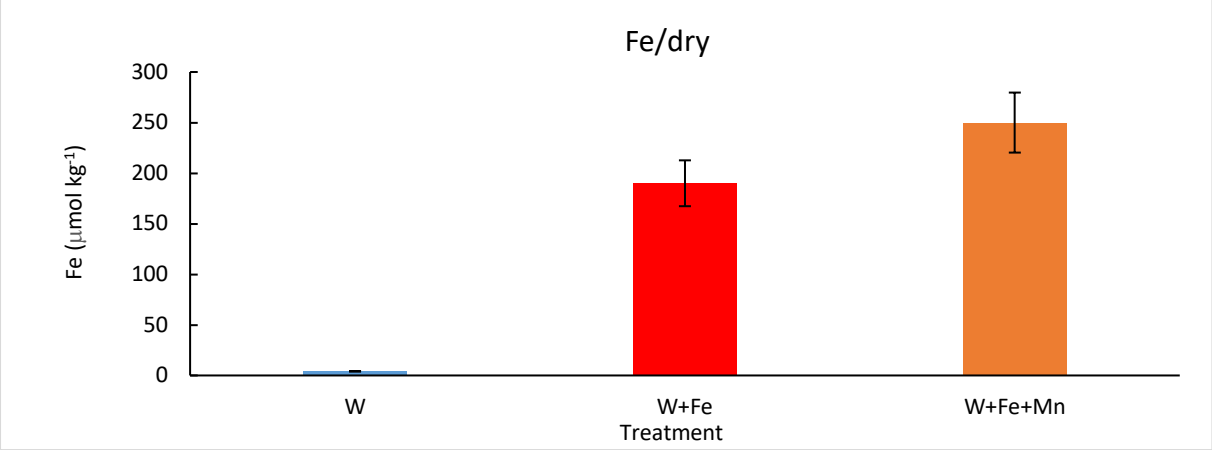
4.0.2. Phosphate extraction

The two functionalised biochar treatments exhibited a higher degree of phosphate absorption compared to the woodchip-only treatment (Figure 11.). This degree of phosphate absorption was determined from the Fe-P/Feox, P/dry and Fe/dry ratios. The Fe-P/Feox ratio refers to the ratio between the concentrations of iron-bound phosphorus (Fe-P) and the concentration of reactive iron species (Feox). The P/dry ratio refers to the concentration of P in relation to the dry weight of substrate and the Fe/dry ratio refers to the concentration of Fe in relation to the

dry weight substrate (Meissner et al., 2008). These ratios provided a comprehensive understanding of the absorption of phosphate taking place in each treatment. The woodchip-only treatment displayed a high Fe-P/Feox ratio and low Fe/dry and P/dry ratios, while the two biochar treatments demonstrated lower Fe-P/Feox ratios and higher Fe/dry and P/dry ratios. The fractions in which these ratios were calculated from can be observed in Table 4A in the appendix.

Standard error bars showed differences between the Fe-P/Feox, Fe/dry and P/dry ratios for each treatment. Error bars display higher variability in the woodchip-only treatment and lower variability in the two biochar treatments.





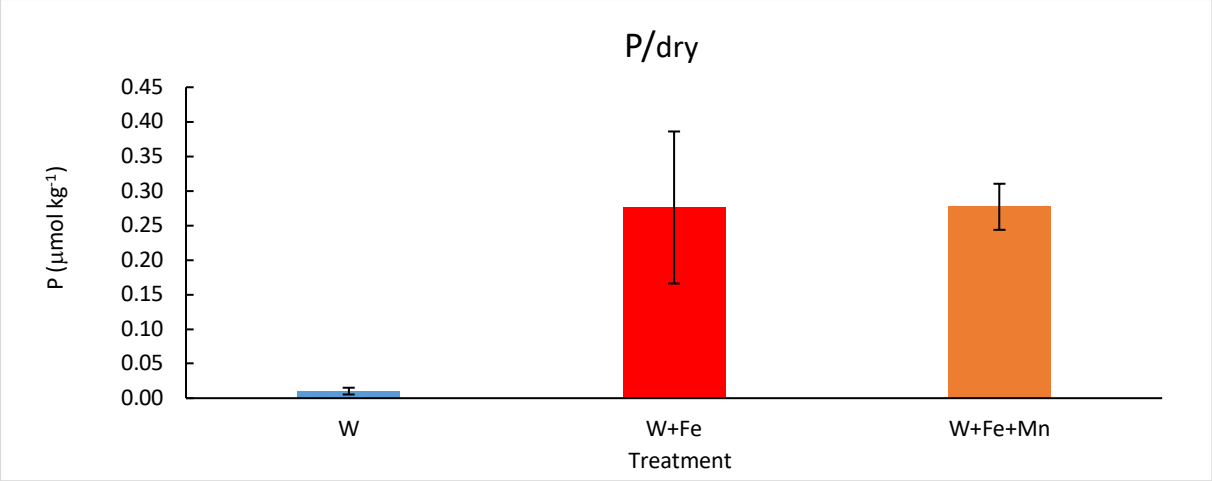


Figure 11. Bar graphs displaying the Fe-P/Feox, Fe/dry and P/dry ratios for each treatment, along with their standard error bars.

To gain better insight into where phosphate absorption was occurring within the columns of each treatment, the Fe-P/Feox ratio (Figure 12), Fe/dry ratio (Figure 13), and P/dry ratio (Figure 14) were recorded for the different sections down the column. The highest FeP/Feox ratio was measured in the top sections for both the woodchip-only and W+Fe treatments. This is supported by a high P/dry and low Fe/dry ratio. This indicated that most of the phosphate was concentrated in the upper layer of W and W+Fe treatments as opposed to being evenly distributed throughout the core, as seen in the W+Fe+Mn treatment. Again, the fractions in which these ratios were calculated from can be observed in Table 4A in the appendix.

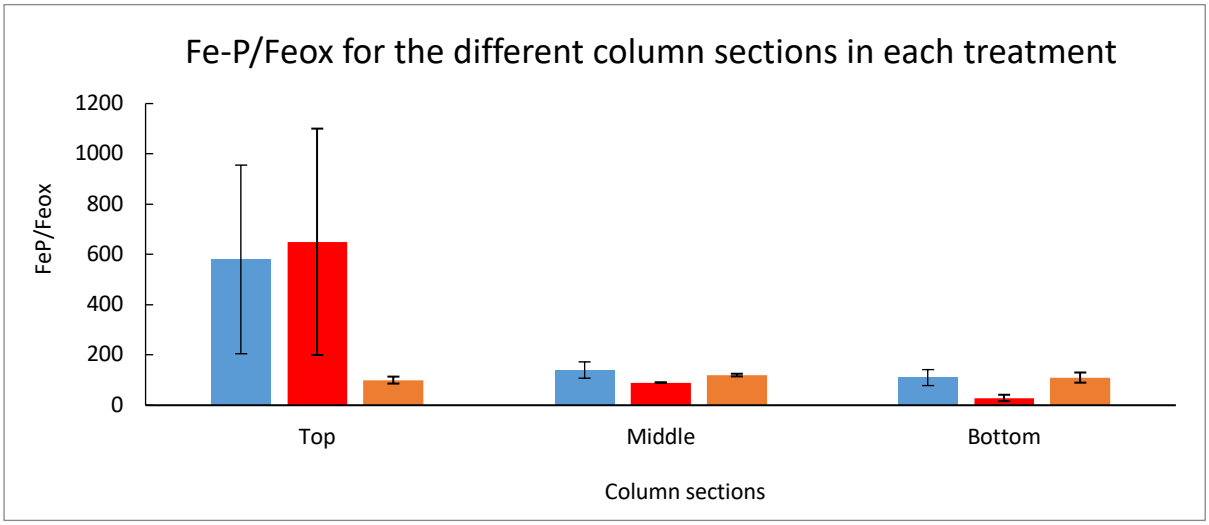


Figure 12. Fe-P/Feox ratio for the different column sections within each treatment. Blue (W), red (W+Fe) and yellow (W+Fe+Mn).

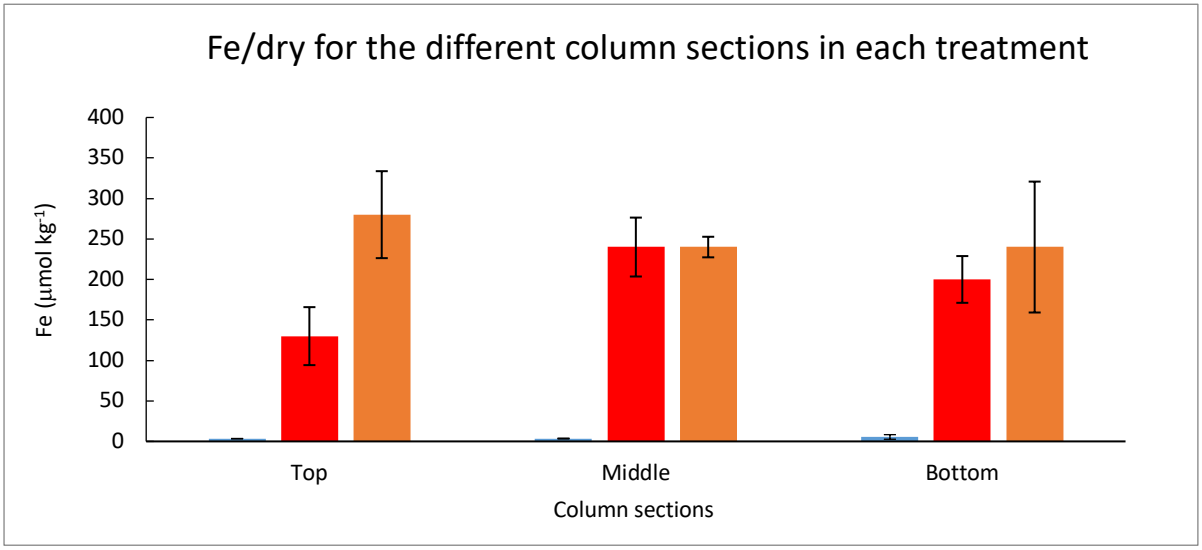


Figure 13. Fe/dry ratio within the different column sections for each treatment. Blue (W), red (W+Fe) and yellow (W+Fe+Mn).

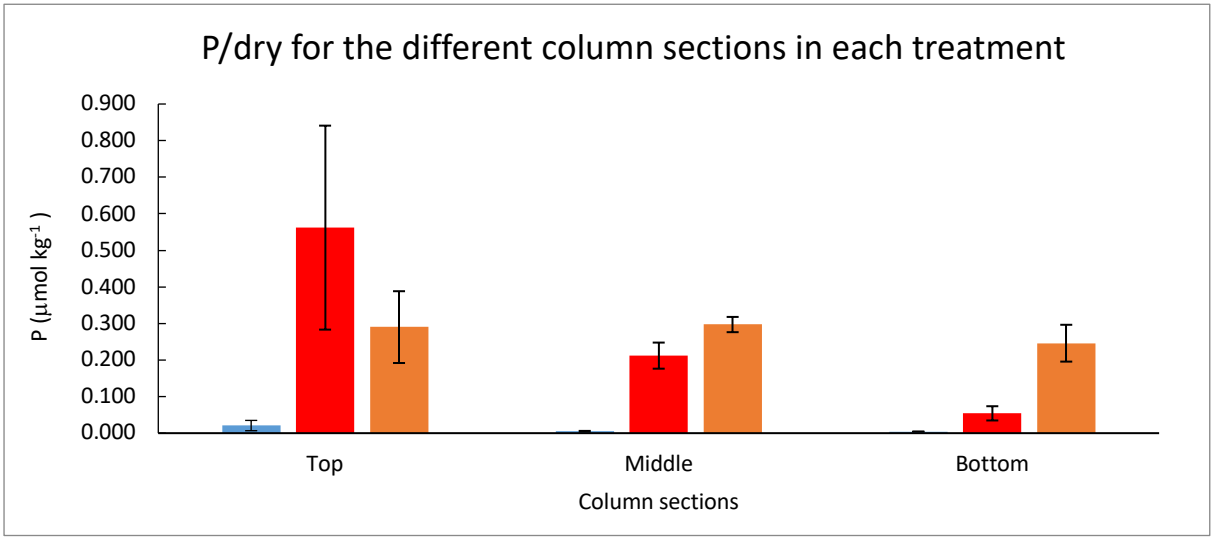


Figure 14. P/dry ratio within the different column sections for each treatment. Blue (W), red (W+Fe) and yellow (W+Fe+Mn).

Standard errors were used to show the variation amongst the Fe-P/Feox, Fe/dry and P/dry ratios for all the different sections, demonstrating higher variability in the woodchip-only and W+Fe treatments and lower variability in the W+Fe+Mn treatment.

In the W+Fe treatment, a low Fe/dry ratio was observed for the top section. This was suggested to be attributed to iron reduction to soluble Fe^{2+} which moved down and through the column.

4.0.3. Nitrate concentration

There was no consistent nitrate removal observed across all three treatments (Figure 15). All treatments resulted in higher concentrations in outflow than inflow (1.36 mg L^{-1} NO^{-}_{3}-N). The woodchip-only treatment produced more nitrate than the other two biochar treatments. This was supported by the considerable deviation of average nitrate concentrations from the inflow concentration. The two biochar treatments exhibited lower nitrate losses. The data used to calculate nitrate concentration is shown in Table 5A in the appendix.

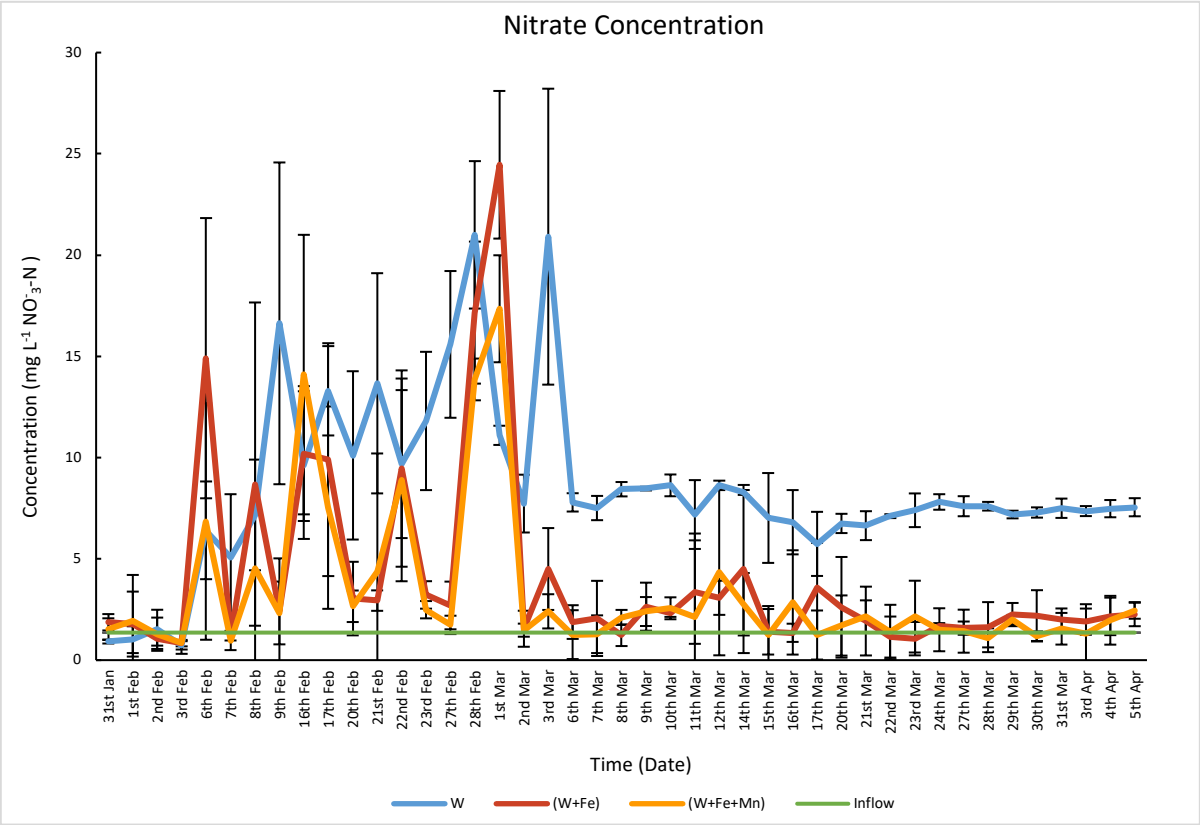


Figure 15. Daily average nitrate concentrations for each treatment, along with their 95% error bars for each sampling occasion.

Like phosphate concentrations, larger variations in mean nitrate concentrations occurred at the beginning of the experiment compared to the end.

4.1. Sharing of mātauranga Māori

This section focuses on the mātauranga shared in response to questions posed at the wānanga. This includes members past engagement with researchers, background history of Lake Waikare, pūrākau associated to the lake, tikanga linked to the lake, and proposed recommendations to enhance the cultural aspects of woodchip bioreactors.

4.1.1. Prior engagement with researchers

Members were queried about their prior engagement in research focused on Lake Waikare. Members have met researchers in the past looking to gain information about the lake's history and current state but stated that this was their first time engaging with myself. Previous engagements with other researchers have been generally positive, but subsequent communications from some research groups were limited to only one or two instances. In previous years, members have been involved in restoration projects related to the lake. Within these projects, members imparted their tikanga to researchers, some which can be traced back to the Rangiriri invasions. However, members noted that researchers sometimes struggled to comprehend this tikanga and found it difficult to accept. Nonetheless, Matahuru Marae have formed strong partnerships with crown institutions and all members agreed that research that benefits the aera is commendable.

4.1.2. Background history of Lake Waikare

Members and their whanau have owned land and lived in the area since birth. Their childhood consisting of swimming in the lake, fishing, catching tuna, duck shooting, gathering kai near the swamps and playing in the gardens and around the dairy shed. Food was abundant during this time but due to the current, toxic state of the lake it is now not. With the installation of the flood gates, everything in the lake, including food, puna sites, native plants and native fish species were flushed away. When the lake was given back to the iwi, it was in an unhealthy state, prompting the iwi to seek assistance from crown institutions. Proposed solutions included raising the water level in the lake, however, this was decided against due to its potential to cause greater long-standing problems persistent across generations. Another solution was to drain the lake but was immediately stopped due to traditional reasons, such as disturbing ancestral remains. Recent solutions have involved engaging with farmers to reduce their farming intensity and establish fencing around waterways, but members said that farmers in the region were reluctant to change their practices. Members expressed a strong desire to revert the lake back to what it once was so that their children and mokopuna can use it in the future.

4.1.3. Pūrākau of Lake Waikare

One member told that during duck hunting session, hunters are advised to use caution if they spotted a white duck on the lake and that pursuing this bird was deemed unwise as it would result in the hunter's disappearance. In another story, a friend of a member witnessed one

morning a pair of twin taniwha playing and sitting on petrified wood on top of the lake. The friend described it as a bad omen regarding to the current state of lake, as she felt very unwell afterwards.

4.1.4. Tikanga of Lake Waikare

Members expressed that the mana and mauri of Lake Waikare has been significantly diminished to the extent where even their tūpuna can feel it. The tikanga of the lake consists of karakia that pays respect to the ancestral remains of iwi members that reside in the depths of Lake Waikare. There are also areas on the lake that members refrain from accessing, again as sign of respect. Members expressed that for years they have been restoring and enhancing their ancestral home by planting native trees along the lake to revive the biodiversity and stop sediment entering the lake. Biodiversity has slowly revived in the area, as evidenced by the number of returning native birds, but nutrient pollution still poses a challenge.

4.1.5. Recommendations to enhance woodchip bioreactors

Members conveyed a favourable outlook towards the implementation of woodchip bioreactors. In the past, farmers cut down the native trees on the hillsides to set up their farms in the area, resulting in increased runoff entering the lake. Restoration planting, soil monitoring and mussel filtration have been used to mitigate nutrient in the water, with the goal of using the environment to look after the environment. Members confirmed that woodchip bioreactors can be used as a form of kaitakitanga because they help restore the environment. When queried about how woodchip bioreactors could be enhanced culturally, members suggested that the utilization of indigenous woodchips could be a viable approach. This is because unlike pine wood, native woodchips were reviewed to foster a better connection to the people, as it would give a sense of whakapapa. It would also give Māori a better understanding of where the woodchips have come from, being locally sourced. Members concluded that native woodchips would be the best solution because the whenua be used to working with it instead of pine, which doesn't whakapapa to the whenua or the people.

Members enjoyed their participation and stated that the concern of lake is a responsibility that we all need to take care of. Members would have continuous communication and updates from myself regarding the dissertation and it was proposed that a second visit be arranged after my research was done to speak to the rangatahi to help inspire them into the sciences.

Chapter 5
Discussion

Enhancing phosphorus removal in woodchip bioreactors is essential because both N and P are responsible for nutrient pollution. Incorporating functionalized biochar in woodchip bioreactors is one potential method of enhancing P removal, due to its ability to absorb nutrients (Sanchez Bustamante-Bailon., 2022; Weidner et al., 2022). Recognising the need for solutions to mitigate nutrient pollution in New Zealand, the integration of western science and Mātauranga Māori is called upon. By combining the strengths of both knowledge systems, collaborative solutions can be established to effectively address nutrient pollution in New Zealand waterways.

This dissertation proposed two hypotheses: (i) The two functionalised biochar treatments will be more efficient at removing phosphorus compared to the woodchip-only treatment, and (ii) Matahuru Marae members will share their mātauranga of Lake Waikare and offer insight to enhance the cultural aspects of woodchip bioreactors.

5.0.1 Phosphorus removal efficiencies between functionalised biochar and woodchips.

In the column experiment, functionalised biochar displayed higher phosphate reduction than woodchips only. This was indicated by the difference in average daily phosphate removal and percentage across each treatment. Functionalised biochar removed between 1.43 to 5.72 PO^{-}_{4}-P m^{-3} d^{-1}, averaging 85% phosphate removal, while woodchips only removed between 0.005 to 2.21 mg PO^{-}_{4}-P m^{-3} d^{-1}, averaging 13% phosphate removal. Furthermore, in the phosphate extraction of column materials at the end of the experiment, functionalised biochar had greater phosphate absorption compared to woodchips only. Following phosphate extraction, functionalised biochar had a lower Fe-P/Feox ratio and higher Fe/dry and P/dry ratios compared to woodchips only. The enhanced capabilities were attributed to the presence of Fe and Mn metal oxides within the biochar treatments. The removal efficiency and absorption of P within the woodchips-only treatment was relatively poor. These poor capabilities were attributed to the lack of metal oxides present in the treatment. Several published studies, such as Liu et al. (2015) and Wu et al. (2020) on functionalised biochar, and Husk et al. (2018) and

Sanchez Bustamante-Bailon et al. (2022) on woodchips show similar findings that support these conclusions discussed below.

Liu et al. (2015) investigated iron (II) sulphate ($FeSO_4$) functionalised corn straw biochar for P removal from agricultural runoff. The study utilized a column experiment to compare concentrations of outflow P to inflow P. The results of their study revealed that outflow P concentrations reduced to below 0.02 mg P L^{-1} and achieved a 99% P removal rate from the inflow P that concentration varied between 1.86 to 2.47 mg P L^{-1}. This outcome was like the results made in my column experiment, which indicated significant P removal in the outflow compared to the inflow (Liu et al., 2015). A second study by Wu et al. (2020) investigated P absorption and retention in saline-alkaline soils using iron-oxide biochar composites. The study utilized rice straw biochar, ferrous chloride ($FeCl_2$) biochar, and ferric chloride ($FeCl_3$) biochar. Based on their results, a high P absorption of 39.2 mg PO^{-}_4 g^{-1} was observed in ferrous chloride ($FeCl_2$) biochar compared to the other two biochar substrates. Again, this outcome was like the results from my PO^{-}_4-P extraction, where functionalised biochar demonstrated high P absorption capabilities. Additionally, in a column leachate experiment, $FeCl_2$ biochar leached the least P per day while the other biochar substrates the most P per day. The authors attributed this enhanced absorption and retention to iron-oxide in $FeCl_2$ being in an amorphous state. Being in an amorphous state enhances biochar porosity and surface area to facilitate increased phosphate bonding, thereby prompting better phosphate absorption (Wu et al., 2020).

A study by Husk et al. (2018) investigated P absorbent efficiencies between activated alumina gravel (mix media woodchips) and untreated woodchips and their capacity to lower P concentrations in drainage water to the critical environmental threshold of 0.030 mg P L^{-1}. Activated alumina gravel refers to a form of activated alumina that is structured in the shape of gravel. Its porous, high-surface-area structure makes it easy to integrate into organic material. Using four full-scale field bioreactors, they showed that woodchips alone were not as effective at reducing P levels as the mix-media woodchips did. Mix-media woodchips reduced P levels by 0.015 mg P L^{-1}, corresponding to a P removal rate of 9% (Husk et al., 2018). Sanchez Bustamante-Bailon et al. (2022) investigated woodchips with varying amounts of metals known to absorb P by conducting batch tests with various woodchip metal combinations. They showed that woodchips with lower aluminium (AI) and Fe content were less effective at removing phosphate compared to woodchips with higher AI and Fe content. Woodchips with high AI and Fe content removed an average of 13 ± 2.5 mg of DRP per kg of woodchip. The authors attributed high reduction in phosphate to both the presence of

amorphous (hydr)oxide forms of AI and Fe, as well as higher concentrations of AI and Fe. Both factors collectively contribute to an increase of surface area on the woodchips, facilitating enhanced phosphate absorption (Sanchez Bustamante-Bailon et al., 2022). The findings of both these studies are consistent with the results. Specifically, woodchips alone showed negligible phosphate reduction compared to functionalised biochar.

5.0.2. Functionalised biochar's phosphate-absorbing properties.

The efficacy of biochar, both in its original carbon-rich form and when modified with metal oxides, as a phosphate absorbent can be attributed to several properties (Ambaye et al., 2021). Biochar possesses a highly porous structure and a large surface area because of its formation through pyrolysis. One way phosphate absorption can occur is through the physical binding of P molecules to the porous surface of the biochar through weak van der Waal forces of electrostatic attraction. A greater surface area facilities more available sites for P molecules to bind to (Qiu et al., 2022; Ambaye et al., 2021). The incorporation of metal oxides, such as iron oxide (Fe_2O_3) and aluminium oxide (AI_2O_3), has the potential to improve biochar surface area by leveraging its own porous structure to facilitate more areas for physical phosphate absorption (Luo et al., 2023). Functional groups on the surface of the biochar, such as carboxyl (COOH), hydroxyl (COH) and phenolic functional groups, contribute to enhanced P removal via chemical bonding (Qiu et al., 2022). Negative phosphate molecules (PO^{-}_4) bind via mainly ion exchange to the positively charged functional groups on the biochar, resulting in the absorption of phosphate. Metal oxides enhance the biochar surface by introducing additional functional groups to the biochar surface, thereby increasing sites for ion exchange, prompting better chemical P absorption (Munera-Echeverri et al., 2018; Qiu et al., 2022).

5.0.3. Functionalised biochar as a phosphorus removal enhancement for woodchip bioreactors.

Based on the result from this dissertation and previous published studies, it is reasonable to suggest that the incorporation of functionalised biochar in woodchip bioreactors has the potential of enhancing their phosphorus removal capabilities. Published studies have already demonstrated the effectiveness of implementing non-functionalised biochar in woodchip bioreactors. For instance, Bock et al. (2015) investigated the effects of adding biochar to denitrifying woodchip bioreactors for the removal of P and N from nutrient contaminated water. The study utilized nine small scale bioreactors: one filled with woodchips-only and others with different biochar treatments. The results found that the biochar bioreactors had

significantly lower concentrations of DRP in the outflow, averaging a phosphate removal rate of 65%. In contrast, the woodchip-only treatment experienced an increase in DRP concentrations by 0.6 mg L^{-1} over the course of the experiment. Biochar also showed improved N removal, achieving an average N removal rate of 86%. The addition of functionalised biochar may further enhance the P removal capabilities of woodchip bioreactors (Bock et al., 2015).

Although studies have demonstrated the favourability of biochar as a phosphate absorbent it is important to acknowledge that several studies have shown instances where biochar fails to support P removal. A study by Coleman et al. (2019) investigated the effects of biochar on the removal of N and P in woodchip bioreactors. Their study utilized a column experiment with woodchips, 10% biochar and 30% biochar. A significant release of P from the pine-feedback biochar was exhibited, with a substantial 170% increase in P concentration in the outflow compared to the inflow. Average N removal across all treatments was 11.0 g m^3 N d^3 (Coleman et al., 2019). Another study by Vismontienė & Povilaitis. (2021) investigated biochar in denitrifying woodchip bioreactors to remove P and N from tile drainage water. Their study utilized 3 small scale bioreactors: one containing woodchips and two containing 10% and 20% biochar content. Biochar released P in the outflow with high P concentrations ranging from 0.720 to 2.50 mg P L^{-1}. Woodchips removed P with lower P concentrations ranging from 0.013 to 0.080 mg P L^{-1} in the outflow (Vismontienė & Povilaitis., 2021).

Overall, functionalized biochar exhibited high efficiency in the absorption and removal of phosphate, as observed in both the column experiment and phosphate extraction, in comparison to woodchips only. When implemented into woodchip bioreactors, functionalized biochar has the capacity to enhance P removal within their systems, thereby contributing to the mitigation of nutrient pollution in freshwater ecosystems.

5.0.4 Mātauranga of Laka Waikare

The wānanga was an important opportunity to delve into the history, pūrākau and tikanga of Lake Waikare. The wānanga facilitated an immersive learning environment in which mātauranga was exchanged. This offered the opportunity to actively engage in Māori knowledge and perspectives, as understood and shared by mana whenua. It was discussed that Lake Waikare has undergone a devastating decline in its health and quality over the past several years. This decline has significantly impacted various amenities, such as fishing and swimming, which were once abundant in the area and contributed to the well-being of mana whenua. Waikato Regional Council (WRC) characterises the lake as being in a hypertrophic

state, referring to the lake being excessively nutrient enriched, thereby prohibiting swimming in the lake. Monitoring conducted between 1993 to 2004 revealed notable increases in total N and P levels. The current condition of the lake remains in a hypertrophic state. WRC believes that this is attributed to runoff from neighbouring farmlands and discharge from the Te Kauwhata effluent treatment facility (Waikato Regional Council, n.d.). Mana whenua said that the lake remains in a deteriorated state today.

Lake Waikare functions as a flood reservoir due to its low-lying area, shallow depth and flat bottom that makes it well suited for storing water (Reeves et al., 2002). In 1965, Lake Waikare underwent both a 1.5 meter lowering in water level and construction of a floodgate under the Lower Waikato-Waipa Flood Control Scheme (LWWFCS) aimed at improving flood control in the area for agricultural land (Wildlands, 2012). Mana whenua stated that they encountered significant challenges to these changes, including the depletion of food resources and the loss of seasonal wetlands, subsequently converted into agricultural pastures. The return of the lake to Waikato Tainui, stipulated in the Waikato Tainui Deed of Settlement 1995, returned Lake Waikare to mana whenua but under poor water quality conditions. Currently, initiatives implemented to reduce nutrient levels in the lake have been through riparian planting. Mānuka riparian planting established at Nikau farms has proven to be instrumental at mitigating nutrient levels in the lake. Analysis of pore water samples collected from beneath the mānuka plot revealed a decrease in leaching of N and P into the water, which was attributed to the uptake of these nutrients by the plant (Institute of Environmental Science and Research [ESR], 2022).

The wānanga showed that Lake Waikare holds a deep cultural and spiritually connection to mana whenua, encompassing tikanga and pūrākau that have been passed down through generations. Tikanga refers to the customs, practises and values that govern various aspect of Māori life. Tikanga is deeply rooted in Māori culture and embodies the collective wisdom and values of Māori people (Mead, 2016). Pūrākau refers to traditional narratives that convey cultural, spiritual, and historical knowledge. Pūrākau is rooted in Māori oral traditions and plays a significant role in passing down ancestral teachings (Hikuroa, 2017). Through pūrākau and personal experiences, mana whenua revealed that Lake Waikare is guarded by taniwha (*guardian spirits*) whose presence ensures the protection of the lake and its surrounding environments. A notable aspect of these narratives was the unsettling nature that the story conveyed. This was evident when mana whenua used terms such as “disappearance”, “petrified” and “sick feeling” when telling the stories. It was suggested this unsettling nature was attributed to the current degraded conditions of the lake, further emphasising the need for

its restoration. The tikanga of the lake embodies karakia and kaitiakitanga. Karakia would be done to express deep respect towards the deceased buried at the bottom of the lake. Additionally, specific areas of the lake were refrained from visiting out of respect for the dead. Mana whenua have exhibited kaitiakitanga through their ongoing efforts of resorting and enhancing the biodiversity of Lake Waikare through native planting.

To enhance woodchip bioreactors, the integration of native woodchips was recommended by mana whenua. Woodchip bioreactors commonly use a variety of wood types depending on availability and regional preferences (Sanchez Bustamante-Bailon et al., 2022). This dissertation utilised pine wood (*Pinus radiata*) as the main woodchip substrate (Torres-Rojas et al., 2023). Utilizing native woodchips can offer cultural suitability. Mana whenua conveyed that native woodchips would foster a deeper connection to Māori people and give a sense of whakapapa. Native plants hold great significance in Māori culture because they reflect the lands history and connection to the people (McAllister et al., 2019). It was suggested that utilizing native woodchips would show respect to Māori traditions and reinforce a sense of identity, belonging and kaitaikitanga when involved in woodchip bioreactor projects. Collaborating with Māori communities can also provide insight into the selection and management of native woodchips. Māori communities residing in the area can possess a deep understanding of the land. By involving them, guidance can be given in woodchip bioreactor projects regarding what native woodchips should be used, their availability and sustainable sourcing methods.

5.0.5. Integrating mātauranga Māori and western science.

Integrating mātauranga Māori and western science has the capabilities of being an effective approach for addressing environmental issues in New Zealand. Mātauranga Māori provides a holistic and interconnected Māori worldview that recognizes the interdependence of all living things, the relationship we have with them, recognition to the spiritual realm and the significance of maintaining harmony with the natural world (Hikuroa, 2017). Mātauranga Māori encompasses knowledge of New Zealand's natural environment that has been developed and refined by our ancestors and eventually passed down from generation to generation (McAllister et al., 2019). By integrating western science and mātauranga Māori, we can provide more effective strategies to manage the environment and foster a more collaborative and comprehensive approach in knowledge generation and problem-solving to resolve environmental challenges, such as nutrient pollution, in New Zealand.

Overall, the collaboration with mana whenua revealed that incorporating native woodchips can enhance the cultural appropriateness of woodchip bioreactors, as native woodchips hold significant cultural value and tikanga to the land and people. The integration of mātauranga Māori and western science can provide a comprehensive and cultural inclusive approach for addressing environmental issues, such nutrient pollution, in New Zealand.

Conclusion

This dissertation investigated how functionalized biochar can improve P removal in woodchip bioreactors and how a Te Ao Māori approach can improve the cultural aspects of woodchip bioreactors. Woodchip bioreactors are well known to remove excess N subsurface drainage before it reaches waterbodies. However, woodchip bioreactors are generally inefficient at P removal. Functionalized biochar has the potential to enhance P removal efficiency owing to its superior P absorption properties. The integration of mātauranga Māori and western science to solve environmental issues in New Zealand is expanding. mātauranga Māori encompasses traditional knowledge and sustainable practices rooted from the deep connection Māori have to the natural environment. Previous studies have demonstrated collaboration between mātauranga Māori and western science, but little has been done to explore this collaboration in the context of woodchip bioreactors. The results from a column experiment and phosphate extraction demonstrated that functionalized biochar exhibited enhanced P removal efficiencies compared to woodchips-only. The results from the wānanga revealed that Lake Waikare has suffered severe declines in water quality over the years owing to nutrient pollution. Member of Matahuru Marae suggested that native woodchips is recommended to be used in bioreactors because they foster better connections to the land and people. This dissertation showed that functionalised biochar in woodchip bioreactors improves P removal and that from a Te Ao Māori perspective, native woodchips can be used to enhance the cultural aspect of woodchip bioreactors.

Based on the findings from this dissertation, several areas warrant further research. Further statistical analysis is needed to better assess the P removal efficiencies between Fe functionalised biochar and Fe and Mn functionalised biochar. By identifying the most effective P removal treatment, P removal efficiency in woodchip bioreactors can be increased. Additionally, this would need to be tested in a field scale woodchip bioreactor to understand the effectiveness of the two functionalised biochar treatments in removing P when applied to a larger scale bioreactor and subjected to environmental conditions. Experimental analysis, either through batch testing or column experiment, should be conducted to examine the affinity of native woodchips as a viable nutrient absorbent. This analysis should be conducted in collaboration with iwi, as it would provide guidance in selecting the appropriate native woodchips and facilitate a stronger relationship between Māori and western science. There is potential for further exploration within the incorporation of mātauranga Māori in woodchip

bioreactors. Different marae communities around Lake Waikare have different insights and perspectives. Engaging in further conversations with them, wither through wānanga or environmental projects, might provide insight on further enhancing woodchip bioreactors using mātauranga Māori. There is need to further explore other mātauranga that can mitigate nutrient pollution. Indigenous knowledge systems often hold much insight into sustainable practises. Enhanced involvement with iwi and mana whenua, either through participations in collaborative projects, wānanga's, gatherings or cultural occasions, can foster better connections and promote the sharing of knowledge.

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Appendix

Human Research Ethics Committee
Postal Address: The Secretary, Human Research Ethics Committee
Private Bag 3105
Hamilton 3240

E-mail: humanethics@waikato.ac.nz

Before applying for approval applicants must familiarise themselves with the Ethical Conduct in Human Research and Related Activities Regulations in the University Calendar
http://calendar.waikato.ac.nz/assessment/ethicalConduct.html.

Use this application if your research project involves the collection, use, and/or reuse of human data. This form is to be completed by staff and students doing research **prior to** the collection of any data from human participants.

Upon completion of this form please submit to/or email to your Faculty/School Human Research Ethics Committee [HREC]. Health Research and Health, Sport & Human Performance applications should be submitted to the central HREC (humanethics@waikato.ac.nz).

Note 1: This application has been formatted as a series of tables to enhance stability. Please type your responses to questions in the cells beside or below the prompts. The table will expand to accommodate the length of your responses. At times, tables in word do not display correctly onscreen, although the underlying formatting is stable and the file will print to hard copy or pdf correctly. To fix this problem, position the cursor in an empty cell, and press enter or tab. This should fix the display. You can then delete the formatting you have added and continue.

Note 2: Use the file naming convention 2019_Surname_HRECApplication (e.g. **2019_Smith_HRECApplication**). When you submit your application, we would prefer a single pdf file including all documents associated with the application, in the order you intend us to read them. If you have difficulty combining files, please number your files in the order that you intend us to read them (e.g. **2019_Smith_HRECApplication01, 2019_Smith_HRECApplication02**, etc.)

A positive answer to one or more of the questions below indicates the need for review by the University of Waikato Human Research Ethics Committee (Health), which is accredited by the Health Research Council. Health Applications should be submitted by email to humanethics@waikato.ac.nz.

n Are you investigating a topic that concerns health, disability or well-being?
n Are you using an instrument intended to assess health, disability or well-being?
n Is referral to a health service provider anticipated as a potential outcome of participation?
n Are participants being recruited in their capacity as DHB employees?
n Is the researcher intending to collect tissue samples (e.g. bloods, saliva, urine) from healthy individuals?
n Is the researcher intending to utilize interventions related to exercise and nutrition?

Submit this application form when the checklist and the Application Cover Sheet is complete and has been signed.

y Personal details (on Application Cover Sheet)
(Information Sheet (attached
y Consent Form (attached)
y Academic Details (on Cover Sheet)
y Signatures (where required)
y Research Instruments (attached)

Human Research Ethics Committee
Postal Address: The Secretary, Human Research Ethics Committee
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THE UNIVERSITY OF WAIKATO
Te Whare Wānanga o Waikato

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School / Faculty / Institute:	School of Science
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Student ID (if applicable):	1276896
Proposed start date of field research / data collection:	10th Dec 2022
This is an application for approval of: (indicate all that apply)	n Staff research project n PhD Research y Masters Research n Other
Name of degree / paper (if applicable):	Master of Science (Research) in Environmental Science
Supervisor's name (if applicable):	Louis Schipper
Supervisor's approval (signature):	
Funding sources:	University of Waikato and NIWA
Project sponsors (e.g. equipment sponsors):	University of Waikato
Research locations (if not within University of Waikato facilities)	Matahuru marae, Waikato
Associated Applications (provide the associated application code and title):	NA

I request approval for this research or related activity and attach all relevant documentation necessary for evaluation under the Ethical Conduct in Human Research and Related Activities Regulations. http://calendar.waikato.ac.nz/assessment/ethicalConduct.html
I have read and complied with the University's Ethical Conduct in Human Research and Related Activities Regulations.
Principal Investigator's signature:

Date: 11/15/22

Please provide us with basic information about your project.

1. Project Title: Enhancing denitrifying woodchip bioreactors for phosphorus removal for the purpose of improving mahinga kai areas.
2. Briefly state the **research topic, research questions** and/or **research objectives**.
   Mahinga kai areas are disappearing because high concentrations of nutrient contaminated wastewater from agricultural runoff is polluting waterways. Denitrifying woodchip bioreactors have been used to reduce the quantity of nutrient contaminants entering the waterways, however this goal is only partially met because woodchip bioreactors are more effective at removing nitrogen than phosphorus. Our question is how we can enhance phosphorus removal within denitrifying woodchip bioreactors in order to protect waterways and mahinga kai areas. Our objectives are that we will be using different substrates that are known to enhance phosphorus removal and from an mātauranga perspective, we want to gain a deeper understanding of the cultural context around nutrient wastewater pollution and the idea of implementing woodchip bioreactors from the perspective of Māori.
3. What specific research activities are you planning to undertake? Respond to this question with a list of research activities. You will be asked to provide further details under Q.18.
   We are wanting to talk and ask questions on the mātauranga involving the concept of a woodchip bioreactor and nutrient pollution to members of the Matahuru marae community in order to gain a Māori perspective and understanding.
4. To justify your project, provide a summary of the research, its methods, anticipated academic benefits, value and/or contribution to the field.
   As world populations continue to grow, it is expected that farmers will use more nutrient fertilizers to speed up crop growth in order to keep up with rising demands for food. A consequence of this will be a rise in nutrient contaminates (nitrogen and phosphorus) entering waterways by agricultural wastewater runoff and increasing nutrient pollution which has serious environmental repercussions.
   One approach in resolving this issue is by using denitrifying woodchip bioreactors that remove nutrients from wastewater runoff. Published research have indicated that woodchip bioreactors are effective at removing high quantities of nitrogen but ineffective at removing the same concentrations of phosphorus and so this research looks at ways of enhancing phosphorus removal from woodchip bioreactors. Using a column experiment, we intend to fill these with our chosen substrates and run phosphorus farm water through them. We then collect the filtered water samples and measure the amount of phosphorus removed from them through colorimetry techniques. This method will be done in the lab. Our mātauranga approach will be discussing woodchip bioreactors and nutrient pollution with members from Matahuru marae with the goal of gaining a deeper understanding of these two topics from an mātauranga Māori point of view. This method will be done through a wananga. Improving phosphorus removal in woodchip bioreactors will be beneficial to overall reducing nutrient pollution within New Zealand waterways. Freshwater ecosystems and inhabitants will benefit from improved water qualities, especially areas of mahinga kai. Enhanced mahinga kai areas will overall be beneficial for Māori as areas for food, drinking water and safe areas to utilize.

Please tell us about your research team.

5. List all members of the research team and briefly describe their roles within the research project.
   Brandon Taoho – Masters Student and main researcher.
   Loui Schipper – University of Waikato supervisor.
   Tim Manukau – Senior Research Fellow and mātauranga Co-Director.
   Te Taka Keegan – Associated Dean of Māori.
   Rupert Craggs - Principle Scientist at NIWA/ NIWA supervisor.
   Chris Tanner – Principle Scientist at NIWA/ NIWA supervisor.
   Nikita Toataua – Māori advisor for NIWA.
6. Outline your qualifications to undertake this research. Include such things as prior experience, training in relevant research methods, and/or personal knowledge of the subject.
   Bachelors of Science (Technology) majoring in Ecology and Biodiversity.
   Currently undertaking a Masters in Environmental Research.
   Prior experience: Have collaborated with iwi on river management strategy plans and projects at the Waikato Regional Council and on native planting restoration with iwi trusts at Waterside Planting.
   Personal knowledge: I whakapapa to my research area (Lake Waikare, where Matahuru marae is located) through being Waikato Tainui affiliated.
7. What, if any, discipline-specific codes of ethics or professional standards will guide your research?
   I will be undergoing my research for Māori and the benefits it can be bring for Māori. I will adhere to the rules within this ethics approval and the professional standards for which are expected of me from the University of Waikato and NIWA.

Please provide the following information about your potential participants:

8. Broadly, who will your participants be? (Indicate the population, not the names of participants) How many participants will there be? Provide an estimate if you are unsure of exact numbers.
   Participants will be members of Matahuru marae. At least 30 people are expected, although the exact number will vary depending on availability of all participants.
9. How will you recruit participants? Summarise your process.
   Initially contact was through Matahuru marae member Tawera Nikau. A notice email will be sent to all Matahuru members notifying them of the wānanga and their option of participating. Members will be sent an information poster, participation information sheet and consent form to sign.
10. How will you inform them about the project and their part in it? Summarise your process.
    All Matahuru members will be sent a participation information sheet outlining their participation in the project.
    Attach *a copy of the information sheets for participants. Ensure that the content of the information sheet is written in language suited to the relevant participants.*
    Attach *a copy of any recruitment emails, posts, posters or similar.*
11. Are the participants vulnerable? No
    If yes, then:
    In what ways are they vulnerable? NA
    Why do you need to involve them in your research? NA
    How will you protect them from harm? Na
12. Will you select participants on the basis of their ethnicity, iwi, culture, gender, sexuality, religion, ethical belief or disability?
    Iwi, ethnicity and culture.

If yes, then specify the basis for selection, and state how you will tell participants about the selection criteria.
I have picked members of the Matahuru marae who are Māori. I have stated this in my summary document.

Are your participants likely to be from a particular ethnic group or other distinct population even if you are not selecting them on that basis?
Yes. Participants will be Māori.

What cultural and other competencies do you have to work with your selected participant group (e.g. language, membership, professional training)?
I have been brought up in a Māori environment. I have people advising me on cultural approaches. These people are 1) Nikita Toataua, 2) Tim Manukau and 3) Te Taka Keegan.

13. Do you have any type of relationship with your participants already (e.g. employer/employee, supervisor/worker, personal relationship)?
Yes.

If yes, then you will have a dual role in the research, both as researcher and, for example, as friend or family member. How will your pre-existing relationship affect your role as a researcher?
I shall maintain my research topic as the focal point of the whole wānanga by concentrating only on the issue under discussion. If the talk seems to be going personal, I will lead it back to my core questions.

Consider potential ethical issues associated with your pre-existing relationship. How will you address these issues in your project?
I will stay focus on my questions and advice participants of this.

14. Will participants receive any form of compensation or incentive for participation? (See guidelines on compensation, and note that reimbursement for travel expenses can be stated, but does not need justification.)
Yes.

If yes, what will they receive? (e.g. vouchers, prizes, shared refreshments, course credits etc.)
They will receive a koha from the University of Waikato of minimum of $100 to cover their catering.

Please provide the following information about consent processes:

15. How will you gain informed consent from your participants?
    I will create a consent document to give to my participants in order to obtain their consent.
    Who will gain consent from participants? Note that where dual roles exist (Q.13 above), coercion to participate may be avoided by asking a third party to undertake the informed consent process.
    Tawera Nikau.
    When will participants give their consent?
    On the day of the wānanga.
    How will you record their consent?
    Their signed consent papers will be returned to me, and I will save them on my laptop and in the cloud as a backup.
    Attach *a copy of the consent forms for participants. If you intend to seek oral consent, include a procedure sheet to describe the process by which consent will be negotiated.*
    If vulnerable, are your participants able to give informed consent? Not vulnerable.
    If no, then:
    How will you obtain consent from their proxy? NA
    What steps will you take to ensure that their participation is voluntary at all times? NA
16. With the exception of participants who are anonymous to the researcher, participants have the right to withdraw entirely or in part from the research. Please provide the following information:
    How long will participants have to withdraw? (e.g. three weeks after data collection, or receipt of a
    transcript)
    2 weeks after the wānanga when the data has been collected.
    How will they withdraw? (e.g. by informing the researcher)
    By informing myself the researcher.
17. Data collection activities may be planned for off-campus locations. Please list all off-campus location where you will engage in data collection.
    Matahuru marae.
    Do you need consent or permission from any organisation, community representative, and/or anyone
    other than the individual participants? If yes, list all the required permissions, consents, and/or approvals.
    Yes. The Faculty/School Human Research Ethics Committee at the University of Waikato. I have already been given approval from Tawera Nikau on behalf of Matahuru through verbal agreement.
    How and when will you gain these permissions, consents and/or approvals?
    On completion of this Human Research Ethics Application I will gain approval from the Faculty/School Human Research Ethics Committee at the University of Waikato.
    Attach *any statements, letters, or emails of permission or approval that have been secured in advance of your application to the Human Research Ethics Committee.*

Please tell us about what you will be asking your participants to do.

18. What will participants be doing and how long will each activity take? Please provide these details for each of the items on your list in Q.3 above. Participants will be asked to answer question involving the mātauranga of woodchip bioreactors and Lake Waikare. The wānanga is estimated to be 2 hours but may proceed longer depending on the length of discussion and questions by participants.
Attach *all research instruments that you intend to use to collect data. (e.g. interview schedules, questionnaire/survey items). Indicate whether the research instruments are drafts or final versions. The final versions of research instruments must be lodged with the committee prior to data collection.*
How will participants benefit from their involvement in the research?
More nutrient contamination removal from waterways, better health of waterways, and improved areas of mahinga kai.
19. Could participants be harmed in your research? No
If yes, please describe all potential harms to your participants.
How will you minimize the risk of these harms occurring?
NA
What will you do if a participant is harmed? Describe your processes in detail.
NA
Is it likely that concerns could arise regarding the health and wellbeing of your participants, through their participation in your project? How will this be managed?
NA
20. How will you analyse the data that you collect from your participants?
I will critically review the information given and include this in my thesis. Any sensitive information given (if not given permission to include within my thesis) will not be used.
Will your research involve comparing one group to another? No
If yes, then explain how the comparison will be done.
How are the participants categorized into specific groups? NA
Why is it important to do this? NA
21. Does your research involve any deception of participants?
No
If yes, then describe the deception.
Why is it necessary to deceive participants? How and when will participants be told of the deception?
No
22. Will the true identity of the researcher(s) be concealed from participants at any time during the researcher? (Such research is called 'covert research'.)
No
If yes, then describe the concealment.
Why is it necessary?
How and when will participants be told of the concealment?
If never, then, explain why the concealment will not be disclosed to participants.
NA

Te Whare Wānanga o Waikato, the University of Waikato, through its official *Charter,* has an explicit commitment to partnership with Māori, to kaupapa and tikanga Māori, and to the interests of New Zealand- born and Island-born Pacific people.

Through the *Ethical Conduct and Human Research and Related Activities Regulations*, researchers are required to respect the **cultural, social** and **language preferences** and **sensitivities** of participants. When applying for ethical approval, researchers should demonstrate an awareness of social and cultural difference, consult advisors regarding the appropriate conduct of their research, and present the outcome of consultation in their ethics application.

Two resources that are particularly relevant to research at the University of Waikato are *Te Ara Tika – Guidelines for Māori Research Ethics* and the *Pacific Health Research Guidelines.*

23. Does the research project have particular relevance or potential implications for Māori, or for other social and cultural groups?
    Yes.
    If yes, then please provide the following information about your consultation processes:
    Who are the stakeholders? (That is, whom do you have to consult?)
    What are the results of your consultation with them so far? (e.g. describe advice taken on appropriate
    procedures and approaches to research, decisions made about appropriate ways to return research findings)
    Stakeholders will include Matahuru and members from Matahuru marae.
    To date, I have consulted with Tawera Nikau and Aarkea Hopkins of Matahuru, Louis Schipper, Tim Manukau, and Te Taka Keegan of the University of Waikato, and Rupert Craggs, Chris Tanner, and Nikita Toataua of NIWA. The advice I have been given is as follows: To attend a pōwhiri to Matahuru marae where I will be welcomed onto the marae by Matahuru members and will present a koha to Matahuru marae on behalf of myself and the University of Waikato. My discussion will be accompanied by a PowerPoint presentation outlining my masters research topic and questions. When the wananga concludes, a kai will be held at Matahuru marae.
    Do you have at least one cultural advisor for this project? Please provide their name(s) and specific role(s).
    Yes.
    Tim Manukau – cultural advisor University of Waikato.
    Aareka Hopkins – cultural advisor Matahuru marae.
24. Describe how you will show respect and sensitivity towards participants (e.g. having support persons present during interviews, having an interpreter if you are not fluent in the language, being vouched for by elders, using appropriate gestures, dressing inoffensively, or participating in cultural ceremonies or rituals).
    On the day, I will have the assistance of Aareka Hopkins, Tim Manukau, and Louis Schipper. Te Wera Niku and Aareka Hopkins will be vouching for me. When conveying biophysical facts, only little motions will be employed. To demonstrate our respect and professionalism, we shall all wear formal clothing. In addition, I will be wearing a koru necklace that was a gift from my grandfather.
25. How will the identities of participants (and their communities and/or organisations where relevant) be represented in the research?
    Participants will be referred to in the research as member/members of Matahuru marae.
    Is it important to maintain the confidentiality of participants (and their communities/organisations where relevant) in the research reporting?
    Yes
    If yes, how will you preserve confidentiality?
    I will not use their names and refer to participants as member/members of Matahuru marae.

26. In addition to the lead researcher(s), who else will see information provided by the participants? Will any of the shared information be linked to the participant's names, or will it be anonymised before sharing?
    For grading reasons, the research output will be shared with my university supervisor Louis Schipper, Te Taka Keegan and Tim Manukau, NIWA representees Rupert Cragg, Chris Tanner and Nikita Toataua. No personal information of the participants will be shared.
    It may be appropriate to ask additional parties (e.g. student researchers, transcribers) to sign a confidentiality agreement. ***Attach*** *the confidentiality agreement that you intend to use.*
27. How and where will the data be stored and protected **during** the research project?
    Information will be stored on my laptop and cloud storage for back up.

28. List all the anticipated research outputs for the project (e.g. thesis, conference papers, journal articles, other sorts of presentation, book, media release, pedagogic materials).
    Masters research thesis.
    What provision is there to provide participants with information about the outcomes of the research?
    Continuous communication will be upheld through me and the members of Matahuru marae about the outcomes of the research.
29. Research data must be stored for a minimum of 5 years after the completion of a research project.
    Where and how will you store your data after the project has been completed? Supervisors are responsible for storing research data on behalf of their students.
    Data will be submitted to the Waikato University's Indigenous Research Archives via email method.
    If archiving is appropriate for your project data, where will you archive the data and under what conditions?

    Data will be stored within the Waikato University's Indigenous Research Archives for minimum of 5 years under the University of Waikato's research ethics conditions.
    If you do not intend to store your data indefinitely, how will you ensure that your data is safely destroyed?
    NA

30. Ownership of Human Research Data
    It is usual to state that participants own the data that they provide, and that the researcher will use the data for the specified purposes, with the consent of participants. Please explain any variation from this arrangement.
    No variation. I will adhere to this agreement.
31. Copyright
    The researcher's ownership of scholarly publications and other forms of research outputs is governed by the University of Waikato's Intellectual Property Rights Policy. Crucially the policy states in Clause 8 that*, "the University recognises and endorses the traditional academic freedom of staff to publish research and scholarly documents and to produce*

creative and artistic works without restriction; the University does not assert ownership of copyright of such works (e.g. books, journal articles, conference papers, art works and musical recordings) unless specified in clauses 12-18 of [the] policy."
Please explain any variation from this policy.
No variation. I will adhere to this agreement.
Clause 9 states that, *"When dealing with intellectual property that includes Mātauranga Māori, and in the context of the WAI262 claim report, the principles of Te Tiriti o Waitangi will be applied by the University".*
Please indicate if intellectual property is subject to the principles of Te Tiriti o Waitangi.
Yes.

32. Other legal or ethical issues
Describe any other legal or ethical issues related to this project. Consider particularly relationships between members of the research team, and project funders, sponsors, or other stakeholders.
No.

Figure 1A. Ethics approval consent sheet for the approval of the wānanga.

Participant Information Sheet

Woodchip bioreactors for mahinga kai areas

Formal Study title**: Enhancing denitrifying woodchip bioreactors for phosphorus removal for the purpose of improving mahinga kai areas**

Sponsors: **University of Waikato and NIWA:**

Lead Researcher: **Brandon Taoho**

Study Site: **Lake Waikare**

Phone number: **0279076748**

Email: **b.taoho007@gmail.com**

Tēnā tātou

Ko Tainui te waka, Ko Taupiri te Maunga, Ko Waikato Tainui tōku iwi, Ko Ngāti Māhuta tōku hapuu. Ko Waahi Pa tōku marae. Ko Potetau Te Wherowhero te tangata. Waikato taniwharau. Ko Brandon Taoho toku ingoa.

You and your whanau have been invited to take part in a wānanga at Ohinewai Hall on the 10th Dec 2022 to kōrero about Mātauranga Māori around nutrient pollution in waterways and to share your thoughts on a new technology called a denitrifying woodchip bioreactor that is used to mitigate nutrient pollution.

I am currently undertaking my Master's in Environmental Research where I am focusing on enhancing the phosphorus removal in woodchip bioreactors and understanding the Mātauranga of woodchip bioreactors so that this technology can seek opportunities for Māori and be led by Māori.

The purpose of this wānanga will help me understand the cultural aspects of nutrient pollution in waterways and help me gain an understanding of woodchip bioreactors from the perspective of Māori. With your help, I will be able to use traditional practices and knowledge to guide the development and use of this technology so that I can build its potential so that it can be led by Māori in the near future.

Whether or not you take part in the wānanga is your choice. If you don't want to take part, you don't have to give a reason.

This Participant Information Sheet will help you decide if you'd like to take part. It sets out why we are doing the study, what your participation would involve and what will happen to

your information after the wānanga. We will go through this information with you during the wānanga and answer any questions you may have.

If you agree to take part in this study, please sign the Consent Form on the last page of this document. You will be given a copy of both the Participant Information Sheet and the Consent Form to keep.

WHAT IS THE PURPOSE OF THE STUDY?

Mahinga kai areas are disappearing because nitrogen and phosphorus rich agricultural effluent is polluting waterways. Denitrifying woodchip bioreactors are a new technology that can help decrease the amount of nutrient pollutants entering these waterways.

A denitrifying woodchip bioreactor is essentially a subterranean ditch where runoff water can enter and pass through a woodchip medium before being discharged into lakes, rivers and streams. Large amounts of nitrogen are removed from this runoff water as it filters through the woodchips but a drawback to this technology is that woodchip bioreactors are not as efficient at removing large amounts of phosphorus.

The reason being is that woodchips do not as easily absorb phosphorus from runoff water like they do for nitrogen and so the purpose of this master's research is to enhance phosphorus removal in woodchip bioreactors.

From a cultural viewpoint, woodchip bioreactors can be a way of restoring and protecting the mana and mauri of waterways throughout New Zealand. Nutrient pollution is slowly killing our native waterways by poisoning their water quality and killing precious toanga species. One area in particular which are of concerns are areas of mahinga kai.

These areas are greatly important to Māori because they are places that provide sustainable natural resources, such as food and drinking water to be used by Māori communities. By enhancing phosphorus removal in woodchip bioreactors, these areas can be further protected by the harmful effects of nutrient pollution so that they can still be utilized by Māori for generations. And so, the second purpose of this master's research is to enhance phosphorous removal within woodchip bioreactors for the purpose of protecting mahinga kai areas.

WHAT WILL MY PARTICIPATION IN THE STUDY INVOLVE?

To enhance woodchip bioreactors for the protection of mahinga kai areas, I am wanting to understand both the cultural mātauranga around nutrient pollution and what perspective do Māori have about woodchip bioreactors from a collective Māori viewpoint.

These understandings will help me guide the development of enhancing woodchip bioreactor technologies to incorporate traditional knowledge and practices for the potential of it to be led by Maori in the future.

Your participation in this study will be asking you to share your cultural knowledge, tikanga and perspective about nutrient pollution, woodchip bioreactor technology and its potential for mahinga kai enhancement.

This will be an open kōrero about your thoughts and perspectives. You do not need to have a full understanding of woodchip bioreactors or nutrient pollution.

WHO CAN TAKE PART IN THE STUDY?

For the purpose of this research study, participants are required to be of Māori descent and affiliate with Matahuru marae.

HOW IS THE STUDY DESIGNED?

You and your whanau will be seated within Ohinewai Hall, along with others who have chosen to take part in the wānanga. Myself, along with my supporting team of member from the University of Waikato and NIWA, will present a slide show detailing my master's project to you.

At the end of the slide show presentation, I will then open the discussion to the audience by asking you questions that offer you to share your knowledge with me and my team. You do not need to share if you do not want to.

Your answers will be recorded so that your information can be incorporated into my master's research writing. Any answers that are asked to not be recorded will be granted and will not be used in the research.

Food will be provided to all participants at the end of the wānanga.

PARTICIPATION WITHDRAWAL FROM THIS STUDY

Rights to Withdraw Your Information.

You may withdraw your consent for the collection and use of your information at any time, by informing myself via the contact information provided.

If you withdraw your consent, your study participation will end, and the study team will stop collecting information from you.

If you agree, information collected up until your withdrawal from the study will continue to be used and included in the study. You may ask for it to be deleted when you withdraw, unless you withdraw after the study analyses have been undertaken.

If at any time you feel as though a question or an answer is culturally inappropriate to share or be recorded and used within the study than either the question or answer will be removed.

WHAT WILL HAPPEN TO MY INFORMATION?

All information gathered from the wānanga will be stored on both cloud storage and my personal laptop.

Identifiable Information

Participants can consent to allowing to use their name directly towards any answers or discussions that they individually ask or participant in within the master's thesis.

Identifiable information is any data that could identify you (e.g. your name, date of birth, or address).

Your identifiable information is held by myself during the study. After the study it is transferred to a secured University of Waikato archiving site and stored for at least 5 years. Your information will be entered into electronic case report forms and sent through a secure server to the sponsor. Your information will be kept by the sponsor in secure, cloud-based storage indefinitely. All storage will comply with local and/or international data security guidelines.

CAN I FIND OUT THE RESULTS OF THE STUDY?

Rights to Access Your Information.

You have the right to request access to your information held by the research team. You also have the right to request that any information you disagree with is corrected.

Please provide consent below if you would like to access the results by contacting myself with the contact information given.

If you have any questions about the collection and use of information about you please feel free to contact myself via the contact information provided.

WILL ANY COSTS BE REIMBURSED?

A koha of $100 will be presented to the Matahuru marare to cover food costs.

WHO IS FUNDING THE STUDY?

Funding is sourced by the University of Waikato, Waikato Tainui and NIWA.

WHO DO I CONTACT FOR MORE INFORMATION OR IF I HAVE CONCERNS?

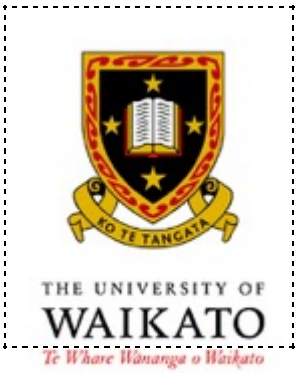
If you have any questions, concerns or complaints about the study at any stage, you can contact:

Brandon Taoho

Phone : 0279076748
Email : b.taoho007@gmail.com

Consent Form

Woodchip bioreactors for mahinga kai areas



Please tick to indicate you consent to the following

I have read the Participant Information Sheet and I fully comprehend what it says.		
I am satisfied with the answers I have been given regarding the study and I have a copy of this consent form and information sheet.		
I understand that taking part in this study is voluntary (my choice) and that I may withdraw from the study at any time.		
I consent to the researcher collecting and processing my information within their Master's thesis.		
If I decide to withdraw from the study, I agree that the information collected about me up to the point when I withdraw may continue to be processed.	Yes ☐	No ☐
I consent for my identifiable information to be used within the master's research thesis.	Yes ☐	No ☐
If no, then I understand that my participation in this study is confidential and that no material, which could identify me personally, will be used in any reports on this study upon my consent.		
I know who to contact if I have any questions about the study in general.		
I understand my responsibilities as a study participant.		
I wish to receive a summary of the results from the study.	Yes ☐	No ☐

.

Declaration by participant:
I hereby consent to take part in this study.

Participant's name:

Signature: Date:

Declaration by member of research team:

I have given a verbal explanation of the research project to the participant, and have answered the participant's questions about it.

I believe that the participant understands the study and has given informed consent to participate.

Researcher's name: Brandon Taoho

Signature: Date: 11/15/22

Figure 2A. Participant information sheet and consent form for the wānanga.

Three sections to this presentation

Section 1: Basics of a woodchip bioreactor

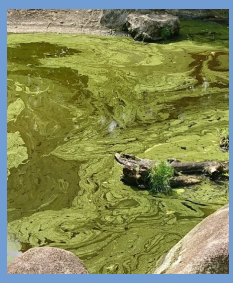
Section 2: Introduction to my maters project

Section 3: Incorporating Mātauranga Māori

Basics of a woodchip bioreactor

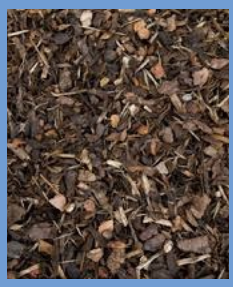
Nutrient pollution is a major environmental issue in Aotearoa.



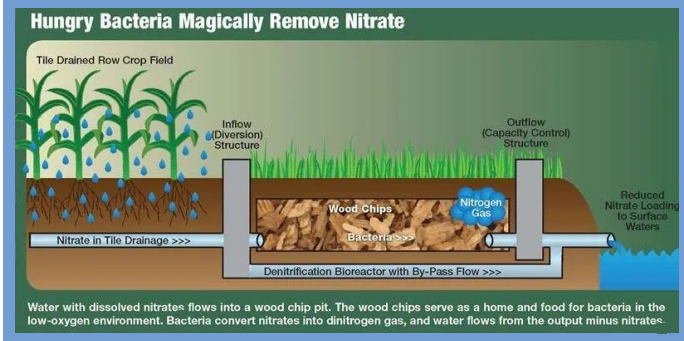



Woodchip bioreators as a remedy for nutrient pollution.



What is a woodchip bioreactor?



Water with dissolved nitrates flows into a wood chip pit. The wood chips serve as a home and food for bacteria in the low-oxygen environment. Bacteria convert nitrates into dinitrogen gas, and water flows from the output minus nitrates.

Benefits:

Reduces nutrients within agricultural runoff

Low cost

Requires little maintenance

Expected to last 20+ years

No land needs to be taken out of production

How a woodchip bioreactor works

How a woodchip bioreactor works

Image 1

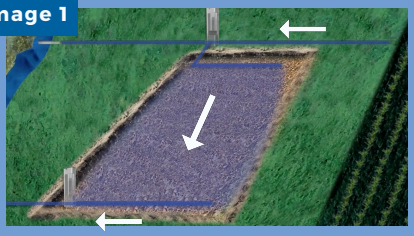


Image 2

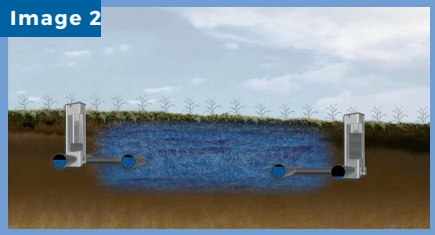
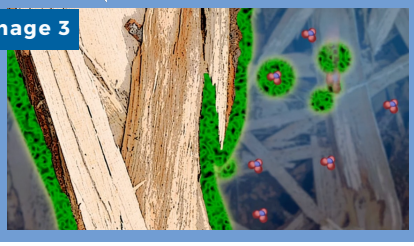


Image 3



- Image 1: Runoff enters bioreactor.
- Image 2: Bioreactor can store large amounts of runoff.
- Image 3: Bacteria remove nutrients by denitrification.

Where WB are currently being used around the world

American Society of Agronomy, United States

Lincoln Agritech, New Zealand

Clarifications?

Three sections to this presentation

Section 1: Basics of a woodchip bioreactor

Section 2: Introduction to my maters project

Section 3: Incorporating Mātauranga Māori

My masters project

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The problem

Woodchip bioreactors are less effective at removing phosphorus from agricultural wastewater runoff compared to nitrogen.

To test three known phosphates absorptive substrates to determine which one is more efficient at removing phosphorus from phosphorus-contaminated river water.

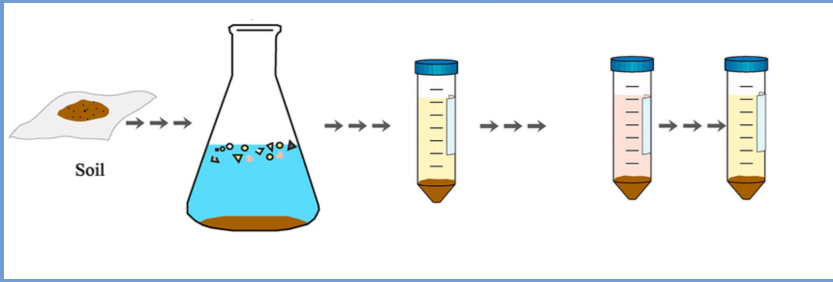
Woodchips

Iron (Fe) biochar

Iron (Fe)/manganese (Mg) biochar

Columns experiment

Sequential extraction will determine which substrate has absorbed more phosphate and overall determine which media is better at removing phosphorous in wastewater compared to the others.



Hypothesis

We think that...

1st - Iron/manganese biochar

2nd - Iron biochar

3rd - Woodchips

Clarifications?

Three sections to this presentation

Section 1: Basics of a woodchip bioreactor

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Section 3: Incorporating Mātauranga Māori

Incorporating Mātauranga Māori

What Mātauranga Māori is to me

Mātauranga Māori refers to indigenous Māori knowledge that explains the natural world from a Māori point of view.

Mātauranga Māori is communicated by oral narratives, like pūrākau, waiata, whakapapa and many others

Mātauranga Māori draws upon the spiritual connection that we as Māori have with the world and its environment.

Why Mātauranga Māori is important to me

The heart of Mātauranga Māori is a proactive attitude of reciprocation and protection between Māori and the environment.


Integrating Mātauranga Māori and Western Science

Over the years, the idea of integrating Western science and Mātauranga Māori has become more and more important to the way Aotearoa takes care of its environment.

Today, Māori knowledge and cultural practices are becoming increasingly incorporated within environmental conservation/restoration.

Woodchip bioreactors for mahinga kai areas

Nutrient pollution is slowly killing our natural waterways. Poisonings our native taonga species and destroying mahinga kai areas.

Mahinga kai areas are areas that provide sustainable natural resources like food and drinking water to Māori people, making them very important.

Woodchip bioreactors have the potential of restoring and protecting the mana and mauri of waterways and mahinga kai areas throughout Aotearoa.

By enhancing phosphorus removal in woodchip bioreactors, mahinga kai areas can be protected from nutrient pollution so that Māori may use them for generations.



Figure 3A. Woodchip bioreactor presentation for wānanga.

Table 1A. Data of daily phosphate removal.

	Daily phosphate removal (mg P m^{-3} d^{-1})		
Date	W	(W+Fe)	(W+Fe+Mn)
31st Jan	0.54	2.86	3.69
1st Feb	0.75	4.05	4.97
2nd Feb	1.43	5	5.44
3rd Feb	0.67	4.94	4.8
6th Feb	1.44	3.5	2.12
7th Feb	1.47	4.39	4.1
8th Feb	2.21	3.69	3.86
9th Feb	1.68	5.06	5.04
10th Feb	1.8	4.9	5.05
13th Feb	1.61	4.72	4.54
14th Feb	1.16	4.79	4.69
15th Feb	0.64	3.03	3.07
16th Feb	1.22	3.42	3.86
17th Feb	0.74	3.14	3.76
20th Feb	1.21	5.19	4.69
21st Feb	0.61	5.32	4.71
22nd Feb	1.79	3.7	4.55
23rd Feb	2.03	4.35	4.67
24th Feb	1.79	4.99	4.66
27th Feb	0.09	5.68	5.6
28th Feb	0.25	2.39	4.32
1st Mar	0.61	3.49	4.83
2nd Mar	0.39	4.52	5.05
3rd Mar	0.36	2.18	1.43
6th Mar	0.13	4.86	4.52
7th Mar	0.05	4.97	4.11

8th Mar	0.06	5.66	5.65
9th Mar	0.45	5.57	5.66
10th Mar	0.29	5.59	5.37
11th Mar	0.39	5.61	5.47
12th Mar	0.32	5.45	5.36
14th Mar	0.48	5.43	5.5
15th Mar	0.65	5.59	5.59
16th Mar	0.77	5.55	5.38
17th Mar	0.3	5.39	5.52
20th Mar	0.64	5.46	5.47
21st Mar	0.58	5.46	5.46
22nd Mar	0.34	5.72	5.71
23rd Mar	0.64	5.68	5.7
24th Mar	0.34	5.59	5.49
27th Mar	0.39	5.55	5.25
28th Mar	0.29	5.33	5.59
29th Mar	0.34	5.34	5.37
30th Mar	0.77	5.45	5.22
31st Mar	0.84	5.62	5.62
3rd Apr	0.25	5.15	5.08
4th Apr	0.23	5.27	5.27
5th Apr	0.59	5.36	5.27

Table 2A. Data of percentage daily phosphate removal.

	Daily percentage phosphate removal (%)		
Date	W	(W+Fe)	(W+Fe+Mn)
31st Jan	9	50	64
1st Feb	13	71	87
2nd Feb	25	87	95
3rd Feb	12	86	84
6th Feb	25	61	37
7th Feb	26	77	72
8th Feb	39	64	67
9th Feb	29	88	88
10th Feb	31	85	88
13th Feb	28	82	79
14th Feb	20	84	82
15th Feb	11	53	54
16th Feb	21	60	67
17th Feb	13	55	66
20th Feb	21	91	82
21st Feb	11	93	82
22nd Feb	31	65	79
23rd Feb	35	76	81
24th Feb	31	87	81
27th Feb	2	99	98
28th Feb	4	42	75
1st Mar	11	61	84
2nd Mar	7	79	88
3rd Mar	6	38	25
6th Mar	2	85	79

7th Mar	1	87	72
8th Mar	1	99	99
9th Mar	8	97	99
10th Mar	5	98	94
11th Mar	7	98	95
12th Mar	6	95	94
14th Mar	8	95	96
15th Mar	11	97	97
16th Mar	13	97	94
17th Mar	5	94	96
20th Mar	11	95	95
21st Mar	10	95	95
22nd Mar	6	100	100
23rd Mar	11	99	99
24th Mar	6	97	96
27th Mar	7	97	92
28th Mar	5	93	97
29th Mar	6	93	94
30th Mar	13	95	91
31st Mar	15	98	98
3rd Apr	4	90	89
4th Apr	4	92	92
5th Apr	10	93	92

Table 3A. Data of phosphate concentrations from column experiment.

	Phosphate concentrations (mg L^{-1} PO^{-}_{4}-P)								
	Column replicate and treatment								
Date	A1 (W)	B2 (W+Fe+Mn)	C3 (W+Fe)	D4 (W+Fe)	E5 (W)	F6 (W+Fe)	G7 (W)	H8 (W+Fe+Mn)	I9 (W+Fe+Mn
31st Jan	8.67	5.41	2.88	7.44	7.95	7.71	7.84	0.51	3.68
1st Feb	7.63	2.05	1.97	3.63	8.19	4.96	7.65	0.45	1.07
2nd Feb	8.37	0.4	1.55	1.41	6.48	1.63	5.41	0.53	0.45
3rd Feb	8.61	0.91	2.16	1.57	8.21	1.23	7.01	1.97	1.49
6th Feb	7.36	4.35	3.7	3.72	7.71	6.57	5.14	5.92	6.74
7th Feb	7.24	0.03	0.26	2.13	6.47	6.07	6.37	7.04	0.61
8th Feb	5.67	0.78	0.93	6.04	5.17	5.84	5.74	4.15	3.9
9th Feb	6.07	0.78	0.66	2.78	6.34	0.78	6.67	1.13	1.35
10th Feb	5.67	1.23	0.63	3.95	6.17	0.66	6.67	1.13	0.86
13th Feb	6.16	1.73	1.61	3.43	8.03	1.32	5.26	2.22	1.68
14th Feb	8.03	1.83	0.93	3.9	7.43	1.1	6.09	1.68	1.42
15th Feb	8.01	4.38	4.75	6.21	7.91	6.06	8.06	4.19	3.97
16th Feb	7.23	3.07	3.68	4.94	6.4	5.89	7.64	3.14	2.61
17th Feb	7.35	3.14	3.95	6.16	8.06	6.18	8.11	3.8	2.32
20th Feb	7.7	0.86	0.28	2.09	7.49	1.04	6.11	2.27	1.77
21st Feb	8.02	1.83	0.54	0.04	8.08	2.04	8.05	2.21	0.77
22nd Feb	6.02	3.12	1.01	6.64	6.35	5.11	6.2	1.45	1.01
23rd Feb	5.88	3.3	3.77	0.1	5.67	4.82	5.91	0.89	0.83
24th Feb	6.02	2.45	1.77	0.22	6.32	2.71	6.23	1.39	1.24
27th Feb	8.72	0.19	0.16	0.01	8.99	0.19	8.87	0.1	0.33
28th Feb	8.49	2.27	3.71	8.78	8.99	8.46	8.37	3.09	1.27
1st Mar	6.52	0.07	2.45	5.32	8.87	6.32	8.75	2.53	1.62
2nd Mar	8.11	0.1	3	0.45	8.46	4.21	8.6	1.89	1.21
3rd Mar	8.81	7.96	7.55	6.05	8.31	8.72	8.19	6.49	5.82
6th Mar	8.64	1.83	1.36	1.39	8.72	2.75	9.01	1.2	2.67

7th Mar	8.93	1.2	1.28	0.86	8.88	2.59	8.95	4.14	2.3
8th Mar	8.88	0.21	0.24	0.13	8.85	0.08	8.98	0.11	0.08
9th Mar	8.35	0.11	0.5	0.5	8.53	0.05	8.01	0.08	0.13
10th Mar	8.9	0.18	0.21	0.31	8.35	0.34	8.38	0.63	0.89
11th Mar	8.38	0.05	0.42	0.11	8.33	0.29	8.43	0.21	0.97
12th Mar	8.53	0.31	0.97	0.45	8.74	0.34	8.22	0.47	0.94
14th Mar	8.9	0.38	0.9	0.68	8.44	0.33	7.4	0.3	0.44
15th Mar	8.11	0.27	0.11	0.52	8.22	0.3	7.62	0.25	0.16
16th Mar	8.14	0.05	0.03	0.7	8.77	0.41	6.47	1.12	0.49
17th Mar	8.41	0.08	0.25	0.93	8.49	0.96	8.68	0.22	0.68
20th Mar	7.49	0.33	0.71	0.38	8.52	0.63	7.95	0.11	0.79
21st Mar	7.71	0.17	0.74	0.33	8.28	0.6	8.28	0.38	0.71
22nd Mar	8.36	0.06	0.01	0.03	8.87	0.03	8.17	0.01	0.03
23rd Mar	8.49	0.06	0.11	0.11	7.03	0.11	8.47	0.03	0.06
24th Mar	8.55	0.11	0.17	0.33	8.28	0.44	8.55	0.44	0.57
27th Mar	8.68	0.06	0.74	0.25	8.87	0.11	7.6	1.01	1.22
28th Mar	8.71	0.38	0.82	0.9	8.66	0.79	8.28	0.11	0.2
29th Mar	8.87	0.66	0.68	0.79	8.3	0.98	8.22	0.76	0.3
30th Mar	8.28	0.38	0.6	0.82	7.22	0.33	7.87	0.9	1.11
31st Mar	8.44	0.28	0.22	0.28	7.2	0.2	7.41	0.03	0.22
3rd Apr	8.71	0.71	0.93	1.25	8.66	1.49	8.44	1.44	0.9
4th Apr	8.6	0.63	1.01	0.79	8.55	1.11	8.76	0.76	0.79
5th Apr	8.44	0.52	0.76	0.79	7.79	0.79	8.01	1.22	0.44

Table 4A. Data of phosphate fractions from phosphate extraction experiment.

Treatment	Column	FeP/Feox	Fe/dry (μmol kg^{-1})	P/dry (μmol kg^{-1})
W	A1	1.32007	0.003695	4.88E-05
W	A1	0.207215	0.004318	8.95E-06
W	A1	0.057613	0.011162	6.43E-06
W+Fe+Mn	B2	0.087297	0.238656	0.000208
W+Fe+Mn	B2	0.133772	0.243629	0.000326
W+Fe+Mn	B2	0.149738	0.177752	0.000266
W+Fe	C3	0.07758	0.195977	0.000152
W+Fe	C3	0.089873	0.193815	0.000174
W+Fe	C3	0.054757	0.168354	9.22E-05
W+Fe	D4	0.331847	0.132877	0.000441
W+Fe	D4	0.087217	0.205627	0.000179
W+Fe	D4	0.016417	0.259636	4.26E-05
W	E5	0.295835	0.003321	9.82E-06
W	E5	0.10016	0.003581	3.59E-06
W	E5	0.167901	0.002638	4.43E-06
W+Fe	F6	1.539351	0.071093	0.001094
W+Fe	F6	0.091887	0.308736	0.000284
W+Fe	F6	0.015736	0.177294	2.79E-05
W	G7	0.128408	0.00306	3.93E-06
W	G7	0.126829	0.002539	3.22E-06
W	G7	0.105702	0.002764	2.92E-06
W+Fe+Mn	H8	0.082924	0.212452	0.000176
W+Fe+Mn	H8	0.118138	0.260183	0.000307
W+Fe+Mn	H8	0.11295	0.132862	0.00015
W+Fe+Mn	I9	0.12624	0.384753	0.000486
W+Fe+Mn	I9	0.118008	0.217175	0.000256
W+Fe+Mn	I9	0.079907	0.401357	0.000321

Table 5A. Nitrate concentrations from column experiment.

	Nitrate concentrations (mg L^{-1} NO^{-}_{3}-N)								
	Column replicate and treatment								
Date	A1 (W)	B2 (W+Fe+Mn)	C3 (W+Fe)	D4 (W+Fe)	E5 (W)	F6 (W+Fe)	G7 (W)	H8 (W+Fe+Mn)	I9 (W+Fe+Mn)
31st Jan	0.99	1.68	1.46	2.11	0.82	2.04	0.94	1.91	1
1st Feb	0.55	4.25	0.94	0.99	0.82	3.42	1.67	0.93	0.62
2nd Feb	0.77	0.8	0.9	0.87	1.33	1.41	2.45	0.94	2.12
3rd Feb	0.93	1.39	0.71	0.82	0.67	0.99	0.58	0.67	0.49
6th Feb	8.86	4.34	19.9	8.08	4.95	16.7	5.43	12.8	3.44
7th Feb	4.46	1.15	0.97	1.21	8.08	1.27	2.66	1.27	0.49
8th Feb	4.4	7.42	17.7	5.55	8.8	2.78	8.32	2.78	3.44
9th Feb	19.9	0	0.91	5.07	8.56	1.21	21.4	2.05	2.6
16th Feb	7.26	20.8	12.8	10.7	8.34	6.99	13.3	12.6	8.88
17th Feb	5.28	15.6	15.4	5.37	8.61	8.97	8.7	8.16	16
20th Feb	5.87	2.16	4.51	1.33	12.23	3.3	12.23	2.39	3.45
21st Feb	8.3	0.87	2.61	2.77	15.3	3.45	17.5	10.3	1.93
22nd Feb	6.55	3.98	8.3	14.2	13	5.87	9.51	10.3	12.5
23rd Feb	9.2	2.92	2.77	3.9	11.1	2.99	15.11	2.31	2.23
27th Feb	12.06	1.29	1.96	2.25	16.39	3.89	18.31	2.06	1.87
28th Feb	17.35	12.93	20.43	16.77	22.25	14.27	23.41	14.75	13.89
1st Mar	10.81	14.75	24.56	21.2	10.91	27.64	11.58	18.02	19.27
2nd Mar	7.54	1.2	1.2	1	9.08	2.45	6.58	1.77	1.48
3rd Mar	13.79	1.58	6.48	3.02	22.54	3.98	26.39	3.02	2.64
6th Mar	8.23	0.03	2.14	1.05	7.69	2.45	7.45	1.98	1.75
7th Mar	6.91	0.5	2.06	3.7	7.69	0.42	7.92	2.14	1.2
8th Mar	8.78	1.75	1.67	0.73	8.39	1.28	8.16	2.38	2.22
9th Mar	8.39	1.83	3.39	3.08	8.55	1.44	8.47	2.3	3.08
10th Mar	8.08	2.45	2.38	2.45	8.86	2.14	8.94	2.14	3.08
11th Mar	8.55	2.3	5.97	2.06	5.58	2.06	7.45	2.06	2.06

12th Mar	8.55	2.14	3.55	3.47	8.86	2.22	8.47	2.38	8.55
14th Mar	8.4	1.9	3.55	8.55	8.19	1.4	8.26	4.33	2.05
15th Mar	4.76	0.4	2.05	1.9	8.19	0.26	8.12	2.69	0.69
16th Mar	6.26	1.76	1.55	0.9	8.4	1.62	5.76	5.47	1.33
17th Mar	7.19	1.19	2.97	5.76	5.62	1.97	4.4	2.33	0.19
20th Mar	7.11	0.52	3.12	4.5	6.29	0.2	6.86	3.12	1.5
21st Mar	6.13	1.66	0.2	2.8	6.46	2.8	7.35	2.96	1.82
22nd Mar	7.11	2.23	0.11	1.66	7.19	1.66	7.02	0.03	1.9
23rd Mar	7.11	2.8	0.68	1.9	8.24	0.6	6.86	0.36	3.28
24th Mar	8.08	2.47	1.66	1.82	7.43	1.58	7.92	0.6	1.41
27th Mar	7.88	2.42	1.41	1.91	7.81	1.41	7.09	0.55	1.34
28th Mar	7.53	1.34	1.99	2.49	7.81	0.4	7.45	1.34	0.62
29th Mar	7.38	2.2	1.77	2.2	7.09	2.78	7.09	1.99	1.77
30th Mar	7.24	1.12	0.98	3.14	7.09	2.49	7.53	0.98	1.41
31st Mar	7.81	2.35	1.7	1.7	7.67	2.56	7.02	1.12	1.19
3rd Apr	7.12	2.79	2.44	1.94	7.4	1.3	7.55	0.67	0.45
4th Apr	7.19	2.65	1.23	2.44	7.33	2.79	7.9	2.51	0.74
5th Apr	7.12	2.79	1.87	2.09	7.9	2.87	7.62	2.44	2.09

Table 6A. Iron analysis data.

Column and column section	Iron, as Fe (mg/kg)
A (Bottom)	2.8
A (Middle)	3.2
A (Top)	8.0
B (Bottom)	190
B (Middle)	180
B (Top)	150
C (Bottom)	140
C (Middle)	160
C (Top)	110
D (Bottom)	88
D (Middle)	150
D (Top)	190
E (Bottom)	2.3
E (Middle)	2.6
E (Top)	1.9
F (Bottom)	49
F (Middle)	200

F (Top)	120
G (Bottom)	2.2
G (Middle)	1.9
G (Top)	2.0
H (Bottom)	140
H (Middle)	170
H (Top)	94
I (Bottom)	270
I (Middle)	170
I (Top)	260